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1 **Seasonal and spatial variability of sea ice and phytoplankton**
2 **biomarker flux in the Chukchi Sea (western Arctic Ocean)**

3

4 **Youcheng Bai^{a, b}, Marie-Alexandrine Sicre^c, Jianfang Chen^{b, d*}, Vincent Klein^c,**
5 **Haiyan Jin^{b, d}, Jian Ren^b, Hongliang Li^b, Bin Xue^b, Zhongqiang Ji^b, Yanpei**
6 **Zhuang^b, Meixun Zhao^{a, e}**

7

8 *^aKey Laboratory of Marine Chemistry Theory and Technology (Ocean University of China),*
9 *Ministry of Education, Qingdao 266100, China*

10 *^bKey Laboratory of Marine Ecosystem and Biogeochemistry, Second Institute of Oceanography,*
11 *State Oceanic Administration, Hangzhou 310012, China*

12 *^cSorbonne Universités (UPMC, Université Paris 06) -CNRS-IRD-MNHN, LOCEAN Laboratory, 4*
13 *place Jussieu, F-75005 Paris, France*

14 *^dState Key Laboratory of Satellite Ocean Environment Dynamics, Second Institute of*
15 *Oceanography, State Oceanic Administration, Hangzhou, 310012, China*

16 *^eLaboratory for Marine Ecology and Environmental Science, Qingdao National Laboratory for*
17 *Marine Science and Technology, Qingdao 266071, China*

18 ***Corresponding author. E-mail: jfchen@sio.org.cn (Jianfang Chen).**

19 **Abstract**

20 Sediment traps were deployed at 870 m water-depth from August 2008 to
21 September 2009 at station DM in the Chukchi Sea (western Arctic Ocean) in an area
22 covered by sea ice in winter to determine seasonal fluxes of HBIs and phytoplankton
23 sterols in order to improve our understanding of sea ice proxies. HBI-III fluxes and
24 $P_{III}IP_{25}$ are for the first time documented in the Arctic Ocean to evaluate their
25 significance for paleoclimate reconstructions. Highest mass fluxes were found from
26 mid-July 2009 to September 2009 contrasting with low values during all other months
27 (i.e., December 2008 to early July 2009). Indeed, during the winter months IP_{25} was
28 not detected but increased by a factor of nine over summer 2009 reflecting sea ice
29 algae and pelagic phytoplankton production at the sea ice edge. High HBIs and low
30 sterol fluxes at the end of summer 2008 are consistent with the complete melting of
31 sea ice and post-bloom conditions. We found that HBI-III was more abundant in the
32 early stage of sea ice retreat that characterizes the marginal ice zone. These sea ice
33 biomarkers were also measured in surface sediments across a wide range of sea ice
34 cover in the western Arctic region. Higher IP_{25} values were found in the southeastern
35 Chukchi Sea and decreased westwards where sea ice conditions are less severe.
36 Stronger positive linear relationship were found between the sea ice proxy indexes
37 P_BIP_{25} and $P_{III}IP_{25}$ and spring sea ice concentrations than with IP_{25} in agreement with
38 earlier findings from other Arctic and sub-Arctic regions.

39 **Keywords:** sea ice, biomarkers, Chukchi Sea, sediment trap, IP_{25} , HBI-III, $P_{III}IP_{25}$,

40

41 **1. Introduction**

42 Sea ice plays an important role in the global climate and contributes to the large
43 seasonal and inter-annual climate variability in the Arctic region. It also exerts a
44 strong control on the exchange of heat, moisture, and gas between polar waters and
45 the atmosphere (Haas, 2017). Brine rejection during sea ice formation contributes to
46 deep-water formation and convection (Killworth, 1983). Sea ice is also a key driver of
47 primary production and the polar marine ecosystem via its control on light availability
48 and surface water nutrient supply (Arrigo, 2017). Indeed, the release of freshwater
49 from sea ice melting leads to the build-up of a halocline that affects the renewal of
50 nutrients in surface waters (Dickson et al., 2007; Coupel et al., 2015; Petrich and
51 Eicken, 2017).

52 The unprecedented decline in Arctic sea ice cover and thickness in September 2007
53 and 2012 attracted the attention of the scientific community (Stroeve et al., 2005;
54 2007; Arrigo et al., 2008; Boetius et al., 2013). Furthermore, satellite observations
55 revealed that perennial sea ice cover dramatically declined (by 38%) in the recent
56 decades (Comiso, 2012). At the current rate of retreat, the Arctic Ocean could be
57 ice-free in summer within 30 years (Wang and Overland, 2009, 2012; Liu et al., 2013),
58 which could have a profound impact on primary production and the carbon cycle
59 (Grebmeier et al., 2006; Cai et al., 2010; Lee et al., 2012; Thomas, 2017). Yet, our
60 knowledge on the role of sea ice on the polar ecosystem remains limited mainly due
61 to the lack of *in situ* observations. The limited number of paleo-reconstructions either
62 based on geochemical proxies or dinoflagellate cysts, diatoms, and foraminifera is

63 another cause for our incomplete understanding of the long-term evolution of the
64 Arctic climate (Polyak et al., 2010).

