



# Sea ice-associated algae and zooplankton fecal pellets fuel organic particle export in the seasonally ice-covered northwest Labrador Sea

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# 11 Abstract.

- 12 Ocean warming and Arctic sea ice decline are expected to affect biological pump efficiency by altering the timing, quantity, quality,
- 13 and composition of export production. However, the origins and composition of sinking organic matter are still understudied for
- the oceans generally, and in ice-covered areas especially. Here we use compound-specific isotope analysis (CSIA) of amino acids
- 15 (AAs) to investigate the sources and composition of exported organic matter from a sediment trap-derived time-series of sinking
- 16 particles collected at depths of 469 m and 915 m at the edge of Saglek Bank in the northwest Labrador Sea from October 2017 to
- 17 July 2019. The outer edge of Saglek Bank is located at the confluence of cold and fresh Arctic outflow and relatively warmer
- 18 Atlantic waters. The area is subject to seasonal sea ice cover and is a biological hotspot for benthic organisms including deep-sea
- 19 corals and sponges. Sea ice was present for ~50-60% of the deployment days in both cycles. Phytoplankton blooms at our study
- 20 site cooccurred with the onset of sea ice melt. Microalgal taxonomy indicated the presence of ice-associated diatoms in the sinking
- 21 particles during the spring bloom in 2018, confirming that sea ice algae contributed to the organic particle export at our study site.
  22 Abundant copepods and copepod nauplii caught in the sediment traps was consistent with a high abundance of copepods in
- overlying epipelagic waters. Stable carbon isotopes ( $\delta^{13}$ C) of essential amino acids (EAAs) of the sinking particles revealed a
- 24 potentially important contribution of sea ice algae as a carbon source at the base of the food web to sinking particles, with only
- 25 minor modification by microbial resynthesis. Stable nitrogen isotopes ( $\delta^{15}N$ ) of AAs of sinking particles provided independent
- 26 evidence of the minor bacterial degradation and Bayesian mixing models based on normalized  $\delta^{15}$ N-AA values revealed dominant
- 27 contribution of fecal pellets (76-96%) to the sinking particles. Our study demonstrates the importance of sea ice algae and fecal
- 28 pellets to the biological pump in the seasonally ice-covered northwest Labrador Sea, with sea ice algae exported either directly via
- 29 passive sinking or indirectly via zooplankton grazing, with fecal pellets dominating the organic particle fluxes.

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# 32 1 Introduction

33 The ocean's biological pump sequesters about 10 Pg of carbon per year, which represents up to one-third of anthropogenic carbon 34 emissions to the atmosphere (Sabine et al., 2004; Sabine and Tanhua, 2010). The pump operates by exporting unrespired particulate 35 organic matter (POM) via three pathways: passive sinking ("gravitational pump"), active transport by animals ("migrant pump"), 36 and physical mixing ("mixing pump"; Volk and Hoffert, 1985; Turner, 2015; Nowicki et al., 2022). Despite its importance in 37 global biogeochemical models, the proportional contribution of each biological pump export pathway is poorly estimated. The 38 effects of climate change (i.e., rising temperatures, enhanced ocean stratification and acidification, and changing nutrient 39 availability) compound the uncertainties in biological pump functioning and efficiency (Finkel et al., 2010; Passow and Carlson, 40 2012; Arrigo and van Dijken, 2015). Arctic and subarctic seas are thought to represent a globally important carbon sink (Bates and 41 Mathis, 2009; MacGilchrist et al., 2014) due to high rates of primary productivity across the expansive continental shelves (Kaltin 42 and Anderson, 2005; Harrison et al., 2013), high nutrient availability (Kaltin et al., 2002, Murata and Takizawa, 2003), and sea-43 ice and solar dynamics (Rysgaard et al., 2007; Harrison et al., 2013). However, ongoing declines in seasonal sea ice extent and 44 enhanced freshwater input due to global warming has affected particulate organic carbon (POC) export in these regions (Steele et 45 al., 2008; Lalande et al., 2009b; Grebmeier, 2012; Arrigo and van Dijken, 2015). An increase in primary production has been 46 observed in the Arctic (Arrigo and van Dijken, 2015), which could lead to an increase in POC export (Lalande et al., 2009a, b). 47 On the other hand, the loss of sea ice has also been shown to cause a reduction in surface nutrient availability and a shift in plankton 48 community structure from larger celled plankton to picoplankton, which may decrease the POC export to the deep sea (Li et al., 49 2009; Finkel et al., 2010). The accelerating loss of sea ice necessitates a deeper understanding of factors controlling POC export 50 in ice-covered ecosystems and responses.

- 51 In remote regions, sinking particles are typically collected, measured, and characterized using moored sediment traps (Honjo and 52 Doherty, 1988), especially in regions where seasonal sea ice cover constrains remote sensing of ocean colour, preventing the 53 detection of under-ice algal blooms (Strass and Nöthig, 1996; Yager et al., 2001; Fortier et al., 2002; Mundy et al., 2009; Arrigo 54 et al., 2012, 2014). Export flux measurements, phytoplankton and zooplankton identification, and geochemical analyses of sinking 55 particles provide information on 1) sources, cycling, and fate of key elements in the ocean, e.g., carbon and nitrogen, and their 56 biogeochemical roles; and 2) processes and mechanisms that control the fluxes of sinking particles. Nevertheless, it is difficult to 57 identify and quantify the main sources contributing to sinking particles collected in sediment traps. Microalgae and zooplankton 58 taxonomic enumeration can be complicated by large morphological variability within and between species, lack of taxonomic 59 expertise, and inconsistency in identification methods (McQuatters-Gollop et al., 2017). Estimates of biomass or particulate organic 60 carbon (POC) based on composition and abundance data can also be confounded by the wide range in cell sizes within and between 61 functional groups (e.g., diatoms, dinoflagellates, etc; Leblanc et al., 2012). Combining taxonomic methods with biomarker 62 approaches will enhance quantification of the composition of exported sinking particles. This improvement is key to better 63 understanding and predicting the responses of Arctic/subarctic biological pump, marine ecosystems, and benthic communities to 64 a rapidly changing climate.
- Stable isotopes of carbon ( $\delta^{13}$ C) and nitrogen ( $\delta^{15}$ N) have been widely used to investigate biogeochemical processes in marine ecosystems (Peterson and Fry, 1987; Altabet et al., 1999). Isotopic compositions of sinking organic matter collected in long-term
- 67 sediment traps record information about sources and cycling of carbon and nitrogen on timescales of months to years (Nakatsuka





68 et al., 1997; Altabet et al., 1999; Montes et al., 2013). However, traditional measurements of stable isotope values of bulk organic 69 matter can be difficult to interpret due to confounding factors of source variability and heterotrophic modifications (Boecklen et 70 al., 2011). Recent advances in carbon and nitrogen compound-specific isotope analysis (CSIA) of amino acids (AAs) has helped to address these complications (Larsen et al., 2009; Larsen et al., 2013; McMahon et al., 2013; Batista et al., 2014; Ohkouchi et 71 72 al., 2017; Close, 2019; Shen et al., 2021). Interpretation of  $\delta^{13}$ C-AA analysis is based on the classification of AAs into essential 73 and non-essential groups. Essential amino acids (EAAs) are synthesized only by autotrophs, and hence their  $\delta^{13}$ C values remain 74 unchanged with trophic transfers (Larsen et al., 2013; McMahon et al., 2013). Diverse biosynthetic pathways and associated 75 isotopic effects result in distinct and consistent  $\delta^{13}$ C-EAA signatures of different primary producers, which are reflected in  $\delta^{13}$ C-76 EAA patterns of consumers (Hayes, 1993; Larsen et al., 2009). Interpretation of  $\delta^{15}$ N-AA, on the other hand, is based on different 77 groupings that are independent of those based on  $\delta^{13}$ C. The  $\delta^{15}$ N values of source AAs (SrcAAs) undergo little or no  $\delta^{15}$ N 78 enrichment during trophic transfers while those of trophic AAs (TrAAs) are enriched with increasing trophic position or modified 79 by microbial processing (McClelland & Montoya, 2002). Hence, the complementary but fully independent  $\delta^{13}$ C-AA and  $\delta^{15}$ N-AA 80 analyses offer detailed insights about carbon and nitrogen origins, trophic changes, and microbial degradation and allow for more 81 accurate and detailed interpretation of stable isotope data (McMahon et al., 2013; McMahon & McCarthy, 2016).

82 The goal of this study is to investigate the organic carbon and nitrogen sources and trophic and microbial processing of sinking

83 particles in the seasonally ice-covered northwest Labrador Sea. Two sediment traps were deployed at different depths (469 m and

84 915 m, respectively) at the outer edge of Saglek Bank from October 2017 to August 2018 and from August 2018 to July 2019.

85 Measurements of particle flux, phytoplankton and zooplankton taxonomy, and bulk stable isotopes were combined with CSIA-AA

86 to characterize the origins, alteration, and transport mechanisms of sinking particles. Together these data help constrain the sources

87 and relative contributions of different components to the sinking particles in the northwest Labrador Sea.

