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1 **Quantitative estimates of sinking sea ice particulate organic carbon based on the**
2 **biomarker IP₂₅**

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19 Running head – Quantifying sea ice organic carbon

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ABSTRACT

Sea ice derived particulate organic carbon (iPOC) represents an important contribution of carbon to Arctic ecosystems, yet our ability to obtain realistic quantitative estimates of iPOC outside of the sea ice matrix is currently somewhat limited. To address this challenge, we applied a novel approach to quantifying iPOC within the water column under melting sea ice by first measuring the proportion of the sea ice diatom biomarker IP₂₅ within iPOC in bottom ice samples obtained from Resolute Passage in spring 2012. We then compared this value with corresponding values obtained from a time series of water samples. Together, these reflected a period of ice melt and rapid release of iPOC, indicated by changing ice temperature and thickness, in addition to changes in the stable carbon isotope composition, and concentration of iPOC, IP₂₅ and chlorophyll *a* within bottom ice. Estimates of iPOC in seawater were highest (0.15 – 0.22 mg l⁻¹) in the upper 2 m, coincident with the reduction of iPOC in sea ice near the beginning of sampling, with iPOC accounting for an estimated 84 - 125% of total POC (tPOC). Collectively, this biomarker approach yielded realistic estimates of %iPOC, both numerically, and in the context of melting sea ice following a spring bloom in the Canadian Arctic. We also describe some assumptions of this approach and consider the impacts of possible caveats on quantitative estimates of iPOC derived from it.

KEY WORDS: IP₂₅, diatom, spring sea ice bloom, POC, carbon budget, Resolute Passage, quantitative,

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INTRODUCTION

Sea ice associated primary production can represent an important contribution of carbon to Arctic pelagic and benthic marine ecosystems (Arrigo et al. 2010). Optimal conditions for sea ice associated primary production occur in spring when nutrient rich water coupled with sufficient solar radiation provide the stimulus for phototrophic growth (Arrigo et al. 2010). This part of the productive period, commonly referred to as the spring bloom, is terminated when sea ice melts, releasing accumulated organic carbon biomass into the underlying ocean (Michel et al. 1996, 2002, Fortier et al. 2002, Leventer 2003, Dieckmann & Hellmer 2010, Arrigo 2014). With estimated sea ice carbon production ranging from 0.2 – 23 g C m⁻² y⁻¹ (Arrigo et al. 2010), sea ice can provide an important contribution to the carbon available to pelagic heterotrophs (Søreide et al. 2010, Forest et al. 2011a, Brown & Belt 2012a, Wang et al. 2014) in a relatively short time. Indeed, it is known that some organisms time their grazing activities to coincide with spring sea ice blooms (Renaud et al. 2007, Søreide et al. 2010, Leu et al. 2011), thus enabling effective uptake of sea ice carbon into the pelagic and benthic ecosystem. In some cases, sea ice carbon concentration exceeds the grazing potential of pelagic organisms (Forest et al. 2011b), such that sedimentation occurs, making sea ice carbon also accessible to benthic ecosystems (Arrigo 2014). However, challenges associated with distinguishing sea ice carbon from that derived from marine and terrestrial sources, complicates attempts to quantify the former in the pelagic environment. Despite these challenges, however, some approaches have been used for distinguishing sea ice carbon in samples that also contain carbon derived from additional sources. For instance, determination of the stable carbon isotope composition ($\delta^{13}\text{C}$) of particulate organic carbon (POC) can potentially provide information on the relative contributions of different organic carbon sources since sea ice particulate organic carbon (iPOC) is usually more enriched in ¹³C (e.g. $\delta^{13}\text{C} -11\%$; Pineault et al. 2013) compared to pelagic particulate organic carbon

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72 (pPOC) (e.g. $\delta^{13}\text{C}$ -27‰ ; Pineault et al. 2013). However, end-member values are not fixed,
73 in practice, and temporal changes in the isotopic composition of dissolved inorganic carbon
74 (Munro et al. 2010, Pineault et al. 2013) can complicate the interpretation of isotopic data,
75 especially within samples of sea ice. As such, the isotopic signature ($\delta^{13}\text{C}$) of iPOC is
76 strongly influenced by sea ice DIC and, in some cases, overlaps with values obtained from
77 pPOC. For example, Tremblay et al. (2006) observed overlap in the isotopic composition of
78 iPOC ($\delta^{13}\text{C}$ -9 to -26‰) with pPOC ($\delta^{13}\text{C}$ -20 to -27‰) in the North Water Polynya in
79 spring 1998, noting that the greatest overlap occurred early in sampling from relatively thin
80 ice (<80 cm). Similarly, Forest et al. (2011a) reported the isotopic composition of both sea
81 ice and pelagic particulate organic matter in the Amundsen Gulf during spring 2008, where
82 mean values ranged -24 to -31‰ and overlapped most closely at the beginning of sampling
83 where ice and pelagic samples were almost indistinguishable, isotopically, from each other.

84 The determination of the stable isotopic composition of specific lipid biomarkers has
85 also been used to provide information on the source of individual components of iPOC
86 (Budge et al. 2008). Fatty acids are routinely measured for this purpose since they are a major
87 component of algal lipids and contribute substantially to carbon biomass in both iPOC and
88 pPOC. Budge et al. (2008) determined the isotopic composition of certain fatty acids in sea
89 ice algae from Barrow, Alaska, in 2002, reporting $\delta^{13}\text{C}$ values of $-24.0 \pm 2.4\text{‰}$ and $-18.3 \pm$
90 2.0‰ for 16:4n-1 and 20:5n-3, respectively. In contrast, the same fatty acids in the co-
91 sampled phytoplankton were lighter, with $\delta^{13}\text{C}$ $-30.7 \pm 0.8\text{‰}$ and $-26.9 \pm 0.7\text{‰}$. While the
92 reported end-members were clearly different in this study, Budge et al. (2008) noted that
93 there may be further isotopic variations in pelagic iPOC at other times of the year, thus
94 making it more difficult to establish reliable end-member values. In addition, Budge et al.
95 (2008) noted that some 20:5n-3 may be derived from non-diatom sources (Volkman et al.
96 1998) and these would likely influence the isotopic composition of this biomarker.

97 The analysis of phototrophic microorganism accessory pigments can provide
98 information on the biological composition of POC (Morata & Renaud 2008). For example,
99 fucoxanthin (from diatoms) was found to be particularly abundant in Barents Sea surface
100 sediments collected in spring from 2003 to 2005 (Morata & Renaud 2008). Further,
101 chlorophyll *b*, a marker of green algae, was found in Arctic-influenced sediments, while 19'-
102 hex-fucoxanthin, a marker of prymnesiophytes, was found in Atlantic-influenced sediments.
103 Measurement of chlorophyll *a* (chl *a*) and phaeopigments also provided information on the
104 freshness of sinking organic carbon, leading to the conclusion that fresh diatom material was
105 being sedimented in spring due to close pelagic-benthic coupling. However, since sea ice and
106 pelagic microorganisms can produce the same pigments, analysis of these alone does not
107 provide a means of unambiguously distinguishing between individual POC sources.

108 Limitations of individual methods can, to some extent, be overcome by employing
109 multiple approaches. For example, Michel et al. (1996) combined pigment analysis with
110 physical and biological measurements made in Resolute Passage (central Canadian Arctic) to
111 estimate that >65% of iPOC released from melting sea ice remained suspended in the water
112 and was subsequently grazed upon by heterotrophs. Similarly, Forest et al. (2011b) combined
113 pigment and carbon stable isotope analysis with physical and biological measurements in the
114 southeast Beaufort Sea, to estimate that ice algae contributed ~6% to gross primary
115 production in spring-summer 2008. What remains clear, however, is that the development of
116 further complementary approaches for estimating the contribution of sea ice carbon after its
117 release from sea ice would enhance our understanding of its importance to pelagic and
118 benthic ecosystems.

