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A novel biomarker-based proxy for the spring phytoplankton bloom in Arctic and sub-arctic settings – HBI T₂₅

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1 **Abstract**

2 The spring phytoplankton bloom is a characteristic feature of mid-high latitudes in
3 modern times, but can be challenging to identify in palaeo records. In the current
4 study, we investigated the absolute and relative distributions of two diatom-derived
5 tri-unsaturated highly branched isoprenoid (HBI) lipids, at least one of which has
6 previously been suggested to be a possible proxy for the productive region of the
7 marginal ice zone (MIZ) in the Polar Regions. Based on a comparison of their
8 distributions in surface sediments from the Barents Sea and neighbouring regions
9 with a range of oceanographic parameters, we identify, via principal component
10 analysis, a strong association between the relative proportion of the two HBIs and
11 satellite-derived spring chlorophyll *a* (chl *a*) concentration. Further, based on
12 agglomerative hierarchical clustering, we identify two clusters of HBI biomarker ratios
13 and spring chl *a* together with a potential threshold biomarker ratio (termed HBI
14 TR₂₅) for the spring phytoplankton bloom. A modified version of HBI TR₂₅ (i.e. HBI
15 T₂₅) provides a potentially more straightforward binary measure of the spring
16 phytoplankton bloom. Analysis of HBI TR₂₅ and HBI T₂₅ values in a series of short
17 (spanning recent centuries) and long (Holocene) sediment cores from the region
18 provides an initial evaluation of the applicability of this novel proxy in the palaeo
19 record. Outcomes are mainly consistent with the findings from the surface sediments
20 and with other proxy-based reconstructions, including estimates of past sea ice
21 cover, which is well-known to influence primary production in the region. Indeed, we
22 suggest that the new HBI T₂₅ phytoplankton bloom proxy may also represent an
23 important new tool for characterising the MIZ in palaeo records, especially when
24 used alongside well-established sea ice proxies, such as IP₂₅ and PIP₂₅. Despite the
25 largely empirical nature of the study, we also provide a possible explanation for the

26 observed biomarker ratio-chl *a* relationship. Thus, a previous laboratory investigation
27 showed that the distributions of the same two HBIs analysed herein in their likely
28 source (viz. *Rhizosolenia setigera*) was strongly influenced by culture temperature
29 and growth rate. Confirmation of the generality of our findings and of the causal
30 relationship between HBI T₂₅ and the spring phytoplankton bloom will, however,
31 require further laboratory- and field-based studies in the future.

32

33 **1. Introduction**

34 The spring phytoplankton bloom is a particularly characteristic and important
35 feature of mid- to high-latitude settings in the northern hemisphere (Mahadevan et
36 al., 2012 and references cited therein). Relatively high photosynthetic light intensity
37 combined with eddy-driven stratification and increased nutrient levels following
38 winter vertical mixing, provide the necessary stimuli and growth conditions for rapid
39 phytoplankton development, such that growth rates can outcompete those of
40 grazing. As a consequence, phytoplankton blooms can contribute significantly to
41 global fixing of atmospheric carbon and its subsequent export from surface waters.
42 High phytoplankton productivity is also critical for the development and maintenance
43 of primary consumers and higher trophic level marine ecosystems, more generally
44 (Legendre, 1990; Søreide et al., 2010; Wassman et al., 2006).

45 As a response to recent and rapid climate change in the Arctic and sub-arctic
46 regions, and a reduction in sea ice cover, in particular, various changes to
47 phytoplankton dynamics are beginning to emerge. For example, spring blooms in
48 sub/low-Arctic regions are developing earlier due to a more rapid retreat of the
49 productive marginal ice zone (MIZ), and the productive period, in general, is
50 lengthening due to both earlier ice retreat in late winter/spring and later freeze-up in
51 late summer/autumn (Renaut et al., 2018 and references cited therein). Further, in
52 ice-marginal locations such as the Barents Sea and the Kara Sea, which exhibit
53 greatest sensitivity to modern sea ice change (Lind et al., 2018 and references cited
54 therein), northward expansion of phytoplankton blooms (Renaut et al., 2018) and
55 increased prevalence of under-ice phytoplankton blooms have been reported, which
56 likely result from thinning of sea ice, reduced precipitation (snow) and an increase in
57 the frequency of open-water leads between ice floes (Arrigo et al., 2012).