65 Over the past decade, a new proxy for seasonal sea ice has been developed based
66 on the concentration of the mono-unsaturated C₂₅ highly branched isoprenoid (HBI)
67 alkene (Fig. 1) biosynthesized by sea ice diatoms, termed IP₂₅ (Belt et al., 2007) and
68 successfully applied for the first time to paleo-reconstructions by Massé et al. (2008).
69 In seasonally ice-covered areas, IP₂₅ contributes to the biogenic material exported to
70 the sea floor. IP₂₅ has been described in sea ice and marine sediments from many
71 areas across the Arctic and sub-Arctic regions (e.g. Müller et al., 2009, 2011; Vare et
72 al., 2010; Fahl and Stein, 2012; Belt and Müller, 2013; Cabedo-Sanz et al., 2013;
73 Méheust et al., 2013; Stoyanova et al., 2013; Xiao et al., 2013, 2015; Belt and
74 Cabedo-Sanz, 2015), and over long time periods, as long ago as the late Miocene
75 prior to 5.3 Ma (Stein et al., 2016). Ice-free and permanently thick ice cover areas
76 encountered in the Arctic are characterized by a zero to near-zero IP₂₅ (Belt et al.,
77 2007; Müller et al., 2011; Navarro-Rodriguez et al., 2013). To distinguish between
78 these two end-member cases, open water phytoplankton biomarker brassicasterol and
79 dinosterol (Fig. 1) have been used in combination with IP₂₅. The so-called PIP₂₅
80 (Phytoplankton-IP₂₅) index was initially developed to better assess sea ice conditions
81 (Müller et al., 2011). More recently, a tri-unsaturated HBI alkene, hereafter named
82 HBI-III, found in the vicinity of the sea ice edge has been suggested as an indicator of
83 retreating sea ice (Belt et al., 2015; Smik et al., 2016, Smik and Belt, 2017). Indeed,
84 HBI-III has been found in high abundances in the marginal ice zone (MIZ) where

85 primary production is enhanced. Although the use of HBI-III for calculating the PIP₂₅
86 is thought to improve sea ice description, this proxy still requires further assessment.
87 Finally, a di-unsaturated highly branched isoprenoid (HBI-II; Fig. 1) has been found
88 in the surface sediments of polar and more temperate oceans (Belt and Müller, 2013)
89 and has been used as a novel Antarctic sea ice proxy (Massé et al., 2011; Belt et al.,
90 2016). The positive correlation between this compound and sea ice diatoms in
91 Antarctic Ocean sediments has led to the suggestion of its potential application as a
92 proxy for the duration of the sea ice season when combined to HBI-III (Collins et al.,
93 2013).

94 In this study, we investigate the seasonal pattern of production and export of HBIs
95 and phytosterols found in sinking particles collected during a one-year sediment trap
96 experiment conducted in the Chukchi Sea in order to improve our understanding and
97 use of these proxies to reconstruct past sea ice changes. We combine for the first time
98 IP₂₅ and HBI-III fluxes measured in the Arctic Ocean to provide a more accurate
99 description of sea ice conditions. Surface sediments retrieved from across the western
100 Arctic Ocean where sea ice ranges from perennial sea ice to ice-free conditions were
101 also analysed to see how well they reflect sea ice distribution. Our approach is thus (i)
102 to document the seasonal production and export mechanisms of HBIs over one year in
103 parallel with sterols for PIP₂₅ calculations and alkanes as a by-product and (ii) to
104 assess the spatial distribution of sea ice and phytoplankton production over the recent
105 years based on surface sediments from the western Arctic Ocean.

106

107 **2. Regional setting**

108 Our mooring site is located in the Chukchi Sea, one of the largest marginal seas in
109 the Arctic Ocean covered by sea ice in winter. This area is influenced by the
110 northward flowing Pacific Water (PW), which has an annual mean transport rate of
111 0.8 Sv (1 Sv = 10^6 m³/s; Roach et al., 1995) and strong seasonal and interannual
112 variability (Woodgate et al., 2005). The PW is primarily driven by salinity gradients
113 between the Pacific and the Arctic oceans (Coachman et al., 1975). The surface
114 circulation in the Chukchi Sea (Fig. 2) is described in detail by Overl and Roach
115 (1987) and Woodgate et al. (2005). In brief, water masses flow across the Chukchi
116 Sea along three main pathways: the saline (>32.5) and nutrient-rich ($\text{NO}_3^{-1} \geq 20 \mu\text{M}$)
117 Anadyr Waters (AW; Grebmeier et al., 1988; Weingartner et al., 2005); the relatively
118 warm, fresher (<31.8) and nutrient-poor Alaska Coastal Waters (ACW; Woodgate and
119 Aagaard, 2005; Hunt et al., 2013); and the Bering Shelf Waters in the central channel
120 with moderate nutrient and salinity values (31.8–32.5; Weingartner et al., 2005).

121 Changes in sea ice extent, thickness, and motion depends on atmospheric and
122 oceanic factors. The Arctic oscillation (AO) affects the frequency of cyclones entering
123 the Arctic Ocean thereby contributing to the redistribution of sea ice (Zhang et al.,
124 2000; Rigor et al., 2002; Serreze et al., 2003). A positive wintertime AO promotes
125 advection of sea ice away from the Eurasian and Alaskan coasts whereas under a
126 negative AO southeasterly winds in summer bring warm air over the ocean causing
127 sea ice to decline in the Beaufort and Chukchi seas (Rigor et al., 2002). Ocean heat
128 transport also impacts on sea ice (Woodgate et al., 2010). The inflow of PW has been

129 shown to accelerate sea ice retreat in the Chukchi Sea (Woodgate et al., 2010, 2012).