# 88 2 Material and methods

# 89 2.1 Study site

90 Located in the north-western section of the Atlantic Ocean, the Labrador Sea is a high-latitude marginal sea of the Atlantic Ocean 91 and an important transition zone connecting Arctic and subarctic ecosystems, bounded by the Labrador and Newfoundland shelves 92 to the west and the southern tip of Greenland to the east (Fragoso et al., 2017). The overall circulation of the Labrador Sea is 93 cyclonic, with layers of distinct water masses in the boundary currents. The upper layer of boundary currents comprises cold and 94 fresh Arctic waters from mixing between the water entering Baffin Bay from eastern Davis Strait, that is cooled in the winter as it 95 circulates within the bay, and the inflow from the Arctic Ocean, that are mainly identified as the Baffin Island Current (BIC) and the Labrador Current (LC; Fig. 1; Tang et al., 2004). Underneath are the relatively warm and saline waters of West Greenland 96 97 Current (WGC), with a dominant inflow through eastern Davis Strait and a branch deflecting westwards forming a counter-98 clockwise gyre (Irminger Current) while the remaining waters propagate north (Fig. 1; Yashayaev, 2007; Frajka-Williams et al., 99 2009). In Baffin Bay, below the WGC water lies the Baffin Bay Deep Water at 1200-1800 m and the Baffin Bay Bottom Water 100 below 1800 m, which have no direct access to the Arctic and Atlantic Oceans due to the relatively shallow sill depths of the Arctic 101 channels and Davis Strait (Tang et al., 2004). The inner shelf of the Labrador Sea is covered by landfast ice with drifting pack ice 102 cover further offshore from January to May each year (Hall et al., 1999; National Snow and Ice Data Center). The study area lies 103 in a transitional zone between the ice-dominated Boreal Polar Province (BPLR) of the Labrador Shelf, and the largely ice-free and





105 drifts from the north (Baffin Bay) and the west (Hudson Strait; Marson et al., 2018). Differences in physical-chemical parameters 106 shape variability in phytoplankton community composition and the seasonality of phytoplankton blooms between and within these 107 two provinces (Fratantoni and Pickart, 2007; Yashayaev, 2007; Frajka-Williams and Rhines, 2010; Fragoso et al., 2017). 108 Phytoplankton blooms start on the Labrador shelf from April to early May. These blooms are typically dominated by diatoms, 109 favoured by high silicate concentrations in Arctic waters (Fragoso et al., 2018), and facilitated by vigorous tidal mixing in Hudson 110 Strait (Drinkwater and Harding 2001). From mid-May to June, weaker blooms occur in the central Labrador Sea induced by 111 increased light levels (Frajka-Williams and Rhines, 2010). The strong bottom currents on the Labrador shelf expose hard substrates, 112 providing suitable habitats for deep-sea corals and sponges (Wareham & Edinger, 2007). Observations of abundant and diverse 113 deep-sea corals and sponges are reported at Saglek Bank, forming important habitats for many fish and invertebrate species 114 (Wareham & Edinger, 2007; Dinn et al., 2020). With ongoing global warming and sea ice decline, ice conditions at the study site 115 are projected to be impacted, with up to 70% decrease in winter sea ice extent and a shorter winter ice duration (Han et al., 2019),

116 which may have cascading effects on the phytoplankton community, export fluxes, and in turn, benthic communities.

## 117 2.2 Remote sensing

- 118 Satellite derived daily-average sea ice concentrations were retrieved at a 12.5 km resolution from the Centre ERS d'Archivage et
- 119 de Traitement (CERSAT) of the French Research Institute for the Exploration and Exploitation of the Sea (IFREMER) and
- 120 averaged for a  $3^{\circ} \times 3^{\circ}$  grid centred at the mooring location (59-62°N, 60-63°W; Fig. 1). Weekly-average chlorophyll *a* (chl *a*)
- 121 concentrations for the same selected grid (59-62°N, 60-63°W) were derived from Ocean Color (Aqua MODIS, 4 × 4 km; missing
- 122 data are due to obstacles in observing conditions; https://oceancolor.gsfc.nasa.gov/) and BIO remote sensing group
- 123 (https://github.com/BIO-RSG). The large areal grid (333 km × 172 km) grid used for sea ice and chl *a* retrieval was necessary to
- 124 smooth out data coverage gaps.

# 125 2.3 Sediment trap and zooplankton net sampling and processing

- 126 Two sediment traps were deployed off Saglek Bank on the northwest Labrador slope from October 2017 to August 2018 at a depth 127 of 469 m (bottom depth: 509 m; 60.47°N, 61.26°W; SB-500) and from August 2018 to July 2019 at a depth of 915 m (bottom depth: 1015 m; 60.46°N, 61.16°W; SB-1000) during the annual ArcticNet expeditions of the CCGS Amundsen (Table 1; Fig. 1). 128 Both sediment traps (Technicap PPS 3/3; 0.125 m<sup>2</sup> aperture) were equipped with a baffle sieve (diameter: 9.5 mm) covering the 129 130 trap opening and 24 sampling bottles (265 ml) programmed to rotate every 14 days. Before deployment, each sampling bottle was 131 filled with filtered seawater with a salinity > 36 PSU adjusted using sodium chloride. Sodium borate-buffered formaldehyde (2% 132 v/v) was added to preserve the collected particles during and after deployment. In August 2018 and July 2019, both sediment traps 133 were recovered before the final sampling bottle rotation, therefore the last sampling bottles remained open and were excluded from 134 the study. Zooplankton were sorted from half of the volume of each trap sample under a stereomicroscope and preserved in 4% 135 formalin solution. Zooplankton were counted and identified to the lowest taxonomic level possible (Dezutter et al., 2021). 136 Following the removal of zooplankton, subsamples were analyzed for total particulate matter (TPM), particulate organic carbon (POC) and particulate nitrogen (PN) and converted to daily fluxes (mg m<sup>-2</sup> d<sup>-1</sup>) following Dezutter et al. (2021). Microalgal cells 137 138 were enumerated and counted to the lowest taxonomic level possible using an inverted microscope (Wild Herbrugg) in accordance 139 with Lund et al. (1958). For each sample, a minimum of 100 cells were enumerated along three transects (Genin et al., 2021) at a 140 magnification of 20x for the 2017-2018 deployment and of 60x for the 2018-2019 deployment. Microalgal counts were converted 141 to daily fluxes (cells m<sup>-2</sup> d<sup>-1</sup>). For bulk and amino acid stable isotope analyses, samples were washed with Milli-Q water, freeze-
- 142 dried, and homogenized prior to further analyses.



153



- 143 Zooplankton was opportunistically sampled with a multi-net plankton sampler (Hydrobios, mesh size 200 µm) close to the HiBio-
- 144 C mooring site (60.47°N, -61.16°E) on July 25, 2021, during the annual CCGS *Amundsen* expedition. Once retrieved, zooplankton
- from the 200-0 m layer were gently poured into incubation chambers filled with filtered seawater (0.2  $\mu$ m) to clear their gut content
- 146 for 6-12 hours (Doherty et al., 2021; Stamieszkin et al., 2021). After incubation, zooplankton were transferred into a labelled plastic
- 147 bag and immediately frozen and stored at -20 °C until further analysis.
- 148 In the laboratory, 30 to 50 copepods were subsampled from the zooplankton samples using a binocular microscope (Motic SMZ-
- 149 168). The subsampled copepods were freeze-dried and homogenized until further analysis. Detritus aggregates (clumps of dark-
- 150 color materials; Fig. 4b) that were collected along with the zooplankton from the incubation chambers were hand-picked into a
- 151 Petri dish filled with Milli-Q water under the microscope. The collected detritus aggregates were then filtered onto 0.7-µm GF/F
- 152 filters (Whatman) and freeze-dried until further analysis.



Figure 1 Map and inset detail of study site off Labrador and Nunavut, Canada (a) with bathymetry (grey contours), simplified representation of the main boundary currents (arrows) and sediment trap locations (circles), and (b) cross section of the continent slope where the two sediment traps (SB-500 and SB-1000) were deployed and their depth profiles. Black rectangle represents the area where sea ice concentration and surface chlorophyll *a* concentration were derived for (59-62°N, 60-63°W). Abbreviations: BIC, Baffin Island Current; LC, Labrador Current; IC, Irminger Current; WGC, West Greenland Current. Figure made with Ocean Data View, Schlitzer, 2021.





Trap	Mooring	Latitude	Longitude	Trap depth	Deployment date	Recovery date*	Deployment days*	Date of sea ice freeze-up (> 10%)	Date of sea ice melt (<10%)	Deployment days with >10% ice cover (%)	Average areal extent of i cover during ice-in
		(°N)	(°W)	(m)							
SB-500	HiBioA-17	60.47	61.26	469	16-Oct-17	16-Jul-18	274	01-Jan-18	30-Jun-18	62%	$44 \pm 19\%$
	HiBioC-18	60.46	61.16	015	03-Aug-18	18-Jun-19	319	19-Dec-18	28-May-19	49%	$42 \pm 14\%$





# 162 **2.4 Bulk and amino acid** $\delta^{13}$ **C and** $\delta^{15}$ **N analysis**

163 Subsamples were taken for bulk and amino acid stable isotope analyses (Table S1, S2). Bulk  $\delta^{13}$ C and  $\delta^{15}$ N were measured in 164 duplicate or triplicate based on the available dry weight of sinking particles. Subsamples for bulk  $\delta^{13}$ C analysis were decarbonated 165 in 4% HCl at 80°C for one hour and rinsed in Milli-Q water repeatedly until pH neutralized, following the method of Galy et al. (2007). Decarbonated samples were dried at 50°C overnight. Subsamples for bulk  $\delta^{15}N$  analysis were not pre-treated. Bulk  $\delta^{13}C$ 166 167 and  $\delta^{15}$ N analysis were carried out at the Canada Excellence Research Chairs Laboratory at Dalhousie University using an 168 Elemental Analyzer (EA; Elementar microcube) coupled with an Isotope Ratio Mass Spectrometer (IRMS; Isoprime 100). Isotopic 169 values were calibrated to co-analyzed reference material and reported in delta notation ( $\delta$ ) in units of per mill "%" relative to Vienna PeeDee Belemnite (VPDB) and air for  $\delta^{13}$ C and  $\delta^{15}$ N, respectively. Analytical precision based on differences between 170 171 sample replicates was < 0.15 ‰ for both  $\delta^{13}$ C and  $\delta^{15}$ N.

