ELUCIDATING CARBON FLOW IN SETTLING AGGREGATES

Dissertation

Zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften
- Dr. rer. nat. -
Fachbereich Geowissenschaften (FB5) der Universität Bremen

Anna Biastoch
Mai 2024

Gutachter
Prof. Dr. Morten H. Iversen
Dr. Isabell Klawonn

Datum des Kolloquiums
21.06.2024

Hauptbetreuer
Jack J. Middelburg

SUMMARY

The ocean inherits a major role in atmospheric CO_2 drawdown. A key driver in carbon sequestration the biological carbon pump, where primary producers photosynthetically fix CO_2 in surface waters, convert it into particulate organic forms and transport it into the ocean interior. The main fraction of the particulate organic carbon occurs in forms of sinking phyto- and zooplankton, detritus, zooplankton fecal pellets and microbes. When these marine particles coagulate, they form macroscopic aggregates. The formation of aggregates and the resulting specific sinking velocity are considered as key factors determining the efficiency of carbon export, whereby the sinking velocity defines the time an aggregate is exposed to mineralization and consumption processes, conducted by microbes and zooplankton. Within this thesis I investigated the process of aggregate formation influenced by nutrient availability, possible causes of episodic flux events and the overall carbon and nitrogen flow in the biological carbon pump.

In **Manuscript I** I studied the influence of macronutrient availability on aggregate formation imitating phytoplankton conditions during the end of bloom. Within a steady phytoplankton assemblage, comprised of *Phaeocystis antarctica*, *Chaetoceros debilis* and *Pseudo-nitzschia subcurvata*, I observed that aggregate morphology was highly variable and aggregate composition mainly relied on available nutrient levels. I was able to distinguish between two aggregate types, white colored aggregate, indicating the presence of *P. antarctica* related structures and empty diatom frustules, and yellowish aggregates indicating the formation from living diatom cells. Moreover, these differences in aggregate structures were also reflected in differences in size-specific sinking velocities, assuming that living silica-enriched diatoms ballasted the yellow aggregates and in turn increased the sinking velocity. Moreover, I discovered that the absence of macronutrients resulted in high total aggregate volume and high production of transparent exopolymeric particles (TEP). Whereby, under nutrient replete conditions the production of TEP was also enhanced but did not end up in high aggregate formation. Consequently, high TEP formation does not always induces high aggregate formation.

In **Manuscript II** I investigated temporal changes of carbon flux and related aggregate properties in combination with abundance and community structure of zooplankton during a cruise in the area of Porcupine Abyssal Plain from April to May. I observed a drastic change in carbon flux dynamics over a short period of time. While the upper water column was dominated by small compact aggregates at the beginning of the cruise, within days we observed a sudden shift, towards the formation of large mucus aggregates related to an increasing carbon flux from 100 to 200 mg C m^{-2} d^{-1}. Generally, such rapid changes in carbon flux are mediated by changes in water masses, driven by eddy activity or passing fronts, or changes in conditions of the surface ocean terminating a phytoplankton bloom. With CTD profiles, moored sensors and satellite observations I could show that the peak of carbon flux was not induced by those physical fluctuations. Instead, there seemed to be a link between the changes in carbon flux and aggregate types and the abundance of gelatinous zooplankton, mainly appendicularians and pteropods. Specifically, the formation of mucus aggregates due to high quantities of appendicularian houses and pteropod feeding nets, seemed to cause the two-order of magnitude increase in carbon flux within a few days during the second half of the cruise.

In **Manuscript III** I surveyed the aggregate formation from two prevalent phytoplankton species in the Southern Ocean, *Phaeocystis antarctica* and *Chaetoceros debilis*. Moreover, I examined the carbon and nitrogen flow from phytoplankton towards aggregated material and the utilization of the aggregated carbon and nitrogen by microbes. I observed that the carbon fraction in the aggregates were primarily derived from *P. antarctica*, which accounted for 70% of the total aggregated carbon, while the aggregated nitrogen was from the two phytoplankton species in equal (47 % and 56% for *P. antarctica* and *C. debilis*). Moreover, with NanoSIMS imaging I revealed that carbon and nitrogen were efficiently transferred from *P. antarctica* to bacteria, while nitrogen and carbon fixed by diatoms was utilized much less efficient by bacteria. Therefore, it emerged that *Phaeocystis antarctica* has a pivotal role for aggregate formation and the microbial loop in comparison to *Chaetoceros debilis*.

ZUSAMMENFASSUNG

Der Ozean spielt eine wesentliche Rolle bei der Reduktion des atmosphärischen Kohlenstoffdioxids. Eine treibende Kraft bei der Kohlenstoffeinlagerung ist die biologische Kohlenstoffpumpe, in der Primärproduzenten im Oberflächenwasser CO_2 durch Fotosynthese fixieren, es in partikuläre organische Formen umwandeln und es anschließend in den tiefen Ozean transportiert wird. Vorwiegend tritt partikulärer organische Kohlenstoff in Form von Phyto- und Zooplankton, Detritus, Zooplankton Kotballen und Mikroorganismen auf. Kommt es zur Koagulation dieser Partikel bilden sich makroskopische Aggregate. Die Bildung von Aggregaten und die daraus resultierende spezifische Sinkgeschwindigkeit werden als ausschlaggebende Faktoren in der Bestimmung der Effizienz des Kohlenstoffexportes angesehen, wobei die Sinkgeschwindigkeit die Zeit definiert in der ein Aggregate Mineralisations- und Konsumierungsprozessen durch Mikroorganismen und Zooplankton ausgesetzt ist. Im Rahmen dieser Abschlussarbeit untersuchten ich die Beeinflussung der Aggregatbildung durch Nährstoffverfügbarkeit, mögliche Ursachen für episodenhafte Veränderungen der Kohlenstoffflüsse und die Gesamtflüsse von Kohlenstoff und Stickstoff in der biologischen Kohlenstoffpumpe.

In **Manuskript I** untersuchte ich den Einfluss der Verfügbarkeit von Makronährstoffen auf die Aggregatbildung durch Phytoplankton, dessen Zustand am Ende einer Blütezeit entsprach. Innerhalb einer unveränderten Phytoplanktongemeinschaft, bestehend aus *Phaeocystis antarctica*, *Chaetoceros debilis* and *Pseudo-nitzschia subcurvata*, konnten wir beobachten, dass die Aggregatmorphologie sehr unterschiedlich war und die Zusammensetzung hauptsächlich auf der Verfügbarkeit von Nährstoffen beruhte. Wir waren in der Lage zwischen zwei Aggregattypen zu unterschieden, weiße Aggregate, die auf die Anwesenheit von *P. antarctica* Strukturen und leeren Kieselalgenschalen hindeuten, und gelbliche Aggregate, die signalisieren, dass lebende Kieselalgen Aggregate gebildet haben. Die unterschiedlichen Aggregatstrukturen spiegelten sich auch in den Größen-spezifischen Sinkgeschwindigkeiten wider, was vermuten lässt, dass lebende Kieselalgen, die mit Silica angereichert sind, gelb gefärbte Aggregate schwerer machen und das wiederum die Sinkgeschwindigkeit erhöht. Darüber hinaus konnten wir beobachten, dass die Abwesenheit von Makronährstoffen dazu führte, dass insgesamt ein großes Aggregatvolumen

entstand und eine Vielzahl an transparenten, exopolymerischen Partikeln (TEP) gebildet wurden. Wobei, unter dem Zustand einer ausreichenden Nährstoffmenge, wurde ebenfalls eine hohe Menge an TEP produziert aber die Aggregatbildung blieb vermindert. Demzufolge, induziert eine hohe TEP Bildung nicht immer eine hohe Aggregatbildung.

In **Manuskript II** untersuchte ich zeitliche Veränderungen des Kohlenstoffflusses und setzten diese, im Zusammenhang mit Partikeleigenschaften, in Verbindung mit der Abundanz und gemeinschaftlichen Zusammensetzung von Zooplankton während einer Ausfahrt in dem Bereich des Porcupine Abyssal Plain, im Zeitraum von April bis Mai. Ich beobachtete eine drastische Veränderung in der Kohlenstoffflussdynamik über einen kurzen Zeitraum hinweg. Während die obere Wassersäule am Anfang der Studie durch kleine, kompakte Aggregate dominiert wurde, kam es innerhalb von Tagen zu der Bildung von großen, schleimigen Aggregaten verbunden mit einem starken Anstieg des Kohlenstoffflusses von 100 zu 200 mg C m^{-2} d^{-1}. Generell werden solche drastischen Veränderungen im Kohlenstofffluss durch Veränderungen in den Wassermassen, Strudelaktivitäten oder passierende Fronten oder auch Veränderungen im Zustand des Oberflächenwassers, was wiederum zu einer Eliminierung der Algenblüte führt, hervorgerufen. Mit Hilfe von CTD Profilen, fest verankerten Sensoren und Satellitenbeobachtungen war ich in der Lage zu beweisen, dass der hohe Anstieg im Kohlenstofffluss nicht durch solche physikalischen Fluktuationen hervorgerufen wurde. Vielmehr scheint die Veränderungen im Kohlenstofffluss und im Partikeltyp mit der Anwesenheit von gelatinösem Zooplankton, hauptsächlich vertreten durch Appendikularien und Pteropoden, verknüpft zu sein. Insbesondere die Bildung von schleimigen Aggregaten durch eine hohe Anzahl von Appendikularien Häusern und Pteropoden Fraßnetzen scheint die Ursache für die Verdopplung des Kohlenstoffflusses in der zweiten Hälfte der Ausfahrt zu sein.

In **Manuskript III** untersuchte ich die Aggregatbildung durch zwei Phytoplanktonarten, die im Südlichem Ozean vorherrschende sind, *Phaeocystis antarctica* and *Chaetoceros debilis*. Desweiteren, untersuchte ich die Kohlenstoff- und Stickstoffflüsse von Phytoplankton über aggregiertes Material hin zur mikrobiellen Aufnahme des aggregierten Kohlen- und Stickstoffes. Wir fanden heraus, dass bis zu 70% Kohlenstoffanteil des Gesamtkohlenstoffes in Aggregaten hauptsächlich von *P. antarctica* stammt, wohingegen der Stickstofftransfer von beiden Phytoplanktonarten ähnliche Anteile aufwies (47 % für *P. antarctica* und 56 % für *C. debilis*). Zudem fand ich, mit der Hilfe von Bildgebungsverfahren unter der Verwendung von NanoSIMS, heraus, dass Kohlenstoff und Stickstoff effizienter von *P. antarctica* zu Mikroorganismen transferiert wurde, wohingegen Kieselalgenmaterial weniger effizient durch Mikroorganismen genutzt wurde. Aufgrund dieser Beobachtungen, schlussfolgern wir, dass *Phaeocystis antarctica* im direkten Vergleich zu *Chaetoceros debilis*, sowohl in der Aggregatbildung, als auch im mikrobiellen Kreislauf, eine hervorgehobene Rolle spielt.

TABLE OF CONTENTS

1. INTRODUCTION

1.1 OCEANIC CARBON BUDGETS

The increase in atmospheric CO_2 from 280 ppm (parts per million) in 1750 to 422 ppm in 2024 (Monthly average at Mauna Loa; https://gml.noaa.gov/ccgg/trends/) is considered as the key driver of global climate change. During this period, atmospheric carbon has increased by 48%, reaching about 879 Gt of atmospheric carbon in 2021 (Friedlingstein et al. 2022). Rising CO_2 concentration in the atmosphere causes global warming, which in turn melts sea-ice, ice sheets and glaciers, accelerating rising sea-level and changing precipitation (IPCC 2023). Anthropogenic CO_2 emission due to deforestation and the use of fossil fuels is the driving force of increasing CO_2 concentrations in the atmosphere since pre-industrial times. Since 1850 the land and ocean domains have removed 31% and 26%, respectively, of the total anthropogenic CO_2 emissions (Friedlingstein et al. 2022), while the remaining CO_2 has accumulated in the atmosphere. The cumulative CO_2 emission due to land use changes is similar to the cumulative terrestrial carbon uptake; consequently, the ocean is the main sink for anthropogenic emissions of CO_2 to the atmosphere (Hauck et al. 2020, Friedlingstein et al. 2022).

Globally, the oceans contain about 38,000 Pg Carbon, but only 700-1000 Pg is found in surface waters and the remaining part is mainly stored in ocean's interior (Houghton 2007). Carbon in the world's oceans can be classified in four different pools; dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), particulate inorganic carbon (PIC), and particulate organic carbon (POC). The DIC pool is the largest, comprising approximately 37,000 Gt C (Hedges 1992, Friedlingstein et al. 2022) and is mainly present in the form of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions, carbonic acid, and dissolved CO_2 (Brewin et al. 2021). The DOC pool is the second largest pool comprising approximately 662 Pg C (Hansell and Carlson 2013), followed by the POC pool covering 2.3 Pg C (Stramska and Cieszyńska 2015). The PIC pool is the smallest carbon fraction in the oceans pool with 0.03 Pg C (Hopkins et al. 2019).

The capacity of the oceans to take up atmospheric CO_2 and its conversion into its dissolved ionic form relies mainly on the alkalinity (dominance of proton acceptors over donors, Zeebe and Wolf-Gladrow 2001, Middelburg et al. 2020), water temperature, and ocean circulation. Cold, high-latitude systems (e.g., the North Atlantic and Southern Ocean) play a major role in CO_2 uptake from the atmosphere (Takahashi et al. 2009, Friedlingstein et al. 2022). At these high latitudes, cold-water masses are formed and as their density increase, they sink to greater depth, which also transport the dissolved DIC downwards simultaneously. The cold temperatures of the water also increase the solubility of CO_2 compared to warm waters. As long as the cold waters remain at depth in the ocean interior, the CO_2 is stored and not able to exchange with the atmosphere. However, these waters are upwelled at one of the eastern boundary upwelling regions, which are mainly found in warm regions near the equator (Takahashi et al. 2009, Gruber et al. 2009), the air temperatures are warming the cold, upwelled water and, thus, lower the solubility of CO_2, resulting in outgassing of CO_2 from the water to the atmosphere. Hence, the solubility of CO_2 in surface waters in cold regions e.g., the North Atlantic and the Southern Ocean, is nearly 2-fold higher than the solubility of CO_2 in surface waters that have temperatures of around 20°C (DeVries 2022, Weiss 1974). The process of high CO_2 uptake by cold surface waters at low latitudes, their subsequent subduction and transport as deep and intermediate water via the ocean thermohaline circulation, and finally their upwelling, warming, and outgassing at warm, low latitudes is referred to as the *solubility pump* (Volker and Hoffert 1985, Raven and Falkowski 1999, Fig. 1). The solubility pump is responsible for the majority of the net uptake of carbon, whereby 70% of the vertical gradient of increasing DIC concentrations with increasing depth is maintained by one of the oceans other pumps, the *biological carbon pump* (Volk and Hoffert 1985).

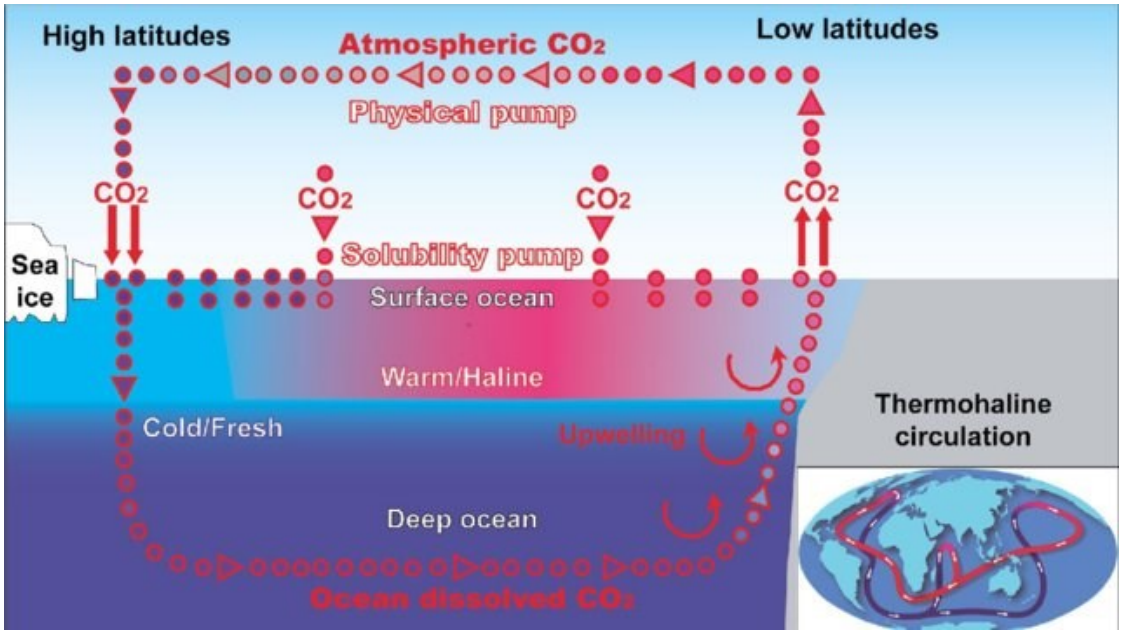


Fig.1: Graphical overview of CO_2 transport between the oceans and the atmosphere including the global thermohaline circulation (Baxter et al. 2014).

1.2 THE BIOLOGICAL CARBON PUMP

The biological carbon pump refers to the processes where CO_2 is photosynthetically fixed by primary producers in the surface ocean and subsequently transported vertically to deep ocean seafloor (Volk and Hoffert 1985). Globally, about 50 Pg of carbon is fixed into organic matter annually by marine primary producers (Field et al. 1998, Carr et al. 2006). However, most of the fixed organic carbon is remineralized within the surface ocean, and only 5-25% of the fixed carbon sinks out of the euphotic zone (>100m) (De La Rocha and Passow 2007). Once the organic material leaves the euphotic zone, it is considered as part of the export flux (Buesseler et al. 2020, Iversen 2023, Sulpis et al. 2023). Still, 80% or more of the export flux is remineralized or utilized by bacteria, microzooplankton or mesozooplankton within the mesopelagic and will never sink to bathypelagic depths (Iversen 2023, Sulpis et al. 2023). The remaining <20% of the export flux i.e., 1-5% of the carbon fixed in the surface ocean, may sink to the bathypelagic (>1000 m) where the organic matter has the potential to be stored in the ocean interior on time-scales exceeding 100 years, we refer to the flux to depths below 1000 m as sequestration flux (Passow and Carlson 2012). Still, as the organic matter sinks through the bathypelagic water column, it is being degraded and respired by microbes, and <1% of the organic matter that was fixed by primary

producers in the surface ocean will reach the seafloor in the deep ocean where it will further be turned over by early diagenesis in the surface sediments before it can be considered sequestered and stored for millennials or longer (Ducklow et al. 2001, Iversen 2023). Still, despite only a fraction of the CO_2 fixed into organic matter will sink out and be sequestered in the deep seafloor, the carbon storage via the biological carbon pump has been responsible for a 50% reduction in the atmospheric CO_2 concentrations since the industrial revolution compared to what it would have been without the biological carbon pump (Sarmiento et al. 2004). In general, the biological carbon pump can be dived into three major forms: (I) the gravitational pump, (II) the mixing pump and (III) the migration pump (Fig. 2).

The **gravitational pump** is defined as the downward settling of organic material from the surface ocean to the deep sea, in the form of POC (Lampitt et al. 2008, Siegel et al. 2016, Boyd et al. 2019). Sinking POC can be classified as phytoplankton cells, resting spores or cysts, aggregated phytoplankton, marine snow, which defines particles >500 μm in diameter, including accumulated phytoplankton material from the surface ocean (DiTullio et al. 2000, Simon et al. 2002, Leblanc et al. 2018), and zooplankton fecal pellets (Turner 2002, Cavan et al. 2015). Therefore, the gravitational pump includes the settling aggregates, which is primarily comprised of marine snow aggregates, large phytoplankton that is ballasted by biominerals, and zooplankton fecal pellets (Le Moigne 2019).

The **mixing pump** refers to the process where neutrally buoyant organic carbon is transported to greater depth by water mixing or circulation (Le Moigne 2019). Carbon in this scenario can be present in the form of DOC or suspended particles that do not sink due to small sizes or low excess density (Hansell et al. 2009, Le Moigne 2019).

The **active migration pump** describes the downward carbon transport into the ocean interior due to active vertical migrating of fish and zooplankton (Steinberg et al. 2000, Landry and Calbet 2004, Le Moigne 2019), which can occur on a daily or seasonal frequency. For example, in terms of diurnal vertical migration organisms remain in deeper, dark waters during the day to avoid predation and they only migrate up to the surface water to feed during night (Longhurst 1990, Steinberg and Landry 2017, Le Moigne 2019).

In terms of their global importance, the gravitational, mixing and vertical migration pumps contribute about 70, 20 and 10% to the total carbon export by the biological carbon pump, respectively (Nowicki et al. 2022). This highlights the importance of the gravitational pump and the necessity of a better understanding of the factors that influence the efficiency of the biological carbon pump in general.

The efficiency of the biological carbon pump is described as the proportion of primary production in surface waters, that is exported to the deep ocean (Buesseler and Boyd 2009). The efficiency of the biological carbon pump is determined by several factors, which may vary regionally and seasonally. (Martin et al. 1987, Legendre and Rivkin 2002, De La Rocha and Passow 2007). For example, polar regions export 30% - 100% of the primary production in surface waters, whereas the export in central gyres covers is often only 1-10% of the primary production (Buesseler 1998, Neuer et al. 2002, Laws et al. 2011). The differences in export efficiency can explained by changes in the prevalent phytoplankton, zooplankton, and microbial assemblages, which in turn causes variations in primary production, grazing rates, aggregate formation, aggregate composition, aggregate sinking velocities, and remineralization rates. Furthermore, it was observed that fluxes of biogenic and lithogenic material, such as silicate or carbonate, often correlate with the POC flux (Armstrong et al. 2001, Francois et al. 2002). The incorporation of these minerals into aggregated material leads to an additional ballasting factor. Ballast minerals can support aggregate formation and can increase aggregate specific density resulting in higher sinking velocities, which in turn can enhance the POC flux (Hamm 2002, Engel et al. 2009, Iversen and Robert 2015).

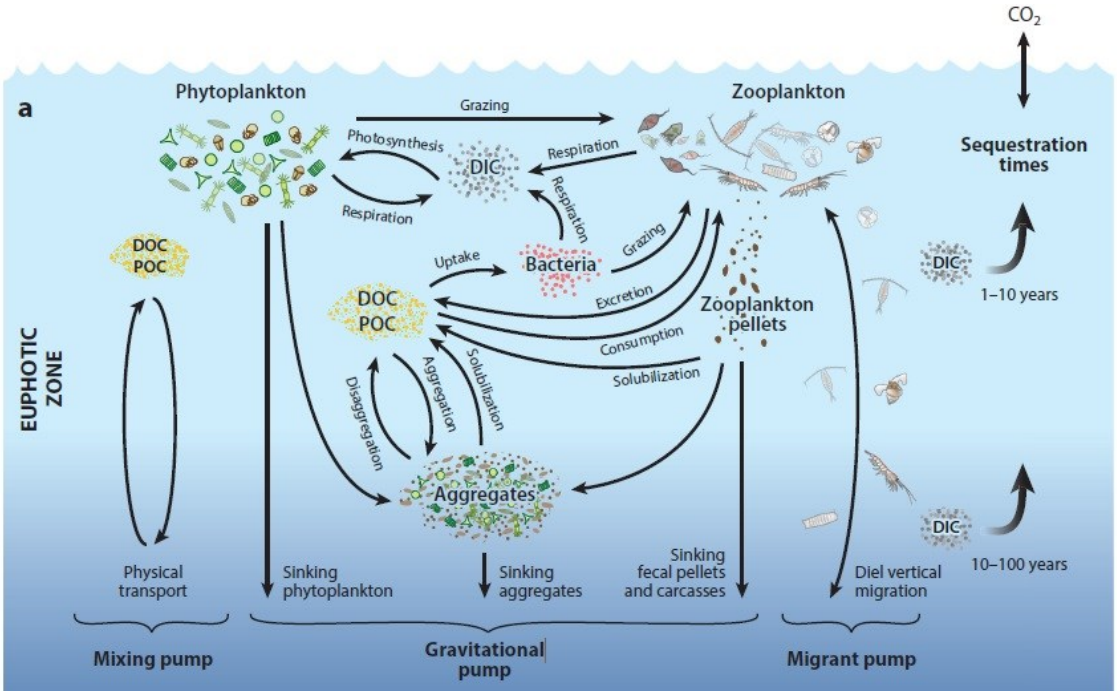


Fig.2: Schematic overview of the oceanic food web structure of the euphotic zone including relevant biochemical processes within the three different biological carbon pump types and the sequestration times of produced dissolved inorganic carbon as a depth related variable (Modified from Siegel et al. 2023).

1.3 AGGREGATE FORMATION

Aggregates in pelagic systems are ubiquitous and differ in their composition, size, and morphological structure, depending on their source material. The size range covered by marine aggregates is typically from 1 µm for picoplankton cells to quite a few centimeters for cyanobacterial filaments (Simon et al. 2002). The largest aggregates were observed in the Northern Adriatic Sea reaching several meters in diameter (Herndl et al. 1999). Because of the complex structure and shape of an aggregate, the size is a useful measure to classify aggregates into three major groups: (I) submicron particles (< 1 µm), (II) microscopic aggregates (1 – 500 µm), and (III) macroscopic aggregates (> 500 µm, also named marine snow) (Longhurst et al. 1992, Simon et al. 2002).

The formation of an aggregate and the resulting specific sinking velocity are one of the crucial processes within the biological carbon pump. Marine aggregates are mainly formed in the euphotic zone where phytoplankton is growing and reaching concentrations high enough to cause encounters between individual phytoplankton cells (Jackson and Kiørboe 2008). The formation of macroscopic aggregates often occurs at the end of a phytoplankton bloom when cell concentrations are highest and typically at depths immediately below the depth of chlorophyll maximum (Alldredge and Gottschalk 1989, Lampitt et al. 1993, Becquevort and Smith 2001). The availability of organic biomass is the initial step of aggregate formation, which is driven by a variety of physical and biological processes.

Physically induced aggregation takes place on small-scales and relies on brownian motion of submicron particles, shear forces of larger particles or turbulence, which brings the particles together and causes them to collide (Simon et al. 2002, Burd and Jackson 2009). In this way, polysaccharides can encounter and coagulate with particles, making them sticky. Another physical process is differential settling, which refers to the collision between two different particles with different sinking velocities i.e., the faster settling particle will encounter the slower sinking particle and, if the particles are sticky, they will form an aggregate (Simon et al. 2002, Burd and Jackson 2009, Fig. 3).

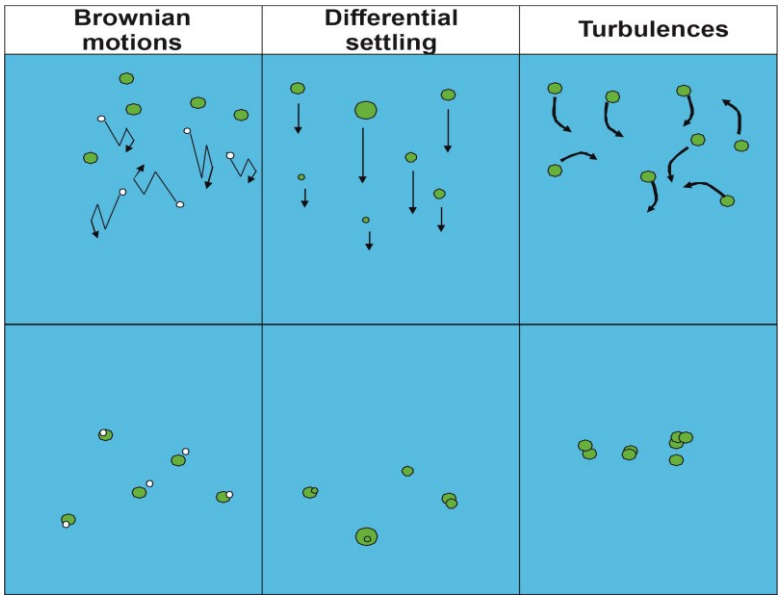


Fig.3: Schematic overview of the main processes inducing aggregate formation

In terms of biologically produced aggregates, zooplankton fecal pellets are very common in the ocean and is an efficient mechanism to package single cells into dense aggregates (Simon et al. 2002). Since fecal pellets are often very compact and dense, they can be efficient vehicles for carbon export due to their high carbon content and fast size-specific settling velocities (Lampitt 1990, Turner 2002, Turner 2015). The contribution of zooplankton fecal pellets to the export flux varies between 1 -100%, depending on region, season, and plankton community composition (Turner 2015). Additionally, some zooplankton form mucus structures such as feeding nets, which can be discarded and become a sinking aggregate that can have a substantial contribution to the total carbon export.

Appendicularians are producing mucus houses, which they use to capture food from the surrounding via a filtration system. Those houses consist of an outer coarse filter that captures large particles before the water is passed through an inner fine filter, which can capture particles < 2 μm (Deibel and Powell 1987, Lombard et al. 2011). The appendicularians ingest the fine filter with the captured particles. If the coarse filter is clogged up by a high concentration of large particles, appendicularians can jump out of the clogged houses and immediately inflate a new and already prepared house (Gorsky & Fenaux 1998, Sato et al. 2003). The abandoned house will deflate and start to sink and, hence, become part of the export flux (Lombard and Kiørboe 2010). Appendicularians are ubiquitous in the marine environment and are able to build up >20 houses per day (Alldredge and Silver 1988, Silver et al. 1998, Sato et al. 2001). Their contribution to the total export flux is estimated to be between 13 – 83 % (Hansen et al. 1996, Silver et al. 1998, Lombard and Kiørboe 2010). As another mucus producing zooplankton organism, pteropods form mucus feeding nets, which they use to capture sinking particles. These mucus nets are ingested together with the captured food particles by the pteropod. However, if the pteropods are interrupted by e.g., predators while their net is deployed, they discard the net in order to escape the predator and the net becomes a settling organic aggregate (Simon et al. 2002, Hunt et al. 2008, Iversen 2023).

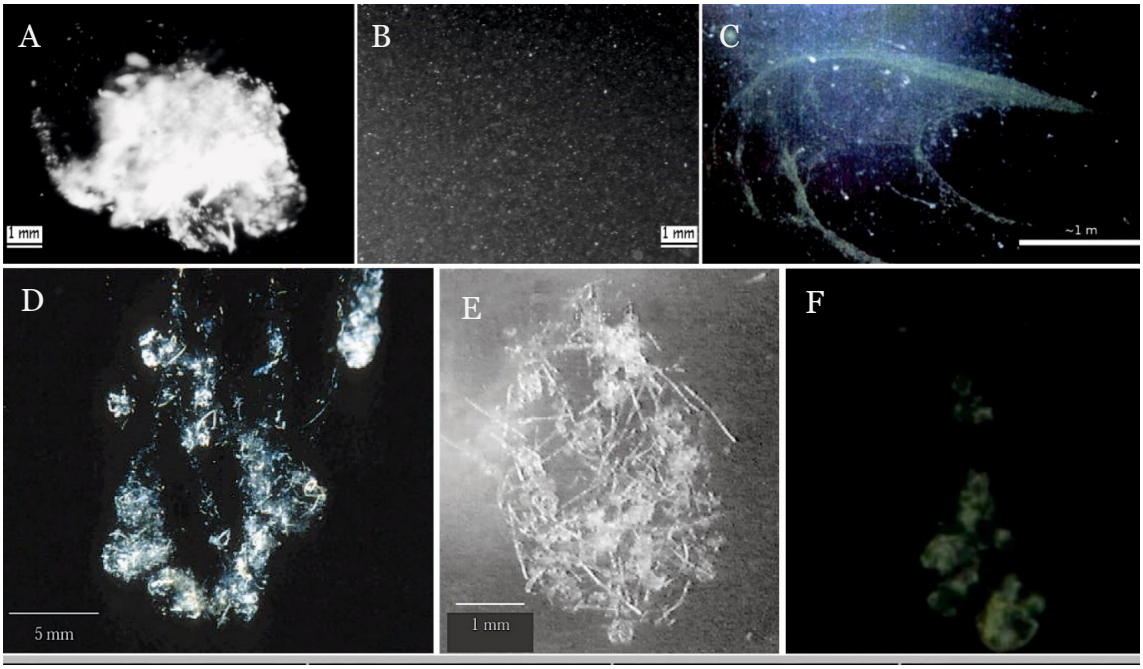


Fig. 4: Different aggregate types formed by a variety of phytoplankton: (A) in-situ photos of a macroaggregate from the pelagic, (B) microaggregates in shallow waters with high turbidity (Simon et al. 2002) and (C) a giant mucus aggregate formed in the northern Adriatic subjected to eddy activity (Stachowitsch 1984). In-situ pictures were taken of (D) an aggregate formed by diatoms with trapped fecal pellets, (E) an aggregate formed from Chaetoceros sp. (Kiorboe 2001), and (F) an aggregate formed by appendicularian mucus structures (Giménez et al. 2023).

Due to the high complexity of aggregation processes, which involves aggregation of phytoplankton cells and production of fecal pellets and mucus structures by zooplankton, aggregate composition is not uniformly across aggregate types (Fig. 4). This makes aggregates very heterogenous and they can be composed of a variety of different materials, including dead or living algae, diatom frustules, fecal pellets, mucus structures, detritus, lithogenic and biogenic material, cysts dinoflagellates, and cyanobacteria (Alldredge and Gottschalk 1989, Grossart and Simon 1993, Kiørboe et al. 1998, Simon et al. 2002, Fig. 4). Simon et al. (2002) mentioned that aggregates from the pelagic environment are mainly composed of diatoms, fecal pellets, larvacean houses, and miscellaneous material and typically there are large regional and temporal differences. Moreover, marine aggregates were found to act as a habitat for a broad range of bacteria with bacterial abundances three orders of magnitude higher within aggregates relative to the surrounding waters (Alldredge et al. 1986, Herndl 1988, Simon et al. 2002). Though Kiørboe (2000) showed that

the bacterial enrichment factor on aggregates decreases with increasing size, they are still considered hot-spots of microbial abundance and activity.

When considering aggregates that are formed via physical encounters and coagulation, the crucial steps are that the single particles reach high enough concentrations to have frequent encounters and that they are sticky enough to form aggregates. The success of these process is mainly defined by their coagulation efficiency also named stickiness (Jackson 1990, Kiørboe et al. 1990). The stickiness of particles is influenced by the excretion of extracellular polysaccharides (Passow 2000, Engel 2000), especially due to the production of transparent exopolymeric particles (TEP) (Alldredge et al. 1993, Engel 2000). TEP in the oceanic environment is mainly present in the form of discrete particles characterized by an enhanced stickiness coefficient ($\alpha>1$) (Chin et al. 1998, Engel 2000). Diatoms are known to produce high amounts of TEP at the end of a bloom period (Kiørboe and Hansen 1993, Engel 2000, Fukao et al. 2010). However, the TEP production is depending on the species composition, growth conditions, and nutrient availability (Engel 2000, Simon et al. 2002). Although TEP enhances aggregate formation, it will not directly enhance carbon export since TEP has low density and is neutral buoyant, hence high TEP amounts may decrease the excess density of an aggregate and, thus, reduce their size-specific sinking velocity (Alldredge 1999, Engel and Schartau 1999, Azetsu-Scott and Passow 2004). Nevertheless, TEP plays a key role in aggregate formation and in the efficiency by which organic aggregates scavenge suspended ballast material and increase settling of organic matter. As a result, TEP plays a crucial role in efficiency of the biological carbon pump and the magnitude carbon flux from the surface ocean to the deep sea.

1.4 IMPACT FROM ZOOPLANKTON ON CARBON FLUX

Often the efficiency of the biological carbon pump is measured as the ratio between particulate organic carbon flux and the rate of fixing CO_2 to organic carbon via primary production. Hence, the efficiency of the biological carbon pump is a measure for how well phytoplankton cells form aggregates, sink out of the euphotic zone, and are being grazed by zooplankton and remineralized by bacteria (Lutz et al. 2007, Buesseler and Boyd 2009, Iversen 2023). Typically, POC flux decreases with increasing depth and often this decrease is much more pronounced in upper

water column compared to the deep ocean, hence, POC flux profiles tend to follow a power-law or exponential decrease over depth (Suess 1980, Martin et al. 1987, Armstrong et al. 2001, Iversen 2023, Fig. 5). The time an aggregate is available for remineralization and consumption within a specific depth-interval is defined by the sinking velocity of the aggregate. Hence, aggregate settling velocity is often proportional to the magnitude of POC export (Boyd and Newton 1999). In general, the size, density and porosity of an aggregate are considered as controlling factors for size-specific sinking velocity of organic aggregates (Turner 2002, Iversen and Ploug 2010). Still, several factors can also have a direct influence on the size-specific sinking velocity of an aggregate. For example, TEP structures can lower the excess density and therefore the sinking velocity, whereas the incorporation of lithogenic and biogenic material, such as diatom silica frustules and calcium carbonate from coccolithophores, can enhance the sinking velocity of an aggregate (Iversen and Ploug 2010). The sinking velocities of macroaggregates range from <5 to several hundred meters per day (Alldredge and Gottschalk 1988, Kiørboe et al. 1994, Lombard and Kiørboe 2010). Due to their high density and compact structure, zooplankton fecal pellets sink rapidly through the water column. For example, pteropod and salp fecal pellets can reach sinking velocities > 2000 m d^{-1}, whereas the settling velocity of copepod fecal pellets only reach 220 m d^{-1}, depending on the copepod species that produced the fecal pellets and what the composition of the fecal pellets were (Turner 2002). Moreover, appendicularian houses, as an important component of macroscopic aggregates, are characterized by sinking velocities <200 m d^{-1} (Alldredge and Gottschalk 1988, Hansen et al. 1996, Sato et al. 2003). In terms of carbon export, the mucous houses of two abundant appendicularians were measured to contribute by 12- 83% to the total POC flux from the epipelagic (Lombard and Kiørboe 2010).

In general, zooplankton can enhance POC export due to passive mechanisms, including molts, carcasses, sinking feal pellets and released mucous structures. Additionally, since zooplankton are performing diel vertical migration, they can also contribute actively to the downward transport of organic carbon by feeding in the surface during night and producing fecal pellets and respiring at depth during day (Steinberg and Landry 2017). The passive versus active contribution to POC flux by zooplankton is difficult to quantify and tends to vary regionally and

temporally. For example, several studies have reported that zooplankton fecal pellets contribute <40% to the total POC flux via passive settling through the water column, however, the POC flux in the upwelling system off California was solely composed of fecal pellets during spring time (Stukel et al. 2013, Turner 2015). The proportion of fecal pellets to carbon export depends on species assemblage, zooplankton biomass and available food sources (Dagg et al. 2014), which in turn directly impact the carbon content and settling velocity of the produced fecal pellets. Some studies have suggested that the active transport of carbon via diel vertical migration is equal to that of passively settling fecal pellets (Longhurst et al. 1990, Steinberg et al. 2000, Steinberg and Landry 2017). Hence, it is possible that zooplankton play a great role for carbon export than we generally give them credit for.

1.5 CARBON FLUX ATTENUATION

Only 0.66 GtC of the annual primary production of 50 Gt C sinks to depths below 1000 m annually, which means that only a small fraction of the primary production has the potential to be sequestered in the oceans on time-scale beyond hundreds of years (Boyd et al. 2019, Henson et al. 2012, Iversen 2023). This poor efficiency of carbon export is due to intense degradation and grazing of the settling organic matter in the upper water column. Since the shape of the POC flux profiles are determined by a combination of biological degradation processes and physical settling processes, the prediction and description of remineralization profiles, as well as their mathematical expressions are highly debated (Martin et al. 1987, Middelburg 2019, Armstrong et al. 2001, Kriest and Oschlies 2008, Lauderdale and Cael 2021). A commonly used remineralization profile is a power-law function assuming that slow sinking and fragile particles are subjected to degradation processes in the first hundred meters of the water column and that most of the carbon loss occurs here, this remineralization profile is termed the Martin-curve (Martin et al. 1987) and described by the following function:

$$F(z) = F(z_0) * (\frac{z}{z_0})^{-b} \quad (1)$$

with $F_{(z)}$ as the POC flux at a specific depth z, POC flux $F_{(z0)}$ at depth z_0<z defined at the lower epipelagic and b as the flux attenuation exponent. The so called "Martin b parameter" is a combined measure for sinking velocity and

remineralization rate subjected to water depth (Middelburg 2019). There is a large body of research dedicated to identify the best fitting flux attenuation coefficient for the global, as well as regional, ocean. The study by Martin (1987) calculated a b value of 0.858, but these observations were restricted to the area of the Pacific Ocean. Several studies showed, that b is highly variable depending on region, temperature, aggregate composition, microbial community, and mineral ballasting (Guidi et al. 2015, Marsay et al. 2015, Armstrong et al. 2002, Boyd and Newton 1999, Gehlen et al. 2006). However, while the chase for the perfect b is ongoing, all studies agree that there is intense flux attenuation in the upper ocean, which gradually decreases with increasing depth. Iversen (2023), classified four depth layers with different attenuation rates and mechanisms by calculation the corresponding depth- and carbon-specific degradation rate (Cspec): (I) the upper mesopelagic (50 - 300 m) with the highest attenuation and the highest Cspec of 0.31 d^{-1} explained by an interplay of microbial remineralization and zooplankton grazing, (II) the mid mesopelagic (300 – 500 m) with a Cspec of 0.18 d^{-1}, (III) the lower mesopelagic (500 – 1000 m) with Cspec of 0.09 d^{-1} and (IV) the deep bathypelagic (>1000 m) with Cspec of 0.02 d^{-1} (Fig. 5). The decrease in carbon specific degradation correlates with decreasing zooplankton abundance at greater depth, indicating that microbial remineralization become increasingly more important for flux attenuation at depths below the lower mesopelagic (Stemmann et al. 2004, Iversen et al. 2010, Iversen 2023). Furthermore, the low attenuation at greater depth also indicates that microbial activity is limited due to decreasing temperature and increasing pressure (Tamburini et al. 2002, Iversen and Ploug 2013, Iversen 2023).

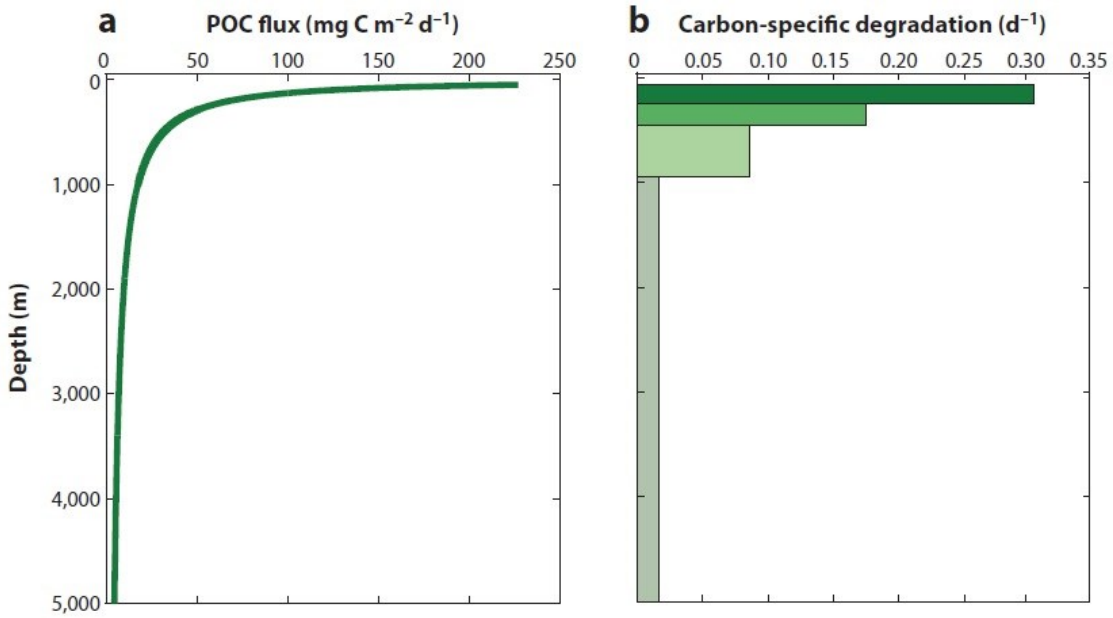


Fig.5: (a) Depth related POC flux plotted as vertical profiles from Martin et al. (1987). (b) Vertical profile of the flux attenuation defined by their depth dependent carbon specific degradation rates according to depth of 50-300m, 300 – 500m, 500 – 1000m and 1000 – 5000m (Iversen 2023).

1.6 ZOOPLANKTON MEDIATED FLUX ATTENUATION

Besides this positive influence of zooplankton on POC export, zooplankton also attenuates POC fluxes in the euphotic zone. The strong flux attenuation in the upper-water column often correlates with high zooplankton abundances (Jackson and Checkley 2011, Christiansen et al. 2018, Iversen 2023). Different mechanisms have been proposed regarding the role of zooplankton for flux attenuation. First, the so-called filter-feeders can directly control phytoplankton abundance in surface waters, which in turn reduce primary production and therefore also reduce POC flux to the deeper ocean (Hernández-León and Ikeda 2005, Iversen 2023). Second, zooplankton that directly feed on aggregates can cause fragmentation of large, fast sinking aggregates into small slow sinking ones, which extends their residence time in the upper water column and can thereby further increase the flux attenuation (Dilling et al. 1998, Iversen and Poulsen 2007, Cavan et al. 2021). Flux feeding zooplankton, such as polychaetes or pteropods, reduce the particle flux by intercepting sinking particles with their expanded feeding net structures, (Silver and Bruland 1981, Christiansen et al. 2018, Iversen 2023). Zooplankton can also reduce the efficiency of the biological carbon pump by directly feeding on settling fecal pellets, which both removes the organic matter from the export flux and also

fragment the pellets into smaller and slower settling fecal pellet parts. Furthermore, fragmentation of fecal pellets disrupts their peritrophic membrane and providing easier access for microbial degraders to the center of the pellets, which enhances degradation and decreases the efficiency of the biological carbon pump (Lampitt et al. 1990, Noji et al. 1991, Iversen and Poulsen 2007). The role of zooplankton for flux attenuation is highly variable and depends on seasons and regions where their contribution to flux attenuation varies between 8 - 70% (Steinberg et al. 2008, Van der Jagt et al. 2020, Iversen 2023). Within the euphotic zone it was estimated that zooplankton feeding is responsible for ingestion and turnover of 75 – 91% of the total primary production (Steinberg and Landry 2017). However, with increasing depth the importance of zooplankton for flux attenuation decreases and microbial remineralization becomes relatively more important.

1.7 THE ROLE OF MICROBES WITHIN THE BIOLOGICAL CARBON PUMP

Marine aggregates are habitats for diverse microbial communities, whereby the abundance is typically three orders of magnitude higher compared to the same volume of surrounding waters (Azam 1998, Herndl and Reinthaler 2013, Thiele et al. 2015). The aggregate associated microbial assemblages are composed of prokaryotes, nanoflagellates, ciliates, and heterotrophic flagellates (Alldredge 1986, Kiørboe 2001, Iversen and Robert 2015). The microbial carbon turnover during the settling of an aggregate relies on O_2 and nutrient availability and the DOM concentration (Simon et al. 2002, Ploug and Bergkvist 2015). Moreover, due to the decrease of Cspec degradation rates, which correlate with decreasing temperature and increasing pressure, it is assumed that microbial activity is conditional on these environmental factors (Grossart and Gust 2009, Nagata et al. 2010, Iversen and Ploug 2013). Some studies have shown that with increasing pressure, microbial respiration activity, as well as their extracellular enzyme activity decrease, but the composition of the microbial assemblage seems to be unaffected (Grossart and Gust 2009, Herndl and Reinthaler 2013, Stief et al. 2021). Therefore, it is assumed that aggregate associated microbes within aggregates collected in deeper waters originated from surface communities that colonized the aggregates during their formation in the surface ocean (Thiele et al. 2015, Bachmann et al. 2018). This in turn leads to the suggestion that microbial

remineralization activity is adapted to temperatures and pressures in surface waters.

More recently, the concept of the microbial carbon pump was introduced, which is based on the production of refractory DOC by microbes and that this refractory carbon can last several hundreds of years in the oceans and therefore contribute to carbon sequestration (Legendre et al. 2015). The production of such long-lived DOC fractions was found to be closely linked to heterotrophic respiration activity (Jiao et al. 2010, Jiao and Zheng 2011). Even other marine organisms can produce such long-lived DOC, for example due to phytoplankton exudation or viral lysis processes (Jiao and Azam 2011). How much the microbial carbon pump contributes towards carbon sequestration into the ocean interior is still not clear, due to knowledge gaps in transforming short term DOC into longer lived forms (Legendre et al. 2015). One attempt was done by Legendre et al. (2015), who calculated that the microbial carbon pump sequestered 0.18 Pg C $year^{-1}$, based on the assumption that primary production fixes 50 Pg C $year^{-1}$.

1.8 STOICHIOMETRY CHANGES WITHIN THE BIOLOGICAL CARBON PUMP

The central role of the biological carbon pump is the downward transport of carbon and nutrients in the forms of particulate organic matter (POM) and dissolved organic matter (DOM) from the surface ocean into the ocean interior. During the sinking, this organic material will be consumed, respired, transformed, or fragmented, which in turn releases DIC i.e., CO_2, and nutrients into the surrounding. It is widely accepted that the composition of POM that is produced by photosynthetic primary producers on average has a more or less constant molar ratio of C:N:P:O of 106:16:1 in terms of composition, also termed the Redfield ratio (Redfield et al. 1963). This ratio is subject to regional and seasonal variations, depending on the plankton community composition (Redfield et al. 1963). By measuring dissolved inorganic nutrients in marine environments, it was also shown that changes in the Redfield ratio were caused by remineralization (Anderson and Sarmiento 1994, Schneider et al. 2003) and the downward transport of DOC and inorganic nutrients through aggregates (Arrigo et al. 1999).

Most studies on stoichiometry of POM in marine environments focus on the carbon to nitrogen (C:N) ratio, which is fundamental to explain the relationship between the oceanic carbon and nitrogen cycle (Sterner et al. 1992, Oschlies et al. 2008, Martiny et al. 2013). Within particulate matter the C:N ratio varies regional and seasonal, but it generally seems to exceed that of the Redfield ratio (6.6) (Schneider et al. 2003, Sterner et al. 2008, Martiny et al. 2013). Martiny et al. (2013) reviewed five mechanisms that can causes variations in the C:N ratio of POM: (I) Nitrogen limitation tends to result in low amounts of nitrogen in the cells, which enhances the C:N ratio. (II) Low light irradiation hampers the accumulation of carbon polymers within phytoplankton, which decreases carbon relative to nitrogen and, hence, lowers the C:N ratio. (III) Nutrient stress during phytoplankton growth causes a negative relation of growth rate and cell-specific C:N ratio. It is assumed that the decrease in cellular C:N ratios is provoked by an accumulation of proteins and nucleic acid as well as a preventive nutrient storage. (IV) Variations in C:N ratio can be caused by phylogenetical differences and (V), the proportion of detritus to marine particles can alter the C:N ratio of sinking particles. Generally, the C:N ratios of POM increases with increasing depth, indicating a preferential mineralization of nitrogen compared to carbon at greater depth (Suess and Müller 1980, Schneider et al. 2003, Martiny et al. 2013).

Nitrogen and phosphate are the most limiting factors for primary production since they are often only present in low concentrations in the sunlit surface ocean. At low-latitudes, the surface oceans are mainly characterized by a constant nutrient limitation during phytoplankton blooms. Nitrogen and phosphate are immediately consumed by phytoplankton and repacked into sinking aggregates. Due to ocean circulation, upwelling systems and episodical eddy activity, those nutrients return in surface waters in oceanic equatorial regions (Deutsch und Weber 2012). Redfield and colleagues (1963) observed that the average N:P ratio (NO_3^-:PO_4^{3-}) in the open ocean is close to the N:P ratio of surface phytoplankton. It was found that nitrogen and phosphate were enriched in dissolved organic material relative to carbon (Church et al. 2002), whereby phosphate showed much more variability in the concentration due to faster turnover rates and the nitrogen pool seems to be more stable (Clark et al. 1998, Abell et al. 2000, Torres-Valdes et al. 2009). Moreover, the role of N:P within the export flux was intensively studied in the last

decades (Rubin et al. 1998, Arrigo et al. 2002, Deutsch and Weber 2012). Weber and Deutsch (2012) observed that the N:P drawdown shows a spatial distribution with an increasing ratio from the Antarctic to subantarctic zone. In the Antarctic zone low N:P (10:1) ratios within the export were found to correlate with diatom blooms (Rubin et al. 1998, Green and Sambrotto 2006, Deutsch and Weber 2012), whereas high N:P (20:1) ratios of the export flux were found in regions dominated by *Phaeocystis antarctica*, indicating that the prevalent phytoplankton assemblage is also having a main impact on the stoichiometry of the exported organic matter and the removal of nutrients from the surface ocean (Arrigo et al. 1999). In general, with increasing depth the N:P ratio decreases to values below the Redfield ratio (Deutsch and Weber 2012).