130

131 **3. Material and Methods**

132 **3.1 Sediment trap material and sediment samples**

133 During the 3rd Chinese Arctic Research Expedition (CHINARE; summer 2008), a
134 long-term mooring system with a multi-sampling sediment trap (McLane
135 Mark78H-21; aperture area: 0.5 m²) was deployed from the icebreaker RV *Xuelong* in
136 the Chukchi Sea at station DM (Fig. 2; DM: 74°24.0' N, 158°14.0' W, 1650 m water
137 depth). The sediment trap was installed at about 800 m above the seafloor (870 m
138 water depth). The 21 collecting cups were filled with deionized water brought to a
139 salinity of 35 by the addition of NaCl and poisoned with HgCl₂ before deployment.
140 After trap recovery, wet samples were refrigerated until further processing. Large
141 swimmers were removed using a 1-mm mesh nylon sieve. The fine particle fractions
142 (< 1 mm) were split into equal aliquots by means of a rotary splitter wet-sample
143 divider (McLane WSD-10) and filtered onto pre-weighed polycarbonate filters (47
144 mm diameter and 0.45µm pore size). Therefore, one aliquot (1/4 or 1/8 of total cup
145 sample) taken from each cup represents an average of each of the 21 samples time
146 periods. Samples were subsequently dried at 45°C in an oven for 72 h and weighed
147 for total mass determination. Total mass flux was obtained by dividing dried weight
148 by collection time. Note that replicate analyses could not be performed because of the
149 generally low amount of available material.

150 Surface sediment samples (0-2 cm; n = 36) were collected using a box corer during

151 several CHINARE cruises between 2008 and 2014 (Fig. 2). They were stored in clean
152 glass vials at -20°C prior to freeze-drying and further analysis for biomarkers. This
153 sample set covers a broad range of sea ice conditions within the western Arctic Ocean.

154

155 **3.2 Methods**

156 **3.2.1 Particulate organic carbon analysis**

157 Prior to use, filters were dried overnight at 65°C , acid washed and pre-combusted
158 at 450°C for 2 hours in scintillation vials. After filtration, the sediment trap material
159 was placed overnight in a desiccator saturated with HCl fumes to remove carbonates.
160 The air in the desiccator was kept saturated by placing an opened HCl container in its
161 lower compartment. The filters were then dried in an oven at 45°C . Particulate
162 organic matter (POC) and particulate organic nitrogen (PON) were measured on a
163 CHNOS elemental analyser (Elementar, Germany). The daily total mass ($\text{mg m}^{-2}\text{d}^{-1}$)
164 and POC ($\text{mg C m}^{-2}\text{d}^{-1}$) fluxes were calculated for each sediment trap cup. POC
165 fluxes were not corrected for possible dissolution of organic material and should thus
166 be considered as minimum estimates.

167

168 **3.2.2 Biomarker analysis**

169 The filters were placed in a clean glass tube containing a mixture of
170 dichloromethane/methanol to extract the freeze-dried sediment trap material (2:1, v/v).
171 The glass tubes were placed in an ultrasonic bath for 15 minutes and then centrifuged
172 for 15 minutes at 3000 rotations per minute. The supernatant was recovered and

173 transferred in a pre-combusted glass vial. This operation was repeated twice and the
174 three extracts combined to yield total lipid extracts. Prior to extraction, a known
175 amount of internal standard containing 7-hexylnonadecane was added to the sediment
176 trap filters to determine the HBI relative abundances. N-alkanes, HBIs, and sterols
177 were separated by silica gel chromatography (Sicre et al., 2001). Hydrocarbons were
178 eluted with 100% hexane, alkenones with a mixture of 10% ethyl acetate in hexane
179 and sterols in 20% ethyl acetate in hexane. For the surface sediment analysis, 3 to 4 g
180 of freeze-dried sediment was extracted using the same procedure as for the sediment
181 trap samples.

182 Sterols and *n*-alkanes were analyzed by gas chromatography (GC) using a Varian
183 3300 equipped with a septum programmable injector and a flame ionization detector.
184 For sterols, the temperature was programmed from 50 °C to 100 °C (30°C/min), then
185 from 100 °C to 150 °C (1.5 °C/min) and then to 300 °C (3 °C/min) and held for 20
186 min. Prior to the GC analysis, sterols were silylated with 100 µL BSTFA at 80 °C for
187 1 h. For *n*-alkanes, the GC oven temperature was programmed from 80 °C to 300 °C
188 (8 °C/min). A 30 m DB-5MS column (0.25 mm i.d., 0.25 µm film thickness) was used
189 for both compound classes. In both cases, a known amount of 5 α -cholestane was
190 added to the sample prior GC analysis for quantitation.

191 HBIs were analysed using a GC coupled to a mass spectrometer (GC/MS) using an
192 Agilent Technologies 7890 GC equipped with an Agilent 262 Technologies 5975C
193 inert XL mass selective detector. A 30-m HP-5MS column was used for GC/MS
194 analysis (0.25 mm i.d., 0.25 µm film thickness). The oven temperature was

195 programmed from 40 °C to 300 °C at 10 °C/min and held at the final temperature for
196 10 min. The operating conditions for the MS were 250 °C for the ion source
197 temperature and 70 eV for the ionization energy. The HBIs were identified by
198 comparing their GC retention times and mass spectra with those of authentic
199 compounds. Selective ion monitoring (SIM) was used to detect the IP₂₅ (*m/z* 350),
200 HBI-II (*m/z* 348), and HBI-III Z isomers (*m/z* 346) using their peak areas. The HBI
201 concentrations were quantified based on the area of the individual compounds and
202 that of the 7-hexylnonadecane (*m/z* 266) obtained by GC/MS. The HBIs are thus
203 expressed as relative abundances based on the individual GC/MS response of each
204 HBI relative to the internal 7-hexylnonadecane (Belt et al., 2007; Müller et al., 2011).
205 Maps of sea ice distribution and biomarkers were produced using the Ocean Data
206 View software (Schlitzer, 2013).

