

RESEARCH ARTICLE

The importance of transparent exopolymer particles over ballast in determining both sinking and suspension of small particles during late summer in the Northeast Pacific Ocean

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Gravitational sinking of particles is a key pathway for the transport of particulate organic carbon (POC) to the deep ocean. Particle size and composition influence particle sinking velocity and thus play a critical role in controlling particle flux. Canonically, sinking particles that reach the mesopelagic are expected to be either large or ballasted by minerals. However, the presence of transparent exopolymer particles (TEP), which are positively buoyant, may also influence particle sinking velocity. We investigated the relationship between particle composition and sinking velocity during the Export Processes in the Ocean from RemoTe Sensing (EXPORTS) campaign in the Northeast Pacific Ocean using Marine Snow Catchers. Suspended and sinking particles were sized using FlowCam for particle imaging, and their biogeochemical composition was assessed by measuring the concentration of particulate organic carbon (POC) and nitrogen, particulate inorganic carbon, biogenic and lithogenic silica, and TEP. Sinking fluxes were also calculated. Overall, both suspended and sinking particles were small (<51 μm , diameter) in this late summer, oligotrophic system. Contrary to expectation, the ratio of ballast minerals to POC was higher for suspended particles than sinking particles. Further, suspended particles showed TEP-to-POC ratios three times higher than sinking particles. These ratios suggest that TEP content and not ballast dictated whether particles in this system would sink (low TEP) or remain suspended (high TEP). Fluxes of POC averaged $4.3 \pm 2.5 \text{ mmol C m}^{-2} \text{ d}^{-1}$ at 50 m ($n = 9$) and decreased to $3.1 \pm 1.1 \text{ mmol C m}^{-2} \text{ d}^{-1}$ at 300–500 m ($n = 6$). These flux estimates were slightly higher than fluxes measured during EXPORTS with drifting sediment traps and Thorium-234. A comparison between these approaches illustrates that small sinking particles were an important component of the POC flux in the mesopelagic of this late summer oligotrophic system.

Keywords: Biological carbon pump, Ocean Station Papa, Bioelements, Particle sinking velocity, Marine gels, Particulate fluxes

1. Introduction

The biological carbon pump (BCP) comprises the processes that mediate the transfer of organic carbon from the euphotic zone, where it is produced, to the deep ocean (Volk and Hoffert, 1985). Without the BCP the concentrations of atmospheric CO_2 would be approximately 200 ppm higher than present (Parekh et al., 2006). The

efficiency of the BCP depends primarily on the gravitational settling of particles, the physical advection and mixing of particles, and the active vertical transport of particles due to migrating zooplankton and fish (Boyd et al., 2019). These processes shape the flux of carbon and other elements through the mesopelagic and abyssopelagic zones, where carbon can be locked away from the atmosphere, impacting atmospheric CO_2 concentrations over climatologically relevant timescales (Kwon et al., 2009; DeVries et al., 2012). Accurately predicting the response of the ocean carbon storage to already underway and future climate changes requires a mechanistic knowledge of the processes making up the BCP (e.g., Siegel et al., 2023).

The largest component of the BCP is settling particles (Boyd et al., 2019; Nowicki et al., 2022). Particles in the open ocean are mainly produced in the surface layer and consist of living and dead phytoplankton cells, detritus,

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carcasses, fecal material, and minerals. Their size range spans between less than a micrometer (typical threshold defined as 0.7 μm in diameter) to many millimeters, with those of a diameter >0.5 mm being referred to as “marine snow” (Alldredge and Silver, 1988). The fate and distribution of particles are influenced by the transformation processes that change particle size, composition and, consequently, sinking velocity. Particles can aggregate, disaggregate, solubilize or be remineralized back to inorganic forms via mechanical forcing, bacterioplankton activity, and interaction with zooplankton (Stemmann et al., 2004; Burd et al., 2010; Giering et al., 2014; Collins et al., 2015). When particles aggregate or are repackaged into fecal matter, they have the potential to sink rapidly (approximately 50 to $\geq 2,000$ m d^{-1}) and hence more easily escape consumption, fragmentation, and dissolution at shallow depths, thus bringing organic matter to the deep ocean more efficiently than smaller particles (Alldredge and Silver, 1988; Ebersbach and Trull, 2008).

Particle sinking velocities are typically thought to be determined largely by size. Stokes' Law, which quantifies the sinking velocity of spherical solid particles under laminar flow conditions, assumes that particle sinking velocity increases as the product of the spherical particle diameter squared and the excess density with respect to seawater. The implication for sinking particles in the ocean is that large particles should sink rapidly and are hence effective vectors for carbon transport to depth, whereas small particles should sink slowly and be remineralized within the upper mesopelagic, contributing little to BCP-mediated ocean carbon storage (Kriest, 2002; Marsay et al., 2015; Cavan et al., 2017). Nevertheless, the presence of small particles (0.2–20 μm) has been observed at great depths (>1000 m; e.g., Dall'Olmo and Mork, 2014; Briggs et al., 2020). Furthermore, recent studies have shown that the downward flux of particulate organic carbon (POC) via small particles (<100 μm) can be significant in specific ecosystems and seasons, at times constituting the bulk of the total POC flux through the mesopelagic (e.g., Durkin et al., 2015; Giering et al., 2016; Bisson et al., 2020; Dever et al., 2021).

The presence of ballast minerals (biogenic silica from diatoms, particulate inorganic carbon from coccolithophores and foraminifera, and lithogenic material from aeolian and riverine inputs) is also thought to increase particle sinking velocity by increasing particle excess density in respect to seawater (Armstrong et al., 2001; Passow and De La Rocha, 2006; Laurenceau-Cornec et al., 2020; Iversen and Lampitt, 2020; Iversen, 2023). However, cause and effect in the relationship between organic matter and minerals is not clear, and sinking aggregates originating from biological activity in the mixed layer could scavenge and subsequently transport small, suspended mineral particles to depth (Passow, 2004).

The presence of transparent exopolymer particles (TEP; Alldredge et al., 1993) also has the potential to influence the sinking of particles. TEP are composed largely of polysaccharides released by phytoplankton and bacteria as extracellular surface-active exopolymers (Passow, 2002), especially under nutrient-limited conditions (Obernosterer

and Herndl, 1995). TEP may act as biological glue and thus enhance particle coagulation rate by increasing particle “stickiness” (Passow and Alldredge, 1994; Jackson, 1995). However, by being positively buoyant, TEP may also reduce aggregate sinking velocities, especially when aggregates are characterized by a high ratio of TEP to solid particles (Engel and Schartau, 1999; Azetsu-Scott and Passow, 2004). Although TEP has the potential to play an important role in controlling the downward transport of particles, we lack a robust mechanistic understanding of this process (e.g., Mari et al., 2017; Nagata et al., 2021).

Our hypothesis is that TEP play a critical role in determining the sinking velocity of particles, potentially out-competing the role of ballast minerals. We assessed how particle size and composition regulate the partitioning between sinking and suspended particles within the upper mesopelagic in an iron-limited region of the Northeast Pacific Ocean. Particles were collected using Marine Snow Catchers (MSC) during the Export Processes in the Ocean from RemoTe Sensing field (EXPORTS) campaign. In addition, we considered the possible mechanisms driving the formation of small sinking particles in the mesopelagic and highlighted the importance of studying small particle characteristics and particle patchiness to enhance our understanding of the functioning of the biological carbon pump.

2. Materials and methods

2.1. Ocean Station Papa

This study is part of the first EXPORTS field campaign, which took place in late summer 2018 (August 14 to September 9) at Ocean Station Papa (“Station P”). Station P is a time-series site located in the Northeast Pacific Ocean (nominally 50°N 145°W) that has been monitored regularly since 1949 (e.g., Tabata, 1965). It is a high-nutrient low-chlorophyll system with a “muted” spring bloom owing to persistently low concentrations of iron (Martin and Fitzwater, 1988; Boyd et al., 1996). During our study, Station P was characterized by a shallow mixed layer (average: 29 ± 4 m, $n = 226$) and strong vertical and weak horizontal gradients in hydrographic properties (Siegel et al., 2021). Mixed layer macronutrient concentrations were elevated and chlorophyll *a* concentrations were low (0.10 – 0.35 $\mu\text{g L}^{-1}$) and lower than typical August values (2000–2017) for Station P (Siegel et al., 2021). This condition resulted in an isolume depth of the 1% photosynthetically available radiation (PAR) between 70 m and 90 m (Siegel et al., 2021), which was slightly deeper than climatological conditions (Siegel et al., 2021). The site was characterized by a highly recycled food web in the mixed layer (Meyer et al., 2022; McNair et al., 2023), with low POC fluxes (Buesseler et al., 2020; Estapa et al., 2021), which were in line with previous observations performed at Station P (Charette et al., 1999; Wong et al., 2002; Kawakami et al., 2010; Timothy et al., 2013; Mackinson et al., 2015). An in-depth discussion of how POC fluxes measured during EXPORTS compare to previous POC flux measurements is provided by Buesseler et al. (2020).

The observations presented here were conducted from the R/V *Roger Revelle*, which sampled ecological and

biogeochemical properties following an instrumented Lagrangian float at a depth of approximately 100 m. Detailed operations of the EXPORTS North Pacific field campaign have been described by Siegel et al. (2021).

2.2. Sample collection with the Marine Snow Catchers

Profiles of suspended and sinking particles were collected using three Marine Snow Catchers (MSC, OSIL, UK; Lam-pitt et al., 1993). The MSC is a large volume (volume: V_{MSC} 89.8 L, height: h_{MSC} 1.5 m) water sampler with a removable base section (approximately 8 L) that enables the partitioning of particles according to a predefined settling time (Riley et al., 2012; Giering et al., 2016). The MSCs were deployed at two to three depths ranging between 20 m and 500 m at 13 stations (Table S1). Deployment depths were chosen to include (1) just below the mixed layer depth (20–65 m), (2) at approximately 100 m (Lagrangian float depth), and (3) between 100 m and 500 m. Depths were adjusted to match where particle maxima were detected immediately before the MSC deployments, either via chlorophyll fluorescence profile, or particle counts from the Underwater Vision Profiler-5 (UVP, Hydroptic, France; Picheral et al., 2010). MSC casts were conducted in the afternoons on days 1, 3, and 6 of each of the three 8-day sampling epochs, with additional two-depth casts on day 5 of epochs 2 and 3 (Table S1).