119 To be considered complementary, any new approach should address at least some of
120 the limitations of existing methods and, ideally, be based on the measurement of a physical,
121 biological or chemical parameter that is unique to iPOC and is quantifiable in samples of sea

122 ice, seawater and sediment from any part of the Arctic. Furthermore, in order for such a
123 measure to be effective, its native proxy signature must be retained following release from
124 melting sea ice into the water column (and beyond). For biological- or chemical-based
125 proxies, this means retention of the source composition of the proxy per unit carbon being
126 retained within, for example, seawater or sediment. Finally, the identification and
127 quantification of such a proxy needs to be unambiguous and reliable. In recent years, a novel
128 lipid produced by certain Arctic sea ice-dwelling diatoms has been identified that possesses
129 these attributes and analytical requirements.

130 IP₂₅ ('Ice-Proxy with 25 carbon atoms') is a highly branched isoprenoid (HBI) lipid
131 biomarker made by certain Arctic sea ice diatoms (Belt et al. 2007, Brown et al. 2014c)
132 during the spring bloom (Brown et al. 2011, Belt et al. 2013b) and IP₂₅ concentrations in sea
133 ice correlate well with other major components of iPOC, including chl *a* and fatty acids
134 (Brown et al. 2011, Belt et al. 2013b). In addition, IP₂₅ has an isotopic signature ($\delta^{13}\text{C}$ -19 to
135 -22‰) consistent with biosynthesis in sea ice (Belt et al. 2008), even when detected in
136 sediments. In contrast, IP₂₅ has not been identified in Arctic phytoplankton so it appears to be
137 only produced by sea ice diatoms. However, although IP₂₅ is only made by a relatively small
138 number of diatom species, these are, nevertheless, pan-Arctic in distribution (Brown et al.
139 2014c). Consistent with this, IP₂₅ has been identified in seawater containing sinking iPOC
140 (Brown 2011), sediments (Belt & Müller 2013) and animals (Brown & Belt 2012b, Brown et
141 al. 2012, Brown et al. 2014a) across the Arctic.

142 Laboratory experiments have demonstrated that IP₂₅ is substantially more stable to
143 oxidation than other major components of iPOC, including chl *a* and fatty acids (Rontani et
144 al. 2011). Additionally, the identification of IP₂₅ within marine animal tissues spanning
145 various trophic levels (Brown et al. 2014d), and in ancient marine sediments as old as 3.9 Ma
146 old (Knies et al. 2014), confirms that IP₂₅ is particularly resilient to alteration following

147 biosynthesis. Finally, rigorous analytical protocols for the identification and quantification of
148 IP₂₅ in sea ice, seawater and sediments have been developed (Brown et al. 2011, Belt et al.
149 2012, 2013a). Combined, these attributes suggest that the analysis of IP₂₅ represents a
150 potentially ideal candidate for the quantification of iPOC in the Arctic.

151 For the analysis of IP₂₅ to provide quantitative estimates of iPOC in seawater (rather
152 than simply a qualitative indicator of presence/absence), the proportion of IP₂₅ to total iPOC
153 in sea ice needs to be known. This can be expressed as the ratio $iPOC_i/IP_{25i}$ where $iPOC_i$ and
154 IP_{25i} correspond to the measured concentrations of ice-derived POC and IP₂₅, respectively.
155 Quantification of iPOC in seawater (i.e. $iPOC_w$) can then be determined by combining IP₂₅
156 concentrations measured in seawater with $iPOC_i/IP_{25i}$ on the assumption that there is no
157 significant change to this ratio. In addition, since both IP₂₅ and iPOC are transferred to the
158 water column during ice melt, and become incorporated into total particulate organic carbon
159 in the water column ($tPOC_w$), there should be an overall dilution of IP₂₅ and a subsequent
160 increase in POC/IP_{25} compared to that found in ice. As a result, it is hypothesised that
161 comparison of $iPOC_w$ (calculated) with $tPOC_w$ (measured) in seawater samples should
162 provide an estimate of the proportion of iPOC in seawater POC (i.e. $\%iPOC_w$).

163 The purpose of this study, therefore, was to test this hypothesis by measuring IP₂₅ and
164 POC in sea ice and seawater samples obtained during springtime ice melt to see if these
165 provided realistic estimates of $iPOC_w$ and $\%iPOC_w$ following a spring bloom. To achieve
166 this, a time series of bottom sea ice cores and seawater samples was collected from Resolute
167 Passage, Canada and analysed for IP₂₅, POC and other physical and biochemical parameters
168 to provide some necessary context.

169 **MATERIALS AND METHODS**

170 **Sampling**

171 Sampling was conducted at a landfast ice station (74° 43.6' N, 95° 33.5' W) located
172 between Griffith Island and Sheringham Point (Cornwallis Island) in Resolute Passage
173 (central Canadian Arctic archipelago) from 22 May to 23 June 2012, within the framework of
174 the Arctic-ICE project (Mundy et al. 2014). Vertical profiles of temperature and salinity were
175 measured from 2 – 80 m (max water depth = 90 m) with a Sea-Bird SBE 19plus V2
176 conductivity-temperature-depth (CTD) probe every 1 – 2 days throughout the study period.

177 Sectioned sea ice core samples (bottom 0 – 3 cm) were collected every 3 – 4 days from
178 an area of low snow cover (<10 cm) using a 9 cm internal diameter core barrel (Kovacs Mark
179 II). To compensate for biomass heterogeneity in sea ice (Gosselin et al. 1986), 2 – 3 core
180 bottoms were pooled for each sampling day in isothermal containers. Pooled sea ice cores
181 were then melted in 0.2 µm filtered seawater (3 part FSW to 1 part melted ice) to minimize
182 osmotic stress on the microbial community during melting (Garrison & Buck 1986). A
183 further ice core was obtained to measure the bottom ice (approximately 2.5 cm from the
184 ice/water interface) temperature by drilling a 2 mm hole to the centre of the core and inserting
185 a temperature probe (Testo 720 probe). Water samples were collected at the same frequency
186 at 2, 5, 10, 25, 50 and 80 m under the sea ice using large (5 l) Niskin bottles to accommodate
187 any within sample heterogeneity.

188 **Diatom cell counts and chlorophyll *a* analysis**

189 At the shore laboratory, and within 24 h of sampling, duplicate samples of sea-ice and
190 seawater were filtered through Whatman GF/F glass-fibre filters (nominal pore size of 0.7
191 µm) for chl *a* determination. Chl *a* retained on the filters was measured using a 10-005R
192 Turner Designs fluorometer, after 24 h extraction in 90% acetone for 18 h at 4° C in the dark
193 (acidification method of Parsons et al. 1984). The fluorometer was calibrated with a
194 commercially available chl *a* standard (*Anacystis nidulans*, Sigma). Selected subsamples of
195 sea ice (bottom 0 – 3 cm; 27 May and 21 Jun) and seawater (2 m depth; 30 May and 23 Jun)

196 for cell identification and enumeration were preserved with acidic Lugol's solution (Parsons
197 et al. 1984) and stored in the dark at 4 °C until analysis. Diatom cells were enumerated at the
198 lowest possible taxonomic rank using inverted microscopy (Zeiss Axiovert 10) according to
199 Lund et al. (1958) where three transects were made and at least 400 cells were counted at
200 400x.

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Particulate organic carbon analysis

203 Single subsamples of sea ice and seawater were filtered onto precombusted (450° C for
204 5 h) Whatman GF/F filters and stored frozen at -80° C for analysis at the Université du
205 Québec à Rimouski. Filters for the POC and stable carbon isotope determination were dried
206 at 60°C for at least 24 h, placed in a desiccator saturated with HCl fumes for 24 h to remove
207 carbonate and pelletized. Samples were then analysed for POC concentrations and stable
208 carbon isotope ratios using an ECS 4010 elemental analyser (Costech Analytical
209 Technologies Inc.) coupled to a Delta^{Plus} XP continuous flow isotope ratio mass spectrometer
210 (Thermo Electron Corporation). Stable carbon isotope ratios are expressed as a deviation
211 ($\delta^{13}\text{C}$ in ‰) from the PeeDee Belemnite (PDB) standard, according to the following
212 equation: $\delta X = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$, where X is ^{13}C of the sample and R is the
213 corresponding ratio $^{13}\text{C}/^{12}\text{C}$. Instrumental analytical error was 0.2‰ for $\delta^{13}\text{C}$, based on
214 internal standards (limestone and sucrose) from the National Institute of Standards and
215 Technology (NIST).