Approximately 5 mg of organic carbon per sample was required for  $\delta^{13}$ C-AA and  $\delta^{15}$ N-AA analyses. Samples with insufficient 172 173 organic carbon were combined with adjacent samples, if available. Each sample composite included not more than three samples 174 (6 weeks) in total. Combined periods are January 31 to March 3, 2018; April 3 to May 1, 2018; and August 3 to September 18, 175 2018. Sample composites were hydrolyzed in 6-N HCl (Sigma-Aldrich) at 110 °C for 20 hours, purified and derivatized in batches 176 of 6-7 samples following previously established protocols (Silfer et al. 1991; Larsen et al. 2013; Batista et al. 2014; McMahon et al. 2015; Chen et al. 2022). Each sample batch contained two calibration standards of AA mixtures with known  $\delta^{13}$ C and  $\delta^{15}$ N 177 178 values and a lab standard (homogenized Chlorella powder; Organika) processed in the same way as samples. Samples were 179 measured in triplicate for  $\delta^{13}$ C and  $\delta^{15}$ N, bracketed by triplicate injections of calibration standards, using a Trace 1310 Gas 180 Chromatograph (GC) coupled with a Delta V IRMS (Thermo Scientific). A total of twelve AAs were typically resolved: alanine 181 (Ala), glycine (Gly), proline (Pro), valine (Val), leucine (Leu), isoleucine (Ile), asparagine + aspartic acid (Asx), threonine (Thr), 182 serine (Ser), glutamine + glutamic acid (Glx), phenylalanine (Phe), and lysine (Lys). Final  $\delta^{13}$ C values were corrected for the 183 isotopic fractionation and the introduction of carbon atoms during derivatization according to Silfer et al. (1991) and normalized 184 against instrument drift between successive triplicate injections of the amino acid standard by applying linear regression (Yarnes 185 and Herszage, 2017). Final  $\delta^{15}$ N values were calibrated based on the offset between known and measured values of calibrated 186 standards and normalized against instrument drift by applying linear regression. The average reproducibility of  $\delta^{13}$ C was  $\pm 0.3\%$ 187 for the internal standard Nle (n = 12), and from  $\pm 0.3\%$  (Ala, Leu, Asp, and Phe) to  $\pm 0.8\%$  (Lys) for AA standards, respectively (n = 12 for each AA). The average reproducibility of  $\delta^{15}N \text{ was } \pm 0.4\%$  for the internal standard Nle (n = 11), and from  $\pm 0.2\%$ 188 189 (Glu) to  $\pm 0.6\%$  (Ala, Val, and Ile) for AA standards, respectively (n = 11 for each AA). The absolute (mol) and relative (mol%) 190 abundances of amino acids were estimated by calibration of mass 44 peak areas against that of internal standard (Nle) using a 191 relative response factor for each AA, following Kaiser and Benner (2005). Yields of total hydrolysable AAs (THAAs) were 192 determined by dividing the total abundance of AAs by the amount of hydrolyzed material.

# 193 2.5 Calculations and statistical analyses

194 To account for the spatio-temporal variations in baseline  $\delta^{13}C$  (Larsen et al. 2015; Chen et al. 2022), the  $\delta^{13}C$ -AA values were

195 internally normalized by subtracting the mean of 5 EAAs (Phe, Leu, Ile, Thr and Val) for each sample (denoted as normalized

- 196  $\delta^{13}$ C). Normalization accounts for influences from inorganic carbon sources and other environmental parameters, whereas the
- 197 internal variations between AAs reveal the underlying biochemical mechanisms (Larsen et al., 2015; McMahon et al., 2015; Stahl,
- 198 2021; Elliott Smith et al., 2022).





199 The  $\delta^{15}$ N values for THAAs ( $\delta^{15}$ N<sub>THAA</sub>) were calculated by summing the mol%-weighted  $\delta^{15}$ N values following McCarthy et al. 200 (2013):

201  $\delta^{15} N_{THAA} = \sum (\delta^{15} N_i \times mol\%_i)$ (1)

202 Where  $\delta^{15}N_i$  is the calibrated  $\delta^{15}N$  value of individual AA and  $mol\%_i$  is the mol% of the corresponding AA.

203 The "metazoan" trophic position ( $TP_{met}$ ) of samples was calculated based on calibrated  $\delta^{15}N$  values of Glx and Phe, following the

204 equation proposed by Chikaraishi et al. (2009) and modified by Nielsen et al. (2015):

205 
$$TP_{met} = \frac{(\delta^{15}N_{Glx} - \delta^{15}N_{Phe} - 2.9\%_0)}{6.6\%_0} + 1$$
(2)

The "protozoan" trophic position (TP<sub>pro</sub>) was calculated based on calibrated  $\delta^{15}$ N values of Ala and Phe, following Décima et al. (2017) and Décima and Landry (2020):

208 
$$TP_{pro} = \frac{(\delta^{15}N_{Ala} - \delta^{15}N_{Phe} - 3.2\%_0)}{4.5\%_0} + 1$$
(3)

Three proxies are commonly used to evaluate the degree of heterotrophic bacterial degradation in organic material, based on changes in AA composition or average deviation of  $\delta^{15}$ N-TrAAs. The percentage of N represented by THAA in total N (THAA-N%) is used as a degradation indicator, where THAA-N% below 38% is considered to indicate diagenetic alteration (Cowie and Hedges, 1992). THAA-N% was calculated, following:

213 
$$THAA - N\% = \frac{\sum (mol_i \times n_i)}{DW \times TN\% \div M_N} \times 100\%$$
(4)

Where n is the number of N atoms in individual AA,  $mol_i$  is the absolute abundance of this AA, DW is the dry weight of hydrolyzed material, TN% is the weight percentage of total N, and  $M_N$  is the atomic mass of N. Similarly, the percentage of carbon represented by THAA in total organic carbon (THAA-C%) was calculated based on the number of carbon atoms, total organic carbon percentage, and the atomic mass of carbon.

The degradation index (DI) is based on the changes in the mol% of AAs with diagenetic alteration (Dauwe and Middelburg, 1998;
Dauwe et al., 1999), and was calculated following Dauwe et al. (1999):

220 
$$DI = \sum_{i} \left[ \frac{var_{i} - AVG_{i}}{STD_{i}} \right] \times fac. coef_{i}$$
(5)

Where  $var_i$  is the mol% of each AA in this dataset (Ala, Asp, Glu, Gly, Ile, Leu, Phe, Thr, and Val), and  $AVG_i$  and  $STD_i$  are the mean and standard deviation of individual AA in the reference dataset from Dauwe et al. (1999), and *fac.coef<sub>i</sub>* is the factor coefficient for the corresponding AA based on the first principal component factor from Table 1 in Dauwe et al. (1999). Note that DI was calculated without Ser in this study due to unavailability of Ser data for some samples.

The degree of heterotrophic resynthesis can also be evaluated by calculating the  $\sum V$  based on the average deviation of calibrated  $\delta^{15}N$  values of TrAAs from their mean, following the formula from McCarthy et al. (2007):

$$\Sigma V = \frac{1}{n} \sum ABS(\delta^{15}N_i - \delta^{15}N_{mean})$$
(6)





- 228 Where n is the number of TrAAs used in the calculation,  $\delta^{15}N_i$  are the calibrated  $\delta^{15}N$  values of each TrAA (Ile, Leu, Asx, Glx,
- where it is the number of Third's used in the calculation,  $b = h_1$  are the calculated b = h values of each Third' (he, Ecu, Asx, Gix,
- Pro, and Ala) and  $\delta^{15}N_{mean}$  is the average  $\delta^{15}N$  of these AAs. Higher  $\sum V$  values suggest a higher degree of heterotrophic resynthesis (McCarthy et al., 2007).
- 231 Differences in CSIA-AA patterns and parameters were tested between sediment traps, detritus, copepods, and other published end-
- 232 members using Two Sample T-tests. Prior to carrying out the Two Sample T-test, the residuals of normalized  $\delta^{13}$ C and calibrated
- 233  $\delta^{15}$ N values were tested for univariate normality with Shapiro-Wilks test (R package: stats). To compare the normalized  $\delta^{13}$ C
- signatures between sediment traps and sea ice and pelagic algae, principal component analysis (PCA, R package: FactoMineR)
- and linear discriminant analysis (LDA, R package: MASS) were performed in R version 4.1.1 with Rstudio interface version
- 236 1.4.1717. Standard ellipse areas (SEA) were plotted for each group's bivariate means in the PCA, each enclosing ~40% of the data
- 237 (Batschelet 1981; Jackson et al., 2011).
- 238 Bayesian mixing models were performed in R (MixSIAR; Stock and Semmens, 2016) to estimate the proportional contributions
- 239 of three end-members (phytoplankton, fecal pellets, and zooplankton) using Phe-normalized  $\delta^{15}$ N-Ala and  $\delta^{15}$ N-Thr to sediment
- traps. The models were parameterized using means and standard deviations of chosen biotracers with an uninformative prior and
- 241 a MCMC chain length of 10<sup>6</sup> (Stock and Semmens, 2016). Model convergence was tested with Geweke and Gelman-Rubin
- 242 diagnostic tests (Stock and Semmens, 2016). We report the median of results for each end-member to account for skewed
- 243 distributions of model results.

## 244 3 Results

## 245 3.1 Environmental Conditions

- 246 Sea ice in the study area began forming in early January for both sediment trap deployments and persisted until June in 2018, and
- May in 2019 (Table 1, Fig. 2a). Sea ice concentration during the ice season averaged around 40% during both deployments (Table
- 248 1).
- 249 Remotely sensed chl a concentration showed peaks in late April 2018 and in early May 2019, when ice concentration was still >
- 250 25% (Fig 2a). The timing of these blooms coincided with the onset of > 15 hours of daylight (Astronomical Applications
- 251 Department of the United States Naval Observatory, "Duration of Daylight"), followed by smaller peaks in chl a concentrations
- $(< 2 \text{ mg m}^{-3})$  during the open-water period (defined as sea ice concentration < 10%; Fig. 2a).
- 253