A full description of the MSC and its sampling methodology has been published by Riley et al. (2012) and Giering et al. (2016). We modified the protocol slightly as follows. During deployment, the terminal apertures of the top and base sections of the MSC were kept open and then were closed at the target depth through a wire-guided messenger trigger mechanism. A tray (height: $h_{\text{tray}} = 4.4$ cm, area: $A_{\text{tray}} 0.028$ m², approximate volume: 1 L) was placed at the bottom of the MSC base section prior to each deployment. Immediately following deployment and retrieval, the MSC was secured in an upright position, the initial bulk population of particles was sampled from the MSC central tap (time zero, T_0), and particles were allowed to settle for 2 hours. We operationally defined three particle fractions, *top*, *base* and *tray*, according to their sampling locations within the MSC after the 2-hour settling period. The *top* fraction was collected from the central tap in the top section of the MSC and represents the suspended particle pool, i.e., particles that did not sink during the 2-hour settling period. Subsequently, the water contained in the upper part of the MSC was gently drained, and the upper part of the MSC removed. The water in the base section overlying the tray was siphoned off, constituting the *base* fraction (volume: V_{base} 4.5–5.5 L). Water in the tray was considered as the *tray* fraction (volume: V_{tray} 0.33–0.98 L). The *base*- and *tray*-sampled volumes varied across deployments depending on sampling efficiency (i.e., how much volume was lost during sampling). In the laboratory, the tray was visually investigated for the presence of marine-snow-sized particles. In two instances (settling time experiments; Section 2.6) the *tray* and *base* fractions were combined before sampling (referred to as *bottom* fraction).

All three fractions (*top*, *base*, *tray*) were subsampled for various parameters (Table S1). Subsamples for POC and particulate organic nitrogen (PON) analysis and for counts and identification (particle imaging via the FlowCam) were collected at all stations, except on August 17 when no samples were fixed for particle imaging. Subsamples for the analysis of total particulate carbon (TC), from which we obtained particulate inorganic carbon estimates (PIC) by difference ($\text{PIC} = \text{TC} - \text{POC}$), biogenic and lithogenic silica (bSi and lSi, respectively), were taken on days 3 and 5 of each epoch. Subsamples for the determination of TEP were collected on days 1 and 5 of each epoch, and the abiotic aggregation potential was determined on seawater collected on day 1 of each epoch.

2.3. Particle imaging and sizing with the FlowCam

Particle size distribution of suspended and sinking particles was assessed using particle imaging. Subsamples (50 mL) were fixed with 37% formalin (hexamethylenetetramine buffered) to a final concentration of 1%–2% and stored in dark at 4°C until analysis. Subsamples were analyzed using a FlowCam 8000 Series (Yokogawa Fluid Imaging Technologies, US; Sieracki et al., 1998) in auto-image mode (particles imaged at a pre-defined flow rate; Table S2). To assess relevant particle sizes, we first analyzed subsamples using a 40× objective combined to a 300- × 1500-μm flow cell and then a 200× objective with a 50- × 300-μm flow cell. Of 30 suspended particle samples, 13 were not analyzed with the 40× objective due to time constraints. The minimum sizes reliably resolved by the objectives were 30 μm (40×) and 3 μm (200×). The maximum size, dictated by the flow cell size, was 300 μm for the 40× objective and 50 μm for the 200× objective. *Base* and *tray* fractions were pre-filtered using a 44-μm mesh filter to avoid clogging the 50- × 300-μm flow cell when using the 200× objective.

Based on the size of the particles and the FlowCam resolution, we chose to restrict our analysis to particles with an equivalent spherical diameter (ESD) between 4 μm and 128 μm. We calculated the minimum number of particles required to estimate a robust particle size spectrum using the empirical relationship given by Blanco et al. (1994) and assuming that a size bin is well represented if there are at least 10 particles in it (Álvarez et al., 2011). Thus, we imaged around 1,300 particles (i.e., minimum desired count and lowest number of counted particles) to cover a size range of 4 μm to <32 μm at 200× and a size range of ≥32 μm to 128 μm at 40×.

Imaged particles were sized using FlowCam VisualSpreadsheet© software version 4.15.1. and grouped in the 5 size bins based on their ESD. The complete method settings and example images are presented in Table S2. Particle concentrations of *top*, *base* and *tray* were calculated by dividing the counted number of particles in each size bin by the sample volume imaged. Suspended and sinking particle abundances were calculated as explained in Section 2.7. Particle size distributions (PSDs) were estimated as differential number size distributions $N(D)$ (# particle mL⁻¹ μm⁻¹) for *top* and *tray* fractions. The slope of the PSDs was calculated as the slope of

a one-degree polynomial fit to the \log_{10} -transformed PSD and \log_{10} -transformed arithmetic mean of each size bin (μm) over the entire measured size range (polyfit function, Matlab R2021b).

2.4. Biogeochemical analyses

Typically, 1 L of each of the T_0 , *top* and *base* fractions and approximately 0.1 L of the *tray* fraction were filtered for analysis of POC and PON, TC, bSi and lSi, and TEP. For the occasions when we carried out the settling time methodological test, 0.5–1.5 L of the *top* and *bottom* subsamples were filtered instead.

Concentrations of POC and PON were determined by filtering subsamples onto two replicate pre-combusted (450°C, 30 minutes) GF/F filters (25 mm, Whatmann, UK). The filters were dried at 60°C and stored at room temperature until analysis. Filters were analyzed using a CEC 440HA elemental analyzer (Control Equipment, US) after treatment with 10% HCl. Replicates were averaged (see average of the relative standard deviations of the filter replicates in Table S3). The range for the detection limit of POC and PON was 0.8–16 μg and 0.2–3.9 μg , respectively. All POC values were above the detection limit of the instrument. However, for PON, 24 of 237 values were below detection, seven of which were negative and therefore substituted with zero ($\mu\text{g L}^{-1}$). Values were corrected to account for non-target carbon on the filter using the average POC and PON mass (12.6 μg for POC; 2.1 μg for PON) of 28 blanks obtained using a multiple volume (0.5 L, 1 L and approximately 2 L) regression approach (Moran et al., 1999) for water collected with Niskin Bottles from the CTD-rosette system within the mixed layer (campaign-wide correction). A detailed explanation of the blank correction method and a reconciliation of all the POC and PON measurements obtained using different methodologies during the EXPORTS field campaign is presented by Graff et al. (n.d.).

TC was measured following procedures similar to POC but without prior acidification. Only one filter per fraction was generated due to volume constraints. No measured values fell below the instrument detection limit (1.2–4.5 μg). PIC was calculated by subtracting the uncorrected POC from TC.

Biogenic and lithogenic silica concentrations were determined by filtering samples onto 0.6 μm pore size polycarbonate membrane filters (47 mm diameter, Isopore, Millipore), which were dried at 60°C and stored at room temperature until analysis. Filters were digested in Teflon tubes by adding 4 mL of 0.2 N NaOH (95°C, 40 minutes) and cooled immediately afterwards. The resulting solutions were neutralized by adding 1 mL of 1 M HCl and centrifuged (10 minutes, 2,500 rpm) to separate lSi from bSi. Four mL of the solution was diluted with 6 mL of Milli-Q water and assessed via the molybdo-silicic acid spectrophotographic method to measure bSi (Strickland and Parsons, 1968). The remaining 1 mL of solution, which was left at the bottom of the Teflon tube together with the filter, was rinsed using Milli-Q water, left to dry, and cooled. To extract lSi, 0.25 mL of 2.5 M hydrofluoric acid was added. After 48 hours 9.75 mL of 1 M

saturated boric acid solution were added, and filters were centrifuged. Eight mL of the resulting solution was added to 2 mL of 1 M saturated boric acid solution and assessed spectrophotometrically as aforementioned.

Concentrations of TEP were determined colorimetrically on triplicate samples. Subsamples were filtered onto 0.4 μm pore size polycarbonate filters (25 mm, Whatmann, UK), stained with Alcian blue, and stored frozen until analysis. Filter blanks, prepared by staining and rinsing wet filters, were processed like the samples. Stained filters were soaked for at least 2 hours in 80% sulfuric acid (95% w/w; Fisher Scientific), and the absorption at 787 nm was measured spectrophotometrically (Thermo Scientific GENESYS 10 S UV-VIS; Passow and Alldredge, 1995). The stained filters were compared to a standard curve developed using xanthan gum (Sigma-Aldrich), and hence TEP determinations were expressed as standardized xanthan gum equivalents (Xgeq; Bittar et al., 2018). TEP determinations were considered above detection if the absorbance value of a sample at 787 nm was at least twice the absorbance value of the blank at 787 nm (Passow and Alldredge, 1995). A total of 28 of 112 TEP determinations measured from the MSC were below this detection limit. TEP values associated with sinking particles between 300 m and 500 m were always at or below detection limit. In addition to the MSC samples, we also determined water column TEP on water collected using Niskin bottles fitted to a CTD rosette (depth range: 5–500 m; $n = 153$). A total of 22 of 153 TEP measurements on the water column sampled with the Niskin bottles were at or below the detection limit. We did not remove TEP values at or below the limit of detection but instead considered these observations an upper bound estimate of the true in situ concentrations. We expressed TEP in carbon units (TEP-C) using a conversion factor of $0.75 \mu\text{g C } \mu\text{g L}^{-1} / \text{Xgeq L}^{-1}$ (Engel and Passow, 2001).

Several values of the biogeochemical measurements were considerably higher than the average concentrations at their collection depth. If at least twice the average concentration for that depth layer, a value was defined as an outlier; approximately 5% of the total number of observations were *outliers*. We refer to background concentrations when these outliers were removed to assess the baseline biogeochemical composition of suspended and sinking particles. The nature of the outliers and the implication of their presence is discussed in Section 4.5.

2.5. Abiotic aggregation potential experiments

The potential for the abiotic formation of aggregates was evaluated using rolling tanks experiments. Four experiments were conducted using MSC T_0 (August 25 at 95 m), *top* (August 25 at 95 m) or *base* (August 17 at 55 m and August 19 at 55 m and 95 m) sample fractions. Each experiment was conducted for 36 hours in 1.1 L rolling tanks at near in situ temperature (13°C or 4°C) in the dark. Aggregate formation was monitored by visually checking every 6 hours for the appearance of marine snow-sized particles (ESD > 0.5 mm).

2.6. Settling time experiments for MSC

Methodological experiments to determine the effect of settling time on particle fraction partitioning were conducted twice (on August 20 and September 03; Table S1) on samples from MSC deployments at depths of 60 m and 80 m, respectively. Each time, all three MSCs were deployed at the same depth, but settling times after retrieval varied: particles were allowed to settle for 1, 2 and 4 hours after recovery of the MSCs. Subsamples of *top* and *bottom* fractions were analyzed for POC and PON, bSi, and TEP.