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Lipid analysis

218 At the University of Plymouth, 9-octyl-8-heptadecene (10 μl ; 2 $\mu\text{g ml}^{-1}$) and
219 nonadecanoic acid (10 μl ; 4 mg ml^{-1}) internal standards were added to dedicated filters for
220 quantification of IP_{25} and fatty acids respectively from sea ice (15 – 400 ml filtered) and

221 seawater (1 – 4 l filtered). Filters were then saponified (5% KOH; 70°C; 30 min), after which
222 non-saponifiable lipids (including IP₂₅) were extracted with hexane (3 × 2 ml) and purified by
223 open column chromatography (SiO₂; hexane; 3 column volumes). Fatty acids were obtained
224 by adding concentrated HCl (1 ml) to the saponified solution (after extraction of non-
225 saponifiable lipids) and re-extracted with hexane (3 × 2 ml). Identification of IP₂₅ was
226 achieved following analysis by selective ion monitoring (SIM; m/z 350.3, limit of detection =
227 1 ng l⁻¹) using an Agilent 7890A gas chromatograph coupled to an Agilent 5975c quadrupole
228 EI mass spectrometer (GC-MS; HP5ms; Belt et al. 2012). Comparison of IP₂₅ in sample
229 extracts to the retention index obtained from a pure standard of IP₂₅ provided unambiguous
230 identification, while monitoring of m/z 348.3 enabled evaluation of the co-eluting C_{25:2} HBI
231 (Belt et al. 2013a). Fatty acids were derivatised (BSTFA; 50 µl; 80°C; 60 min) and analysed
232 using an HP 6890 gas chromatograph with flame ionising detector (GC-FID; HP5).
233 Individual fatty acids were identified by comparison of their chromatographic properties with
234 those of authentic standards. For quantification, IP₂₅ abundances were normalised according
235 to a response factor, derived from a calibration of the IP₂₅ standard to 9-octyl-8-heptadecene
236 (Belt et al. 2012), and both IP₂₅ and fatty acids were further normalised to quantities of
237 internal standards and sample volume.

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Quantification of iPOC

240 Lower and upper values for the iPOC_i/IP_{25i} (g:g) ratio were calculated from bottom
241 ice sampled in Resolute Passage on the 23 and 27 May 2012 (see Discussion). Range
242 estimates of iPOC concentration in individual seawater samples (iPOC_w) were obtained by
243 multiplying IP₂₅ concentrations measured in seawater (IP_{25w}) with these lower and upper
244 iPOC_i/IP_{25i} ratios determined from analysis of sea ice (Eq. 1). Temporal range estimates of
245 iPOC_w were derived from the lowest and highest individual values across the time series.

246 (1)

$$247 \quad \text{iPOC}_w = \text{IP}_{25w} \times \frac{\text{iPOC}_i}{\text{IP}_{25i}}$$

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249 Percentage concentration estimates of iPOC in seawater (iPOC_w) were calculated using Eq. 2.

250 (2)

$$251 \quad \% \text{iPOC}_w = 100 \times \frac{\text{iPOC}_w}{\text{tPOC}_w}$$

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253 **Statistical analysis**

254 Mann-Whitney *U*-test was performed to assess significant differences between bottom
255 ice and seawater samples. Spearman's rank order correlation (*r*) was used to infer the strength
256 of associations between two variables. These statistical tests were carried out using R 3.1
257 software.

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Results

Measurements in sea ice

Bottom (0 – 3 cm) sea ice temperature increased steadily throughout sampling from –2.2 to –0.2°C, while sea ice thickness reduced from 127 – 93 cm (Fig. 1a, b). The concentration of iPOC_i was highest early on in the sampling period, on 23 and 31 May (99 – 72 mg l⁻¹), corresponding to 64% of the total cumulative iPOC_i measured throughout sampling (Fig. 1c). Over the same dates, the stable carbon isotopic composition of iPOC_i was relatively enriched in ¹³C (δ¹³C –7.7 to –8.3‰) (Fig. 1d). iPOC_i concentration was lower (14 – 2 mg l⁻¹) after 4 June and remained low until the end of the sampling period. At the same time, a change in the isotopic composition of iPOC_i (δ¹³C –11.4 to –23‰) was evident (Fig. 1c, d). Chl *a* followed a similar trend to iPOC_i (r = 0.93, p = <0.01), such that initial concentrations (1.3 – 0.9 mg l⁻¹) reduced substantially after 4 June (0.1 – 0.003 mg l⁻¹) (Fig. 1e), although bottom ice protist composition did not change noticeably between 27 May and 21 June (Fig. 2). The two highest concentrations of IP_{25i} (45 and 26 µg l⁻¹) occurred on 23 and 27 May, respectively, with much lower concentrations from 31 May to 21 June (9 – 0.01 µg l⁻¹). During the interval of highest IP_{25i}, the iPOC_i/IP_{25i} ratio ranged from 2,167 to 3,224 (mean 2,695) and generally increased up to 6 x10⁵ thereafter (Fig. 3).

Measurements in seawater

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Under-ice seawater exhibited relatively consistent hydrographic conditions from 2 – 80 m (–1.7 to –1.8 °C and 32.1 to 32.4 salinity) up to 13 June (Fig. 4). After 14 June, near surface water (2 – 5 m) temperature began to increase (–1.5 °C) and, by 23 June, this extended down to 40 m, along with a reduction in salinity (< 32). Temperature increased further (–1.4 °C), while salinity continued to decrease (31.5) at 2 m at the end of sampling (Fig. 4), which coincided with the lowest sea ice thickness (< 1 m) (Fig. 1b). Concentrations

283 of tPOC_w measured across the time series were most variable at 2 m water depth (i.e. close to
284 the ice/water interface) (Fig. 5a; mean \pm SD; 0.19 ± 0.12 mg l⁻¹). Between 30 May and 7
285 June, tPOC_w at 2 m water depth was relatively high (mean \pm SD; 0.17 ± 0.02 mg l⁻¹),
286 coincident with a reduction in iPOC_i (Fig. 1c). A further increase in tPOC_w at 2 m occurred
287 towards the end of sampling, reaching a maximum on 23 June (0.48 mg l⁻¹), despite there
288 being no further reduction in iPOC_i. Importantly, the protist composition on 30 May at 2 m
289 was extremely similar ($r = 0.99$, $p = < 0.01$) to that of the overlying sea ice on 27 May (Fig.
290 2). In contrast, protist composition in 2 m water on 23 June was not well correlated to the
291 corresponding compositions in 2 m water on 30 May ($r = 0.28$, $p = 0.40$) or the overlying sea
292 ice on 21 June ($r = 0.37$, $p = 0.26$), largely due to an increase in unidentified flagellates (Fig.
293 2).