1.9 REGIONAL DIFFERENCES IN CARBON EXPORT AND SEQUESTRATION

The high variability of the biological pump in terms of carbon export and sequestration efficiency is closely linked to regional variations in primary production, remineralization, sinking velocity, and input of ballast minerals (Buesseler 1998, Neuer et al. 2002, Iversen 2023). The work of this thesis comprises two different areas, the Porcupine Abyssal Plain (PAP) in the North-East Atlantic and the Southern Ocean. Due to pandemic restriction, it was not possible to get in-situ data from the Southern Ocean due to cancelled or postponed cruises. Therefore, in the following section the differences of these ecosystems, with focus on the biological carbon pump, will be explained. Both regions are characterized by high variability in POC transfer into the mesopelagic and sequestration efficiency (Cavan et al. 2019).

There are strong seasonal differences in carbon export in the temperate Northeast Atlantic, where the spring bloom is dominated by diatoms, which can enhance carbon export due to their silicate frustules (Cavan et al. 2019). In contrast the summer bloom is mainly composed of smaller dinoflagellates, which do not form biominerals and therefore not ballast themself, implying that they sink slower than diatom aggregates and, hence are potentially more efficiently degraded in the water column (McQuatters-Gollop et al. 2007, Cavan et al. 2017). Moreover, the collection of settling POM by deep ocean sediment traps during a spring bloom revealed little transformation of the settling organic matter (Honjo and Manganini

1993, Buesseler and Boyd 2009). This may be due to lower abundance of heterotrophic bacteria in the euphotic zone during the spring bloom, while summer events often have higher numbers of heterotrophic bacteria (Colebrook 1979, Cavan et al. 2019). Additionally, or as an alternative explanation, calcifying organisms, such as coccolithophores and foraminifera, could also have ballasted the settling aggregates via their production of calcium carbonate and caused the formation of aggregates with high settling velocities, which resulted in rapid sinking, high flux events (Daniels et al. 2018, Cavan et al. 2019). This is similar to the sporadic dust input from the Sahara Dessert where intense export events take place due to efficient ballasting (Iversen et al. 2010, Nowald et al. 2015, Van der Jagt et al. 2018). Overall, the total carbon export for the region of the North Atlantic is 37.7 g C m^{-2} yr^{-1}, whereby the gravitational pump is less important compared to other carbon pumps covering only 17% of the total export. The main part of carbon export with 26% of the total POC export in the North Atlantic can be explained by the mixing pump (Nowicki et al. 2022).

The Southern Ocean shows a strong seasonality regarding POC export. While summer has high primary production and relatively high POC export, winter is mainly characterized by low primary production and carbon export (Buesseler 1998, Hill and Cota 2005). In comparison to the Atlantic Ocean, the POC export and sequestration is mainly due to the gravitational pump, whereby zooplankton fecal pellets contribute >50% of the POC export (Nowicki et al. 2022). Combined, fecal pellets and sinking phytoplankton aggregates account for 75% of the total carbon sequestration in the Southern Ocean. Regions with high POC export in the Southern Ocean were mainly dominated by *Chaetoceros* sp. and large phytoplankton species, whereas other regions were dominated by smaller phytoplankton, like *Phaeocystis antarctica* (Smetacek et al. 1984, Schoemann et al. 2005). Generally, regions in the Southern Ocean, which are characterized by high POC production via primary production do not correlate with high carbon export efficiency. Only a small proportion of POC reaches depth >200 m (Noji et al.1999), whereby the high flux attenuation is supposed to be caused by zooplankton grazing of both phytoplankton and settling aggregates (Cavan et al. 2019).

1.10 OBJECTIVES OF THIS THESIS

In the last the biological carbon pump gained much interest, due to its high relevance for atmospheric CO_2 drawdown by the oceans. However, in consequence of the high complexity and reliance on variable factors, like regionality and seasonality, operational parameters in the biological carbon pump are not fully understood yet. Specifically, grey shaded areas remain in topics of, aggregate formation drivers, carbon flux attenuation, aggregate composition, and influencing factors on sinking velocity. During my PhD, I performed laboratory experiments with Antarctic phytoplankton and used *in-situ* measurements from the Porcupine Abyssal Plain with reference to crucial steps in the biological carbon pump. To reveal uncertainties and fill knowledge gaps, this thesis addressed unsolved queries regarding aggregate formation, zooplankton-aggregate interactions, aggregate stoichiometry and settling velocity from a biological perspective. The overall questions in this thesis were:

I. How does nutrient availability impact aggregate formation?
II. How do gelatinous zooplankton and bacteria mediate flux attenuation?
III. What causes changes in the stoichiometry?
IV. How is the sinking velocity of aggregates impacted by changes in oceanic community structures?

2. MANUSCRIPTS

LIST OF MANUSCRIPTS

MANUSCRIPT 1

Nutrient depletion induces aggregation of Phaeocystis antarctica

Anna Biastoch, Morten H. Iversen, Jack J. Middelburg

Authors contribution: conceptualized by AB, MHI and JJM; laboratory work performed by AB; data analysis performed by AB and MHI; writing by AB under supervision of MHI and JJM

In advanced state of submission

MANUSCRIPT 2

The role of pelagic appendicularians and pteropods for carbon export and flux attenuation over the Porcupine Abyssal Plain, Northeast-Atlantic

Anna Biastoch, Richard S. Lampitt, Corinne Pebody, Jack J. Middelburg, Morten H. Iversen

Authors contribution: sample collection by MHI, RSL and CP; measurements by MHI and CP; data analysis AB, MHI and CP ; writing by AB supervised by MHI and JJM with contribution from RSL and CP

In advanced state of submission to Limnology and Oceanography

MANUSCRIPT 3

Phaeocystis antarctica, an underestimated key driver of the biological carbon pump

Anna Biastoch, Morten H. Iversen, Lubos Polerecky, Jack J. Middelburg

Authors contribution: conceptualized by all authors; laboratory work performed by AB; data analysis performed by AB and LP; writing by AB supervised by MHI and JJM with contribution from LP

In preparation

CONTRIBUTIONS TO OTHER MANUSCRIPTS

Three-dimensional visualization of marine snow using magnetic resonance imaging

Steffen Swoboda, Ekkhard Küstermann, Gerhard Bartzke, Ricarda Gatter, Nasrollah Moradi, Anna Biastoch, Wolfgang Dreher, Morten H. Iversen

Authors contribution: conceptualized by SS, EK, GB, WD, NM and MHI; laboratory work performed by SS and AB; magnetic resonance imaging, processing and analysis performed EK, SS, RG and GB; flow model analyses performed by GB; data analysis performed by SS with contributions from GB and EK; writing by SS with contribution from all authors

In preparation

MANUSCRIPT 1. NUTRIENT DEPLETION INDUCES AGGREGATION OF *PHAEOCYSTIS ANTARCTICA*

Anna Biastoch, Morten H. Iversen, Jack J. Middelburg

ABSTRACT

The biological carbon pump (BCP) is a key driver in ocean's carbon sequestration via its formation and export of organic aggregates. Aggregate formation in the upper ocean is the first crucial step that determines the efficiency of the BCP. Multiple processes are involved in aggregate formation, for which the driving factors governing still remain unclear, but nutrient depletion towards the end of phytoplankton blooms seem to increase aggregate formation. To test this, we investigated the role of macronutrient availability for aggregate formation in order to stimulate phytoplankton conditions at the end of a bloom. Our study showed that aggregate formation, size-distribution, composition, and morphology is affected by nutrient availability. While whitish aggregates indicate the presence of *Phaeocystis antarctica* structures and empty diatom frustules, yellowish aggregates were an indication of living diatoms. Size-specific sinking velocity were related to macronutrient concentration and showed high variability, which was related to TEP concentration and ballasting effects. The absence of macronutrients increased the total aggregate volume due to high production of transparent exopolymeric particles (TEP). Though TEP concentrations increased over time under nutrient replete conditions, this did not result in elevated aggregation formation or increase volume of the formed aggregates. Hence, high TEP concentrations alone does not result in high aggregate formation. Accordingly, TEP was produced irrespective of nutrient availability, but aggregate formation was primarily taking place during nutrient depleted conditions. Co-depletion of multiple nutrients resulted in higher aggregate volume than single nutrient depletion or no nutrient depletion.

INTRODUCTION

The biological carbon pump (BCP) is a major pathway for the downward transport of particulate organic carbon and thus plays an important role in atmospheric CO_2 uptake by the oceans. The BCP is a combination of processes that causes photosynthetically produced particulate organic carbon to form settling aggregates and subsequently sink from surface waters to the ocean interior (Volk and Hoffert 1985, Falkowski et al. 1998, Ducklow & Steinberg 2001, Turner 2015). The efficiency of the BCP is mainly driven by aggregate formation, their size-specific sinking velocity, and their susceptibility to degradation (De La Rocha and Passow 2007, Passow and Carlson 2012, Petrou et al. 2016). The efficiency of the BCP may change due to future climate change, which in turn may impact ocean CO_2 uptake (Wohlers et al. 2009, Steinacher et al. 2010, Barange et al. 2017). The direction and strength of this climate feedback is poorly understood, but it is expected that increased stratification in the surface ocean will cause less upward mixing of nutrients, causing nutrient depletion and changes in plankton community composition.

Sinking particulate organic matter appears in the form of marine snow (particles with diameters > 0.5 μm) and fecal pellets (e.g., Turner 2002). Marine snow is mainly formed via coagulation of inorganic matter, phytodetritus, living organisms, and colloids (Alldredge and Silver 1988). Several factors determine the process of aggregation, including particle concentration, stickiness of the individual particles, and their collision frequency (McCave, 1984; Jackson, 1990, Karakas et al. 2009), which in turn depend on plankton community composition and physical forces within the water column (Kiorboe et al. 1990, Kiorboe and Hansen 1993, Guidi et al. 2009). Aggregate formation from phytoplankton cells is stimulated by increasing the stickiness of cells (Hill, 1992; Riebesell and Wolf-Gladrow, 1992, Kiorboe and Hansen 1993). Several studies have demonstrated that the stickiness of phytoplankton cells differs among species (Kiorboe et al. 1990, Kiørboe and Hansen, 1993; Waite et al., 1997). Transparent exopolymeric particles (TEP) play a major role in aggregate formation of phytoplankton cells (Alldredge et al. 1993, Engel 2000, Passow 2002). TEP is a ubiquitous structure in the oceans and has a sticky character (Alldredge et al. 1993, Engel 2000, Engel et al. 2004), which is thought to enhance the efficiency of the BCP by intensifying the process of aggregate formation (Passow and Alldredge 1994, Kiorboe et al. 1994, Jackson

1995, Jackson and Burd 1998). However, recent studies demonstrated that high TEP concentrations do not always correlate with a high efficiency of the biological carbon pump (Passow et al. 2001, Mari et al. 2017, Prairie et al. 2019), indicating that other factors are involved as well.

Diatoms are known to secrete generous amounts of exopolymeric substances during bloom conditions (Becker 1996, Passow and Alldredge 1995 a, Mari 1999, Engel 2000, Leandro et al. 2003). However, all diatom blooms do not culminate in aggregate formation, implying that TEP alone does not cause aggregation and that other factors like environmental conditions, prevailing diatom species, and the nature of secreted polysaccharides also play a role (Kiørboe et al. 1990, Passow 2002, Grossart et al. 2006). Moreover, the secretion of sticky polysaccharides is usually enhanced at the end of a diatom bloom, when cells become nutrient limited (Passow and Alldredge 1994, Engel 2000, Fukao et al. 2010, Kahl et al. 2008). Another phytoplankton group playing a key role in the ocean's carbon cycle is the ubiquitous haptophyte *Phaeocystis spp.*, hereafter Phaeocystis (Smith et al. 1991, Riebesell et al. 1995, Moisan et al. 1998, Schoemann et al. 2005, Verity et al., 2007). Due to their ability to fix high amounts of carbon during blooms (Smith et al. 1991, Thingstad and Billen 1994, Hamm et al. 1999, Solomon et al. 2003, Schoemann et al. 2005, Rousseau et al. 2007) as well as their release of copious amounts of organic carbon into the surrounding waters, Phaeocystis is a key driver in ocean biogeochemistry (Alderkamp et al. 2007, Hamm et al. 1999, Schoemann et al. 2005, Verity et al., 2007, Bender et al. 2018). Phaeocystis has a complex lifecycle including two dominant manifestations: (1) single flagellated cells and (2) colonies, where a high number of cells are embedded in a gelatinous matrix consisting of mucopolysaccharides (Becquevort et al. 1998, Hamm et al. 1999, Hamm 2000, Schoemann et al. 2005). When these colonial forms of Phaeocystis become nutrient depleted, the colonies break apart and release high amounts of sticky mucus material into the surrounding waters (Rousseau et al. 1994, Riebesell et al. 1995, Reigstad et al. 2000, Schoemann et al. 2005). In this way, Phaeocystis could have a high impact on aggregate formation via coagulation.

Here, we study the process of aggregate formation induced by nutrient reduction. We assembled a community consisting of two diatom species and one Phaeocystis species common to Antarctic waters, *Phaeocystis antarctica*, and exposed them to different nutrient conditions to induce aggregate formation. We determined aggregate characteristics, including morphology, size, and sinking velocity, as well as changes in TEP concentration and residual nutrient concentrations.

MATERIAL & METHODS

Cultures and incubation

Cultures of *Pseudo-nitzschia turgidula* (Hustedt) Hasle 1993, *Chaetoceros debilis* Cleve 1894, and the colony forming *Phaeocystis antarctica* Karsten 1905 were grown for 21 days at 2°C in sterile filtered seawater (salinity 33) that was supplemented with nutrients according to f/2 (Guillard, 1975). Cultures were exposed to a light:dark cycle (16:8h) with a light intensity of 150 µmol photons m^{-2} s^{-1}. The three phytoplankton cultures were combined at a ratio of 1:1:1 and at a total density of 21000 cells ml^{-1}. This phytoplankton assemblage was incubated in roller tanks (Plexiglas cylinder: diameter = 14 cm, height = 7.5 cm, Volume = 1.15 L). The roller tanks were rotated at 3 rpm (rotation per minute) on a roller table, which was kept in the dark at 2°C. We tested a range of nutrient concentrations in artificial seawater for the roller tank incubations (Table 1) .

Table 1: List of treatments used for the roller tank incubations.

Nutrient concentration	Abbreviation
Full Nutrient concentration following f/2	f/2
Half of nutrient concentration following f/2	f/4
No Nutrients	f/0
f/2 with Nitrate reduction by 50%	N
f/2 with Phosphate reduction by 50%	P
f/2 with Trace element reduction by 50%	TE
f/2 with Silicate reduction by 50%	Si
f/2 with Vitamin reduction by 50%	Vi
f/2 with Nitrate and Phosphate reduction by 50%	N+P
f/2 with Nitrate and Trace Element reduction by 50%	N+TE
f/2 with Phosphate and Trace element reduction by 50%	P+TE

Aggregate morphology and total aggregate volume

After aggregates had formed in the roller tanks, we picked individual aggregates and measured their size before we gently destroyed the aggregate by shaking it in a falcon tube that was filled with artificial seawater. A subsample was collected from the known volume of destroyed and diluted aggregate and the phytoplankton cells were counted and identified using a Sedgewick Rafter counting chamber. For the colony forming *Phaeocystis antarctica,* colonial cell number was determined from the colony volume following the equation of Mathot et al. (2000):

$$Vc = 417 * Nc^{1.67} \quad (2)$$

with Vc describing the Volume of a colony and Nc the Number of cells within a colony.

For the determination of aggregate abundance and morphology the roller tanks were gently rotated by 90° and placed with the bottom side on top of a Perspex disc. The aggregates were allowed to settle on the bottom for 30 min and a picture was taken with a Sony camera (Sony α 6000, f/3.5) from below. Images were analyzed with the free software Fiji version 1.53-c (Schindelin et al. 2012). The equivalent spherical diameter (ESD) of an aggregate was calculated from its specific area (A), estimated with the polygon tool in Fiji, using the following equation:

$$ESD = 2 * \sqrt{\frac{A\,(Aggregate)}{\pi}} \quad (3)$$

Sinking velocity

Aggregate sinking velocity was estimated from aggregate orbits in rotating roller tanks, which were identified from images captured by a Sony camera (Sony α 6000) for at least two full orbits of an aggregate. This method relies on the assumption that aggregates at steady states follow specific orbital trajectories (Tooby et al. 1977). Under this precondition the sinking velocity can be calculated using the following equation (Tooby et al. 1977, Jackson 1994):

$$x_b = \frac{w_s * T}{2 * \pi} \quad (4)$$

with x_b (cm) defined as the distance from the aggregate specific orbital center to the center of the roller tank, ws as the sinking velocity in cm d^{-1} and T as the rotation

period (s). The x and y positions of an aggregate on their orbit were determined using the MTrackJ plugin (Meijering et al. 2012) in Fiji. For the calculation of the orbit center from the analysed positions we used the method published in Ploug et al. (2010).

Transparent exopolymeric particles

Transparent exopolymeric particles (TEP) concentrations were measured using the semi-quantitative method described by Passow and Alldredge (1995b). From each incubation we sampled between 50 and 100 ml water without aggregates to estimate the suspended TEP concentration. Additionally, we sampled and analysed TEP from between 25 and 50 ml of an aggregate slurry. All samples were taken in triplicate and gently filtered onto 0.4 µm polycarbonate filters (Whatman, Maidstone, England). The filters were stained with 1 ml Alcian Blue solution (0.02%, pH=2.5) for 5 s to stain mucopolysaccharides and rinsed with milliQ water. After staining, each filter was transferred into a 10 ml glass cuvette that was filled with 6 ml 80% H_2SO_4 and left for at least 2 h. The cuvettes were gently shaken every 30 min to ensure dissolution of the Alcian Blue solution from the filters. After dissolution, the filters were removed and the concentration of dissolved Alcian Blue was determined spectrophotometrically at 787 nm. TEP concentrations were calculated in relation to polysaccharide Xanthan Gum standard and reported with the unit xanthan gum equivalents per liter (µg XG eq L^{-1}).

Inorganic nutrients

To assess changes in dissolved nutrients, water without aggregates was sampled from each treatment and filtered through a combusted GF/F filter (Whatman, 0.7 µm pore size). 50 ml of the filtrate was immediately frozen and stored in the dark until further analysis at the ZMT in Bremen. Inorganic nutrients within the background water were analyzed with a TECAN-plate reader (version 1.14). Phosphate (PO_4^{3-}), silicate ($Si(OH)_4$), nitrite (NO_2^-), and the total amount of nitrite and nitrate (NO_x^-) were analyzed spectrophotometrically, whereas ammonium (NH_4^+) concentration was determined fluorometrically. Nitrate was quantified by subtracting NO_2^- from NO_x^-.

RESULTS

Aggregate morphology and total aggregate volume

Nutrients had a major impact on aggregate morphology and volume for all treatments, whereas incubations with vitamin reduction did not result in aggregate formation. Total aggregate volume was smallest for the f/2 and Si reduction treatments and highest for the no-nutrient addition treatment (f/0). Furthermore, we observed a steady increase in total aggregated volume with nutrient reduction, which showed the lowest total aggregate volume for f/2, intermediate total aggregate volume for f/4, and the highest total aggregate volume for f/0. Generally, all treatments had aggregates larger than 1 mm^3 contributing most to the total aggregate volume.

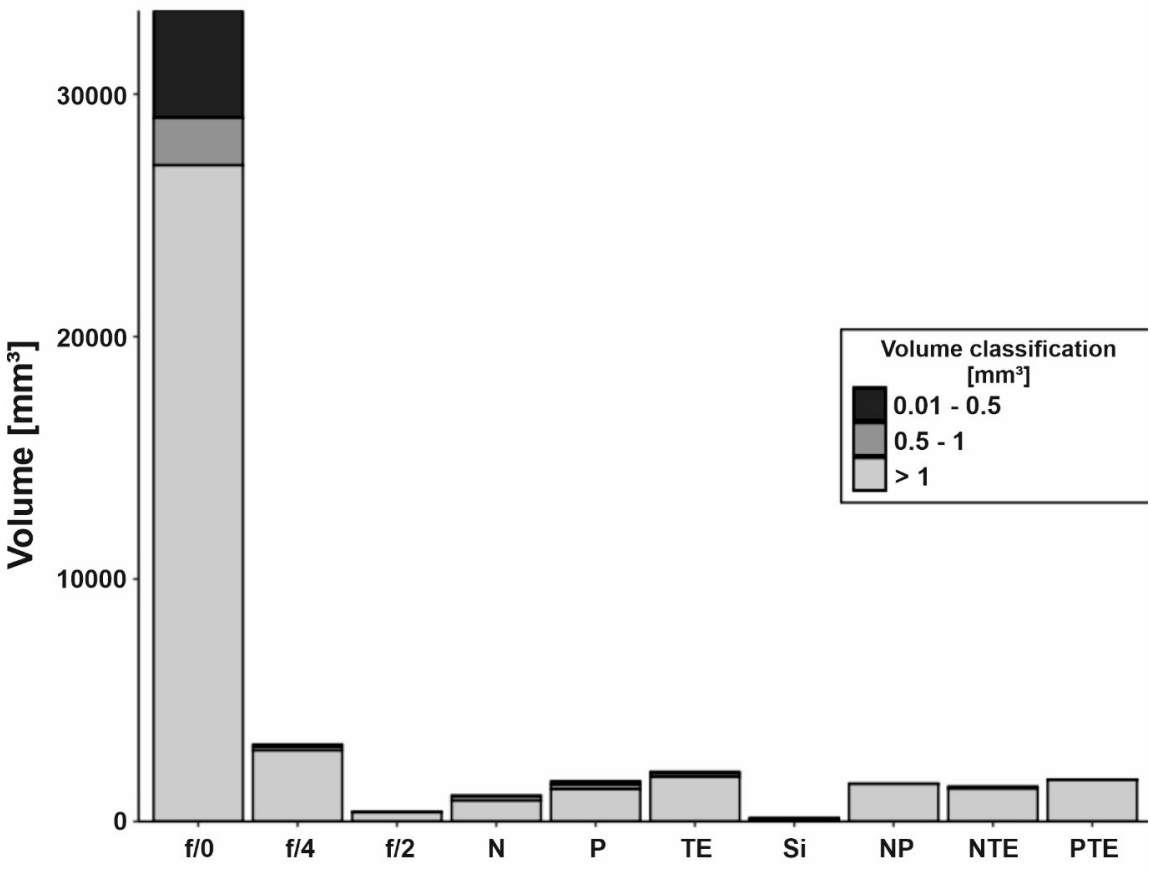
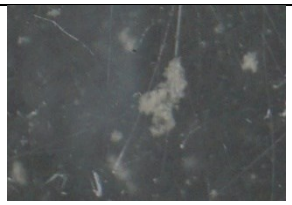
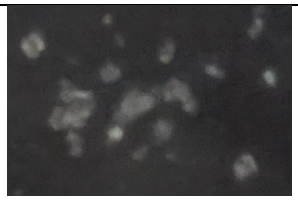
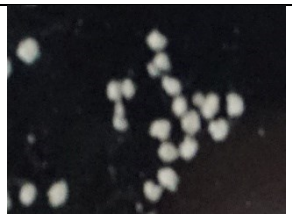
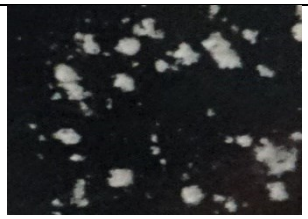
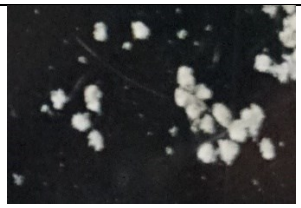
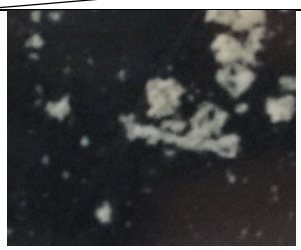
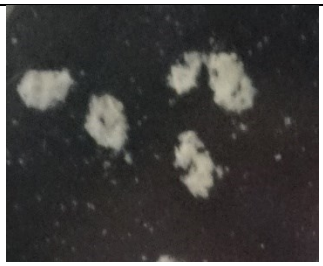


Fig. 6: Total aggregated volume within the different nutrient reduction treatments determined after 24 h with optical measurements.

Nutrient reduction caused changes in aggregate colour from yellow-white (f/2) to yellow (f/4) and white for single nutrient reductions (N, P, TE, Si) and full nutrient reduction (f/0). Aggregates formed during co-reduction of two nutrients simultaneous (NP, NTE, PTE) were yellow-white. These colour changes were accompanied with changes in aggregate compactness, e.g., from fluffy for f/2 to compact in f/4, N, P, TE and N+TE reductions (Table 2). It is important to note that camera settings were all set to manual and light conditions for the photos captured for all the treatments.

Table 2: Aggregate characterisation in terms of morphology for nutrient manipulation treatments determined by optical measurements through a constant camera set up

Treatment	Picture	Characterization
f/2		• yellow and white • fluffy
f/4		• yellow • compact
f/0		• white • fluffy • dense clouds
N		• white • compact
P		• white • compact

TE		• white • compact
Si		• white • fluffy
Vi		
N+P		• yellow and white • compact and fluffy
N+TE		• yellow and white • compact
P+TE		• yellow and white • compact and fluffy

Sinking velocity

Nutrient reduction treatments had major impact on aggregate size and size-specific sinking velocity. The slowest size specific sinking velocities were determined for the aggregates that were formed within the full nutritional treatment (f/2) and within the treatment that had reduced Si, both treatments had settling velocities below 50 m d^{-1}. In contrast, highest sinking velocities were observed in the treatments with reduced N, P and PTE, as well as in the treatment where all nutrients were reduced by half (f/4). The majority of the formed aggregates had ESDs ranging between 0.5 and 2.5 mm. Only the PTE and f/2 treatments formed

aggregates with ESDs up to 4 mm. Correlations between ESD and sinking velocities were poor to moderate for most treatments ($R^2 \leq 0.25$), while co-reductional treatments (NP, NTE, PTE) showing moderate to high correlations. Comparing among treatments, all treatments showed significant differences in ESDs and size-specific sinking velocities using a significance level of $p<0.01$ (Kruskal-Wallis; Table S1).

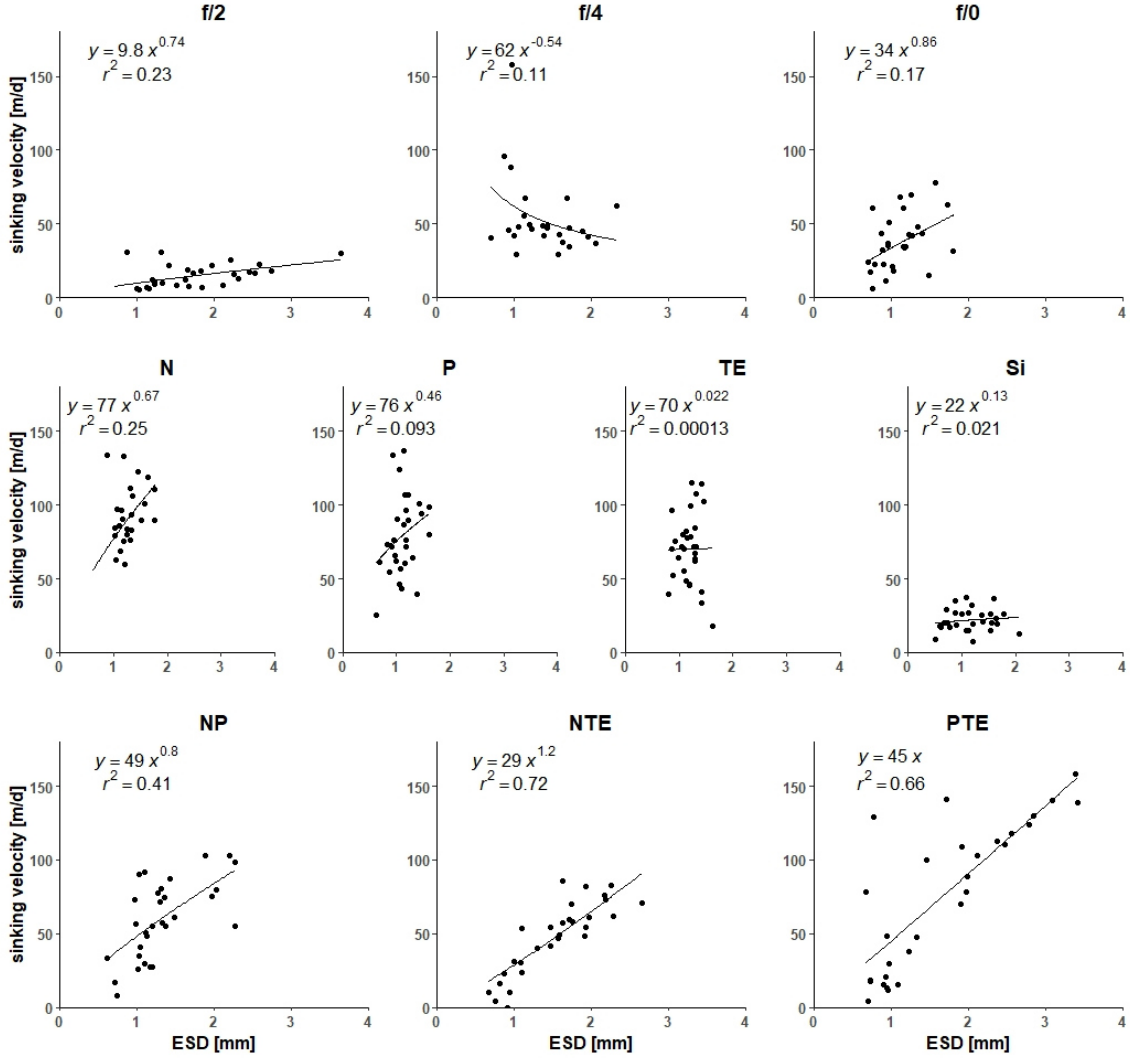


Fig. 7: Relationship of aggregate size (ESD in mm) and their specific sinking velocity (m d^{-1}) after 24 h of incubation in roller tank for the different nutrient reduction treatments. The correlation of size and settling velocity within the treatments is displayed by a power law function and the corresponding R^2 value.

Transparent exopolymeric particles

Total final TEP concentrations were highest in both the full f/2 and lowest f/0 nutrient treatments and lowest for the treatments TE, NP and PTE. Normalising TEP concentration per mm^3 aggregate revealed that the highest final TEP concentration relative to aggregate volume was for the treatment's f/2 and Si. All other treatments showed values under 1.2 µg Xeq mm^{-3} aggregate with the lowest for f/0. We observed significant differences in TEP concentrations between t0 and t1 for all aggregates and all treatments showed significant different total TEP concentrations at t1 when compared to the f/0 treatment (t-test; $p<0.05$). Considering the non-aggregated TEP, all treatments showed significantly similar TEP concentrations when using a significance level of $p<0.01$ (t-test), however, when tested at a significance value of $p<0.05$, TEP concentrations in f/0 showed significantly higher TEP concentrations compared to the TEP concentrations in the treatment with reduced nitrogen (- N) (Table S1).

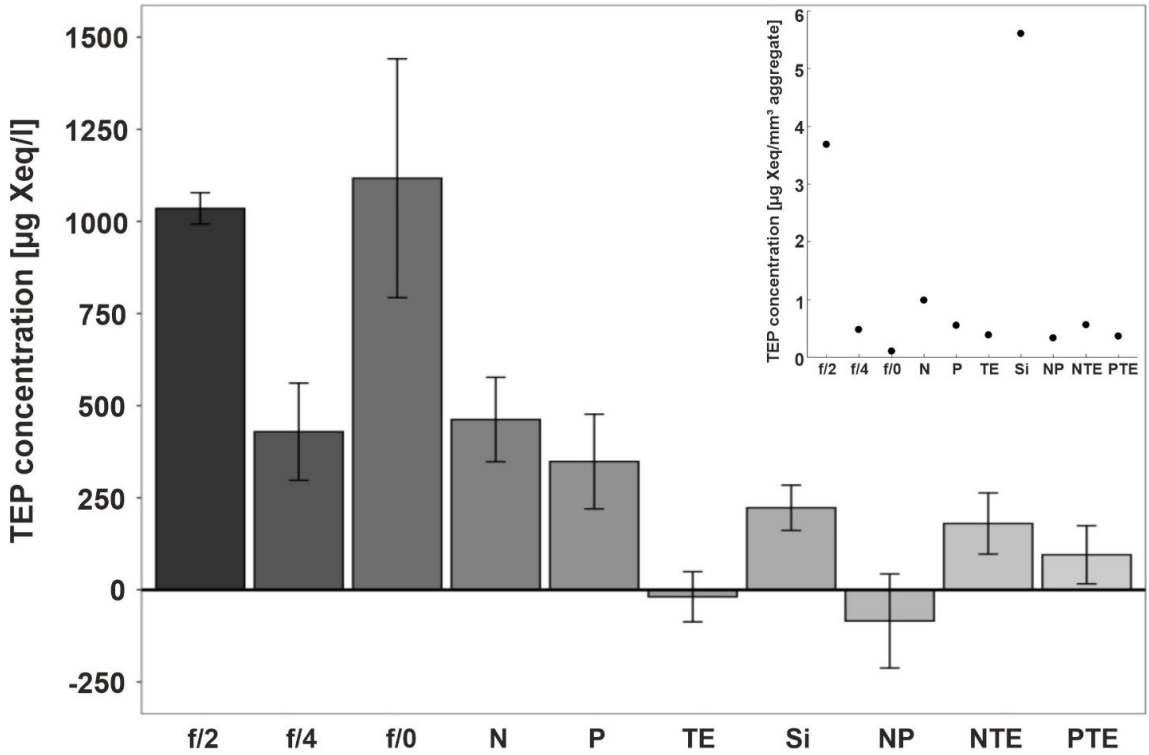


Fig. 8: Changes in TEP concentration after 24 hours for the different nutrient reduction treatments. Positive values describe an increase over time, while negative values describe a decrease. The incorporated plot shows TEP values normalized to the average aggregate volume within different treatments.

Inorganic nutrients

The nutrient concentrations revealed a few remarkable trends: (1) the f/0 treatment showed an increase in nitrate, nitrite, ammonium, and silicate and a decrease in phosphate. (2) Nitrogen reduction resulted in nitrate, ammonium, phosphate, and silicate release. (3) Phosphor reduction was accompanied by nitrate, nitrite, and ammonium consumption as well as phosphate and silicate release. (4) Trace element reduction induced nitrogen and phosphate uptake, but silicate release. (5) Silicate was released to solution for all single nutrient reductional treatments (N, P, TE, Si) and full reduction (f/0), while it was taken up for treatments with co-nutrient reductions (NP, NTE, PTE). Significant differences could be observed for the treatments at each timepoint (Kruskal-Wallis or ANOVA, $p<0.05$) with the exception of nitrite (Table S1).

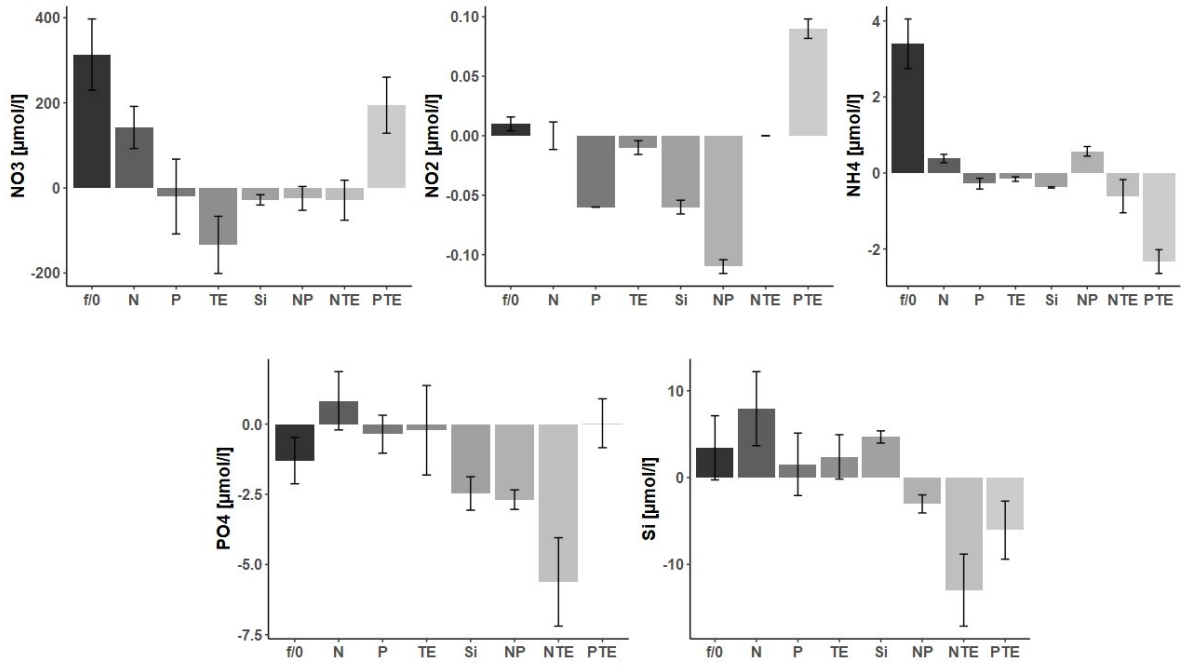


Fig. 9: Changes in inorganic nutrients between the start and after 24 hours of incubation. Positive values describe an increase and negative values describe a decrease in nutrients during the 24 h incubation.

DISCUSSION

We assembled a community of three phytoplankton species that are commonly found in Antarctic surface waters and studied how nutrient deficiency impacts their aggregate formation and aggregate characteristics. Aggregation of phytoplankton often occurs during at the end of phytoplankton blooms when nutrients and/or trace metals become limited (Kiorboe et al. 1990, Passow 2002, Thornton 2002, Prairie et al. 2019), however, the impact of single or combinations of various nutrients on aggregation dynamics is poorly understood.

Reduction of specific nutrients had a major impact on aggregate morphology, color, and density. Single nutrient reductions (N, P, TE) resulted in the formation of highly compact aggregates, whereas aggregates that were formed in other nutritional treatments (Si, NP, PTE, f/0) showed a looser structure. While aggregates that were formed in the f/2, f/4, and every co-reduction treatment appeared yellowish, aggregates formed under single nutrient reduction and the f/0 treatment had a more whitish color. In general, aggregate morphology is mainly defined by size, shape, and porosity, which in turn is influenced by factors such as surface roughness and permeability (Laurenceau-Cornec et al. 2015, Trudnowska et al. 2021). Of course, aggregate composition also relies on several other factors in natural environments, including the prevailing phytoplankton assemblage, released TEP structures, as well as water properties such as stratification, turbulence, and shear (Alldredge et al. 1990, Rousseau et al. 1994, Laurenceau-Cornec et al. 2015, Takeuchi et al. 2019). Flocculation's of the phytoplankton *Chaetoceros gracilis* were found to be more loosely structured with a high amount on mucilage components compared to aggregates formed from *Nitzschia angularis* (Crocker and Passow, 1995). Moreover, aggregates formed from *Chaetoceros spp.* were loosely with inconsistent shapes (Zetsche et al. 2020). Ploug et al. (2002) also observed a less compact structure for aggregates formed from *Chaetoceros sp.,* irrespective of whether they originated from in-situ samples or formed in roller tanks from batch cultures. Microscopic observations of in-situ aggregates showed, that yellow-colored aggregates tend to include living diatom cells (observation made by M. H. Iversen). Conversely, Hamm and Rousseau (2003) observed, that aggregates formed through the matrix material from *Phaeocystis globosa* appeared grey colored with irregular shapes and a sticky mucus envelop (Rousseau et al. 1994, Putt et al. 1994, Becquevort et al. 1998, Garrison et al. 1998). A

comparison of our findings and literature observations is not straightforward, because aggregate morphology was highly variable between the different nutritional treatments. Elucidating the relative importance of phytoplankton species identity and type of nutrient limitation on aggregate morphology appears to be challenging, in particular given the co-variances and the many parameters influencing aggregate size, structure, and morphology. However, yellow colored aggregates appear to indicate the presence of living diatom cells, while white colored aggregates are likely to include mainly *P. antarctica*, the matrix from *P. antarctica* colonies, and empty frustules of diatoms.

Largest total aggregate volume was observed in the treatment with full nutrient depletion (f/0). Increasing nutrients from f/0 over f/4 to f/2 caused a steady decrease in particle volume. Reduction of one or two nutrients caused a modest increase in aggregate volume, with the lowest total aggregate volume observed for the Si reduction treatment. Diatoms are known to be efficient in forming aggregates (Smetacek 1985, Alldredge and Silver 1988, Kranck and Milligan, 1988; Riebesell 1991, Thornton 2002). Diatom aggregation is induced via coagulation and cell stickiness and relies on encounters between cells i.e., is proportional to the squared cell concentration and with coagulation dependent on the stickiness of the cells, which is increased by the production of TEP (Riebesell 1991, Alldredge et al. 1993, Passow and Alldredge. 1994, Passow et al. 2001, Grossart et al. 1997, Engel 2004, Mari et al. 2017). Multiple studies have shown that *Chaetoceros sp*. plays a crucial role in the formation of settling aggregates and, thus, downward vertical carbon fluxes in the open oceans (Logan and Alldredge, 1989; Kiørboe and Hansen 1993; Passow and Alldredge 1994; Logan et al. 1995). Kiorboe et al. (1990) showed a correlation between cell stickiness and nutrient depletion for phytoplankton cells. This was shown for the species *Chaetoceros debilis*, which only form aggregates under nutrient limitation (Logan and Alldredge 1989). The aggregation potential of *Phaeocystis sp*. and its role in the biological carbon pump seems more complex because Phaeocystis aggregates are mainly formed at the end of a bloom, when the colonies are senescent (Rousseau et al. 1994, Putt et al. 1994, Becquevort et al. 1998, Garrison et al. 1998). For example, *Phaeocystis pouchetii* formed aggregates when the senescent colonies fell apart and high amounts of TEP were released (Riebesell et al. 1995, Reigstad et al. 2000). It is also known that

Phaeocystis sp. colonies are neutrally buoyant, which in turn means that aggregates formed from *Phaeocystis sp.* colonies need to be ballasted in order to have densities higher than seawater and thereby be able to settle out of the mesopelagic zone (Skreslet 1988, Becquevort and Smith 2001, Jakobson and Tang 2002, Wang and Tang 2010). As a consequence, *Phaeocystis sp.* formed aggregates that sink to depths deeper than 100 m are very heterogenous, consisting of diatoms, ciliates, nanoflagellates, mucus structures and Phaeocystis cells (Weisse et al. 1994, Passow and Wassmann 1994). Several studies reported that senescence of intact *Phaeocystis sp.* colonies were induced under light and nutrient limitation (van Boekel et al. 1992, Schoemann et al. 2005, Smith Jr. and Trimborn 2023), resulting in high TEP concentration, which encourage the formation of fast sinking aggregates in combination with ballasting material. Massive deposition of *Phaeocystis sp.* derived material to the seafloor has been observed in polar regions (Wassmann et al. 1990, Asper and Smith 1999, DiTullio et al. 2000). However, most of the *Phaeocystis sp.* related material is readily remineralized in the upper ocean (Von Bodungen 1986, Passow and Wassmann 1994, Sweeney et al. 2000, Reigstad and Wassmann 2007), with the consequence that Phaeocystis is thought to have a limited role in carbon transfer to the deep sea. *Chaetoceros debilis* and Phaeocystis have the ability to induce aggregation at the end of a bloom i.e., during periods where nutrients are depleted. Consistently our results, showed that nutrient depletion enhances the total volume of formed aggregates.

Highest TEP concentration and production were observed for the nutrient depleted treatment f/0. The same treatment also had the highest total particle volume. However, TEP production was also high in the nutrient replete f/2 treatment, but this was associated with low particle volume. Diatoms are known to steadily excrete TEP structures during their growth phase (Myklestad 1974, Decho 1990). Passow et al. (2004) showed that the aggregation process of *Chaetoceros gracilis* is predominantly induced by TEP released structures. In the Adriatic and Tyrrhenian Sea, TEP rich structures were associated with the presence of the diatoms *Chaetoceros sp.* and *Nitzschia sp.* (Schuster and Herndl 1995, Alldredge and Crocker 1995, Radic et al. 2005, De Philippis et al. 2005). Moreover, the release of TEP triggered aggregation of diatoms and other particles and facilitates the downward transport of organic matter (Crocker and Passow 1995), including

particles that otherwise would never sink. Several studies showed that exopolymeric particle excretion by diatoms is enhanced when they become nutrient limited (Myklestad 1974, Myklestad et al. 1989, Corzo et al. 2000, Deng et al. 2016). Corzo et al. (2000) found evidences that nitrogen limited cultures of *Chaetoceros sp*. excrete a large proportion of TEP in comparison to nutrient replete cultures. It is also known that colonial *Phaeocystis spp*. contribute greatly towards the TEP pool in the oceans (Riebesell et al., 1995; Reigstad et al., 2000, Schoemann et al. 2005, Mari et al. 2005). TEP production appears to occur continuously for *Phaeocystis sp*. colonies during their growth as well as by colony disruption mainly caused by senescence (Verity et al. 1991, Alderkamp et al. 2005, Mari et al. 2005, Li et al. 2023). *Phaeocystis antarctica* colonies are known to produce more TEP during a bloom in comparison to coastal diatom blooms through the disruption of the colonial matrix (Hong et al. 1997). In a mesocosm experiment, *Phaeocystis globosa* produced TEP at concentrations between 60 to > 1500 µg Xan. Eq. L^{-1} (Mari et al. 2005), consistent with our results where TEP concentration never exceed 1200 µg Xan. Eq. L^{-1} with the exception of the f/0 treatment. The function of TEP within biological carbon pump has received much interest because it is considered as a key factor within the aggregation (Passow and Alldredge 1995 a , Engel 2000, Passow 2002, Engel 2004). Here, we show that TEP is produced during nutrient replete conditions (f/2), but with limited aggregation, while nutrient reduction caused high TEP production and high aggregation.

The highest correlation between size (ESD) and settling velocity was observed for nutritional treatments with co-reductions (NP, NTE, PTE; Fig. 7). Additionally, single nutrient reductions showed more compact aggregates (Table 2) and had ESDs below 2 mm. Sinking velocities of aggregates are affected by shape, density, and composition (Alldredge and Gotschalk, 1988, De La Rocha and Passow 2007, Iversen and Ploug 2010, Bach et al. 2019, Laurenceau-Cornec et al. 2020). Aggregates that are primarily formed from the diatom *Chaetoceros sp*. tend to have slow sinking velocities, presumably caused by high amounts of TEP structures embedded in their porous spaces (Zetsche et al. 2020). TEP is characterized by its low density (Engel and Schartau 1999, Prairie et al. 2019) and near-neutral buoyancy (Azetsu-Scott and Passow 2004; Mari et al. 2017), which lower the excess density of an aggregate and consequentially also results in low sinking velocities.

Prairie et al. (2019) observed that the growth phase of phytoplankton affected the TEP release with higher secretion during the later growth phase. Diatom aggregates are ballasted by their own silica frustule material, positively influencing their settling to greater depth (Passow and De La Rocha 2006, Engel et al. 2009, Bach et al. 2016). In comparison, Phaeocystis colonies that do not contain ballast material have low sinking velocities (Van Boekel et al. 1992, Ploug et al. 1999, Becquevort and Smith 2001). As an example, Becquevort and Smith Jr. (2001) measured sinking velocities between 0 and 1 m d^{-1} for non-ballasted Phaeocystis aggregates in the Ross Sea. In comparison, aggregates formed from Chaetoceros in the laboratory showed sinking velocities between 13 and 123 m d^{-1} (Engel and Schartau 1999). The different treatments in our study showed high variations in size-specific sinking velocities, which is a direct result of the different excess densities of the aggregates due to different amounts of TEP and ballast material (in our case diatom cells) within the aggregates.

Monitoring of dissolved nutrient changes allowed us to identify patterns in nutrient dynamics among treatments. In the nutrient depleted f/0 treatment dissolved nitrogen increased via increasing concentrations of ammonium, nitrate, and nitrite, while the treatments of P, TE, and Si showed removal of available nitrogen sources. Aggregates in marine environments are known as nutritional hot spots, especially for carbon- and nitrogen sources (Shanks and Trent 1979, Alldredge 1979, Alldredge and Cohen 1987). When these aggregates are remineralized by attached heterotrophic bacteria, ammonia is released into the surrounding waters (Glibert et al. 1988). Moreover, under increasing light irradiance diatoms release dissolved nitrogen compounds with highest rates for ammonia (Lomas et al. 2000). Such release of nitrogen sources has not been reported for Phaeocystis colonial species or Phaeocystis derived materials. On the contrary, several studies reported that Phaeocystis colonies remove nitrate and ammonia from the surrounding waters as they grow (Smith 1993, Cochlan and Bronk 2001, Arrigo et al. 2002, Tungaraza et al. 2003, Wang et al. 2011). Less is known about the impact from nutrient limitation on the nitrogen cycling within aggregates and most studies have addressed the change in photochemical activity of phytoplankton and resulting changes in carbon cycling under nutrient limitation (Myklestad and Haug 1972, Myklestad et al. 1989, Myklestad 1995, Corzo et al.

2000, Berman-Frank et al. 2007). Based on our observations, it seems that nutrient reduction affects the composition of the aggregates and potentially the attached bacterial assemblage, which then in turn impact nitrogen and carbon cycling. Another interesting observation was that silica concentrations were reduced over time in all co-nutritional reductions (NP, NTE, PTE), while dissolved silicate increased in the single nutrient reduction treatments (N, P, TE) and full reduction (f/0) treatments. It is known that the cellular silica content of diatoms relies on several conditions, including temperature, salinity, and nutrient concentrations (Paasche 1980, Martin-Jézéquel et al. 2000, Milligan et al. 2004). Consequently, an uptake of dissolved silicate from the water is likely due to the presence of living diatom cells within aggregates, while silicate release might reflect diatom cells degradation or dissolution (Oehler 1979, Nelson et al. 1995, Passow et al. 2003, Treguer and De La Rocha 2013, Treguer et al. 2021). Accordingly, it appears that nutritional co-reductions (NP, NTE, PTE) had living Chaetoceros cells, which contributed to the aggregation, while the single nutrient reductions (N,P, TE) or a total lack of nutrients (f/0) had fewer active diatoms and the aggregation was mainly mediated by Phaeocystis and then ballasted by diatoms.

Aggregate formation and settling involve multiple processes. This study showed the important role of nutrient availability for aggregate formation, composition, and size-specific settling velocity. Specifically, we observed that reduction of macronutrients encouraged the process of aggregation. Furthermore, we were able to show that high TEP concentrations do not always result in high aggregate volume. Additionally, our results revealed that living diatoms play a more important role in aggregation during co-nutritional reductions compared to situations where only one nutrient was depleted. Understanding the process of aggregation and therefore the first step of the biological carbon pump, is the key towards a better understanding of the efficiency in carbon sequestration in the oceans. This study focused on phytoplankton species living in the Southern Ocean. The Southern Ocean account for 20% of the global oceans (Boyd, 2002) and takes up 40% of the global athropogenic carbon emission (Mikaloff Fletcher et al. 2006, Khatiwala et al. 2009). Future climate conditions will yield changes in the prevailing phytoplankton assemblage in the Southern Ocean. Especially the Marginal Ice Zone (MIZ) is predicted to have a loss in sea-ice coverage, which will

make this region accessible to wind induced mixing (Flynn et al. 2023). Thus, it is likely that more light will penetrate a well-mixed future Southern Ocean, which will favor those species which are better adapted towards changes in light irradiances, such as *Phaeocystis antarctica (*Trimborn et al. 2017, Trimborn 2019, Nissen and Vogt 2021). In this scenario, Phaeocystis could become more abundant within the MIZ region and we hypothesize that this will result in a loss in natural ballasting material originating from Chaetoceros frustules. The lack of ballasting will hamper the potential of aggregates to sink to greater depth and resulting in a less efficient biological carbon pump.

ACKNOWLEDGEMENTS

This work was conducted in the framework of the HGF Infrastructure Program FRAM of the Alfred-Wegener-Institute Helmholtz Center for Polar and Marine Research. This work was part of the Helmholtz Program "Changing Earth—Sustaining our Future" supported by the Helmholtz Program-Orientated Funding (POF IV) to topic 6 (Marine Life) and the sub-topic 6.3 (The Future Biological Carbon Pump). The work was funded by DFG-Research Center/Cluster of Excellence "The Ocean Floor—Earth's Uncharted Interface": EXC-2077-390741603.

CONFLICT OF INTEREST

The authors have no conflict of interest.

REFERENCES

Alderkamp, A. C., Buma, A. G., & van Rijssel, M. (2007). The carbohydrates of Phaeocystis and their degradation in the microbial food web. Biogeochemistry, 83, 99-118.

Alldredge, A. L. (1979). The chemical composition of macroscopic aggregates in two neretic seas 1. Limnology and Oceanography, 24(5), 855-866.

Alldredge, A. L., & Cohen, Y. (1987). Can microscale chemical patches persist in the sea? Microelectrode study of marine snow, fecal pellets. Science, 235(4789), 689-691.

Alldredge, A. L., & Crocker, K. M. (1995). Why do sinking mucilage aggregates accumulate in the water column?. Science of the total environment, 165(1-3), 15-22.

Alldredge, A. L., & Gotschalk, C. (1988). In situ settling behavior of marine snow 1. Limnology and Oceanography, 33(3), 339-351.

Alldredge, A. L., & Silver, M. W. (1988). Characteristics, dynamics and significance of marine snow. Progress in oceanography, 20(1), 41-82.

Alldredge, A. L., Granata, T. C., Gotschalk, C. C., & Dickey, T. D. (1990). The physical strength of marine snow and its implications for particle disaggregation in the ocean. Limnology and Oceanography, 35(7), 1415-1428.