2.7. Calculations of particle concentrations and fluxes

Following Riley et al. (2012) and Giering et al. (2016), concentrations of suspended (c_{NS}), slow-sinking (c_{SS}) and fast-sinking (c_{FS}) particles were calculated as follows:

$$c_{NS} = \text{top concentration} \quad (1)$$

$$c_{SS} = (\text{base} - \text{top concentrations}) \times V_{\text{base}} / V_{\text{MSC}} \quad (2)$$

$$c_{FS} = (\text{tray} - \text{base concentrations}) \times V_{\text{tray}} / (A_{\text{tray}} \times h_{\text{MSC}}) \quad (3)$$

Occasionally after applying the corrections, we obtained negative values; i.e., the *top* concentration exceeded the *base* concentration, or the *base* concentration exceeded the *tray* concentration. We assigned a zero concentration to the specific observations. The negative values could reflect a lack of sinking particles, the presence of ascending particles and/or actively moving zooplankton. In the analyses that follow, little differences were found between slow- and fast-sinking particle concentrations (Section 3.2). Hence, these two sinking particle fractions are combined. In four deployments, TEP and TC were measured only in the *top* and *tray* fractions. In these cases, sinking TEP and TC concentrations were estimated following Equation 3 but subtracting the *top* fraction from the *tray* fraction.

The standard particle sinking velocity for the MSC is assumed to be 18 m d^{-1} , as determined geometrically by dividing the sinking distance (height of the MSC; $h_{\text{MSC}} = V_{\text{MSC}} / A_{\text{MSC}} = 1.5 \text{ m}$) by the settling time ($t = 2 \text{ hours}$). We assumed that the 18 m d^{-1} sinking velocity estimate for sinking particles represents a lower bound estimate because the sinking particles could have reached the bottom of the MSC much sooner (Giering et al., 2016).

2.8. Statistical analyses

The relative uncertainties in the calculated concentrations and fluxes were determined by using a Monte Carlo error propagation, with mean values obtained by averaging the replicate filters and the precision estimated by calculating the average of the relative standard deviations of the filter replicates (Table S3). A 1% uncertainty was assumed for the measured values (V_{MSC} , A_{tray} , h_{MSC} , V_{base} , V_{tray} , h_{MSC} and sinking time). Final estimates of the averages and standard deviations of particle concentrations and fluxes were then calculated from the simulation results. Simple linear regression was used to test (Student's t-test, 95% confidence) for statistically significant temporal and depth

trends displayed by the biogeochemical content of suspended and sinking particles, and their partitioning to total. The linear analyses were performed using the function `fitlm` in Matlab (R2021b). The same approach was used to test for significant temporal trends displayed by the biogeochemical content of suspended and sinking particles during the settling tests. Paired t-test was used to test for differences among particle fractions. The data presented in this study, and all the data generated during the first EXPORTS field campaign, can be found at NASA SeaBASS data repository (<https://seabass.gsfc.nasa.gov/cruise/EXPORTSNP>).

3. Results

3.1. Marine snow and abiotic aggregation potential

No visible sinking marine snow particles (diameter $> 0.5 \text{ mm}$) were found in the tray fractions from any of the MSCs deployments. This observation suggests that the concentration of sinking marine-snow-sized particles was less than 0.02 L^{-1} . Furthermore, during the four aggregation potential experiments, no visible marine snow-sized aggregates formed in the rolling tanks regardless of depth (55 m and 95 m) or sample fraction (T_0 , *top* or *base*).

3.2. Particle concentrations and size

Most of the imaged particles (approximately 95%) were smaller than $16 \mu\text{m}$ in diameter (ESD), whether suspended or sinking (Figure 1). Furthermore, particle concentrations measured in the tray were equal to or lower than the ones measured in the base for 20 of 30 MSC deployments. These observations suggest that the concentration differences between *base* and *tray* particle fractions were too small to be detected with this method. We hence summed the concentrations of slow- and fast-sinking particles into a single sinking particle fraction. This decision is also supported by the lack of marine snow, which would have contributed appreciably to the fast-sinking particle fraction.

Our results, based on the analysis of particles with diameters (ESD) between $4 \mu\text{m}$ and $128 \mu\text{m}$, suggest that $>70\%$ of suspended and sinking particles had a diameter of $4\text{--}8 \mu\text{m}$ and that particles larger than $32 \mu\text{m}$ were at the detection limit of our method (i.e., too rare to be quantified). The partitioning of particles across the size bins was consistent among particle fractions (paired t-test, $p = 0.33\text{--}0.63$, $n = 17$), indicating that suspended and sinking particles were of a similar size (Figure 1 and Table S4).

Additionally, we calculated the particle size distribution (PSD, $4\text{--}128 \mu\text{m}$) of suspended particles and of sinking (*tray*) particles (uncorrected fraction) to assess differences in slopes among fractions with depth. Overall, throughout the entire water column, PSD slopes of suspended particles were similar (-3.3 ± 0.3 , $n = 17$) to those of sinking particles (-3.5 ± 0.2 , $n = 17$; Figure S1). Yet below 100 m, PSDs of sinking particles were significantly steeper than those of suspended particles (paired t-test, $p = 0.03$, $n = 5$; Figure S1). Furthermore, the slope of suspended PSD became significantly shallower with depth between 20 m and 500 m ($R^2 = 0.33$, $p < 0.02$, $n = 17$), while the slopes

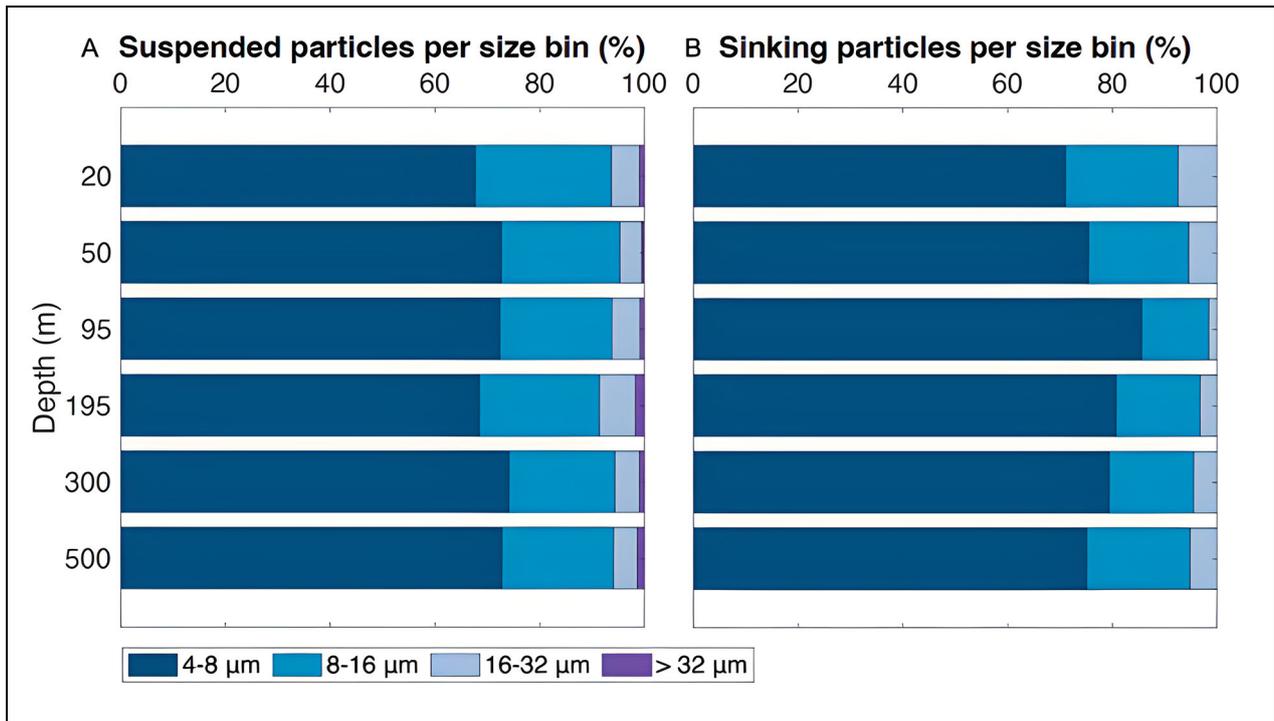


Figure 1. Relative contribution of particle abundances per size (4 to >32 μm) versus depth. Bar plots display the contribution (%) of A) suspended and B) sinking particle concentrations in 4 size bins based on the octave scale (4–8, 8–16, 16–32 and >32 μm) and on the particle equivalent spherical diameter. Concentrations are calculated as cruise-wide averages for 6 depth layers (20–25 m, 50–65 m, 95 m, 195 m, 300–350 m and 500 m). Numbers of stations per depth layer are 2, 10, 10, 2, 4 and 2, respectively, for bins between 4 μm and 32 μm and 2, 4, 5, 2, 2 and 1 for the largest size bin (>32 μm). Sinking particles (>32 μm) were at the detection limit of our method.

of sinking PSDs remained constant ($R^2 = 0.01$, $p = 0.75$, $n = 17$; Figure S1).

The determination of particle size using this approach is associated with uncertainties due to sample handling. We cannot exclude the possibility that fragile and larger aggregates ($ESD > 0.5$ mm) may have broken up due to physical disturbance developed during the sampling and partitioning of the three particle fractions and during injection of subsamples into the FlowCam flowcell used in combination with the 40× objective (minimum size of 300 μm). Therefore, the size characterization performed with the FlowCam must be taken with caution. Particle type and shape could not be resolved reliably with the FlowCam due to the small size of the particles.

3.3. Biogeochemical partitioning by particle sinking fraction

The background suspended POC concentrations decreased significantly with depth in the euphotic zone between 20 m and 65 m ($R^2 = 0.43$, $p = 0.03$, $n = 11$) and in the upper mesopelagic between 95 m and 500 m ($R^2 = 0.59$, $p = 0.001$, $n = 14$; Figure 2A), whereas background sinking POC concentrations did not attenuate significantly with depth ($R^2 = 0.01$, $p = 0.62$, $n = 24$). The relative contribution of background suspended POC to total background POC decreased significantly in the upper mesopelagic ($R^2 = 0.70$, $p < 0.001$, $n = 13$), resulting in a concomitant increase in the contribution of the background sinking POC

($R^2 = 0.70$, $p < 0.001$, $n = 13$) (Figure 2A). Nearly all the background POC was found in suspended particles, which contributed to the total POC on average $89\% \pm 9\%$ ($n = 23$). In respect to outliers, in 5 of 29 MSC deployments, the measured POC of either suspended or sinking particle fractions was at least twice as high as POC concentrations measured at other stations in the same depth layer (Table S5).