294 Throughout sampling, tPOC_w concentrations generally decreased with water depth (Fig. 5a).
295 From 22 May to 3 June (i.e. before the reduction of iPOC_i in sea ice), the concentration of
296 tPOC_w was relatively low and less variable between 5 – 80 m water depth (mean \pm SD; 0.07
297 ± 0.02 mg l⁻¹) than at 2 m. From 7 to 23 June, following the reduction of iPOC_i in sea ice,
298 tPOC_w increased between 5 and 80 m (mean \pm SD; 0.13 ± 0.05 mg l⁻¹), with tPOC_w (80 m)
299 reaching 0.14 mg l⁻¹ from 16 June. The chl *a* concentration profile broadly paralleled tPOC_w
300 throughout ($r = 0.53$, $p = < 0.01$; Fig. 5b) and was also most variable at 2 m (mean \pm SD; 0.85
301 ± 0.51 μ g l⁻¹). In contrast to tPOC_w, however, maximum chl *a* occurred between 30 May and
302 7 June (mean \pm SD; 1.45 ± 0.25 μ g l⁻¹), coincident with a rapid reduction of iPOC_i and chl *a*
303 in sea ice (Fig. 1c, e). Fatty acid concentrations were more closely correlated to those of
304 tPOC_w ($r = 0.66$, $p = < 0.01$), while maximum values coincided with highest chl *a* (Fig. 5c; 30
305 May; 7.7 μ g l⁻¹) and tPOC_w (23 June; 6.7 μ g l⁻¹). IP₂₅ was identified in all water samples and,
306 like tPOC_w, exhibited greatest concentration variability at 2 m (mean \pm SD; 24.0 ± 19.7 ng l⁻¹
307 ¹) (Fig. 5a, d). The highest IP₂₅ concentration in water (IP_{25w}) was at 2 m (30 May; 67.4 ng l⁻¹

308 ¹) which coincided with the late May increase of tPOC_w and chl *a* at the same depth. A
309 second, but less pronounced increase in IP_{25w} (20 June; 30.3 ng l⁻¹) was limited to a single
310 sampling date (Fig. 5d). Between 22 and 30 May, (i.e. prior to the release of iPOC from sea
311 ice), the mean IP_{25w} concentration from 5 – 80 m was 7.1 ± 3.6 ng l⁻¹ which then increased to
312 12.0 ± 4.1 ng l⁻¹ from 3 to 23 June as iPOC_i declined. In seawater, IP_{25w} was well correlated
313 to chl *a* ($r = 0.80$, $p = <0.01$) and, to a certain extent, fatty acid ($r = 0.65$, $p = <0.01$), but
314 poorly correlated to tPOC_w ($r = 0.33$, $p = 0.02$).

315

316 **Calculated iPOC_w in seawater**

317 Concentrations of ice-derived POC in the water column (iPOC_w) were obtained by
318 combining IP₂₅ concentrations in seawater (IP_{25w}) with lower and upper values for iPOC_i/IP_{25i}
319 of 2,167 and 3,224, respectively (mean = 2,695) (Eqn. 1), in order to provide range estimates
320 (see Discussion). Using this approach, iPOC_w concentrations across the sampling dates were
321 found to be most variable at 2 m ($0.02 - 0.22$ mg l⁻¹), with the maximum iPOC_w estimate
322 occurring on 30 May (Fig. 6a). Prior to the reduction of iPOC_i (22 to 30 May), iPOC_w
323 concentrations were lower (mean \pm SD; 0.02 ± 0.01 mg l⁻¹) between 5 – 80 m compared to
324 those at 2 m (Fig. 6a). Following the surface (2 m) iPOC_w maximum (30 May), iPOC_w
325 concentrations increased in the mid-water column (5 – 25 m; mean \pm SD; 0.04 ± 0.01 mg l⁻¹),
326 yet remained low in the deeper water column (50 – 80 m; mean \pm SD; 0.02 ± 0.006 mg l⁻¹).

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Discussion

329 Our discussion focuses on an assessment of whether the calculated concentrations of
330 $iPOC_w$ and $\%iPOC_w$ represent realistic quantitative estimates of $iPOC$ in seawater both
331 numerically and within the context of a spring bloom. Such an evaluation can be divided into
332 a number of key considerations.

333 Firstly, it was important to establish that our sea ice and seawater samples reflected
334 the period of $iPOC$ transfer from ice to the water column, as would be expected at the end of
335 a spring sea ice bloom (Fortier et al. 2002, Leventer 2003, Lavoie et al. 2005, Forest et al.
336 2010, Arrigo 2014). Confirmation of this was achieved on the basis that highest IP_{25i} , $iPOC_i$
337 and chl a (all in ice) occurred at the beginning of the sampling interval, with 76% of the
338 protists consisting of diatoms with intact chloroplasts. At the same time, the stable carbon
339 isotopic composition of $iPOC_i$ was at its heaviest ($\delta^{13}C = -7.7\text{‰}$), consistent with biomass
340 formed within sea ice (Pineault et al. 2013). As the sampling interval progressed,
341 concentrations of IP_{25i} , $iPOC_i$ and chl a rapidly declined as biomass was released from
342 bottom ice, and remained low until the end of the sampling interval. Comparison of the
343 timing of the decrease in IP_{25i} , $iPOC_i$ and chl a , with other spring blooms recorded
344 previously from Resolute and the Amundsen Gulf (Michel et al. 1996, Belt et al. 2013b),
345 provides further evidence that our period of sampling coincided with the decline of the sea
346 ice algal bloom.

347 At the end of May, the $iPOC$ material that was lost from the bottom ice appeared
348 within the surface water. Thus, a sharp increase in IP_{25} concentration at 2 m, together with an
349 extremely similar ($r = 0.99$, $p = <0.01$) composition of protists to that in sea ice, demonstrated
350 that parallel increases in $tPOC_w$, chl a and fatty acid concentrations could most likely be
351 attributed to the transfer of $iPOC$ from ice to the water. Although absolute surface ocean
352 current velocities in Resolute Passage are typically ca. 10 cm s^{-1} , and regularly up to 30 cm s^{-1}

353 ¹ or more (Marsden et al 1994, Mundy et al. 2014), the residual flow at 15 m is $<10 \text{ cm s}^{-1}$,
354 and averages $<4 \text{ cm s}^{-1}$ (Marsden et al 1994). Since this corresponds to ca. 0.4 km d^{-1} , it is
355 also feasible that some of the constituents within the water column samples were present as a
356 result of relatively small-scale advection. Therefore, our tPOC_w data may reflect a
357 combination of both local (autochthonous) and advected (allochthonous) material. In any
358 case, the similarity between iPOC and tPOC_w in terms of lipid and protist composition
359 provides evidence for their consistency in sea ice from the wider geographical region.
360 Clarification of this consistency could potentially be achieved through examination of sea ice
361 samples with greater spatial coverage. As sea ice thickness declined, an under-ice bloom
362 began to occur towards the end of the sampling period (Fig. 5). However, while this later
363 under-ice bloom was also evident in tPOC_w , chl *a* and fatty acid profiles, IP_{25w} did not
364 increase at this time. Additionally, the proportion of pennate diatoms declined from 71 to
365 14% and unidentifiable flagellates increased from 12 to 47% compared to surface water at the
366 end of May (Fig. 2). Accordingly, our data are more consistent with pelagic productivity,
367 rather than further ice-released POC at this time.

368 Combined, the profiles of IP_{25} , POC, chl *a*, fatty acid, stable isotopes and protist
369 composition confirmed that our samples corresponded to a period where iPOC was
370 transferred from sea ice to the water column. The source selectivity of IP_{25} permitted the
371 identification of input of both iPOC_w and pPOC_w based on increases and decreases in IP_{25w}
372 concentrations, relative to POC, chl *a* and fatty acid in water. Since the sampling site
373 remained ice covered, throughout the period of sampling (ice $>90 \text{ cm}$ thick), we attribute
374 increases in pPOC_w toward the end of the sampling interval to an under-ice phytoplankton,
375 rather than open water bloom (Fortier et al. 2002, Arrigo et al. 2014, Mundy et al. 2014). As
376 such, the sample set represents a useful template for testing our hypotheses against two
377 contrasting source inputs of POC.