58 Although such observations and possible attributions can be made through
59 contemporary in situ measurements, deducing the same within palaeo records is
60 much less straightforward to achieve, partly due to the challenge of finding suitable
61 proxy measures, especially of the spring bloom, uniquely. Several proxy methods for
62 estimating past changes in overall marine primary productivity exist (see Ragueneau
63 et al., 2000 for an overview), including those based on elemental composition, stable
64 isotopes and microfossil assemblages, although, as with all proxies, each have their
65 limitations. Biogenic silica can potentially more accurately reflect the dominance of
66 diatoms and radiolarians commonly associated with the spring bloom, although
67 dissolution and often poor sedimentary preservation are limitations (Ragueneau et
68 al., 2000). Similarly, the accumulation rates of certain benthic foraminifera, known to
69 be opportunistic consumers of fresh phytodetritus and thus a potential proxy
70 measure of the spring bloom, may be negatively influenced by significant carbonate
71 dissolution, especially in high latitude locations (Polyak et al., 2013; Seidenkrantz et
72 al., 2013).

73 Certain source-specific lipids in marine sediments from high latitude settings
74 have emerged as useful paleoceanographic proxies over the last decade or so. For
75 example, the mono- and di-unsaturated highly branched isoprenoid (HBI) biomarkers
76 IP₂₅ and IPSO₂₅ (Fig. 1) have been proposed as binary measures of seasonal sea
77 ice in the Arctic and Antarctic, respectively, a signature based on their selective
78 production by certain sea ice-associated (i.e. sympagic) diatoms only (see Belt, 2018
79 for a recent review). Further, by considering the variable concentrations of IP₂₅ and
80 IPSO₂₅ alongside those of some open-water (i.e. pelagic) biomarkers, either
81 individually or in the form of the so-called PIP₂₅ index (Müller et al., 2011), more
82 semi-quantitative estimates of sea ice conditions have been proposed (Belt, 2018).

83 In some recent studies, a tri-unsaturated HBI lipid biomarker (often referred to
84 as HBI III; Fig. 1) has been suggested to represent a suitable open-water counterpart
85 to IP₂₅ and IPSO₂₅, partly due to its source-specific production by certain pelagic
86 diatoms (Belt, 2018). Interestingly, based on water column and sediment data from
87 the Arctic and the Antarctic, it has been suggested that HBI III might represent a
88 useful proxy for the MIZ, with its elevated abundance in such regions (Belt et al.,
89 2015; Schmidt et al., 2018; Belt, 2018; Bai et al., 2019), reflecting the more general
90 feature of higher productivity commonly observed along the retreating ice margin
91 (Sakshaug et al., 2009; Wassmann et al., 2006). More generally, however, the
92 establishment of a robust proxy for the MIZ remains an interesting research
93 challenge.

94 Despite these previous reports, there have been no dedicated studies aimed
95 at identifying any quantitative relationship(s) between HBI III and other well-
96 recognised measures of primary production such as chlorophyll a (chl a) or indeed
97 any other oceanographic feature. In the current study, we therefore compared the
98 distribution of HBI III in ca. 200 surface sediments with a range of modern-day
99 oceanographic parameters, including sea surface temperature, salinity, water depth,
100 sea ice concentration, photosynthetically active radiation (PAR) and chl a. Here, we
101 focus on the Barents Sea and neighbouring regions on the basis of well-documented
102 and contrasting spring bloom dynamics, together with the availability of suitable
103 surface and downcore sediment material. We also considered biomarker-based
104 estimates of spring sea ice concentration (SpSIC; Smik et al., 2016) due to its
105 influence over seasonal phytoplankton dynamics, and the distribution of a geometric
106 isomer of HBI III (HBI IV; Fig. 1), not least because HBIs III and IV are often co-
107 produced by certain common diatoms (e.g. *Rhizosolenia setigera*; Rowland et al.,

108 2001), with HBI IV having been shown recently to be a useful predictor of sea ice
109 classification in the Barents Sea when used alongside IP₂₅ (Köseoğlu et al., 2018a).