Patterns of PON (Figure S2) were similar to those of POC, with molar POC-to-PON ratios of the suspended fraction on average slightly higher than the Redfield ratio of 6.6 (average: 7.9 ± 3.9 , $n = 24$). The molar POC-to-PON ratios did not show any trend with depth ($R^2 = 0.06$, $p = 0.25$) and were in general agreement with molar POC-to-PON ratios measured during the EXPORTS field campaign (Graff et al., n.d.). Molar POC-to-PON for sinking particles varied between 3 and 16 (average: 7.2 ± 3.8 , $n = 26$) and did not show any significant trend with depth ($R^2 = 0.11$, $p = 0.10$).

PIC was below detection in 20% of the suspended particle fractions, and in 60% of sinking particle fractions. Suspended PIC concentrations increased significantly with depth ($R^2 = 0.40$, $p = 0.05$, $n = 10$; Figure 2B). Background sinking PIC was on average 0.4 ± 0.3 ($n = 8$) $\mu\text{g C L}^{-1}$ and remained constant with depth ($R^2 = 0.05$, $p = 0.59$, $n = 8$). Background molar PIC-to-POC ratios calculated for suspended particles increased significantly with depth ($R^2 = 0.80$, $p < 0.001$, $n = 10$) and were significantly higher than PIC-to-POC ratios of sinking particles in the mesopelagic (paired t-test, $p = 0.01$, $n = 5$; Figure 3A).

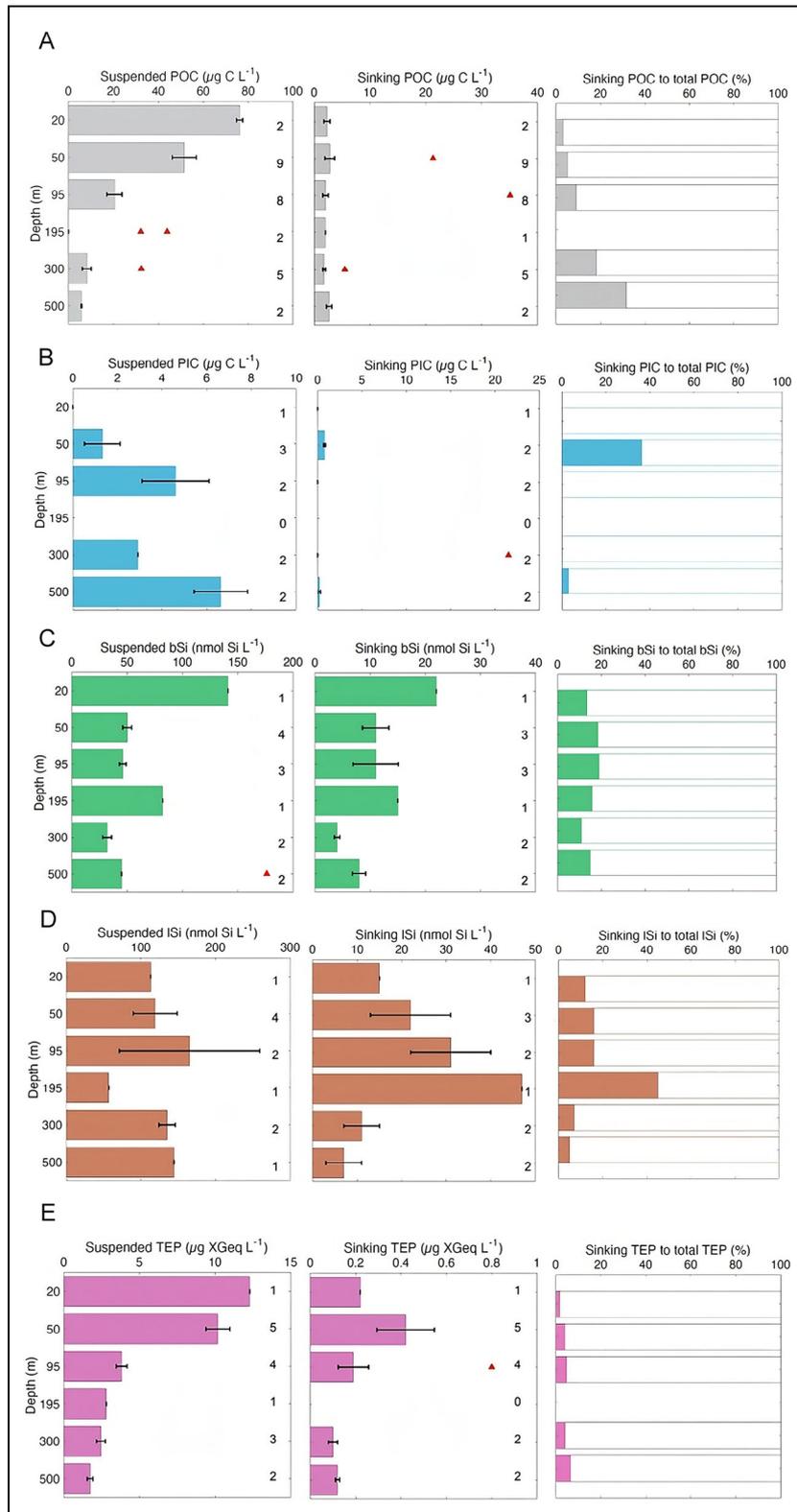


Figure 2. Concentrations of biogeochemical components in suspended and sinking particles and contributions of sinking to total. Bar graphs display time-averaged concentrations of A) particulate organic carbon (POC), B) particulate inorganic carbon (PIC), C) biogenic silica (bSi), D) lithogenic silica (ISi), and E) transparent exopolymer particles (TEP) in (left) suspended particles and (middle) sinking particles, along with (right) the contribution (%) of sinking particle to total concentrations. Outliers are represented as red triangles. The values are cruise-wide averages calculated for six depth layers (20–25 m, 50–65 m, 95 m, 195 m, 300–350 m and 500 m). Error bars are the standard deviations of the concentrations averaged within each depth layer and thus reflect dataset variability rather than the propagated uncertainty of each datapoint. Numbers to the right of each bar indicate total number of observations per depth layer including outliers. The differences in number of observations between sinking and suspended particles reflect loss of samples during analysis. Note differences in scales.

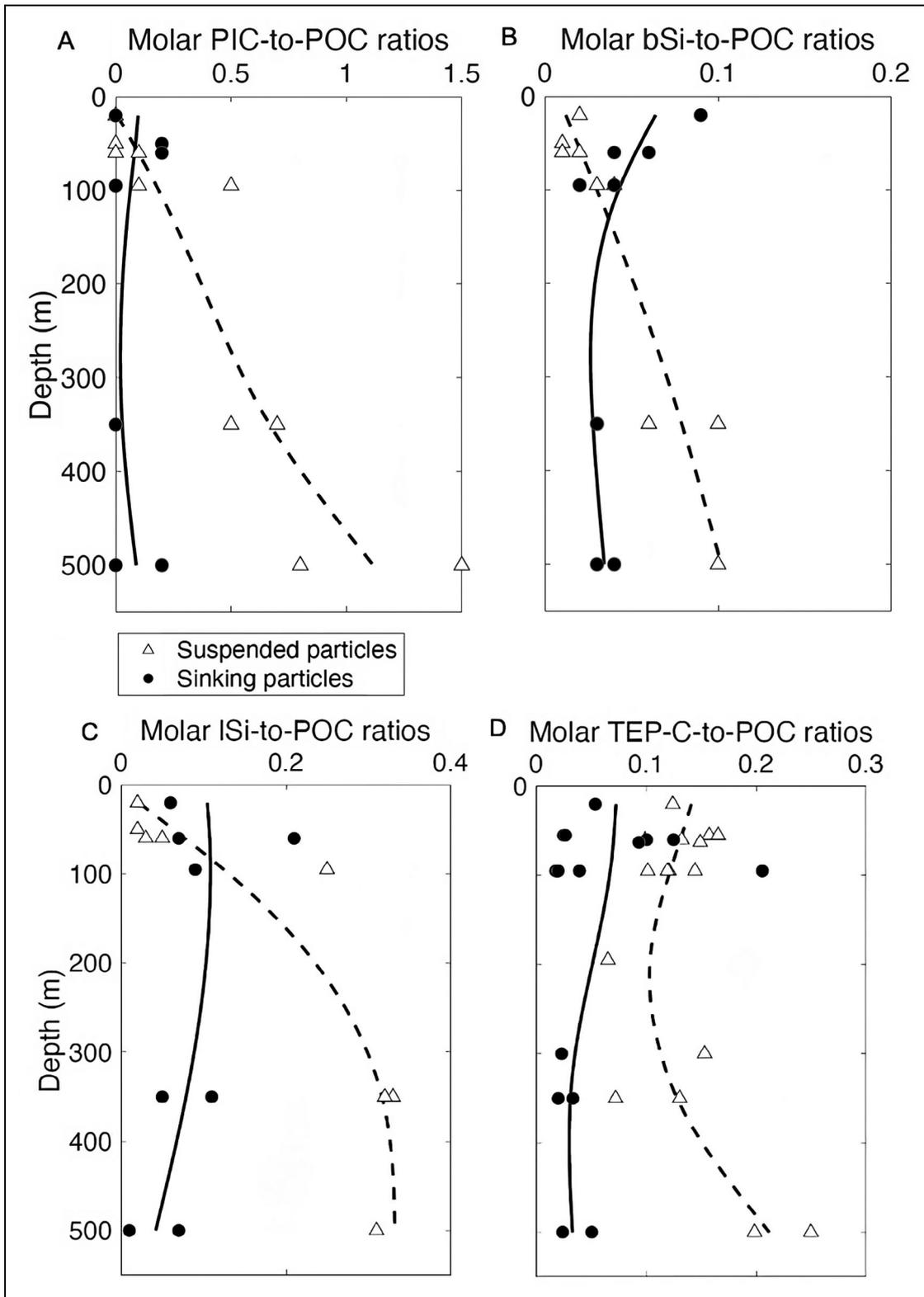


Figure 3. Ratios of ballast minerals and TEP to POC in suspended and sinking particles with depth. Depth profiles of molar ratios of A) particulate inorganic carbon to particulate organic carbon (PIC:POC), B) biogenic silica to POC (bSi:POC), C) lithogenic silica to POC (lSi:POC) and D) transparent exopolymer particles to POC (TEP-C:POC) calculated for suspended (white triangles) and sinking (black circles) particles. Dashed and continuous lines are smoothing spline used to enhance visualization of trends and thus do not have statistical significance. Outliers of the suspended molar bSi-to-POC ratio (0.35 at 500 m) and sinking PIC-to-POC ratio (12.4 at 350 m) have been removed to better display depth trends, which are not affected by their exclusion.