Alldredge, A. L., Passow, U., & Logan, B. E. (1993). The abundance and significance of a class of large, transparent organic particles in the ocean. Deep Sea Research Part I: Oceanographic Research Papers, 40(6), 1131-1140.

Asper, V. L., & Smith Jr, W. O. (1999). Particle fluxes during austral spring and summer in the southern Ross Sea, Antarctica. Journal of Geophysical Research: Oceans, 104(C3), 5345-5359.

Azetsu-Scott, K., & Passow, U. (2004). Ascending marine particles: Significance of transparent exopolymer particles (TEP) in the upper ocean. Limnology and oceanography, 49(3), 741-748.

Bach, L. T., Boxhammer, T., Larsen, A., Hildebrandt, N., Schulz, K. G., & Riebesell, U. (2016). Influence of plankton community structure on the sinking velocity of marine aggregates. Global Biogeochemical Cycles, 30(8), 1145-1165.

Bach, L. T., Stange, P., Taucher, J., Achterberg, E. P., Algueró-Muñiz, M., Horn, H., ... & Riebesell, U. (2019). The influence of plankton community structure on sinking velocity and remineralization rate of marine aggregates. Global Biogeochemical Cycles, 33(8), 971-994.

Barange, M., Butenschön, M., Yool, A., Beaumont, N., Fernandes, J. A., Martin, A. P., & Allen, J. I. (2017). The cost of reducing the North Atlantic Ocean biological carbon pump. Frontiers in Marine Science, 3, 290.

Becker, K. (1996). Exopolysaccharide production and attachment strength of bacteria and diatoms on substrates with different surface tensions. Microbial ecology, 32, 23-33.

Becquevort, S., & Smith Jr, W. O. (2001). Aggregation, sedimentation and biodegradability of phytoplankton-derived material during spring in the Ross Sea, Antarctica. Deep Sea Research Part II: Topical Studies in Oceanography, 48(19-20), 4155-4178.

Becquevort, S., Rousseau, V., & Lancelot, C. (1998). Major and comparable roles for free-living and attached bacteria in the degradation of Phaeocystis-derived organic matter in Belgian coastal waters of the North Sea. Aquatic Microbial Ecology, 14(1), 39-48.

Bender, S. J., Moran, D. M., McIlvin, M. R., Zheng, H., McCrow, J. P., Badger, J., ... & Saito, M. A. (2018). Colony formation in Phaeocystis antarctica: connecting molecular mechanisms with iron biogeochemistry. Biogeosciences, 15(16), 4923-4942.

Berman-Frank, I., Rosenberg, G., Levitan, O., Haramaty, L., & Mari, X. (2007). Coupling between autocatalytic cell death and transparent exopolymeric particle production in the marine cyanobacterium Trichodesmium. Environmental microbiology, 9(6), 1415-1422.

De La Rocha, C. L., & Passow, U. (2007). Factors influencing the sinking of POC and the efficiency of the biological carbon pump. Deep Sea Research Part II: Topical Studies in Oceanography, 54(5-7), 639-658.

Cochlan, W. P., & Bronk, D. A. (2001). Nitrogen uptake kinetics in the Ross Sea, Antarctica. Deep Sea Research Part II: Topical Studies in Oceanography, 48(19-20), 4127-4153.

Corzo, A., Morillo, J. A., & Rodríguez, S. (2000). Production of transparent exopolymer particles (TEP) in cultures of Chaetoceros calcitrans under nitrogen limitation. Aquatic Microbial Ecology, 23(1), 63-72.

Crocker, K. M., & Passow, U. (1995). Differential aggregation of diatoms. Marine ecology progress series. Oldendorf, 117(1), 249-257.

De Philippis, R., Faraloni, C., Sili, C., & Vincenzini, M. (2005). Populations of exopolysaccharide-producing cyanobacteria and diatoms in the mucilaginous benthic aggregates of the Tyrrhenian Sea (Tuscan Archipelago). Science of the total environment, 353(1-3), 360-368.

De Tommasi, E., Gielis, J., & Rogato, A. (2017). Diatom frustule morphogenesis and function: a multidisciplinary survey. Marine genomics, 35, 1-18.

Decho, A. W. (1990). Microbial exopolymer secretions in ocean environments: their role (s) in food webs and marine processes. Oceanogr Mar Biol Annu Rev, 28(7), 73-153.

Deng, W., Cruz, B. N., & Neuer, S. (2016). Effects of nutrient limitation on cell growth, TEP production and aggregate formation of marine Synechococcus. Aquatic Microbial Ecology, 78(1), 39-49.

DiTullio, G. R., Grebmeier, J. M., Arrigo, K. R., Lizotte, M. P., Robinson, D. H., Leventer, A., ... & Dunbar, R. B. (2000). Rapid and early export of Phaeocystis antarctica blooms in the Ross Sea, Antarctica. Nature, 404(6778), 595-598.

Drapeau, D. T., Dam, H. G., & Grenie, G. (1994). An improved flocculator design for use in particle aggregation experiments. Limnology and oceanography, 39(3), 723-729.

Ducklow, H. W., Steinberg, D. K., & Buesseler, K. O. (2001). Upper ocean carbon export and the biological pump. Oceanography, 14(4), 50-58.

Engel, A. (2000). The role of transparent exopolymer particles (TEP) in the increase in apparent particle stickiness (α) during the decline of a diatom bloom. Journal of Plankton Research, 22(3), 485-497.

Engel, A. (2004). Distribution of transparent exopolymer particles (TEP) in the northeast Atlantic Ocean and their potential significance for aggregation processes. Deep Sea Research Part I: Oceanographic Research Papers, 51(1), 83-92.

Engel, A., & Schartau, M. (1999). Influence of transparent exopolymer particles (TEP) on sinking velocity of Nitzschia closterium aggregates. Marine Ecology Progress Series, 182, 69-76.

Engel, A., Szlosek, J., Abramson, L., Liu, Z., & Lee, C. (2009). Investigating the effect of ballasting by CaCO3 in Emiliania huxleyi: I. Formation, settling velocities and physical properties of aggregates. Deep Sea Research Part II: Topical Studies in Oceanography, 56(18), 1396-1407.

Falkowski, P. G., Flagg, C. N., Rowe, G. T., Smith, S. L., Whitledge, T. E., & Wirick, C. D. (1988). The fate of a spring phytoplankton bloom: export or oxidation?. Continental Shelf Research, 8(5-7), 457-484.

Fernandez, E., Serret, P., de Madariaga, I., Harbour, D. S., & Davies, A. G. (1992). Photosynthetic carbon metabolism and biochemical composition of spring phytoplankton assemblages enclosed in microcosms: the diatom-Phaeocystis sp. succession. Marine ecology progress series. Oldendorf, 90(1), 89-102.

Flynn, R. F., Haraguchi, L., McQuaid, J., Burger, J. M., Mutseka Lunga, P., Stirnimann, L., ... & Fawcett, S. E. (2023). Nanoplankton: The dominant vector for carbon export across the Atlantic Southern Ocean in spring. Science Advances, 9(48), eadi3059.

Fukao, T., Kimoto, K., & Kotani, Y. (2010). Production of transparent exopolymer particles by four diatom species. Fisheries science, 76(5), 755-760.

Garrison, D. L., Gowing, M. M., & Hughes, M. P. (1998). Nano-and microplankton in the northern Arabian Sea during the Southwest Monsoon, August–September 1995 A US–JGOFS study. Deep Sea Research Part II: Topical Studies in Oceanography, 45(10-11), 2269-2299.

Gehlen, M., Beck, L., Calas, G., Flank, A. M., Van Bennekom, A. J., & Van Beusekom, J. E. E. (2002). Unraveling the atomic structure of biogenic silica: evidence of the structural association of Al and Si in diatom frustules. Geochimica et Cosmochimica Acta, 66(9), 1601-1609.

Glibert, P. M., Dennett, M. R., & Caron, D. A. (1988). Nitrogen uptake and NH4+ regeneration by pelagic microplankton and marine snow from the North Atlantic. Journal of Marine Research, 46(4), 837-852.

Grossart, H. P., Simon, M., & Logan, B. E. (1997). Formation of macroscopic organic aggregates (lake snow) in a large lake: The significance of transparent exopolymer particles, plankton, and zooplankton. Limnology and Oceanography, 42(8), 1651-1659.

Grossart, H. P., Czub, G., & Simon, M. (2006). Algae–bacteria interactions and their effects on aggregation and organic matter flux in the sea. Environmental Microbiology, 8(6), 1074-1084.

Guidi, L., Stemmann, L., Jackson, G. A., Ibanez, F., Claustre, H., Legendre, L., ... & Gorskya, G. (2009). Effects of phytoplankton community on production, size, and export of large aggregates: A world-ocean analysis. Limnology and Oceanography, 54(6), 1951-1963.

Guillard, R. R. (1975). Culture of phytoplankton for feeding marine invertebrates. In Culture of marine invertebrate animals: proceedings—1st conference on culture of marine invertebrate animals greenport (pp. 29-60). Boston, MA: Springer US.

Hamm, C. E., Simson, D. A., Merkel, R., & Smetacek, V. (1999). Colonies of Phaeocystis globosa are protected by a thin but tough skin. Marine Ecology Progress Series, 187, 101-111.

Hamm, C. E. (2000). Architecture, ecology and biogeochemistry of Phaeocystis colonies. Journal of Sea Research, 43(3-4), 307-315.

Hamm, C. E., & Rousseau, V. (2003). Composition, assimilation and degradation of Phaeocystis globosa-derived fatty acids in the North Sea. Journal of Sea Research, 50(4), 271-283.

Hill, P. S. (1992). Reconciling aggregation theory with observed vertical fluxes following phytoplankton blooms. Journal of Geophysical Research: Oceans, 97(C2), 2295-2308.

Hong, Y., Smith Jr, W. O., & White, A. M. (1997). Studies on transparent exopolymer particles (Tep) produced in the Ross Sea (Antarctica) and by Phaeocystis antarctica (Prymnesiophyceae) 1. Journal of Phycology, 33(3), 368-376.

Iversen, M. H., & Ploug, H. (2010). Ballast minerals and the sinking carbon flux in the ocean: carbon-specific respiration rates and sinking velocity of marine snow aggregates. Biogeosciences, 7(9), 2613-2624.

Jackson, G. A. (1990). A model of the formation of marine algal flocs by physical coagulation processes. Deep Sea Research Part A. Oceanographic Research Papers, 37(8), 1197-1211.

Jackson, G. A. (1994). Particle trajectories in a rotating cylinder: implications for aggregation incubations. Deep Sea Research Part I: Oceanographic Research Papers, 41(3), 429-437.

Jackson, G. A. (1995). Comparing observed changes in particle size spectra with those predicted using coagulation theory. Deep Sea Research Part II: Topical Studies in Oceanography, 42(1), 159-184.

Jackson, G. A., & Burd, A. B. (1998). Aggregation in the marine environment. Environmental science & technology, 32(19), 2805-2814.

Jakobsen, H. H., & Tang, K. W. (2002). Effects of protozoan grazing on colony formation in Phaeocystis globosa (Prymnesiophyceae) and the potential costs and benefits. Aquatic Microbial Ecology, 27(3), 261-273.

Kahl, L. A., Vardi, A., & Schofield, O. (2008). Effects of phytoplankton physiology on export flux. Marine Ecology Progress Series, 354, 3-19.

Karakaş, G., Nowald, N., Schäfer-Neth, C., Iversen, M., Barkmann, W., Fischer, G., ... & Schlitzer, R. (2009). Impact of particle aggregation on vertical fluxes of organic matter. Progress in Oceanography, 83(1-4), 331-341.

Khatiwala, S., Primeau, F., & Hall, T. (2009). Reconstruction of the history of anthropogenic CO2 concentrations in the ocean. Nature, 462(7271), 346-349.

Kiørboe, T., & Hansen, J. L. (1993). Phytoplankton aggregate formation: observations of patterns and mechanisms of cell sticking and the significance of exopolymeric material. Journal of Plankton Research, 15(9), 993-1018.

Kiørboe, T., Andersen, K. P., & Dam, H. G. (1990). Coagulation efficiency and aggregate formation in marine phytoplankton. Marine Biology, 107, 235-245.

Kiørboe, T., Lundsgaard, C., Olesen, M., & Hansen, J. L. (1994). Aggregation and sedimentation processes during a spring phytoplankton bloom: A field experiment to test coagulation theory. Journal of Marine Research, 52(2), 297-323.

Kranck, K., & Milligan, T. G. (1988). Macroflocs from diatoms: in situ photography of particles in Bedford Basin, Nova Scotia. Marine ecology progress series. Oldendorf, 44(2), 183-189.

Laurenceau-Cornec, E. C., Trull, T. W., Davies, D. M., Christina, L., & Blain, S. (2015). Phytoplankton morphology controls on marine snow sinking velocity. Marine Ecology Progress Series, 520, 35-56.

Laurenceau-Cornec, E. C., Le Moigne, F. A., Gallinari, M., Moriceau, B., Toullec, J., Iversen, M. H., ... & De La Rocha, C. L. (2020). New guidelines for the application of Stokes' models to the sinking velocity of marine aggregates. Limnology and Oceanography, 65(6), 1264-1285.

Leandro, S. M., Gil, M. C., & Delgadillo, I. (2003). Partial characterisation of exopolysaccharides exudated by planktonic diatoms maintained in batch cultures. Acta Oecologica, 24, S49-S55.

Li, J., Xu, M., Wang, J., Lan, C., & Lai, J. (2023). Effects of nutrient limitation on cell growth, exopolysaccharide secretion and TEP production of Phaeocystis globosa. Marine Environmental Research, 183, 105801.

Logan, B. E., & Alldredge, A. L. (1989). Potential for increased nutrient uptake by flocculating diatoms. Marine Biology, 101, 443-450.

Logan, B. E., Passow, U., Alldredge, A. L., Grossartt, H. P., & Simont, M. (1995). Rapid formation and sedimentation of large aggregates is predictable from coagulation rates (half-lives) of transparent exopolymer particles (TEP). Deep Sea Research Part II: Topical Studies in Oceanography, 42(1), 203-214.

Lomas, M. W., Rumbley, C. J., & Glibert, P. M. (2000). Ammonium release by nitrogen sufficient diatoms in response to rapid increases in irradiance. Journal of Plankton Research, 22(12), 2351-2366.

Mari, X. (1999). Carbon content and C: N ratio of transparent exopolymeric particles (TEP) produced by bubbling exudates of diatoms. Marine Ecology Progress Series, 183, 59-71.

Mari, X., Rassoulzadegan, F., Brussaard, C. P., & Wassmann, P. (2005). Dynamics of transparent exopolymeric particles (TEP) production by Phaeocystis globosa under N-or P-limitation: a controlling factor of the retention/export balance. Harmful algae, 4(5), 895-914.

Mari, X., Passow, U., Migon, C., Burd, A. B., & Legendre, L. (2017). Transparent exopolymer particles: Effects on carbon cycling in the ocean. Progress in Oceanography, 151, 13-37.

Martin-Jézéquel, V., Hildebrand, M., & Brzezinski, M. A. (2000). Silicon metabolism in diatoms: implications for growth. Journal of phycology, 36(5), 821-840.

Mathot, S., Smith Jr, W. O., Carlson, C. A., Garrison, D. L., Gowing, M. M., & Vickers, C. L. (2000). Carbon partitioning within Phaeocystis antarctica (Prymnesiophyceae) colonies in the Ross Sea, Antarctica. Journal of Phycology, 36(6), 1049-1056.

McCave, I. N. (1984). Size spectra and aggregation of suspended particles in the deep ocean. Deep Sea Research Part A. Oceanographic Research Papers, 31(4), 329-352.

Meijering, E., Dzyubachyk, O., & Smal, I. (2012). Methods for cell and particle tracking. Methods in enzymology, 504, 183-200.

Mikaloff Fletcher, S. E., Gruber, N., Jacobson, A. R., Doney, S. C., Dutkiewicz, S., Gerber, M., ... & Sarmiento, J. L. (2006). Inverse estimates of anthropogenic CO2 uptake, transport, and storage by the ocean. Global biogeochemical cycles, 20(2).

Milligan, A. J., Varela, D. E., Brzezinski, M. A., & Morel, F. M. (2004). Dynamics of silicon metabolism and silicon isotopic discrimination in a marine diatomas a function of pCO2. Limnology and Oceanography, 49(2), 322-329.

Moisan, T. A., Olaizola, M., & Mitchell, B. G. (1998). Xanthophyll cycling in Phaeocystis antarctica: changes in cellular fluorescence. Marine Ecology Progress Series, 169, 113-121.

Myklestad, S. (1974). Production of carbohydrates by marine planktonic diatoms. I. Comparison of nine different species in culture. Journal of Experimental Marine Biology and Ecology, 15(3), 261-274.

Myklestad, S., & Haug, A. (1972). Production of carbohydrates by the marine diatom Chaetoceros affinis var. willei (Gran) Hustedt. I. Effect of the concentration of nutrients in the culture medium. Journal of Experimental Marine Biology and Ecology, 9(2), 125-136.

Myklestad, S., Holm-Hansen, O., Vårum, K. M., & Volcani, B. E. (1989). Rate of release of extracellular amino acids and carbohydrates from the marine diatom Chaetoceros affinis. Journal of Plankton Research, 11(4), 763-773.

Myklestad, S. M. (1995). Release of extracellular products by phytoplankton with special emphasis on polysaccharides. Science of the total Environment, 165(1-3), 155-164.

Nelson, D. M., Tréguer, P., Brzezinski, M. A., Leynaert, A., & Quéguiner, B. (1995). Production and dissolution of biogenic silica in the ocean: revised global estimates, comparison with regional data and relationship to biogenic sedimentation. Global biogeochemical cycles, 9(3), 359-372.

Nissen, C., & Vogt, M. (2021). Factors controlling the competition between Phaeocystis and diatoms in the Southern Ocean and implications for carbon export fluxes. Biogeosciences, 18(1), 251-283.

Oehler, J. H. (1979). Deposition and diagenesis of biogenic silica. In Studies in Environmental Science (Vol. 3, pp. 467-483). Elsevier.

Paasche, E. (1980). Silicon content of five marine plankton diatom species measured with a rapid filter method 1. Limnology and Oceanography, 25(3), 474-480.

Passow, U. (2002). Transparent exopolymer particles (TEP) in aquatic environments. Progress in oceanography, 55(3-4), 287-333.

Passow, U., & Alldredge, A. L. (1995a). Aggregation of a diatom bloom in a mesocosm: The role of transparent exopolymer particles (TEP). Deep Sea Research Part II: Topical Studies in Oceanography, 42(1), 99-109.

Passow, U., & Alldredge, A. L. (1995b). A dye-binding assay for the spectrophotometric measurement of transparent exopolymer particles (TEP). Limnology and Oceanography, 40(7), 1326-1335.

Passow, U., & De La Rocha, C. L. (2006). Accumulation of mineral ballast on organic aggregates. Global Biogeochemical Cycles, 20(1).

Passow, U., & Wassmann, P. (1994). On the trophic fate of Phaeocystis pouchetii (Hariot): IV. The formation of marine snow by P. pouchetii. Marine Ecology Progress Series, 153-161.

Passow, U., & Alldredge, A. L. (1994). Distribution, size and bacterial colonization of transparent exopolymer particles (TEP) in the ocean. Marine Ecology Progress Series, 185-198.

Passow, U., & Carlson, C. A. (2012). The biological pump in a high CO2 world. Marine Ecology Progress Series, 470, 249-271.

Passow, U., Alldredge, A. L., & Logan, B. E. (1994). The role of particulate carbohydrate exudates in the flocculation of diatom blooms. Deep Sea Research Part I: Oceanographic Research Papers, 41(2), 335-357.

Passow, U., Shipe, R. F., Murray, A., Pak, D. K., Brzezinski, M. A., & Alldredge, A. L. (2001). The origin of transparent exopolymer particles (TEP) and their role in the sedimentation of particulate matter. Continental Shelf Research, 21(4), 327-346.

Passow, U., Engel, A., & Ploug, H. (2003). The role of aggregation for the dissolution of diatom frustules. FEMS Microbiology Ecology, 46(3), 247-255.

Petrou, K., Kranz, S. A., Trimborn, S., Hassler, C. S., Ameijeiras, S. B., Sackett, O., ... & Davidson, A. T. (2016). Southern Ocean phytoplankton physiology in a changing climate. Journal of Plant Physiology, 203, 135-150.

Ploug, H., Stolte, W., & Jørgensen, B. B. (1999). Diffusive boundary layers of the colony-forming plankton alga Phaeocystis sp.—implications for nutrient uptake and cellular growth. Limnology and Oceanography, 44(8), 1959-1967.

Ploug, H., Hietanen, S., & Kuparinen, J. (2002). Diffusion and advection within and around sinking, porous diatom aggregates. Limnology and oceanography, 47(4), 1129-1136.

Ploug, H., Terbrüggen, A., Kaufmann, A., Wolf-Gladrow, D., & Passow, U. (2010). A novel method to measure particle sinking velocity in vitro, and its comparison to three other in vitro methods. Limnology and Oceanography: Methods, 8(8), 386-393.

Prairie, J. C., Montgomery, Q. W., Proctor, K. W., & Ghiorso, K. S. (2019). Effects of phytoplankton growth phase on settling properties of marine aggregates. Journal of Marine Science and Engineering, 7(8), 265.

Putt, M., Miceli, G., & Stoecker, D. K. (1994). Association of bacteria with Phaeocystis sp. in McMurdo Sound, Antarctica. Marine Ecology Progress Series, 179-189.

Radić, T., Kraus, R., Fuks, D., Radić, J., & Pečar, O. (2005). Transparent exopolymeric particles' distribution in the northern Adriatic and their relation to microphytoplankton biomass and composition. Science of the Total Environment, 353(1-3), 151-161.

Reigstad, M., & Wassmann, P. (2007). Does Phaeocystis spp. contribute significantly to vertical export of organic carbon?. Phaeocystis, major link in the biogeochemical cycling of climate-relevant elements, 217-234.

Reigstad, M., Wassmann, P., Ratkova, T., Arashkevich, E., Pasternak, A., & Øygarden, S. (2000). Comparison of the springtime vertical export of biogenic matter in three northern Norwegian fjords. Marine Ecology Progress Series, 201, 73-89.

Riebesell, U. (1991). Particle aggregation during a diatom bloom II. Biological aspects. Marine Ecology Progress Series, 69, 281-291.

Riebesell, U., Reigstad, M., Wassmann, P., Noji, T., & Passow, U. (1995). On the trophic fate of Phaeocystis pouchetii (Hariot): VI. Significance of Phaeocystis-derived mucus for vertical flux. Netherlands Journal of Sea Research, 33(2), 193-203.

Riebesell, U., & Wolf-Gladrow, D. A. (1992). The relationship between physical aggregation of phytoplankton and particle flux: a numerical model. Deep Sea Research Part A. Oceanographic Research Papers, 39(7-8), 1085-1102.

Rousseau, V., Vaulot, D., Casotti, R., Cariou, V., Lenz, J., Gunkel, J., & Baumann, M. (1994). The life cycle of Phaeocystis (Prymnesiophycaea): evidence and hypotheses. Journal of marine systems, 5(1), 23-39.

Rousseau, V., Chrétiennot-Dinet, M. J., Jacobsen, A., Verity, P., & Whipple, S. (2007). The life cycle of Phaeocystis: state of knowledge and presumptive role in ecology. Biogeochemistry, 83, 29-47.

Schindelin, J., Arganda-Carreras, I., Frise, E., Kaynig, V., Longair, M., Pietzsch, T., ... & Cardona, A. (2012). Fiji: an open-source platform for biological-image analysis. Nature methods, 9(7), 676-682.

Schoemann, V., Becquevort, S., Stefels, J., Rousseau, V., & Lancelot, C. (2005). Phaeocystis blooms in the global ocean and their controlling mechanisms: a review. Journal of Sea Research, 53(1-2), 43-66.

Schuster, S., & Herndl, G. J. (1995). Formation and significance of transparent exopolymeric particles in the northern Adriatic Sea. Marine Ecology Progress Series, 124, 227-236.

Shank A. L., & Trent D.T. (1979). Marine snow: Microscale nutrient patched. Limnol. Oceanogr, 24, 850-854.

Skreslet, S. (1988). Buoyancy in Phaeocystis pouchetii (Hariot) Lagerheim. Journal of experimental marine biology and ecology, 119(2), 157-166.

Smetacek, V. S. (1985). Role of sinking in diatom life-history cycles: ecological, evolutionary and geological significance. Marine biology, 84, 239-251.

Smith Jr, W. O., Codispoti, L. A., Nelson, D. M., Manley, T., Buskey, E. J., Niebauer, H. J., & Cota, G. F. (1991). Importance of Phaeocystis blooms in the high-latitude ocean carbon cycle. Nature, 352(6335), 514-516.

Smith Jr, W. O. (1993). Nitrogen uptake and new production in the Greenland Sea: The spring Phaeocystis bloom. Journal of Geophysical Research: Oceans, 98(C3), 4681-4688.

Smith Jr, W. O., & Trimborn, S. (2023). Phaeocystis: A global enigma. Annual Review of Marine Science, 16.

Solomon, C. M., Lessard, E. J., Keil, R. G., & Foy, M. S. (2003). Characterization of extracellular polymers of Phaeocystis globosa and P. antarctica. Marine Ecology Progress Series, 250, 81-89.

Steinacher, M., Joos, F., Frölicher, T. L., Bopp, L., Cadule, P., Cocco, V., ... & Segschneider, J. (2010). Projected 21st century decrease in marine productivity: a multi-model analysis. Biogeosciences, 7(3), 979-1005.

Sweeney, C., Hansell, D. A., Carlson, C. A., Codispoti, L. A., Gordon, L. I., Marra, J., ... & Takahashi, T. (2000). Biogeochemical regimes, net community production and carbon export in the Ross Sea, Antarctica. Deep Sea Research Part II: Topical Studies in Oceanography, 47(15-16), 3369-3394.

Takeuchi, M., Doubell, M. J., Jackson, G. A., Yukawa, M., Sagara, Y., & Yamazaki, H. (2019). Turbulence mediates marine aggregate formation and destruction in the upper ocean. Scientific Reports, 9(1), 16280.

Thingstad, F., & Billen, G. (1994). Microbial degradation of Phaeocystis material in the water column. Journal of marine systems, 5(1), 55-65.

Thornton, D. C. (2002). Diatom aggregation in the sea: mechanisms and ecological implications. European Journal of Phycology, 37(2), 149-161.

Tooby, P. F., Wick, G. L., & Isaacs, J. D. (1977). The motion of a small sphere in a rotating velocity field: a possible mechanism for suspending particles in turbulence. Journal of geophysical research, 82(15), 2096-2100.

Tréguer, P. J., & De La Rocha, C. L. (2013). The world ocean silica cycle. Annual review of marine science, 5, 477-501.

Tréguer, P. J., Sutton, J. N., Brzezinski, M., Charette, M. A., Devries, T., Dutkiewicz, S., ... & Rouxel, O. (2021). Reviews and syntheses: The biogeochemical cycle of silicon in the modern ocean. Biogeosciences, 18(4), 1269-1289.

Trimborn, S., Thoms, S., Brenneis, T., Heiden, J. P., Beszteri, S., & Bischof, K. (2017). Two Southern Ocean diatoms are more sensitive to ocean acidification and changes in irradiance than the prymnesiophyte Phaeocystis antarctica. Physiologia Plantarum, 160(2), 155-170.

Trimborn, S., Thoms, S., Bischof, K., & Beszteri, S. (2019). Susceptibility of two Southern Ocean phytoplankton key species to iron limitation and high light. Frontiers in Marine Science, 6, 167.

Trudnowska, E., Lacour, L., Ardyna, M., Rogge, A., Irisson, J. O., Waite, A. M., ... & Stemmann, L. (2021). Marine snow morphology illuminates the evolution of phytoplankton blooms and determines their subsequent vertical export. Nature communications, 12(1), 2816.

Tungaraza, C., Rousseau, V., Brion, N., Lancelot, C., Gichuki, J., Baeyens, W., & Goeyens, L. (2003). Contrasting nitrogen uptake by diatom and Phaeocystis-dominated phytoplankton assemblages in the North Sea. Journal of Experimental Marine Biology and Ecology, 292(1), 19-41.

Turner, J. T. (2015). Zooplankton fecal pellets, marine snow, phytodetritus and the ocean's biological pump. Progress in Oceanography, 130, 205-248.

Van Boekel, W. H. M. (1992). Phaeocystis colony mucus components and the importance of calcium ions for colony stability. Marine Ecology-Progress Series, 87, 301-301.

Verity, P. G., Smayda, T. J., & Sakshaug, E. (1991). Photosynthesis, excretion, and growth rates of Phaeocystis colonies and solitary cells. Polar research, 10(1), 117-128.

Verity, P. G., Brussaard, C. P., Nejstgaard, J. C., van Leeuwe, M. A., Lancelot, C., & Medlin, L. K. (2007). Current understanding of Phaeocystis ecology and biogeochemistry, and perspectives for future research. Biogeochemistry, 83, 311-330.

Volk, T., & Hoffert, M. I. (1985). Ocean carbon pumps: Analysis of relative strengths and efficiencies in ocean-driven atmospheric CO2 changes. The carbon cycle and atmospheric CO2: Natural variations Archean to present, 32, 99-110.

von Bodungen, B. (1986). Phytoplankton growth and krill grazing during spring in the Bransfield Strait, Antarctica—implications from sediment trap collections. Polar Biology, 6, 153-160.

Vrieling, E. G., Gieskes, W. W. C., & Beelen, T. P. (1999). Silicon deposition in diatoms: control by the pH inside the silicon deposition vesicle. Journal of Phycology, 35(3), 548-559.

Waite, A., Gallager, S., & Dam, H. G. (1997). New measurements of phytoplankton aggregation in a flocculator using videography and image analysis. Marine Ecology Progress Series, 155, 77-88.

Wang, X., & Tang, K. W. (2010). Buoyancy regulation in Phaeocystis globosa Scherffel colonies. Open Marine Biology Journal, 4, 115.

Wang, X., Wang, Y., & Smith Jr, W. O. (2011). The role of nitrogen on the growth and colony development of Phaeocystis globosa (Prymnesiophyceae). European Journal of Phycology, 46(3), 305-314.

Wassmann, P., Vernet, M., Mitchell, B. G., & Rey, F. (1990). Mass sedimentation of Phaeocystis pouchetii in the Barents Sea. Marine Ecology Progress Series, 183-195.

Weisse, T., Tande, K., Verity, P., Hansen, F., & Gieskes, W. (1994). The trophic significance of Phaeocystis blooms. Journal of Marine Systems, 5(1), 67-79.

Wohlers, J., Engel, A., Zöllner, E., Breithaupt, P., Jürgens, K., Hoppe, H. G., ... & Riebesell, U. (2009). Changes in biogenic carbon flow in response to sea surface warming. Proceedings of the national academy of sciences, 106(17), 7067-7072.

Zetsche, E. M., Larsson, A. I., Iversen, M. H., & Ploug, H. (2020). Flow and diffusion around and within diatom aggregates: effects of aggregate composition and shape. Limnology and Oceanography, 65(8), 1818-1833.

SUPPLEMENTARY

Table S1: Summary of statistic tests for all measurements

Measurement	Timepoint	Comparison	statistic test	p.value
ESD	t1	between the nutritional treatments	Kruskal-Walis	3.832*10-5
Sinking velocity	t1	between the nutritional treatments	Kruskal-Walis	<2.2*10-16
Macronutrients	t0	NO3-	ANOVA	1.58*10-6
	t0	NO2-	ANOVA	0.436
	t0	NH4+	Kruskal-Walis	0.01504
	t0	PO42-	Kruskal-Walis	0.003056
	t0	Si(OH)4	Kruskal-Walis	0.01661
	t1	NO3-	Kruskal-Walis	0.00743
	t1	NO2-	Kruskal-Walis	0.6106
	t1	NH4+	Kruskal-Walis	0.01192
	t1	PO42-	Kruskal-Walis	0.004893
	t1	Si(OH)4	ANOVA	2.03*10-11
TEP	t0	f/0 - f/2	t-test	0.002792
	t0	f/0 - f/4	t-test	0.01756
	t0	f/0 - N	t-test	0.005948
	t0	f/0 - P	t-test	0.005579
	t0	f/0 - TE	t-test	0.008881
	t0	f/0 - Si	t-test	0.0058
	t0	f/0 - NP	t-test	0.009877
	t0	f/0 - NTE	t-test	0.005235
	t0	f/0 - PTE	t-test	0.005718
	t1_background	f/0 - f/2	t-test	0.4584
	t1_background	f/0 - f/4	t-test	0.2459
	t1_background	f/0 - N	t-test	0.02499
	t1_background	f/0 - P	t-test	0.7819
	t1_background	f/0 - TE	t-test	0.3697
	t1_background	f/0 - Si	t-test	0.1236

Table S1 (continued): Summary continued of statistic tests for all measurements

Measurement	Timepoint	Comparison	statistic test	p.value
	t1_background	f/0 - NP	t-test	0.8309
	t1_background	f/0 - NTE	t-test	0.377
	t1_background	f/0 - PTE	t-test	0.2697
	t1_aggregate	f/0 - f/2	t-test	0.01863
	t1_aggregate	f/0 - f/4	t-test	0.01294
	t1_aggregate	f/0 - N	t-test	0.006181
	t1_aggregate	f/0 - P	t-test	0.003014
	t1_aggregate	f/0 - TE	t-test	0.008671
	t1_aggregate	f/0 - Si	t-test	0.009972
	t1_aggregate	f/0 - NP	t-test	0.006523
	t1_aggregate	f/0 - NTE	t-test	0.008604
	t1_aggregate	f/0 - PTE	t-test	0.00908
	t1_total	f/0 - f/2	t-test	0.00426
	t1_total	f/0 - f/4	t-test	0.007089
	t1_total	f/0 - N	t-test	0.00257
	t1_total	f/0 - P	t-test	0.002288
	t1_total	f/0 - TE	t-test	0.001673
	t1_total	f/0 - Si	t-test	0.00167
	t1_total	f/0 - NP	t-test	0.001092
	t1_total	f/0 - NTE	t-test	0.001812
	t1_total	f/0 - PTE	t-test	0.001591

MANUSCRIPT 2. THE ROLE OF PELAGIC APPENDICULARIANS AND PTEROPODS FOR CARBON EXPORT AND FLUX ATTENUATION OVER THE PORCUPINE ABYSSAL PLAIN, NORTHEAST-ATLANTIC

Anna Biastoch, Richard S. Lampitt, Corinne Pebody, Jack J. Middelburg, Morten H. Iversen

ABSTRACT

The biological carbon pump in the Northeast Atlantic display's large local and temporal variability with high peaks of carbon flux lasting a matter of days during the spring period. Yet, it is still unclear what drives these sudden flux peaks. This study investigates a sudden shift in carbon flux dynamics at the Porcupine Abyssal Plain Sustained Observatory (PAP-SO). At the start of the study period, the upper water column was dominated by small aggregates, but within days, a shift occurred and large mucus aggregates prevailed, increasing peak flux from 100 to 200 mg C m^{-2} d^{-1}. Despite an initial decrease in chlorophyll concentration, in-depth analyses ruled out that the change in carbon flux was not driven by changing water masses, the influence of storms, or plankton blooms. Instead, we could link the fluctuations to the influence of gelatinous zooplankton, especially pteropods and appendicularians. In particular, the enhanced carbon flux in the second half of the study seemed to be caused by a high number of sinking appendicularian houses and pteropod mucus feeding nets. This study indicates that appendicularians and pteropods are a vector for efficient carbon export in the region and underscored their significant role in shaping carbon flux dynamics.

INTRODUCTION

The biological carbon pump is pivotal in ocean carbon uptake. Primary producers in the surface water convert carbon dioxide into particulate organic forms and these are partly exported to the ocean interior (Falkowski et al. 1998, Turner 2015). The exported organic carbon is eventually either respired in deep waters or buried in sediments where it is locked away on geological timescales (Volk & Hoffert 1985, Longhurst & Harrison 1989, Longhurst 1991, Ducklow & Steinberg 2001). Without detailed understanding of the biological pump, we cannot anticipate how future climate change will impact the ocean's capability to sequester carbon from the atmosphere; this will hamper the accuracy of ocean carbon uptake projections.

Most of the downward transport of Particulate Organic Material (POM) occurs in the form of faecal pellets produced by zooplankton and marine snow (macroscopic particles with a diameter > 500 μm) (Fowler & Knauer 1986, Simon et al. 2002), whereby faecal pellets can also be included in marine snow. Marine snow is mainly formed via coagulation of phytodetritus, attached microbes and colloids or via the production of mucus structures, for example discarded appendicularian houses and feeding net structures from polychaetes and pteropods, which have an adhesive character (Gilmer 1972, Silver & Bruland 1981, Noji et al. 1997, Sutherland et al. 2010). Despite decades of research, the role of zooplankton within the biological carbon pump is not yet fully understood. In the euphotic zone, organic matter consumption processes are very efficient and normally, less than 25%, often less than10%, of net primary production reaches depths below the euphotic zone (>100 m) (Christina & Passow 2007). The water depth of maximum Particulate Organic Carbon (POC) flux attenuation correlates often with high zooplankton abundance, suggesting that zooplankton act as gatekeepers for POC fluxes (Napp et al. 1988, Forest et al. 2011, Möller et al. 2012, Christiansen & Weikert 2018, Van der Jagt et al. 2020, Whitmore & Ohman 2021). Several laboratory experiments documented that zooplankton can directly feed on settling POM (Lampitt et al. 1990, Noji et al. 1991, Steinberg et al. 1994, Green & Dagg 1997, Dilling & Brzezinski 2004, Poulsen & Kiørboe 2005, Iversen & Poulsen 2007, Lombard et al. 2013, Cavan et al. 2021). However, zooplankton not only contribute to POC flux attenuation, but can also increase the downward transport of particles, hence increase POC fluxes. Highly compact fecal pellets increase sinking velocities of the organic matter and, hence, increase the vertical particle flux (Lampitt et al.

1990, Marty et al. 1994, Ducklow & Steinberg 2001, Fortier et al. 2002). Turner (2002) showed, that the contribution of faecal pellets to the POC flux is highly variable: it can vary from <1 to 100%, depending on zooplankton community composition and available food types. Furthermore, some species, including pteropods but often driven by crustaceans, migrate vertically, which increases POC fluxes at depth greater than 100 m and remineralization at depth via respiration (Hays 1995, Steinberg et al. 2002, Steinberg et al. 2008). Zooplankton also play an important role in aggregation and settling of POM (Karl et al. 1988, Taylor 1989, Koski et al. 2005) through discarded mucus structures (Alldredge 1976, Silver et al. 1978, Davoll & Silver 1986, Kiorboe & Hansen 1993, Robinson et al., 2005). In combination with phytodetritus and fecal pellets, mucus scaffolds form particles called mucus aggregates with relatively high sinking velocities. For example, discarded houses of appendicularians and mucus aggregates produced by the Pteropod Limacina retroversa can achieve sinking velocities in excess of 800 m/d (Hamner & Robison 1992, Noji et al. 1997).

Here, we study a fairly short time-period which was characterized by rapid fluctuations in carbon flux at PAP-SO in the Northeast Atlantic. We link these fluctuations to the influence of gelatinous zooplankton, especially pteropods and appendicularians, on the POC flux. To this end, we combined in situ imaging with zooplankton net tows to follow the zooplankton community and particle dynamics during a period of 15 days.

MATERIAL AND METHODS

Study site

We quantified the temporal changes in vertical size-distribution and abundance of particles and aggregates in combination with zooplankton community structure and abundance during a cruise from the 18th April to 8th May 2016 on board of the British RRS Discovery (DY050) in the area of the Porcupine Abyssal Plain Sustained Observatory (PAP-SO). The site is located southwest of Ireland in the Northeast Atlantic in a region where the abyssal plain is at 4840 m water depth (Billett & Rice 2001). PAP-SO is an open ocean region with little impact from land and with seasonal large spring blooms of phytoplankton followed by a smaller summer bloom, which also drive similar seasonal peaks in particulate organic carbon (POC) export to the deep sea (Lampitt et al. 2010). There is generally a

strong flux attenuation in the upper water column, which is determined by microbial remineralization and feeding by zooplankton (Lampitt et al. 1990, Giering et al. 2014). We performed a high-resolution time-series sampling at the PAP-SO at position 49°0.3` N and 16°23.8` W with daily sampling between the 20th April and 10th May during the RV Discovery cruise DY050 (Fig. 10B).

Hydrography

Physical variables in the upper 300 m of the water column were determined using a CTD (Conductivity, Temperature and Depth; see 2.4) during the cruise. The calculation of the mixed layer depth was defined as the depth at which temperature is 0.2°C below that at the surface (de Boyer Montegut et al. 2004). Chlorophyll distribution was determined by CTD and chlorophyll satellite data provided by the OC-CCI (Sathyendranath et al. 2019). Satellite data for sea level anomaly and currents was provided by C3S (Copernicus Climate Change Service, Climate Data Store, 2018). Data for current velocities at greater depth were provided by the Global Ocean Forecast System 3.1 (Metzger et al. 2017).

Size-specific sinking velocities and carbon content of in situ sampled aggregates

In-situ aggregates were sampled from 10 m below the chlorophyll a maximum using a Marine Snow Catcher (MSC). The MSC consisted of a 95L PVC closing water bottle with a removeable 5L bottom chamber, which was deployed open to the target depth and closed by a messenger weight (Lampitt et al. 1993). After closure of the MSC and recovery to the ship, it was left on deck for two hours to allow the collected particles and aggregates to settle to the bottom part of the MSC. We therefore used the settling velocities of the different particles and aggregate fractions to classify them into two fractions: (1) fast sinking particle fraction, which were the aggregates that reached the bottom plate of the collector tray of the MSC after a settling period of two hours and (2) slow sinking particle fraction, which reached the base section of the MSC without sinking to the bottom plate. A 1.5 L sample was taken from the top and the bottom chamber for size fractionated POC and chlorophyll analysis. The collector tray was stored in a 10°C temperature-controlled laboratory for further analysis.

Size and sinking velocity of individual in situ collected fast-settling aggregates were measured using a flow chamber (Ploug and Jørgensen 1999). The flow chamber

was filled with GF/F filtered water from the water that was collected by the MSC for each station. For each deployment, all fast-settling aggregates that were collected on ¼ of the bottom plate in the collection tray were analysed. This was typically between 5 and 15 particles, which were transferred individually with a wide pore pipette to a flow chamber. The upward flow was adjusted for each aggregate so it balanced the downward settling velocity of the aggregates, positioning the aggregate in suspension one particle diameter above the mesh in the flow chamber (see Ploug and Jørgensen 1999). The sinking velocity of the aggregate was determined by dividing the flow rate by the area of the flow chamber. Sinking velocity was measured three times for each aggregate. The x-, y- and z-dimensions of each aggregate (height, length, and width) were determined using a horizontal dissection microscope with a calibrated ocular. Aggregate volume was calculated for each aggregate by assuming an ellipsoidal shape. Furthermore, the equivalent spherical diameter (ESD) was calculated for comparison between different aggregate sizes.

Vertical size-distribution and abundance of particles and aggregates

The PELAGRA Cam is an in situ camera system, which enables determination of abundance and size-distribution of particles and aggregates larger than 100 µm. We deployed the PELAGRA Cam as a profiling system attached to the Red Camera Frame (RCF) to determine vertical particle abundance and size-distribution of particles in the upper 300 m of the water column (Giering et al. 2020, Iversen and Lampitt 2020). The RCF was equipped with an Idronaut CTD sensor (Conductivity, Temperature and Depth) and captured an image every five seconds. The pixel-size of the PELAGRA Cam on the RCF was 54 µm per pixel and the field of view was 157 mm wide and 101 mm high with a depth of 135 mm, resulting in an image volume of 2.15 L. The PELAGRA Cams consisted of a Canon EOS 6D digital SLR camera, a 50 mm macro lens and a Canon Speedlite 600EX RT flash gun. A Hahnel Giga T Pro II remote timer ensured the timing between each image. The camera as well as flash gun were put in manual mode with following settings:

Tab. 3: Flash gun settings of the PELAGRA Cam integrated in the Red Camera Frame

Characteristics	Settings
shutter speed	1/160 [s]
Aperture	f/32
Lens focus	1.5 [ft]
Flash direction	straight
Flash output	0

Additional information about vertical profiles of particle abundance and size-distribution can be found in the supplementary information (Fig. S1).

Particulate organic carbon flux

The POC flux was calculated based on the method described by Guidi et al. (2008) and Iversen et al. (2010). This method uses the vertical abundance and size-distribution of particles to calculate total POC flux (F, mg C m^{-2} d^{-1}) by multiplying with the size-specific carbon content and sinking velocities of each aggregate size:

$$F = CF * \int_0^\infty n(d) * POC(d) * w(d) * d(d) \quad (5)$$

where n is the particle size-spectra (# cm^{-4}), POC is the measured size-specific POC content (µg POC), w is the measured size-specific sinking velocity of the aggregates collected in situ using the marine snow catcher (cm s^{-1}), d is the width of each size-bin in the particle size-spectra (cm) and CF is a conversion factor to go from µg C cm^{-2} s^{-1} to mg C m^{-2} d^{-1}. Since we measured POC for pooled aggregates of different sizes, we calculated the size-specific POC content for the aggregates collected at different time points. This was done by measuring POC content for different fractions of the particles collected with the MSC (suspended particles, slow sinking particles, and fast sinking aggregates; see section 2.3). The different fractions were filtered through a pre-combusted (450°C, 24 h) glass fibre filter (Ø 25 mm, GF/F, Whatman), rinsed with Milli-Q water, and oven dried at 50°C for 24 h. Hereafter, the filters were fumed with 37% HCl in a vacuum desiccator over night to remove inorganic carbon and placed into tin cups. POC and PON were measured with an elemental analyser (Elementar vario EL III). Since marine snow particles have fractal dimension i.e., their porosity increases with increasing size, we followed van

der Jagt et al. (2020) and used a power law function to determine the size-specific POC content as a function of aggregate volume for the fast-settling aggregates:

$$POC = A * V^b \quad (6)$$

where V is the aggregate volume (cm^3) and the constant b was 0.5 (see van der Jagt et al. 2020). The constant A was found by calculating total POC flux for all aggregate sizes and numbers that were pooled for POC analysis using the power function (Eq. 6) and identifying the A value that gave the least difference in total POC compared to the measured POC for the pooled aggregates.

Zooplankton abundance

A zooplankton net (Working Party 2, WP2) with a mesh-size of 200 µm was deployed as vertical hauls with 0.16 m s^{-1} to collected zooplankton in the upper 200 m of the water column. After deployment, the collected samples were gently concentrated in the cod-end and fixed with borate buffered formaldehyde (4%) until analyses in the home laboratory. A 1/8 or 1/16 subsample from each net was diluted in 1 L of seawater and gently pumped through a FlowCam Macro. The same context file was used for every sample (Flow Cell type FC5000X5, auto image frame rate 10 frames per second, pump flow rate 603 mL min^{-1}). The flow cell depth was 5000 µm and the width was 10000 µm. Once the subsample had been run through the FlowCam Macro it was added to the rest of the sample and re-preserved to a concentration of 4% borate buffered formaldehyde. Visual Spreadsheet 4.19.3 was used to classify the individual mesozooplankton vignettes to the lowest possible taxonomic group. Debris or parts of animals were deleted and any unclassified particles were grouped together. Twenty-nine different zooplankton groups were quantitatively identified, however, for the purpose of this study we clustered those groups into the eight most abundant groups: i) Appendicularia (Larvaceans), ii) Pteropods, iii) Large Copepods, iv) Small Copepods, v) *Oithona sp.,* vi) *Oncaea sp.,* and vii) *Euchaeta sp.*. We calculated the zooplankton biomass from the abundance and size-specific biomass of each identified zooplankton group using literature data (see Table 4).

Tab. 4: References for biomass calculation from zooplankton abundance

Zooplankton	Reference	Biomass [µg C/Individual]
Small Copepods	Thompson et al. 2013	0.35
Large Copepods	Thompson et al. 2013	84.66
Oncaea	De Melo Junior et al. 2021	4.44
Oithona	Castellani et al. 2008	0.62
Euchaeta	Dias et al. 2015	5.40
Appendicularia	Sato et al. 2008	5.00
Pteropod	Bednarsek et al. 2012	46.72

RESULTS

Hydrography

The vertical profiles of the temperature showed variations over time in the upper mixed layer (Fig. 10A and C). The mixed layer depth (MLD) was at a depth of 143.7 m during the beginning of the cruise, whereafter it became shallower and was 36.8 m until the 30th April. On 1st May, vertical temperature profiles showed more stratification and the MLD was reduced to 29.9 m (Fig. 10C). After 1st May vertical temperature profiles appeared more consistence with a MLD of almost 50 m. Data from the moored buoy at 30 m depth and satellites showed that the region was characterized by low and stable chlorophyll-a concentration in surface waters before 1st May, whereafter this doubled subsequently (Fig. 10A and B). Comparing the temperature and salinity between 1 m and 30 m from the moored buoy and the vertical CTD profiles showed a stable system without large changes in water masses during the study period (Fig. 10A and C).

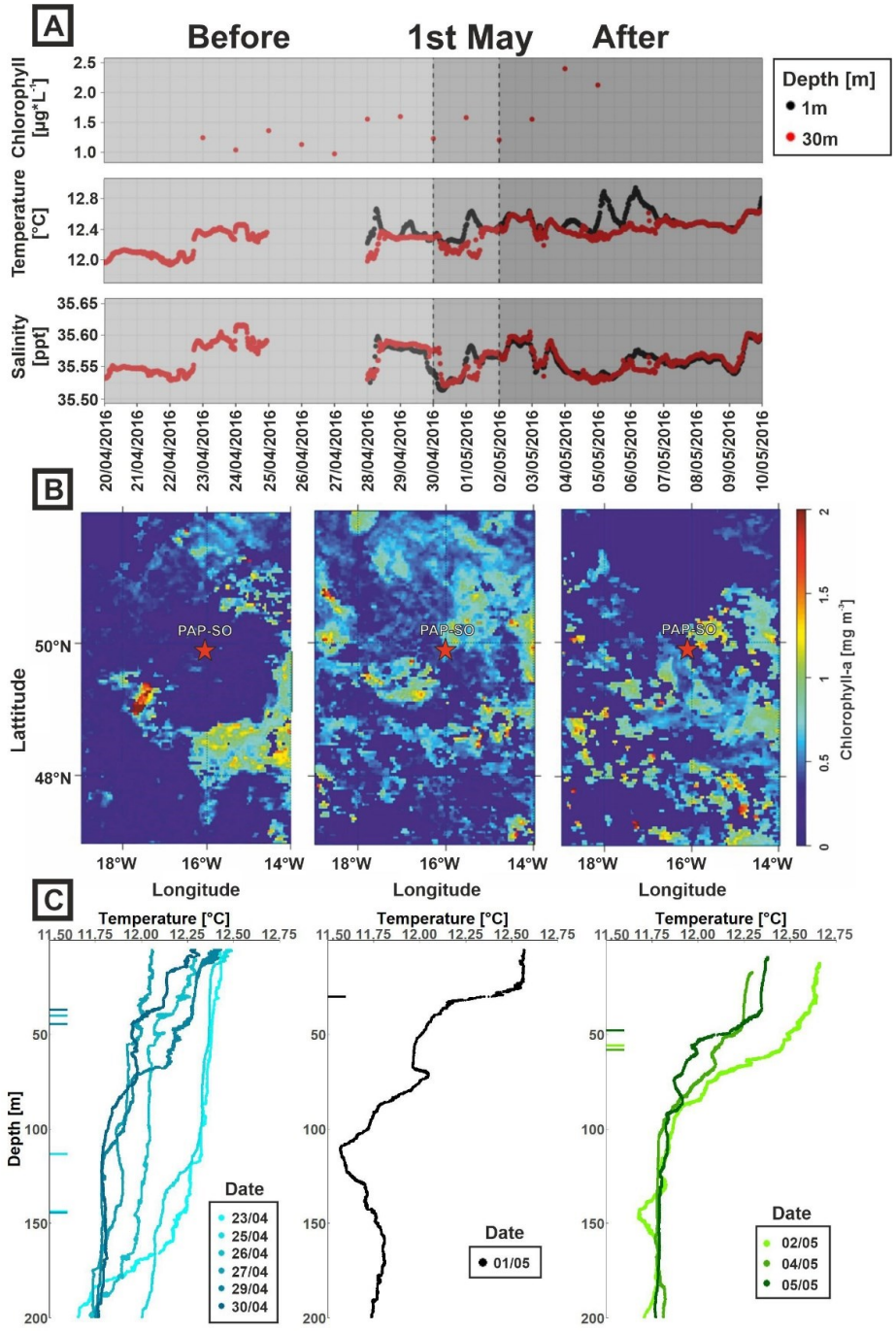


Fig. 10: Changes in chlorophyll-a concentration, temperature, and salinity throughout the study and separated into the periods where we observed the largest changes in POC flux; before 1st May (left), on 1st May (middle), and after 1st May (right). The moored PAP Observatory buoy recorded chlorophyll-a concentration, temperature, and salinity at 1 m and 30 m depth over time, however, during our study, chlorophyll-a was only measured at 30 m (A). Satellite based surface chlorophyll-a concentrations were five days averages for the study region (B). CTD profiles measured vertical daily temperature profiles throughout the entire cruise with the calculated mixed layer depth indicated by the coloured bars on the y-axis (C).