207

208 ***3.2.3 Sea ice distributions***

209 The HBIs at the mooring site were compared with the average biweekly sea ice
210 concentration derived from the daily field of sea ice concentrations provided by the
211 National Snow and Ice Data Center (NSIDC) for the deployment period. These data
212 were obtained from the DMSP-F13 Special Sensor Microwave/Imager (SSM/I) daily
213 brightness temperatures at a spatial resolution of 25 km (Cavalieri et al., 1996). For
214 the surface sediments, the sea ice biomarker data were compared with the satellite sea
215 ice concentrations obtained from the Nimbus-7 SMMR and DMSP SSM/I-SSMIS
216 passive microwave sensors collected by NSIDC between 1988 and 2007 to generate

217 average sea ice distributions for spring (April–June) and summer (July–September).
218 Since most calibrations of PIP₂₅ index to date use quantitative sea ice data from this
219 period (Xiao et al., 2015; Smik et al., 2016), we selected the same time interval in
220 order to compare our results with those of previous studies. Furthermore,
221 Navarro-Rodriguez et al. (2013) demonstrated that a 20-year time-interval
222 satellite–derived mean sea ice concentration data are reasonably consistent with
223 known sea ice cover datasets in recent decades, regardless of their exact time frame.
224 Therefore, comparison between satellite-derived mean sea ice data and proxy data
225 from surface sediments given the different time frames is thus meant for broadly
226 assessing how well proxy data reproduce sea ice cover at a regional scale, being
227 aware of the range of sedimentation rates in the study area (e.g., Stein et al., 2010;
228 Pearce et al., 2017).

229 The PIP₂₅ index that combines an open water phytoplankton biomarker (P) with
230 IP₂₅ was calculated using the equation of Müller et al. (2011):

$$231 \quad \text{PIP}_{25} = \text{IP}_{25} / (\text{IP}_{25} + (\text{phytoplankton} \times c))$$

232 where c is the ratio of the mean IP₂₅ concentration to the mean phytoplankton
233 biomarker concentration. Brassicasterol and HBI-III were used to calculate the P_BIP₂₅
234 and P_{III}IP₂₅ indexes respectively.

235 The c factor was introduced by Müller et al. (2011) to compensate for the generally
236 higher phytoplankton biomarker concentrations (e.g., brassicasterol) when compared
237 with IP₂₅. Although there are limitations and difficulties associated with the use of the
238 c factor (Müller et al., 2011; Belt et al., 2013) the PIP₂₅ index has been extensively

239 applied to surface sediments (Navarro-Rodriguez et al., 2013; Stoyanova et al., 2013;
240 Xiao et al., 2013, 2015) and sediment cores to reconstruct sea ice conditions in the
241 past (Müller et al., 2012; Cabedo-Sanz et al., 2013; Stein and Fahl, 2013; Müller and
242 Stein, 2014; Hörner et al., 2016; Stein et al., 2017a; Kremer et al., 2018). The recent
243 comprehensive dataset collected from across the modern Arctic Ocean by Xiao et al.
244 (2015) and determination of a global c factor has also proven that brassicasterol-based
245 P_BIP_{25} better reflects spring–summer sea ice than IP_{25} alone.

246 Belt et al. (2015) proposed that the $P_{III}IP_{25}$, based on HBI-III, is less dependent on c
247 because of the similar abundances and diagenetic sensitivity of this compound and
248 IP_{25} . Consequently, its use is seen to be an improvement for paleo sea ice
249 reconstructions and for comparison of records from different Arctic Ocean areas (Belt
250 et al., 2015; Smik et al., 2016; Berben et al., 2017; Stein et al., 2017b). In this study, we
251 used the P_BIP_{25} values of sinking particles and surface sediments with the following c
252 values: $c_{\text{trap}} = 0.00393$ and $c_{\text{surface sediment}} = 0.1063$. The $P_{III}IP_{25}$ values were
253 determined with c values of $c_{\text{trap}} = 10.943$ and $c_{\text{surface sediment}} = 3.7111$.

254

255 **4. Results and discussion**

256 ***4.1 Relationship between particulate organic carbon fluxes and satellite sea ice data***

257 Our mooring was deployed in the Chukchi Borderland under ice-free conditions in
258 August 2008. The area quickly became ice-covered by the end of September and was
259 fully frozen by November 2008. Ice cover remained high (94%) until around early
260 July 2009 when it started to decrease to ~30% in August and 0% by mid-September

261 (Fig. 3a).

262 At high latitudes, the seasonal variations in sea ice cover have a strong influence on
263 marine production and thus on the vertical fluxes and characteristics of the sinking
264 material (Hebbeln and Wefer, 1991). Indeed, total mass fluxes show a pronounced
265 seasonal pattern that follows the temporal evolution of sea ice cover (Fig. 3a–c).
266 Values varied between $6.57 \text{ mg m}^{-2} \text{ d}^{-1}$ in June 2009 and $836.32 \text{ mg m}^{-2} \text{ d}^{-1}$ in
267 September 2009. Persistently lowest fluxes occurred from December 2008 to early
268 July 2009 under the permanent sea ice cover of boreal winter (Fig. 3c; Table 1). From
269 July to August–September 2009, fluxes increased by one order of magnitude with
270 retreating sea ice and the concomitant penetration of sunlight into the upper ocean
271 waters. These high fluxes indicate the rapid response of surface-water productivity to
272 changing environmental conditions as sea ice melted (Hill and Cota, 2005).