Background suspended and sinking bSi concentrations and their contribution to total bSi concentrations did not change significantly with depth between 50 m and 500 m ($R^2 = 0.06\text{--}0.18$, $p = 0.17\text{--}0.49$, $n = 11$; **Figure 2C**). Suspended particles stored on average $83\% \pm 9\%$ ($n = 10$) of the total background bSi pool. Molar bSi-to-POC ratios associated with background suspended particles increased significantly with depth between 50 m and 500 m ($R^2 = 0.84$, $p < 0.001$, $n = 8$), whereas ratios of sinking particles remained constant ($R^2 = 0.16$, $p = 0.32$, $n = 8$). Furthermore, molar bSi-to-POC ratios of sinking particles were on average higher than the ratios associated with suspended particles above 95 m ($n = 3$), and lower between 350 and 500 m ($n = 4$). Ratios above and below 95 m were statistically different (paired t-test, $p = 0.01$ and $p = 0.008$, respectively; **Figure 3B**).

Suspended and sinking lSi concentrations and relative contribution to the total lSi pool showed high variability and did not display a significant trend with depth ($R^2 = 0.004\text{--}0.19$, $p = 0.18\text{--}0.85$, $n = 11$; **Figure 2D**). Suspended lSi accounted on average for $82\% \pm 19\%$ ($n = 10$) of the total lSi pool. Molar lSi-to-POC ratios associated with suspended particles increased significantly with depth between 20 and 500 m depth ($R^2 = 0.76$, $p < 0.005$, $n = 8$). For sinking particles, molar lSi-to-POC ratios displayed the tendency of decreasing with depth between 20 m and 500 m, although the trend was not statistically significant ($R^2 = 0.25$, $p = 0.21$, $n = 8$; **Figure 3C**). Ratios between suspended and sinking particles differed statistically below the euphotic zone (paired t-test, $p < 0.01$), with suspended particles characterized by consistently higher ratios than sinking particles.

Suspended TEP decreased significantly with depth ($R^2 = 0.53$, $p = 0.001$, $n = 16$) and, like POC, displayed the sharpest decrease between 50 m and 95 m. On average, $95\% \pm 4\%$ of TEP was suspended, and sinking TEP was often at or near detection (average = $0.3 \pm 0.2 \mu\text{g XGeq L}^{-1}$, $n = 15$; **Figure 2E**). TEP concentrations measured in the MSCs were in line with the concentrations measured in the water collected with the CTD rosette (Figure S3). After converting TEP to TEP-C, we estimated, in 11 of 15 deployments, that $15\% \pm 5\%$ of suspended POC was TEP and only $3\% \pm 1\%$ of sinking POC was TEP. In 4 observations collected above 100 m, TEP-C accounted for 13% of the sinking POC (**Figure 3D**). Ratios of TEP-C to POC associated with suspended and sinking particles were statistically different (paired t-test, $p < 0.001$, $n = 15$).

Background POC, TEP, bSi and lSi concentrations in the suspended and sinking particle pools did not display a significant variability over time at 50–65 m, 95 m or 300–500 m (t-test, 95% confidence). Temporal trend for PIC could not be tested owing to the limited number of observations available.

To provide an overall assessment of the relative changes in the measured biogeochemical composition of suspended and sinking particles with depth, we summed the background cruise-wide averaged concentrations of organic TEP-C, POC and PON, and ballast minerals and evaluated the differences in their relative contributions (**Figure 4**). We found that the composition of suspended

particles was dominated by POC ($62\% \pm 1\%$, $n = 2$) in the euphotic zone and on average ($n = 3$) by POC ($30\% \pm 12\%$), lSi ($36\% \pm 8\%$) and PIC ($17\% \pm 9\%$) in the upper mesopelagic, whereas sinking particles were on average ($n = 5$) composed mainly of POC ($50\% \pm 10\%$), followed by lSi ($20\% \pm 7\%$), bSi ($14\% \pm 7\%$) and PON ($9\% \pm 3\%$) throughout the water column. The relative contribution of TEP-C in suspended particles was on average twice that in sinking particles (**Figure 4B**).

3.4. Constraining the particle sinking velocity

The settling time experiments showed no consistent differences in the fraction of sinking particles to the whole particle population (suspended plus sinking) as a function of settling time (t-test, 95% confidence). After 1, 2 and 4 hours of settling, sinking POC made up 10%, 11% and 10%, and sinking PON 6%, 7% and 8%, of the whole particle population (Table S6). Sinking bSi made up 23%, 25% and 25%, whereas sinking TEP made up 6%, 3% and 5%; (Table S6). Thus, the concentrations of POC, PON, bSi and TEP in sinking particles were effectively the same regardless of the settling time. However, our experiment was limited to only two casts within the euphotic zone; hence, we cannot assume that all sinking particles collected had the potential to sink within one hour at 36 m d^{-1} . We therefore present fluxes calculated assuming the standard sinking velocity of 18 m d^{-1} , and we reinforce that these fluxes represent a lower bound as suggested by our settling time experiments (**Figure 5**). Background POC fluxes averaged 4.3 ± 2.5 ($n = 9$), 3.1 ± 1.5 ($n = 7$) and 3.1 ± 1.1 ($n = 6$) $\text{mmol C m}^{-2} \text{ d}^{-1}$ at 50–65 m, 95 m, and 300–500 m, respectively. When including the outliers, the estimates increased to 7 ± 10 ($n = 10$), 9 ± 18 ($n = 8$) and 4 ± 2 ($n = 7$) $\text{mmol C m}^{-2} \text{ d}^{-1}$, respectively, at these same depth intervals. Fluxes of bSi averaged 0.2 ($n = 3$), 0.2 ($n = 3$) and 0.1 ($n = 4$) $\text{mmol Si m}^{-2} \text{ d}^{-1}$ and lSi fluxes 0.3 ($n = 4$), 0.4 ($n = 3$) and 0.2 ($n = 4$) $\text{mmol Si m}^{-2} \text{ d}^{-1}$, at 50–65 m, 95 m and 300–500 m, respectively.

4. Discussion

In this discussion, we first put our results into the overall cruise context and then focus on the causes that drive the differences between the suspended and sinking particles as measured with the MSC. Specifically, we discuss why—despite all particles being small—some particles sank while others remained suspended. Furthermore, we discuss the potential mechanisms that can explain the presence of small, slowly sinking particles in the mesopelagic. We finally address several aspects of the methodology by comparing sinking particle fluxes derived from different methods and interpreting the observed outliers in our data set and their implications, including the potential role of “patchiness” in ocean particle distributions.

4.1. Comparison with other particulate biochemical measurements made during EXPORTS: Consistency in responses by size

A variety of methods and sampling equipment were used to measure the biogeochemical composition of particulate matter during the first EXPORTS field campaign (Siegel et

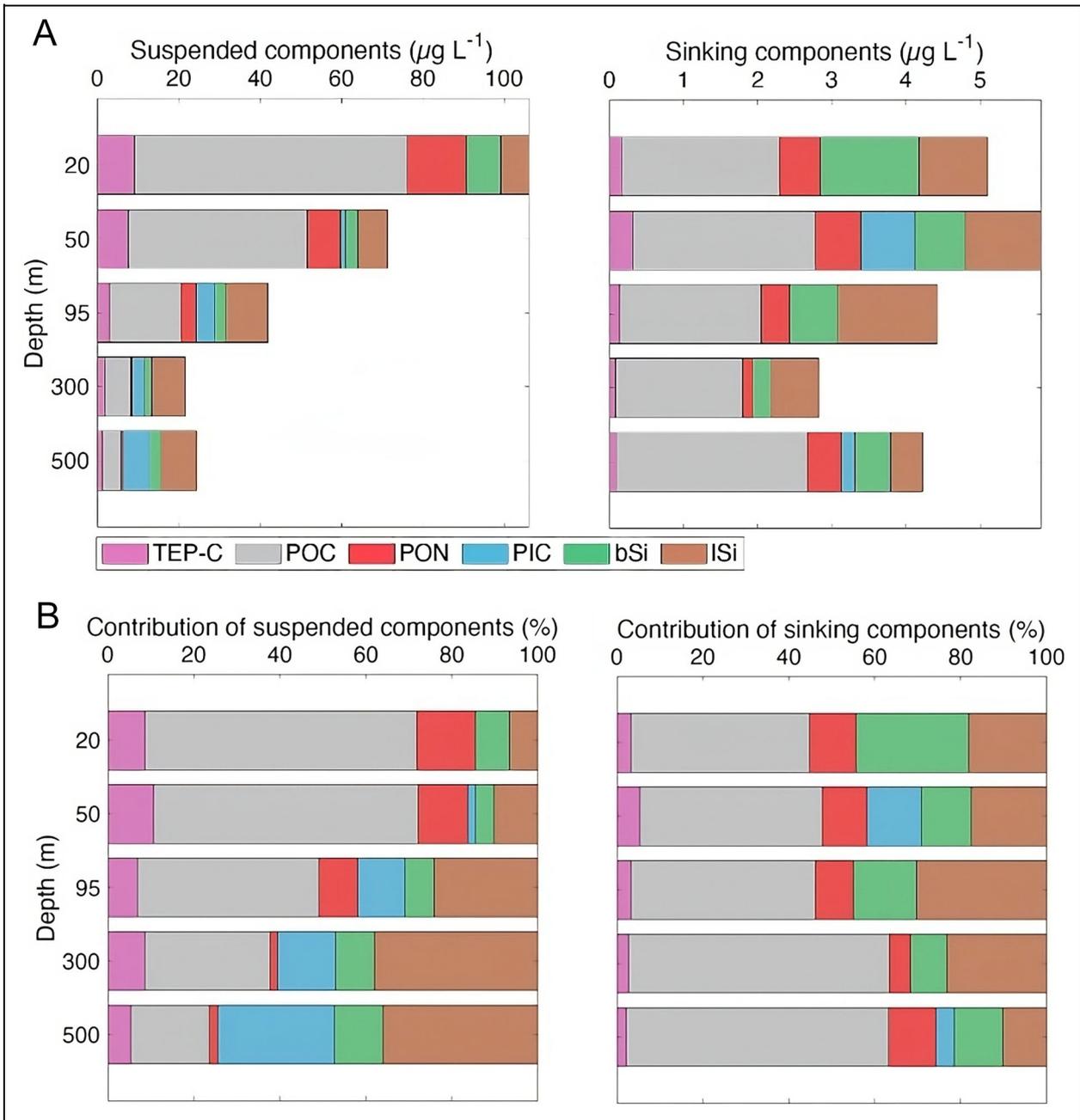


Figure 4. Concentrations of organic and inorganic components in suspended and sinking particles and contributions to totals. Bar plots display A) the summed biogeochemical concentrations (in $\mu\text{g L}^{-1}$) of the measured organic (TEP-C, POC, PON) and inorganic (PIC, bSi and ISi) components and B) their relative contributions (%) in (left) suspended and (right) sinking particles at five depth layers (50–65 m, 95 m, 300–350 m and 500 m). Biogenic silica (bSi) and lithogenic silica (ISi) were converted to mass units using a molar mass of 61 g mol^{-1} . Here we display particulate organic carbon (POC, grey) as total POC minus transparent exopolymer particle carbon (TEP-C). The compositional plots display background concentrations; i.e., outliers were removed.