Size-distribution and size-specific sinking velocities of in situ collected aggregates

We observed clear changes in MSC collected aggregate types, size-distribution, and size-specific settling velocities throughout the study (Fig.11). Before 1st May, the size-range was small with a maximum aggregate size of 0.9 mm ESD and sinking velocities below 100 m d^{-1}. The aggregate types were more or less evenly distributed between zooplankton fecal pellets and marine snow aggregates before 1st May. On 1st May, the aggregate sizes increased and reached maximum sizes of 2.5 mm ESD, however, the sinking velocities were still below 100 m d^{-1}, as observed for the smaller aggregates before 1st May. Hence, the 1st May had lower size-specific settling velocities compared to the period before the 1st May. The aggregate types on 1st May were dominated by marine snow aggregates and we did not observe any zooplankton fecal pellets. After 1st May, the aggregate sizes did not become much larger than 1 mm ESD, but had velocities above 100 m d^{-1} for marine snow aggregates. Generally, we only observed few fecal pellets after 1st May and the majority of the aggregates were marine snow.

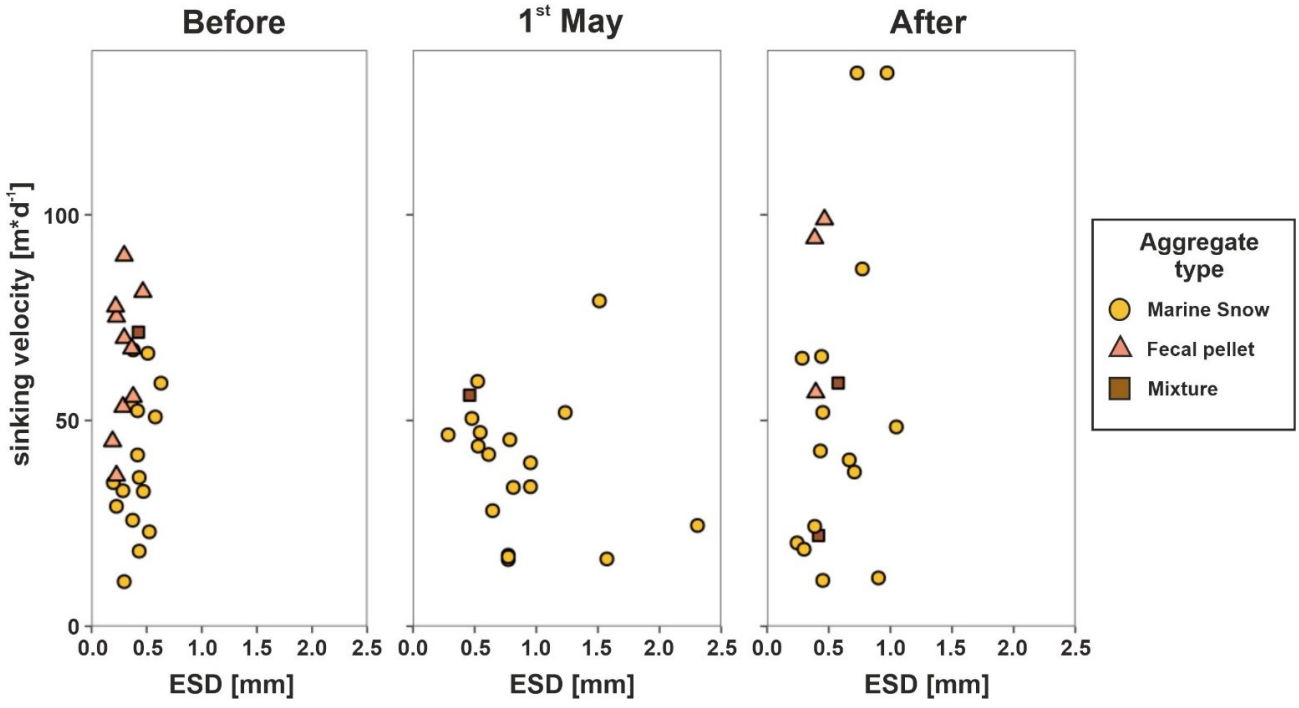


Fig.11: Sizes and sinking velocities measured in the flow chamber for different types of in situ collected aggregates. Left: aggregates collected during the period before 1st May (four MSC deployments). Middle: aggregates collected on 1st May (one MSC deployment). Right: aggregates collected after 1st May (three MSC deployments).

Total particulate organic carbon and nitrogen content

We made a mechanical separation of the organic aggregates that were collected by MSC into fast- and slow-settling aggregates (see section 2.3). Fast-sinking aggregates dominated both the POC and PON pools before and after the 1st May, but on 1st May slow sinking particles constituted the main part of POC and PON (Fig. 12A and B). Compared to 1st May, the period after 1st May showed a decrease in the contribution of slow sinking particles while the contribution of fast sinking particles increased. Both POC and PON varied much throughout the cruise periods with a POC range between ~200 and 700 μg l^{-1} and a PON range between ~25 and ~125 μg l^{-1} (Fig. 12A and B). Although the dynamics in POC and PON seemed to be linked (Fig. 12A and B), we also observed variability in the molar C:N ratio for both the fast- and slow-sinking aggregates (Fig.12C). In the first period before the 1st May, the C:N ratio of fast- and slow-sinking aggregates was between 2-12 and 4-12, respectively. On 1st May the C:N ratios of both aggregate types decreased to values of around 7.5. After the 1st May, we initially observed a rapid increase to 18 for fast-settling aggregates, which lasted for a few days whereafter it dropped to ~2. For the slow-settling aggregates after 1st May, we only observed an increase in C:N ratio on 4th May to 13, but on 5th May it dropped to 8 again (Fig. 12C).

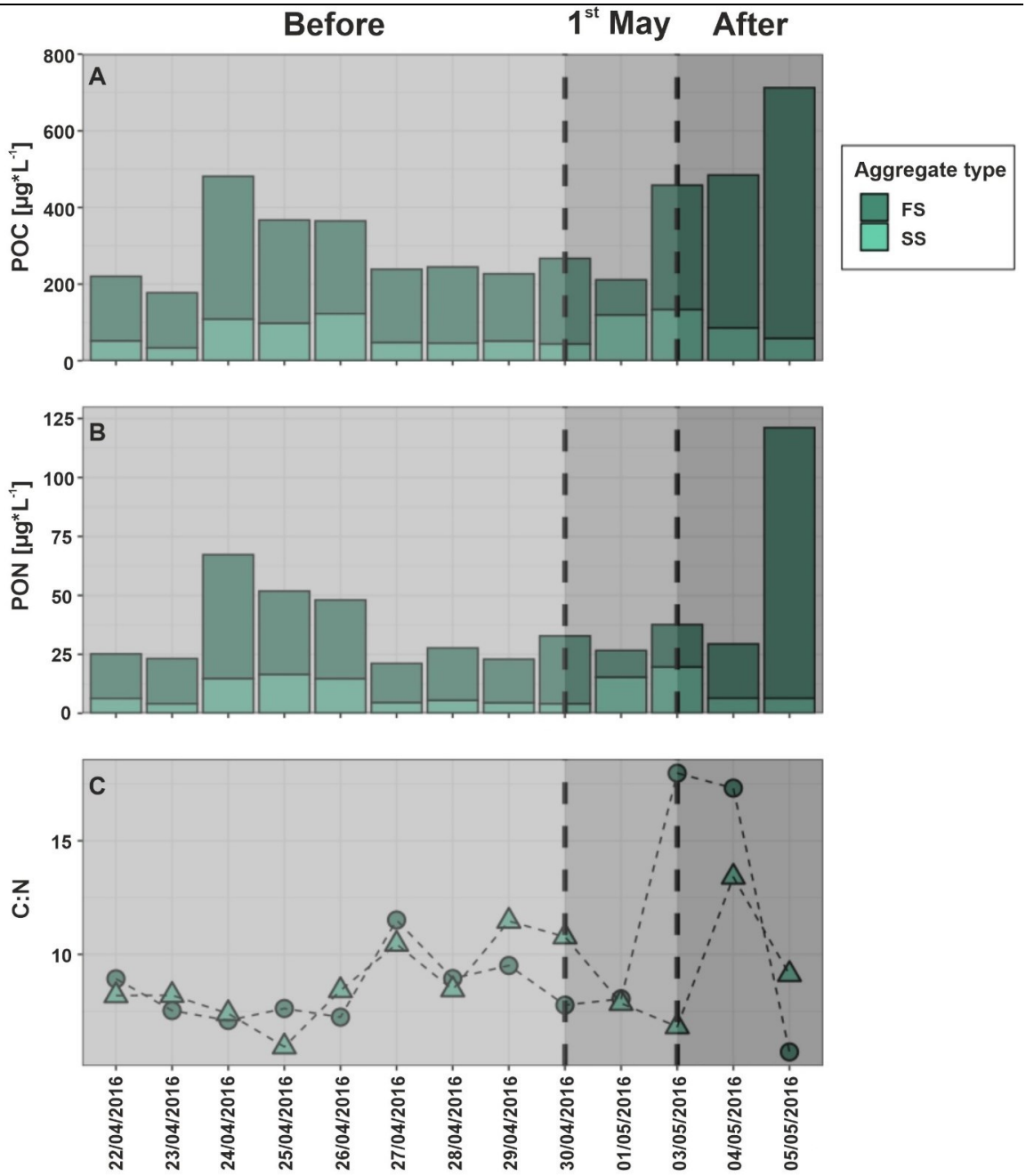


Fig. 12: Changes in POC (A), PON (particulate organic nitrogen, (B) and molar C:N ratio (C) for fast- and slow-sinking aggregate types throughout the cruise period.

Particulate organic carbon flux

The POC flux was calculated from the vertical size-distribution and abundance of aggregates and the measure size-specific POC content and size-specific settling velocities of the aggregates (see Eq. 5 and 6). POC flux showed distinct differences over time (Fig. 13) where the period before 1st May showed POC fluxes in the upper water column of ~50 mg C m^{-2} d^{-1} with a subsurface maximum of about 80-100 mg C m^{-2} d^{-1} at ~20 m depth. On 1st and 2nd May, we observed very low POC fluxes with maximum values lower than 2.5 mg C m^{-2} d^{-1}. After 2nd May, POC fluxes increased 2-fold compared to the period before the 1st May and around two-orders of magnitude compared to 1st and 2nd May (Fig. 13).

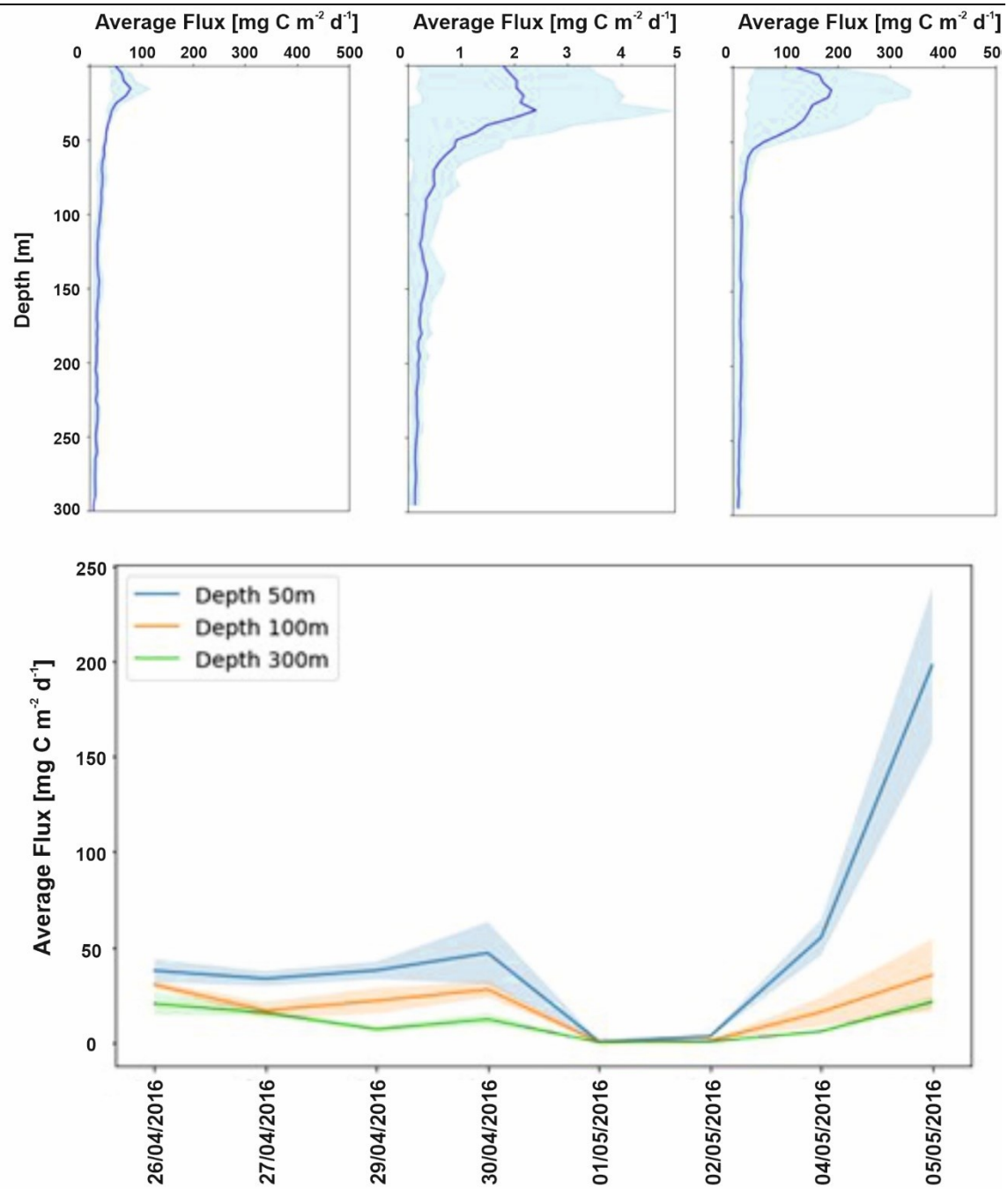


Fig. 13: Upper: Estimated POC fluxes (mg C m^{-2} d^{-1}) calculated from Eqs. (5) and (6) based on vertical particle size distributions. The deep blue line shows the mean organic carbon fluxes. The light blue shadowed area specifies the minimum and maximum range of POC fluxes calculated within specific timescales. Left: POC flux including calculations from four RCF deployments before 1st May. Middle: POC flux calculated at 1st May (Note the 100 times difference in scale). Right: POC flux including calculations from three RCF deployments after 1st May. Lower: average POC flux for three different depth-layers over time i) 30-50 m, ii) 50-100 m, and iii) 100-300 m.

Zooplankton biomass

Zooplankton net samples from the upper 200 m of the water column showed that before 1st May, the zooplankton community was dominated by large copepods (357 to 428 µg C m^{-3}), followed by appendicularia (178 to 267 µg C m^{-3}) and pteropods (20 to 92 µg C m^{-3}) (Fig. 14). While the biomass of large copepods remained rather constant on the 1st May, the biomass of appendicularia increased to 452 µg C m^{-3}. However, on the 3rd May the Appendicularia decreased to the previous values while large copepod biomass remained similar. The main difference on the 3rd May was that pteropods increased in biomass and exceeded that of the appendicularia (Fig. 14).

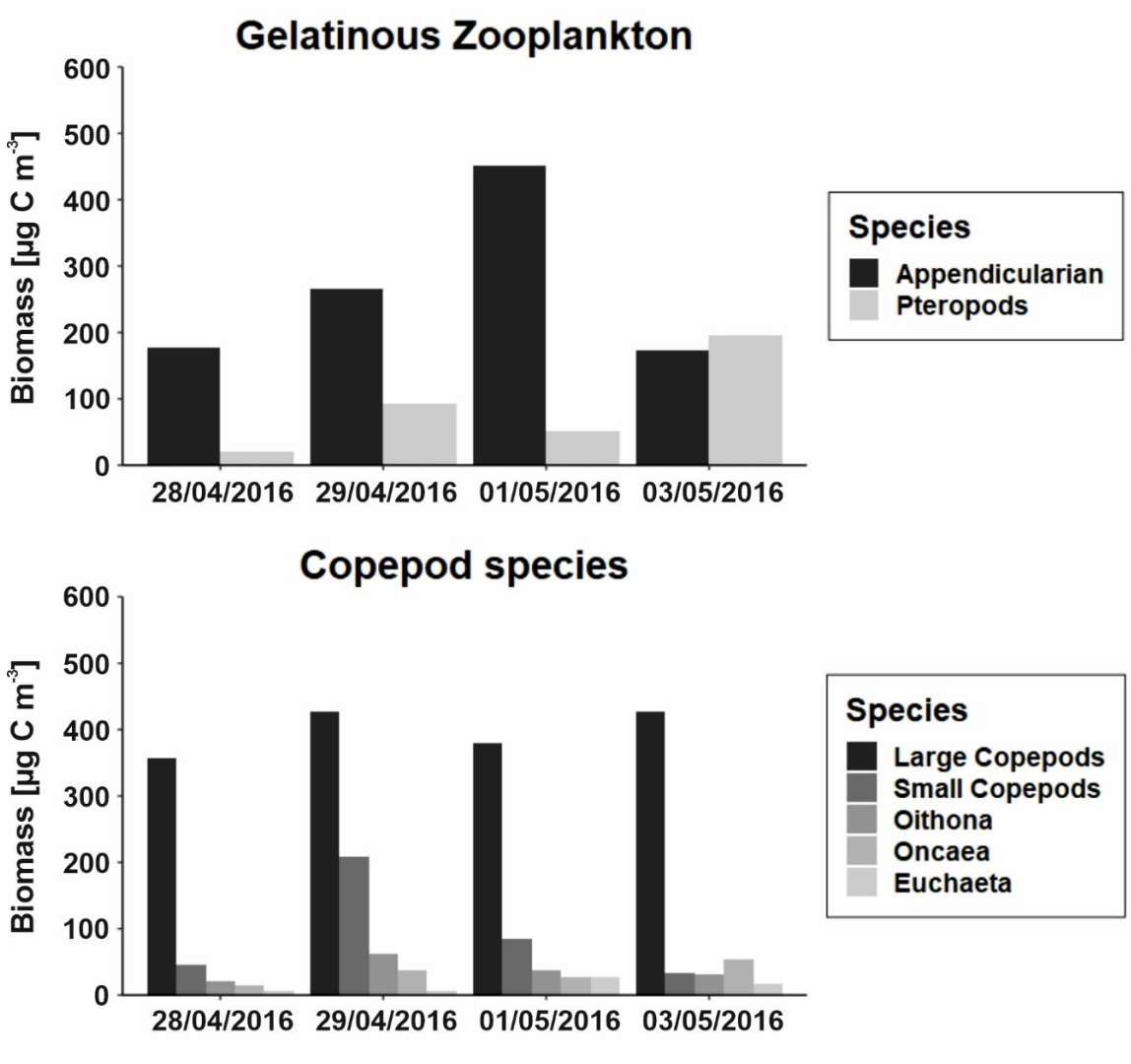


Fig. 14: Biomass of the eight main zooplankton groups sampled in the upper 200 m of the water column. (A) major gelatinous zooplankton and (B) major copepod groups.

DISCUSSION

On 1st May, we observed a large change in aggregate properties and carbon flux. Before 1st May, the flux was composed of many small and compact aggregates, however, those aggregates disappeared on the 1st May and the peak carbon flux decreased from 100 to 3.0 mg C m^{-2} d^{-1} (Fig. 13). After the 2nd May, the settling aggregates were dominated by large mucus aggregates (Fig. 15), which had slightly higher size-specific settling velocities compared to the small and compact aggregates observed before (Fig. 11). These large mucus aggregates increased the peak flux to 200 mg C m^{-2} d^{-1}. Typically, such rapid changes in export flux (an order of magnitude within days), suggest changes in either water masses i.e., passing of a front or an eddy, or surface ocean conditions such as the passing of a storm or the demise of a plankton bloom. However, our in-situ observations of chlorophyll, temperature, and salinity using ship-deployed CTD profiles, moored sensors at 1 m and 30 m depths, and satellite observations of fluorescence, current velocities, temperature anomalies, and sea-height anomalies, all showed that we were sampling in the same water mass and there was no evidence for a storm. (Fig.10, Fig. S2). A closer look into surface currents during the cruise period revealed that strongest surface current velocity was measured at the 5th of May with approximately 0.078 m s^{-1} (Fig. S3). Using the highest value as a standard for the water mass movement over the whole cruise period, showed that the daily water mass movement was low with a total daily movement of around 6.75 km, which could not explain the large variabilities in POC flux over short-time scale. Furthermore, we analysed the average current velocities for the upper mixed layer (surface to 50 m depth) and below the MLD from 50 m to 300 m (Fig.S4). We observed that the current velocity was relatively constant and similar both above and below the MLD with velocities of around 0.01 m s^{-1}, except on the 1st of May, were the eastward current above the MLD increased to 0.066 m s^{-1}. When we consider the constant value over the whole cruise period, the daily water mass movement was <1 km per day, which is neglectable and fits with the comparable chlorophyll concentrations measured throughout the study from the moored CTD and cannot explain the large variability in POC flux. Moreover, we did observe a decrease in MLD after the 2nd May, which concentrated the phytoplankton in a shallower surface layer (from 50 m to around 25 m) and increased the chlorophyll a concentration from 1 to 2 mg m^{-3}. Hence, we conclude that the doubling from 1.2

to 2.2 mg chl-a m^{-3} 4th May in chlorophyll concentrations was due to a shallowing of the MLD and not due to lateral advection of different water masses with higher chlorophyll a concentration. Still, a doubling in phytoplankton concentration is unlikely to explain the occurrence of mucus aggregates or the strong increased POC flux after the 2nd May compared to a few days earlier. Hence, POC flux dynamics was be driven by other processes than changes in water masses, physical mixing, or growth of phytoplankton.

There is a growing amount of literature showing that zooplankton are more important than microbes for flux attenuation in the upper water column (e.g., Iversen et al. 2010, van der Jagt et al. 2020, Pauli et al. 2021), suggesting that zooplankton might have shaped the temporal and spatial flux dynamics. The biomass of large copepods showed little variation during the study period and had the largest contribution to total mesozooplankton biomass, which is consistent with previous observations in oceanic waters (Vargas et al. 2002, Hidaka 2008, Yilmaz & Besiktepe 2010, Andersen et al. 2011), especially in the region of the Northeast Atlantic (Morales et al. 1991, Morales et al. 1993, Christiansen et al. 1999, Christiansen et al. 2010). Still, despite the large contribution to the total biomass from large copepods, their actual numbers only ranged between one and five copepods per cubic meter. Therefore, even when allowing for very high filtration rates, the few large copepods within one cubic meter of water would only have been able to filter less than five litres of water per day, suggesting that the large copepods were only responsible for a minor fraction of the vertical and temporal changes in carbon flux. Furthermore, though the small copepods showed a small increase in abundance and biomass on the 29th April, this was not reflected in the carbon flux and during the period of large fluctuations in carbon flux, the small copepod biomass steadily decreased. Hence, we assume that copepods had limited impact on carbon export and attenuation during our study.

The biomass of appendicularia made the second largest contribution to the total mesozooplanktonic biomass, consistent with literature findings about the general assemblage of zooplankton communities (Hopcroft et al. 1998, Sommer & Stibor 2002, Jaspers et al. 2009, Yilmaz & Besiktepe 2010). Moreover, we observed a constant increase in appendicularian biomass until the 1st May whereafter their biomass decreased 2.5-fold. In comparison to copepods, appendicularians grow

much faster (Hopcroft & Roff 1995, Uye & Ichino 1995, Hopcroft et al. 1998, Zubkov & Lopez-Urrutia et al. 2003), which might explain why we observed large change in appendicularian biomass while copepod biomass remained relatively constant during the study. Considering a maximum clearance rate of 12±1 µg C m^{-3} d^{-1} (Lombard et al. 2009), the appendicularian biomass observed the 1st May could potentially remove 5.4 mg C m^{-3} d^{-1} via filtration. When calculating the flux attenuation for the upper 50 m of the water column according to Iversen (2023), the loss in carbon flux was only 0.7±0.7 mg C m^{-3} d^{-1}, suggesting that appendicularians could have been responsible for both the vertical and temporal changes in carbon flux until the 1st May.

Several studies reported that the growth of appendicularian is limited by food concentration, with decreasing body size and individual carbon content as a result of low food concentration (Lopez-Urrutia et al. 2003, Lombard et al. 2009). If this is the case, then the low food availability in the water column on 1st and 2nd May could potentially have caused the decrease in appendicularian biomass that we observed on the 3rd May. The shift from small and compact to large mucus aggregates after the 2nd May is co-occurring with this and may well reflect a large contribution of appendicularian houses to the carbon flux. The filtration system of appendicularian houses consists of two filters, one outer coarse filter to capture large particles and one inner and fine filter that allow them to capture and ingest small particles down to a size of 0.2 µm (Deibel & Powell 1987, Lombard et al. 2011). When the outer coarse filter becomes clogged by large particles, the appendicularia abandons its house and can immediately inflate a new and already prepared house (Gorsky & Fenaux 1998, Sato et al. 2003). Sato et al. (2001) found that Larvaceans are able to discard 26 houses per day. Once the houses are discarded, they slowly start to sink and become part of the settling marine snow (Alldredge 1976, Silver & Alldredge 1981, Taguchi 1982, Alldredge et al. 1990, Hamner & Robison 1992, Hansen et al. 1996, Sato et al. 2001). At first, when the houses are still inflated, they sink slowly, but as they start collapsing, their settling velocities increase and can reach velocities of several hundred meters per day (Lombard and Kiørboe 2010), enhancing export production up to 55% (Berline et al. 2011). Comparing the appearance of the large mucus aggregates with the observations of settling appendicularian houses by Lombard and Kiørboe (2010,

Fig. 3), they show great similarities and suggests that appendicularian houses account for the majority of the large mucus aggregates (Fig. 15). Assuming a carbon content per house to be 0.8 µg C and a daily production and release of 26 houses (Sato et al. 2001), 90 appendicularians could contribute by 93.6 mg C m^{-2} d^{-1} in the upper 50 m of the water column. Furthermore, assuming that these first sink slowly until the collapse, the grazing and house production by appendicularians could explain the initial rapid decrease and subsequent increase in carbon flux observed from the 1st May.

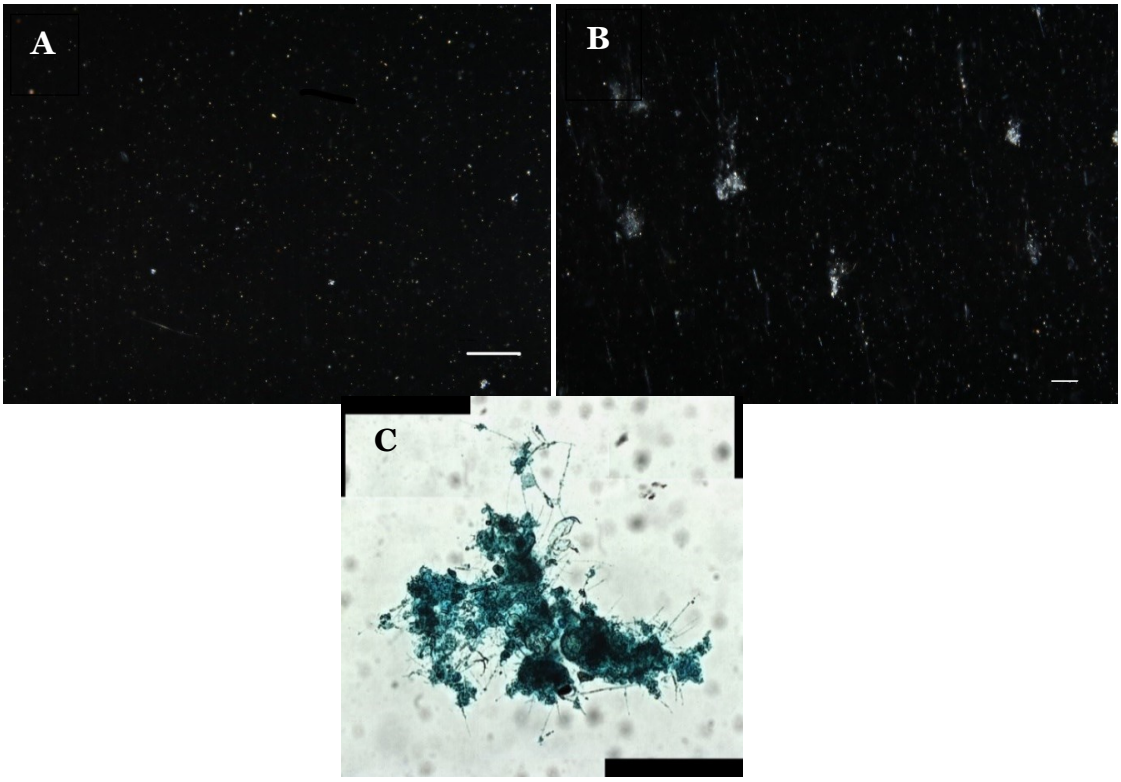


Fig. 15: Examples of in situ particles captured with the PELAGRACam in the upper 50m of the water column. (A) shows particles from 30th April 2016 and (B) from 5th May 2016. The white bar in the right lower corner of both images is defined as a 5 mm scale bar. (C) Alcian blue stained aggregate collected with the Marine Snow Catcher after 1st May. Alcian Blue stained regions appear blue and show dyable Polysaccharides structures within the aggregate. The photo was taken with an inverted microscope at a 100x magnification. The image width is 1.14 mm and the aggregate diameter is around 1 mm.

The biomass of pteropods increased to 200 µg C m^{-3} on 3rd May. Pteropods are passive flux feeders and feed by releasing mucus feeding nets that capture sinking particles (Silver and Bruland 1981, Noji et al. 1997, Jackson 1993). They are

therefore efficient flux attenuators, but due to their low abundance on 1st May, they probably contributed little to flux attenuation during our study. However, pteropods could have contributed to the increased carbon flux after 2nd May via the production and release of mucus feeding nets (Gilmer & Harbison 1986, Tsurumi et al. 2005) and are considered important contributors to the carbon flux. Generally, mucus feeding nets are only released when the pteropods are disturbed, the sticky mucus structures enhance the aggregation and accumulate to small dense particles reaching average settling velocities of 300 m d^{-1} (Noji et al. 1997). The high carbon flux observed after 2nd May was also due to contributions from pteropods faecal pellets and abandoned mucus feeding nets.

To gain further insights into changes in aggregate type within the upper water column, we analyzed the chemical composition of different particle classes. Fast-sinking, as well as slow sinking particles showed a steady decrease in their C:N ratio until 1st May. These could be caused by export of phytoplankton cells over detritus (Xu et al. 2021), the incorporation of clay minerals (Müller 1977), the fragmentation of large particles into smaller ones. In general, gelatinous zooplankton is known for their high protein content, which could also lower C:N ratios when these species were incorporated in aggregate material (Madin et al. 1981). Furthermore, Alldredge (1998) assumed that newly discarded appendicularian houses results in decreased C:N ratio of the bulk flux, due to the clogging of fresh large phytoplankton to the coase filters of the houses. After 1st May, we observed an increased variability in C:N ratios ranging between 5 and 18 during the period until 6th May. The high values are similar to previous observations at the PAP-SO where a C:N ratio of 18 were observed for fast settling aggregates (Lampitt 2010). However, we propose that polysaccharides from the mucus structures increased the C:N ratios, similar to previous observations for transparent exopolymeric particles (TEP) (Engel 2000, Engel & Passow 2001). Interestingly, the C:N ratio decreased to around 2 on the 5th May, it is difficult to explain what caused this decrease, but the average C:N ratio of an appendicularian body is around 3.6 (Gorsky et al. 1988), so we can only speculate that it is possible that some of the organisms themselves died and sank out towards the end of our study.

Overall, our study suggests that appendicularians and to some extent pteropods are able to determine carbon fluxes to the mesopelagic at the Porcupine Abyssal Plain. With the release of mucus feeding nets or discarded houses, pteropods and appendicularian can enhance the carbon content and velocities of settling aggregates. Hence, pteropods and appendicularians can be key contributors to regional pulse events of carbon export, leading to a more efficient carbon pump. Due to the production of mucus rich aggregates, there was a preferential export of carbon over nutrients and the carbon to nitrogen ratios were much higher than what is typically observed for phytoplankton aggregates. This study therefore agrees with the recent suggestions that heterotrophic activity at the base of the euphotic zone may increase the overall efficiency of the BCP by promoting export of carbon-rich aggregates (Iversen 2023). Moreover, if these findings at the PAP-SO are typical for the Northeast Atlantic, then the contribution of gelatinous zooplankton to the BCP has been significantly underestimated.

ACKNOWLEDGEMENTS

We thank the captains and crew of the British RRS Discovery. This work was conducted in the framework of the HGF Infrastructure Program FRAM of the Alfred-Wegener-Institute Helmholtz Centre for Polar and Marine Research. This work was part of the Helmholtz Program "Changing Earth—Sustaining our Future" supported by the Helmholtz Program-Orientated Funding (POF IV) to topic 6 (Marine Life) and the sub-topic 6.3 (The Future Biological Carbon Pump). The work was funded by DFG-Research Centre/Cluster of Excellence "The Ocean Floor—Earth's Uncharted Interface": EXC-2077-390741603. We thank Catherine Broster who ran the flow cam samples as part of her MSc dissertation "TRAIT-BASED APPROACH REVEALS PATTERNS IN MESOZOOPLANKTON DIEL VERTICAL MIGRATION AT THE PORCUPINE ABYSSAL PLAIN FIXED-POINT SUSTAINED OBSERVATORY (PAP-SO)".

CONFLICT OF INTEREST

The authors have no conflict of interest.

REFERENCES

Alldredge, A. L. (1976). Discarded appendicularian houses as sources of food, surface habitats, and particulate organic matter in planktonic environments. Limnology and Oceanography, 21(1), 14-24.

Alldredge, A. (1998). The carbon, nitrogen and mass content of marine snow as a function of aggregate size. Deep Sea Research Part I: Oceanographic Research Papers, 45(4-5), 529-541.

Alldredge, A. L., Granata, T. C., Gotschalk, C. C., & Dickey, T. D. (1990). The physical strength of marine snow and its implications for particle disaggregation in the ocean. Limnology and Oceanography, 35(7), 1415-1428.

Andersen, N. G., Nielsen, T. G., Jakobsen, H. H., Munk, P., & Riemann, L. (2011). Distribution and production of plankton communities in the subtropical convergence zone of the Sargasso Sea. II. Protozooplankton and copepods. Marine Ecology Progress Series, 426, 71-86.

Ashjian, C. J., Campbell, R. G., Welch, H. E., Butler, M., & Van Keuren, D. (2003). Annual cycle in abundance, distribution, and size in relation to hydrography of important copepod species in the western Arctic Ocean. Deep Sea Research Part I: Oceanographic Research Papers, 50(10-11), 1235-1261.

Bednaršek, N., Možina, J., Vogt, M., O'Brien, C., & Tarling, G. A. (2012). The global distribution of pteropods and their contribution to carbonate and carbon biomass in the modern ocean. Earth System Science Data, 4(1), 167-186.

Berline, L., Stemmann, L., Vichi, M., Lombard, F., & Gorsky, G. (2011). Impact of appendicularians on detritus and export fluxes: a model approach at DyFAMed site. Journal of Plankton Research, 33(6), 855-872.

Billett, D. S. M., & Rice, A. L. (2001). The BENGAL programme: introduction and overview. Progress in Oceanography, 50(1-4), 13-25.

Caron, D. A., Madin, L. P., & Cole, J. J. (1989). Composition and degradation of salp fecal pellets: implications for vertical flux in oceanic environments. Journal of Marine Research, 47(4), 829-850.

Castellani, C., Irigoien, X., Mayor, D. J., Harris, R. P., & Wilson, D. (2008). Feeding of Calanus finmarchicus and Oithona similis on the microplankton assemblage in the Irminger Sea, North Atlantic. Journal of Plankton Research, 30(10), 1095-1116.

Cavan, E. L., Kawaguchi, S., & Boyd, P. W. (2021). Implications for the mesopelagic microbial gardening hypothesis as determined by experimental fragmentation of Antarctic krill fecal pellets. Ecology and evolution, 11(2), 1023-1036.

Christiansen, B., Drüke, B., Koppelmann, R., & Weikert, H. (1999). The near-bottom zooplankton at the abyssal BIOTRANS site, northeast Atlantic: composition, abundance and variability. Journal of Plankton Research, 21(10).

Christiansen, B., Bühring, S. I., Pfannkuche, O., & Weikert, H. (2010). The near-bottom plankton community at the Porcupine Abyssal Plain, NE-Atlantic: Structure and vertical distribution. Marine Biology Research, 6(2), 113-124.

Christiansen, B., & Weikert, H. (2018). High temporal variability of zooplankton, but only weak evidence for a near-bottom effect on composition and distribution in the deep Levantine Basin, eastern Mediterranean. Marine Biology Research, 14(1), 76-86.

Christina, L., & Passow, U. (2007). Factors influencing the sinking of POC and the efficiency of the biological carbon pump. Deep Sea Research Part II: Topical Studies in Oceanography, 54(5-7), 639-658.

Copernicus Climate Change Service, Climate Data Store, (2018): Sea level gridded data from satellite observations for the global ocean from 1993 to present. Copernicus Climate Change Service (C3S) Climate Data Store (CDS). DOI: 10.24381/cds.4c328c78 (Accessed on 13-12-2023)

Davoll, P. J., & Silver, M. W. (1986). Marine snow aggregates: life history sequence and microbial community of abandoned larvacean houses from Monterey Bay, California. Mar. Ecol. Prog. Ser, 33(11), l-120.

de Boyer Montégut, C., Madec, G., Fischer, A. S., Lazar, A., & Iudicone, D. (2004). Mixed layer depth over the global ocean: An examination of profile data and a profile - based climatology. Journal of Geophysical Research: Oceans, 109(C12).

de Melo Júnior, M., Miyashita, L. K., & Lopes, R. M. (2021). A 3-year study of the seasonal variability of abundance, biomass and reproductive traits of Oncaea venusta (Copepoda, Oncaeidae) in a subtropical coastal area. Journal of plankton research, 43(5), 751-761.

Deibel, D., & Powell, C. V. L. (1987). Ultrastructure of the pharyngeal filter of the appendicularian Oikopleura vanhoeffeni: implications for particle size selection and fluid mechanics. Marine Ecology Progress Series, 243-250.

Dias, C. O., Araujo, A. V., Vianna, S. C., Fernandes, L. L., Paranhos, R., Suzuki, M. S., & Bonecker, S. L. C. (2015). Spatial and temporal changes in biomass, production and assemblage structure of mesozooplanktonic copepods in the tropical south-west Atlantic Ocean. Journal of the Marine Biological Association of the United Kingdom, 95(3), 483-496.

Dilling, L., & Brzezinski, M. A. (2004). Quantifying marine snow as a food choice for zooplankton using stable silicon isotope tracers. Journal of Plankton Research, 26(9), 1105-1114.

Ducklow, H. W., Steinberg, D. K., & Buesseler, K. O. (2001). Upper ocean carbon export and the biological pump. Oceanography, 14(4), 50-58.

Engel, A. (2000). The role of transparent exopolymer particles (TEP) in the increase in apparent particle stickiness (α) during the decline of a diatom bloom. Journal of Plankton Research, 22(3), 485-497.

Engel, A., & Passow, U. (2001). Carbon and nitrogen content of transparent exopolymer particles (TEP) in relation to their Alcian Blue adsorption. Marine Ecology Progress Series, 219, 1-10.

Falkowski, P. G., Barber, R. T., & Smetacek, V. (1998). Biogeochemical controls and feedbacks on ocean primary production. science, 281(5374), 200-206.

Forest, A., Tremblay, J. É., Gratton, Y., Martin, J., Gagnon, J., Darnis, G., ... & Piepenburg, D. (2011). Biogenic carbon flows through the planktonic food web of the Amundsen Gulf (Arctic Ocean): A synthesis of field measurements and inverse modeling analyses. Progress in Oceanography, 91(4), 410-436.

Fortier, M., Fortier, L., Michel, C., & Legendre, L. (2002). Climatic and biological forcing of the vertical flux of biogenic particles under seasonal Arctic sea ice. Marine Ecology Progress Series, 225, 1-16.

Fowler, S. W., & Knauer, G. A. (1986). Role of large particles in the transport of elements and organic compounds through the oceanic water column. Progress in oceanography, 16(3), 147-194.

Giering, S. L., Sanders, R., Lampitt, R. S., Anderson, T. R., Tamburini, C., Boutrif, M., ... & Mayor, D. J. (2014). Reconciliation of the carbon budget in the ocean's twilight zone. Nature, 507(7493), 480-483.

Giering, S. L., Hosking, B., Briggs, N., & Iversen, M. H. (2020). The interpretation of particle size, shape, and carbon flux of marine particle images is strongly affected by the choice of particle detection algorithm. Frontiers in Marine Science, 7, 564.

Gilmer, R. W. (1972). Free-floating mucus webs: a novel feeding adaptation for the open ocean. Science, 176(4040), 1239-1240.

Gilmer, R. W., & Harbison, G. R. (1986). Morphology and field behavior of pteropod molluscs: feeding methods in the families Cavoliniidae, Limacinidae and Peraclididae (Gastropoda: Thecosomata). Marine Biology, 91, 47-57.

Gorsky, G., Dallot, S., Sardou, J., Fenaux, R., Carré, C., & Palazzoli, I. (1988). C and N composition of some northwestern Mediterranean zooplankton and micronekton species. Journal of Experimental Marine Biology and Ecology, 124(2), 133-144.

Gorsky, G., & Fenaux, R. (1998). The role of Appendicularia in marine food webs. The biology of pelagic tunicates, 161-169.

Green, E. P., & Dagg, M. J. (1997). Mesozooplankton associations with medium to large marine snow aggregates in the northern Gulf of Mexico. Journal of Plankton Research, 19(4), 435-447.

Guidi, L., Jackson, G. A., Stemmann, L., Miquel, J. C., Picheral, M., & Gorsky, G. (2008). Relationship between particle size distribution and flux in the mesopelagic zone. Deep Sea Research Part I: Oceanographic Research Papers, 55(10), 1364-1374.

Hamner, W. M., & Robison, B. H. (1992). In situ observations of giant appendicularians in Monterey Bay. Deep Sea Research Part A. Oceanographic Research Papers, 39(7-8), 1299-1313.

Hansen, J. L., Kiørboe, T., & Alldredge, A. L. (1996). Marine snow derived from abandoned larvacean houses: sinking rates, particle content and mechanisms of aggregate formation. Marine Ecology Progress Series, 141, 205-215.

Hays, G. C. (1995). Ontogenetic and seasonal variation in the diel vertical migration of the copepods Metridia lucens and Metridia longa. Limnology and Oceanography, 40(8), 1461-1465.

Hidaka, K. (2008). Species composition and horizontal distribution of the appendicularian community in waters adjacent to the Kuroshio in winter–early spring. Plankton and Benthos Research, 3(3), 152-164.

Hopcroft, R. R., & Roff, J. C. (1995). Zooplankton growth rates: extraordinary production by the larvacean Oikopleura dioica in tropical waters. Journal of Plankton Research, 17(2), 205-220.

Hopcroft, R. R., Roff, J. C., & Bouman, H. A. (1998). Zooplankton growth rates: the larvaceans Appendicularia, Fritillaria and Oikopleura in tropical waters. Journal of Plankton Research, 20(3), 539-555.

Iversen, M. H., & Lampitt, R. S. (2020). Size does not matter after all: no evidence for a size-sinking relationship for marine snow. Progress in Oceanography, 189, 102445.

Iversen, M. H., & Poulsen, L. K. (2007). Coprorhexy, coprophagy, and coprochaly in the copepods Calanus helgolandicus, Pseudocalanus elongatus, and Oithona similis. Marine Ecology Progress Series, 350, 79-89.

Iversen, M. H. (2023). Carbon Export in the Ocean: A Biologist's Perspective. Annual Review of Marine Science, 15, 357-381.

Iversen, M. H., Nowald, N., Ploug, H., Jackson, G. A., & Fischer, G. (2010). High resolution profiles of vertical particulate organic matter export off Cape Blanc, Mauritania: Degradation processes and ballasting effects. Deep Sea Research Part I: Oceanographic Research Papers, 57(6), 771-784.

Jackson, G. A. (1993). Flux feeding as a mechanism for zooplankton grazing and its implications for vertical particulate flux 1. Limnology and Oceanography, 38(6), 1328-1331.

Jaspers, C., Nielsen, T. G., Carstensen, J., Hopcroft, R. R., & Møller, E. F. (2009). Metazooplankton distribution across the Southern Indian Ocean with emphasis on the role of Larvaceans. Journal of plankton research, 31(5), 525-540.

Karl, D. M., Knauer, G. A., & Martin, J. H. (1988). Downward flux of particulate organic matter in the ocean: a particle decomposition paradox. Nature, 332(6163), 438-441.

King, K.R. 1981. The quantitative natural history of Oikopleura dioica (Urochordata, Larvacea) in the laboratory and in enclosed water columns. Ph.D. thesis, University of Washington.

Kiørboe, T., & Hansen, J. L. (1993). Phytoplankton aggregate formation: observations of patterns and mechanisms of cell sticking and the significance of exopolymeric material. Journal of Plankton Research, 15(9), 993-1018.

Koski, M., Kiørboe, T., & Takahashi, K. (2005). Benthic life in the pelagic: aggregate encounter and degradation rates by pelagic harpacticoid copepods. Limnology and oceanography, 50(4), 1254-1263.

Lampitt, R. S., Noji, T., & Von Bodungen, B. (1990). What happens to zooplankton faecal pellets? Implications for material flux. Marine Biology, 104, 15-23.

Lampitt, R. S., Wishner, K. F., Turley, C. M., & Angel, M. V. (1993). Marine snow studies in the Northeast Atlantic Ocean: distribution, composition and role as a food source for migrating plankton. Marine Biology, 116, 689-702.

Lampitt, R. S., Salter, I., de Cuevas, B. A., Hartman, S., Larkin, K. E., & Pebody, C. A. (2010). Long-term variability of downward particle flux in the deep northeast Atlantic: Causes and trends. Deep Sea Research Part II: Topical Studies in Oceanography, 57(15), 1346-1361.

Lombard, F., Renaud, F., Sainsbury, C., Sciandra, A., & Gorsky, G. (2009). Appendicularian ecophysiology I: Food concentration dependent clearance rate, assimilation efficiency, growth and reproduction of Oikopleura dioica. Journal of Marine Systems, 78(4), 606-616.

Lombard, F., Selander, E., & Kiørboe, T. (2011). Active prey rejection in the filter - feeding appendicularian Oikopleura dioica. Limnology and Oceanography, 56(4), 1504-1512.

Lombard, F., Koski, M., & Kiørboe, T. (2013). Copepods use chemical trails to find sinking marine snow aggregates. Limnology and oceanography, 58(1), 185-192.

Longhurst, A. R., & Harrison, W. G. (1989). The biological pump: profiles of plankton production and consumption in the upper ocean. Progress in Oceanography, 22(1), 47-123.

Longhurst, A. R. (1991). Role of the marine biosphere in the global carbon cycle. Limnology and Oceanography, 36(8), 1507-1526.

López-Urrutia, Á., Acuña, J. L., Irigoien, X., & Harris, R. (2003). Food limitation and growth in temperate epipelagic appendicularians (Tunicata). Marine Ecology Progress Series, 252, 143-157.

Madin, L. P., Cetta, C. M., & McAlister, V. L. (1981). Elemental and biochemical composition of salps (Tunicata: Thaliacea). Marine Biology, 63, 217-226.

Martiny, A. C., Vrugt, J. A., Primeau, F. W., & Lomas, M. W. (2013). Regional variation in the particulate organic carbon to nitrogen ratio in the surface ocean. Global Biogeochemical Cycles, 27(3), 723-731.

Marty, J. C., Nicolas, E., Miquel, J. C., & Fowler, S. W. (1994). Particulate fluxes of organic compounds and their relationship to zooplankton fecal pellets in the northwestern Mediterranean Sea. Marine Chemistry, 46(4), 387-405.

Metzger E.J., Helber R.W., Hogan P.J., Posey P.G., Thoppil P.G., Townsend T.L., Wallcraft A.J., Smedstad O.M., and Franklin D.S., 2017: Global Ocean Forecast System 3.1 Validation Testing. NRL Report NRL/MR/7320--17-9722

Möller, K. O., John, M. S., Temming, A., Floeter, J., Sell, A. F., Herrmann, J. P., & Möllmann, C. (2012). Marine snow, zooplankton and thin layers: indications of a trophic link from small-scale sampling with the Video Plankton Recorder. Marine Ecology Progress Series, 468, 57-69.

Morales, C. E., Bedo, A., Harris, R. P., & Tranter, P. R. G. (1991). Grazing of copepod assemblages in the north-east Atlantic: the importance of the small size fraction. Journal of Plankton Research, 13(2), 455-472.

Morales, C. E., Harris, R. P., Head, R. N., & Tranter, P. R. (1993). Copepod grazing in the oceanic northeast Atlantic during a 6 week drifting station: the contribution of size classes and vertical migrants. Journal of Plankton Research, 15(2), 185-212.

Müller, P. J. (1977). CN ratios in Pacific deep-sea sediments: Effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. Geochimica et Cosmochimica Acta, 41(6), 765-776.

Napp, J. M., Brooks, E. R., Matrai, P., & Mullin, M. M. (1988). Vertical distribution of marine particles and grazers. II. Relation of grazer distribution to food quality and quantity. Marine Ecology Progress Series, 59-72.

Noji, T. T., Estep, K. W., Macintyre, F., & Norrbin, F. (1991). Image analysis of faecal material grazed upon by three species of copepods: evidence for coprorhexy, coprophagy and coprochaly. Journal of the Marine Biological Association of the United Kingdom, 71(2), 465-480.

Noji, T. T., Bathmann, U. V., Bodungen, B. V., Voss, M., Antia, A., Krumbholz, M., ... & Rey, F. (1997). Clearance of picoplankton-sized particles and formation of rapidly sinking aggregates by the pteropod, Limacina retroversa. Journal of Plankton Research, 19(7), 863-875.

Pauli, N. C., Flintrop, C. M., Konrad, C., Pakhomov, E. A., Swoboda, S., Koch, F., ... & Iversen, M. H. (2021). Krill and salp faecal pellets contribute equally to the carbon flux at the Antarctic Peninsula. Nature Communications, 12(1), 7168.

Ploug, H., & Jørgensen, B. B. (1999). A net-jet flow system for mass transfer and microsensor studies of sinking aggregates. Marine Ecology Progress Series, 176, 279-290.

Poulsen, L. K., & Kiørboe, T. (2005). Coprophagy and coprorhexy in the copepods Acartia tonsa and Temora longicornis: clearance rates and feeding behaviour. Marine Ecology Progress Series, 299, 217-227.

Robison, B. H., Reisenbichler, K. R., & Sherlock, R. E. (2005). Giant larvacean houses: rapid carbon transport to the deep sea floor. Science, 308(5728), 1609-1611.

Sathyendranath, S., Brewin, R. J., Brockmann, C., Brotas, V., Calton, B., Chuprin, A., ... & Platt, T. (2019). An ocean-colour time series for use in climate studies: the experience of the ocean-colour climate change initiative (OC-CCI). Sensors, 19(19), 4285.

Sato, R., Tanaka, Y., & Ishimaru, T. (2001). House production by Oikopleura dioica (Tunicata, Appendicularia) under laboratory conditions. Journal of plankton research, 23(4), 415-423.

Sato, R., Tanaka, Y., & Ishimaru, T. (2003). Species-specific house productivity of appendicularians. Marine Ecology Progress Series, 259, 163-172.

Sato, R., Ishibashi, Y., Tanaka, Y., Ishimaru, T., & Dagg, M. J. (2008). Productivity and grazing impact of Oikopleura dioica (Tunicata, Appendicularia) in Tokyo Bay. Journal of Plankton Research, 30(3), 299-309.

Silver, M. W., & Alldredge, A. L. (1981). Bathypelagic marine snow: deep-sea algal and detrital community.

Silver, M. W., & Bruland, K. W. (1981). Differential feeding and fecal pellet composition of salps and pteropods, and the possible origin of the deep-water flora and olive-green "cells". Marine Biology, 62, 263-273.

Silver, M. W., Shanks, A. L., & Trent, J. D. (1978). Marine snow: microplankton habitat and source of small-scale patchiness in pelagic populations. Science, 201(4353), 371-373.

Simon, M., Grossart, H. P., Schweitzer, B., & Ploug, H. (2002). Microbial ecology of organic aggregates in aquatic ecosystems. Aquatic microbial ecology, 28(2), 175-211.

Sommer, U., & Stibor, H. (2002). Copepoda–Cladocera–Tunicata: the role of three major mesozooplankton groups in pelagic food webs. Ecological Research, 17, 161-174.

Steinberg, D. K., Silver, M. W., Pilskaln, C. H., Coale, S. L., & Paduan, J. B. (1994). Midwater zooplankton communities on pelagic detritus (giant larvacean houses) in Monterey Bay, California. Limnology and Oceanography, 39(7), 1606-1620.

Steinberg, D. K., Goldthwait, S. A., & Hansell, D. A. (2002). Zooplankton vertical migration and the active transport of dissolved organic and inorganic nitrogen in the Sargasso Sea. Deep Sea Research Part I: Oceanographic Research Papers, 49(8), 1445-1461.