										SB-1000																				SB-500		Trap
Ξ	10	9	8	7	6	5	4	3*	2*	1*	Annua	Mean ±	18	17	16	15	14	13*	12*	Ξ	10	9*	8*	7	6	5	4	ω	2	1		Cup
03-Jan-19	19-Dec-18	03-Dec-18	18-Nov-18	03-Nov-18	19-Oct-18	03-Oct-18	18-Sep-18	03-Sep-18	19-Aug-18	03-Aug-18	l flux (g m <sup>-2</sup> yr <sup>-1</sup>	ESD	01-Jul-18	16-Jun-18	01-Jun-18	16-May-18	01-May-18	17-Apr-18	03-Apr-18	18-Mar-18	03-Mar-18	15-Feb-18	31-Jan-18	16-Jan-18	01-Jan-18	16-Dec-17	01-Dec-17	16-Nov-17	01-Nov-17	16-Oct-17		Date opened
19-Jan-19	03-Jan-19	19-Dec-18	03-Dec-18	18-Nov-18	03-Nov-18	19-Oct-18	03-Oct-18	18-Sep-18	03-Sep-18	19-Aug-18	)		16-Jul-18	01-Jul-18	16-Jun-18	01-Jun-18	16-May-18	01-May-18	17-Apr-18	03-Apr-18	18-Mar-18	03-Mar-18	15-Feb-18	31-Jan-18	16-Jan-18	01-Jan-18	16-Dec-17	01-Dec-17	16-Nov-17	01-Nov-17		Date closed
1029	210	282	798	1181	719	1436	1085	587	248	243	214		167	139	86	285	132	384	294	379	179	449	785	603	1007	591	1116	982	959	1955	$(mg m^{-2} d^{-1})$	TPM
22.9	5.2	9.9	16.8	25.2	18.8	30.4	23.7	16.3	9.3	8.4	4.3		4.4	5.3	4.3	12.5	4.6	8.5	7.3	7.8	5.7	10.5	15.1	10.6	12.9	14.3	22.2	19.3	22.8	25.5	$(mg C m^{-2} d^{-1})$	POC
-24.6	-26.0	-25.4	-25.1	-25.5	-25.4	-25.0	-25.2	-25.0	-25.9	NA		$\textbf{-24.9}\pm0.6$	-24.8	-25.8	-23.8	-24.3	-24.9	NA	-25.4	NA	-24.6	NA	-25.6	-25.0	-24.6	-24.7	-25.3	-25.3	NA	NA	(‰)	Bulk 8 <sup>13</sup> C
7.5	NA	7.6	NA	6.7	NA	6.7	6.0	8.6	NA	NA		$6.9\pm0.9$	9.3	6.1	5.6	5.9	6.3	6.3	8.1	7.7	7.2	6.7	6.3	7.2	7.0	7.5	6.8	6.8	NA	NA	(‰)	Bulk δ <sup>15</sup> N
2.2	NA	NA	2.1	NA	2.2	NA	2.1		2.3			$2.0\pm0.1$	NA	NA	NA	2.0	NA	<u>t:</u>	с С	2.0	NA	<u>.</u>	ر ۱	NA	NA	NA	2.0	2.1	NA	NA		TPmet
2.9	NA	NA	2.6	NA	2.6	NA	2.5		NA			$2.4\pm0.1$	NA	NA	NA	2.0	NA	2.0	y (	2.4	NA	2.7	20	NA	NA	NA	2.3	2.3	NA	NA		$TP_{pro}$
2.8	NA	NA	2.1	NA	2.2	NA	2.3		1.5			$2.0\pm0.2$	NA	NA	NA	1.8	NA	1.7	10	2.2	NA	1.0	1 0	NA	NA	NA	1.8	2.2	NA	NA	(%)	Σv
-1.3	NA	NA	-0.8	NA	-0.9	NA	-0.7		0.0			$\textbf{-0.8}\pm0.3$	NA	NA	NA	-0.4	NA	-0.0	208	-0.9	NA		NA	NA	NA	NA	-1.1	NA	NA	NA		DI
129.3	NA	NA	71.0	NA	86.0	NA	78.2		120.0			$97.8\pm46.0$	NA	NA	NA	170.8	NA	/ 4.4	74 4	69.9	NA		NIA	NA	NA	NA	59.1	114.9	NA	NA	(µmol g <sup>-1</sup> )	THAA yield
17.9	NA	NA	9.4	NA	11.6	NA	11.5		NA			$14.3\pm3.6$	NA	NA	NA	18.9	NA	12.7	104	NA	NA			NA	NA	NA	10.7	15.2	NA	NA	(%)	THAA-C
53.1	NA	NA	NA	NA	NA	NA	30.3		NA			$38.3\pm8.7$	NA	NA	NA	42.4	NA	20.1	<u> 28 1</u>	36.4	NA	TANT.	NA	NA	NA	NA	33.6	50.7	NA	NA	(%)	THAA-N







								•	periods (cups)	nt sampling	ned for adjacer	es were combin	*CSIA-AA valu
									7.2	438	)	al flux (g m <sup>-2</sup> yr <sup>-1</sup>	Annu
$24.9\pm15.9$	$9.2\pm4.7$	$65.8\pm39.5$	$\textbf{-0.3}\pm1.0$	$2.0\pm0.4$	$2.5\pm0.3$	$2.0\pm0.2$	$6.8\pm1.1$	$\textbf{-25.2}\pm0.5$				$\pm$ SD	Mear
NA	NA	NA	NA	NA	NA	NA	6.5	-25.2	28.4	2036	18-Jun-19	03-Jun-19	21
19.9	7.8	36.8	0.0	1.9	2.3	1.9	5.3	-24.9	35.1	2784	03-Jun-19	19-May-19	20
NA	NA	NA	NA	1.6	2.0	1.8	4.5	-24.7	28.4	2241	19-May-19	03-May-19	19
NA	NA	NA	NA	NA	NA	NA	NA	-25.0	19.3	1360	03-May-19	18-Apr-19	18
NA	11.2	61.8	-1.1	1.8	2.8	2.1	NA	-24.9	13.4	884	18-Apr-19	03-Apr-19	17
9.3	3.5	12.4	2.2	1.9	2.7	2.0	7.2	-24.8	32.0	3017	03-Apr-19	19-Mar-19	16
11.7	1.9	17.5	0.5	NA	2.5	1.9	7.8	-24.5	28.4	2383	19-Mar-19	03-Mar-19	15
24.8	8.4	44.6	-1.0	1.9	2.3	2.0	7.1	-24.8	24.5	1711	03-Mar-19	16-Feb-19	14
NA	NA	NA	NA	NA	NA	NA	6.9	-25.1	11.4	631	16-Feb-19	02-Feb-19	13
NA	NA	NA	NA	NA	NA	NA	NA	-26.6	5.9	223	02-Feb-19	19-Jan-19	12

256 \*









Figure 2 Time-series of (a) satellite derived daily sea ice concentration at a 12.5 km resolution from the Centre ERS d'Archivage et de Traitement (IFREMER) and weekly-averaged chl *a* concentration derived from Ocean Color (Aqua MODIS, 4 × 4 km; missing data are due to obstacles in observing conditions; https://oceancolor.gsfc.nasa.gov/) and BIO remote sensing group (https://github.com/BIO-RSG) for the 3° × 3° grid centred at the mooring site (59-62°N, 60-63°W), (b) total particulate matter (TPM) and particulate organic carbon (POC) fluxes, (c) microalgal flux (diatoms + Chlorophyceae + flagellates) and copepod flux (including copepod nauplii), (d) bulk  $\delta^{13}$ C and average  $\delta^{13}$ C of five essential amino acids (Avg EAA; Phe, Thr, Ile, Leu, Val), and (e) bulk  $\delta^{15}$ N, average  $\delta^{15}$ N of trophic AAs (Avg TrAA), Phe, and total hydrolysable AAs (THAA) of SB-500 and SB-1000 sinking particles. Vertical error bars show ±1 standard deviation for each sample (n = 3-4). Horizontal error bars show temporal ranges of individual or combined samples (see Sect. 2.4).

266





# 267 **3.2 Particulate matter and organic carbon fluxes**

- 268 Daily fluxes of TPM shared similar trends with POC for each cycle (Fig. 2b). In SB-500, TPM and POC showed an overall
- decreasing trend from late October 2017 to July 2018, with a small peak in May (Fig. 2b). In SB-1000, TPM and POC peaks were
- 270 observed in early October and late March and May 2019 (Fig. 2b).

# 271 3.3 Microalgal fluxes and swimmers

- 272 Diatoms, green algae (Chlorophyceae) and flagellates composed most of the microalgal flux (~97%). Algal fluxes peaked in late
- 273 October 2017 and late May 2018 at SB-500 and in early November 2018 at SB-1000 (Fig. 2c). Peaks of diatom fluxes were
- observed in late October, 2017, and from May to June 2018 at SB-500 (Fig. 3a). Centric diatoms contributed the majority of the
- diatom export in both cycles (Fig. 3b). Shortly before the peak in diatom flux in late May 2018, surface chl *a* maximum was
- observed in April (Fig. 2a, 3a). During the peak diatom flux in late May 2018, sea ice exclusive species Nitzschia frigida and
- 277 Melosira arctica were reported (Fig. 3). Centric and pennate diatom species that are ice-associated, for example, Fragilariopsis
- spp. and *Nitzschia/Pseudo-Nitzschia* spp., were also reported during the peak flux in 2018 (Fig. 3). Relatively high fluxes of green
- algae (> 2 million cells  $m^{-2} d^{-1}$ ) were observed in late October and November and in early December 2017 at SB-500 and from
- 280 early September to early November 2018 at SB-1000 (Fig. 3a). Flagellates dominated the algal fluxes at SB-1000, contributing up
- 281 to  $\sim$ 75% of the flux (Fig. 3b).





282



Figure 3 (a) fluxes of diatoms, Chlorophyceae (listed as "unknown" in 2017-2018 cycle), and flagellates and (b) percent contribution of
 diatoms, Chlorophyceae, and flagellates in sinking particles collected in SB-500 and SB-1000 sediment traps.

Copepods and copepod nauplii dominated the zooplankton community for most of both deployment periods, except when the empty shells of pteropod *Limacina spp.* were dominant in late November 2017 and in September 2018 (data not shown). Peaks of copepod abundances were observed in early November 2017, and early April and late May 2018 at SB-500, and in early August

288 2018, and late March and late May 2019 at SB-1000 (Fig. 4a). In July 2021, large copepods, e.g., Calanus spp., dominated the

289 zooplankton community collected near the sediment trap site (Fig. 4b, c).







290

Figure 4 (a) stacked fluxes of copepods and copepod nauplii in sinking particles collected in SB-500 and SB-1000 sediment traps and example images of zooplankton collected in the northwest Labrador Sea in 2021. (b) A mixture of copepods and detritus aggregates in the multi-net samples and (c) example of individual copepod subsampled for CSIA-AA analyses.