al., 2021). Values of POC and PON measured in the MSC T_0 fraction were slightly higher than those obtained from the 12 L Niskin bottles sampled from the CTD/rosette system from the same ship (Graff et al., n.d.). The differences between the two measurements may be explained by a combination of the following: 1) under-sampling of sinking particles by Niskin bottles compared to the MSC, 2) slight overestimation of MSC POC values due to a possibly higher POC blank than the one used to correct the

measured POC masses (Section 2.4), and 3) spatiotemporal differences in sampling (Graff et al., n.d.).

Our PIC concentrations were low but consistent with low productivity regimes in the global ocean (Mitchell et al., 2017) and complementary measurements made at Station P during EXPORTS (Roca-Martí et al., 2021), suggesting a limited presence of calcifying microorganisms. In situ pump observations showed low PIC concentrations and small contributions to particle stocks during EXPORTS

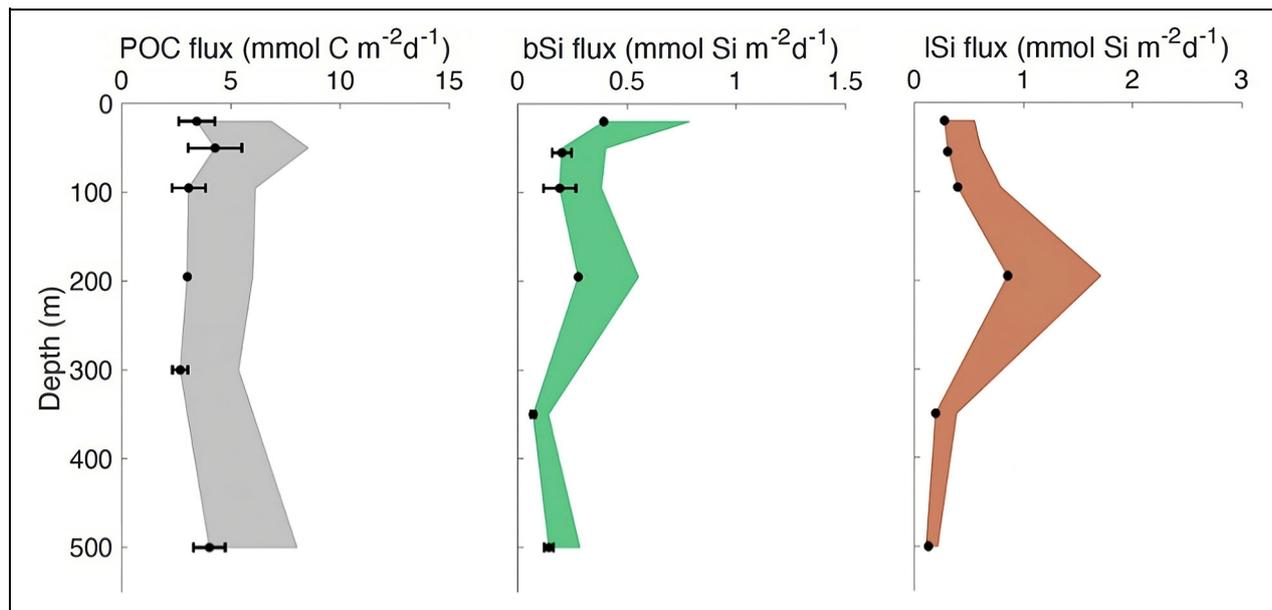


Figure 5. Calculated fluxes of particulate organic carbon, biogenic and lithogenic silica with depth. Plots represent fluxes of particulate organic carbon (POC, grey), biogenic silica (bSi, green) and lithogenic silica (lSi, brown) calculated using the background biogeochemical concentrations (outliers removed) and a conservative sinking velocity of 18 m d^{-1} . The filled area represents the upper bound fluxes estimated using a sinking velocity of 36 m d^{-1} . The values are cruise-wide averages calculated for five depth layers (50–65 m, 95 m, 195 m, 300–350 m and 500 m). Error bars are standard deviations averaged within each depth layer and thus reflect the dataset variability rather than the propagated uncertainty of each datapoint. Only one observation is available for each biogeochemical component at 195 m and only one for bSi and lSi at 20 m; hence, these depths are not well represented by our dataset.

(Roca-Martí et al., 2021). Our PIC estimates were higher than the in situ pump observations, which may be attributed to the use of a larger filter pore size with in situ pumps (QMA; $1.0 \mu\text{m}$ nominal pore size) compared to the smaller pore size of glass fiber filters used with Niskin bottles and MSC analyses (GF/F; $0.3 \mu\text{m}$ nominal pore size after combustion; Nayar and Chou, 2003; Graff et al., n.d.). Indeed, during EXPORTS, most of the PIC was associated with the smallest size particle fraction measured by in situ pumps (i.e., in the $1\text{--}5 \mu\text{m}$ fraction rather than the $5\text{--}51 \mu\text{m}$ or $>51 \mu\text{m}$ fraction; Roca-Martí et al., 2021).

Our measurements of bSi standing stocks were in good agreement with measurements performed on seawater collected with Niskin bottles (Brzezinski et al., 2022) and measurements obtained with in situ pumps (Roca-Martí et al., 2021), which used similar pore sizes (0.6 , 0.6 and $0.8 \mu\text{m}$, respectively). Our molar bSi-to-POC ratios associated with suspended and sinking particles were in the same range as the $1\text{--}51 \mu\text{m}$ particle size fractions (bSi: POC = $0.03\text{--}0.16$; Roca-Martí et al., 2021), except for one outlier (0.35 at 500 m ; Section 4.5). Molar bSi-to-POC ratios measured from larger sized particles with in situ pumps and drifting sediment traps were higher (Estapa et al., 2021; Roca-Martí et al., 2021). This comparison suggests that the MSC sampled on average small particles ($<51 \mu\text{m}$) and under-sampled large particles, and that using GF/F filters allowed a better representation of particles $<1 \mu\text{m}$ in diameter than in situ pumps. Overall, the concentrations and flux values (see also

Section 4.4) obtained by the MSCs agreed with other measurements obtained during the cruise; we are therefore confident that the MSC observations are representative of the conditions present in situ during our visit.

4.2. Partitioning of TEP and ballast minerals in suspended and sinking particles

When comparing sinking to suspended particles, we expected to find either larger particles or a higher ratio of ballast materials to POC (or both) in the sinking fraction. However, neither expectation was met (Figures 1, 3 and 4). Both fractions were characterized by small particles which, from a simplistic view, would suggest that sinking particles contained a higher fraction of ballast material than suspended particles. Contrary to this idea, however, suspended particles were characterized by the higher ratio of ballast material in the mesopelagic. This finding begs the question of why the small non-ballasted particles sank (and, why the ballasted particles did not sink).

The partitioning of particles into suspended and sinking pools must have been controlled by another factor. So far, we looked at the composition in context of the traditional constituents: POC, PIC and silicate. However, the molecular makeup of POC can have a large effect on particle density. For example, diatoms have been shown to be positively buoyant (i.e., float; Villareal, 1988; Moore and Villareal, 1996; Woods and Villareal, 2008); however, the phytoplankton community consisted predominantly of very small non-diatom cells (McNair et al., 2021). Alternatively, TEP are

positively buoyant and thus could reduce the sinking velocity of aggregates (Engel and Schartau, 1999; Azetsu-Scott and Passow, 2004). Overall, we observed low concentrations of water column TEP between 5 m and 500 m ($17.3\text{--}1.2 \mu\text{g Xgeq L}^{-1}$). This result is in line with low productivity systems such as the Southern Ocean (from undetectable values to $48 \mu\text{g Xgeq L}^{-1}$; Ortega-Retuerta et al., 2009), the tropical western Pacific Ocean ($5.3\text{--}40 \mu\text{g Xgeq L}^{-1}$; Yamada et al., 2017), the Eastern Mediterranean Sea ($5.7\text{--}25.1 \mu\text{g Xgeq L}^{-1}$; Ortega-Retuerta et al., 2019) and the Indian and subtropical South West Pacific oceans ($<20 \mu\text{g Xgeq L}^{-1}$; Engel et al., 2020). Despite the observed low TEP concentrations, TEP-C accounted for approximately 15% of the suspended POC pool. According to theoretical calculations, a 1 mm aggregate composed solely of TEP and diatoms can sink only if less than 5% of its carbon content consists of TEP (Mari et al., 2017). Here we show that the relative contribution of TEP-C was on average three times that threshold (15%) in suspended particles, while in sinking particles on average only 3% of the POC was TEP. While the model used diatoms as the primary particle pool, in our case most of the suspended particle pool consisted of very small cells (*Synechococcus* spp, picoeukaryotes and nanoeukaryotes; McNair et al., 2021), and possibly fragments of old cells, minerals, and detritus. Nonetheless, our data support the model implication (Mari et al., 2017) and provide evidence that the chemical composition of POC, and especially the contribution of organic exudates, is critical to understanding particle sinking velocity.