378

379 Secondly, to obtain quantitative estimates of iPOC within the water column, it was
380 necessary to determine a value (or range) for the $iPOC_i/IP_{25i}$ ratio that could be considered
381 representative of iPOC in sea ice. One approach to achieving this would be through direct
382 measurement from cultures of IP_{25} producing diatoms. However, since such data (or cultures)
383 are not currently available, we instead first calculated a range of theoretical iPOC/ IP_{25} ratios
384 using data from cultures of diatoms that produce other HBI lipids similar to IP_{25} . To do this,
385 we took the measured TOC/HBI ratio in cultures of *Haslea ostrearia* (TOC/HBI ca. 70;
386 Brown et al. 2014c) and *Berkeleya rutilans* (TOC/HBI ca. 50; Brown et al. 2014b) and
387 combined these with the proportion of IP_{25} -producing species in our samples (0.5 – 3.2%);
388 the latter being consistent with values reported previously for Arctic sea ice (0.3 – 5 %; Belt
389 et al. 2007, 2013b, Belt & Müller 2013, Brown et al. 2014c). Using this method, we
390 estimated a theoretical range of iPOC/ IP_{25} ratios in ice to be between ca. 10^3 and 10^4 . A
391 complementary (and likely more accurate) approach for obtaining a suitable iPOC/ IP_{25} ratio,
392 however, is one that uses concentration data specific to the location and timing of sampling,
393 especially considering how sea ice and the underlying water column are coupled. Since it is
394 also likely that the $iPOC_i/IP_{25i}$ ratio may be sensitive to the sampling interval (as was the case
395 here) and might, potentially, also be quite variable in sea ice from other locations or
396 seasons/years, we decided to determine $iPOC_i/IP_{25i}$ ratio from sea ice, rather than from
397 cultures. In the current study, we used $iPOC_i/IP_{25i}$ values for sea ice samples collected from
398 23 to 27 May to provide lower and upper estimates of $iPOC_w$ since these corresponded to
399 samples with the highest overall $iPOC_i$ and IP_{25} , the majority of protists (>70%) comprised
400 diatoms, and the stable isotopic composition (mean $\delta^{13}C = -8.2\text{‰}$) of $iPOC_i$ all confirmed
401 that the majority (if not all) of the biomass was produced within sea ice (Pineault et al. 2013).
402 Significantly, the mean value of $iPOC_i/IP_{25i}$ in sea ice from 23 to 27 May (ca. 2.7×10^3) falls

403 within the theoretical range based on HBI concentrations in diatom cultures and the %IP₂₅
404 producers in sea ice (i.e. 10³ -10⁴), while our lower (2,167) and upper (3,224) iPOC_i/IP_{25i}
405 ratios also fall within this range and differ by less than 20%. In contrast, after June 12, and
406 following the release of the majority of iPOC in May, values of iPOC_i/IP_{25i} increased above
407 10⁴ (Fig. 3), while the stable isotopic composition of iPOC changed substantially (mean δ¹³C
408 = -21.3‰), reducing confidence in a sea ice assignment of iPOC at this time. Such changes
409 in iPOC_i/IP_{25i}, however, illustrate that, in the future, it will be important to establish the
410 variability in the iPOC_i/IP_{25i} ratio in sea ice samples from different locations and
411 seasons/years but, in any case, parallel measurement of IP₂₅ and POC in sea ice and
412 underlying water samples are likely required for estimation of iPOC_w and %iPOC_w using the
413 method described herein.

414 Thirdly, having identified suitable lower and upper limits for the iPOC/IP₂₅ ratio for
415 the current sample set, we next combined these with IP₂₅ concentrations measured in the
416 water column to see if this provided realistic range estimates of iPOC_w concentrations. Since
417 IP₂₅ could be quantified in all water samples, these values covered all stages of the release of
418 iPOC_i to the water column, with estimates of iPOC_w and %tPOC_w ranging from 0.01 – 0.22
419 mg l⁻¹ and 6 – 125%, respectively. To the best of our knowledge, there have been no previous
420 reports of equivalent data with similar depth and temporal resolution to compare with our
421 findings, but we are able to evaluate the numerical values, to some extent, on the basis of
422 theoretical limits and an understanding of the system under study (viz. the transfer of iPOC_i
423 into the water column following the spring bloom). For example, since iPOC_w cannot exceed
424 the tPOC_w within the same sample, tPOC_w concentrations provide an upper limit for iPOC_w
425 estimates in all samples. Significantly, therefore, we note that nearly all %iPOC_i values were
426 <100%. Exceptionally the highest values we found ranged between 85-125% (mean 105%),
427 based on the upper and lower limits of the ratio. This finding was consistent with our

428 observation of overall protist composition in seawater (30 May) being almost identical ($p =$
429 <0.01) to that of sea ice (27 May). Similarly, the percentage of IP₂₅ producers to total diatoms
430 (1.3%) and total protists (0.97%) in water on 30 May, was extremely similar (1.4 and 1.03%)
431 to that found in sea ice on 27 May. Collectively, these observations suggest that the majority
432 of the tPOC_w in the upper water depth was derived from iPOC; a conclusion also arrived at
433 by Michel et al. (1996) who used a carbon budget model based on pigment concentrations to
434 estimate that iPOC corresponded to 98 – 138% of upper 0 – 15 m water column POC, and
435 coincided with iPOC loss from bottom ice.

436 In addition to finding that virtually all of the calculated %iPOC_i values were $<100\%$,
437 we also identified two statistically different (Wilcoxon ranked sum $p = <0.001$) and
438 contextually relevant zones (Fig. 6b) in the water column on the basis of the entire
439 estimated %iPOC_w dataset. The high spatial and temporal resolution of our data enabled us to
440 determine that these zones were partially stratified, as well as being temporally divided in
441 early June. The first of these zones, Zone-a, corresponded to the first half of sampling (i.e. 22
442 May to 11 June) and from 2 – 50 m and contained iPOC_w that ranged from 9 to 125% of
443 tPOC_w, but with mean lower and upper estimates (37 - 55%) indicating comparable
444 contributions of iPOC_w and other POC from additional sources. In contrast, Zone-b
445 comprised samples where %iPOC_w ranged from 6 – 52% and was defined by all samples at
446 80 m and all depths after 16 June to the end of sampling and included the onset of the under-
447 ice bloom at the end of the sampling period. We note, however, that the major difference
448 between these zones was due to a more significant difference ($p = 0.003$) in tPOC_w between
449 the two zones rather than differences in the estimated iPOC_w concentration ($p = 0.08$),
450 presumably due to increased POC from the growing under-ice bloom observed here towards
451 the end of the sampling interval. Previous studies have identified that the bloom period
452 consists of changes in POC export in relation to pre- and post-bloom conditions, based on

453 quantitative measurements of parameters such as POC (Michel et al. 1996, Fortier et al. 2002,
454 Forest et al. 2008, Juul-Pedersen et al. 2008). For example, Michel et al. (1996) reported a
455 significant difference between pre- and post-iPOC input in Resolute. This transition from
456 iPOC to pPOC dominance is very important in the Arctic, and models have been created in
457 an attempt to quantify the relative importance of iPOC, in particular (Michel et al. 1996, Deal
458 et al. 2011, Forest et al. 2011b). For example, Forest et al. (2011b) integrated data spanning
459 spring-summer in the Amundsen Gulf to estimate that ice algae contributed 6% of the total
460 primary production throughout this time. In the current study, our sampling has provided
461 further insights into the temporal evolution of iPOC to pPOC on a more highly resolved
462 temporal scale which is useful for gaining a better understanding of this important springtime
463 transition.

464 Finally, our estimated $iPOC_w$ concentrations have been made on the assumptions that
465 the measured range in the $iPOC_i/IP_{25i}$ ratio, determined through analysis of sea ice samples
466 from a single location, are both representative of Resolute Passage (see earlier) and remained
467 unaltered in seawater. Our data support these assumptions, with additional contributions to
468 tPOC resulting in an enhancement of $tPOC_w/IP_{25w}$, and a decrease in $\%iPOC_w$, as predicted.
469 Nevertheless, we believe it valuable to consider the impacts of a number of other theoretical
470 scenarios on the derived $iPOC_w$ and $\%iPOC_w$ values.