# 294 3.4 Temporal changes in bulk and amino acid $\delta^{13}C$ and $\delta^{15}N$

- $295 \qquad \text{Bulk } \delta^{13}\text{C values for the SB-500 and SB-1000 traps were similar, varying from -25.8\% to -23.8\% and from -26.6\% to -24.5\%,}$
- respectively (Fig. 2d). The average  $\delta^{13}$ C-EAA values of the sinking particles were more variable than the bulk  $\delta^{13}$ C values,
- fluctuating from -26.0% to -22.3% with no significant difference (Fig. 2d). Bulk  $\delta^{15}$ N values of the SB-500 and SB-1000 traps
- ranged from 5.6% to 9.3% and from 4.5% to 8.6%, respectively (Fig. 2e). The  $\delta^{15}$ N-Phe values, which is commonly used to
- 299 indicate N source  $\delta^{15}$ N value, averaged 6.6 ± 0.7‰ and 6.8 ± 0.6‰ for the SB-500 and SB-1000 traps, respectively, with both





- 300 minima occurring in May shortly after the surface water chlorophyll peaks (Fig. 2e). The  $\delta^{15}$ N-TrAA values in both sediment traps
- 301 averaged ~8.0% more elevated than the  $\delta^{15}$ N-Phe, varying from 11.5% to 17.2% (Fig. 2e). The  $\delta^{15}$ N of total hydrolysable AAs
- 302 (THAA) averaged 10.5  $\pm$  1.7‰ and 10.7  $\pm$  1.2‰ for the SB-500 and SB-1000 traps, respectively, ranging between  $\delta^{15}$ N-Phe and
- $303 \qquad \delta^{15} \text{N-TrAA} \text{ (Fig. 2e)}.$

# 304 3.5 Amino acid $\delta^{13}$ C and $\delta^{15}$ N patterns

- 305 To explore potential carbon sources to export production, we compared the normalized  $\delta^{13}$ C-AA patterns with algae collected from
- 306 melted brash ice and pelagic algae collected from deep chlorophyl maximum depth in the northwest Labrador Sea and Baffin Bay
- 307 in 2019 and 2021 (see details in Chen et al., 2022). Sinking particles obtained during both sampling periods and at both depths
- 308 shared similar  $\delta^{13}$ C-EAA patterns, with  $\delta^{13}$ C values of ~-4.3‰ for Phe and Val, ~12.5‰ for Thr, ~2.9‰ for Ile and ~-6.8‰ for
- 309 Leu (Fig. 5a). The  $\delta^{13}$ C-EAA patterns of sinking particles were overall similar to those measured previously for sea ice algae (Two-
- $\label{eq:sample} 310 \qquad \text{Sample T-Test on individual EAAs, } p > 0.05 \text{ except Leu; Chen et al., } 2022 \text{) than to those of pelagic algae (< 0.05 for Phe, Thr, the sample algae (< 0.05 for Phe, the sample alg$
- 311 and Leu; Fig. 5a; Chen et al., 2022).
- 312 Patterns of calibrated  $\delta^{15}$ N-AA (Fig. 5b) were broadly similar to those for sinking particles reported in other geographical locations,
- 313 with more enriched  $\delta^{15}$ N-TrAA and more depleted  $\delta^{15}$ N-Thr compared to  $\delta^{15}$ N-SrcAA (Monterey Bay, Shen et al., 2021; Gulf of
- 314 Maine, Golombek et al., 2024). No significant differences were found in  $\delta^{15}$ N-AA values between SB-500 and SB-1000 particles
- 315 (Two Sample T-test, p > 0.05). The  $\delta^{15}N$  values of individual TrAAs fluctuated from ~12.0% to ~17.0% (Fig. 5b). The  $\delta^{15}N$
- 316 values of TrAAs and Thr for sinking particles showed significant distinctions from sea ice and pelagic algae (p < 0.05) and detritus
- 317 (p < 0.05 except Val). No significant differences were observed in  $\delta^{15}$ N-TrAAs between sediment traps and copepods (except Ala).
- 318 The  $\delta^{15}$ N-Phe of sinking particles was comparable with sea ice algae (p > 0.05) but significantly higher than pelagic algae,
- 319 copepods, and detritus (p < 0.05; Fig. 5b).







320

321Figure 5 Normalized  $\delta^{13}$ C-AA patterns (a) and calibrated  $\delta^{15}$ N-AA patterns (b) of SB-500and SB-1000 sinking particles, copepods and322detritus collected close to the mooring site. Data are compared with normalized  $\delta^{13}$ C-AA and calibrated  $\delta^{15}$ N-AA patterns of > 3 µm and3230.2-3 µm sea ice and pelagic algae collected from the northwest Labrador Sea and Baffin Bay, respectively (Chen et al., 2022; dashed324and dotted rectangles; range: mean ±1 stdev). Error bars show ±1 standard error for each group (SB-500: n = 4-6; SB-1000: n = 7-11;325Copepods: n = 3; Detritus = 3). EAA, essential amino acid; NEAA, non-essential amino acid; TrAA, trophic amino acid; SrcAA, source326amino acid.

#### 327 **3.6 Microalgal and bacterial contribution to sinking particles**

328 To evaluate the potential contributions of sea ice and pelagic algae to the sinking particle fluxes, normalized  $\delta^{13}$ C-AA patterns

329 were compared using PCA (Fig. 6a). PCA based on normalized  $\delta^{13}$ C-EAA explained 66.3% of the total variation, with the first





- two principal components (PC1 and PC2) accounting for 36.5% and 29.8%, respectively (Fig. 6a). The standard ellipses of sinking
- particles mostly overlapped with each other as well as sea ice algae while clustered apart from pelagic algae (Fig. 6a).
- 332 To investigate the degree of bacterial biomass in sinking particles, we performed LDA based on a training dataset comprising
- eukaryotic microalgae and bacteria from Larsen et al. (2009; 2013). While bacteria and eukaryotic microalgae demonstrated
- 334 distinct  $\delta^{13}$ C-EAA patterns from each other, 13 out of 14 sinking particle samples were classified as eukaryotic microalgae with
- 335 100% probability (one classified as bacteria with 58% probability; Fig. 6b).



336

Figure 6 Principal component analysis (a) based on normalized δ<sup>13</sup>C values of five essential amino acids of sinking particles collected in
 SB-500 and SB-1000 sediment traps, > 3 μm and 0.2-3 μm sea ice algae and pelagic algae and (b) linear discriminant analysis based on
 normalized δ<sup>13</sup>C values of five essential amino acids of a training dataset comprising bacteria (open crosses) and eukaryotic microalgae
 (open diamonds) from Larsen et al. (2009; 2013). Values in parentheses of the axis titles are the percentage variation explained by each
 axis. The coloured ellipses represent standard ellipse area (SEA) for each corresponding group, containing ~40% of the data. Sea ice and
 pelagic algae data are from Chen et al., 2022.

343

The "metazoan" trophic position ( $TP_{met}$ ) values of both sediment traps averaged 2.0 (Fig. 7a). The "protozoan" trophic position ( $TP_{pro}$ ) averaged 2.4 and 2.6 for the SB-500 and SB-1000 traps, respectively, significantly different from but ranging between detritus ( $1.7 \pm 0.3$ ) and copepods ( $3.4 \pm 0.3$ ; Two Sample T-test, p < 0.01; Fig. 7b). Values of the  $\Sigma V$  parameter for microbial resynthesis for SB-500 and SB-1000 sediment traps ranged from 1.8 to 2.2‰ and from 1.5 to 2.8‰, respectively, similar to detritus (1.6-1.9‰; Two Sample T-test, p > 0.1) and slightly lower than copepods (2.2-2.7%; p < 0.05; Fig. 7c). No significant offsets were found in  $TP_{met}$ ,  $TP_{pro}$ , and  $\Sigma V$  values between SB-500 and SB-1000 sediment traps (p > 0.1).

- 350 Phe-normalized  $\delta^{15}$ N of Ala and Thr has been shown to improve characterization of potential end-member contributors to sinking
- 351 particles (Doherty et al., 2021; Chen et al., 2022; Wojtal et al. 2023). The Phe-normalized  $\delta^{15}$ N-Ala and  $\delta^{15}$ N-Thr values were
- 352 similar between SB-500 and SB-1000 sediment traps (Two Sample T-test, p > 0.1), ranging around 10.0% and -9.5%, respectively
- and overlapping with fecal pellets (p > 0.1; Fig. 7d). Copepods shared similar  $\delta^{15}$ N-Ala and  $\delta^{15}$ N-Thr values with zooplankton (p
- 354 > 0.1). Detritus values ranged between phytoplankton, fecal pellets, and degraded OM end-members (Fig. 7d).





- A three-end-member Bayesian mixing model based on Phe-normalized  $\delta^{15}$ N of Ala and Thr demonstrated a dominant contribution
- (76–96%) of fecal pellets to sinking particles in both sediment traps (Fig. 8). Degraded OM contributed 1-3% and phytoplankton
   contributed 2-17% to the sinking particles (Fig. 8). Phytoplankton contribution peaked during the spring bloom in 2018 (Fig. 2a,
- 358 3a, 8). No significant differences were found in the modelled contributions of phytoplankton, degraded OM, and fecal pellets to
- *538 53, 5).* No significant differences were found in the modelled controlutions of phytophankton, degraded Owi, and recar penets to





360

361Figure 7 δ<sup>15</sup>N-AA parameters for trophic positions and microbial resynthesis of sinking particles collected in SB-500 and SB-1000362sediment traps, detritus, and copepods (semi-transparent shapes), compared with means of phytoplankton, fecal pellets, zooplankton,363and degraded OM end-members (shapes with error bars). (a) "metazoan" trophic position (TP<sub>met</sub>), (b) "protozoan" trophic position364(TP<sub>pro</sub>), and (c) the ΣV parameter in different water layers. (d) Phe-normalized δ<sup>15</sup>N of Ala and Thr. Error bars show ±1 standard errors365for (a)-(c) and standard deviations for (d). End-member distributions are from previously published literature: McClelland and366Montoya, 2002; Chikaraishi et al., 2009; Hannides et al., 2009, 2013; Doherty et al., 2021.





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Figure 8 MixSIAR-derived relative contributions of different end-members in sinking particles. The relative N contributions from phytoplankton, fecal pellets, and degraded OM were estimated based on Phe-normalized δ<sup>15</sup>N of Ala and Thr. End-member source data are from previously published literature: McClelland and Montoya, 2002; Chikaraishi et al., 2009; Hannides et al., 2009, 2013;
 Yamaguchi and McCarthy, 2018; Doherty et al., 2021.