Steinberg, D. K., Van Mooy, B. A., Buesseler, K. O., Boyd, P. W., Kobari, T., & Karl, D. M. (2008). Bacterial vs. zooplankton control of sinking particle flux in the ocean's twilight zone. Limnology and Oceanography, 53(4), 1327-1338.

Sutherland, K. R., Madin, L. P., & Stocker, R. (2010). Filtration of submicrometer particles by pelagic tunicates. Proceedings of the National Academy of Sciences, 107(34), 15129-15134.

Taguchi, S. (1982). Seasonal study of fecal pellets and discarded houses of Appendicularia in a subtropical inlet, Kaneohe Bay, Hawaii. Estuarine, Coastal and Shelf Science, 14(5), 545-555.

Taylor, G. T. (1989). Variability in the vertical flux of microorganisms and biogenic material in the epipelagic zone of a North Pacific central gyre station. Deep Sea Research Part A. Oceanographic Research Papers, 36(9), 1287-1308.

Thompson, G. A., Dinofrio, E. O., & Alder, V. A. (2013). Structure, abundance and biomass size spectra of copepods and other zooplankton communities in upper waters of the Southwestern Atlantic Ocean during summer. Journal of Plankton Research, 35(3), 610-629.

Tsurumi, M. 1., Mackas, D. L., Whitney, F. A., DiBacco, C., Galbraith, M. D., & Wong, C. S. (2005). Pteropods, eddies, carbon flux, and climate variability in the Alaska Gyre. Deep Sea Research Part II: Topical Studies in Oceanography, 52(7-8), 1037-1053.

Turner, J. T. (2002). Zooplankton fecal pellets, marine snow and sinking phytoplankton blooms. Aquatic microbial ecology, 27(1), 57-102.

Turner, J. T. (2015). Zooplankton fecal pellets, marine snow, phytodetritus and the ocean's biological pump. Progress in Oceanography, 130, 205-248.

Uye, S. I., & Ichino, S. (1995). Seasonal variations in abundance, size composition, biomass and production rate of Oikopleura dioica (Fol)(Tunicata: Appendicularia) in a temperate eutrophic inlet. Journal of Experimental Marine Biology and Ecology, 189(1-2), 1-11.

Van der Jagt, H., Wiedmann, I., Hildebrandt, N., Niehoff, B., & Iversen, M. H. (2020). Aggregate feeding by the copepods Calanus and Pseudocalanus controls carbon flux attenuation in the Arctic shelf sea during the productive period. Frontiers in Marine Science, 7, 543124.

Vargas, C. A., Tönnesson, K., Sell, A., Maar, M., Møller, E. F., Zervoudaki, T., ... & Tiselius, P. (2002). Importance of copepods versus appendicularians in vertical carbon fluxes in a Swedish fjord. Marine Ecology Progress Series, 241, 125-138.

Verity, P. G., Williams, S. C., & Hong, Y. (2000). Formation, degradation, and mass: volume ratios of detritus derived from decaying phytoplankton. Marine Ecology Progress Series, 207, 53-68.

Volk, T., & Hoffert, M. I. (1985). Ocean carbon pumps: Analysis of relative strengths and efficiencies in ocean - driven atmospheric CO2 changes. The carbon cycle and atmospheric CO2: Natural variations Archean to present, 32, 99-110.

Whitmore, B. M., & Ohman, M. D. (2021). Zooglider - measured association of zooplankton with the fine - scale vertical prey field. Limnology and Oceanography, 66(10), 3811-3827.

Xu, Z., Wang, B., Luo, Y., Li, H., Zhang, J., Jin, H., & Chen, J. (2021). Changes of carbon to nitrogen ratio in particulate organic matter in the marine mesopelagic zone: A case from the South China Sea. Marine Chemistry, 231, 103930.

Yılmaz, A. Z., & Besiktepe, S. (2010). Annual variations in biochemical composition of size fractionated particulate matter and zooplankton abundance and biomass in Mersin Bay, NE Mediterranean Sea. Journal of Marine Systems, 81(3), 260-271.

SUPPLEMENTARY

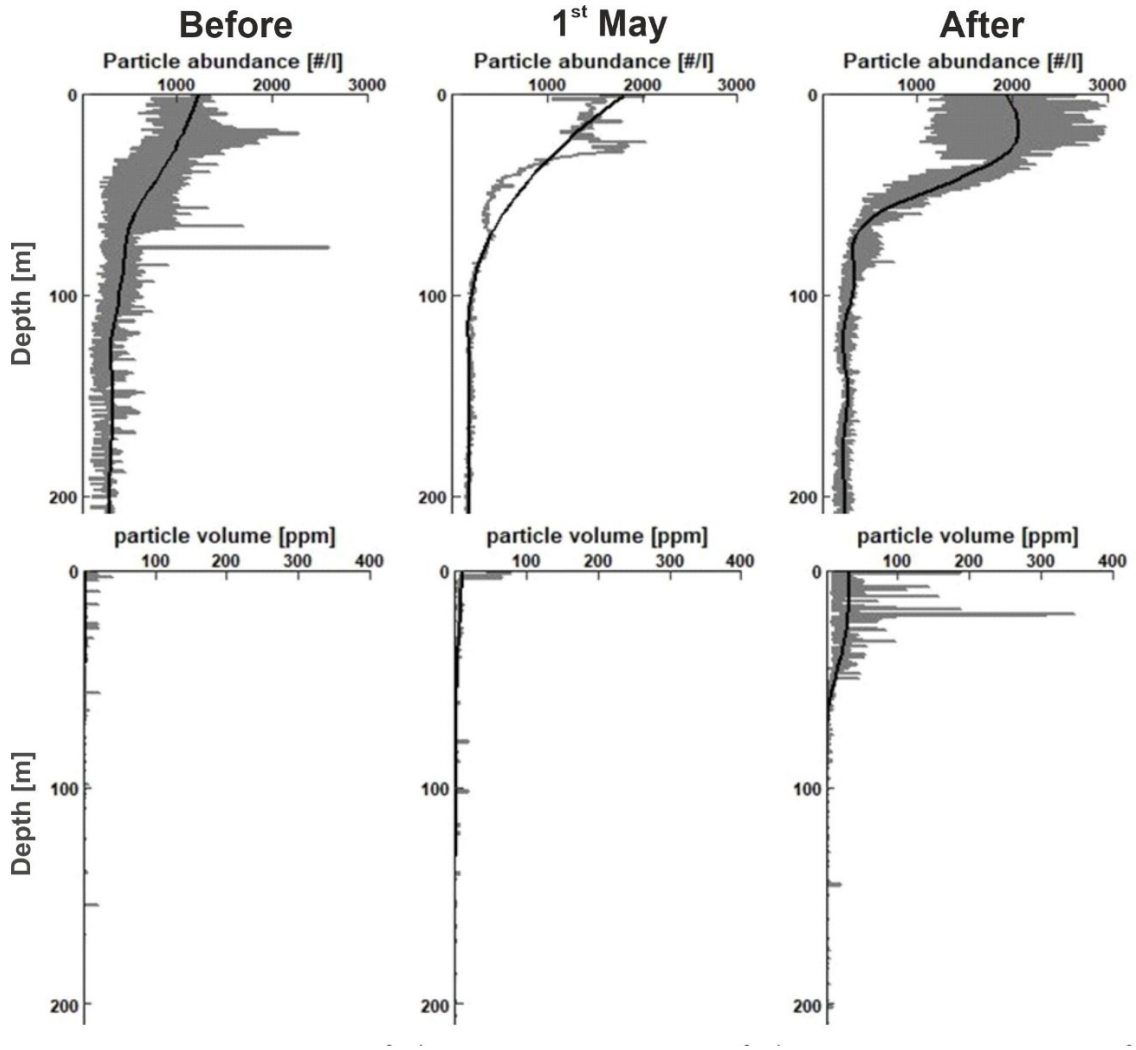


Fig. S1: Vertical profiles of particle abundance (A) and volume (B) measured with the PELAGRACam attached to the Red Camera frame. The black line shows the mean. The grey shadowed area specifies the minimum and maximum range of particle characteristics measured within specific timescales: Left: values including every 4 casts before 1st May. Middle: values directly measured at 1st May. Right: values including 3 casts after 1st May.

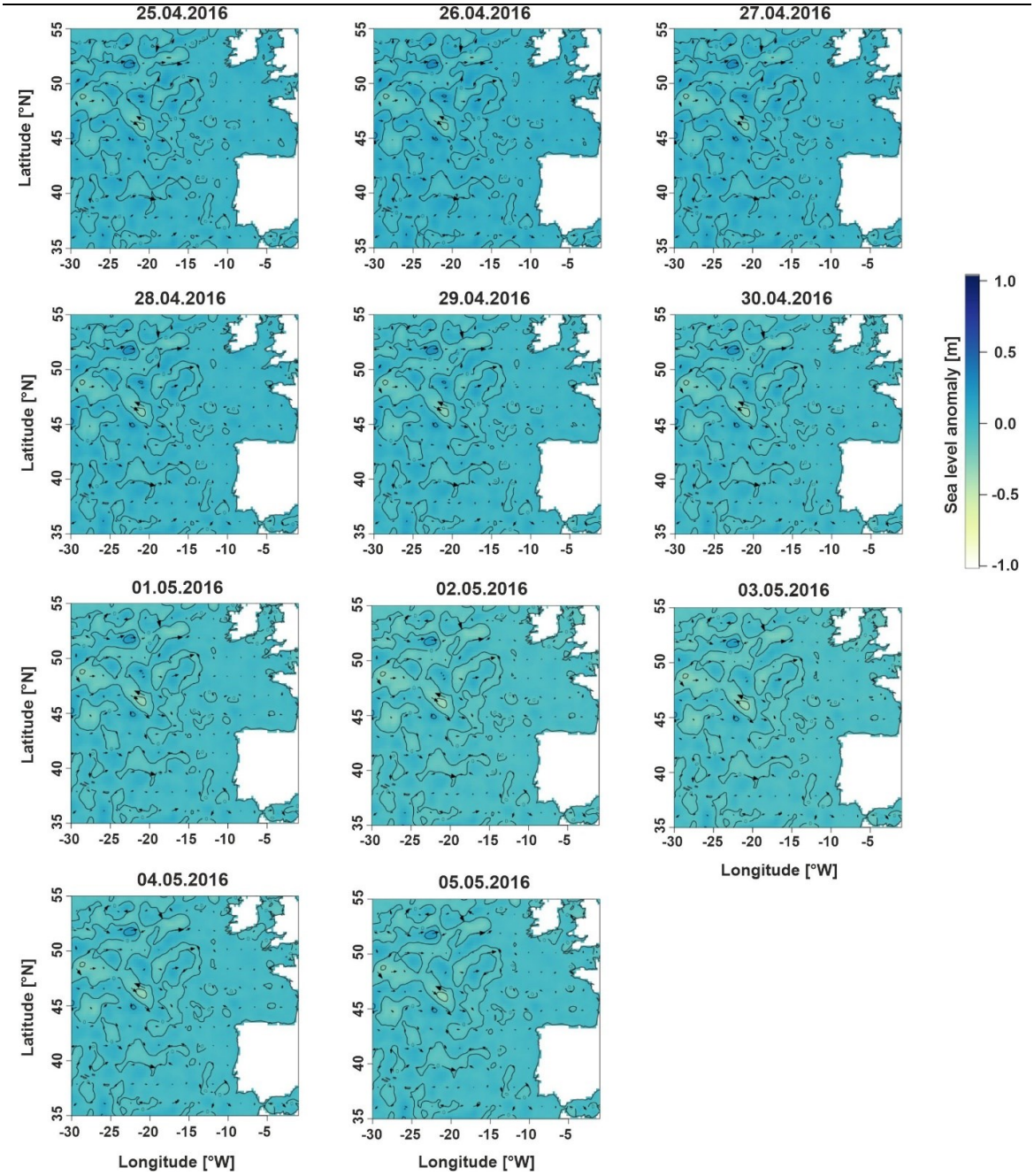


Fig. S2: Daily Sea level anomaly and currents starting from 25th April 2016 to 5th May 2016. Sea level anomaly is displayed colourful and currents display with arrows. The head of arrows specifies the direction and the size defines the strength.

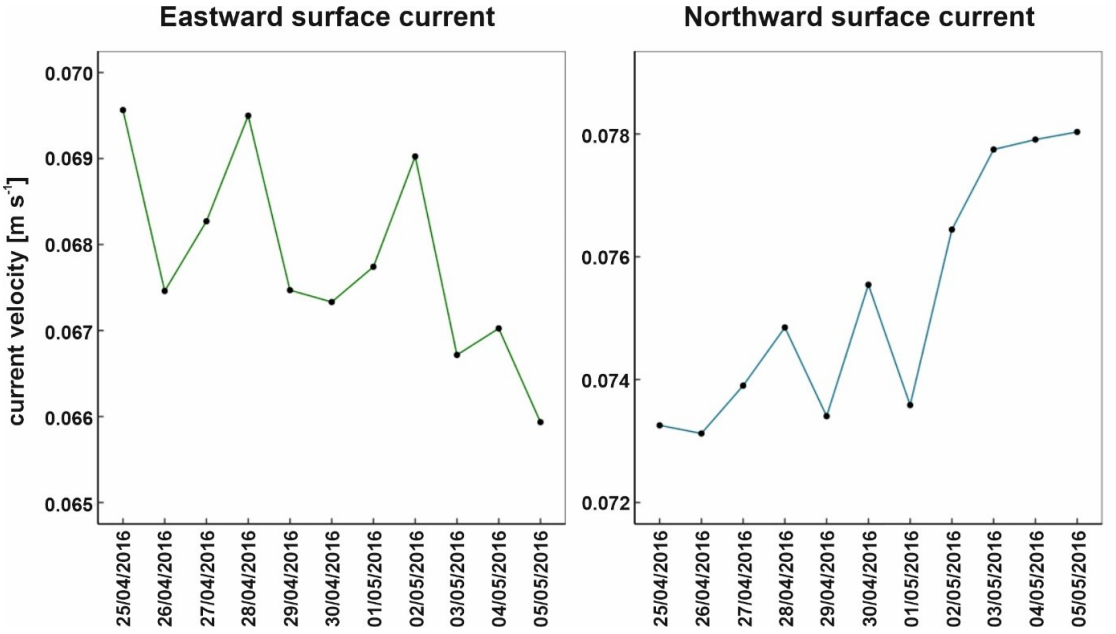


Fig. S3: Daily averaged surface currents for the region of -30° to -5°W as longitude and 35° to 55°N as latitude. Left: The mean of the eastward surface current. Right: The mean of the northward current.

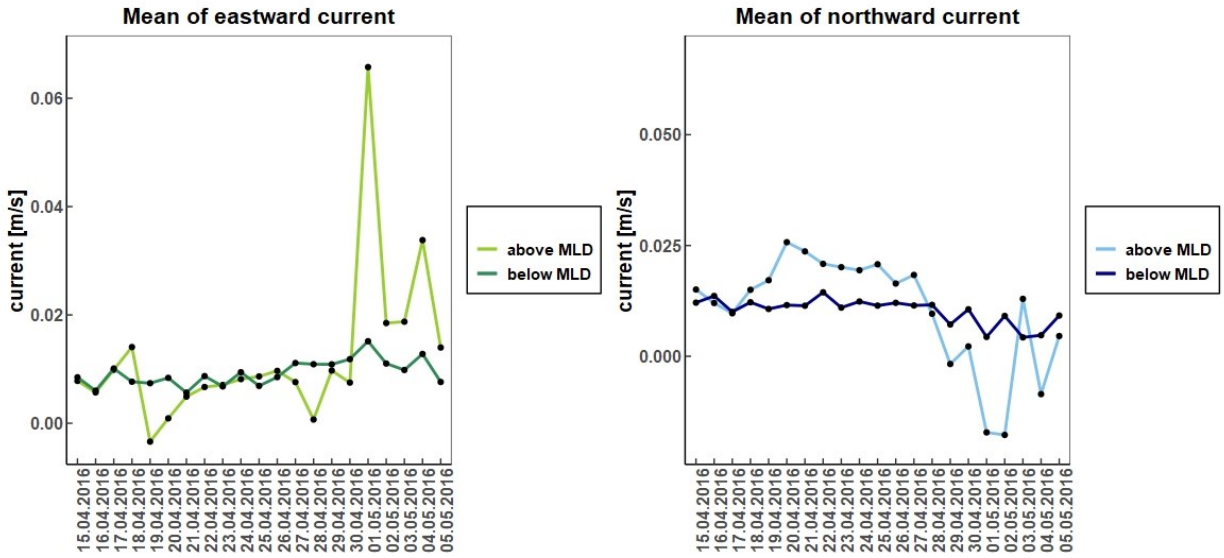


Fig. S4: Daily averaged water depth currents above and below the mixed layer depth (MLD) for the region of -30° to -5°W as longitude and 35° to 55°N as latitude. Left: The mean of the eastward currents. Right: The mean of the northward currents

MANUSCRIPT 3. *PHAEOCYSTIS ANTARCTICA*, AN UNDERESTIMATED KEY DRIVER OF THE BIOLOGICAL CARBON PUMP

Anna Biastoch, Morten H. Iversen, Lubos Polerecky, Jack J. Middelburg

ABSTRACT

The biological carbon pump plays a major role in ocean carbon uptake. Multiple phytoplankton species are involved but their relative contributions to carbon pathways are poorly characterized. *Phaeocystis antarctica* and the diatom *Chaetoceros debilis* are major players in Southern Ocean plankton communities. Here we studied aggregate formation and carbon and nitrogen flows from phytoplankton to bacteria in assembled communities of *P. antarctica* and *C. debilis* that were incubated in roller tanks with either ^{13}C-bicarbonate labelled *P. antarctica* and ^{15}N-nitrate labelled *C. debilis* (13C Phaeo/15N Chae) or ^{13}C-bicarbonate labelled *C. debilis* and ^{15}N-nitrate labelled *P. antarctica* (13C Chae/15N Phaeo). Although aggregate formation and size-specific settling rates were similar, carbon and nitrogen transfer from phytoplankton to aggregated material differed. About 70% of the carbon fixed by Phaeocystis formed aggregates, whereas only 3% of the carbon fixed by diatom contributed to aggregate formation. Nitrogen transfers from phytoplankton to aggregated material were more similar (47% and 56% for *P. antarctica* and *C. debilis*, respectively). NanoSIMS imaging revealed high transfer of *P. antarctica* carbon and nitrogen to bacteria, while diatom organic matter was hardly used by bacteria. Accordingly, in our study, *Phaeocystis antarctica* plays a major role in aggregation and supports microbial secondary production, while diatoms contribute little to the aggregated carbon and microbial carbon and nitrogen resources. Still, the silica production by diatoms acted as a ballasting material that provided density to the Phaeocystis dominated aggregates and enabled them to sink at rates of several hundred meters per day.

INTRODUCTION

The Southern Ocean is located south of the subtropical front and is a major carbon dioxide (CO_2) sink (Boyd 2002). Specifically, the Southern Ocean is responsible for 40% of marine CO_2 uptake (Raven and Falkowski 1999, Sabine et al. 2004, Takahashi et al. 2009, Frölicher et al. 2015). Part of this CO_2 uptake involves the biological carbon pump: the set of processes governing aggregation in the photic zone and at the base of the mixed layer, export to the mesopelagic and deep ocean, and sequestration in the deep ocean and seafloor (Volk and Hoffert 1985, Longhurst and Harrison 1989, Longhurst 1991, Ducklow et al. 2001). A diverse community of phytoplankton fixes CO_2 into organic matter. This newly formed organic material is either consumed within the food web by zooplankton or bacteria, assimilated into biomass, hydrolyzed to dissolved organic carbon, respired back to CO_2, or aggregated and then exported to the deeper water column where further degradation and remineralization takes place (Iversen 2023).

In the Southern Ocean diatoms are important contributors to carbon sequestration (Wilson et al. 1986, Brown and Landry 2001, Flynn et al. 2023). However, recent studies showed a dominance of prymnesiophytes in some regions, such as Prydz Bay and the Ross Sea where especially the prymnesiophyte *Phaeocystis antarctica* forms large blooms (Davidson and Marchant 1992, Trimborn et al. 2017, Smith and Trimborn 2023). In general, *Phaeocystis spp*. are ubiquitous in the world's oceans and play a crucial role in oceanic carbon and sulfur cycling (Hamm et al. 1999, Schoemann et al. 2005, Smith and Trimborn 2023). The role of Phaeocystis in carbon export and sequestration is highly debated. On the one hand, Phaeocystis plays a significant role in carbon fixation (Hamm et al. 1999, Schoemann et al. 2005, Verity et al. 2007) due to their high release of dissolved organic carbon (Hamm et al. 1999, Alderkamp et al. 2007), which subsequently is an important driver for aggregate formation (DiTullio et al. 2000). The potential of Phaeocystis to form aggregates is mainly described by a process where senescent colonies are colonized by auto- and heterotrophic microorganisms (Rousseau et al. 1994, Putt et al. 1994, Garrison et al. 1998). On the other hand, Phaeocystis cells and the colony stage are characterized by slow sinking rates or by being neutrally buoyant when they aggregate (Becquevort and Smith 2001, Peperzak et al. 2003, Schoemann et al. 2005). Hence, Phaeocystis are

generally considered of little importance for carbon export to the deep ocean (Wassmann et al. 1990).

The diatom *Chaetoceros debilis* has been shown to form large blooms in spring and contributes much to the Southern Ocean carbon export (Smetacek et al. 2004, Thomson et al. 2006, Flynn et al. 2023). From a global perspective, diatoms account for about 40% of the total oceanic primary production and 40% of the total POC export reaching to and beyond the mesopelagic zone (Boyd et al. 2010, De Jong et al. 2012). This important role of diatoms towards carbon sequestration is due to their ability to form large blooms, the relative low grazing pressure, and the role of silicate frustules, which function both as a protection against grazing and as a ballasting factor for sinking particles (Timmermans et al. 2001, Alderkamp et al. 2012). Aggregates formed form diatoms are characterized by being highly porous structures that contain a large volume fraction of transparent exopolymeric particles (TEP), which can reach values >90% (Alldredge and Gottschalk 1988, Ploug and Passow 2007, Iversen and Ploug 2010). TEP can increase the stickiness of particles and phytoplankton cells, which in return encourages aggregate formation (Alldredge et al. 1993, Passow 2002, Mari et al. 2017). Especially, aggregates from *Chaetoceros sp*. are highly enriched in TEP (Zetsche et al. 2020).

Here, we study the carbon (and nitrogen) pathways within the biological carbon pump from growing phytoplankton through aggregate formation and microbial remineralization. To do this, we formed aggregates from mixed *Phaeocystis antarctica* and *Chaetoceros debilis* communities to study their characteristics (aggregate size, settling velocity, and composition), the transfer of carbon and nitrogen to from phytoplankton to aggregates and bacteria, and elucidated the roles of *Phaeocystis antarctica* and *Chaetoceros debilis* in mixed communities for aggregate formation using cell-specific isotope data.

MATERIAL AND METHODS

Experimental design

Cultures of *Phaeocystis antarctica Karsten* 1905 and *Chaetoceros debilis Cleve 1894* were grown for 21 days at 2°C in artificial seawater enriched with nutrients according to f/2 (Guillard 1975) with phosphate concentration reduced by half to enhance aggregation potential (Biastoch et al. 2024, chapter 2). Cultures were exposed to a light intensity of 150 µmol photons m^{-2} s^{-1} at a l6 to 8 hour light-dark cycle. Both algae were labeled with either ^{13}C carbon isotopes or ^{15}N nitrogen isotopes in separate incubations that were enriched with 10% $NaH^{13}CO_3$ or 5% $Na^{15}NO_3$. The labelled algae were incubated in roller tanks that were rotated at 3 rpm (rotation per minutes) on roller tables at 2°C in the dark. Isotopically enriched cultures were crosswise incubated to trace the flow from phytoplankton to aggregates and heterotrophic bacteria: i.e., ^{13}C labelled *C. debilis* with ^{15}N labelled *P. antarctica* (15N Phaeo /13C Chae) and ^{15}N labelled *C. debilis* with ^{13}C labelled *P. antarctica* (13C Phaeo/15N Chae). Samples were taken at the start (t0), after 21 h (t1), 42 h (t2) and 90 h (t3), corresponding to initial conditions, ongoing aggregation, visual appearance of aggregates, and mature conditions, respectively.

Aggregate characteristics

Aggregate abundances and their specific areas i.e., sizes, were determined via imaging of the roller tanks after 21 and 42 h of incubations, at timepoints t2 and t3. To this end, roller tanks were gently rotated by 90° and placed on a perspex disc. Aggregates were allowed to settle to the bottom for 30 min. Pictures were taken from below with a Sony camera (Sony α 6000, f/3.5) and images were analysed with the free software Fiji version 1.53-c (Schindelin et al. 2012). The area of individual aggregates was determined with the polygon tool in Fiji, used as a basis for the calculation of the equivalent spherical diameter (ESD) with the following equation:

$$ESD = 2 * \sqrt{\frac{A\,(Aggregate)}{\pi}} \qquad (3)$$

For the determination of sinking velocity, rotating roller tanks were recorded with a Sony camera (Sony α 6000) in a fixed installation set up for at least two full orbits of an aggregate. This method is based on the specific orbital trajectories that settling aggregates follow in a rotating roller tank (Tooby et al. 1977). The following

equation was used to calculate the sinking velocity of the aggregates (Jackson, 1994):

$$x_b = w_s * T/(2 * \pi) \quad (4)$$

whereby x_b (cm) defines the distance between the center of the roller tank and the specific orbital center of an aggregate, ws describes the sinking velocity in cm d^{-1} and T marks the rotation period (s). The MTrackJ plugin (Meijering et al. 2012) from Fiji was used to determine x and y positions of an aggregate on their trajectory. The center of the aggregate specific orbit relays on the analyzed positions was calculated by using the method from Ploug et al. (2010).

Chemical aggregate composition

Total organic carbon (TOC) and total organic nitrogen (TON), as well as stable isotopic ratios were determined for the incubated phytoplankton cells at the start of the incubation, t0, and for collected aggregates with diameters between 1.4 and 2 mm after 42 h of incubation at t2. To determine the chemical composition of the phytoplankton cells, 45 ml of incubation water was filtered directly onto a pre-combusted and pre-weighed 25 mm GF/F filter, while aggregates collected at t3 were picked individually with a wide pore pipette and transferred to pre-combusted 25 mm GF/F filters. The filters were rinsed with ultrapure water to remove background signals and dried for at least 24 h at 50°C. Inorganic carbon was removed by fuming the filters in a 37% fuming hydrochloric acid vapor, dried again for 48 h at 50°C and re-weighed on a Mettler Toledo XP26 balance with a sensitivity of 1 µg. Filters were carefully packed into tin capsules and analysed with a Thermo Scientific Flash 2000 elemental analyzer that was connected to a Thermo Delta V Plus IRMS. Analyses were performed in triplicates or, when material was limiting, in duplicates. TOC and TON values were calculated as µg/mg dry weight with detection limit for carbon 0.04 µg and for nitrogen 0.66 µg. This relatively high detection limit for nitrogen was chosen to accommodate for any possible leakage of nitrogen via the autosampler, which enhanced nitrogen background noise by small proportions of air injections. Stable isotopic ratios were reported in the delta notation ($\delta^{13}C$ and $\delta^{15}N$) relative to the Vienna Pee Dee Belemnite (V-PDB) standard and atmospheric nitrogen standard (‰). The precision of $\delta^{13}C$ and $\delta^{15}N$ measurements complied 0.1 ‰.

NanoSIMS

Two types of samples were prepared for Nanoscale Secondary Ion Mass Spectrometry (NanoSIMS): (1) non-aggregated phytoplankton cells that were collected from each treatment at the start of the incubation, t0, and after 21 hours of incubation, t1, and (2) aggregated material collected with a wide-bore pipette after 42 and 90 h of incubation. For analysis of aggregated material, an intact aggregate was gently transferred with a wide pore pipette into a 2 ml Eppendorf tube filled with ultrapure water and 4% glutaraldehyde. Afterwards, the aggregate was ultrasonicated for 15 min to break up the aggregate. For the non-aggregated phytoplankton cell, one ml of aggregate-free water was transferred to an Eppendorf container that did not contain any ultrapure water where it was fixed with a 4% glutaraldehyde. The prepared material was then filtered onto polycarbonate filters and coated with a 10 nm gold layer (25 mm, 0.2 µm pore size) and washed three times with 20 ml ultrapure water. Samples were air dried and stored in the dark at room temperature until further analysis. Target identification for each of the filters was performed by imaging with a table-top SEM (JEOL JCM-6000PLUS NeoScope Benchtop SEM) with high accelerating voltage (10 kV). NanoSIMS imaging was performed with a NanoSIMS 50L instrument (Cameca, Gennevilliers, France) operated at the Utrecht University. Fields of view were pre-sputtered with Cs+-ions until secondary ion yields stabilized. Afterwards, secondary ions $^{12}C-$, $^{13}C-$, $^{16}O-$, $^{12}C^{14}N-$, $^{12}C^{15}N-$, $^{31}P-$, and $^{32}S-$ were detected with a primary Cs+ primary ion beam (<1 – 2pA, dwell time of 1 ms pixel−1) scanning over the sample (areas between 25 µm × 25 µm and 40 µm × 40 µm in size). Signal increase was caused by imaging the same area several times. The resulting ion count images were aligned and accumulated. The output data was processed with the Look@NanoSIMS software (Polerecky et al. 2012) for ^{13}C and ^{15}N atom fraction quantification. For each cell the specific ^{13}C atom fraction was calculated from the total counts of ^{12}C and ^{13}C ions (or $^{12}C^{14}N-$ and $^{13}C^{14}N-$ ions) and accumulated over all regions of interest (ROI) pixels. Likewise, cell specific ^{15}N atom fraction was calculated from the total counts of the $^{12}C^{14}N-$ and $^{12}C^{15}N-$ ions accumulated over all ROI pixels. ROIs classification resolved Phaeocystis, diatoms, and bacteria cells and was done microscopically based on phenotypically differences, whereby detected organisms at t2 and t3 were incorporated into aggregated material.

RESULTS

Aggregate characteristics

Visible aggregates occurred after 42 hours and aggregate measurements were performed at t2 (42 h) and t3 (90h). Total aggregated volume increased from 978 mm^3 for 15N Phaeo/13C Chae and 1325 mm^3 for 13C Phaeo/15N Chae at t2 to 1651 and 1718 mm^3 for 15N Phaeo/13C Chae and 13C Phaeo/15N Chae at t3, respectively.

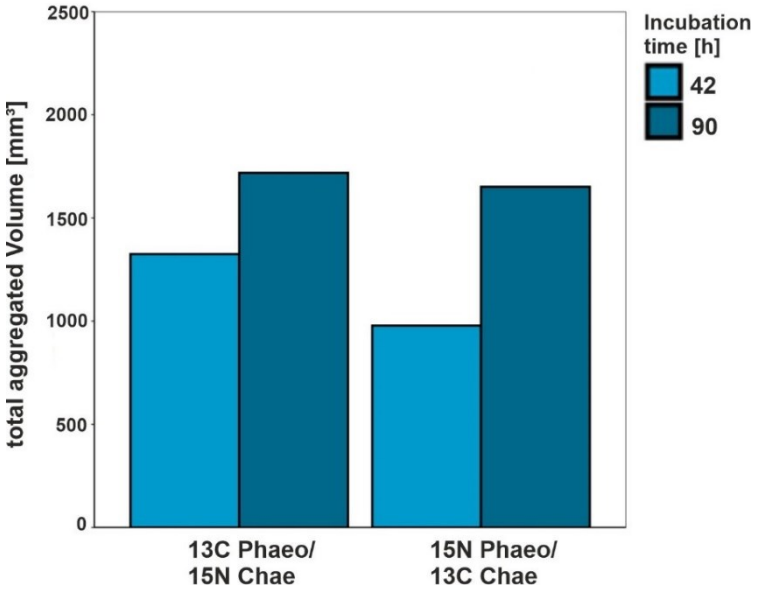


Fig. 16: Total aggregated Volume within the mesocosms after 42 hours (t2) and 90 hours (t3)

Aggregate size (ESD) and settling velocity were significantly correlated and the more mature aggregates at t3 had a smaller size-range with significantly steeper size-to-settling slopes compared to t2 ($p<0.01$, ‚Supplementary: Table S2). This shows that the aggregates became more compact and denser over time.

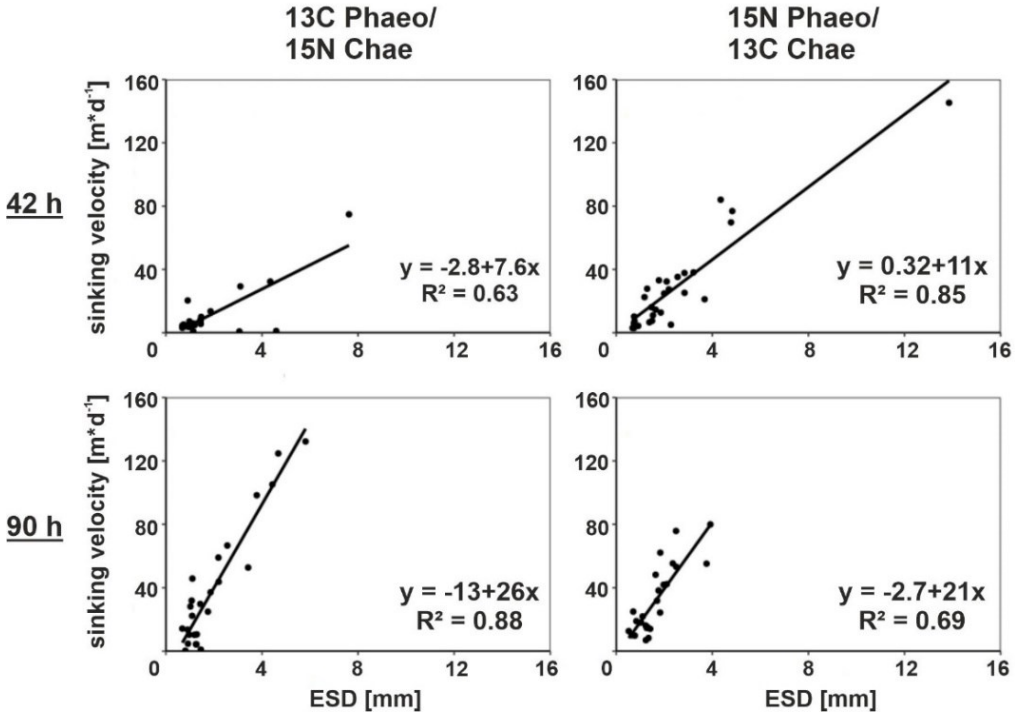


Fig. 17: The relationship between size (applied as the ESD in mm) and the corresponding sinking velocity (in m d-1) of individual aggregates within the different treatments (13C Phaeo/15N Chae and 15N Phaeo/13C Chae) after 42h (t2) and 90h (t3) and plotted with their linear correlations.

Chemical aggregate composition

The molar C:N ratio increased from 5.4 at the start of the incubation (t0) to 6.35 and 6.8 for the 15N Phaeo/13C Chae and 13C Phaeo/15N Chae, respectively.

Table 5: Changes in carbon to nitrogen ratio over the course of time

Treatment	Incubation time [h]	Molar C:N ratio	Standard deviation
13C Phaeo/15N Chae	0	5.37	0.15
13C Phaeo/15N Chae: Aggregate	90	6.80	0.03
15N Phaeo/13C Chae	0	5.36	0.07
15N Phaeo/13C Chae: Aggregate	90	6.35	0.18

At the start of the incubation, the 13C Phaeo/15N Chae treatment had higher carbon and nitrogen contents compared to 15N Phaeo/13C Chae. This pattern was also reflected in isotopic ratios: the 13C Phaeo/15N Chae treatment was more enriched in ^{13}C and ^{15}N compared to the 15N Phaeo/13C Chae. This difference reflects the variations in the number of active cells per incubation. However, similar proportions of carbon and nitrogen were transferred to aggregates: 73.2% of the C and 65.8 % of the N for 13C Phaeo/15N Chae and 69.2% of the C and 67.2% of the N for 15N Phaeo/13C Chae. While the transfer of ^{15}N was also similar between the two treatments (56.4 and 46.7% for 13C Phaeo/15N Chae and 15N Phaeo/13C Chae, respectively), this was not the case for ^{13}C transfer: about 70% of the ^{13}C labelled Phaeocystis material was recovered in the aggregates compared to a smaller transfer (3.4%) of Chaetoceros ^{13}C to aggregates.

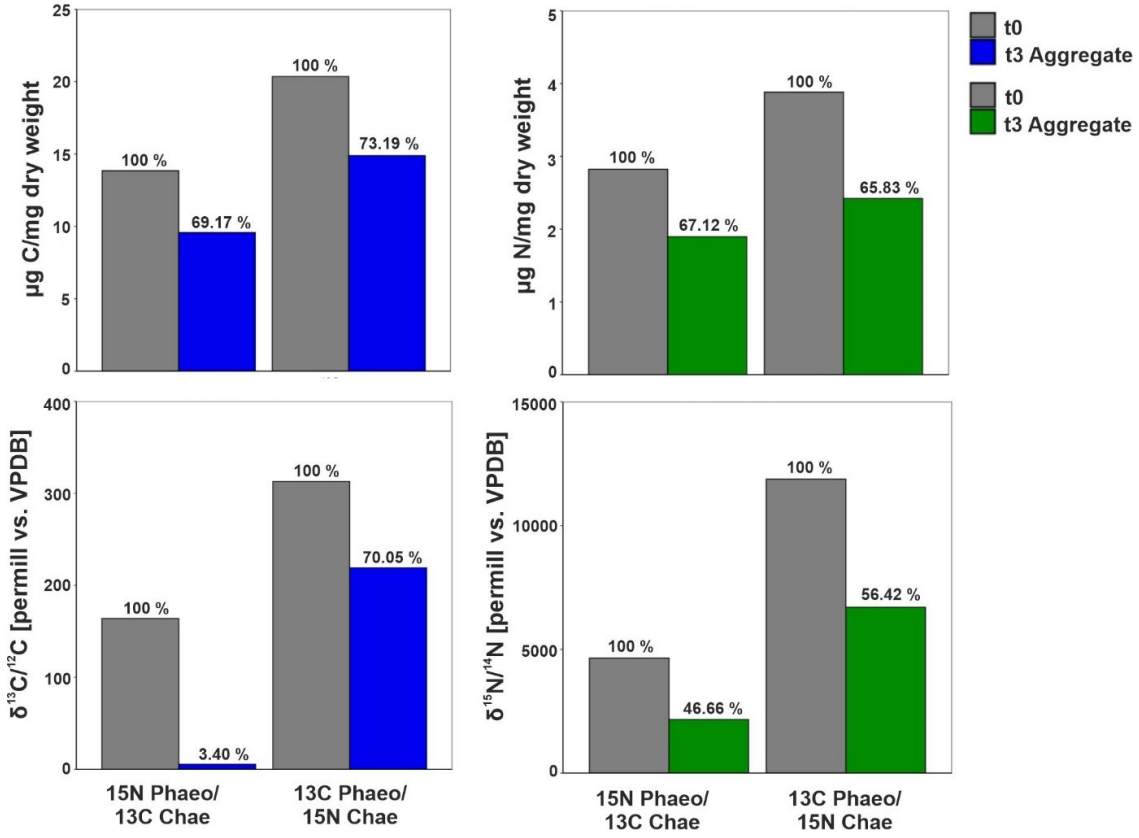


Fig.18: Chemical composition of the total system defined at t0 (grey) and the proportion within aggregates at t3 (coloured) for the treatments: (1) ^{13}C bicarbonate labelled Chaetoceros and ^{15}N Nitrate labelled Phaeocystis and (2) ^{13}C bicarbonate labelled Phaeocystis and ^{15}N Nitrate labelled Chaetoceros. The upper row shows carbon and nitrogen values in µg / mg dry weight. The percentage in the plots indicates how much carbon or nitrogen ended in the aggregated material in comparison to the amount in the whole system which is defined as 100%. The lower row shows the increase in stable isotopic ratios of δ13C/12C and δ15N/14N in ‰ relative to the Vienna Pee Dee Belemnite (V-PDB) standard. The percentage in the plots indicates how much of the labelled material ended in the aggregated pool in comparison to the amount in the whole system which is defined as 100%.

NanoSIMS

Within the 13C Phaeo/15N Chae treatment, we detected an enrichment in ^{13}C label in Phaeocystis cells with ^{13}C fraction values in the range 0.014 to 0.015. The ^{15}N labelling enrichment for Chaetoceros cells was variable with maximum values of 0.042. The ^{13}C labelling signal of bacteria cells increased over the course of time, while bacteria did not incorporate much ^{15}N. The 15N Phaeo/13C Chae treatment displayed a moderate ^{13}C labelling for Chaetoceros cells with values between 0.011 and 0.013 and a variable, but high ^{15}N labelling of Phaeocystis cells attaining 0.048 as maximum. Within this treatment the ^{13}C signal of bacteria cells remained low,

while the ^{15}N labelling showed high enrichment in bacteria cells reaching a maximum of 0.032. Standard deviations and mean values are displayed in a boxplot (Supplementary Fig. S5). Statistical analyses showed significant differences between the measurements of ^{13}C and ^{15}N within the single cells of *Phaeocystis antarctica*, *Chaetoceros debilis,* and bacteria, with the exception of ^{15}N measurements of *Chaetoceros debilis* (p-value<0.01, Supplementary: Table S3).

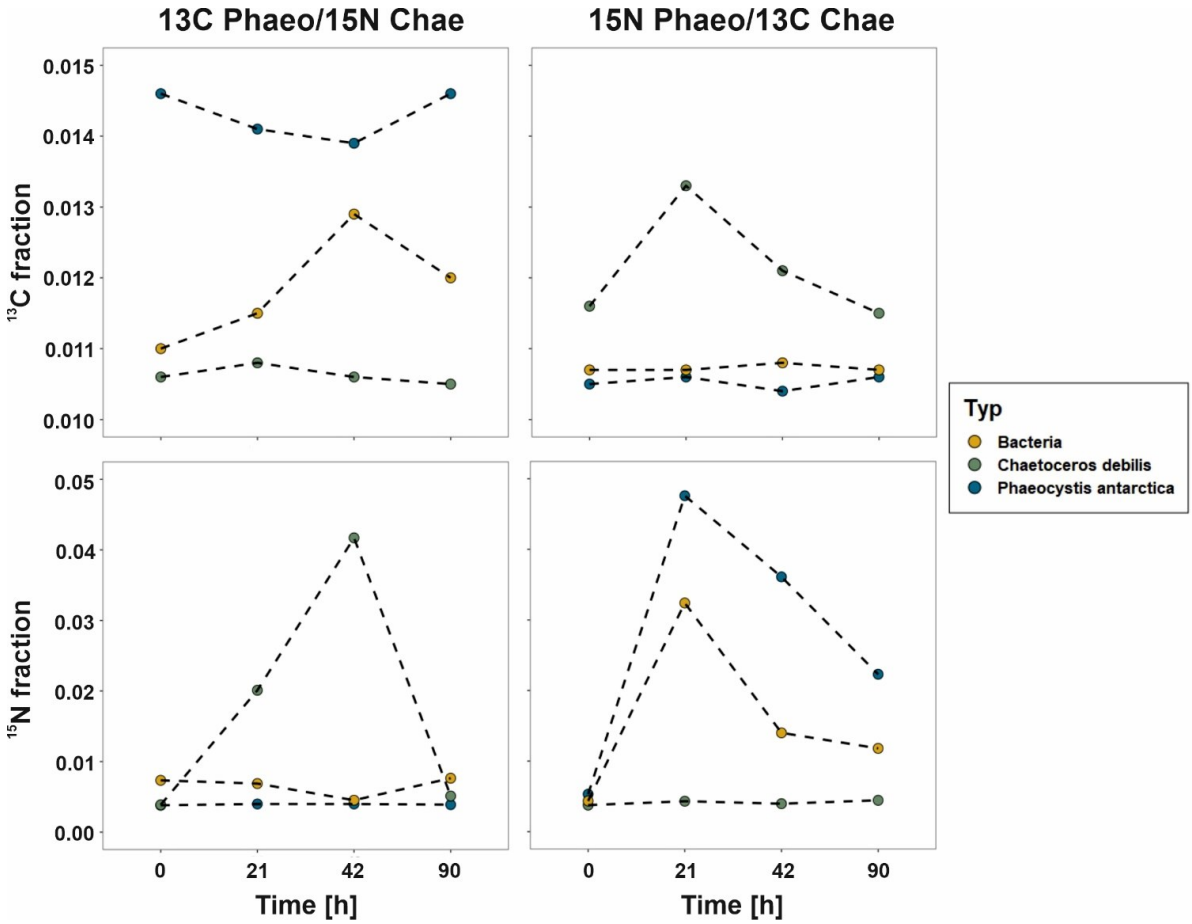


Fig.19: NanoSIMS measurements of mean ^{13}C fraction, calculated from secondary ion counts (0.5*12C13C)/(12C2+(0.5*12C13C)) and mean ^{15}N fraction, calculated from secondary ion counts 12C15N/(12C214N+12C15N). In both treatments, 13C Phaeo/15N Chae and 15N Phaeo/13C Chae individual cells of *Phaeocystis antarctica, Chaetoceros debilis* and Bacteria were monitored over time at 0h, 21h, 42h and 90h, whereby cells at 42h and 90h were included in aggregated material.

DISCUSSION

Here, we study the role of *Phaeocystis antarctica* versus *Chaetoceros debilis* for aggregation in the Southern Ocean. Aggregates were formed with either carbon or nitrogen labelled diatoms and Phaeocystis. In the first incubation we labelled *Phaeocystis antarctica* with ^{13}C-bicarbonate and *Chaetoceros debilis* with ^{15}N-nitrate, while the second incubation had ^{15}N-nitrate labeled *Phaeocystis antarctica* and ^{13}C-bicarbonate labeled *Chaetoceros debilis*. Using this cross-labelling strategy, we were able to follow the flow of carbon and nitrogen from the phytoplankton and into aggregates and bacteria.

In both treatments visible aggregates occurred after 42 hours and reached total aggregated volumes of ~ 1700 mm^3 after 90 hours, indicating similar aggregation potential, independent of the labelling strategy (Fig. 16). The contribution of Phaeocystis towards aggregation and the resulting particulate organic carbon flux in natural environments has been highly debated. Schoemann et al. (2005) described three possible pathways for Phaeocystis to form aggregates, self-aggregation, the exudation of matrix polysaccharides and the settlement of auto- and heterotrophic organisms onto senescent colonies, whereby the last appears to be most efficient. Colonization of senescent Phaeocystis colonies by microorganisms result in the aggregation of Phaeocystis derived material due to an enhanced release of TEP structures after disruption (Riebesell et al. 1995, Schoemann et al. 2005). This strategy was observed for *P. globosa* in the North Sea and Arabian Sea and for *P. antarctica* in the Ross Sea (Rosseau et al. 1994, Putt et al. 1994, Becquevort et al. 1998, Garrison et al. 1998). Moreover, it was found that fractured senescent Phaeocystis colonies release transparent exopolymer particles (TEP), stimulating aggregation of Phaeocystis (Riebesell et al. 1995, Reigstad et al. 2000). Despite the high aggregation potential of Phaeocystis colonies, they are often remineralized in the upper water column and not exported to the mesopelagic zone (Lutter et al. 1989, Wassmann et al. 1990, Riebesell 1993, Sweeney et al. 2000). Thingstad and Billen (1994) discovered that it is mostly the colony matrix of Phaeocystis and not the individual cells that are aggregating. This matrix consists of mucopolysaccharides, which are highly degradeable (Janse et al. 1999, Hamm and Rousseau 2003, Mari et al. 2005). Despite this, some studies observed the presence of Phaeocystis derived aggregates at greater depth,

suggesting that they were not efficiently remineralized in the surface ocean (Wassmann et al. 1990, Riebesell 1993, Asper and Smith 1999).

The role of diatoms for aggregate formation and downward transport of organic carbon to greater depth is much clearer, where especially *Chaetoceros sp*. seems of great importance (Alldredge and Gottschalk 1989, Kiorboe and Hansen 1993, Crocker and Passow 1995, Corzo et al. 2000, Zetsche et al. 2020). *Chaetoceros sp*. is known for high TEP production, where TEP coating causes high stickiness and aggregation of the diatom cells (Kiørboe and Hansen 1993, Passow et al. 1994, Logan et al. 1995). Hence, *Chaetoceros sp*. is a main contributor to aggregation and carbon export. The structure of *Chaetoceros sp*. aggregates appears loose since their TEP covered spines result in highly porous structures (Alldredge and Gotschalk 1989, Kiørboe and Hansen 1993, Crocker and Passow 1995, Iversen and Ploug 2010, Zetsche et al. 2020). Despite the high porosity of the *Chaetoceros sp*. aggregates, their pore-space is generally composed of TEP, which fills the pore-space and causes low permeability and little to no lateral advection through the aggregates, despite their highly porous nature, despite the high TEP content, they sink at high velocities (Ploug and Passow 2007). For homogenous aggregates, the sinking velocity is mainly determined by the compactness, i.e., the size of the composite aggregates, which can be packed tightly for small cell sizes and thereby cause high excess densities of aggregates formed from small diatoms (Iversen and Ploug 2013, Iversen and Lampitt 2020).

In this study the size-specific sinking velocities where not significantly different between the treatments and we only observed variations in size-specific sinking velocities between the different timepoints and not between the different labeling treatments, i.e., faster size-specific settling velocities for older aggregates (Fig. 17). This indicates that the aggregates became more compact or more ballasted by diatoms over time and hence sank faster. Phaeocystis aggregates without any ballasting are mainly characterized by slow sinking velocities or neutral buoyancy (Riebesell et al. 1995, Hamm 2000, Hamm and Rousseau 2003), which also applied for single colonies themselves, which have sinking velocities ranging from -0.37 to 14 m d^{-1} (Schoemann et al. 2005). Hence, aggregates formed by Phaeocystis rely on an external ballasting in order to sink out of the euphotic zone. Several studies observed a correlation between mineral fluxes (calcium carbonate,

biogenic silica and lithogenic silica) and the POC flux within sediment trap analysis (Armstrong et al. 2001, Francois et al. 2002, Klaas and Archer 2002), which lead to the concept that the sinking velocity of an aggregate can be positively influenced by ballasting. This ballast hypothesis can be explained by minerals that are trapped within aggregates and, thereby, increase the downward transport of particulate organic carbon by enhancing the sinking velocity due to increasing density of the aggregates. The highest correlation between mineral flux and POC flux was found for calcium carbonate, whereby the correlation between POC flux and opal flux (biogenic silica) played a minor role, but was still significant (Ragueneau et al. 2000, Francois et al. 2002, Klaas and Archer 2002). Diatom frustules mainly consist of biogenic silica, which simultaneously also causes a self-ballasting of aggregated diatoms and lead to a more efficient downward transport compared to Phaeocystis aggregates (Riebesell et al. 1995, Hamm and Rousseau 2003). Aggregates formed in this study were characterized by a homogenous composition. However, it was clear from the proportions of labelled carbon that Phaeocystis initiated aggregate formation and diatoms were subsequently scavenged from the background water and added to the ballast of the aggregates and caused them to have faster size-specific settling velocities over time.

Independent of the labelling treatments we observed the same trends for C:N ratios over time, where the C:N ratios were around 5.4 at t0 and increased to 6.6 after 90h, with slightly higher values for the treatment of 13C Phaeo/15N Chae. The colonial matrix of Phaeocystis was characterized by a high content of mucopolysaccharides (Wassmann et al. 1990, Baumann et al. 1994, Riebesell et al. 1995), which might explain the elevated C:N values, though, several other studies found that C:N ratios of Phaeocystis colonies were similar to the Redfield ratio, as also observed in our study (Smith et al. 1998, Alderkamp et al. 2019, O. Smith Jr. and Trimborn 2023). Solomon et al. (2003) suggested that amino sugars act as natural antagonists towards the high carbon accumulation. Studies of different Chaetoceros species reported a broader range of C:N ratios than that observed here, however, this was likely caused by limiting factors during growth in their experiments. Low carbon to nitrogen ratios of 3.2 were detected for a non-limited *Chaetoceros debilis* cultures (Harrison et al. 1977) and of 4.3 for *Chaetoceros sp.* incubated at 4°C coupled with low irradiance (Thomas et al. 1992). Contrastingly,

several studies reported molar C:N ratios exceeding the Redfield ratio for different Chaetoceros species (Tantanasarit et al. 2013, Pausch et al. 2019, Schiffrine et al. 2020). In situ aggregates from the Southern Ocean showed C:N ratio within the Redfield ratio or slightly higher (Salter et al. 2007, Rembauville et al. 2015). Through the use of stable isotope as tracer our study showed a limited transfer of carbon (3.4%) from diatoms to aggregates while carbon transfer form *Phaeocystis antarctica* to aggregates was much higher (70%). This indicated that, in terms of carbon, *Phaeocystis antarctica* had a much high aggregation potential compared to *Chaetoceros debilis*. At the same time, we did not observe significant differences in the aggregation potential for nitrogen between the two phytoplankton species, suggesting that production of carbon-rich TEP by *P. antarctica* was the driving mechanism for aggregation in our study.