110 Having identified a strong relationship between the relative proportions of
111 HBIs III and IV (but not the individual biomarkers) and spring chl a, but no other
112 measured parameter, we then measured the same relative biomarker distribution in
113 a series of short cores spanning recent centuries and longer (early-late Holocene)
114 downcore records from the region. Our findings suggest that the proportion of HBIs
115 III and IV in marine archives may provide a proxy measure of the past occurrence (or
116 otherwise) of the spring phytoplankton bloom, at least for the Barents Sea and
117 neighbouring regions. On the basis of an earlier laboratory investigation into the
118 distributions of HBIs (including III and IV) in the cosmopolitan pelagic diatom *R.*
119 *setigera*, we also suggest a possible origin of the proxy relationship between HBIs III
120 and IV, and the spring phytoplankton bloom.

121

122 **2. Regional setting**

123 Detailed descriptions of Barents Sea oceanography can be found in Loeng
124 (1991). In brief, the Barents Sea is characterised by three distinct water masses (Fig.
125 2a): northward inflow of warm and saline Atlantic Water (AW) via the North Atlantic
126 Current (NAC), which continues further north as the North Cape Current (NCaC) and
127 the West Spitsbergen Current (WSC), fresher and colder Arctic Water (ArW) flowing
128 southwest via the East Spitsbergen Current (ESC) and the Persey Current (PC), and
129 brackish coastal water topographically steered along the Norwegian coast by the
130 Norwegian Coastal Current (NCC) (Sakshaug et al., 2009). The northern region of
131 the Barents Sea also experiences seasonal sea ice cover, reaching its maximum

132 extent in March–April; however, inter-annual fluctuations can be large due to variable
133 inflow of AW (Smedsrød et al., 2013). Overall, sea ice in the Barents Sea has
134 decreased by >50% in the last 40 years or so (Fetterer et al., 2016), a negative trend
135 that has likely existed since 1850 AD (Divine and Dick, 2006). The region is almost
136 entirely ice-free at the September sea ice minimum, while the position of the
137 maximum winter ice margin is important for defining the highly productive MIZ (e.g.
138 Wassmann et al., 2006). The advection of AW also contributes to longer productive
139 seasons compared to other Arctic areas making the Barents Sea one of the most
140 productive areas of the Arctic Continental Shelf (Wassmann et al., 2006 and
141 references cited therein).

142

143 **3. Materials and methods**

144 *3.1 Surface sediment material*

145 198 surface sediment sub-samples were taken from a range of grab samples,
146 multicores, box cores and gravity cores reflecting regions of variable sea ice cover
147 and seasonal primary productivity (Fig. 2b). All surface sediments are assumed to
148 represent recent deposition, as described previously (Belt et al., 2015; Smik et al.,
149 2016; Köseoğlu et al., 2018a and references therein). Sampling locations, core
150 types, biomarker data and various physical parameters used for the calibration
151 component of this study can be found in Supplementary Table 1.

152 *3.2 Downcore sediment material*

153 Downcore data spanning recent centuries were obtained from six short
154 sediment cores (Fig. 2a) described in detail elsewhere (Vare et al., 2010; Dylmer,

155 2013; Cabedo-Sanz and Belt, 2016; Köseoğlu et al., 2018a). In brief, Cores BASICC
156 1, BASICC 8, and BASICC 43, hereafter referred to as cores 1, 8, and 43, were
157 recovered aboard the RV *Ivan Petrov* as part of the ‘Barents Sea Ice Edge in a
158 Changing Climate’ (BASICC) project (Cochrane et al., 2009). We used the age
159 models given elsewhere (Vare et al., 2010). Core MSM5/5-712-1 (hereafter, core
160 712) was collected aboard the RV *Maria S. Merian* during the MSM5/5 cruise and
161 the age model is based on five ^{14}C Accelerated Mass Spectrometry (AMS) dates
162 (Spielhagen et al., 2011). Multicores R248MC010 and R406MC032 (hereafter cores
163 10 and 32, respectively) were retrieved within the framework of the MAREANO
164 programme (www.mareano.no) on-board F/F G.O. Sars, with chronologies based on
165 ^{210}Pb data (see Dylmer, 2013 and references cited therein).