#### 373 4 Discussion

The benthic habitats of Saglek Bank area, including the Labrador Shelf slope, are known to support abundant deep-sea corals and sponges, for example, the gorgonian *Primnoa resedaeformis* and the large sponge *Geodia* spp. (Wareham and Edinger, 2007; Dinn et al., 2020). These deep-water sessile organisms rely on deposition of POM from the surface (Sherwood et al., 2005; Sherwood and Edinger, 2009; Dinn et al., 2020). Therefore, an enhanced understanding of the organic carbon and nitrogen sources and trophic and microbial processing in the sinking particles at the Saglek Bank area is critical. In our study,  $\delta^{13}$ C-EAA results revealed dominance of relatively "fresh" organic matter (i.e., less microbially degraded) and a potentially high baseline contribution of sea ice algae to sinking particles. The  $\delta^{15}$ N-AA data suggested sinking particles were dominated by fecal pellets. Together, these results

381 suggested that sea ice algae and exported zooplankton fecal pellets can be a critical source of POC and PN for the benthic fauna.

# 382 4.1 Contribution of microalgae

- Bulk  $\delta^{13}$ C values of sinking particles at the study site (-26.6 to -23.8‰) fell toward the lower end of the typical range of marine particulate organic matter from Arctic/subarctic regions (-19 to -26‰; Schubert and Calvert, 2001; Søreide et al., 2006; Belt et al.,
- 2008). The temporal variability of bulk  $\delta^{13}$ C was relatively small (~2.0‰) and was not correlated to the more variable  $\delta^{13}$ C-EAA
- $(\sim 4.0\%; r^2 = 0.004; Fig. 2d)$ . Given the low THAA-C% (< 20%), the bulk  $\delta^{13}$ C signal in the sinking particles was likely driven by
- 387 other (non-EAA) carbon-containing compounds (i.e., NEAAs, amino sugars, carbohydrates, lipids, molecularly uncharacterizable
- organic compounds) and was therefore largely decoupled from  $\delta^{13}$ C-EAA due to biogeochemical and/or metabolic processing
- 389 during sinking.
- 390 In a previous study,  $\delta^{13}$ C-EAA in sinking particles collected in sediment traps deployed at 1,200 m depth in Monterey Bay was
- 391 shown to quantitatively track the bulk  $\delta^{13}$ C of surface primary production (Shen et al., 2021). If this principle applies to sinking
- 392 particles generally, then the  $\delta^{13}$ C-EAA measured in the Saglek Bank traps would imply that the bulk  $\delta^{13}$ C of surface water primary
- 393 production ranges from -26.0 to -22.3‰ over an annual cycle. These values bracket a recently modelled estimate of mean annual



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394 baseline  $\delta^{13}$ C (-23.5‰) at 60°N/60°W in the Labrador Sea but exceed the modelled annual variability by about 3 ‰ (Espinasse et 395 al. 2022). Given the negligible microbial influence on  $\delta^{13}$ C-EAA values (discussed below), the  $\delta^{13}$ C-EAA results imply a 396 potentially wider variability in primary producer  $\delta^{13}$ C than currently captured in isoscape models of baseline  $\delta^{13}$ C.

- 397 Beyond tracking the  $\delta^{13}$ C of primary production,  $\delta^{13}$ C-EAA signatures are potentially even more useful for quantifying the relative 398 contributions of different primary producer functional groups in marine food webs (Lehman, 2009; Larsen et al., 2013; Schiff et
- 399 al., 2014; Vokhshoori et al., 2014). Sinking particles collected during both cycles demonstrated similar  $\delta^{13}$ C-EAA patterns with
- 400 sea ice and pelagic algae collected from northwest Labrador Sea and Baffin Bay (Chen et al., 2022; Fig. 5), suggesting that exported
- organic carbon primarily originated from surface primary production, assuming that sea ice and pelagic algae are the major 402 autotrophic sources (Irwin, 1990; Gosselin et al., 1997). Sea ice algae are generally acknowledged to play an important role in
- 403 primary and export production in the Arctic Ocean, especially in higher latitudes of the Arctic (Hsiao, 1980; Michel et al., 1996;
- 404 Gosselin et al., 1997; Fernández-Méndez et al, 2014; Fadeev et al., 2021). In our study, a higher similarity was observed between
- 405 sinking particles and sea ice algae (Two Sample T-test, p > 0.1 except Leu), compared to pelagic algae (p < 0.05 for Phe, Thr, and
- 406 Leu; Fig. 5a). This resemblance was further evidenced by the overlap of sinking particles with sea ice algae in the PCA (Fig. 6b),
- 407 suggesting the carbon in EAAs of the sinking particles may originate largely from sea ice algae.
- 408 The large contribution of sea ice algae to the sinking particles is operated via two pathways: direct sinking of ice algal biomass 409 and indirect transfers via heterotrophic processing (e.g., zooplankton grazing). Sea ice algal biomass is generally composed of 410 relatively large cells (> 5 µm; 50-100%) in the Arctic (Gosselin et al., 1997) and hence is exported more efficiently to depth, 411 compared to pelagic algae. Sea-ice or under-ice diatoms typically form large aggregates; when detached from ice, the strands sink 412 rapidly, sporadically contributing large amounts of C to the benthic ecosystem (Fernández-Méndez et al, 2014). Fast-sinking ice-413 associated diatom aggregates contribute to higher export efficiency and enhanced pelagic-benthic coupling, whereas smaller and 414 slow-sinking flagellate-dominated aggregates are largely recycled in the epipelagic waters (Fadeev et al., 2021). At our study site, 415 sea ice was present for  $\sim$ 50-60% of the deployment days in both cycles (Table 1). Both chl *a* maxima in early April, 2018 and early 416 May, 2019 coincided with sea ice breakups (defined as sea ice concentration < 50% for more than five consecutive days), 417 suggesting a potential release of sea ice algae to the water column by the ice melt (Fig. 2a; Michel et al., 1993). Following the chl 418 a maxima, the persistent phytoplankton blooms with a smaller magnitude ( $\leq 2 \text{ mg m}^{-3}$ ) during the open-water period could be 419 governed by nutrient limitation (Fig. 2a; Leu et al., 2015). In the Labrador Sea, light is the primary limiting factor to primary 420 production for most of the year, which is largely governed by daylight periods, sea ice cover, and snow depth, controlling the 421 timing and initiation of under-ice blooms (Mundy et al., 2009, 2014; Leu et al., 2015), whereas nutrients becomes co-limiting or 422 limiting in summer/autumn as they become depleted within the mixed layer, especially for nitrate on the Labrador Shelf (Harrison 423 and Li, 2007). Nevertheless, remote-sensing of ocean color only accounted for phytoplankton blooms in open water and thus under-
- 424 ice algal growth remained "invisible" and its magnitude was uncertain.
- 425 Direct sinking of sea ice algae was also evident by the microalgal taxonomy of our sinking particles. Sea ice and pelagic algae are
- 426 often dominated by centric and pennate diatoms with species reported in both habitat types (Hsiao, 1980; Melnikov, 1998; Poulin
- 427 et al., 2011), for example, Fragilariopsis spp. and Nitzschia/Pseudo-Nitzschia spp, which were also observed in our samples (Fig.
- 428 3). Microalgal counts revealed a dominance of Chaetoceros/Attheya spp. in the fall diatom fluxes in 2017 and the fluxes in 2018
- 429 while unidentified centric diatoms dominated the fall fluxes in 2018 and the spring fluxes in 2019 (Fig. 3b). Although it is difficult
- 430 to tell what fraction of the observed diatoms were originated from sea ice or pelagic habitats, the observation of sea ice exclusive
- 431 species N. frigida and M. arctica in the sinking particles of the northwest Labrador Sea confirmed the cooccurrence of sea ice algae





432 in exported carbon (Fig. 3; Lalande et al., 2019a). The occurrence of Nitzschia frigida and Melosira arctica cooccurred with the 433 dominance of Chaetoceros/Attheya spp. in May 2018, shortly after the surface chl a maximum in April associated with the ice 434 melt, suggesting concurrent pelagic production and sea ice algal release induced by sea ice breakup in 2018 (Fig. 2a, 3). Although 435 the direct export of Nitzschia frigida and Melosira arctica accounted for only a small fraction, the magnitude of sea ice algal export 436 remains unknown, given the fact that many diatom species can be either from sea ice or pelagic habitats (Fig. 3b). Further, 437 taxonomic analysis provides a visual representation of plankton cells exported through passive sinking but does not account for 438 other organic matter components, such as fecal pellets and detritus. Therefore, the taxonomic counts only represent a portion of 439 exported sea ice algae whereas  $\delta^{13}$ C-EAA can trace the other portion that cannot be visually identified (e.g., degraded, assimilated,

440 or excreted).

441 In terms of indirect carbon export from surface primary producers, flux of fecal pellets from zooplankton grazing is an important 442 but highly variable component, which is governed by variation in sea ice/pelagic algae and zooplankton biomass and community 443 composition (Turner, 2015). Sea ice algae were found to have higher nutritional quality compared to phytoplankton with an 444 elevated essential fatty acid content and thereby may be a better food source for consumers (Park et al., 2002; Arrigo and Thomas, 445 2004; McMahon et al., 2006; Amiraux et al., 2021). The importance of sea ice algae as food supply for zooplankton grazers has 446 been reported in Hudson Bay (Runge and Ingram, 1988), Frobisher Bay (Grainger and Hsiao, 1990), Canadian Arctic Archipelago 447 (Michel et al., 1996), Barents Sea (Scott et al., 1999, 2001), and northern Baffin Bay (Michel et al., 2002). A more recent 448 biomolecular study also revealed active feeding on sea ice algae by copepods Calanus glacialis under seasonal sea ice long before 449 ice melt and the development of ice-edge blooms in the Northern Bering Sea (Durbin and Casas, 2014). Overall,  $\delta^{13}$ C-EAA 450 signatures revealed a dominance of relatively "fresh" organic matter (i.e., less microbially degraded) and a potentially high baseline 451 contribution of sea ice algae in sinking particles (via direct or indirect export), which was consistent with previous observations 452 that sea ice algae could be either exported via fast-sinking aggregates (e.g., in Beaufort Sea, Carey, 1987; in Eurasian Basin, 453 Fernández-Méndez et al, 2014), or ingested by zooplankton and exported as fecal materials (e.g., in Canadian Arctic Archipelago, 454 Michel et al., 1996). The contribution of fecal pellets to our sinking particles was further evidenced by the presence of intact fecal 455 pellets and the independent  $\delta^{15}$ N-AA analyses, discussed in the section below.