471 The first of these alternative scenarios represents a sea ice dominated system, where
472 iPOC is transferred to the water column with no additional contribution of POC from other
473 sources. In this setting, an unaltered $iPOC_i/IP_{25i}$ ratio would lead to $\%iPOC_w$ being
474 consistently 100% of $tPOC_w$ (or very close to this value). In practice, such an observation
475 was confined to a single 2 m water sample, and this coincided with the timing of maximum
476 delivery of iPOC from melting sea ice (30 May). In addition, the consistency in the protist
477 composition of the sea ice and water samples at this time also suggested that the majority (if

478 not all) of the POC in the surface water was derived from sea ice biota; a conclusion arrived
479 at previously for upper water in Resolute Passage (Michel et al. 1996). However, the majority
480 of our %iPOC_w estimates were less than 100%, and as low as 6%, indicative, therefore, of a
481 second scenario, whereby iPOC is transferred to the water column where it becomes
482 combined with additional sources of POC with an increase to the tPOC_w/IP_{25w} ratio and a
483 reduction in %iPOC_w, consistent with the range observed (i.e. 6 – 125%). Of course, pending
484 further investigation, the potential alteration of the iPOC composition following release from
485 ice, resulting from, for example, increased production of exopolymeric substances (e.g.
486 Underwood et al. 2013), cannot be ignored, especially as this would also lead to increases in
487 the tPOC_w/IP_{25w} ratio, regardless of any contributions from pPOC_w.

488 A third scenario considers the impact of preferential degradation of IP_{25w} over other
489 components within iPOC, which might potentially occur both with and without additional
490 POC input. As a consequence of such a degradation process, a modified iPOC_i/IP_{25i} ratio
491 would result in substantial underestimates of %iPOC_w. In an extreme case, such a scenario
492 may even prevent the calculation of iPOC_w if IP_{25w} became sufficiently degraded to prevent
493 detection. In practice, however, IP₂₅ was readily quantified in all samples. On the other hand,
494 it is not possible to discount this scenario entirely since %iPOC_w estimates covered a broad
495 range, with some values less than 10%. However, it has been previously shown that IP₂₅ is far
496 less reactive than some other components of POC, including fatty acids and chl *a*, under
497 laboratory conditions designed to represent the euphotic zone (Rontani et al. 2011). As a
498 consequence, therefore, we suggest that preferential degradation of IP₂₅ compared to other
499 components of POC is an unlikely scenario. In contrast, a fourth scenario, whereby iPOC
500 degrades at a higher rate compared to IP₂₅, likely represents a more realistic modifier of the
501 iPOC_i/IP_{25i} ratio, especially given the enhanced reactivity of some components of iPOC (e.g.
502 fatty acids) to processes such as oxidation in the euphotic zone (Rontani et al. 2003b, Rontani

503 et al. 2011, Rontani et al. 2012). However, the primary degradation processes tend to result in
504 relatively minor alterations to chemical structures, rather than complete degradation
505 (mineralisation). For example, the primary photo-oxidation of POC components such as fatty
506 acids leads to the formation of structurally similar hydroperoxides (Rontani et al. 2003a,
507 Rontani et al. 2012), which would not have significant impacts on iPOC/IP₂₅ ratios. In any
508 case, any enhanced loss of iPOC_w (relative to IP₂₅) would result in overestimates of %iPOC_w
509 and, in particular, values that are in a large excess of 100%, which is not the case. Of course,
510 it is possible that losses in iPOC_i may be compensated for by the addition of POC from other
511 sources, but this seems unlikely given the generally similar composition, and thus reactivity,
512 of POC derived from different sources. Finally, changes in the protist composition in favour
513 of IP₂₅ producers, or further production of IP₂₅ within the water column, would also result in
514 overestimates of %iPOC_i. However, this would also result in %iPOC_w values >100% and, in
515 any case, there have been no reports of IP₂₅ in the pelagic environment. We also note that
516 the %IP₂₅-producing diatoms in mixed Arctic sea ice diatom assemblages is reasonably
517 consistent (Brown et al., 2014c).

518

519 In conclusion, we describe a novel biomarker-based approach that not only provides a
520 means of identifying the transfer of POC from sea ice to the water column, but also allows
521 quantification of concentrations and percentage contributions of ice-algae derived POC in
522 seawater. We present these outcomes from a case study location (Resolute Passage) that has a
523 well-defined spring sea ice melt and algal bloom. In contrast to the limited number of
524 previous studies, which are temporally and spatially integrated, the current approach also
525 permits higher resolution assessments of ice-derived POC to be conducted which will enable
526 the evaluation of changes in source POC to be investigated in more detail. As a next stage in
527 the development of this approach, it will be important to establish the variability in, and

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528 influences over, the $iPOC_i/IP_{25i}$ ratio, together with the impacts that these have on

529 quantitative estimates of ice-derived organic matter in the water column.

530

531

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547

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Figure legends

697 Fig. 1. Time series of (a) temperature and (b) total ice thickness, (c) particulate organic
698 carbon (iPOC_i), (d) carbon stable isotope composition ($\delta^{13}\text{C}$), (e) chlorophyll *a* (Chl *a*), and
699 (f) sea ice diatom biomarker IP₂₅ (IP_{25i}) measured in the bottom 0 – 3 cm of sea ice in
700 Resolute Passage from 23 May to 21 June 2012

701

702 Fig. 2. Relative abundance of protists in the bottom 3 cm of sea ice and in seawater (2 m) in
703 Resolute Passage at the end of May and towards the end of June.

704

705 Fig. 3. Time series of measurements in the bottom 3 cm of sea ice in Resolute Passage from
706 23 May to 21 June 2012. Bar: iPOC_i, % relative abundance of the total iPOC_i measured in sea
707 ice during the sampling interval. Scatter: iPOC_i/IP_{25i} (g:g). Cross represents outlier

708

709 Fig. 4. Time series of water column (a) temperature and (b) salinity in Resolute Passage from
710 21 May to 23 June 2012. Data from 36 hydrocasts (black dots) were interpolated and plotted
711 in Ocean Data View v. 4.6.1. Schlitzer, R., Ocean Data View, <http://odv.awi.de>, 2015.

712

713 Fig. 5. Time series of water column (a) particulate organic carbon (tPOC_w), (b) chlorophyll *a*,
714 (c) C_{14:0} fatty acid, and (d) the sea ice diatom biomarker IP₂₅ (IP_{25w}) in Resolute Passage from
715 21 May to 23 June 2012. Data from 54 discrete samples were interpolated and plotted using
716 Ocean Data View v. 4.6.1. Schlitzer, R., Ocean Data View, <http://odv.awi.de>, 2015.