Hence, the higher TEP-to-POC ratio in suspended particles compared to sinking particles may have led to the difference in the partitioning of the two particle fractions as collected by the MSC by reducing the sinking velocity of small, ballasted particles that in the absence of TEP would have been part of the collected sinking fraction. Whereas the suspended POC was associated with ballasting material and consisted of a large fraction of TEP, the sinking POC consisted of relatively small fractions of ballasting material and TEP. This result suggests that the ratio of ballasting material to POC cannot be used as a sole predictor for sinking velocity, but that organic carbon composition needs to be considered.

The importance of TEP for potentially reducing sinking velocity and thus flux was first suggested by Mari et al. (2017), and here we present the first in situ measurements suggesting that high TEP concentrations reduce particle sinking velocities. Yet, our observations are limited to one field campaign only, and hence we cannot generalize. We observed this phenomenon in a low productivity system where particle concentrations were low and TEP concentrations were high. Our dataset was collected during late summer, when the system was characterized by low concentrations of chlorophyll *a*, nutrients, particles, and ballast minerals (Roca-Martí et al., 2021; Siegel et al., 2021; Brzezinski et al., 2022). The TEP-to-POC ratio may have been higher compared to other seasons, due to stressful conditions for phytoplankton growth and high light levels (Ortega-Retuerta et al., 2009), implying that the observed mechanisms could be seasonal (Mari et al., 2017). Regardless, our data suggest that future biological pump studies

should characterize POC composition, including TEP, to help gain a mechanistic understanding of how these gels influence particle sinking velocities and, in turn, the role of particle dynamics in ocean biogeochemical cycles across different productivity systems and seasons.

4.3. Potential mechanisms explaining small particles at depth

Our observations suggest that suspended particles were increasingly reworked with depth; e.g., a larger fraction of POC was remineralized with depth, leading to the relative increase in the ratio between ballasting material and POC with depth. Sinking POC did not decrease with depth, suggesting that either the attenuation of the sinking particle population was negligible, or an input of sinking material balanced the expected losses. If we assume that sinking particles collected at 500 m were produced at 30 m (within the mixed layer) and sank at 18 m d^{-1} , those particles would require 26 days to reach 500 m. We can estimate the loss rate assuming a temperature-dependent remineralization rate of 0.04 d^{-1} measured experimentally using a temperature of 7°C (average temperature between 30 and 500 m from CTD data) and a Q_{10} of 3.5 (Iversen and Ploug, 2013; Giering et al., 2017). If particles were to sink undisturbed, 30% of the POC would have been remineralized by bacteria during that time window (26 days). Yet, such a decrease was not observed.

One theoretical explanation for a lack of flux attenuation of sinking particles would be rapid physical transport processes (Omand et al., 2015; Giering et al., 2016; Siegel et al., 2023). Particle subduction or convective mixing can be excluded, however, as during our visit density stratification beneath the mixed layer was strong and consistent and lateral density gradients were weak (Siegel et al., 2021).

Alternatively, an input of sinking particles at depth may have balanced their loss. Large sinking phytodetrital aggregates were rare, implying that disaggregation of sinking aggregates was not the prevailing source of small sinking particles. However, if suspended POC existed as loosely packed aggregates within a buoyant TEP matrix (e.g., low-density aggregates; Mari et al., 2017), their disaggregation would allow dense components to sink, albeit at a relatively slow velocity. Such disaggregation could be caused by zooplankton (Passow and Alldredge, 1999) or by microbially mediated degradation processes (Passow, 2002). During microbially mediated degradation, lighter C-components may be consumed preferentially, leaving denser and more recalcitrant material in the sinking fraction (Hamanaka et al., 2002). In fact, extracellular particulate carbohydrates released by phytoplankton (i.e., TEP) are remineralized by bacteria at a faster rate than non-TEP carbon (i.e., 0.53 and 0.21 d^{-1} , respectively; Harvey et al., 1995; Mari et al., 2017).

Particle flux was dominated by fecal pellets during EXPORTS (approximately 80%; Durkin et al., 2021; Steinberg et al., 2023). Specifically, mini-pellets (ESD $<100 \mu\text{m}$) contributed up to 46% of the total carbon flux in the upper mesopelagic (Durkin et al., 2021), with mesozooplankton and salp pellets contributing the majority of the sinking flux (Durkin et al., 2021; McNair et al., 2023). Fragmentation of fecal pellets, e.g., due to sloppy feeding or

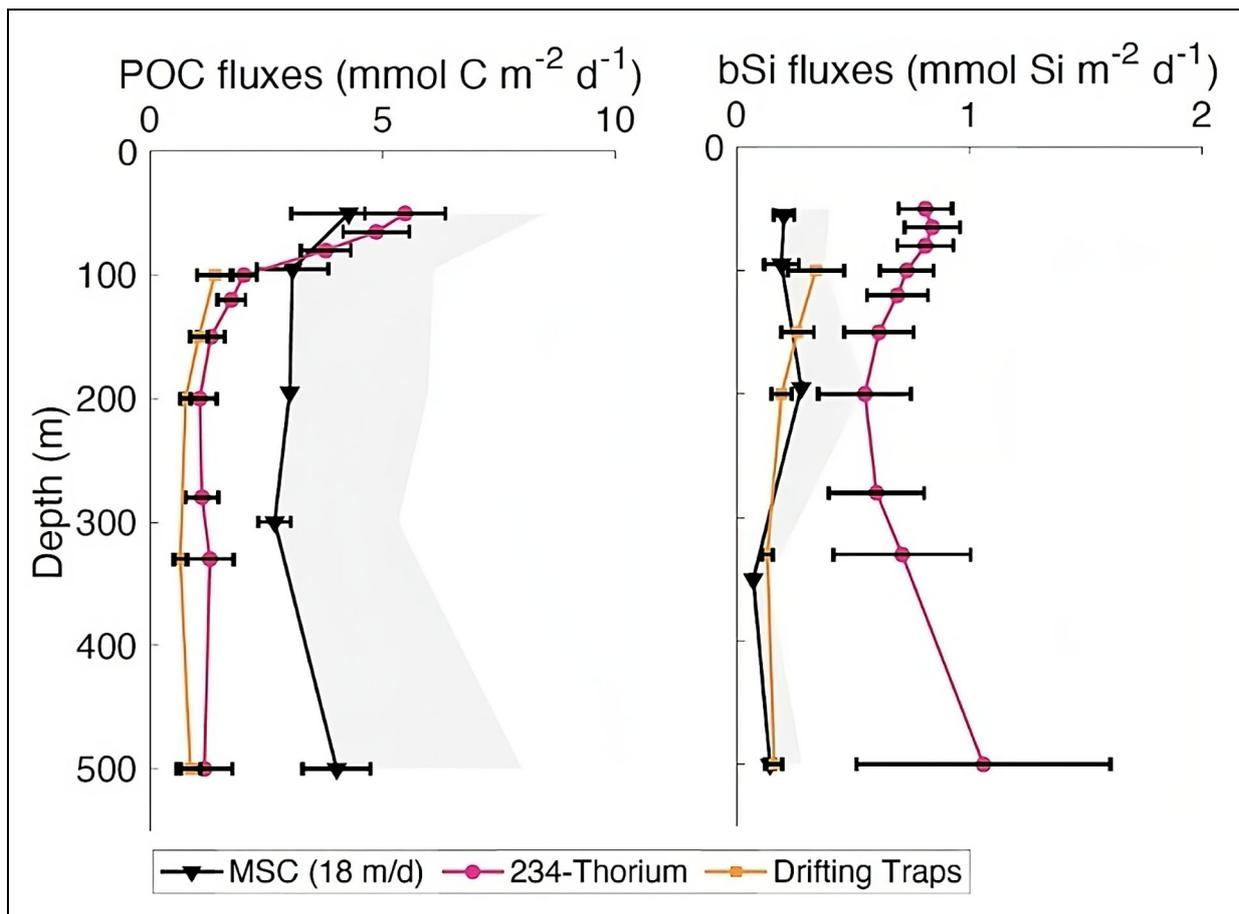


Figure 6. Comparison of particulate organic carbon and biogenic silica fluxes estimated using different approaches during EXPORTS. Depth profiles of fluxes of (left) particulate organic carbon (POC) and (right) biogenic silica (bSi) obtained from the Marine Snow Catchers (MSC), assuming sinking velocities of 18 m d^{-1} (black triangles) to 36 m d^{-1} (filled area), from Thorium-234 assessment (pink circles; Buesseler et al., 2020), and from drifting sediment traps (orange squares; Estapa et al., 2021). The MSC fluxes are calculated using the background biogeochemical concentrations (outliers removed). The 195 m depth is not well represented as only one POC and one bSi observation are available for that depth.

swimming motions (Steinberg and Landry, 2017), could have produced small and dense particles, which may have constituted the bulk of the small sinking particle pool we collected. Such pellet fragments would likely contain a high percentage of organic carbon and a low percentage of TEP, similar to our sinking particle pool. Though we did not observe large fast-sinking pellets in the MSCs, this absence could have been caused by an overall low abundance of pellets or because the MSCs were deployed during the daytime when a large fraction of the zooplankton community likely resided at depth (e.g., Steinberg et al., 2023).

Microzooplankton grazing of suspended POC, and the resulting production of mini-pellets (Stemmann et al., 2004), may have also contributed to the production of small, dense sinking particles. Consumption of small particles by zooplankton and incorporation of their carbon and biogenic silica into sinking particles (Dagg et al., 2003) is especially important for carbon flux if it occurs within relatively short-path food webs (Richardson, 2019). This mechanism could also have been important during our study: compound-specific isotope analyses performed

during our field campaign (Shea et al., 2023) found that the mesopelagic zooplankton food web at Station P was based mainly on small particles ($<6 \mu\text{m}$).

Although we cannot say with certainty why sinking flux of POC did not decrease with depth, likely a series of biologically mediated aggregation or fragmentation processes led to a replenishment of the small sinking particle pool at depth. The described mechanisms are potentially significant contributors in dictating the efficiency of the biological carbon pump, especially in stable low-productivity systems, characterized by small particles in low concentrations.

4.4. Comparison of fluxes derived from different methods during EXPORTS

Our background POC fluxes compared to the cruise mean POC fluxes, obtained using both neutrally buoyant and surface-tethered sediment traps (Estapa et al., 2021) and water column Thorium-234 assessment (Buesseler et al., 2020), were similar in the upper 100 m, but larger below 100 m (Figure 6). These differences between the

estimates for depths >100 m existed even when the lower-bound estimate (assuming a sinking velocity of 18 m d^{-1} ; Section 3.4) was used. In contrast, bSi flux estimates obtained from the MSC were in good agreement with those derived from the traps, but lower than the Thorium-234-based values (Roca-Martí et al., 2021; **Figure 6**).