#### 456 4.2 Organic matter composition of sinking particles

457 The  $\delta^{15}$ N-THAA values represent the mass-balanced N isotopic signature of all AAs and were 2-7‰ more elevated than bulk 458 signals (Fig. 2e), suggesting a contribution of isotopically lighter non-AA compounds to the sinking particles. The changes in bulk 459  $\delta^{15}$ N were positively correlated with  $\delta^{15}$ N-THAA (p < 0.05). This is not surprising given the large contribution of THAA-N to total N (up to ~50%; Table 2). Among TrAAs,  $\delta^{15}$ N of Leu, Ile, Glx, and Ala were positively correlated with bulk  $\delta^{15}$ N (p < 0.05).  $\delta^{15}$ N-460 461 Phe represents the isotopic baseline of source N while  $\delta^{15}$ N-TrAA changes with heterotrophic modifications (McClelland & 462 Montoya, 2002; Ohkouchi et al., 2017). The positive correlation with THAAs and TrAAs indicated that changes in bulk  $\delta^{15}$ N were 463 influenced by AA isotopic fractionations from trophic transfers and/or microbial alteration (McMahon and McCarthy, 2016). 464 However, the discrepancy of bulk  $\delta^{15}$ N from TrAA and THAA  $\delta^{15}$ N values suggests other sources are also controlling the overall 465 bulk signal, i.e., N-containing organic compounds like nucleic acids, lipids, carbohydrates, and uncharacterizable OM (Hedges et 466 al., 2001; Batista, 2016; McMahon and McCarthy, 2016), which made up the other half or more of total N in sinking particles 467 (Table 2). For examples, N-acetyl-D-glucosamine from blue crab and lobster chitin was found to be ~9‰ lighter than the bulk  $\delta^{15}$ N of the whole organisms (Macko et al., 1990) while  $\delta^{15}$ N of chlorophyll was ~5‰ lighter than the bulk  $\delta^{15}$ N of cultured 468 469 phytoplankton, and marine sinking particles and sediments collected across different geographical locations (Sachs et al., 1999).





470 While  $\delta^{13}$ C-EAA traces the ultimate autotrophic carbon sources to the sinking particles, variations in  $\delta^{15}$ N-AA reflect three separate 471 processes: baseline isotopic values of source N, trophic transfers, and microbial resynthesis (Ohkouchi et al., 2017). The  $\delta^{15}$ N-Phe 472 is used as a proxy for baseline  $\delta^{15}$ N because it does not undergo deamination reactions during heterotrophic metabolism 473 (Chikaraishi et al., 2009). To investigate the degree of heterotrophic processing in consumer tissues and detrital materials, several 474 parameters have been developed based on  $\delta^{15}$ N-TrAA and  $\delta^{15}$ N-Phe. The "metazoan" trophic position (TP<sub>met</sub>) is calculated from 475  $\delta^{15}$ N-Glu while the "protozoan" trophic position (TP<sub>pro</sub>) includes both trophic transfers through both metazoans and protozoans 476 (Chikaraishi et al., 2009; Nielsen et al., 2015; Décima et al., 2017; Décima and Landry, 2020). The 5V parameter measures the 477 degree of heterotrophic processing from the deviation of  $\delta^{15}$ N-TrAA (McCarthy et al., 2007). In our study, the elevated  $\delta^{15}$ N of 478 TrAAs in the sinking particles versus sea ice and pelagic algae is indicative of alteration by heterotrophic processing (Fig. 5b). It 479 is hard to infer how much alteration was driven by high trophic materials or heterotrophic microbial biomass by looking at the 480  $\delta^{15}$ N-TrAA values alone. Recent studies have identified several  $\delta^{15}$ N-AA patterns resulting from microbial heterotrophy 481 (McMahon and McCarthy, 2016; Fig. 14 in Ohkouchi et al., 2017): 1) algae-like pattern when microbes synthesize AAs de novo 482 from inorganic N; 2) metazoan-like pattern when microbes incorporate existing AAs; 3) both Glu and Phe increase in the same 483 way when microbes conduct extracellular protein hydrolysis; and 4) scattered pattern when only selected AAs are resynthesized. 484 The algae-like pattern exhibits a  $\delta^{15}$ N-AA pattern similar to that of algae with low TP<sub>met</sub> values (Ohkouchi et al., 2017), which is 485 not consistent with our data (Fig. 5b, 7a). Patterns with high  $\delta^{15}$ N-Glu and Phe from extracellular protein hydrolysis elevates the 486  $\delta^{15}$ N of all AAs with similar amplitudes, including those of SrcAAs (Ohkouchi et al., 2017), contrary to those of our sinking 487 particles which remained low (Fig. 5b) and reflected the regional nitrate  $\delta^{15}N$  (Sherwood et al. 2021). The pattern linked to 488 microbial resynthesis was similar to the metazoan-like pattern but showed more scattered changes in  $\delta^{15}$ N-TrAAs with a large 489 increase in  $\Sigma V$  (Ohkouchi et al., 2017). In our study, given the minimal deviations in  $\delta^{15}$ N-Phe, relatively consistent elevated  $\delta^{15}$ N-Phe, relatively consistent elevated 490 TrAA, a higher TP<sub>met</sub> compared to phytoplankton, and a moderate  $\Sigma V$  overlapping with phytoplankton (except for a few values in

491 the 915m trap), our sinking particles more likely underwent "metazoan" heterotrophy (Fig. 5b, 7a; Ohkouchi et al., 2017).

492 By comparing  $\delta^{15}$ N-AA derived parameters with previously established end-member data of major components reported in marine

493 POM (phytoplankton, fecal pellets, microbial degraded OM, and zooplankton), we can estimate the relative contribution of these

- end-members to the sinking particles (Fig. 7).  $TP_{met}$  and  $\Sigma V$  did not clearly distinguish the three end-members from each other,
- especially for fecal pellets and zooplankton (Fig. 7a, c). This presumably resulted from the underestimation of Glx-based TP ( $TP_{met}$ )
- in plankton food webs, which was observed in experimental studies by Gutiérrez-Rodríguez et al. (2014) and Décima et al. (2017),
- and the confounding effects of microbial reworking (Ohkouchi et al., 2017). Previous studies suggested that Ala and Thr provide
   a better separation of end-members because Ala has a higher trophic sensitivity to protistan consumers while Thr can distinguish
- a better separation of end-members because Ala has a higher trophic sensitivity to protistan consumers while Thr can distinguish
   animal metabolism (zooplankton and fecal pellets) from microbial metabolism (phytoplankton; Gutiérrez-Rodríguez et al., 2014;
- 500 Décima et al., 2017; Doherty et al., 2021). Using Ala to compute the trophic position  $(TP_{pro})$  of our sinking particles, we observed
- 501 a clearer separation between the three end-members (Fig. 7b). The improved separation of TP<sub>pro</sub> was obvious between detritus and
- 502 copepods samples, with detritus overlapping with the fecal pellet end-member and copepods falling within the zooplankton end-
- 503 member (Fig. 7b). The elevated TP<sub>pro</sub> compared to TP<sub>met</sub> in sinking particles suggested a pronounced "protozoan" food web imprint
- on the exported ON, that was not visible in  $TP_{met}$ . This demonstrated the important role of "protozoan" food web in exporting
- 505 surface production to the depth. Plotting Phe-normalized  $\delta^{15}N$  of Ala against Thr further provides two-dimensional separation
- 506 between different samples and end-members (Fig. 7d).





507 Sediment traps may be influenced by lateral transport or resuspension of aged sediment which is more degraded. Our sediment 508 traps were deployed at the outer edge of Saglek Bank (Fig. 1), exposed to strong bottom currents and vertical mixing from the 509 Hudson Strait outflow (Fig. 1; Hecker et al., 1980; Harding, 1998; Drinkwater and Harding, 2001; Wareham & Edinger, 2007; 510 Ostiguy, 2022; de Froe et al., 2024). Continental margins are often subject to vigorous bottom currents and hence lateral transport 511 and resuspension of sediments near the bottom (Rea and Hovan, 1995; Hwang et al., 2010). The fractional proportion of sediment 512 resuspension versus surface production is commonly quantified using two-end-member <sup>14</sup>C mass balance (Hwang et al., 2017; 513 Golombek et al., 2024), which was not available in this study. Nevertheless, the influence of resuspended sediments is considered 514 minor, at least to the AA pool, as evident from  $\delta^{13}$ C-EAA and  $\delta^{15}$ N-AA serving as two independent approaches for estimating 515 microbial POM contribution to our sediment traps (Fig. 6b, 7). The THAA-N% in our sinking particles at times exceeded 38% 516 (Table 2), falling within the range for living biomass reported by Cowie and Hedges (1992) whereas degraded sediments and 517 resuspended materials have much lower values (Cowie and Hedges, 1992; Colombo et al., 1998; Golombek et al., 2024), again

518 evidencing the minor contribution of degraded sediments to our sinking particles.