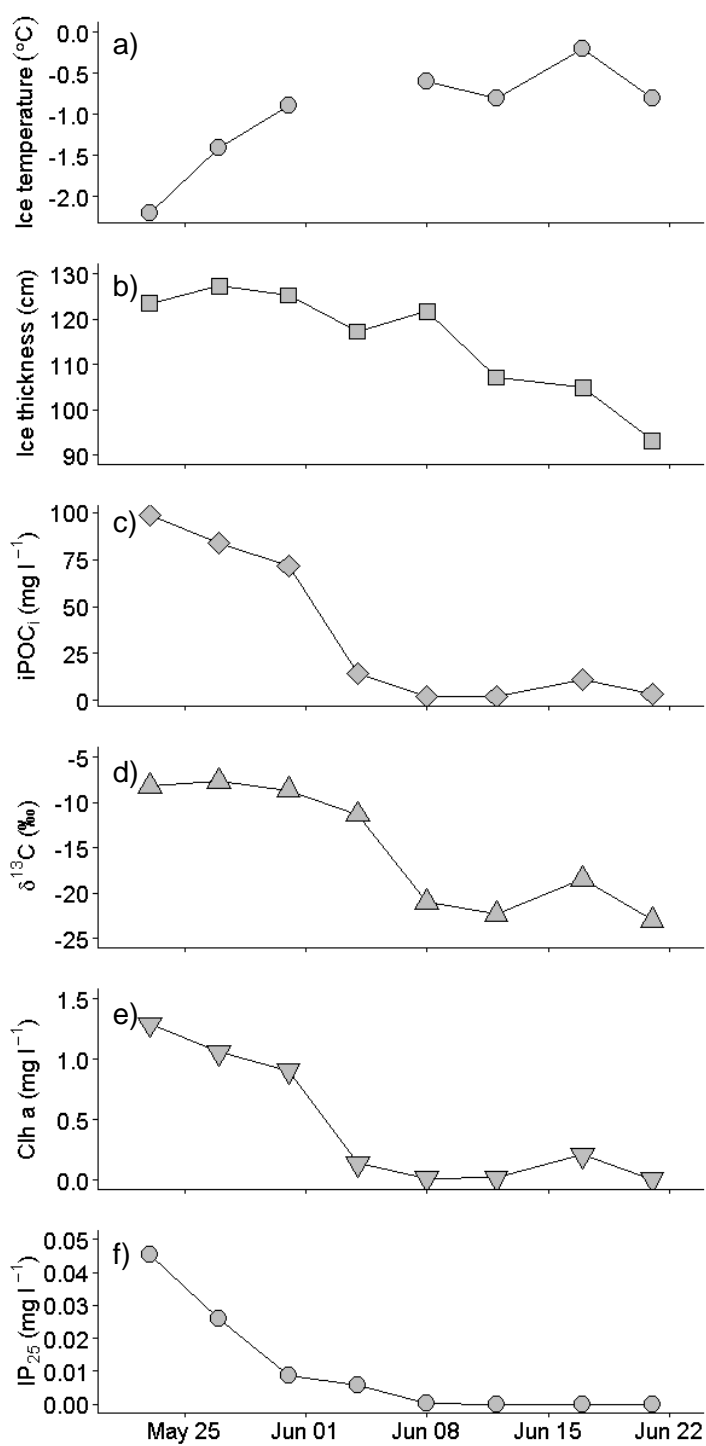
717

718 Fig. 6. Time series of water column (a) mean estimated concentrations of sea ice derived
719 particulate organic carbon (iPOC_w), and (b) iPOC_w as a proportion of total particulate
720 organic carbon (%iPOC_w). Black line divides zone-a and zone-b based on significantly

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721 different ($p = <0.001$) concentrations of total particulate organic carbon (tPOC). Schlitzer, R.,
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723

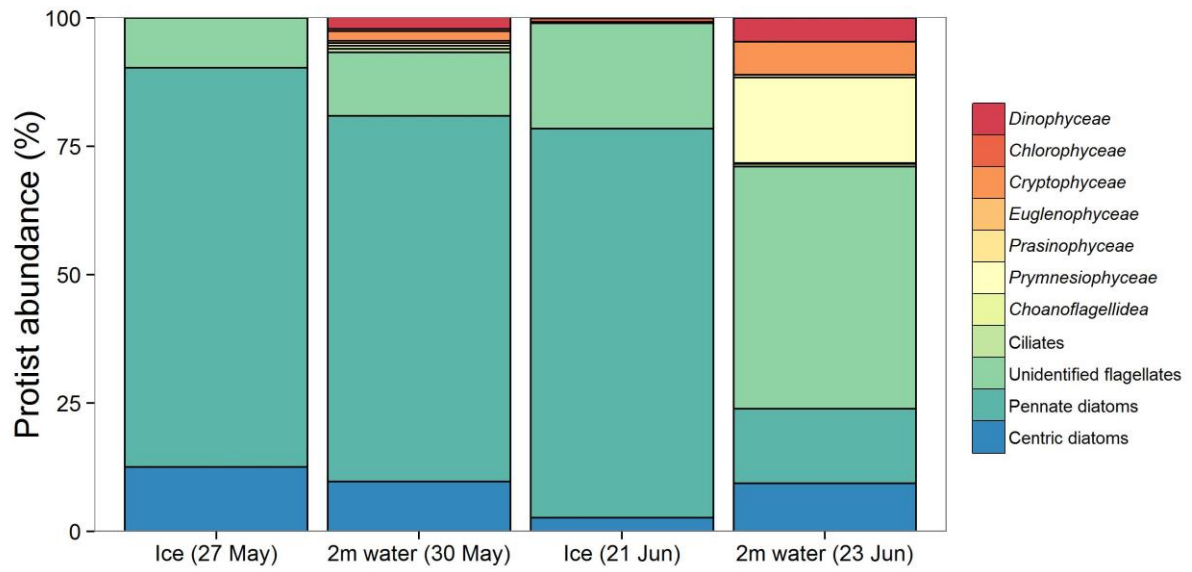


724

725 Figure 1.

726

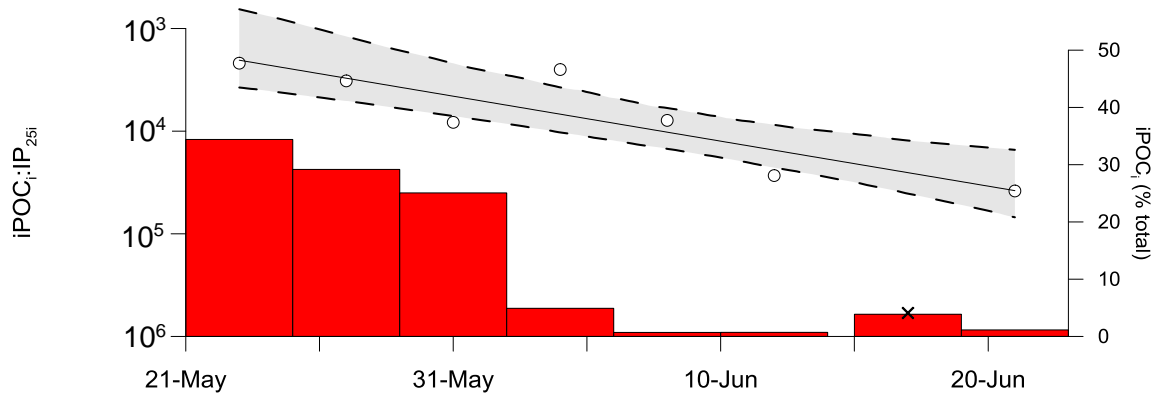
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727