These three approaches for determining sinking particle fluxes differ in the design, spatiotemporal resolutions, and size of collected particles; thus, they may not be directly comparable, and comparisons should be made cautiously. The approaches mainly diverge in four ways: temporal coverage, spatial coverage, and minimum and maximum size of collected particles. Temporally, the MSC provided virtually instantaneous estimates, whereas drifting sediments trap (Gardner, 1977) and water column Thorium-234 carbon flux determinations (Buesseler et al., 1992) integrate over periods of 3–6 days (time to collect sinking particles) and 24 days (the half-life of ^{234}Th), respectively. Spatially, the MSC deployments have the smallest spatial resolution among these methods, with 39 discrete deployments as each MSC deployment assesses the flux from a single, approximately 100 L sample. Drifting sediment traps sampled sinking particles from an area $\leq 10 \text{ km}^2$ (Siegel et al., 2008). Due to the long integration times and abundance of samples (nearly 1000), ^{234}Th particle fluxes average over even larger spatial scales. In terms of minimum size of collected particles, differences in pore sizes of filters can lead to differences in measured biogeochemical concentrations. Here we measured POC using filters with a pore size of approximately $0.3 \mu\text{m}$, while POC from sediment traps (Estapa et al., 2021) and water column Thorium-234 samples (Buesseler et al., 2020) were determined using filters with a pore size of approximately $1 \mu\text{m}$. The filter pore sizes used to estimate bSi were $0.6 \mu\text{m}$, approximately $1 \mu\text{m}$ and $0.8 \mu\text{m}$ for MSC, sediment traps and Thorium-234, respectively. Additionally, drifting sediment traps often underestimate small particles due to hydrodynamics (Buesseler et al., 2007). In terms of maximum size of collected particles, the MSC likely under-sampled the rare larger particles as it collects a limited amount of seawater. During EXPORTS, sediment trap samples were highly impacted by zooplankton “swimmers” and fluxes were corrected to account for the removed biomass (Estapa et al., 2021).

The potential sources of discrepancies between fluxes measured from sediment traps and water column Thorium-234 were addressed in Estapa et al. (2021). Briefly, Thorium-234 fluxes measured in sediment traps were roughly 3-fold smaller than water column Thorium-234 fluxes. The different temporal coverages did not play a major role due to the stability in production and export before the EXPORTS cruise (McNair et al., 2023). The mismatch was attributed largely to under-sampling of both small particles ($<32 \mu\text{m}$) due hydrodynamic biases and rare, large particles ($>1 \text{ mm}$) and zooplankton active-migrant flux by the sediment traps (Estapa et al., 2021). The size of particles collected in the polyacrylamide gel traps, which ranged from 75 to $1461 \mu\text{m}$ (median of $282 \mu\text{m}$), supported this hypothesis

(Estapa et al., 2021). Estimates from the MSC account for the contribution of those small particles close to approximately $0.3 \mu\text{m}$. Thus, the discrepancy between MSC and sediment traps may be partially explained by an under-characterization of very small ($<1 \mu\text{m}$) particles by the traps. We cannot assess whether this statement is applicable when comparing to Thorium-234-based POC fluxes. Th-derived POC fluxes were estimated assuming the POC/Th ratios of 5–51 μm particles, which should be representative of all sinking particles regardless of their size (Buesseler et al., 2020).

However, the MSCs did not capture large, rare particles such as aggregates, salp fecal pellets or the active flux due to migration (Steinberg et al., 2023). We would therefore have expected to see the opposite trend: higher flux measured by traps if large, rare particles played an important role in overall flux at the site. This comparison suggests that POC flux from the MSCs is at least partially complementary to those measured from Thorium-234 and traps. Most importantly, it suggests that small sinking particles were a relevant part of the sinking POC flux in the upper mesopelagic zone, likely exceeding the contribution of rare, large sinking particles. The fact that the MSCs and sediment traps produced similar estimates of bSi fluxes reinforced our finding that the population of sinking particles collected by the MSCs included small sinking particles of organic carbon missed by the other methods, whereas bSi, which was mostly associated with slightly larger particles (Estapa et al., 2021; Roca-Martí et al., 2021; Brzezinski et al., 2022), was equally sampled by all three methods.

4.5. Outliers —Patchiness or artifacts?

The dataset obtained from the MSC holds the potential of highlighting patchiness in the ecosystem through the collection of spatially heterogeneous features. Patchiness in the ocean exists both vertically and horizontally spanning from the microscale to the mesoscale (Cassie, 1962; Siegel, 1998; Robinson et al., 2021) and is in general difficult to map with most oceanographic approaches (McNair et al., 2023). Several of our biogeochemical measurements resulted in values considerably higher than average concentrations for their collection depth (**Figure 2** and Table S5). These “outliers” may be attributed to patchiness or could be due to methodological artifacts. Methodological artifacts could be caused by misfiring of the MSCs at a shallower depth than intended or by contamination of the filter. The latter is improbable as replicate filters and comparisons between T_o and suspended plus sinking particle fractions would have indicated “contamination.” Additionally, filters were always inspected visually for visible particles, such as macrozooplankton, which, if present, were removed. These outliers were specific to the MSC; no outliers were detected by the 12 L Niskin bottles of the CTD on board R/V *Roger Revelle*.

Three of the five outliers in POC were observed on August 16, at 55 m, 95 m, 195 m, one on August 21 at 195 m, and one on September 1 at 350 m. The outlier concentrations of sinking POC measured at 55 m and 95 m, which were an order of magnitude higher than any

other sinking POC values, are likely reflective of in situ patchiness: the respective T_0 and suspended POC concentrations were also within the upper range of the values measured at those depths. The POC measured in the T_0 fraction at 55 m equals the sum of POC measured in the suspended and sinking particle fraction, confirming that the MSC samples were not contaminated. Associated sinking PON values were also marked as outliers and the molar C-to-N ratios were reasonable (10.4 and 12.5 at 55 m and 95 m, respectively), albeit somewhat higher than those of the T_0 and suspended fractions (7.3 and 6.4 at 55 m and 8.3 and 9.7 at 95 m, respectively). Lastly, while the associated sinking TEP concentrations were high (with the observation at 95 m being an outlier), suspended TEP concentrations agreed with TEP measured from water collected with Niskin bottles at those depths (Figure S3). These observations and the fact that the MSC deployment depths were chosen specifically to target “interesting” areas as seen by the CTD or UVP profiles, lead us to believe that the 100 L sample we collected may have included patches of unusually high biochemical concentrations.

The three outlier POC concentrations for suspended POC at 195 m, 195 m and 350 m were associated with outlier values of PON, and could reflect POC and PON concentrations measured at 50–65 m. However, the associated suspended TEP concentrations (2.8, and 3.1 $\mu\text{g XGeq L}^{-1}$) suggest samples stemmed from below 50–65 m (Figure S3). Although uncertain, these concentrations could also reflect patchiness.

One value of biogenic silica (176 nmol Si L^{-1}) at 500 m was >3-fold higher than the bSi measured on other days at that depth either with the Niskin bottles or the MSC (57 and 45 nmol Si L^{-1} , respectively). However, associated POC concentrations were consistent with the deployment depth, and the molar bSi-to-C ratio of this observation (0.35) matched the one measured for particles >5 μm (bSi: POC = 0.16–0.94) collected with in situ pumps (Roca-Martí et al., 2021). Thus, we assume that this sample included a higher-than-average presence of diatoms or Rhizaria. Hot spots of bSi accumulation have previously been found in low productivity systems (Crombet et al., 2011), and this depth was targeted because the UVP profile directly before the MSC deployment indicated a Rhizaria maximum. Similarly, the elevated PIC concentration associated with sinking particles (21.5 $\mu\text{g PIC L}^{-1}$) could potentially be attributed to the presence of foraminifera test fragments or coccoliths.

In summary, the “outliers” measured with the MSC are likely reflective of patchiness in concentrations of small particles in this low productivity system. Patchiness in the distribution of salp swarms was also a prevalent feature during this study (Steinberg et al., 2023). The sporadic nature of patchiness is challenging to quantify and its importance with respect to standing stocks and fluxes of an entire ecosystem hard to assess, especially in a low productivity system.

5. Summary and conclusions

Small, slowly sinking particles are usually under-sampled by canonical particle collection methods and thus have

been poorly characterized. Hence, little is known about their origins, biogeochemical composition, and role in the ocean biogeochemical cycles.

Our study shows that suspended and sinking particles were small and similarly sized. Unexpectedly, sinking particles were not characterized by a higher contribution of ballast materials (bSi, lSi and PIC), which would have justified their sinking behavior. However, they displayed low TEP-to-POC ratios in comparison to suspended particles. This observation suggests that high TEP contribution may have increased the residence time of suspended POC and thus reduced sinking particle fluxes, impacting the efficiency of the biological carbon pump. Hence, we suggest that the composition of POC (i.e., presence of gels like TEP) should be measured routinely to assess how it affects the sinking of particles.

Our data together with other findings from the field campaign support the hypothesis that the pool of small sinking particles in the mesopelagic formed via fragmentation of sinking fecal pellets and zooplankton-mediated repackaging of suspended particles into fecal pellets. A smaller contribution to the small sinking particulate pool may have been provided via the disaggregation of low-density suspended aggregates. Such mechanisms may be especially important in low productivity systems during late summer months.

A comparison between particle fluxes calculated from the MSC and fluxes measured with drifting sediment traps and Thorium-234 suggests that small slowly sinking particles exceeded the contribution of rare, large sinking particles to POC flux in the upper mesopelagic. Our data suggest that such flux of small sinking particles tends to be underestimated by trap and Thorium approaches. Potentially this flux of small sinking particles may contribute towards resolving the budget discrepancies between sinking flux and metabolic carbon requirements in the mesopelagic (Burd et al., 2010).

Data accessibility statement

All data presented here are publicly available on the NASA data repository, SeaBASS along with all other EXPORTS data. The data can be accessed here: <https://seabass.gsfc.nasa.gov/cruise/EXPORTSNP>.

Supplemental files

The supplemental files for this article can be found as follows:

Figures S1–S3.DOCX; Tables S1–S6.DOCX.

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Competing interests

The authors declare no competing interests.

Author contributions

Contributed to conception and design: UP, DAS.

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Contributed to analysis and interpretation of data: ER, UP, DAS, SLCG.

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