These experimental finding showing that Phaeocystis is an efficient driver for aggregate formation are consistent with field observations. Bacterial biomass of free living and attached bacteria increased in natural habitats when *Phaeocystis sp*. colonies become senescent (Davidson and Marchant 1987, Thingstad and Martinussen 1991, Becquevort et al. 1998). It was also observed that the main proportion of POC derived from *Phaeocystis spp*. is mainly mineralized in the euphotic zone (Wassmann et al. 1990, Sweeney et al. 2000, Hamm and Rousseau 2003). Schoemann et al. (2005) showed high biodegradability of *Phaeocystis sp*. under non limiting conditions and suggested that the success of microbial degradation relied on the shape of nutrient limitation in different regions. Within a laboratory experiment from Sheik et al. (2014) it was observed that 20% of carbon from *Phaeocystis globosa* was transferred to *Alteromonas sp*. It was also detected, that within 7 days, 40% of the *Phaeocystis sp*. derived POC was remineralized. When Phaeocystis colonies collapse due to viral lysis or at the end of a bloom, a high accumulation of mucopolysaccharides into the surrounding waters was observed, resulting in the formation of aggregates (Wassmann et al. 1990, Passow and Wassmann 1994, Mari et al. 2004, Brussaard et al. 2005). Bacteria can acquire their carbon and nitrogen directly from Phaeocystis or Chaetoceros, or indirectly via consumption of aggregated exudates from Phaeocystis and Chaetoceros. Our experiment provides clear evidence that bacteria utilize organic carbon and nitrogen produced by *P. antarctica*. However, bacteria might also have utilized

carbon and nitrogen from either aggregated organic matter or *C. debilis*, because bacteria were slightly enriched in ^{13}C in the 15N Phaeo/13C Chae treatment and ^{15}N in the 13C Phaeo/15N Chae treatment. Still, we did have very low t_0 values of ^{15}N labelling for both Phaeocystis and Chaetoceros. We can only speculate that the duration of the iron beam energy was too low to penetrate the silica frustules of the diatoms or that the cultures were not homogenously distributed in the starting mixture and therefore did not appear on the filters used for NanoSIMS. Contrastingly the ^{13}C signal was clear for both Phaeocystis and Chaetoceros at t_0, which suggests that we did have labelled phytoplankton and did penetrate the diatom frustules. Due to the increased ^{15}N signal at t_1 (21h) for both cultures, there is no doubt that both Phaeocystis and Chaetoceros were labelled and since the t_0 came from the same incubations, we have to assume that we had similar or higher labelling percentages at t_0 as those observed at t_1. Nevertheless, our data clearly shows that most organic carbon and nitrogen within aggregates and utilized by bacteria originated from *P. antarctica* and not from *C. debilis*.

This study showed that *P. antarctica* is the main contributor to aggregate formation when incubated together with *C. debilis* and that microbes primarily utilize organic matter from *P. antarctica*, while the diatom *C. debilis* contributed less to both aggregation and bacterial organic matter utilization. While the role of *C. debilis* for carbon contribution to aggregate formation and bacterial utilization may be limited, it seemed to play a major role for ballasting of the Phaeocystis derived aggregates. This may help us to understand how Phaeocystis is often found to contribute substantially to the downward flux of organic matter though it, by itself, should not. We therefore suggest that when Phaeocystis occur together with diatoms, aggregates are efficiently formed and ballasted and, thus, enhancing POC flux, making a more efficient biological carbon pump. Using cell-specific isotope measurements, we could show that *P. antarctica* and/or the derived material is the preferred source for microbial mineralization.

P. antarctica and *C. debilis* are major components of the phytoplankton communities in the Southern Ocean (DiTullio and Smith 1996, Mathot et al. 2000, Smetacek et al. 2004, Trimborn et al. 2017). Under future climate conditions, two possible scenarios could arise with differential effects on phytoplankton community functioning. One, within the marginal ice zone the mixed layer is

predicted to deepen, which could deepen the nutricline and lower the light availability to phytoplankton communities (Lovenduski and Gruber 2005, Hemer et al. 2010, Young et al. 2011, Venables and Meredith 2014). This, would favor Phaeocystis species due to their ability to grow under low light conditions (Moisan and Mitchell 1999). An increase in Phaeocystis abundance with lower diatom occurrence could increase the aggregation potential of Southern Ocean plankton communities. Balaguer et al. (2023) were able to show in on-board laboratory studies, whihc used a natural phytoplankton community from the Weddell Sea, that *Phaeocystis sp.* increased when incubated under conditions of iron and manganese fertilization and that it resulted in a massive increase in POC sequestration. Two, under climate change conditions, plankton communities shift from Phaeocystis dominated towards long chain forming diatom dominance due to increasing CO_2 concentrations (Tortell et al. 2008, Deppeler and Davidson 2017). This might make for a less efficient biological carbon pump compared to a system dominated by Phaeocystis if our findings of less diatom contribution to aggregation is correct. Hence, a shift towards Phaeocystis under future climate conditions could stimulate the biological carbon pump and enhance carbon sequestration, as long as diatoms are present to ballast the Phaeocystis aggregates.

ACKNOWLEDGEMENTS

This work was conducted in the framework of the HGF Infrastructure Program FRAM of the Alfred-Wegener-Institute Helmholtz Center for Polar and Marine Research. This work was part of the Helmholtz Program “Changing Earth—Sustaining our Future” supported by the Helmholtz Program-Orientated Funding (POF IV) to topic 6 (Marine Life) and the sub-topic 6.3 (The Future Biological Carbon Pump). The work was funded by DFG-Research Center/Cluster of Excellence “The Ocean Floor—Earth's Uncharted Interface”: EXC-2077-390741603. The NanoSIMS at Utrecht University was supported by Netherlands Organization for Scientific Research.

CONFLICT OF INTEREST

The authors have no conflict of interest.

REFERENCES

Alderkamp, A. C., van Dijken, G. L., Lowry, K. E., Lewis, K. M., Joy-Warren, H. L., van de Poll, W., ... & Arrigo, K. R. (2019). Effects of iron and light availability on phytoplankton photosynthetic properties in the Ross Sea. Marine Ecology Progress Series, 621, 33-50.

Alldredge, A. L., & Cohen, Y. (1987). Can microscale chemical patches persist in the sea? Microelectrode study of marine snow, fecal pellets. Science, 235(4789), 689-691.

Alldredge, A. L., & Gotschalk, C. (1988). In situ settling behavior of marine snow 1. Limnology and Oceanography, 33(3), 339-351.

Alldredge, A. L., & Silver, M. W. (1988). Characteristics, dynamics and significance of marine snow. Progress in oceanography, 20(1), 41-82.

Armstrong, R. A., Lee, C., Hedges, J. I., Honjo, S., & Wakeham, S. G. (2001). A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals. Deep Sea Research Part II: Topical Studies in Oceanography, 49(1-3), 219-236.

Asper, V. L., & Smith Jr, W. O. (1999). Particle fluxes during austral spring and summer in the southern Ross Sea, Antarctica. Journal of Geophysical Research: Oceans, 104(C3), 5345-5359.

Balaguer, J., Koch, F., Flintrop, C. M., Völkner, C., Iversen, M. H., & Trimborn, S. (2023). Iron and manganese availability drives primary production and carbon export in the Weddell Sea. Current Biology, 33(20), 4405-4414.

Baumann, M. E. M., Lancelot, C., Brandini, F. P., Sakshaug, E., & John, D. M. (1994). The taxonomic identity of the cosmopolitan prymnesiophyte Phaeocystis: a morphological and ecophysiological approach. Journal of Marine Systems, 5(1), 5-22.

Becquevort, S., Rousseau, V., & Lancelot, C. (1998). Major and comparable roles for free-living and attached bacteria in the degradation of Phaeocystis-derived organic matter in Belgian coastal waters of the North Sea. Aquatic Microbial Ecology, 14(1), 39-48.

Boyd, P. W. (2002). Environmental factors controlling phytoplankton processes in the Southern Ocean1. Journal of Phycology, 38(5), 844-861.

Brussaard, C. P. D., Kuipers, B., & Veldhuis, M. J. W. (2005). A mesocosm study of Phaeocystis globosa population dynamics: I. Regulatory role of viruses in bloom control. Harmful algae, 4(5), 859-874.

Carr, M. E., Friedrichs, M. A., Schmeltz, M., Aita, M. N., Antoine, D., Arrigo, K. R., ... & Yamanaka, Y. (2006). A comparison of global estimates of marine primary production from ocean color. Deep Sea Research Part II: Topical Studies in Oceanography, 53(5-7), 741-770.

Cho, H., Hwang, C. Y., Kim, J. G., Kang, S., Knittel, K., Choi, A., ... & Hyun, J. H. (2020). A unique benthic microbial community underlying the Phaeocystis antarctica-dominated Amundsen Sea polynya, Antarctica: a proxy for assessing the impact of global changes. Frontiers in Marine Science, 6, 797.

Constable, A. J., Melbourne - Thomas, J., Corney, S. P., Arrigo, K. R., Barbraud, C., Barnes, D. K., ... & Ziegler, P. (2014). Climate change and Southern Ocean ecosystems I: how changes in physical habitats directly affect marine biota. Global change biology, 20(10), 3004-3025.

Corzo, A., Morillo, J. A., & Rodríguez, S. (2000). Production of transparent exopolymer particles (TEP) in cultures of Chaetoceros calcitrans under nitrogen limitation. Aquatic Microbial Ecology, 23(1), 63-72.

Crocker, K. M., & Passow, U. (1995). Differential aggregation of diatoms. Marine ecology progress series. Oldendorf, 117(1), 249-257.

Crump, B. C., Armbrust, E. V., & Baross, J. A. (1999). Phylogenetic analysis of particle-attached and free-living bacterial communities in the Columbia River, its estuary, and the adjacent coastal ocean. Applied and environmental microbiology, 65(7), 3192-3204.

Davidson, A. T., & Marchant, H. J. (1987). Binding of manganese by Antarctic Phaeocystis pouchetii and the role of bacteria in its release. Marine biology, 95(3), 481-487.

DeLong, E. F., Franks, D. G., & Alldredge, A. L. (1993). Phylogenetic diversity of aggregate - attached vs. free - living marine bacterial assemblages. Limnology and oceanography, 38(5), 924-934.

Deppeler, S. L., & Davidson, A. T. (2017). Southern Ocean phytoplankton in a changing climate. Frontiers in Marine Science, 4, 40.

Diercks, A. R., & Asper, V. L. (1997). In situ settling speeds of marine snow aggregates below the mixed layer: Black Sea and Gulf of Mexico. Deep Sea Research Part I: Oceanographic Research Papers, 44(3), 385-398.

DiTullio, G. R., & Smith Jr, W. O. (1996). Spatial patterns in phytoplankton biomass and pigment distributions in the Ross Sea. Journal of Geophysical Research: Oceans, 101(C8), 18467-18477.

Ducklow, H. W., Steinberg, D. K., & Buesseler, K. O. (2001). Upper ocean carbon export and the biological pump. Oceanography, 14(4), 50-58.

Flynn, R. F., Haraguchi, L., McQuaid, J., Burger, J. M., Mutseka Lunga, P., Stirnimann, L., ... & Fawcett, S. E. (2023). Nanoplankton: The dominant vector for carbon export across the Atlantic Southern Ocean in spring. Science Advances, 9(48), eadi3059.

Fowler, S. W., & Knauer, G. A. (1986). Role of large particles in the transport of elements and organic compounds through the oceanic water column. Progress in oceanography, 16(3), 147-194.

Francois, R., Honjo, S., Krishfield, R., & Manganini, S. (2002). Factors controlling the flux of organic carbon to the bathypelagic zone of the ocean. Global Biogeochemical Cycles, 16(4), 34-1.

Frölicher, T. L., Sarmiento, J. L., Paynter, D. J., Dunne, J. P., Krasting, J. P., & Winton, M. (2015). Dominance of the Southern Ocean in anthropogenic carbon and heat uptake in CMIP5 models. Journal of Climate, 28(2), 862-886.

Garrison, D. L., Gowing, M. M., & Hughes, M. P. (1998). Nano-and microplankton in the northern Arabian Sea during the Southwest Monsoon, August–September 1995 A US–JGOFS study. Deep Sea Research Part II: Topical Studies in Oceanography, 45(10-11), 2269-2299.

Giani, M., Berto, D., Zangrando, V., Castelli, S., Sist, P., & Urbani, R. (2005). Chemical characterization of different typologies of mucilaginous aggregates in the Northern Adriatic Sea. Science of the Total Environment, 353(1-3), 232-246.

Grossart, H. P., Hietanen, S., & Ploug, H. (2003). Microbial dynamics on diatom aggregates in Øresund, Denmark. Marine Ecology Progress Series, 249, 69-78.

Guillard, R. R. (1975). Culture of phytoplankton for feeding marine invertebrates. In Culture of marine invertebrate animals: proceedings—1st conference on culture of marine invertebrate animals greenport (pp. 29-60). Boston, MA: Springer US.

Hamm, C. E. (2000). Architecture, ecology and biogeochemistry of Phaeocystis colonies. Journal of Sea Research, 43(3-4), 307-315.

Hamm, C. E., & Rousseau, V. (2003). Composition, assimilation and degradation of Phaeocystis globosa-derived fatty acids in the North Sea. Journal of Sea Research, 50(4), 271-283.

Harrison, P. J., Conway, H. L., Holmes, R. W., & Davis, C. O. (1977). Marine diatoms grown in chemostats under silicate or ammonium limitation. III. Cellular chemical composition and morphology of Chaetoceros debilis, Skeletonema costatum, and Thalassiosira gravida. Marine Biology, 43, 19-31.

Hedges, J. I. (1992). Global biogeochemical cycles: progress and problems. Marine chemistry, 39(1-3), 67-93.

Hemer, M. A., Church, J. A., & Hunter, J. R. (2010). Variability and trends in the directional wave climate of the Southern Hemisphere. International Journal of Climatology: A Journal of the Royal Meteorological Society, 30(4), 475-491.

Ivančić, I., Paliaga, P., Pfannkuchen, M., Djakovac, T., Najdek, M., Steiner, P., ... & Herndl, G. J. (2018). Seasonal variations in extracellular enzymatic activity in marine snow-associated microbial communities and their impact on the surrounding water. FEMS microbiology ecology, 94(12), fiy198.

Iversen, M. H. (2023). Carbon Export in the Ocean: A Biologist's Perspective. Annual Review of Marine Science, 15, 357-381.

Iversen, M. H., & Lampitt, R. S. (2020). Size does not matter after all: no evidence for a size-sinking relationship for marine snow. Progress in Oceanography, 189, 102445.

Iversen, M. H., & Ploug, H. (2010). Ballast minerals and the sinking carbon flux in the ocean: carbon-specific respiration rates and sinking velocity of marine snow aggregates. Biogeosciences, 7(9), 2613-2624.

Iversen, M. H., & Ploug, H. (2013). Temperature effects on carbon-specific respiration rate and sinking velocity of diatom aggregates–potential implications for deep ocean export processes. Biogeosciences, 10(6), 4073-4085.

Jackson, G. A. (1990). A model of the formation of marine algal flocs by physical coagulation processes. Deep Sea Research Part A. Oceanographic Research Papers, 37(8), 1197-1211.

Jackson, G. A. (1994). Particle trajectories in a rotating cylinder: implications for aggregation incubations. Deep Sea Research Part I: Oceanographic Research Papers, 41(3), 429-437.

Janse, I., van Rijssel, M., Ottema, A., & Gottschal, J. C. (1999). Microbial breakdown of Phaeocystis mucopolysaccharides. Limnology and Oceanography, 44(6), 1447-1457.

Karner, M., & Herndl, G. J. (1992). Extracellular enzymatic activity and secondary production in free-living and marine-snow-associated bacteria. Marine biology, 113, 341-347.

Khatiwala, S., Primeau, F., & Hall, T. (2009). Reconstruction of the history of anthropogenic CO2 concentrations in the ocean. Nature, 462(7271), 346-349.

Kiørboe, T. (2001). Formation and fate of marine snow: small-scale processes with large-scale implications. Scientia marina, 65(S2), 57-71.

Kiørboe, T., & Hansen, J. L. (1993). Phytoplankton aggregate formation: observations of patterns and mechanisms of cell sticking and the significance of exopolymeric material. Journal of Plankton Research, 15(9), 993-1018.

Klaas, C., & Archer, D. E. (2002). Association of sinking organic matter with various types of mineral ballast in the deep sea: Implications for the rain ratio. Global biogeochemical cycles, 16(4), 63-1.

Kulk, G., Platt, T., Dingle, J., Jackson, T., Jönsson, B. F., Bouman, H. A., ... & Sathyendranath, S. (2020). Primary production, an index of climate change in the ocean: satellite-based estimates over two decades. Remote Sensing, 12(5), 826.

Logan, B. E., Passow, U., Alldredge, A. L., Grossartt, H. P., & Simont, M. (1995). Rapid formation and sedimentation of large aggregates is predictable from coagulation rates (half-lives) of transparent exopolymer particles (TEP). Deep Sea Research Part II: Topical Studies in Oceanography, 42(1), 203-214.

Longhurst, A. R. (1991). Role of the marine biosphere in the global carbon cycle. Limnology and Oceanography, 36(8), 1507-1526.

Longhurst, A. R., & Harrison, W. G. (1989). The biological pump: profiles of plankton production and consumption in the upper ocean. Progress in Oceanography, 22(1), 47-123.

Lovenduski, N. S., & Gruber, N. (2005). Impact of the Southern Annular Mode on Southern Ocean circulation and biology. Geophysical Research Letters, 32(11).

Lutter, S., Taasen, J. P., Hopkins, C. C. E., & Smetacek, V. (1989). Phytoplankton dynamics and sedimentation processes during spring and summer in Balsfjord, Northern Norway. Polar Biology, 10, 113-124.

Lyons, M. M., & Dobbs, F. C. (2012). Differential utilization of carbon substrates by aggregate-associated and water-associated heterotrophic bacterial communities. Hydrobiologia, 686, 181-193.

Mari, X., Rassoulzadegan, F., & Brussaard, C. P. (2004). Role of TEP in the microbial food web structure. II. Influence on the ciliate community structure. Marine Ecology Progress Series, 279, 23-32.

Mari, X., Rassoulzadegan, F., Brussaard, C. P., & Wassmann, P. (2005). Dynamics of transparent exopolymeric particles (TEP) production by Phaeocystis globosa under N-or P-limitation: a controlling factor of the retention/export balance. Harmful algae, 4(5), 895-914.

Mathot, S., Smith Jr, W. O., Carlson, C. A., Garrison, D. L., Gowing, M. M., & Vickers, C. L. (2000). Carbon partitioning within Phaeocystis antarctica (Prymnesiophyceae) colonies in the Ross Sea, Antarctica. Journal of Phycology, 36(6), 1049-1056.

McCave, I. N. (1984). Size spectra and aggregation of suspended particles in the deep ocean. Deep Sea Research Part A. Oceanographic Research Papers, 31(4), 329-352.

Meijering, E., Dzyubachyk, O., & Smal, I. (2012). Methods for cell and particle tracking. Methods in enzymology, 504, 183-200.

Moisan, T. A., & Mitchell, B. G. (1999). Photophysiological acclimation of Phaeocystis antarctica Karsten under light limitation. Limnology and Oceanography, 44(2), 247-258.

Nowald, N., Fischer, G., Ratmeyer, V., Iversen, M., Reuter, C., & Wefer, G. (2009, May). In-situ sinking speed measurements of marine snow aggregates acquired with a settling chamber mounted to the Cherokee ROV. In Oceans 2009-Europe (pp. 1-6). IEEE.

Osinga, R., De Vries, K. A., Lewis, W. E., Van Raaphorst, W., Dijkhuizen, L., & Van Duyl, F. C. (1997). Aerobic degradation of phytoplankton debris dominated by Phaeocystis sp. in different physiological stages of growth. Aquatic Microbial Ecology, 12(1), 11-19.

Passow, U., & De La Rocha, C. L. (2006). Accumulation of mineral ballast on organic aggregates. Global Biogeochemical Cycles, 20(1).

Passow, U., & Wassmann, P. (1994). On the trophic fate of Phaeocystis pouchetii (Hariot): IV. The formation of marine snow by P. pouchetii. Marine Ecology Progress Series, 153-161.

Passow, U., Alldredge, A. L., & Logan, B. E. (1994). The role of particulate carbohydrate exudates in the flocculation of diatom blooms. Deep Sea Research Part I: Oceanographic Research Papers, 41(2), 335-357.

Pausch, F., Bischof, K., & Trimborn, S. (2019). Iron and manganese co-limit growth of the Southern Ocean diatom Chaetoceros debilis. PLoS One, 14(9), e0221959.

Ploug, H., & Grossart, H. P. (2000). Bacterial growth and grazing on diatom aggregates: Respiratory carbon turnover as a function of aggregate size and sinking velocity. Limnology and Oceanography, 45(7), 1467-1475.

Ploug, H., Grossart, H. P., Azam, F., & Jørgensen, B. B. (1999). Photosynthesis, respiration, and carbon turnover in sinking marine snow from surface waters of Southern California Bight: implications for the carbon cycle in the ocean. Marine Ecology Progress Series, 179, 1-11.

Ploug, H., Iversen, M. H., & Fischer, G. (2008). Ballast, sinking velocity, and apparent diffusivity within marine snow and zooplankton fecal pellets: Implications for substrate turnover by attached bacteria. Limnology and Oceanography, 53(5), 1878-1886.

Ploug, H., Terbrüggen, A., Kaufmann, A., Wolf - Gladrow, D., & Passow, U. (2010). A novel method to measure particle sinking velocity in vitro, and its comparison to three other in vitro methods. Limnology and Oceanography: Methods, 8(8), 386-393.

Polerecky, L., Adam, B., Milucka, J., Musat, N., Vagner, T., & Kuypers, M. M. (2012). Look@ NanoSIMS–a tool for the analysis of nanoSIMS data in environmental microbiology. Environmental microbiology, 14(4), 1009-1023.

Putt, M., Miceli, G., & Stoecker, D. K. (1994). Association of bacteria with Phaeocystis sp. in McMurdo Sound, Antarctica. Marine Ecology Progress Series, 179-189.

Ragueneau, O., Tréguer, P., Leynaert, A., Anderson, R. F., Brzezinski, M. A., DeMaster, D. J., ... & Quéguiner, B. (2000). A review of the Si cycle in the modern ocean: recent progress and missing gaps in the application of biogenic opal as a paleoproductivity proxy. Global and Planetary Change, 26(4), 317-365.

Raven, J. A., & Falkowski, P. G. (1999). Oceanic sinks for atmospheric CO2. Plant, Cell & Environment, 22(6), 741-755.

Reigstad, M., Wassmann, P., Ratkova, T., Arashkevich, E., Pasternak, A., & Øygarden, S. (2000). Comparison of the springtime vertical export of biogenic matter in three northern Norwegian fjords. Marine Ecology Progress Series, 201, 73-89.

Rembauville, M., Salter, I., Leblond, N., Gueneugues, A., & Blain, S. (2015). Export fluxes in a naturally iron-fertilized area of the Southern Ocean–Part 1: Seasonal dynamics of particulate organic carbon export from a moored sediment trap. Biogeosciences, 12(11), 3153-3170.

Riebesell, U. (1993). Aggregation of Phaeocystis during phytoplankton spring blooms in the southern North Sea. Marine Ecology Progress Series, 96, 281-289.

Riebesell, U., Reigstad, M., Wassmann, P., Noji, T., & Passow, U. (1995). On the trophic fate of Phaeocystis pouchetii (Hariot): VI. Significance of Phaeocystis-derived mucus for vertical flux. Netherlands Journal of Sea Research, 33(2), 193-203.

Rousseau, V., Vaulot, D., Casotti, R., Cariou, V., Lenz, J., Gunkel, J., & Baumann, M. (1994). The life cycle of Phaeocystis (Prymnesiophycaea): evidence and hypotheses. Journal of marine systems, 5(1), 23-39.

Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., ... & Rios, A. F. (2004). The oceanic sink for anthropogenic CO2. science, 305(5682), 367-371.

Salter, I., Lampitt, R. S., Sanders, R., Poulton, A., Kemp, A. E., Boorman, B., ... & Pearce, R. (2007). Estimating carbon, silica and diatom export from a naturally fertilised phytoplankton bloom in the Southern Ocean using PELAGRA: A novel drifting sediment trap. Deep Sea Research Part II: Topical Studies in Oceanography, 54(18-20), 2233-2259.

Schiffrine, N., Tremblay, J. É., & Babin, M. (2020). Growth and elemental stoichiometry of the ecologically-relevant Arctic diatom Chaetoceros gelidus: a mix of polar and temperate. Frontiers in Marine Science, 6, 790.

Schindelin, J., Arganda-Carreras, I., Frise, E., Kaynig, V., Longair, M., Pietzsch, T., ... & Cardona, A. (2012). Fiji: an open-source platform for biological-image analysis. Nature methods, 9(7), 676-682.

Schoemann, V., Becquevort, S., Stefels, J., Rousseau, V., & Lancelot, C. (2005). Phaeocystis blooms in the global ocean and their controlling mechanisms: a review. Journal of Sea Research, 53(1-2), 43-66.

Sheik, A. R., Brussaard, C. P., Lavik, G., Lam, P., Musat, N., Krupke, A., ... & Kuypers, M. M. (2014). Responses of the coastal bacterial community to viral infection of the algae Phaeocystis globosa. The ISME journal, 8(1), 212-225.

Simon, M., Grossart, H. P., Schweitzer, B., & Ploug, H. (2002). Microbial ecology of organic aggregates in aquatic ecosystems. Aquatic microbial ecology, 28(2), 175-211.

Smetacek, V. (1999). Diatoms and the ocean carbon cycle. Protist, 150(1), 25-32.

Smetacek, V., Assmy, P., & Henjes, J. (2004). The role of grazing in structuring Southern Ocean pelagic ecosystems and biogeochemical cycles. Antarctic science, 16(4), 541-558.

Smith, D. C., Simon, M., Alldredge, A. L., & Azam, F. (1992). Intense hydrolytic enzyme activity on marine aggregates and implications for rapid particle dissolution. Nature, 359(6391), 139-142.

Smith Jr, W. O., Carlson, C. A., Ducklow, H. W., & Hansell, D. A. (1998). Growth dynamics of Phaeocystis antarctica-dominated plankton assemblages from the Ross Sea. Marine Ecology Progress Series, 168, 229-244.

Smith Jr, W. O., & Trimborn, S. (2023). Phaeocystis: A global enigma. Annual Review of Marine Science, 16.

Solomon, C. M., Lessard, E. J., Keil, R. G., & Foy, M. S. (2003). Characterization of extracellular polymers of Phaeocystis globosa and P. antarctica. Marine Ecology Progress Series, 250, 81-89.

Sweeney, C., Hansell, D. A., Carlson, C. A., Codispoti, L. A., Gordon, L. I., Marra, J., ... & Takahashi, T. (2000). Biogeochemical regimes, net community production and carbon export in the Ross Sea, Antarctica. Deep Sea Research Part II: Topical Studies in Oceanography, 47(15-16), 3369-3394.

Takahashi, T., Sutherland, S. C., Wanninkhof, R., Sweeney, C., Feely, R. A., Chipman, D. W., ... & de Baar, H. J. (2009). Climatological mean and decadal change in surface ocean pCO2, and net sea–air CO2 flux over the global oceans. Deep Sea Research Part II: Topical Studies in Oceanography, 56(8-10), 554-577.

Tantanasarit, C., Englande, A. J., & Babel, S. (2013). Nitrogen, phosphorus and silicon uptake kinetics by marine diatom Chaetoceros calcitrans under high nutrient concentrations. Journal of Experimental Marine Biology and Ecology, 446, 67-75.

Thingstad, F., & Billen, G. (1994). Microbial degradation of Phaeocystis material in the water column. Journal of marine systems, 5(1), 55-65.

Thingstad, T. F., & Martinussen, I. (1991). Are bacteria active in the cold pelagic ecosystem of the Barents Sea?. Polar research, 10(1), 255-266.

Thomas, D. N., Baumann, M. E., & Gleitz, M. (1992). Efficiency of carbon assimilation and photoacclimation in a small unicellular Chaetoceros species from the Weddell Sea (Antarctica): Influence of temperature and irradiance. Journal of experimental marine biology and ecology, 157(2), 195-209.

Tooby, P. F., Wick, G. L., & Isaacs, J. D. (1977). The motion of a small sphere in a rotating velocity field: a possible mechanism for suspending particles in turbulence. Journal of geophysical research, 82(15), 2096-2100.

Tortell, P. D., Payne, C. D., Li, Y., Trimborn, S., Rost, B., Smith, W. O., ... & DiTullio, G. R. (2008). CO2 sensitivity of Southern Ocean phytoplankton. Geophysical Research Letters, 35(4).

Trimborn, S., Thoms, S., Brenneis, T., Heiden, J. P., Beszteri, S., & Bischof, K. (2017). Two Southern Ocean diatoms are more sensitive to ocean acidification and changes in irradiance than the prymnesiophyte Phaeocystis antarctica. Physiologia Plantarum, 160(2), 155-170.

Venables, H. J., & Meredith, M. P. (2014). Feedbacks between ice cover, ocean stratification, and heat content in Ryder Bay, western Antarctic Peninsula. Journal of Geophysical Research: Oceans, 119(8), 5323-5336.

Volk, T., & Hoffert, M. I. (1985). Ocean carbon pumps: Analysis of relative strengths and efficiencies in ocean - driven atmospheric CO2 changes. The carbon cycle and atmospheric CO2: Natural variations Archean to present, 32, 99-110.

Wassmann, P., Vernet, M., Mitchell, B. G., & Rey, F. (1990). Mass sedimentation of Phaeocystis pouchetii in the Barents Sea. Marine Ecology Progress Series, 183-195.

Young, I. R., Zieger, S., & Babanin, A. V. (2011). Global trends in wind speed and wave height. Science, 332(6028), 451-455.

Zetsche, E. M., Larsson, A. I., Iversen, M. H., & Ploug, H. (2020). Flow and diffusion around and within diatom aggregates: effects of aggregate composition and shape. Limnology and Oceanography, 65(8), 1818-1833.

Ziervogel, K., Steen, A. D., & Arnosti, C. (2010). Changes in the spectrum and rates of extracellular enzyme activities in seawater following aggregate formation. Biogeosciences, 7(3), 1007-1015.

SUPPLEMENTARY

Table S2: Slope comparison with ANCOVA between t2 (42h) and t3 (90h) for the treatments 13C Phaeo/15N Chae and 15N Phaeo/13C Chae

Treatment	Parameters	Df	Sum Sq	Mean Sq	F-value	Pr(>F)
13C Phaeo/15N Chae	Sinking velocity [m/d]	1	59.55	59.55	95.01	9.13E-13
13C Phaeo/15N Chae	Timepoints	1	9.22	9.22	14.71	0.000379
13C Phaeo/15N Chae	Sinking velocity [m/d] : Timepoints	1	12.30	12.30	19.62	5.79E-05
13C Phaeo/15N Chae	Residuals	46	28.83	0.63	NA	
15N Phaeo/13C Chae	Sinking velocity [m/d]	1	141.46	141.46	223.27	<2E-16
15N Phaeo/13C Chae	Timepoints	1	14.01	14.01	22.12	2.12E-05
15N Phaeo/13C Chae	Sinking velocity [m/d] : Timepoints	1	13.67	13.67	21.57	2.59E-05
15N Phaeo/13C Chae	Residuals	49	31.05	0.63	NA	

Equivalent spherical diameter is defined as the dependent variable, Timepoint as the factor and Sinking velocity as the covariate; Abbriviations are defined as follows: Df = Degrees of freedom, Sum Sq = Sum of Squares, Mean Sq = Mean of Squares, F-value = ratio of two mean squares, Pr(>F) = p-value

Table S3: Statistic comparison of 13C and 15N measurements from Phaeocystis antarctica, Chaetoceros debilis and bacteria between the two treatments: (1) 13C Phaeo/15N Chae and (2) 15N Phaeo/13C Chae, whereby 13C/12C signified (0.5*12C13C)/(12C2+(0.5*12C13C)) and 14N/14N signified 12C15N/(12C14N+12C15N)

Measurement	statistic test	p-value
13C/12 C Phaeocystis	Wilcoxon-Test	4.27e-14
15N/14N Phaeocystis	Wilcoxon-Test	1.16e-15
13C/12 C Chaetoceros	Wilcoxon-Test	9.06e-05
15N/14N Chaetoceros	Wilcoxon-Test	5.54e-02
13C/12 C Bacteria	Wilcoxon-Test	2.20e-16
15N/14N Bacteria	Wilcoxon-Test	4.13e-15

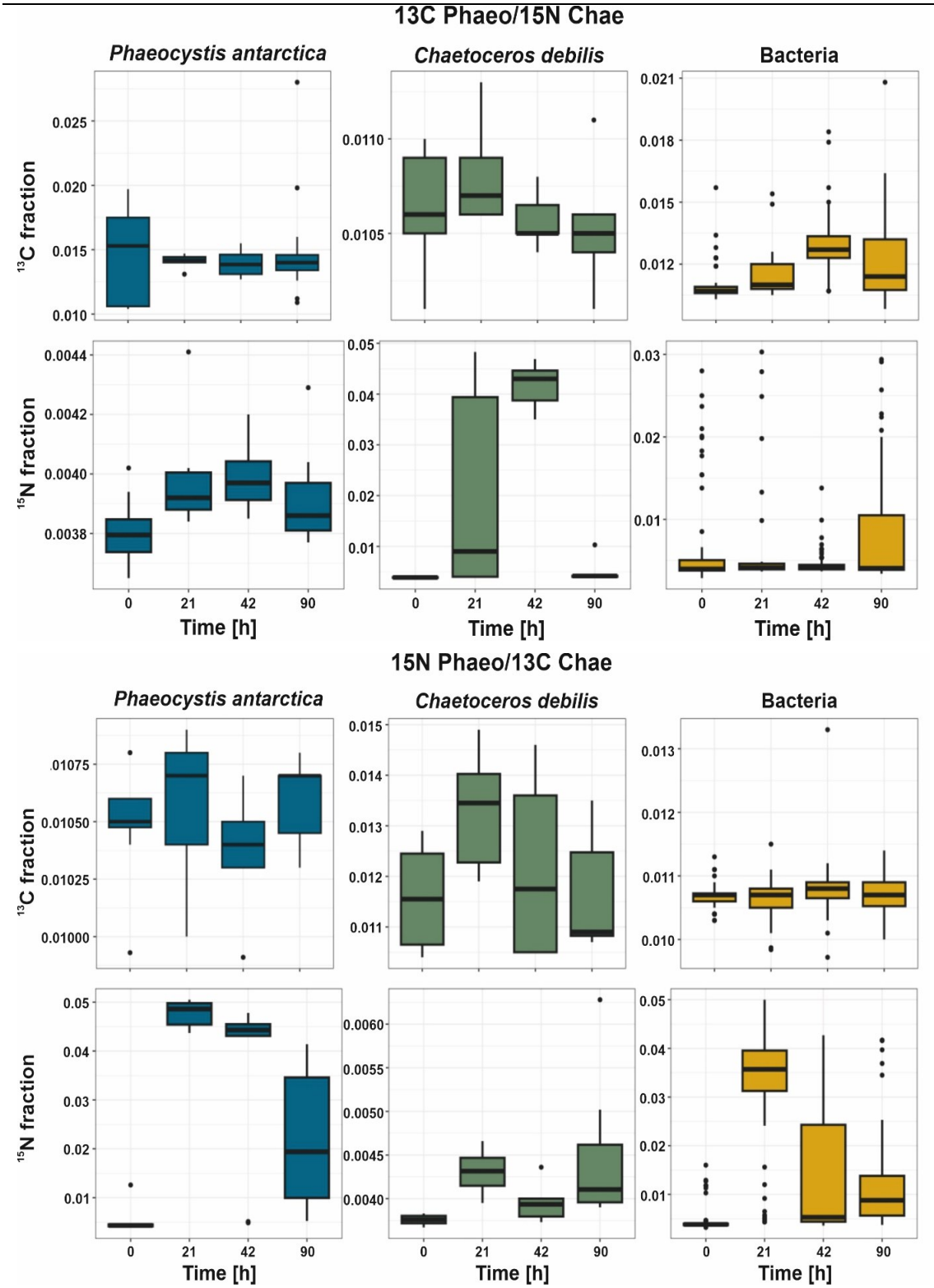


Fig. S5: Mean values and standard deviation of ^{13}C fraction, calculated from secondary ion counts (0.5*12C13C)/(12C2+(0.5*12C13C)) and ^{15}N fraction, calculated from secondary ion counts 12C15N/(12C214N+12C15N). Individual cells of Phaeocystis antarctica, Chaetoceros debilis and bacteria in the treatments of 13C Phaeo/15N Chae and 15N Phaeo/13C Chae were measured following the course of time with 0h, 21h, 42h and 90h, whereby cells at 42h and 90h were included in aggregated material.

3. DISCUSSION

The biological carbon pump is an important process for transport of organic matter from the surface to the deep ocean and has, historically seen, played a crucial role in forming the increasing gradient of carbon with increasing depth in the ocean (Gruber and Sarmiento 2002). The main components of the biological carbon pump are the fixation of carbon dioxide into organic matter via primary production and the formation of settling particles, which, together with vertically migrating animals transports particulate organic matter from the euphotic surface ocean to the deep sea and seafloor. The efficiency and magnitude of the biological carbon pump is driven by aggregate formation, aggregate sinking velocity, and the remineralization rate of the organic matter as it sinks through the water column.

In **Manuscript I**, I simulated a natural phytoplankton community assemblage from the Southern Ocean during laboratory incubations using roller tanks and tested the impact from nutrient availability on aggregate formation.

Direct in-situ observations in **Manuscript II** showed how gelatinous zooplankton can impact the carbon export. Here we found that both pteropods and appendicularians were important for export processes via both episodic flux pulses as well as strong retention of settling aggregates over a short time-scale at the Porcupine Abyssal Plain.

In **Manuscript III** we evaluated the carbon and nitrogen flow from diatoms versus Phaeocystis species from the Southern Ocean. We followed how nitrogen and carbon went from either the diatoms or Phaeocystis to aggregated organic matter and finally to bacterial biomass by labelling the phytoplankton with stable isotopes of ^{13}C-carbon and ^{15}N-nitrogen.

In the following sections, the key findings of each study and the implications for ocean biogeochemistry will be discussed within the wider context of the biological carbon pump.

3.1 HOW DOES NUTRIENT AVAILABILITY IMPACT AGGREGATE FORMATION?

Diatoms have a pivotal role in global carbon fixation, because of their predominance in oceanic environments (Sarthou et al. 2005, Treguer et al. 2018). It is estimated that diatoms contribute about 40% to global primary production in the oceans (Nelson et al. 1995, Treguer and Pondaven 2000, Sarthou et al 2005). The pathway of aggregate formation by diatoms is better understood than that of *Phaeocystis sp*. due to intensive studies during the last decades (Guillard and Wangersky 1958, Alldredge et al. 1993, Treguer et al. 2018). The main points determining the aggregation potential of diatoms are biomass accumulation, phenotypical characteristics, such as chains and spines, and cell stickiness (Riebesell and Wolf-Gladrow 1992, Kiørboe et al. 1998, Thornton 2002, Fig. 20). When diatoms are characterized by chain formation and spines, aggregates can be formed when cells get entangled. Furthermore, diatoms are commonly known to secret large amounts of transparent exopolymeric particles (TEP), which triggers the process of aggregate formation by their high stickiness (Passow et al. 1994, Engel 2000, Treguer et al. 2018, **Manuscript I**). For example, *Chaetoceros gracilis* was found to aggregate indirectly through the production of TEP which scavenge other particles form the surrounding waters via the enhanced stickiness (Crocker and Passow 1995). Moreover, the secretion of TEP is usually enhanced at the end of a diatom bloom, when nutrients become the limiting factor (Passow and Alldredge 1994, Fukao et al. 2010, **Manuscript I**, **Manuscript III**).

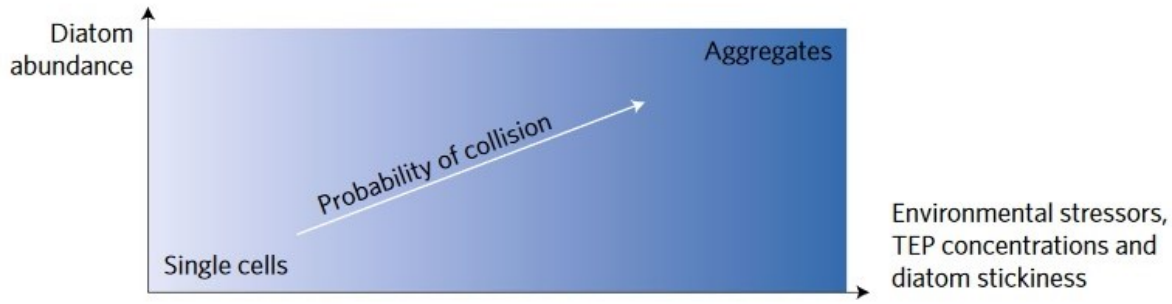


Fig. 20: Factors influencing the aggregation potential of diatoms. While environmental stress could potentially initiate senescence and potentially the production and release of transparent exopolymeric particles (TEP), it is TEP that increase the stickiness of diatoms and, hence, the probability of coagulation when two cells encounter each other. Moreover, increasing diatom abundance causes increased encounters and, together with increasing stickiness, drives the formation of fast-settling, carbon-rich diatom aggregates that are ballasted by silica (Treguer et al. 2018).

The role of *Phaeocystis sp*. in the biological carbon pump is still a matter of debate. Data on aggregate formation, settling velocity of single cells or derived aggregates are scarce. In **Manuscript III** we discovered that the main proportion of aggregated carbon from incubations of equal parts diatoms and Phaeocystis originated from *Phaeocystis antarctica* and that the contribution from diatoms was minor. Moreover, Schoemann et al. (2005) introduced three different potential mechanisms of how Phaeocystis could form aggregates and therefore stimulate the biological carbon pump: (I) due to self-aggregation, (II) due to excretion of mucopolysaccharides from the colony matrix, and (III) due to colonization by microbes. It turned out, that self-aggregation of colonies, solitary cells or a mixture is inefficient (Riebesell 1993, Passow and Wassmann 1994), while particle formation is enhanced when Phaeocystis colonies collapse due to external stressors (Riebesell et al. 1995, Schoemann et al. 2005, Smith Jr. and Trimborn 2023, **Manuscript I**, **Manuscript III**). Furthermore, senescent Phaeocystis colonies release high amounts of TEP, which can enhance the potential for aggregate formation due to high stickiness (Riebesell et al. 1995, Reigstad et al. 2000, **Manuscript I**). It was also shown that the senescent and fragile Phaeocystis colonies were highly colonized by a consortium of heterotrophic- and autotropic organisms, which in turn led to aggregate formation in the North Sea (Rousseau et al. 1994, Becquevort et al. 1998) and in the Ross Sea of the Antarctic (Putt et al.

1994). When studying which components of Phaeocystis colonies are exported, Hamm et al. (1999) primarily observed that the refractory mucus-rich colony skin reached the seafloor while other parts of the colonies seemingly were degraded in the water column. This disproportionate export and sedimentation of different colony material could be due to potential preferential degradation of storage polysaccharides compared to the heteropolysaccharides of the colony skin (Janse et al. 1999). Furthermore, after the collapse of Phaeocystis colonies, a high amount of these mucopolysaccharides are generally released into the surrounding waters, causing an accumulation of TEP, which initiates the process of aggregate formation of a range of particles (Mari et al. 2005, Alderkamp et al. 2007; Fig. 21). Due to the high contribution of the mucus skin of Phaeocystis colonies to aggregate formation, these types of aggregates define a specific class termed as mucus aggregates, which are often very abundant. Hence, our observations of Phaeocystis derived carbon making a substantial proportion of the total aggregated carbon (**Manuscript III**), the high abundance of Phaeocystis in many oceanic regions (Smith Jr. and Trimborn 2023) and the efficiency by which Phaeocystis colonies release of carbon-rich structures to the surrounding waters, we hypothesize that the haptophyte *Phaeocystis antarctica* is playing a key role for phytoplankton aggregation and marine snow formation in the Southern Ocean and speculate that other Phaeocystis species are equally important for aggregation in other oceanic regions.

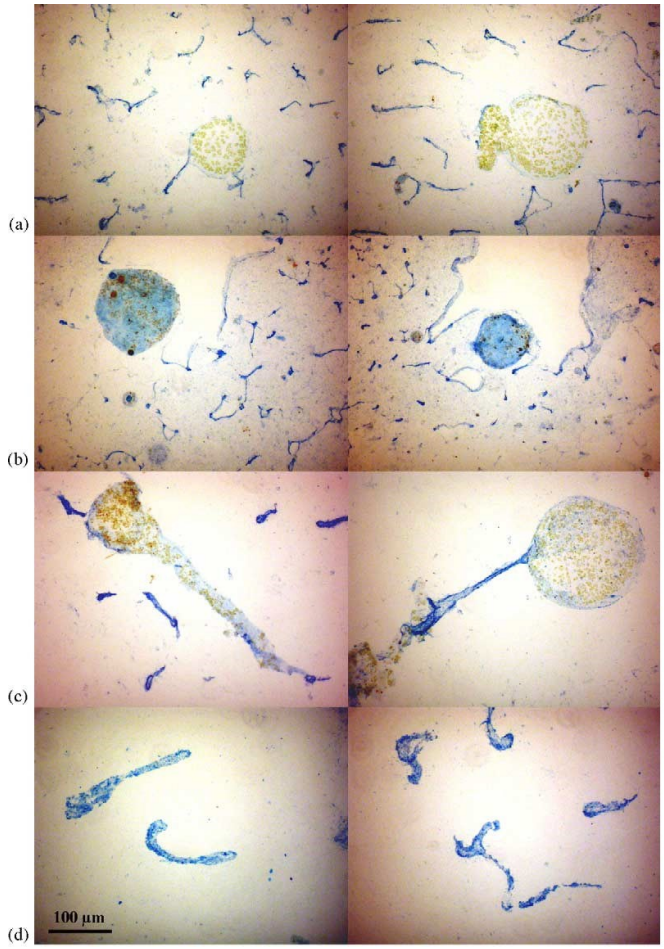


Fig. 21: TEP production and release by the haptophyte *Phaeocystis globosa* at different colonial stages stained with Alcian blue: (a) early stage of the colonies with recently produced TEP structures; (b) more porous structured colonies showing the accumulation of TEP in the colony; (c) initiated disruption of the colonies and the release of TEP and (d) large accumulation of released TEP structures after 14 days (Mari et al. 2005).

In **Manuscript I** we observed that nutrient availability plays a crucial role determining the aggregate formation and composition in a phytoplankton assemblage consisting of diatoms and Phaeocystis. Within a mixture of *Phaeocystis antarctica* and diatoms, the reduction of one nutrient or the absence of all lead to the formation of white aggregates that seemingly were composed of Phaeocystis derived matrix material and empty diatom frustules. This incorporation of primarily empty diatom frustules, might also explain why we observed the aggregates in Manuscript III to be ballasted by silica without have large contributions from diatom carbon to the aggregates (**Manuscript III**). Still, the aggregate composition and appearance was more yellow with seemingly active and living diatoms when two nutrients were simultaneously reduced, interestingly

these aggregates were similar to those formed at replete nutrient conditions. The morphology of an aggregate is highly variable in ocean and relies on several factors (Fig. 22). Aggregates are usually characterized by their size, shape, and porosity (Laurenceau-Cornec et al. 2015, Trudnowska et al. 2021). These factors, in turn, depend on other parameters, such as the predominant phytoplankton and zooplankton assemblage, released TEP structures, nutrient concentration, and water mass characteristics including turbulences and stratification (Alldredge et al. 1990, Rousseau et al. 1994, Takeuchi et al. 2019, **Manuscript I**). Due to the high aggregate diversity and variability, their morphology is seldomly used to describe an aggregate. However, when viewed across several studies, there are some morphological traits of aggregates that can be related to their structure, for instance studies of several species of *Chaetoceros* generally show that they form aggregates with loose structures, inconsistent shapes, and have high amounts on mucilage components (Crocker and Passow 1995, Ploug et al. 2002, Zetsche et al. 2020, **Manuscript I**). Personal observations, made by M.H. Iversen, revealed that yellow colored aggregates include living diatom cells, whereby colorless aggregates were formed with empty diatom frustules. Conversely, aggregates formed from Phaeocystis colony material were described to be colorless, irregular in shape, and covered by a sticky mucus matrix (Putt et al. 1994, Hamm and Rousseau 2003, **Manuscript I**). Our results from **manuscript I** indicated that at least when comparing diatoms and Phaeocystis, nutrient availability could be an important factor that determines aggregate composition and morphology. This may suggest that by identifying different adaptive strategies towards environmental conditions for different phytoplankton species and groups, we may be able to better predict aggregate formation and composition, which again impact aggregate characteristic such as carbon content, settling velocity, and microbial degradation, under different environmental conditions.

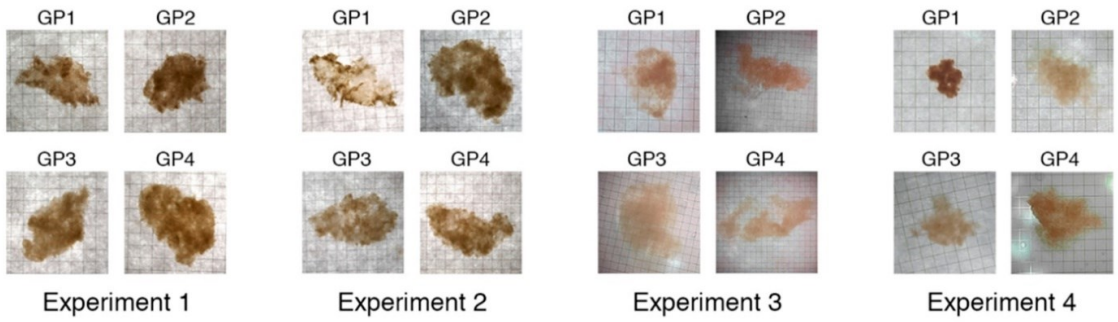


Fig. 22: Differences in aggregate morphology induced by different growth stages with GP1 defining the early exponential phase, GP2 the late exponential growth phase, GP3 the early stationary phase and GP4 the late stationary phase, produced by the phytoplankton *Thalassiosira weissflogii*, whereby the numerated experiments indicate different repetitions of the experiment (Prairie et al. 2019).

Due to different adaptive strategies, the reaction by different phytoplankton species on variable environmental conditions varies widely. But what adaptive strategies to environmental conditions governs the prevalence of diatoms or Phaeocystis concerning a shift in aggregate composition? The growth of phytoplankton relies mainly on the availability of nutrients, like nitrogen, phosphorus, iron, trace metals, and for diatoms silica (Rhee and Gotham 1981, DiTullio et al. 1993, Fitzwater et al. 2000). If these nutrients become limiting or are eliminated, for example at the end of a bloom, the effect on algae cells could be fatal. For example, diatoms require trace metals for specific metabolic processes (Giri et al. 2022) and if the concentration of trace metals is too low or too high, the metabolism is disturbed, which in turn leads to a dysfunctional development or in extreme cases to cell mortality (Giri et al. 2022). Moreover, the photosynthetic apparatus of diatoms requires nitrogen to produce chlorophyll pigments, without which, the photosynthesis will decrease. A reduction of the photosynthesis capability alters carbon fixation and cell growth (Behrenfeld et al. 2008). The most important nutrient for diatom growth is silicon. Diatoms use silicic acid present in the oceanic environment to construct their silica frustules, reflecting a defense strategy towards grazers (Hamm et al. 2003). If less silicon is available, the frustules of diatoms become thinner with less silica, which in turn increases the success potential of grazers (Leynaert et al. 2001, McNair et al. 2018, Giri et al. 2022). It is commonly known that when nutrients become limiting, diatom blooms will be terminated and high amounts of sticky polysaccharides are secreted, which

in turn positively influence the aggregate formation (Passow and Alldredge 1994, Engel 2000, Kahl et al. 2008, **Manuscript I**). For example, the diatom *Chaetoceros debilis* only form aggregates under nutrient limitation at the late stationary growth phase (Logan and Alldredge 1989, **Manuscript I, Manuscript III**).

In general, diatoms can better compete with low iron concentration than most other phytoplankton groups (Ho et al. 2003), which leads to diatoms outcompeting other algae in regions with low iron availability (Boyd et al. 2007). In terms of nutrient uptake, diatom shape is a crucial factor: chain formation lowers nutrient uptake, while elongated solitary cells increase it (Pahlow et al. 1997). An increased diatom cell size due to chain formation or developed spines also reduces the grazing pressure (Verity et al. 2000, Haberman et al. 2003). Moreover, the degree of silicification of the diatom frustule impacts the mortality rate, because heavily silicified cells are protected from mechanical grazing (Hamm et al. 2003). Due to the ability to compete with low iron concentrations, the protective silica frustule against grazing pressure, and their ubiquitous distribution, diatoms are generally clustered as main characters in the ocean carbon cycle. In comparison, some studies reported that Phaeocystis colonies overcome diatoms in the natural environment (Arrigo et al. 1999, Schoemann et al. 2001, Schoemann et al. 2005, Schapira et al. 2006). This was explained by their high adaptivity to fluctuations in light intensity (Arrigo et al. 1999), the formation of a mucus colony skin as a defense strategy against grazing pressure (Hamm et al. 1999) and the development of energy reservoirs in their colony skin (Schoemann et al. 2005). In the Southern Ocean, especially the Ross Sea, Phaeocystis blooms typically occur prior to diatom blooms, because they can better utilize the low light levels (Arrigo et al. 2003, Fig. 23). However, in other regions other factors than light seem to determine the phenology of Phaeocystis blooms, for example in the North Sea Phaeocystis species formed large blooms after a diatom bloom (Smith Jr. and Trimborn 2023), whereby the decrease in diatom abundance was linked to silica limitation while the Phaeocystis bloom correlates with a higher availability of nitrogen and in turn started to dominate the bloom (Lancelot et al. 1998). However, Smith Jr. and Trimborn (2023) reported that in the Ross Sea, the dominance of *P. antarctica* disappears during high stratification of the water column and low iron availability

in early January (Fig. 23). Yet, the impact of nutrient limitation on the mechanism causing senescence of colonies are poorly understood. Regarding aggregate composition, nutrient availability highly impacts the contribution of phytoplankton detritus in the process of aggregate formation, especially in terms of bloom elimination.