728 Figure 2

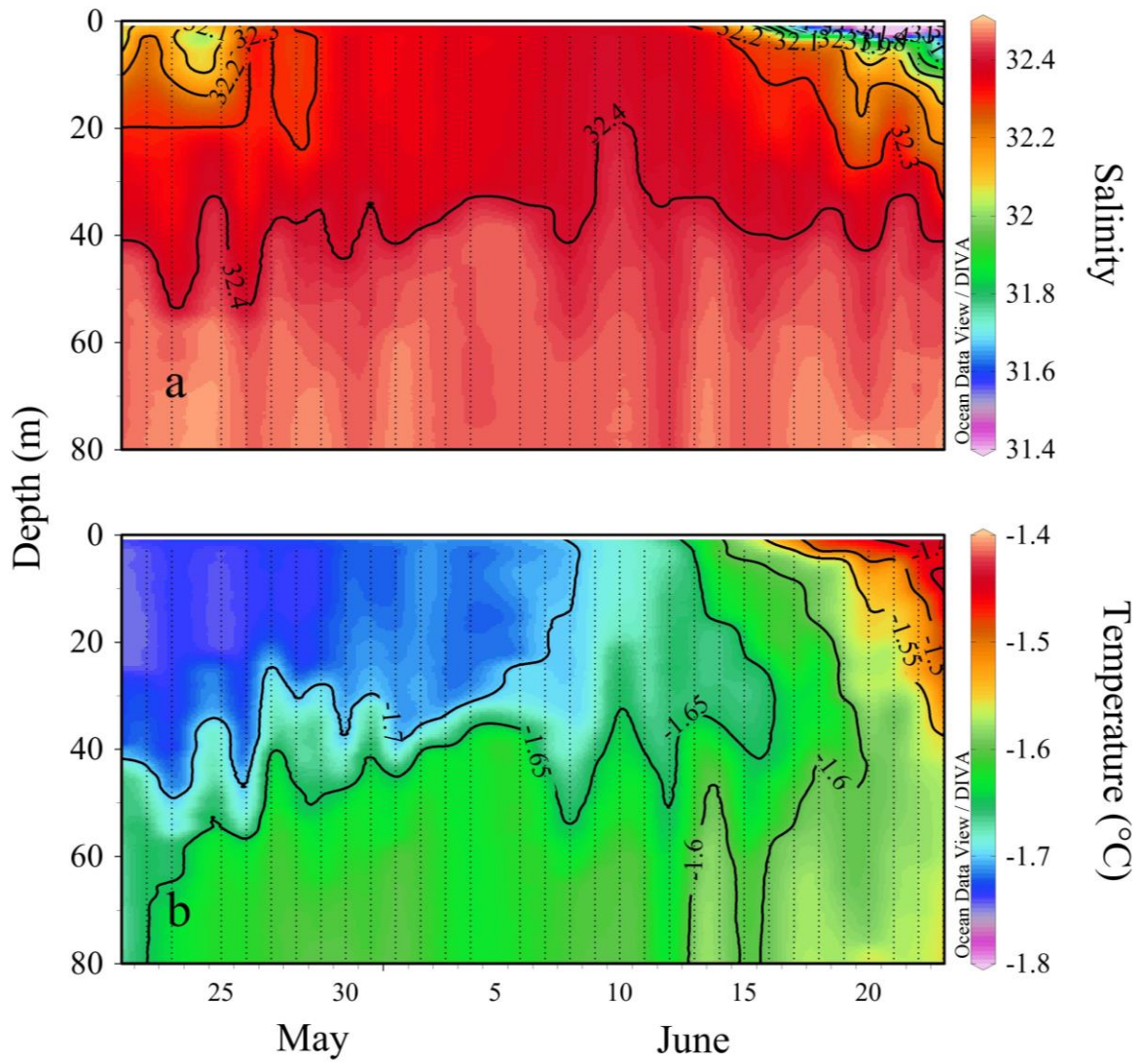
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729

730 Figure 3.

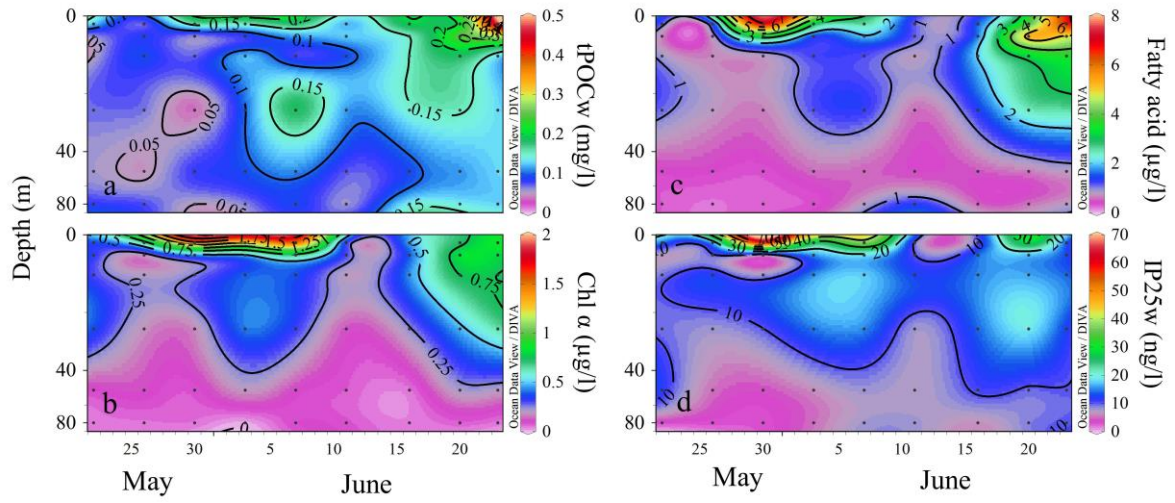
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731

732 Figure 4.

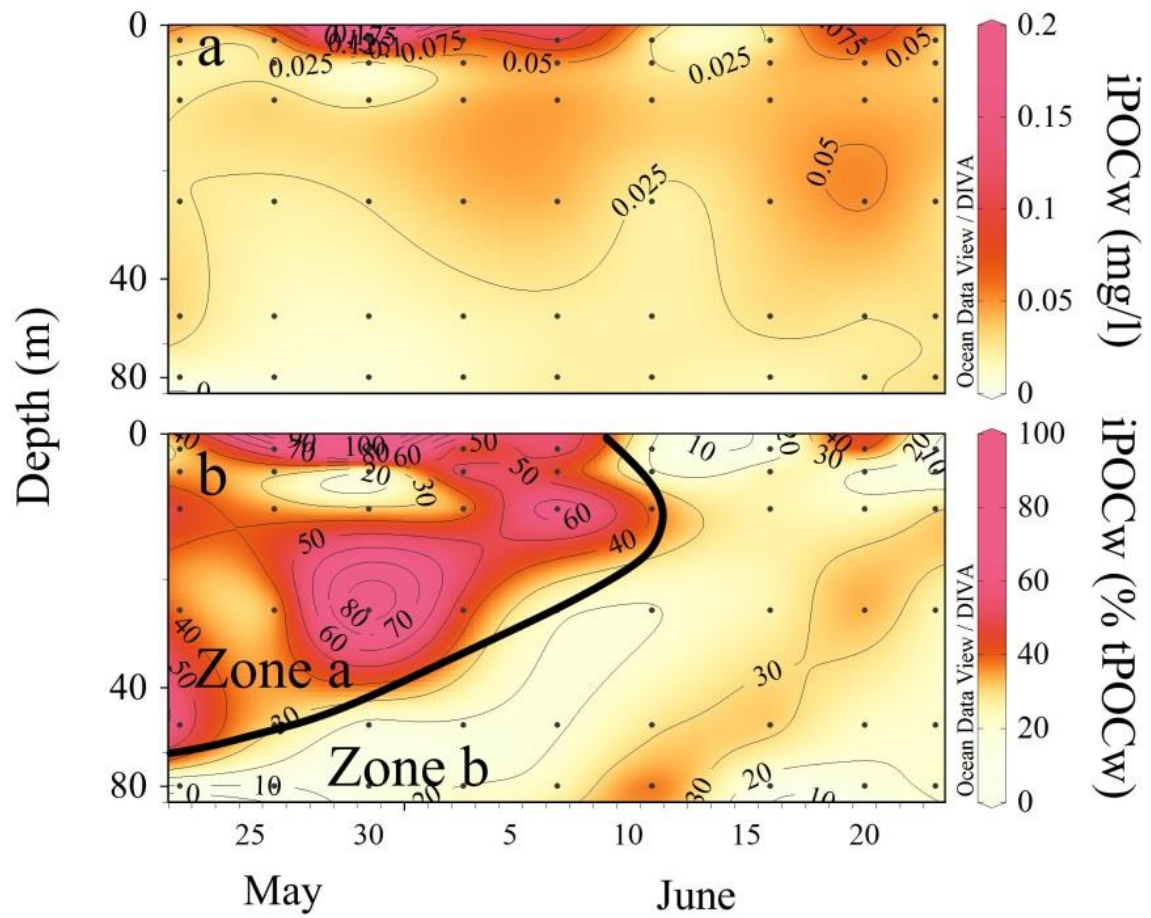
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733

734 Figure 5.

735



736

737 Figure 6.