273 The POC content of the sinking particles varied across a rather wide range lying
274 between 3.5% and 12.3% (Fig. 3b; Table 1) compared to other sediment trap data
275 from the Arctic (Hargrave et al., 1989; Wassmann et al., 2004) due to an outlier in
276 April 2009 (12.3%). The lowest values ($< 4\%$) were found in winter from November
277 to December 2008. Other low values were measured in summer 2009 during the
278 phytoplankton bloom, possibly due to the presence of inorganic biogenic material
279 (e.g., carbonate or opal) in the sinking material. Similarly, the PON percentage was
280 lowest in winter (0.48%) and higher in summer (0.51% – 0.77%) when excluding the
281 outlier in April 2009 (Table 1). The C/N ratios span from 5.7 to 8.5 with higher values
282 in August 2008. These values are typical of predominantly marine material (Meyers,

283 1997). The outlier lowest C/N value (5.7) points to freshly produced marine
284 compounds (Fig. 2c; Table 1). Apart from this episode, the C/N ratio varies within a
285 rather narrow range (6.9 – 8.5) suggesting that the composition of the sinking material
286 was relatively constant and primarily of marine origin with a minor contribution of
287 terrestrial constituents. The POC fluxes range from 0.26 mg m⁻² d⁻¹ in June 2009 to
288 30.53 mg m⁻² d⁻¹ in September 2009 (i.e. over two orders of magnitude) and display a
289 similar seasonal pattern as mass fluxes (Fig. 3d). The POC fluxes in August 2009
290 were larger than those recorded in summer 2008, reflecting their different primary
291 production status (Fig. 3b; Table 1).

292 Based on these bulk parameters and sea ice concentrations, there was a long-lasting
293 period with low mass fluxes when the area was ice-covered in winter (i.e., November
294 2008 to June 2009) and primary production extremely limited. As the sea ice starts
295 melting, both mass and POC fluxes increase indicating the beginning of
296 phytoplankton growth as nutrient-rich waters become exposed to sunlight. Sea ice
297 continues to break up during the summer season and phytoplankton further develops
298 along the retracting ice edge leading to higher export (Sakshaug, 2004). Indeed, the
299 mass and POC fluxes in August 2009 at the sea ice edge reached comparable levels as
300 in August 2008 under ice-free conditions. However, the largest fluxes in boreal
301 summer 2009 occurred in September when waters became ice-free. Late summer thus
302 seems to have provided more favourable conditions for phytoplankton growth and
303 export of biogenic material to the deeper layers.

304 Fluxes at the study site culminated in July–September period reaching levels that

305 are comparable to those found in other Arctic Ocean regions (Fahl and Nöthig, 2007;
306 Lalande et al., 2009). Fahl and Nöthig (2007) reported higher POC fluxes from
307 mid-July to the end of October 1996 at Lomonosov Ridge in the central Arctic Ocean
308 (station LOMO2; Fig. 2). In this area the river discharge is a major nutrient supplier
309 for primary producers (Fig. S1, Supplementary material). Lalande et al. (2009) also
310 found higher fluxes in mid-July and August at mooring site M3 at 175 m water depth
311 in the Laptev Sea (September 2005 – August 2006). However, high POC fluxes were
312 observed as early as mid-June due to earlier ice melting at lower latitudes and more
313 coastal waters, allowing for earlier phytoplankton blooming and longer growth season
314 (Lalande et al., 2009). Interestingly, the flux pattern at station NAP on the Northwind
315 Abyssal Plain near mooring site DM was notably different (Watanabe et al., 2014; Fig.
316 2). The mass fluxes at the NAP station were high in summer (July – August 2011) but
317 even higher in winter (November – December 2010 and 2011) due to the lateral
318 transport of lithogenic particles as well as fresh material produced under low sea ice
319 conditions (Watanabe et al., 2014). According to these authors, transport of large
320 amounts of particles from the Chukchi Sea shelf to NAP would occur by the westward
321 advection of cold eddies developing off Barrow Canyon. Overall, this comparison
322 highlights that the vertical export of biogenic material from surface waters is the
323 dominant process at site DM and that additional contributions via horizontal
324 advection from the shelf, if any, are minor.

325

326 *4.2 Seasonal variations in terrigenous and marine biomarker fluxes*

327 Phytoplankton sterols and *n*-alkanes were examined to identify the major sources of
328 the sinking material over the year (Table 2). The distribution of *n*-alkanes displays a
329 typical higher-plant pattern with prevailing odd-to-even carbon-numbered homologs.
330 To evaluate the land-derived inputs to the sea floor only those homologs with 27 to 31
331 carbon atoms were considered. They were summed and referred to as ΣALK_{27-31} . The
332 marine phytoplankton was assessed using two sterols: brassicasterol and dinosterol
333 (Volkman, 1986; Rampen et al., 2010; Rontani et al., 2014). Brassicasterol
334 (24-methylcholesta-5,22E-dien-3 β -ol) is found primarily in diatoms although
335 coccolithophorids can also produce it (Volkman, 1986). Dinosterol
336 (4 α ,23,24-trimethyl-5 α -cholest-22E-en-3 β -ol) is produced mainly by dinoflagellates
337 that thrive under stratified conditions (Boon et al., 1979; Volkman et al., 1998;
338 Volkman, 2003). Brassicasterol and dinosterol also have terrigenous sources but they
339 are generally minor in open ocean waters (Volkman, 1986; Fahl and Stein, 1999; Fahl
340 et al., 2003) as corroborated by our C/N ratio values. These marine biomarkers were
341 measured here to generate a first-order estimate of phytoplankton occurrence and for
342 PIP₂₅ calculations.