519 The minimal microbial degradation of sinking particles could be attributed to rapid export of fast-sinking diatoms and fecal pellets 520 (Turner, 2015; Lalande et al., 2019; Genin et al., 2021). There is considerable overlap between sinking particles and fecal pellets 521 in the Ala-Thr biplots (Fig. 7c). We then use Bayesian mixing model based on Phe-normalized  $\delta^{15}$ N of Ala and Thr to quantify 522 contributions of end-members to sinking particles. Zooplankton end-member was not included in the mixing model for the sinking 523 particles because zooplankton individuals were sorted and removed from our sinking particle samples (See Sect. 2.3). Assuming 524 phytoplankton, fecal pellets, and microbially degraded OM are the major N sources to the AA pool in sinking particles, our 525 MixSIAR mixing model suggested a dominant contribution of fecal pellets throughout the two years (76-96%; Fig. 8). The 526 contribution of fecal pellets was evidenced by the observation of intact fecal pellet fluxes to the sinking particles in the 2018-2019 527 cycle (Fig. S2; note that fecal pellets were not counted for the 2017-2018 cycle). This was consistent with the observations of 528 sustained copepod communities in removed swimmers from sediment traps (Fig. 4a) and highly abundant large-bodied copepods 529 caught in the plankton sampler at our study site (Fig. 4b, c) as well as previous observations of copepod dominance in subarctic 530 Labrador Sea (Darnis et al., 2022). During phytoplankton blooms, the contribution of direct phytoplankton export was up to 17% 531 (Fig. 8). Note that fecal pellets used in our mixing model consist of data collected from salp, amphipod, krill and mixed community 532 samples that involve herbivory, carnivory, and detritivory feeding (Doherty et al., 2021). We also applied a four end-member 533 mixing model which included zooplankton on our copepod and detritus samples to verify the accuracy of the model (Table S5). 534 Copepod samples were accurately classified within the "zooplankton" end-member (56-87%), while detritus samples were 535 classified as "phytoplankton" (31-55%) and "fecal pellets" (33-54%). Since the detritus aggregates were collected along with the 536 zooplankton from the plankton net (see Sect. 2.3), they were likely contributed by large particles (marine snow) that originate from 537 aggregated phytoplankton (phytodetritus) and fecal matter (Turner, 2015).

# 538 4.3 Exported fecal pellets

539 The fecal-pellet-like  $\delta^{15}$ N-AA signatures in our sinking particles and Bayesian mixing model outputs revealed a potential

- 540 dominance of fecal pellets to exported POM at the study site (Fig. 7d). Sinking fecal pellets serve as an important source of organic
- 541 material for benthic communities but are hard to quantify (Pilskaln and Honjo, 1987; Wilson et al., 2013). The collection of
- 542 recognizable fecal pellets and its proportion in sinking particles largely vary with depth, season, location and is affected by
- 543 zooplankton diets and other enhancing/inhibiting mechanisms during sedimentation (Noji, 1991; Hargrave et al., 1994; Wilson et
- 544 al., 2013). Although fecal pellets are subject to bacterial degradation and/or zooplankton grazing, they may be consumed or





545 repackaged by deep resident zooplankton (that produce larger pellets) or broken down and incorporated into sinking marine snow, 546 and eventually have a greater chance to reach the deep sea (Noji, 1991; Wilson et al., 2013; Stamieszkin et al., 2017). For example, 547 vertical migration of Calanus spp. may promote sinking of particles by feeding in the surface and egesting fecal materials in deeper 548 waters (Noji, 1991; Passow and Carlson, 2012). During sedimentation, fecal pellets are likely to be modified and repackaged 549 several times and become unrecognizable as fecal pellets, making it difficult for visual identification (Noji, 1991). For example, 550 an earlier study estimated a low fecal pellet contribution to POC in a sediment trap collected under permanent ice cover in the 551 Arctic (< 20%), which was derived from enumeration of two types of pellets (cylindrical and ellipsoid; Hargrave et al., 1994). 552 Nevertheless, our results agreed with more recent studies that discovered substantial contribution of fecal pellets from large 553 copepods to vertical export (up to > 60% of the POC flux) in other polar regions; e.g., Fram Strait (Lalande et al., 2011), northern 554 Baffin Bay (Sampei et al., 2004), Beaufort Sea (Juul-Pedersen et al., 2010), and the Southern Ocean (Dagg et al., 2003; Gleiber et 555 al., 2012; Décima et al., 2023). Recent applications of Bayesian mixing model using Phe-normalized  $\delta^{15}$ N of Ala and Thr revealed 556 an increasing contribution of fecal pellets to both small and large particles with increasing depth in North Pacific, indicating fecal 557 pellet production by zooplankton and disaggregation into smaller particles at mesopelagic depths (> 50% in the mid mesopelagic; 558 Doherty, 2021; Wojtal et al. 2023). A recent model study suggested that sinking fecal pellets accounted for 50-90% of total carbon 559 export for most low-latitude seas (Nowicki et al., 2022). Nowicki et al. (2022) found that fecal pellets from "gravitational pump" (i.e., via passive sinking) contributed less to total carbon export in high latitudes (40-50%) because of the larger contribution of 560 561 "mixing pump" (i.e., via active physical transport) from deep water formation. However, the "mixing pump" in their models only 562 includes dissolved organic carbon component and neglected the suspended POC from eddy subduction (Nowicki et al., 2022). Our 563 study, on the other hand, only characterized the particulate portion in the sediment traps, part of which may be transported via the 564 "mixing pump". Hence, our estimates of higher contribution of fecal pellets are reasonable. In fact, physical transport of suspended 565 POC by vertical mixing, seasonal mixed layer detrainment, eddy subduction, and large-scale ocean circulation could play an 566 important role in exporting POC to depth (Omand et al., 2015; Dall'Olmo et al., 2016; Nowicki et al., 2022). For example, based 567 on mixed-layer depth data from Argo floats and satellite estimates of POC, the largest mixed-layer pump can be found in high 568 latitude regions in the North Atlantic, Southern Ocean, and north-west Pacific, accounting for on average 23% of estimates of the 569 biological carbon pump (Dall'Olmo et al., 2016). Glider observations complemented by high-resolution modelling revealed that 570 eddy-driven POC flux can contribute up to half of the total POC export during spring blooms in highly productive subpolar oceans, 571 such as North Atlantic (Omand et al., 2015).

572 Overall, our findings suggested that sea ice algae and zooplankton fecal pellets may fuel export productivity to the mesopelagic 573 zone in a seasonally ice-covered region. This has important ecological implications for global warming and declines in sea ice in 574 the Arctic and subarctic oceans (Pabi et al., 2008). Sea ice declines represent habitat loss and reduced fatty acid quality for sea ice-575 reliant species (Post et al., 2013). This reduction accompanied by younger and thinner ice, freshening surface water, and less ice-576 covered area in the Arctic/subarctic, may also induce changes in community structures and phenology of zooplankton, and hence 577 impacting fecal pellet export and food supply to benthic communities (Post et al., 2013; Leu et al., 2015; Turner, 2015). Although 578 primary production and POC fluxes were predicted to increase in polar oceans as a result of longer ice-free periods, other 579 mechanisms may limit the delivery of POM to benthic ecosystems (Sweetman et al., 2017). First, ocean warming accelerates 580 remineralization and microbial degradation in the water column and hence may reduce the effectiveness of POM export to depth 581 (Riebesell et al., 2009; Turner, 2015). Increased stratification caused by surface warming and freshwater input from sea ice melting 582 limits deep-water ventilation and reduces nutrient supply to surface waters. The weakened deep-water intrusion may reduce the 583 strength of mixed layer pump that acts as an important pathway for POM export in high latitude seas (Dall'Olmo et al., 2016).





- 584 Reduced nutrient supply shifts the surface plankton communities from dominance by diatoms and large zooplankton towards those
- 585 dominated by picoplankton and small zooplankton, thereby reducing the strength of biological pump and the sedimentation of
- 586 organic particles to depth (Li et al., 2009; Finkel et al., 2010; Turner, 2015). This may further deprive benthic communities of 587
- organic matter supply, which are predicted to impact biodiversity hotspots, such as those inhabited by deep-sea corals and sponges
- 588 (Levin and Le Bris, 2015; Sweetman et al., 2017). Hence, these habitats are particularly vulnerable to changes in food quality and
- 589 quantity in the changing Arctic/subarctic oceans.

#### 590 **5** Conclusions

591 In this study, we applied CSIA-AA proxies on sinking particles time series collected in sediment traps at depths of 469 m and 915 592 m in the northwest Labrador Sea (~60°N) to explore the sources and composition of organic carbon and nitrogen in sinking organic 593 matter at the Arctic/subarctic boundary. The sinking particles  $\delta^{13}$ C-EAA patterns indicated that sea ice algae are an important food 594 source to higher trophic levels and that surface primary production was largely preserved in exported organic matter at the study 595 site. Additionally,  $\delta^{15}$ N-AA results independently verified the minor bacterial contribution to sinking particles and revealed 596 dominant animal sources (fecal pellets and zooplankton) to the sinking flux. Overall, these results have significant implications for 597 the use of CSIA-AA in biogeochemical and ecological studies of marine environments. The use of CSIA-AA in sinking particles 598 time series obtained from moored sediment traps provides quantitative estimates of plankton and fecal pellet contributions to 599 carbon export in the ocean, which may help improve the accuracy of flux estimates derived from counting methods and 600 biogeochemical models. Combined with conventional analyses, such as plankton analyses and flux measurements, CSIA-AA may 601 fulfil the promise of precise and high-resolution delineation of marine sinking organic matter in space and time. Climate-related 602 ocean changes may further limit food availability for deep-water benthic assemblages, such as deep-sea corals and sponges (Levin 603 and Le Bris, 2015; Sweetman et al., 2017). We suggest that future work should expand CSIA-AA measurements on sinking 604 particles collected by sediment trap time series globally and establish multi-proxy data repository for vulnerable ecozones. CSIA-605 AA end-member data for estimating sinking particle composition should be better constrained, especially for  $\delta^{13}$ C-EAA. More 606 accurate quantitative estimates of sinking particle composition and processing are beneficial for future studies to predict the 607 biogeochemical and ecological responses in important deep-sea ecosystems to on-going changing climate.

#### 608 Data availability

609 Data are available in the supplementary material (Table S1, S2, S3).

#### 610 Author contribution

- 611 S-MC, DC, EE and OAS contributed to conception and design of the study. S-MC and TD contributed to sampling. TD contributed
- 612 to flux measurements and microalgal and zooplankton counts. S-MC and OAS contributed to sample processing, CSIA-AA and
- 613 bulk stable isotope measurements, and data analysis. DC, EE, and CL contributed to data interpretation. S-MC wrote the manuscript
- 614 with input from all the co-authors.

#### 615 **Competing interests**

616 The authors declare that they have no conflict of interests.





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