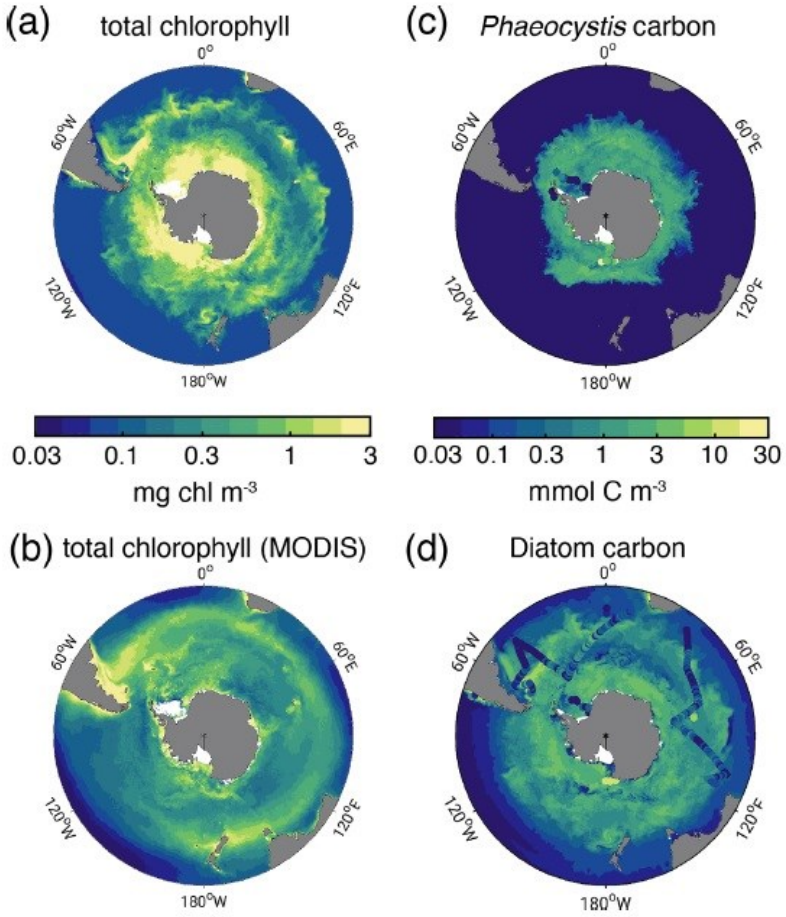


Fig. 23: Average biomass distribution from December to March displayed in: (a) total chlorophyll in surface waters (mg chl m^{-3}) using ROMS-Bec model and (b) using MODIS-Aqua climatology model (NASA-OBPG, 2014) calculated with the algorithm prepared by Johnson et al. (2013); (c) Phaeocystis biomass up to 50m depth and (d) diatom biomass up to 50m water depth (Nissen and Vogt 20021).

Moreover, the formation of aggregates in oceanic environments is stimulated by an increasing stickiness coefficient (Hill 1992, Kiørboe and Hansen 1993, Burd and Jackson 2009). TEP as a ubiquitous structure in the oceans has the potential to increase stickiness and scavenge particles from the surrounding which would otherwise not sink (Alldredge et al. 1993, Engel 2000, Passow 2002), which in turn leads to the assumption that this process also enhances the efficiency of the biological carbon pump due to high aggregate formation (Kiørboe et al. 1994, Jackson 1995, Jackson and Burd 1998). However, recent studies showed that high TEP concentrations not always correlate with high aggregate formation or high carbon export (Passow et al. 2001, Mari et al. 2017, Prairie et al. 2019, **Manuscript I**). Diatom derived TEP has been intensively studied in the last decades (Myklestad 1974, Alldredge and Crocker 1995, Deng et al. 2016). In general, diatoms are known to excrete TEP during their growth steadily (Myklestad 1974, Passow et al. 1994, Chen and Thornton 2015). Passow et al. (1994) showed that aggregation of the diatom *Chaetoceros gracilis* relies mainly on TEP released structures. Moreover, in the Adriatic Sea and Tyrrhenian Sea the occurrence of TEP rich structures correlates with the presence of the diatoms *Chaetoceros sp.* and *Nitzschia sp.* (Alldredge and Crocker 1995, Radić et al. 2005, De Philippis et al. 2005). Several studies found, that the excretion of TEP by diatoms is enhanced when nutrients become limited (Myklestad 1974, Corzo et al. 2000, Deng et al. 2016, **Manuscript I**). *Phaeocystis sp.* is also commonly known to steadily produce TEP during their growth (Verity et al. 1991, Mari et al. 2005, Li et al. 2023). Furthermore, *Phaeocystis sp.* release large amounts of TEP during the disruption of the colony structure caused by senescence (Hong et al. 1997, Mari et al. 2005, Li et al. 2023, **Manuscript I**). The senescence of Phaeocystis colonies is mainly caused by nutrient limitation or viral lysis, which in turn enhances TEP release and triggers aggregate formation (Schoemann et al. 2005, Smith Jr. and Trimborn 2023, **Manuscript I**, **Manuscript III**). Hence, while diatoms are continuously releasing TEP, but at limited and replete nutrient concentration, it seems that both Phaeocystis and diatoms have enhanced TEP production during nutrient limitations and that nutrient limitation causes intense aggregate formation and carbon export.

Zooplankton, like appendicularian and pteropods, also contribute substantially to the formation of aggregates due to mucus feeding structures produced to capture particles from the surrounding (Gorsky and Fenaux 1998, Sato et al. 2001, Noji et al. 1997, Pasternak et al. 2017, **Manuscript II**). In **Manuscript II**, we observed that mucus feeding structures produced by appendicularians and pteropods resulted in the formation of large, loosely structured mucus aggregates and provoked a shift in aggregate type from small and compact aggregates to the presence of high abundances of large and loose aggregates within days. There are still not many direct studies of the impact from zooplankton on aggregate formation and carbon export. Alldredge (1979) observed that, in the Gulf of California gelatinous zooplankton structures accounted for 20% of the total abundance of macroscopic aggregates. Moreover, Noji et al. (1997) reported that large biomass of the pteropod *L. retroversa* in the southern Norwegian Sea correlated with the occurrence of large mucous aggregates. The formation and high abundance of these large mucus aggregates was observed during laboratory incubations of *L. retroversa* and confirmed that the pteropod *L. retroversa* produce high numbers of mucus aggregates (Noji et al. 1997; Fig. 24). Our observations revealed, that the contribution of mucus aggregates led to an episodic flux event in the Porcupine abyssal plain improving carbon sequestration into the deep ocean (**Manuscript II**).

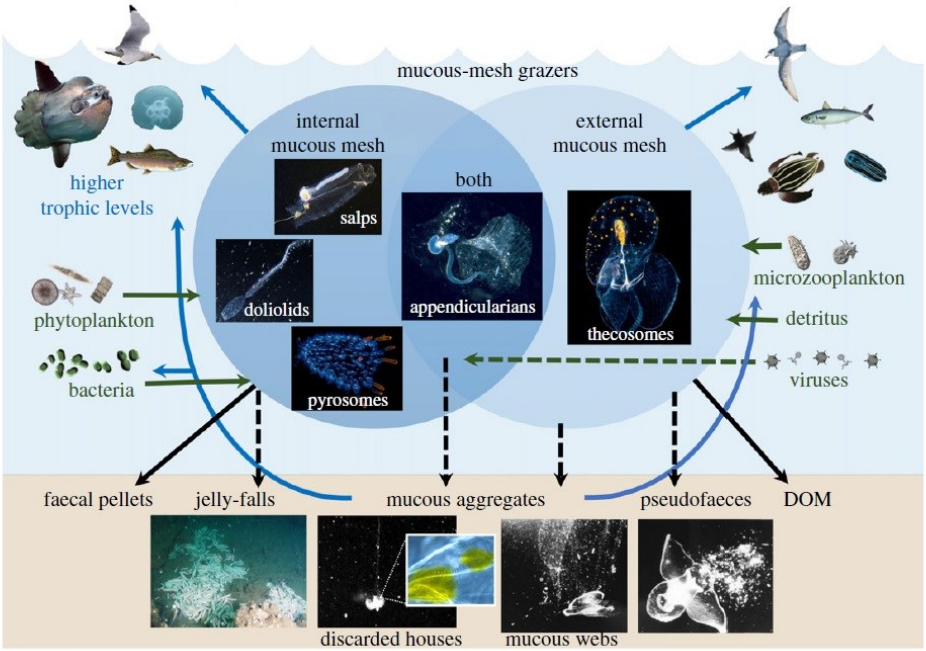


Fig. 24: Food web structure including mucus mesh grazer. General flux pathways are displayed with solid lines and dashed lines represent species specific fluxes. Carbon export pathways by gelatinous zooplankton is represented by jelly-falls, appendicularian houses, mucus web and pseudofaeces production by pteropods (Conley et al. 2018).

3.2 HOW DO GELATINOUS ZOOPLANKTON AND BACTERIA MEDIATE FLUX ATTENUATION?

Flux attenuation is mediated by processes like remineralization, grazing, utilization, and hydrolyzation by microbes, microzooplankton and mesozooplankton within the first 100 m of the water column. This carbon flux attenuation normally decreases with increasing depth, whereby the flux attenuation attributed to microbes becomes more and more important with increasing water depth (Iversen 2023; Fig. 25). It is important to differentiate between free-living and aggregate-attached microbial assemblage. Earlier studies have shown that microbial abundance and activity is enhanced on aggregated material and vary markedly from their free-living equivalents in terms of diversity, phylogeny, and structure (Alldredge and Cohen 1987, Herndl 1988, De Long et al. 1993, Crump et al. 1999, Simon et al. 2002). Moreover, the enzymatic activity and functionality of aggregate-associated microbes are elevated compared to their free-

living counterparts (Karner and Herndl 1992, Simon et al. 2002, Grossart et al. 2007, Ziervogel et al. 2010). A common technique to measure carbon turnover rates by aggregate-attached bacteria is to use oxygen microelectrodes to measure oxygen gradients through the aggregate-water diffusive boundary layer to estimate the flux of oxygen into the aggregate, which is thought to be proportional to the community respiration rate (Alldredge and Cohen 1987, Ploug et al.1997, Iversen et al. 2010). In general, respiration rate and aggregate size correlate positively. However, if the respiration rate is normalized per microbe or aggregate volume, it turns out to correlate inversely (Ploug et al. 1999, Ploug 2001). Moreover, it was shown that carbon turnover by aggregate attached microbes rely on the quality and composition of aggregates (Smith et al. 1992, Grossart and Simon 1998, Ploug et al. 1999). Yet it is still unclear which carbon fraction of the aggregated material is favored by bacteria. Diatoms are main contributors to aggregate formation on a global scale, due to their ubiquitous distribution and the ability to reach high biomasses during bloom conditions. The main proportion of literature about microbial degradation of aggregated material therefor focusses on aggregates formed by diatoms.

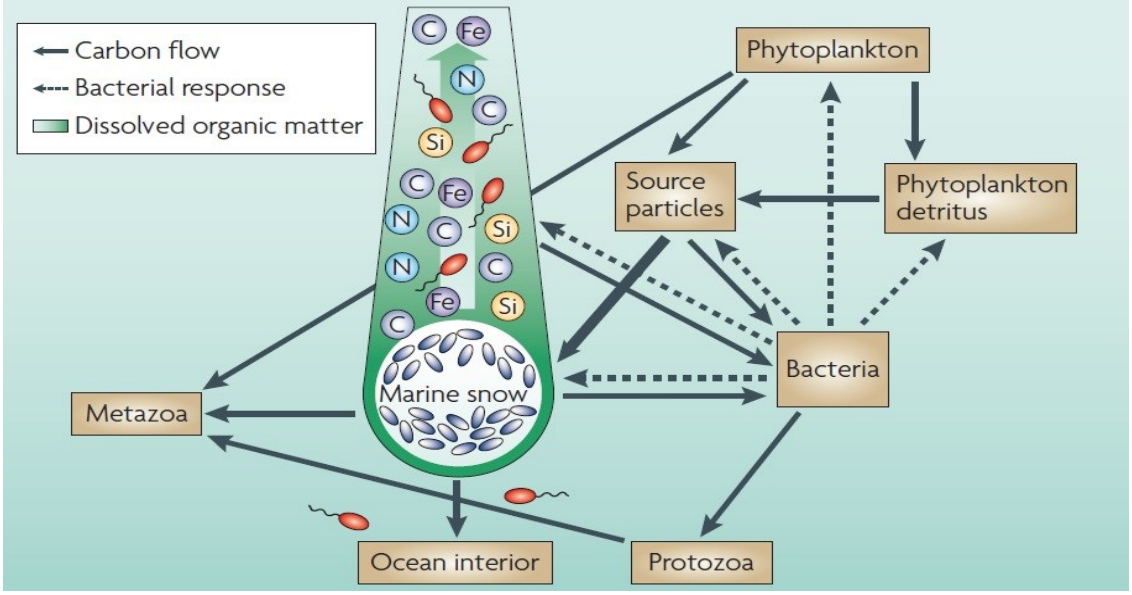


Fig. 25: Microbial food web of a microhabitat linked to marine snow including free-living (red) and aggregate-attached bacteria (blue to white; oval structures in marine snow; Azam and Malfatti 2007)

The microbial degradation of Phaeocystis derived mucopolysaccharides has gained more interest in the last decades as Phaeocystis is becoming more common in many marine environments (Smith Jr. and Trimborn 2023). In **Manuscript III**, we revealed that under phosphate limitation bacteria favor to utilized carbon structures from *Phaeocystis antarctica* compared to carbon from the diatom *Chaetoceros debilis*. Contrastingly, Alderkamp et al. (2007) suggested that phosphate limitation has a much higher negative effect on bacterial degradation of Phaeocystis material compared to the degradation of diatom material. In general, it was observed that Phaeocystis biomass during a bloom is rapidly remineralized by heterotrophic bacteria (Wassmann 1994, Rousseau et al. 2000). Alderkamp et al. (2007) reported that the quality and composition of Phaeocystis organic material impacts the degradation potential by microbes. While freshly excreted DOM can be rapidly degraded, the DOM released during the senescent stage, including mucopolysaccharides, is hardly degraded. Field observation showed that Phaeocystis colonies were colonized by bacteria during late bloom conditions (Thingstad and Billen 1994). Conversely, the accumulation of mucus derived foam or mucus material at the seafloor indicates that the mucus skin from Phaeocystis is less mineralized by attached microbes (Eberlein et al. 1985, Janse et al. 1996, Smith Jr. and Trimborn 2023). Janse et al. (1999) showed that microbial remineralization of mucus polysaccharides occurs under oxic as well as anoxic conditions, whereby remaining carbohydrates, which were not degraded by microbial activity, were protected due to the release of inhibitors. Several studies reported that attached bacterial communities associated with the biomass of Phaeocystis changed during growth (Arrieta and Herndl 2002, Brussaard et al. 2005, Alderkamp et al. 2007). This could be explained by the increasing release of complex carbohydrates such as glucan and mucopolysaccharides during growth of Phaeocystis, which can only be remineralized by specialized bacteria (Alderkamp et al. 2007). Nutrient limitation can also hamper the remineralization capacity of bacteria, with the result that Phaeocystis derived carbon accumulates (Thingstad and Billen 1994). However, apart from the high controversy regarding microbial utilization of Phaeocystis derived carbon, in a mixture of Phaeocystis and diatoms, bacteria prefer to acquire their carbon for secondary production from Phaeocystis (**Manuscript III**).

The main proportion of literature regarding flux attenuation focus on the impact of zooplankton grazing on sinking particles, whereby the role of mucus mesh grazers, like appendicularians and pteropods, in the biological carbon pump is still unclear. Due to limited in-situ observations, their fragile nature and high stickiness, net sampling of these zooplankton species resulted mainly in high stress conditions and therefore high mortality rates (Madin et al. 1996, Hunt et al. 2008, Berline et al. 2011). In **Manuscript II**, we observed that both a complete retention and an increase in carbon flux was driven by appendicularians and pteropods. Appendicularians have specialized feeding structures to capture particles in the euphotic zone and can at times occur in such high abundances that there is high attenuation of the export flux (Sato et al. 2008, Lombard et al. 2009, Iversen 2023, Fig. 26: D-E). Appendicularians, classified as filter feeders, have an exclusive external filter structure, the mucus houses, by which they can capture particles in a size range from 0.2 to 30 µm (Gorsky and Fenaux 1998, Lombard et al. 2011). The massive filtration rate of these houses account for 1L ind^{-1} d^{-1} (Deibel 1998). The clearance rate of appendicularians relies on their weight (Lopez-Urrutia et al. 2003, Broms and Tisselius 2003), food concentration (Acuna and Kiefer 2000, Selander and Tiselius 2003) and particle size (Tiselius et al. 2003, Fernández et al. 2004). Lombard et al. (2009) observed a maximum clearance rate of 12 µg C d^{-1}, while they also reported that the clearance rate increased under limited food concentration. Less is known about pteropods regarding flux attenuation. Pteropods are generally termed as flux feeders. They spawn a mucus feeding net reaching sizes up to several centimeters to capture sinking particles (Silver and Bruland 1981, Jackson 1993, Noji et al. 1997, Fig. 26: A-C). Noji et al. (1997) observed that pteropods can capture particles with sizes <2 µm and were responsible for 50% of the total particle removal under laboratory conditions. Therefore, when appendicularian or pteropod abundances are high, they can remove a significant proportion of the particle flux in the epipelagic (**Manuscript II**).

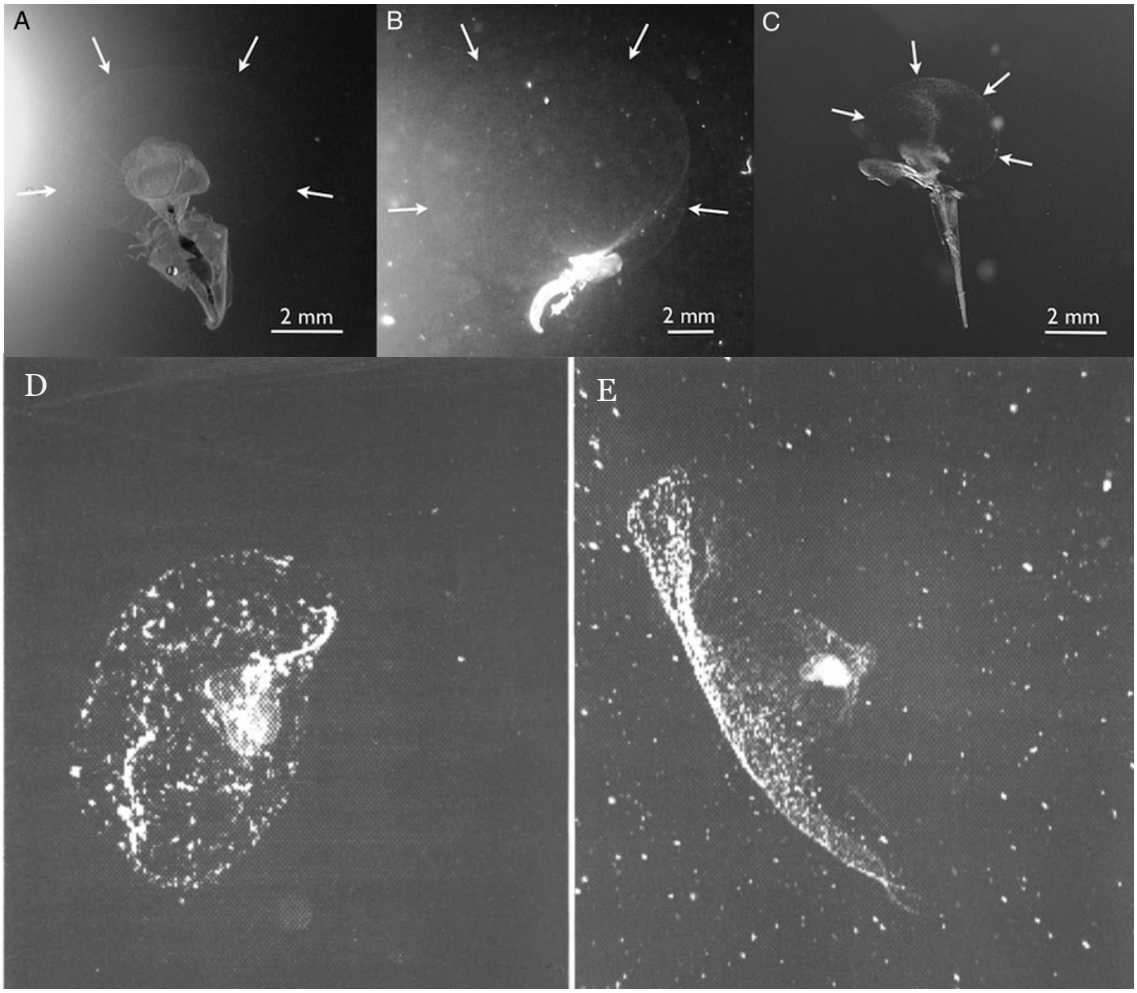


Fig. 26: photo captured mucus mesh structures released by gelatinous zooplankton with (A-C) showing the development of a mucus net (circled by arrows) by pteropods (Howes et al. 2014) and (D-E) showing secretion of a mucus envelope by an appendicularia probably over 7 days (Hamner and Robinson 1992).

3.3 WHAT CAUSES CHANGES IN THE STOICHIOMETRY?

The elemental composition of aggregates impacts the marine carbon cycle. Therefore, it is necessary to understand changes in POC and PON during settling and also differences in C:N ratio between aggregate types. In general, aggregate specific C:N ratios are influenced by several factors, including regionality, determining for example water body stratification, sea surface temperature and water body movements, phytoplankton communities and zooplankton interactions (Caron et al. 1989, Verity et al. 2000, Martiny et al. 2013, **Manuscript II**, **Manuscript III**). Furthermore, Alldredge (1998) showed that, the C:N ratio correlates positively with the aggregate size. Less is known about the C:N ratio of mucus aggregates. In **Manuscript II** we observed that the formation of mucus aggregates by gelatinous zooplankton leads to an increase in the C:N ratio of aggregated material. The impact from gelatinous zooplankton and their released mucus structures on biogeochemical cycles is not well known. It is thought that mucus polysaccharides lead to an increase in carbon to nitrogen ratio, like it was reported for TEP structures in the oceans (Engel 2000, Engel and Passow 2001), which coincided with our observations in **Manuscript II,** that the C:N ratio of aggregates increased, when mucus aggregates become dominant. Regarding Phaeocystis colonies and the derived aggregated material, several studies have shown that the C:N ratios are similar to the Redfield ratio (Smith et al. 1998, Smith Jr. and Trimborn 2023), which correspond to our observation in **Manuscript III,** where aggregates formed from Phaeocystis had a C:N ratio in the range of 6.35 to 6.80. Contrastingly, the C:N ratio of diatoms is highly variable. For example, low carbon to nitrogen ratios of 3.2 were reported for *Chaetoceros sp*. under non-limiting conditions (Harrison et al. 1977), while other studies reported *Chaetoceros sp*. C:N ratios exceeding those of the Redfield ratio (Tantanasarit et al. 2013, Pausch et al. 2019, Schiffrine et al. 2020). These observations confirm that the C:N ratio of aggregated material highly relies on the phytoplankton consortium and their nutritional condition. Moreover, mucus structures from gelatinous zooplankton can increase the carbon content of aggregates and therefore improve the carbon export.

3.4 HOW IS THE SINKING VELOCITY OF AGGREGATES IMPACTED BY CHANGES IN OCEANIC COMMUNITY STRUCTURES?

Aggregate specific sinking velocity in open oceans relies mainly on the composition, which in turn is determined by its origin and the prevalent phytoplankton assemblage. The sinking velocity of diatom cells depends not only on size and shape characteristic, but also on the physiological condition of the cell (Brzezinski and Nelson 1988). The settling of healthy diatom cells usually follows the Stokes' equation (Moore and Villareal 1996). Stoke`s equation is commonly used as a theoretical approach to calculate sinking velocity of an aggregate assuming a spherical shape (Shanks and Trent 1980). However, if diatom cells become senescent the sinking velocity is decreasing (Sarthou et al. 2005). Moreover, nutrient limitation can massively increase the sinking velocity of diatom cells (Bienfang et al. 1982, Harrison et al. 1986, Waite et al. 1992). Muggli et al. (1996) observed, that the sinking rate of the diatom *Actinocyclus sp*. increased fivefold under increasing iron limitation. Diatoms under iron stress condition increase their silification rate, which in turn lead to higher sinking velocities due to an increasing ballasting effect (Takeda 1998, De La Rocha et al. 2008, Sarthou et al. 2005). The senescence of diatom cells, mainly provoked under nutrient limited conditions at the end of a bloom, initiate the formation of marine aggregates. It was shown that diatom aggregates can reach sinking velocities >100 m d^{-1} (Alldredge and Silver 1988, Alldredge and Gottschalk 1989, Iversen and Ploug 2013). TEP structures, secreted by diatoms, are commonly known to lower the sinking velocity of diatom aggregates, due to their low density (Engel and Schartau 1999, Prairie et al. 2019) and near-neutral buoyancy (Azetsu-Scott and Passow 2004, Mari et al. 2017, **Manuscript I**). This in turn, lowers the excess density of an aggregate and consequentially also results in low sinking velocities. However, diatom aggregates are ballasted by their own silica frustule material, positively influencing their settling to greater depth (Passow and De La Rocha 2006, Engel et al. 2009, Bach et al. 2016, **Manuscript I**, **Manuscript III**).

Phaeocystis colonies were found to sink at low rates ranging from -0.37 to 14 m d^{-1}, whereby negative values reflect net positive buoyancy (Schoemann et al. 2005). Low sinking rates were also observed for Phaeocystis derived aggregates (Riebesell et al. 1995, Hamm 2000, Hamm and Rousseau 2003). In **Manuscript I and III**, we showed that Phaeocystis derived aggregates sink more efficient by incorporating an external ballasting factor such as diatom originated silica frustules. Several studies reported, that POC flux within sediment trap analysis often correlates with the mineral flux (calcium carbonate, biogenic silica and lithogenic silica; Armstrong et al. 2001, Francois et al. 2002, Klaas and Archer 2002). This observation led to the concept of the ballast hypothesis, which can be explained by minerals that are incorporated into aggregates and thereby increase the total downward transport of particulate organic carbon to greater depth by enhancing the sinking velocity due to increasing density (Armstrong et al. 2009, De La Rocha et al. 2008, Wilson et al. 2012). The highest correlation was found between POC flux and calcium carbonate flux. The correlation regarding the biogenic silica flux was minor, but still significant (Ragueneau et al. 2000, Francois et al. 2002, Klaas and Archer 2002, Fig. 27). Diatom frustules mainly consist of biogenic silica, which defined their own ballasting material within the process of aggregation and lead to a more efficient downward transport compared to *Phaeocystis* aggregates (Riebesell et al. 1995, Hamm and Rousseau 2003). Therefore, the sinking velocity of Phaeocystis derived aggregates will be enhanced by scavenging silica produced by diatoms, which in turn accelerates carbon export to depth (Le Moigne et al. 2015, **Manuscript I**, **Manuscript III**).

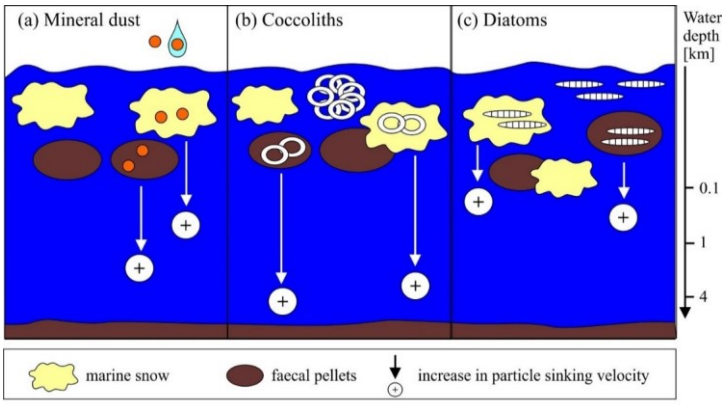


Fig. 27: Graphical abstract of aggregate ballasting with (a) mineral dust, (b) calcium carbonate and (c) silica in surface waters and the resulting effect on sinking velocities displayed by arrow length (Friese 2017).

Less is known about the sinking velocity of mucus aggregates produced by gelatinous zooplankton. In **Manuscript II**, we observed that a shift in aggregate type from small, compact aggregates to large, loosely structured, mucus aggregates enhanced the sinking velocity of marine snow. In general, Noji et al. (1997) observed that the pteropod *Limacina retroversa* initiates the formation of large, fast sinking aggregates by the accumulation of small dense particles reaching values up to 1000 m d^{-1} with a mean of ~ 300 m d^{-1}. Furthermore, it was shown that the fecal pellets of the genus *Clio sp*. also reach high sinking velocities in the range of 120 to 646 m d^{-1} (Yoon et al. 2001). Pasternak et al. (2017) also reported that dead pteropods can reach velocities up to 2000 m d^{-1}. Many studies focused on the sinking velocity of appendicularian houses, which account for a large proportion of macroaggregates. Silver and Alldredge (1981) reported sinking rates of *Oikopleura dioica* houses with a span from 57 to 64 m d^{-1} depending on the temperature. It was shown that the house size has a strong impact on the settling velocity of appendicularian houses. While low latitude appendicularians produce small houses at low temperatures with mean settling rates of 26 m d^{-1}, increasing temperature causes increasing house size and thus led to increasing sinking velocities reaching 157 m d^{-1} (Gorsky et al. 1984). Moreover, high settling rates for appendicularian houses were also reported in calm water bodies with mean values of 189 m d^{-1} (Taguchi 1982). In general, the incorporation of mucus structures, released by pteropods or appendicularians, increase the sinking velocity of aggregated material and may enhance the carbon export in the biological carbon pump (Noji et al. 1997, Berline et al. 2011, **Manuscript II**).

3.5 CONCLUSIONS

The role of Phaeocystis in the oceanic biogeochemical carbon cycle is still a matter of debate. Slow sinking rates or neutral buoyancy of solitary cells and colonies lead to the idea, that Phaeocystis is of little importance for carbon export to the deep ocean (Wassmann et al. 1990, Becquevort and Smith 2001, Schoemann et al. 2005). Contrastingly, it was observed that Phaeocystis releases high amounts of dissolved organic carbon at the end of a bloom, when colonies break apart (Hamm et al. 1999, Schoemann et al. 2005, Verity et al. 2007). It is now appreciated that the release of dissolved organic carbon by Phaeocystis is a key driver for aggregate formation (DiTullio et al. 2000), making Phaeocystis important for the downward transport of carbon in the ocean. In a modelling study, Nissen and Vogt (2021) reported that Phaeocystis contribute to ~40% of the particulate organic carbon export to 100m depth south of 60°S. However, the contribution towards carbon export to greater depth or sequestration is still controversial. It was observed that the majority of Phaeocystis biomass during bloom conditions is rapidly remineralized by heterotrophic bacteria (Wassmann 1994, Rousseau et al. 2000, **Manuscript III**). Contrarily, several studies reported mass deposition events of Phaeocystis derived material, especially in polar waters of the Barents Sea and Ross Sea (Wassmann et al. 1990, Asper et al. 1997, Asper and Smith 1999). The formation of marine aggregates is a crucial and import step in carbon export. It is commonly known that Phaeocystis steadily secrete TEP during growth, which encourage the formation of aggregates (Hong et al. 1997, Passow 2002). In **Manuscript III**, we observed that *Phaeocystis antarctica* is the main contributor to aggregated organic carbon, even when diatoms are available in similar abundances as the Phaeocystis. Moreover, it was observed that Phaeocystis derived aggregates were mainly formed when the colonies collapse due to senescence, typically caused by viral lysis or nutrient restricted conditions (Schoemann et al. 2005, Alderkamp 2007, **Manuscript I**). However, due their low sinking velocities Phaeocystis derived aggregates rely on an external ballasting factor such as diatom frustules for carbon export to the ocean interior (Le Moigne et al. 2015, **Manuscript I**, **Manuscript III**). Nevertheless, with their high biomass during bloom conditions and their capacity to initiate aggregation, Phaeocystis has an important role in the biological carbon pump and in carbon export.

Appendicularians were observed to be the second largest group of mesozooplankton in oceanic environment, but their role in the biological carbon pump is not clear yet (Gorsky and Fenaux 1998, Christiansen et al. 2010, **Manuscript II**). Due to their high physiological rates in fecal pellet production and excretion rates, which usually exceed those of copepods as the largest contributor towards mesozooplankton, this group deserves more attention in revealing the biogeochemical carbon cycle (Lopez-Urrutia et al. 2003, Berline et al. 2011). Moreover, the unique capability to discard up to 26 houses per day and have already prepared new houses at the ready, appendicularians create a carbon rich mucus flux and with the production of dense and rapidly sinking fecal pellets, they are important contributors towards carbon export and eventually also to the sequestration flux in the oceans (Gorsky and Fenaux, Sato et al. 2001, Lombard et al. 2009, **Manuscript II**). One attempt to specify the role of appendicularians to carbon export was done using a model approach by Berline et al. (2011), which showed that the presence of appendicularians in the North-west Mediterranean could enhance the export production by 55% compared to models excluding appendicularians. Contrastingly, due to their high clearance rate, appendicularian where also responsible for a high loss of carbon in form of small slow sinking particles during export in the water column (Lombard et al. 2009, **Manuscript II**).

The contribution of pteropods to carbon export is also not well understood and only few studies have reported on their potential role within the biological carbon pump (Yoon et al. 2001, Hunt et al. 2008, Pasternak et al. 2017). In general, pteropods were described as efficient flux attenuators, due to their passive flux feeding behaviour by releasing mucus nets capturing particles of all sizes larger than 2 μm (Silver and Bruland 1981, Noji et al. 1997, Hunt et al. 2008). In **Manuscript II** we observed that this removal was negligible due to their low biomass. Moreover, pteropods are known to produce large, fast-sinking fecal pellets (Yoon et al. 2001, Hunt et al. 2008). With the ability to turn small particles into large fast-sinking fecal pellets or mucus aggregates, pteropods are important and yet often neglected contributors to carbon export (Noji et al. 1997, Yoon et al. 2001, **Manuscript II**).

3.6 FUTURE OUTLOOK

The ocean is by far the largest reservoir for carbon on Earth and represents a driving force for climate regulation. Through photosynthesis, active marine microorganisms (e.g., phytoplankton) convert atmospheric CO2 into biomass, where most of it is recycled in the surface water layer by diverse processes such as bacterial respiration and zooplankton grazing. Some of this biomass is exported as particulate organic carbon (POC) into deeper regions of the ocean, where zooplankton are the first gatekeepers at the depth of the mixed layer and thereafter bacterial cells play a critical role in regulating the efficiency of carbon export because they colonize and enzymatically hydrolyze photosynthetically derived POC as it sinks. A recent study revealed that bacterial groups are colonizing aggregates at different times, with the Pseudoalteromonas group being the initial colonizer of diatom aggregates, followed by the Alteromonas group (Arandia-Gorostidi et al. 2022). Additionally, both bacterial groups incorporated comparable levels of diatom carbon into their biomass, but Alteromonas bacteria showed significantly higher levels of nitrogen derived from diatoms compared to Pseudoalteromonas. This suggests that sequential colonization by different bacterial groups onto settling marine aggregates can cause a sequential degradation of organic compounds according to the preferential degradation of the individual bacterial groups. These results highlight the importance of bacterial succession within diatom aggregates in influencing taxa-specific carbon and nitrogen uptake, with potential implications for the transformation and molecular composition of organic matter exported to the deep ocean.

Upper ocean carbon export and recycling varies geographically, depending on ecosystem structure and differences in nutrients, light, and temperature (Boyd and Trull 2007). Observations from sediment traps have shown that carbon to nitrogen ratios of sinking organic matter increases between the surface and deep ocean, but that changes are not uniform across seasons or latitudes (Henson et al. 2012). Typically, stoichiometric analyses of exported organic matter collected by sediment traps only includes carbon and nitrogen (e.g., Fischer et al. 2019), while organic compounds are rarely measured. However, in order to understand the driving processes for carbon sequestration, we need to understand if there are depth-specific selective degradation and preservation of organic compounds.

ACKNOWLEDGEMENTS

Of top priority I thank my PhD supervisor Prof. Dr. Jack Middelburg for his steady support and guidance in this process. Moreover, I also say thank you to Prof. Dr. Morten Iversen, who assumed the responsibility as my local supervisor. It was a pleasure to work with both of you and benefit from your knowledge, creativity and experience.

Second, I thank the members of my thesis committee; Morten Iversen, Jack Middelburg, Jan-Hendrik Hehemann and Kai-Uwe Hinrichs for the nice and supportive discussions and improvements. Moreover, I want to say thank you to the members of the PhD defence committee for evaluating my thesis and the nice discussion during the defence.

Great thanks to the co-authors and contributors of my manuscripts. Big thanks go to Michiel Kienhuis from the department of Earth Science at the Utrecht University, who with great enthusiasm and calm nature taught me the process of NanoSIMS imaging. Moreover, I want to say thank you to Jenny Wendt from the organic geochemistry group at MARUM for the support and great patience, in terms of chemical analysis. Special thanks to all members the SeaPump group for the countless chats, coffee breaks, the carefree atmosphere and the good sense of humor.

I also say thank you to my family, which always supported me on this rough way and always believed in me. Chiefly, thanks to my niece, which always put a smile on my face, irrelevant how hard the time was. Last but not least, I say thank you to my wife for being my anchor and creating such a supportive atmosphere regardless how difficult the way was. This journey showed us that we can cope every challenge together.

REFERENCES

Abell, J., Emerson, S., & Renaud, P. (2000). Distributions of TOP, TON and TOC in the North Pacific subtropical gyre: Implications for nutrient supply in the surface ocean and remineralization in the upper thermocline. Journal of Marine Research, 58(2), 203-222.

Alderkamp, A. C., Buma, A. G., & van Rijssel, M. (2007). The carbohydrates of Phaeocystis and their degradation in the microbial food web. Biogeochemistry, 83, 99-118.

Alldredge, A. (1998). The carbon, nitrogen and mass content of marine snow as a function of aggregate size. Deep Sea Research Part I: Oceanographic Research Papers, 45(4-5), 529-541.

Alldredge, A. L. (1979). The chemical composition of macroscopic aggregates in two neretic seas 1. Limnology and Oceanography, 24(5), 855-866.

Alldredge, A. L. (1999). The potential role of particulate diatom exudates in forming nuisance mucilaginous scums. Annali-Istituto Superiore Di Sanità, 35(3), 397-400.

Alldredge, A. L., & Cohen, Y. (1987). Can microscale chemical patches persist in the sea? Microelectrode study of marine snow, fecal pellets. Science, 235(4789), 689-691.

Alldredge, A. L., & Crocker, K. M. (1995). Why do sinking mucilage aggregates accumulate in the water column?. Science of the total environment, 165(1-3), 15-22.

Alldredge, A. L., & Gotschalk, C. (1988). In situ settling behavior of marine snow 1. Limnology and Oceanography, 33(3), 339-351.

Alldredge, A. L., & Gotschalk, C. C. (1989). Direct observations of the mass flocculation of diatom blooms: characteristics, settling velocities and formation of diatom aggregates. Deep Sea Research Part A. Oceanographic Research Papers, 36(2), 159-171.

Alldredge, A. L., & Silver, M. W. (1988). Characteristics, dynamics and significance of marine snow. Progress in oceanography, 20(1), 41-82.

Alldredge, A. L., Cole, J. J., & Caron, D. A. (1986). Production of heterotrophic bacteria inhabiting macroscopic organic aggregates (marine snow) from surface waters 1. Limnology and Oceanography, 31(1), 68-78.

Alldredge, A. L., Granata, T. C., Gotschalk, C. C., & Dickey, T. D. (1990). The physical strength of marine snow and its implications for particle disaggregation in the ocean. Limnology and Oceanography, 35(7), 1415-1428.

Alldredge, A. L., Passow, U., & Logan, B. E. (1993). The abundance and significance of a class of large, transparent organic particles in the ocean. Deep Sea Research Part I: Oceanographic Research Papers, 40(6), 1131-1140.

Anderson, L. A., & Sarmiento, J. L. (1994). Redfield ratios of remineralization determined by nutrient data analysis. Global biogeochemical cycles, 8(1), 65-80.

Arandia-Gorostidi, N., Berthelot, H., Calabrese, F., Stryhanyuk, H., Klawonn, I., Iversen, M., ... & Musat, N. (2022). Efficient carbon and nitrogen transfer from marine diatom aggregates to colonizing bacterial groups. Scientific Reports, 12(1), 14949.

Armstrong, R. A., Lee, C., Hedges, J. I., Honjo, S., & Wakeham, S. G. (2001). A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals. Deep Sea Research Part II: Topical Studies in Oceanography, 49(1-3), 219-236.

Armstrong, R. A., Peterson, M. L., Lee, C., & Wakeham, S. G. (2009). Settling velocity spectra and the ballast ratio hypothesis. Deep Sea Research Part II: Topical Studies in Oceanography, 56(18), 1470-1478.

Arrieta, J. M., & Herndl, G. J. (2002). Changes in bacterial β - glucosidase diversity during a coastal phytoplankton bloom. Limnology and Oceanography, 47(2), 594-599.

Arrigo, K. R., Dunbar, R. B., Lizotte, M. P., & Robinson, D. H. (2002). Taxon - specific differences in C/P and N/P drawdown for phytoplankton in the Ross Sea, Antarctica. Geophysical Research Letters, 29(19), 44-1.

Arrigo, K. R., Robinson, D. H., Worthen, D. L., Dunbar, R. B., DiTullio, G. R., VanWoert, M., & Lizotte, M. P. (1999). Phytoplankton community structure and the drawdown of nutrients and CO2 in the Southern Ocean. Science, 283(5400), 365-367.

Arrigo, K. R., Worthen, D. L., & Robinson, D. H. (2003). A coupled ocean - ecosystem model of the Ross Sea: 2. Iron regulation of phytoplankton taxonomic variability and primary production. Journal of Geophysical Research: Oceans, 108(C7).

Asper, V. L., & Smith Jr, W. O. (1999). Particle fluxes during austral spring and summer in the southern Ross Sea, Antarctica. Journal of Geophysical Research: Oceans, 104(C3), 5345-5359.

Asper, V. L., Diercks, A. R., Lee, J. J., & Smith Jr, W. O. (1997). In situ measurements of aggregate dynamics in the Ross Sea. Report Oceanogr. Soc. Amsterdam.

Azam, F. (1998). Microbial control of oceanic carbon flux: the plot thickens. Science, 280(5364), 694-696.

Azam, F., & Malfatti, F. (2007). Microbial structuring of marine ecosystems. Nature Reviews Microbiology, 5(10), 782-791.

Azetsu-Scott, K., & Passow, U. (2004). Ascending marine particles: Significance of transparent exopolymer particles (TEP) in the upper ocean. Limnology and oceanography, 49(3), 741-748.

Bach, L. T., Boxhammer, T., Larsen, A., Hildebrandt, N., Schulz, K. G., & Riebesell, U. (2016). Influence of plankton community structure on the sinking velocity of marine aggregates. Global Biogeochemical Cycles, 30(8), 1145-1165.

Bachmann, J., Heimbach, T., Hassenrück, C., Kopprio, G. A., Iversen, M. H., Grossart, H. P., & Gärdes, A. (2018). Environmental drivers of free-living vs. particle-attached bacterial community composition in the Mauritania upwelling system. Frontiers in microbiology, 9, 2836.

Baxter, J. M., Laffoley, D., Oliver, J., & Thevenon, F. (2014). The significance and management of natural carbon stores in the open ocean: a summary.

Becquevort, S., & Smith Jr, W. O. (2001). Aggregation, sedimentation and biodegradability of phytoplankton-derived material during spring in the Ross Sea, Antarctica. Deep Sea Research Part II: Topical Studies in Oceanography, 48(19-20), 4155-4178.

Becquevort, S., Rousseau, V., & Lancelot, C. (1998). Major and comparable roles for free-living and attached bacteria in the degradation of Phaeocystis-derived organic matter in Belgian coastal waters of the North Sea. Aquatic Microbial Ecology, 14(1), 39-48.

Behrenfeld, M. J., Halsey, K. H., & Milligan, A. J. (2008). Evolved physiological responses of phytoplankton to their integrated growth environment. Philosophical Transactions of the Royal Society B: Biological Sciences, 363(1504), 2687-2703.

Berline, L., Stemmann, L., Vichi, M., Lombard, F., & Gorsky, G. (2011). Impact of appendicularians on detritus and export fluxes: a model approach at DyFAMed site. Journal of Plankton Research, 33(6), 855-872.

Bienfang, P. K., Harrison, P. J., & Quarmby, L. M. (1982). Sinking rate response to depletion of nitrate, phosphate and silicate in four marine diatoms. Marine Biology, 67, 295-302.

Boyd, P. W., & Newton, P. P. (1999). Does planktonic community structure determine downward particulate organic carbon flux in different oceanic provinces?. Deep Sea Research Part I: Oceanographic Research Papers, 46(1), 63-91.

Boyd, P. W., & Trull, T. W. (2007). Understanding the export of biogenic particles in oceanic waters: Is there consensus?. Progress in Oceanography, 72(4), 276-312.

Boyd, P. W., Claustre, H., Levy, M., Siegel, D. A., & Weber, T. (2019). Multi-faceted particle pumps drive carbon sequestration in the ocean. Nature, 568(7752), 327-335.

Boyd, P. W., Jickells, T., Law, C. S., Blain, S., Boyle, E. A., Buesseler, K. O., ... & Watson, A. J. (2007). Mesoscale iron enrichment experiments 1993-2005: synthesis and future directions. science, 315(5812), 612-617.

Brewin, R. J., Sathyendranath, S., Platt, T., Bouman, H., Ciavatta, S., Dall'Olmo, G., ... & Walker, P. (2021). Sensing the ocean biological carbon pump from space: A review of capabilities, concepts, research gaps and future developments. Earth-Science Reviews, 217, 103604.

Broms, F., & Tiselius, P. (2003). Effects of temperature and body size on the clearance rate of Oikopleura dioica. Journal of plankton research, 25(5), 573-577.

Brussaard, C. P. D., Mari, X., Van Bleijswijk, J. D. L., & Veldhuis, M. J. W. (2005). A mesocosm study of Phaeocystis globosa (Prymnesiophyceae) population dynamics: II. Significance for the microbial community. Harmful algae, 4(5), 875-893.

Brzezinski, M. A., & Nelson, D. M. (1988). Differential cell sinking as a factor influencing diatom species competition for limiting nutrients. Journal of experimental marine biology and ecology, 119(3), 179-200.

Buesseler, K. O. (1998). The decoupling of production and particulate export in the surface ocean. Global Biogeochemical Cycles, 12(2), 297-310.

Buesseler, K. O., & Boyd, P. W. (2009). Shedding light on processes that control particle export and flux attenuation in the twilight zone of the open ocean. Limnology and Oceanography, 54(4), 1210-1232.

Buesseler, K. O., Boyd, P. W., Black, E. E., & Siegel, D. A. (2020). Metrics that matter for assessing the ocean biological carbon pump. Proceedings of the National Academy of Sciences, 117(18), 9679-9687.

Burd, A. B., & Jackson, G. A. (2009). Particle aggregation. Annual review of marine science, 1, 65-90.

Caron, D. A., Madin, L. P., & Cole, J. J. (1989). Composition and degradation of salp fecal pellets: implications for vertical flux in oceanic environments. Journal of Marine Research, 47(4), 829-850.

Carr, M. E., Friedrichs, M. A., Schmeltz, M., Aita, M. N., Antoine, D., Arrigo, K. R., ... & Yamanaka, Y. (2006). A comparison of global estimates of marine primary production from ocean color. Deep Sea Research Part II: Topical Studies in Oceanography, 53(5-7), 741-770.

Cavan, E. L., Kawaguchi, S., & Boyd, P. W. (2021). Implications for the mesopelagic microbial gardening hypothesis as determined by experimental fragmentation of Antarctic krill fecal pellets. Ecology and evolution, 11(2), 1023-1036.

Cavan, E. L., Laurenceau-Cornec, E. C., Bressac, M., & Boyd, P. W. (2019). Exploring the ecology of the mesopelagic biological pump. Progress in Oceanography, 176, 102125.

Cavan, E. L., Le Moigne, F. A., Poulton, A. J., Tarling, G. A., Ward, P., Daniels, C. J., ... & Sanders, R. J. (2015). Attenuation of particulate organic carbon flux in the Scotia Sea, Southern Ocean, is controlled by zooplankton fecal pellets. Geophysical Research Letters, 42(3), 821-830.

Cavan, E. L., Trimmer, M., Shelley, F., & Sanders, R. (2017). Remineralization of particulate organic carbon in an ocean oxygen minimum zone. Nature Communications, 8(1), 14847.

Chen, J., & Thornton, D. C. (2015). Transparent exopolymer particle production and aggregation by a marine planktonic diatom (Thalassiosira weissflogii) at different growth rates. Journal of phycology, 51(2), 381-393.

Chin, W. C., Orellana, M. V., & Verdugo, P. (1998). Spontaneous assembly of marine dissolved organic matter into polymer gels. Nature, 391(6667), 568-572.

Christiansen, B., Bühring, S. I., Pfannkuche, O., & Weikert, H. (2010). The near-bottom plankton community at the Porcupine Abyssal Plain, NE-Atlantic: Structure and vertical distribution. Marine Biology Research, 6(2), 113-124.

Christiansen, S., Hoving, H. J., Schütte, F., Hauss, H., Karstensen, J., Körtzinger, A., ... & Kiko, R. (2018). Particulate matter flux interception in oceanic mesoscale eddies by the polychaete Poeobius sp. Limnology and Oceanography, 63(5), 2093-2109.

Church, M. J., Ducklow, H. W., & Karl, D. M. (2002). Multiyear increases in dissolved organic matter inventories at Station ALOHA in the North Pacific Subtropical Gyre. Limnology and Oceanography, 47(1), 1-10.

Clark, L. L., Ingall, E. D., & Benner, R. (1998). Marine phosphorus is selectively remineralized. Nature, 393(6684), 426-426.

Colebrook, J. M. (1979). Continuous plankton records: seasonal cycles of phytoplankton and copepods in the North Atlantic Ocean and the North Sea. Marine Biology, 51(1), 23-32.

Conley, K. R., Lombard, F., & Sutherland, K. R. (2018). Mammoth grazers on the ocean's minuteness: a review of selective feeding using mucous meshes. Proceedings of the Royal Society B: Biological Sciences, 285(1878), 20180056.

Corzo, A., Morillo, J. A., & Rodríguez, S. (2000). Production of transparent exopolymer particles (TEP) in cultures of Chaetoceros calcitrans under nitrogen limitation. Aquatic Microbial Ecology, 23(1), 63-72.

Crocker, K. M., & Passow, U. (1995). Differential aggregation of diatoms. Marine ecology progress series. Oldendorf, 117(1), 249-257.

Crump, B. C., Armbrust, E. V., & Baross, J. A. (1999). Phylogenetic analysis of particle-attached and free-living bacterial communities in the Columbia River, its estuary, and the adjacent coastal ocean. Applied and environmental microbiology, 65(7), 3192-3204.

Dagg, M. J., Jackson, G. A., & Checkley Jr, D. M. (2014). The distribution and vertical flux of fecal pellets from large zooplankton in Monterey bay and coastal California. Deep Sea Research Part I: Oceanographic Research Papers, 94, 72-86.

Daniels, C. J., Poulton, A. J., Balch, W. M., Marañón, E., Adey, T., Bowler, B. C., ... & Tyrrell, T. (2018). A global compilation of coccolithophore calcification rates. Earth System Science Data, 10(4), 1859-1876.

De La Rocha, C. L., & Passow, U. (2007). Factors influencing the sinking of POC and the efficiency of the biological carbon pump. Deep Sea Research Part II: Topical Studies in Oceanography, 54(5-7), 639-658.

De La Rocha, C. L., Nowald, N., & Passow, U. (2008). Interactions between diatom aggregates, minerals, particulate organic carbon, and dissolved organic matter: Further implications for the ballast hypothesis. Global Biogeochemical Cycles, 22(4).

De Philippis, R., Faraloni, C., Sili, C., & Vincenzini, M. (2005). Populations of exopolysaccharide-producing cyanobacteria and diatoms in the mucilaginous benthic aggregates of the Tyrrhenian Sea (Tuscan Archipelago). Science of the total environment, 353(1-3), 360-368.

Deibel, D. (1998). Feeding and metabolism of Appendicularia. The biology of pelagic tunicates, 139-150.

Deibel, D., & Powell, C. V. L. (1987). Comparison of the ultrastructure of the food-concentrating filter of two appendicularians. Marine Ecology Progress Series, 39, 81-85.

DeLong, E. F., Franks, D. G., & Alldredge, A. L. (1993). Phylogenetic diversity of aggregate - attached vs. free - living marine bacterial assemblages. Limnology and oceanography, 38(5), 924-934.