343 The fluxes of ΣALK_{27-31} and marine sterols appear to be driven mainly by mass
344 flux and thus exhibit broadly similar seasonal patterns (Fig. 4b–d). Brassicasterol and
345 dinosterol fluxes begin to rise in mid-July 2009 as the sea ice retreat to yield their
346 highest values under MIZ conditions (Fig. 4a, c, d). As earlier observed for POC,
347 phytosterols fluxes are weaker in summer 2008 than in 2009. Indeed, export of
348 brassicasterol in September 2009 ($9.74 \mu\text{g m}^{-2}\text{d}^{-1}$) is ~5 times higher than in 2008,

349 while dinosterol flux in September 2009 are ~6 times higher than during the previous
350 summer. These results suggest that ice-free surface waters at the end of summer 2008
351 were less productive than those of the MIZ in summer 2009. Lowest values are
352 consistently found in winter when darkness prevents phytoplankton growth. Flux of
353 ΣALK_{27-31} varied between 0.04 and 1.89 $\mu\text{g m}^{-2}\text{d}^{-1}$ (mean = 0.54 $\mu\text{g m}^{-2}\text{d}^{-1}$) with
354 higher values measured in August 2008 and August 2009 when primary production
355 was also high.

356

357 ***4.3 Biomarker fluxes: sea ice algae and pelagic primary production***

358 In this section, we investigate the relationships between HBIs fluxes and sea ice
359 concentrations provided by the NSIDC and ascertain their links with sea ice diatoms
360 and open ocean primary production.

361 The IP_{25} fluxes exhibit a consistent pattern with the sea ice coverage provided by
362 remote sensing data showing extremely low values during permanent ice cover from
363 November 2008 to June 2009 (Fig. 5a, b). Indeed, during boreal winter the absence of
364 light prevents photosynthetic activity meaning that the sea ice biological community
365 is predominantly heterotrophic (Berge et al., 2015; Leu et al., 2015). The brief IP_{25}
366 production event in November 2008 at the time when sea ice starts to build up
367 suggests a short period of ice algae production when light is still available, which is
368 confirmed by the presence of HBI-II and HBI-III.

369 High IP_{25} are generally seen when sea ice start to retreat. The first step sea ice cover
370 drop from 65% to 30% is coeval with highest IP_{25} fluxes as well as HBI-III and

371 HBI-II in summer 2009 (Fig. 5a, b) as expected from MIZ conditions (Belt et al.,
372 2015). A second peak of IP₂₅ and HBI-II occurs during the second stepwise decrease
373 in sea ice concentration from 30% to 0%, while HBI-III has already significantly
374 dropped. In early August 2008, all three HBIs exhibit high flux values during the final
375 phase of sea ice melting (7% to 0%) (Fig. 5c, d; Table 2).

376 Comparison with phytosterol data shows that from July to September 2009, the IP₂₅
377 fluxes indicate different export timing with respect to brassicasterol and dinosterol
378 (Fig. 5e). Notably, each step of sea ice melting gives rise to enhanced IP₂₅ flux
379 followed by enhanced phytosterol export. This time delay suggests that sea ice export
380 pre-date the open sea phytoplankton production and export that is stimulated by
381 sunlight and nutrient availability upon sea ice melting. Overall, sinking material in
382 summer 2009 would comprise sea ice algae released upon ice melting and open sea
383 phytoplankton produced in the MIZ, whereas the more moderate phytosterol fluxes in
384 late summer 2008 may be indicative of stratified post phytoplankton bloom conditions
385 caused by the complete melting of sea ice and nutrient consumption earlier in the year.
386 The absence of phytosterol production following the three HBI flux peaks in August
387 2008 suggests nutrient exhaustion of the surface waters.

388 These results are in line with the water column data of Coupel et al. (2015)
389 obtained during the CHINARE 2008 cruise. These authors showed that while sea ice
390 melting allows phytoplankton growth as light becomes available, freshening by
391 stratifying the upper ocean progressively reduces the nutrient content of the surface
392 waters and subsequently marine production towards the end of summer. A tight link

393 between primary production, chlorophyll-*a* and the halocline thickness was also
394 demonstrated by Killworth (1983). Overall, our results demonstrate that
395 phytoplankton that thrive during transition periods from ice-covered to ice-free waters
396 experience highly dynamic conditions ranging from a thin halocline of nutrient-rich
397 surface waters promoting marine production to gradually more stratified and nutrient
398 depleted surface waters limiting primary production, as the freshwater layer thickens.

399

400 ***4.4 Assessment of the sea ice index***

401 In the recent years, $P_{\text{B}}\text{IP}_{25}$ and $P_{\text{III}}\text{IP}_{25}$ indexes have emerged as promising proxies
402 for sea ice, providing greater constraints than IP_{25} alone with respect to sea ice
403 coverage (Belt et al., 2015). The temporal evolution of these indexes is investigated
404 here in relation with sea ice cover (Fig. 5f, g).

405 Recently, HBI-III has been proposed as a more suitable biomarker for PIP_{25}
406 calculations than sterols to provide estimates of sea ice conditions (Belt et al., 2015).
407 These authors evidenced a negative correlation between IP_{25} and HBI-III in the
408 Barents Sea sediments, which they attributed to the seasonal advance and retreat of
409 sea ice. In contrast, Smik and Belt (2017) reported a positive linear fit between these
410 two biomarkers in sediments from west of Svalbard that was explained by the
411 dynamical change of the sea ice position caused by the North Atlantic Current
412 variations rather than the seasonal advance and retreat of sea ice as interpreted in the
413 Barents Sea. In our dataset, IP_{25} and HBI-III fluxes are positively correlated ($R^2 =$
414 0.75; Fig. S2, Supplementary material). Note that the removal of the outlier at high

415 values retains and even improves the correlation ($R^2 = 0.88$). This relationship also
416 holds true when using HBI-III and IP_{25} relative abundances instead of fluxes, though
417 weaker ($R^2 = 0.6$). The positive correlation shown here is consistent with HBI-III
418 production being linked to the MIZ as discussed above (i.e. HBI-III increases with
419 IP_{25}).

420 We first calculated the P_BIP_{25} index values using $c = 0.00393$. From August to
421 September 2008, P_BIP_{25} declines from 0.87 to ~ 0.2 reflecting the transition from MIZ
422 to ice-free conditions. High HBI-III fluxes at high P_BIP_{25} are compatible with limited
423 phytoplankton production at the sea ice edge as suggested by low sterol values (Fig.
424 5c, f). From October 2008 to July 2009, the P_BIP_{25} index is highly variable with
425 generally low values in winter, except between January and April 2009 ($P_BIP_{25} > 0.6$).
426 Minor export of IP_{25} under high sea ice cover in the absence of phytoplankton
427 production can account for these values. From August to September 2009, P_BIP_{25}
428 showed large variations (from 0.1 to 0.8) as sea ice rapidly declines towards MIZ
429 conditions.

430 Similar typical ice-edge P_BIP_{25} values (0.5 – 0.8) were found in the shallow
431 sediment trap material (150 m) at the southern Lomonosov Ridge site LOMO2 in
432 July–August 1996 (Fahl and Stein, 2012; Fig. S1, Supplementary material). However,
433 during winter (November 1995 – June 1996) P_BIP_{25} values remained close to zero
434 primarily because IP_{25} was absent or present in minor amounts. The unexpectedly
435 high P_BIP_{25} values in winter at our site highlight the sensitivity and limitation of the
436 use of P_BIP_{25} under extreme situations of low winter IP_{25} at low phytoplankton values.

437 The $P_{III}IP_{25}$ index was also calculated using the c value of our dataset ($c = 10.943$)
438 and a value of $c = 1$ (Fig. 5g). Comparison between the two calculations suggests that
439 $P_{III}IP_{25}$ is less sensitive and cannot distinguish seasonal sea ice changes if we exclude
440 the c factor ($c = 1$). This is particularly obvious for summer 2009 when $P_{III}IP_{25}$ values
441 are all around 1 while estimates of sea ice cover show a reduction when using $c =$
442 10.943. Similar observation can be made for summer 2008. However, from September
443 to October 2008 $P_{III}IP_{25}$ values are close to 1 for both c values due to the absence of
444 production of HBI-III while IP_{25} is present at low levels. This result outlines the
445 limitation of $P_{III}IP_{25}$ at low sea ice cover in our dataset because of the absence or low
446 production of HBI-III towards ice-free waters that is reflected in the positive
447 correlation between IP_{25} and HBI-III (i.e., HBI-III is more abundant in MIZ than ice
448 free waters). Our finding also underline that the c factor is needed as it improves the
449 sensitivity of the $P_{III}IP_{25}$.

450

451 ***4.5 Spatial biomarker distributions and sea ice conditions as derived from surface*** 452 ***sediment data***

453 Lowest concentrations of IP_{25} , HBI-II, brassicasterol and dinosterol are found in the
454 high Arctic (North of $73^{\circ}N$) due to permanent sea ice in spring (Fig. 6a) and summer
455 (Fig. 6b) in this part of the western Arctic, which precludes pelagic phytoplankton
456 growth (Fig. 6c–f; Table 3). Light limitation most probably explains the low
457 brassicasterol ($<5 \mu\text{g/g OC}$) and dinosterol levels ($<5 \mu\text{g/g OC}$) of the northernmost
458 sediments. In the ice-covered high Arctic, insufficient light and nutrients caused by the

459 dominant multiyear sea ice exert a strong control on both beneath-ice and sea ice algal
460 production (Gosselin et al., 1997). Sea ice algae contribute ~60% of primary production
461 in areas with multiyear ice (Legendre et al., 1992; Gosselin et al., 1997).

462 The brassicasterol and dinosterol concentrations increase in ice-free areas and reach
463 their highest values near the summer MIZ (15% summer sea ice concentration; Fig. 6c,
464 d; Table 3). The highest IP₂₅ abundances encountered in the southeastern Chukchi
465 Shelf and off Point Barrow are in accordance with MIZ conditions. Their decrease
466 westwards is explained by the less intense sea ice conditions from east to west
467 (Sharko, 2010; Stoyanova et al., 2013). The co-occurrence of higher IP₂₅ and
468 phytoplankton sterols along Point Barrow and the southeastern Chukchi Shelf
469 indicates that environmental conditions typically found under prevailing ice-edge
470 conditions in summer are favourable for both sea ice algae and open-water
471 phytoplankton development (Fig. 6c–e; Müller et al., 2011; Xiao et al., 2015; Thomas,
472 2017). These areas have high P_BIP₂₅ values ranging from 0.63 to 0.85 (Fig. 7a). In the
473 Chukchi Sea surface waters, algal blooms start as the ice-edge retreats in May and
474 June (Wang et al., 2005). With the thinning and retreat of the sea ice, light transmission
475 through the ice into the upper waters and increased melt-pond coverage provide
476 favourable conditions for both phytoplankton and ice algae production (Arrigo et al.,
477 2014). Phytoplankton blooms driven by upwelling can also take place beneath
478 first-year ice over the Chukchi Sea continental shelf (73 – 74°N; Arrigo et al., 2012).