Deng, W., Cruz, B. N., & Neuer, S. (2016). Effects of nutrient limitation on cell growth, TEP production and aggregate formation of marine Synechococcus. Aquatic Microbial Ecology, 78(1), 39-49.

Deutsch, C., & Weber, T. (2012). Nutrient ratios as a tracer and driver of ocean biogeochemistry. Annual review of marine science, 4, 113-141.

DeVries, T. (2022). The ocean carbon cycle. Annual Review of Environment and Resources, 47, 317-341.

Dilling, L., Wilson, J., Steinberg, D., & Alldredge, A. (1998). Feeding by the euphausiid Euphausia pacifica and the copepod Calanus pacificus on marine snow. Marine Ecology Progress Series, 170, 189-201.

DiTullio, G. R., Hutchins, D. A., & Bruland, K. W. (1993). Interaction of iron and major nutrients controls phytoplankton growth and species composition in the tropical North Pacific Ocean. Limnology and Oceanography, 38(3), 495-508.

DiTullio, G. R., Grebmeier, J. M., Arrigo, K. R., Lizotte, M. P., Robinson, D. H., Leventer, A., ... & Dunbar, R. B. (2000). Rapid and early export of Phaeocystis antarctica blooms in the Ross Sea, Antarctica. Nature, 404(6778), 595-598.

Ducklow, H. W., Steinberg, D. K., & Buesseler, K. O. (2001). Upper ocean carbon export and the biological pump. Oceanography, 14(4), 50-58.

Eberlein, K., Leal, M. T., Hammer, K. D., & Hickel, W. (1985). Dissolved organic substances during a Phaeocystis pouchetii bloom in the German Bight (North Sea). Marine Biology, 89, 311-316.

Engel, A. (2000). The role of transparent exopolymer particles (TEP) in the increase in apparent particle stickiness (α) during the decline of a diatom bloom. Journal of Plankton Research, 22(3), 485-497.

Engel, A., & Passow, U. (2001). Carbon and nitrogen content of transparent exopolymer particles (TEP) in relation to their Alcian Blue adsorption. Marine Ecology Progress Series, 219, 1-10.

Engel, A., & Schartau, M. (1999). Influence of transparent exopolymer particles (TEP) on sinking velocity of Nitzschia closterium aggregates. Marine Ecology Progress Series, 182, 69-76.

Engel, A., Szlosek, J., Abramson, L., Liu, Z., & Lee, C. (2009). Investigating the effect of ballasting by CaCO3 in Emiliania huxleyi: I. Formation, settling velocities and physical properties of aggregates. Deep Sea Research Part II: Topical Studies in Oceanography, 56(18), 1396-1407.

Fernández, D., López-Urrutia, Á., Fernández, A., Acuña, J. L., & Harris, R. (2004). Retention efficiency of 0.2 to 6 μm particles by the appendicularians Oikopleura dioica and Fritillaria borealis. Marine Ecology Progress Series, 266, 89-101.

Field, C. B., Behrenfeld, M. J., Randerson, J. T., & Falkowski, P. (1998). Primary production of the biosphere: integrating terrestrial and oceanic components. science, 281(5374), 237-240.

Fischer, G., Romero, O., Toby, E., Iversen, M., Donner, B., Mollenhauer, G., ... & Wefer, G. (2019). Changes in the dust - influenced biological carbon pump in the Canary Current System: Implications from a coastal and an offshore sediment trap record off Cape Blanc, Mauritania. Global Biogeochemical Cycles, 33(8), 1100-1128.

Fitzwater, S. E., Johnson, K. S., Gordon, R. M., Coale, K. H., & Smith Jr, W. O. (2000). Trace metal concentrations in the Ross Sea and their relationship with nutrients and phytoplankton growth. Deep Sea Research Part II: Topical Studies in Oceanography, 47(15-16), 3159-3179.

Francois, R., Honjo, S., Krishfield, R., & Manganini, S. (2002). Factors controlling the flux of organic carbon to the bathypelagic zone of the ocean. Global Biogeochemical Cycles, 16(4), 34-1.

Friedlingstein, P., Luke, G., Judith, H., Are, O., Wouter, P., Julia, P., ... & Bo, Z. (2022). Global carbon budget 2022. Earth System Science Data, 14(11), 4811-4900.

Friese, C. A. (2017). Modern Saharan dust collected onshore and offshore the northwest African margin: sources, transport and deposition (Doctoral dissertation, Universität Bremen).

Fukao, T., Kimoto, K., & Kotani, Y. (2010). Production of transparent exopolymer particles by four diatom species. Fisheries science, 76(5), 755-760.

Giménez, E. M., Nocera, A. C., Temperoni, B., & Winkler, G. (2023). Appendicularians and marine snow in situ vertical distribution in Argentinean Patagonia. Journal of Plankton Research, 45(2), 239-254.

Giri, T., Goutam, U., Arya, A., & Gautam, S. (2022). Effect of nutrients on diatom growth: a review. Trends in Sciences, 19(2), 1752-1752.

Gorsky, G., & Fenaux, R. (1998). The role of Appendicularia in marine food webs. The biology of pelagic tunicates, 161-169.

Gorsky, G., Fisher, N. S., & Fowler, S. W. (1984). Biogenic debris from the pelagic tunicate, Oikopleura dioica, and its role in the vertical transport of a transuranium element. Estuarine, Coastal and Shelf Science, 18(1), 13-23.

Green, S. E., & Sambrotto, R. N. (2006). Net community production in terms of C, N, P and Si in the Antarctic Circumpolar Current and its influence on regional water mass characteristics. Deep Sea Research Part I: Oceanographic Research Papers, 53(1), 111-135.

Grossart, H. P., & Gust, G. (2009). Hydrostatic pressure affects physiology and community structure of marine bacteria during settling to 4000 m: an experimental approach. Marine Ecology Progress Series, 390, 97-104.

Grossart, H. P., & Simon, M. (1993). Limnetic macroscopic organic aggregates (lake snow): Occurrence, characteristics, and microbial dynamics in Lake Constance. Limnology and Oceanography, 38(3), 532-546.

Grossart, H. P., & Simon, M. (1998). Bacterial colonization and microbial decomposition of limnetic organic aggregates (lake snow). Aquatic Microbial Ecology, 15(2), 127-140.

Grossart, H. P., Tang, K. W., Kiørboe, T., & Ploug, H. (2007). Comparison of cell-specific activity between free-living and attached bacteria using isolates and natural assemblages. FEMS microbiology letters, 266(2), 194-200.

Gruber, N., & Sarmiento, J. L. (2002). Large-scale biogeochemical-physical interactions in elemental cycles. The sea, 12, 337-399.

Gruber, N., Gloor, M., Mikaloff Fletcher, S. E., Doney, S. C., Dutkiewicz, S., Follows, M. J., ... & Takahashi, T. (2009). Oceanic sources, sinks, and transport of atmospheric CO2. Global biogeochemical cycles, 23(1).

Guillard, R. R., & Wangersky, P. J. (1958). The Production of Extracellular Carbohydrates by Some Marine Flagellates 1. Limnology and Oceanography, 3(4), 449-454.

Haberman, K. L., Ross, R. M., & Quetin, L. B. (2003). Diet of the Antarctic krill (Euphausia superba Dana): II. Selective grazing in mixed phytoplankton assemblages. Journal of Experimental Marine Biology and Ecology, 283(1-2), 97-113.

Hamm, C. E. (2000). Architecture, ecology and biogeochemistry of Phaeocystis colonies. Journal of Sea Research, 43(3-4), 307-315.

Hamm, C. E. (2002). Interactive aggregation and sedimentation of diatoms and clay - sized lithogenic material. Limnology and Oceanography, 47(6), 1790-1795.

Hamm, C. E., & Rousseau, V. (2003). Composition, assimilation and degradation of Phaeocystis globosa-derived fatty acids in the North Sea. Journal of Sea Research, 50(4), 271-283.

Hamm, C. E., Merkel, R., Springer, O., Jurkojc, P., Maier, C., Prechtel, K., & Smetacek, V. (2003). Architecture and material properties of diatom shells provide effective mechanical protection. Nature, 421(6925), 841-843.

Hamm, C. E., Simson, D. A., Merkel, R., & Smetacek, V. (1999). Colonies of Phaeocystis globosa are protected by a thin but tough skin. Marine Ecology Progress Series, 187, 101-111.

Hamner, W. M., & Robison, B. H. (1992). In situ observations of giant appendicularians in Monterey Bay. Deep Sea Research Part A. Oceanographic Research Papers, 39(7-8), 1299-1313.

Hansell, D. A., & Carlson, C. A. (2013). Localized refractory dissolved organic carbon sinks in the deep ocean. Global Biogeochemical Cycles, 27(3), 705-710.

Hansell, D. A., Carlson, C. A., Repeta, D. J., & Schlitzer, R. (2009). Dissolved organic matter in the ocean: A controversy stimulates new insights. Oceanography, 22(4), 202-211.

Hansen, J. L., Kiørboe, T., & Alldredge, A. L. (1996). Marine snow derived from abandoned larvacean houses: sinking rates, particle content and mechanisms of aggregate formation. Marine Ecology Progress Series, 141, 205-215.

Harrison, P. J., Conway, H. L., Holmes, R. W., & Davis, C. O. (1977). Marine diatoms grown in chemostats under silicate or ammonium limitation. III. Cellular chemical composition and morphology of Chaetoceros debilis, Skeletonema costatum, and Thalassiosira gravida. Marine Biology, 43, 19-31.

Harrison, P. J., Turpin, D. H., Bienfang, P. K., & Davis, C. O. (1986). Sinking as a factor affecting phytoplankton species succession: the use of selective loss semi-continuous cultures. Journal of experimental marine biology and ecology, 99(1), 19-30.

Hauck, J., Zeising, M., Le Quéré, C., Gruber, N., Bakker, D. C., Bopp, L., ... & Séférian, R. (2020). Consistency and challenges in the ocean carbon sink estimate for the global carbon budget. Frontiers in Marine Science, 7, 571720.

Hedges, J. I. (1992). Global biogeochemical cycles: progress and problems. Marine chemistry, 39(1-3), 67-93.

Henson, S. A., Sanders, R., & Madsen, E. (2012). Global patterns in efficiency of particulate organic carbon export and transfer to the deep ocean. Global Biogeochemical Cycles, 26(1).

Henson, S., Le Moigne, F., & Giering, S. (2019). Drivers of carbon export efficiency in the global ocean. Global biogeochemical cycles, 33(7), 891-903.

Hernández-León, S., & Ikeda, T. (2005). A global assessment of mesozooplankton respiration in the ocean. Journal of Plankton Research, 27(2), 153-158.

Herndl, G. J. (1988). Ecology of amorphous aggregations(marine snow) in the northern Adriatic Sea. 2. Microbial density and activity in marine snow and its implication to overall pelagic processes. Marine ecology progress series. Oldendorf, 48(3), 265-275.

Herndl, G. J., & Reinthaler, T. (2013). Microbial control of the dark end of the biological pump. Nature geoscience, 6(9), 718-724.

Herndl, G. J., Arrieta, J. M., & Stoderegger, K. (1999). Interaction between specific hydrological and microbial activity leading to extensive mucilage formation. Ann. Ist. Super Sanità, 35(3), 405-409.

Hill, P. S. (1992). Reconciling aggregation theory with observed vertical fluxes following phytoplankton blooms. Journal of Geophysical Research: Oceans, 97(C2), 2295-2308.

Hill, V., & Cota, G. (2005). Spatial patterns of primary production on the shelf, slope and basin of the Western Arctic in 2002. Deep Sea Research Part II: Topical Studies in Oceanography, 52(24-26), 3344-3354.

Ho, T. Y., Quigg, A., Finkel, Z. V., Milligan, A. J., Wyman, K., Falkowski, P. G., & Morel, F. M. (2003). The elemental composition of some marine phytoplankton 1. Journal of phycology, 39(6), 1145-1159.

Hong, Y., Smith Jr, W. O., & White, A. M. (1997). Studies on transparent exopolymer particles (Tep) produced in the Ross Sea (Antarctica) and by Phaeocystis antarctica (Prymnesiophyceae) 1. Journal of Phycology, 33(3), 368-376.

Honjo, S., & Manganini, S. J. (1993). Annual biogenic particle fluxes to the interior of the North Atlantic Ocean; studied at 34 N 21 W and 48 N 21 W. Deep Sea Research Part II: Topical Studies in Oceanography, 40(1-2), 587-607.

Hopkins, J., Henson, S. A., Poulton, A. J., & Balch, W. M. (2019). Regional characteristics of the temporal variability in the global particulate inorganic carbon inventory. Global Biogeochemical Cycles, 33(11), 1328-1338.

Houghton, R. A. (2007). Balancing the global carbon budget. Annu. Rev. Earth Planet. Sci., 35, 313-347.

Howes, E. L., Bednaršek, N., Büdenbender, J., Comeau, S., Doubleday, A., Gallager, S. M., ... & Gattuso, J. P. (2014). Sink and swim: a status review of thecosome pteropod culture techniques. Journal of Plankton Research, 36(2), 299-315.

Hunt, B. P. V., Pakhomov, E. A., Hosie, G. W., Siegel, V., Ward, P., & Bernard, K. (2008). Pteropods in southern ocean ecosystems. Progress in Oceanography, 78(3), 193-221.

IPCC, 2023: Summary for Policymakers. In: Climate Change 2023: Synthesis Report. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, H. Lee and J. Romero (eds.)]. IPCC, Geneva, Switzerland, pp. 1-34, doi: 10.59327/IPCC/AR6-9789291691647.001

Iversen, M. H. (2023). Carbon Export in the Ocean: A Biologist's Perspective. Annual Review of Marine Science, 15, 357-381.

Iversen, M. H., & Ploug, H. (2010). Ballast minerals and the sinking carbon flux in the ocean: carbon-specific respiration rates and sinking velocity of marine snow aggregates. Biogeosciences, 7(9), 2613-2624.

Iversen, M. H., & Ploug, H. (2013). Temperature effects on carbon-specific respiration rate and sinking velocity of diatom aggregates–potential implications for deep ocean export processes. Biogeosciences, 10(6), 4073-4085.

Iversen, M. H., & Poulsen, L. K. (2007). Coprorhexy, coprophagy, and coprochaly in the copepods Calanus helgolandicus, Pseudocalanus elongatus, and Oithona similis. Marine Ecology Progress Series, 350, 79-89.

Iversen, M. H., & Robert, M. L. (2015). Ballasting effects of smectite on aggregate formation and export from a natural plankton community. Marine Chemistry, 175, 18-27.

Iversen, M. H., Nowald, N., Ploug, H., Jackson, G. A., & Fischer, G. (2010). High resolution profiles of vertical particulate organic matter export off Cape Blanc, Mauritania: Degradation processes and ballasting effects. Deep Sea Research Part I: Oceanographic Research Papers, 57(6), 771-784.

Jackson, G. A. (1990). A model of the formation of marine algal flocs by physical coagulation processes. Deep Sea Research Part A. Oceanographic Research Papers, 37(8), 1197-1211.

Jackson, G. A. (1993). Flux feeding as a mechanism for zooplankton grazing and its implications for vertical particulate flux 1. Limnology and Oceanography, 38(6), 1328-1331.

Jackson, G. A. (1995). TEP and coagulation during a mesocosm experiment. Deep Sea Research Part II: Topical Studies in Oceanography, 42(1), 215-222.

Jackson, G. A., & Burd, A. B. (1998). Aggregation in the marine environment. Environmental science & technology, 32(19), 2805-2814.

Jackson, G. A., & Kiørboe, T. (2008). Maximum phytoplankton concentrations in the sea. Limnology and Oceanography, 53(1), 395-399.

Jackson, G. A., & Checkley Jr, D. M. (2011). Particle size distributions in the upper 100 m water column and their implications for animal feeding in the plankton. Deep Sea Research Part I: Oceanographic Research Papers, 58(3), 283-297.

Janse, I., van Rijssel, M., Ottema, A., & Gottschal, J. C. (1999). Microbial breakdown of Phaeocystis mucopolysaccharides. Limnology and Oceanography, 44(6), 1447-1457.

Janse, I., Van Rijssel, M., van Hall, P. J., Gerwig, G. J., Gottschal, J. C., & Prins, R. A. (1996). THE STORAGE GLUCAN OF PHAEOCYSTIS GLOBOSA (PRYMNESIOPHYCEAE) CELLS 1. Journal of phycology, 32(3), 382-387.

Jiao, N., & Azam, F. (2011). Microbial carbon pump and its significance for carbon sequestration in the ocean. Microbial carbon pump in the ocean, 10, 43-45.

Jiao, N., & Zheng, Q. (2011). The microbial carbon pump: from genes to ecosystems. Applied and Environmental Microbiology, 77(21), 7439-7444.

Jiao, N., Herndl, G. J., Hansell, D. A., Benner, R., Kattner, G., Wilhelm, S. W., ... & Azam, F. (2010). Microbial production of recalcitrant dissolved organic matter: long-term carbon storage in the global ocean. Nature Reviews Microbiology, 8(8), 593-599.

Johnson, R., Strutton, P. G., Wright, S. W., McMinn, A., & Meiners, K. M. (2013). Three improved satellite chlorophyll algorithms for the Southern Ocean. Journal of Geophysical Research: Oceans, 118(7), 3694-3703.

Kahl, L. A., Vardi, A., & Schofield, O. (2008). Effects of phytoplankton physiology on export flux. Marine Ecology Progress Series, 354, 3-19.

Karner, M., & Herndl, G. J. (1992). Extracellular enzymatic activity and secondary production in free-living and marine-snow-associated bacteria. Marine biology, 113, 341-347.

Kiørboe, T. (2000). Colonization of marine snow aggregates by invertebrate zooplankton: abundance, scaling, and possible role. Limnology and Oceanography, 45(2), 479-484.

Kiørboe, T. (2001). Formation and fate of marine snow: small-scale processes with large-scale implications. Scientia marina, 65(S2), 57-71.

Kiørboe, T., & Hansen, J. L. (1993). Phytoplankton aggregate formation: observations of patterns and mechanisms of cell sticking and the significance of exopolymeric material. Journal of Plankton Research, 15(9), 993-1018.

Kiørboe, T., Andersen, K. P., & Dam, H. G. (1990). Coagulation efficiency and aggregate formation in marine phytoplankton. Marine Biology, 107, 235-245.

Kiørboe, T., Lundsgaard, C., Olesen, M., & Hansen, J. L. (1994). Aggregation and sedimentation processes during a spring phytoplankton bloom: A field experiment to test coagulation theory. Journal of Marine Research, 52(2), 297-323.

Kiørboe, T., Tiselius, P., Mitchell - Innes, B., Hansen, J. L., Visser, A. W., & Mari, X. (1998). Intensive aggregate formation with low vertical flux during an upwelling - induced diatom bloom. Limnology and Oceanography, 43(1), 104-116.

Klaas, C., & Archer, D. E. (2002). Association of sinking organic matter with various types of mineral ballast in the deep sea: Implications for the rain ratio. Global biogeochemical cycles, 16(4), 63-1.

Kriest, I., & Oschlies, A. (2008). On the treatment of particulate organic matter sinking in large-scale models of marine biogeochemical cycles. Biogeosciences, 5(1), 55-72.

Lampitt, R. S., Boorman, B., Brown, L., Lucas, M., Salter, I., Sanders, R., ... & Turnewitsch, R. (2008). Particle export from the euphotic zone: Estimates using a novel drifting sediment trap, 234Th and new production. Deep Sea Research Part I: Oceanographic Research Papers, 55(11), 1484-1502.

Lampitt, R. S., Hillier, W. R., & Challenor, P. G. (1993). Seasonal and diel variation in the open ocean concentration of marine snow aggregates. Nature, 362(6422), 737-739.

Lampitt, R. S., Noji, T., & Von Bodungen, B. (1990). What happens to zooplankton faecal pellets? Implications for material flux. Marine Biology, 104, 15-23.

Lancelot, C., Keller, M., Rousseau, V., Smith Jr, W. O., & Mathot, S. (1998, June). Autoecology of the marine haptophyte Phaeocystis sp. In Physiological Ecology of Harmful Algal Blooms, 1 (pp. 209-224). Springer.

Landry, M. R., & Calbet, A. (2004). Microzooplankton production in the oceans. ICES Journal of Marine Science, 61(4), 501-507.

Lauderdale, J. M., & Cael, B. B. (2021). Impact of remineralization profile shape on the air - sea carbon balance. Geophysical Research Letters, 48(7), e2020GL091746.

Laurenceau-Cornec, E. C., Trull, T. W., Davies, D. M., Christina, L., & Blain, S. (2015). Phytoplankton morphology controls on marine snow sinking velocity. Marine Ecology Progress Series, 520, 35-56.

Laws, E. A., D'Sa, E., & Naik, P. (2011). Simple equations to estimate ratios of new or export production to total production from satellite - derived estimates of sea surface temperature and primary production. Limnology and Oceanography: Methods, 9(12), 593-601.

Le Moigne, F. A. (2019). Pathways of organic carbon downward transport by the oceanic biological carbon pump. Frontiers in Marine Science, 6, 634.

Le Moigne, F. A., Poulton, A. J., Henson, S. A., Daniels, C. J., Fragoso, G. M., Mitchell, E., ... & Zubkov, M. (2015). Carbon export efficiency and phytoplankton community composition in the A tlantic sector of the A rctic O cean. Journal of Geophysical Research: Oceans, 120(6), 3896-3912.

Leblanc, K., Queguiner, B., Diaz, F., Cornet, V., Michel-Rodriguez, M., Durrieu de Madron, X., ... & Conan, P. (2018). Nanoplanktonic diatoms are globally overlooked but play a role in spring blooms and carbon export. Nature communications, 9(1), 953.

Legendre, L., & Rivkin, R. B. (2002). Fluxes of carbon in the upper ocean: regulation by food-web control nodes. Marine Ecology Progress Series, 242, 95-109.

Legendre, L., Rivkin, R. B., Weinbauer, M. G., Guidi, L., & Uitz, J. (2015). The microbial carbon pump concept: Potential biogeochemical significance in the globally changing ocean. Progress in Oceanography, 134, 432-450.

Leynaert, A., Tréguer, P., Lancelot, C., & Rodier, M. (2001). Silicon limitation of biogenic silica production in the Equatorial Pacific. Deep Sea Research Part I: Oceanographic Research Papers, 48(3), 639-660.

Li, J., Xu, M., Wang, J., Lan, C., & Lai, J. (2023). Effects of nutrient limitation on cell growth, exopolysaccharide secretion and TEP production of Phaeocystis globosa. Marine Environmental Research, 183, 105801.

Logan, B. E., & Alldredge, A. L. (1989). Potential for increased nutrient uptake by flocculating diatoms. Marine Biology, 101, 443-450.

Lombard, F., & Kiørboe, T. (2010). Marine snow originating from appendicularian houses: Age-dependent settling characteristics. Deep Sea Research Part I: Oceanographic Research Papers, 57(10), 1304-1313.

Lombard, F., Renaud, F., Sainsbury, C., Sciandra, A., & Gorsky, G. (2009). Appendicularian ecophysiology I: Food concentration dependent clearance rate, assimilation efficiency, growth and reproduction of Oikopleura dioica. Journal of Marine Systems, 78(4), 606-616.

Lombard, F., Selander, E., & Kiørboe, T. (2011). Active prey rejection in the filter - feeding appendicularian Oikopleura dioica. Limnology and Oceanography, 56(4), 1504-1512.

Longhurst, A. R., Bedo, A. W., Harrison, W. G., Head, E. J. H., & Sameoto, D. D. (1990). Vertical flux of respiratory carbon by oceanic diel migrant biota. Deep Sea Research Part A. Oceanographic Research Papers, 37(4), 685-694.

Longhurst, A. R., Koike, I., Li, W. K. W., Rodriguez, J., Dickie, P., Kepay, P., ... & Bird, D. F. (1992). Sub-micron particles in northwest Atlantic shelf water. Deep Sea Research Part A. Oceanographic Research Papers, 39(1), 1-7.

López-Urrutia, Á., Acuña, J. L., Irigoien, X., & Harris, R. (2003). Food limitation and growth in temperate epipelagic appendicularians (Tunicata). Marine Ecology Progress Series, 252, 143-157.

Lutz, M. J., Caldeira, K., Dunbar, R. B., & Behrenfeld, M. J. (2007). Seasonal rhythms of net primary production and particulate organic carbon flux to depth describe the efficiency of biological pump in the global ocean. Journal of Geophysical Research: Oceans, 112(C10).

Madin, L. P., Kremer, P., & Hacker, S. (1996). Distribution and vertical migration of salps (Tunicata, Thaliacea) near Bermuda. Journal of Plankton Research, 18(5), 747-755.

Mari, X., Passow, U., Migon, C., Burd, A. B., & Legendre, L. (2017). Transparent exopolymer particles: Effects on carbon cycling in the ocean. Progress in Oceanography, 151, 13-37.

Mari, X., Rassoulzadegan, F., Brussaard, C. P., & Wassmann, P. (2005). Dynamics of transparent exopolymeric particles (TEP) production by Phaeocystis globosa under N-or P-limitation: a controlling factor of the retention/export balance. Harmful algae, 4(5), 895-914.

Marsay, C. M., Sanders, R. J., Henson, S. A., Pabortsava, K., Achterberg, E. P., & Lampitt, R. S. (2015). Attenuation of sinking particulate organic carbon flux through the mesopelagic ocean. Proceedings of the National Academy of Sciences, 112(4), 1089-1094.

Martin, J. H., Knauer, G. A., Karl, D. M., & Broenkow, W. W. (1987). VERTEX: carbon cycling in the northeast Pacific. Deep Sea Research Part A. Oceanographic Research Papers, 34(2), 267-285.

Martiny, A. C., Vrugt, J. A., Primeau, F. W., & Lomas, M. W. (2013). Regional variation in the particulate organic carbon to nitrogen ratio in the surface ocean. Global Biogeochemical Cycles, 27(3), 723-731.

McNair, H. M., Brzezinski, M. A., & Krause, J. W. (2018). Diatom populations in an upwelling environment decrease silica content to avoid growth limitation. Environmental microbiology, 20(11), 4184-4193.

McQuatters-Gollop, A., Raitsos, D. E., Edwards, M., & Attrill, M. J. (2007). Spatial patterns of diatom and dinoflagellate seasonal cycles in the NE Atlantic Ocean. Marine Ecology Progress Series, 339, 301-306.

Middelburg, J. J. (2019). Marine carbon biogeochemistry: a primer for earth system scientists (p. 118). Springer Nature.

Middelburg, J. J., Soetaert, K., & Hagens, M. (2020). Ocean alkalinity, buffering and biogeochemical processes. Reviews of Geophysics, 58(3), e2019RG000681.

Moore, J. K., & Villareal, T. A. (1996). Size - ascent rate relationships in positively buoyant marine diatoms. Limnology and Oceanography, 41(7), 1514-1520.

Muggli, D. L., Lecourt, M., & Harrison, P. J. (1996). Effects of iron and nitrogen source on the sinking rate, physiology and metal composition of an oceanic diatom from the subarctic Pacific. Marine Ecology Progress Series, 132, 215-227.

Myklestad, S. (1974). Production of carbohydrates by marine planktonic diatoms. I. Comparison of nine different species in culture. Journal of Experimental Marine Biology and Ecology, 15(3), 261-274.

Nagata, T., Tamburini, C., Arístegui, J., Baltar, F., Bochdansky, A. B., Fonda-Umani, S., ... & Bartlett, D. H. (2010). Emerging concepts on microbial processes in the bathypelagic ocean–ecology, biogeochemistry, and genomics. Deep Sea Research Part II: Topical Studies in Oceanography, 57(16), 1519-1536.

NASA-OBPG (2014): NASA Goddard Space Flight Center, Ocean Ecology Laboratory, Ocean Biology Processing Group, Sea-viewing Wide Field-of-view Sensor (SeaWiFS) Chlorophyll Data

Nelson, D. M., Tréguer, P., Brzezinski, M. A., Leynaert, A., & Quéguiner, B. (1995). Production and dissolution of biogenic silica in the ocean: revised global estimates, comparison with regional data and relationship to biogenic sedimentation. Global biogeochemical cycles, 9(3), 359-372.

Neuer, S., Davenport, R., Freudenthal, T., Wefer, G., Llinás, O., Rueda, M. J., ... & Karl, D. M. (2002). Differences in the biological carbon pump at three subtropical ocean sites. Geophysical Research Letters, 29(18), 32-1.

Nissen, C., & Vogt, M. (2021). Factors controlling the competition between Phaeocystis and diatoms in the Southern Ocean and implications for carbon export fluxes. Biogeosciences, 18(1), 251-283.

Noji, T. T., Bathmann, U. V., Bodungen, B. V., Voss, M., Antia, A., Krumbholz, M., ... & Rey, F. (1997). Clearance of picoplankton-sized partides and formation of rapidly sinking aggregates by the pteropod, Limacina reiroversa. Journal of Plankton Research, 19(7), 863-875.

Noji, T. T., Estep, K. W., Macintyre, F., & Norrbin, F. (1991). Image analysis of faecal material grazed upon by three species of copepods: evidence for coprorhexy, coprophagy and coprochaly. Journal of the Marine Biological Association of the United Kingdom, 71(2), 465-480.

Noji, T. T., Rey, F., Miller, L. A., Børsheim, K. Y., & Urban-Rich, J. (1999). Fate of biogenic carbon in the upper 200 m of the central Greenland Sea. Deep Sea Research Part II: Topical Studies in Oceanography, 46(6-7), 1497-1509.

Nowald, N., Iversen, M. H., Fischer, G., Ratmeyer, V., & Wefer, G. (2015). Time series of in-situ particle properties and sediment trap fluxes in the coastal upwelling filament off Cape Blanc, Mauritania. Progress in Oceanography, 137, 1-11.

Nowicki, M., DeVries, T., & Siegel, D. A. (2022). Quantifying the carbon export and sequestration pathways of the ocean's biological carbon pump. Global Biogeochemical Cycles, 36(3), e2021GB007083.

Olli, K., Wassmann, P., Reigstad, M., Ratkova, T. N., Arashkevich, E., Pasternak, A., ... & Jacobsen, A. (2007). The fate of production in the central Arctic Ocean–top–down regulation by zooplankton expatriates?. Progress in Oceanography, 72(1), 84-113.

Oschlies, A., Schulz, K. G., Riebesell, U., & Schmittner, A. (2008). Simulated 21st century's increase in oceanic suboxia by CO2 - enhanced biotic carbon export. Global Biogeochemical Cycles, 22(4).

Pahlow, M., Riebesell, U., & Wolf - Gladrow, D. A. (1997). Impact of cell shape and chain formation on nutrient acquisition by marine diatoms. Limnology and Oceanography, 42(8), 1660-1672.

Passow, U. (2000). Formation of transparent exopolymer particles, TEP, from dissolved precursor material. Marine Ecology Progress Series, 192, 1-11.

Passow, U. (2002). Transparent exopolymer particles (TEP) in aquatic environments. Progress in oceanography, 55(3-4), 287-333.

Passow, U., & Alldredge, A. L. (1994). Distribution, size and bacterial colonization of transparent exopolymer particles (TEP) in the ocean. Marine Ecology Progress Series, 185-198.

Passow, U., & Carlson, C. A. (2012). The biological pump in a high CO2 world. Marine Ecology Progress Series, 470, 249-271.

Passow, U., & de La Rocha, C. L. (2006). Accumulation of mineral ballast on organic aggregates. Global Biogeochemical Cycles, 20(1).

Passow, U., & Wassmann, P. (1994). On the trophic fate of Phaeocystis pouchetii (Hariot): IV. The formation of marine snow by P. pouchetii. Marine Ecology Progress Series, 153-161.

Passow, U., Alldredge, A. L., & Logan, B. E. (1994). The role of particulate carbohydrate exudates in the flocculation of diatom blooms. Deep Sea Research Part I: Oceanographic Research Papers, 41(2), 335-357.

Passow, U., Shipe, R. F., Murray, A., Pak, D. K., Brzezinski, M. A., & Alldredge, A. L. (2001). The origin of transparent exopolymer particles (TEP) and their role in the sedimentation of particulate matter. Continental Shelf Research, 21(4), 327-346.

Pasternak, A. F., Drits, A. V., & Flint, M. V. (2017). Feeding, egg production, and respiration rate of pteropods Limacina in Arctic seas. Oceanology, 57, 122-129.

Pausch, F., Bischof, K., & Trimborn, S. (2019). Iron and manganese co-limit growth of the Southern Ocean diatom Chaetoceros debilis. PLoS One, 14(9), e0221959.

Ploug, H. (2001). Small - scale oxygen fluxes and remineralization in sinking aggregates. Limnology and Oceanography, 46(7), 1624-1631.

Ploug, H., & Bergkvist, J. (2015). Oxygen diffusion limitation and ammonium production within sinking diatom aggregates under hypoxic and anoxic conditions. Marine Chemistry, 176, 142-149.

Ploug, H., Grossart, H. P., Azam, F., & Jørgensen, B. B. (1999). Photosynthesis, respiration, and carbon turnover in sinking marine snow from surface waters of Southern California Bight: implications for the carbon cycle in the ocean. Marine Ecology Progress Series, 179, 1-11.

Ploug, H., Hietanen, S., & Kuparinen, J. (2002). Diffusion and advection within and around sinking, porous diatom aggregates. Limnology and oceanography, 47(4), 1129-1136.

Ploug, H., Kühl, M., Buchholz-Cleven, B., & Jørgensen, B. B. (1997). Anoxic aggregates-an ephemeral phenomenon in the pelagic environment?. Aquatic microbial ecology, 13(3), 285-294.

Prairie, J. C., Montgomery, Q. W., Proctor, K. W., & Ghiorso, K. S. (2019). Effects of phytoplankton growth phase on settling properties of marine aggregates. Journal of Marine Science and Engineering, 7(8), 265.

Radić, T., Kraus, R., Fuks, D., Radić, J., & Pečar, O. (2005). Transparent exopolymeric particles' distribution in the northern Adriatic and their relation to microphytoplankton biomass and composition. Science of the total environment, 353(1-3), 151-161.

Ragueneau, O., Tréguer, P., Leynaert, A., Anderson, R. F., Brzezinski, M. A., DeMaster, D. J., ... & Quéguiner, B. (2000). A review of the Si cycle in the modern ocean: recent progress and missing gaps in the application of biogenic opal as a paleoproductivity proxy. Global and Planetary Change, 26(4), 317-365.

Raven, J. A., & Falkowski, P. G. (1999). Oceanic sinks for atmospheric CO2. Plant, Cell & Environment, 22(6), 741-755.

Redfield, A. C., Ketchum, B. H., & Richards, F. A. (1963). The influence of organisms on the composition of seawater. The sea, 2, 26-77.

Reigstad, M., Wassmann, P., Ratkova, T., Arashkevich, E., Pasternak, A., & Øygarden, S. (2000). Comparison of the springtime vertical export of biogenic matter in three northern Norwegian fjords. Marine Ecology Progress Series, 201, 73-89.

Rhee, G. Y., & Gotham, I. J. (1981). The effect of environmental factors on phytoplankton growth: temperature and the interactions of temperature with nutrient limitation 1. Limnology and Oceanography, 26(4), 635-648.

Riebesell, U. (1993). Aggregation of Phaeocystis during phytoplankton spring blooms in the southern North Sea. Marine Ecology Progress Series, 96, 281-289.

Riebesell, U., & Wolf-Gladrow, D. A. (1992). The relationship between physical aggregation of phytoplankton and particle flux: a numerical model. Deep Sea Research Part A. Oceanographic Research Papers, 39(7-8), 1085-1102.

Riebesell, U., Reigstad, M., Wassmann, P., Noji, T., & Passow, U. (1995). On the trophic fate of Phaeocystis pouchetii (Hariot): VI. Significance of Phaeocystis-derived mucus for vertical flux. Netherlands Journal of Sea Research, 33(2), 193-203.

Rousseau, V., Becquevort, S., Parent, J. Y., Gasparini, S., Daro, M. H., Tackx, M., & Lancelot, C. (2000). Trophic efficiency of the planktonic food web in a coastal ecosystem dominated by Phaeocystis colonies. Journal of Sea Research, 43(3-4), 357-372.

Rousseau, V., Vaulot, D., Casotti, R., Cariou, V., Lenz, J., Gunkel, J., & Baumann, M. (1994). The life cycle of Phaeocystis (Prymnesiophycaea): evidence and hypotheses. Journal of marine systems, 5(1), 23-39.

Rubin, S. I., Takahashi, T., Chipman, D. W., & Goddard, J. G. (1998). Primary productivity and nutrient utilization ratios in the Pacific sector of the Southern Ocean based on seasonal changes in seawater chemistry. Deep Sea Research Part I: Oceanographic Research Papers, 45(8), 1211-1234.

Sarmiento, J. L., Slater, R., Barber, R., Bopp, L., Doney, S. C., Hirst, A. C., ... & Stouffer, R. (2004). Response of ocean ecosystems to climate warming. Global Biogeochemical Cycles, 18(3).

Sarthou, G., Timmermans, K. R., Blain, S., & Tréguer, P. (2005). Growth physiology and fate of diatoms in the ocean: a review. Journal of sea research, 53(1-2), 25-42.

Sato, R., Ishibashi, Y., Tanaka, Y., Ishimaru, T., & Dagg, M. J. (2008). Productivity and grazing impact of Oikopleura dioica (Tunicata, Appendicularia) in Tokyo Bay. Journal of Plankton Research, 30(3), 299-309.

Sato, R., Tanaka, Y., & Ishimaru, T. (2001). House production by Oikopleura dioica (Tunicata, Appendicularia) under laboratory conditions. Journal of plankton research, 23(4), 415-423.

Sato, R., Tanaka, Y., & Ishimaru, T. (2003). Species-specific house productivity of appendicularians. Marine Ecology Progress Series, 259, 163-172.

Schapira, M., Seuront, L., & Gentilhomme, V. (2006). Effects of small-scale turbulence on Phaeocystis globosa (Prymnesiophyceae) growth and life cycle. Journal of Experimental Marine Biology and Ecology, 335(1), 27-38.

Schiffrine, N., Tremblay, J. É., & Babin, M. (2020). Growth and elemental stoichiometry of the ecologically-relevant Arctic diatom Chaetoceros gelidus: a mix of polar and temperate. Frontiers in Marine Science, 6, 790.

Schneider, B., Schlitzer, R., Fischer, G., & Nöthig, E. M. (2003). Depth - dependent elemental compositions of particulate organic matter (POM) in the ocean. Global Biogeochemical Cycles, 17(2).

Schoemann, V., Becquevort, S., Stefels, J., Rousseau, V., & Lancelot, C. (2005). Phaeocystis blooms in the global ocean and their controlling mechanisms: a review. Journal of Sea Research, 53(1-2), 43-66.

Schoemann, V., Wollast, R., Chou, L., & Lancelot, C. (2001). Effects of photosynthesis on the accumulation of Mn and Fe by Phaeocystis colonies. Limnology and Oceanography, 46(5), 1065-1076.

Shanks, A. L., & Trent, J. D. (1980). Marine snow: sinking rates and potential role in vertical flux. Deep Sea Research Part A. Oceanographic Research Papers, 27(2), 137-143.

Siegel, D. A., Buesseler, K. O., Behrenfeld, M. J., Benitez-Nelson, C. R., Boss, E., Brzezinski, M. A., ... & Steinberg, D. K. (2016). Prediction of the export and fate of global ocean net primary production: The EXPORTS science plan. Frontiers in Marine Science, 3, 22.

Siegel, D. A., DeVries, T., Cetinić, I., & Bisson, K. M. (2023). Quantifying the ocean's biological pump and its carbon cycle impacts on global scales. Annual review of marine science, 15, 329-356.

Silver, M. W., & Alldredge, A. L. (1981). Bathypelagic marine snow: deep-sea algal and detrital community.

Silver, M. W., & Bruland, K. W. (1981). Differential feeding and fecal pellet composition of salps and pteropods, and the possible origin of the deep-water flora and olive-green “cells”. Marine Biology, 62, 263-273.

Silver, M. W., Coale, S. L., Pilskaln, C. H., & Steinberg, D. R. (1998). Giant aggregates: Importance as microbial centers and agents of material flux in the mesopelagic zone. Limnology and Oceanography, 43(3), 498-507.

Simon, M., Grossart, H. P., Schweitzer, B., & Ploug, H. (2002). Microbial ecology of organic aggregates in aquatic ecosystems. Aquatic microbial ecology, 28(2), 175-211.

Smetacek, V., von Bodungen, B., Knoppers, B., Peinert, R., Pollehne, F., Stegmann, P., & Zeitzschel, B. (1984). Seasonal stages characterizing the annual cycle of an inshore pelagic system. Rapports et Proces-Verbaux des Reunions Conseil International pour l'Exploration de la Mer, 183, 126-135.

Smith Jr, W. O., & Trimborn, S. (2024). Phaeocystis: A global enigma. Annual Review of Marine Science, 16, 417-441.

Smith Jr, W. O., Carlson, C. A., Ducklow, H. W., & Hansell, D. A. (1998). Growth dynamics of Phaeocystis antarctica-dominated plankton assemblages from the Ross Sea. Marine Ecology Progress Series, 168, 229-244.

Smith, D. C., Simon, M., Alldredge, A. L., & Azam, F. (1992). Intense hydrolytic enzyme activity on marine aggregates and implications for rapid particle dissolution. Nature, 359(6391), 139-142.

Stachowitsch, M. (1984). Mass mortality in the Gulf of Trieste: the course of community destruction. Marine Ecology, 5(3), 243-264.

Steinberg, D. K., & Landry, M. R. (2017). Zooplankton and the ocean carbon cycle. Annual review of marine science, 9, 413-444.

Steinberg, D. K., Carlson, C. A., Bates, N. R., Goldthwait, S. A., Madin, L. P., & Michaels, A. F. (2000). Zooplankton vertical migration and the active transport of dissolved organic and inorganic carbon in the Sargasso Sea. Deep Sea Research Part I: Oceanographic Research Papers, 47(1), 137-158.

Steinberg, D. K., Cope, J. S., Wilson, S. E., & Kobari, T. (2008). A comparison of mesopelagic mesozooplankton community structure in the subtropical and subarctic North Pacific Ocean. Deep Sea Research Part II: Topical Studies in Oceanography, 55(14-15), 1615-1635.

Stemmann, L., Jackson, G. A., & Ianson, D. (2004). A vertical model of particle size distributions and fluxes in the midwater column that includes biological and physical processes—Part I: model formulation. Deep Sea Research Part I: Oceanographic Research Papers, 51(7), 865-884.

Sterner, R. W., Andersen, T., Elser, J. J., Hessen, D. O., Hood, J. M., McCauley, E., & Urabe, J. (2008). Scale - dependent carbon: nitrogen: phosphorus seston stoichiometry in marine and freshwaters. Limnology and Oceanography, 53(3), 1169-1180.

Sterner, R. W., Elser, J. J., & Hessen, D. O. (1992). Stoichiometric relationships among producers, consumers and nutrient cycling in pelagic ecosystems. Biogeochemistry, 17, 49-67.

Stief, P., Elvert, M., & Glud, R. N. (2021). Respiration by “marine snow” at high hydrostatic pressure: Insights from continuous oxygen measurements in a rotating pressure tank. Limnology and Oceanography, 66(7), 2797-2809.

Stramska, M., & Cieszyńska, A. (2015). Ocean colour estimates of particulate organic carbon reservoirs in the global ocean–revisited. International Journal of Remote Sensing, 36(14), 3675-3700.

Stukel, M. R., Ohman, M. D., Benitez-Nelson, C. R., & Landry, M. R. (2013). Contributions of mesozooplankton to vertical carbon export in a coastal upwelling system. Marine Ecology Progress Series, 491, 47-65.

Suess, E. (1980). Particulate organic carbon flux in the oceans—surface productivity and oxygen utilization. Nature, 288(5788), 260-263.

Suess, E., & Müller, P. J. (1980). Productivity sedimentation rate and sedimentary organic matter in the oceans: II. Elemental fractionation. CNRS.

Sulpis, O., Trossman, D. S., Holzer, M., Jeansson, E., Lauvset, S. K., & Middelburg, J. J. (2023). Respiration patterns in the dark ocean. Global Biogeochemical Cycles, 37(8), e2023GB007747.

Taguchi, S. (1982). Seasonal study of fecal pellets and discarded houses of Appendicularia in a subtropical inlet, Kaneohe Bay, Hawaii. Estuarine, Coastal and Shelf Science, 14(5), 545-555.

Takahashi, T., Sutherland, S. C., Wanninkhof, R., Sweeney, C., Feely, R. A., Chipman, D. W., ... & de Baar, H. J. (2009). Climatological mean and decadal change in surface ocean pCO2, and net sea–air CO2 flux over the global oceans. Deep Sea Research Part II: Topical Studies in Oceanography, 56(8-10), 554-577.

Takeda, S. (1998). Influence of iron availability on nutrient consumption ratio of diatoms in oceanic waters. Nature, 393(6687), 774-777.

Takeuchi, M., Doubell, M. J., Jackson, G. A., Yukawa, M., Sagara, Y., & Yamazaki, H. (2019). Turbulence mediates marine aggregate formation and destruction in the upper ocean. Scientific Reports, 9(1), 16280.

Tamburini, C., Garcin, J., Ragot, M., & Bianchi, A. (2002). Biopolymer hydrolysis and bacterial production under ambient hydrostatic pressure through a 2000 m water column in the NW Mediterranean. Deep Sea Research Part II: Topical Studies in Oceanography, 49(11), 2109-2123.

Tantanasarit, C., Englande, A. J., & Babel, S. (2013). Nitrogen, phosphorus and silicon uptake kinetics by marine diatom Chaetoceros calcitrans under high nutrient concentrations. Journal of Experimental Marine Biology and Ecology, 446, 67-75.

Thiele, S., Fuchs, B. M., Amann, R., & Iversen, M. H. (2015). Colonization in the photic zone and subsequent changes during sinking determine bacterial community composition in marine snow. Applied and environmental microbiology, 81(4), 1463-1471.

Thingstad, F., & Billen, G. (1994). Microbial degradation of Phaeocystis material in the water column. Journal of marine systems, 5(1), 55-65.

Thingstad, T. F., & Lignell, R. (1997). Theoretical models for the control of bacterial growth rate, abundance, diversity and carbon demand. Aquatic microbial ecology, 13(1), 19-27.

Thornton, D. C. (2002). Diatom aggregation in the sea: mechanisms and ecological implications. European Journal of Phycology, 37(2), 149-161.Baumann

Tiselius, P., Petersen, J., Nielsen, T., Maar, M., Møller, E., Satapoomin, S., ... & Vargas, C. (2003). Functional response of Oikopleura dioica to house clogging due to exposure to algae of different sizes. Marine Biology, 142, 253-261.

Torres - Valdés, S., Roussenov, V. M., Sanders, R., Reynolds, S., Pan, X., Mather, R., ... & Williams, R. G. (2009). Distribution of dissolved organic nutrients and their effect on export production over the Atlantic Ocean. Global Biogeochemical Cycles, 23(4).

Tréguer, P., & Pondaven, P. (2000). Silica control of carbon dioxide. Nature, 406(6794), 358-359.

Tréguer, P., Bowler, C., Moriceau, B., Dutkiewicz, S., Gehlen, M., Aumont, O., ... & Pondaven, P. (2018). Influence of diatom diversity on the ocean biological carbon pump. Nature Geoscience, 11(1), 27-37.

Trudnowska, E., Lacour, L., Ardyna, M., Rogge, A., Irisson, J. O., Waite, A. M., ... & Stemmann, L. (2021). Marine snow morphology illuminates the evolution of phytoplankton blooms and determines their subsequent vertical export. Nature communications, 12(1), 2816.

Turner, J. T. (2002). Zooplankton fecal pellets, marine snow and sinking phytoplankton blooms. Aquatic microbial ecology, 27(1), 57-102.

Turner, J. T. (2015). Zooplankton fecal pellets, marine snow, phytodetritus and the ocean's biological pump. Progress in Oceanography, 130, 205-248.

Van der Jagt, H., Friese, C., Stuut, J. B. W., Fischer, G., & Iversen, M. H. (2018). The ballasting effect of Saharan dust deposition on aggregate dynamics and carbon export: Aggregation, settling, and scavenging potential of marine snow. Limnology and Oceanography, 63(3), 1386-1394.

Van der Jagt, H., Wiedmann, I., Hildebrandt, N., Niehoff, B., & Iversen, M. H. (2020). Aggregate feeding by the copepods Calanus and Pseudocalanus controls carbon flux attenuation in the Arctic shelf sea during the productive period. Frontiers in Marine Science, 7, 543124.

Verity, P. G. (2000). Grazing experiments and model simulations of the role of zooplankton in Phaeocystis food webs. Journal of Sea Research, 43(3-4), 317-343.

Verity, P. G., Brussaard, C. P., Nejstgaard, J. C., van Leeuwe, M. A., Lancelot, C., & Medlin, L. K. (2007). Current understanding of Phaeocystis ecology and biogeochemistry, and perspectives for future research. Biogeochemistry, 83, 311-330.

Verity, P. G., Smayda, T. J., & Sakshaug, E. (1991). Photosynthesis, excretion, and growth rates of Phaeocystis colonies and solitary cells. Polar research, 10(1), 117-128.

Volk, T., & Hoffert, M. I. (1985). Ocean carbon pumps: Analysis of relative strengths and efficiencies in ocean - driven atmospheric CO2 changes. The carbon cycle and atmospheric CO2: Natural variations Archean to present, 32, 99-110.

Waite, A., & Harrison, P. J. (1992). Role of sinking and ascent during sexual reproduction in the marine diatom Ditylum brightwellii. Marine Ecology Progress Series, 113-122.

Wassmann, P. (1994). Significance of sedimentation for the termination of Phaeocystis blooms. Journal of Marine Systems, 5(1), 81-100.

Wassmann, P., Olli, K., Riser, C. W., & Svensen, C. (2003). Ecosystem function, biodiversity and vertical flux regulation in the twilight zone. Marine science frontiers for Europe, 279-287.

Wassmann, P., Vernet, M., Mitchell, B. G., & Rey, F. (1990). Mass sedimentation of Phaeocystis pouchetii in the Barents Sea. Marine Ecology Progress Series, 183-195.

Weiss, R. (1974). Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Marine chemistry, 2(3), 203-215.

Wilson, J. D., Barker, S., & Ridgwell, A. (2012). Assessment of the spatial variability in particulate organic matter and mineral sinking fluxes in the ocean interior: Implications for the ballast hypothesis. Global Biogeochemical Cycles, 26(4).

Yoon, W., Kim, S., & Han, K. (2001). Morphology and sinking velocities of fecal pellets of copepod, molluscan, euphausiid, and salp taxa in the northeastern tropical Atlantic. Marine Biology, 139, 923-928.

Zeebe, R. E., & Wolf-Gladrow, D. (2001). CO2 in seawater: equilibrium, kinetics, isotopes (Vol. 65). Gulf Professional Publishing.

Zetsche, E. M., Larsson, A. I., Iversen, M. H., & Ploug, H. (2020). Flow and diffusion around and within diatom aggregates: effects of aggregate composition and shape. Limnology and Oceanography, 65(8), 1818-1833.

Ziervogel, K., Steen, A. D., & Arnosti, C. (2010). Changes in the spectrum and rates of extracellular enzyme activities in seawater following aggregate formation. Biogeosciences, 7(3), 1007-1015.

Versicherung an Eides Statt / *Affirmation in lieu of an oath*

gem. § 5 Abs. 5 der Promotionsordnung vom 28.04.2021 /
according to § 5 (5) of the Doctoral Degree Rules and Regulations of 28 April, 2021

Ich / I, _____

(Vorname / First *Name*, Name / *Name*, Anschrift / *Address*, ggf. Matr.-Nr. / *student ID no., if applicable)*

versichere an Eides Statt durch meine Unterschrift, dass ich die vorliegende Dissertation selbständig und ohne fremde Hilfe angefertigt und alle Stellen, die ich wörtlich dem Sinne nach aus Veröffentlichungen entnommen habe, als solche kenntlich gemacht habe, mich auch keiner anderen als der angegebenen Literatur oder sonstiger Hilfsmittel bedient habe und die zu Prüfungszwecken beigelegte elektronische Version (PDF) der Dissertation mit der abgegebenen gedruckten Version identisch ist. / *With my signature I affirm in lieu of an oath that I prepared the submitted dissertation independently and without illicit assistance from third parties, that I appropriately referenced any text or content from other sources, that I used only literature and resources listed in the dissertation, and that the electronic (PDF) and printed versions of the dissertation are identical.*

Ich versichere an Eides Statt, dass ich die vorgenannten Angaben nach bestem Wissen und Gewissen gemacht habe und dass die Angaben der Wahrheit entsprechen und ich nichts verschwiegen habe*. / I affirm in lieu of an oath that the information provided herein to the best of my knowledge is true and complete.*

Die Strafbarkeit einer falschen eidesstattlichen Versicherung ist mir bekannt, namentlich die Strafandrohung gemäß § 156 StGB bis zu drei Jahren Freiheitsstrafe oder Geldstrafe bei vorsätzlicher Begehung der Tat bzw. gemäß § 161 Abs. 1 StGB bis zu einem Jahr Freiheitsstrafe oder Geldstrafe bei fahrlässiger Begehung. / *I am aware that a false affidavit is a criminal offence which is punishable by law in accordance with § 156 of the German Criminal Code (StGB) with up to three years imprisonment or a fine in case of intention, or in accordance with § 161 (1) of the German Criminal Code with up to one year imprisonment or a fine in case of negligence.*

_____ _____

Ort / *Place*, Datum / *Date* Unterschrift / *Signature*