479 The gradual southward decline depicted by IP₂₅ from the central part of the
480 Chukchi Sea reflects the decrease of summer sea ice coverage from North to South (<

481 70°N; Fig. 6e). Concomitantly, brassicasterol and dinosterol increase as a result of the
482 progressive increase of open water phytoplankton production that benefit from ice-free
483 conditions as well as nutrient-rich coastal waters. The P_BIP_{25} index consistently
484 declines to its lowest values towards the southern Chukchi Sea (0.08 – 0.37; Fig. 7a).

485 The distributions of IP_{25} and HBI-II in the sediments are relatively similar as also
486 observed in the sediment traps, confirming that these two HBIs most probably
487 originate from the same source organisms, i.e. sea ice diatoms (Vare et al., 2009;
488 Massé et al., 2011; Xiao et al., 2013). In our study area, these two biomarkers are
489 strongly correlated ($R^2 = 0.93$; Fig. 8a) whereas HBI-III shows a quite different spatial
490 distribution (Fig. 6g). HBI-III levels are relatively low at the northern sites and poorly
491 correlated with IP_{25} and HBI-II (Fig. 8b, c). Enhanced abundances are found in the
492 southeastern part of the Chukchi Shelf near the 15% summer sea ice isoline in the
493 MIZ in late spring to early summer, in accordance with previous results (Belt et al.,
494 2015). HBI-III concentrations in this region of retreating sea ice are much higher than
495 in ice-free areas consistently with sediment trap findings and coherent with higher
496 phytosterol levels within the MIZ.

497 As for sediment trap material, we calculated $P_{III}IP_{25}$ values using the c value
498 obtained from the surface sediment dataset ($c = 3.7111$) and for $c = 1$. $P_{III}IP_{25}$ does not
499 distinguish between moderate and low sea ice conditions when using $c = 1$, but gives
500 better results for $c = 3.7111$ (Fig. 7b) as found in sinking particles (Fig. 5g). Elevated
501 values in the sediments near the central part of the Chukchi Sea are coherent with
502 extended sea ice through spring and summer, while lower values were consistently

503 found in the southern areas of lower sea ice cover. Overall, the $P_{III}IP_{25}$ distribution
504 does not exactly match that of the P_BIP_{25} because of a different habitat of HBI-III
505 producers living preferentially at the sea ice edge while brassicasterol producers tend to
506 thrive in ice-free waters.

507 IP_{25} in surface sediments show no clear correlation with the satellite sea ice
508 concentrations in spring or summer (Fig. S3, Supplementary material). In contrast, the
509 P_BIP_{25} values show a weak positive ($R^2 = 0.33$; Fig. 7c) correlation with spring sea ice,
510 which supports earlier findings in Arctic and sub-Arctic regions that P_BIP_{25} better
511 correlates with satellite-derived (spring) sea ice than IP_{25} (Müller et al., 2011;
512 Stoyanova et al., 2013; Xiao et al., 2013, 2015). The correlation between spring sea ice
513 and the $P_{III}IP_{25}$ index gives slightly better results ($R^2 = 0.44$ for $c = 3.7111$; Fig. 7d).
514 Note that $P_{III}IP_{25}$ is also linearly correlated with summer sea ice concentrations ($R^2 =$
515 0.47 for $c = 3.7111$; Figs 7e, f, and 9e, f). The use of the global value of c proposed by
516 Xiao et al. (2015) does not improve the correlations between P_BIP_{25} and spring sea ice
517 for our dataset (Fig. 9a, c). The same applies when using $c = 1$ for $P_{III}IP_{25}$ (Fig. 9b, d).
518 However, this result is not unexpected, considering that the c values used for each
519 index calculation are not very different (i.e., for P_BIP_{25} $c = 0.1063$ vs. $c = 0.023$, and
520 for $P_{III}IP_{25}$ $c = 3.7111$ vs. $c = 1$).

521

522 **5. Conclusions**

523 Sinking particle fluxes measured from August 2008 to September 2009 in the
524 western Arctic show a strong seasonality with higher values during the Arctic

525 spring–summer season, from mid-July till the end of September 2009, and lower ones
526 during all other months (i.e., from December 2008 to June 2009). Enhanced export of
527 pelagic phytoplankton and sea ice algae biomarkers in July–August 2009 suggests
528 ice-edge production evolving to ice-free conditions. Lower phytosterol fluxes in
529 August 2008 are in turn expected from open-water and post-bloom production under
530 stratified conditions that result from the complete melting of the sea ice. The positive
531 correlation between IP_{25} and HBI-III in sinking particles suggests that the latter is
532 preferentially produced at the sea-ice edge than in ice-free waters. This could explain
533 the high $P_{III}IP_{25}$ values during boreal winter as compared to P_BIP_{25} as well as high
534 values in the northern latitude sediments of the Arctic Ocean.

535 The coeval increase of IP_{25} and phytosterols in surface sediments along Point
536 Barrow and in the southeast Chukchi Sea demonstrate that, on average, over the
537 recent years this region experienced ice-edge conditions in summer. Farther to the
538 north, lower levels in the high Arctic ($> 73^\circ N$) are consistent with permanent sea ice
539 cover whereas in the Southern Chukchi Sea ($< 70^\circ N$) they point to summer ice-free
540 conditions. We found that in the western Arctic Ocean the relationship between
541 satellite-derived spring sea ice cover and P_BIP_{25} was stronger than with IP_{25} , in
542 agreement with previous observations from other sub-Arctic basins. This correlation is
543 not significantly improved using $P_{III}IP_{25}$, at least in our sedimentary dataset, possibly
544 because of the preferential growth of the HBI-III producers at the sea ice edge rather
545 than in ice-free waters.

546

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