166 Longer timeframe data were obtained from gravity cores described previously
167 (Laberg et al., 2002; Dylmer, 2013; Berben et al., 2014, 2017) (Fig. 2a). Gravity core
168 WOO/SC-3 (hereafter core 3) was retrieved from the Norwegian continental margin
169 (Laberg et al., 2002). The age model is based on three ^{14}C AMS dates (Laberg et al.,
170 2002; Dylmer, 2013) and the analysed section corresponds to the last ca. 3.0 cal kyr
171 BP. Core JM09-KA11-GC (hereafter, core 11), was obtained from the Kveithola
172 Trough, south of Svalbard, aboard *RV Jan Mayen*. We use the age model presented
173 in Belt et al. (2015), based on ^{14}C AMS dates from previous studies (Berben et al.,
174 2014 and references therein). Gravity Core NP05-11-70GC (hereafter, core 70) was
175 collected from the Olga Basin, East Svalbard, aboard the *RV Lance*. Core
176 chronology is based on three ^{14}C AMS dates (Berben et al., 2017). For cores 11 and
177 70, we present data covering last ca. 9.5 cal. kyr BP. See Table 1 for a summary of
178 all cores and Supplementary Table 2 for more details regarding core chronologies.

179 3.3 Biomarker data

180 Biomarker data were obtained in two ways. For cores not investigated previously
181 (i.e. cores 3, 10 and 32), lipid analysis was carried out according to Belt et al. (2012),
182 but with a slight modification to the extraction method. Thus, freeze-dried
183 subsamples (ca. 1.5–2.5 g) were saponified in a methanolic KOH solution (ca. 5 mL
184 H₂O:MeOH (1:9); 5% KOH) for 60 min (70 °C). Hexane (3×2 mL) was added to the
185 saponified content, with non-saponifiable lipids (NSLs) transferred to clean vials and
186 dried over N₂. NSLs were then re-suspended in hexane (0.5 mL) and fractionated
187 using column chromatography (SiO₂; 0.5 g). Non-polar fractions containing HBIs
188 were eluted with hexane (6 mL) and purified further using silver-ion chromatography
189 (Belt et al., 2015). Saturated compounds were eluted with hexane (2 mL) and
190 unsaturated compounds, including HBIs III and IV, were collected in a subsequent
191 acetone fraction (3 mL). Prior to extraction, samples were spiked with an internal
192 standard (9-octylheptadec-8-ene, 9-OHD, 10 µL; 10 µg mL⁻¹) to permit quantification.
193 Analysis of purified fractions containing HBIs III and IV was carried out using gas
194 chromatography–mass spectrometry (GC–MS) in total ion current (TIC) and selected
195 ion monitoring (SIM) modes (Belt et al., 2012). HBIs were identified based on their
196 characteristic GC retention indices ($RI_{HP5MS} = 2081, 2044$ and 2091 for IP₂₅, HBI III
197 and HBI IV, respectively) and mass spectra (Belt et al., 2000; Belt, 2018). HBI
198 quantification was achieved by comparison of mass spectral responses of selected
199 ions (e.g. IP₂₅, *m/z* 350; HBIs III and IV, *m/z* 346) in SIM mode with those of the
200 internal standard (9-OHD, *m/z* 350) and normalized according to their respective
201 instrumental response factors (Belt et al., 2012). For cores analysed previously, we
202 used the data reported by Köseoğlu et al. (2018b). The proportions of the two tri-

203 unsaturated HBIs (III and IV) in the form of an HBI triene ratio ($HBI\ TR_{25}$) and a re-
204 arranged version of this ($HBI\ T_{25}$) were calculated according to Eqn. 1 and 2.

205 Biomarker-based spring sea ice concentration (%SpSIC) estimates (and their
206 root-mean-square errors (RMSE)) were either obtained from the new biomarker data
207 sets (i.e. for cores 3, 10 and 32) based on the relative concentrations of IP_{25} and HBI
208 III and a regional calibration (Eqn. 3 and 4; Smik et al., 2016), or have been reported
209 previously using the same approach (Berben et al., 2017; Köseoğlu et al., 2018b).
210 Square brackets denote absolute HBI concentrations (ng g⁻¹ dry sed.). All downcore
211 biomarker related data can be found in Supplementary Table 3.

212

213

$$HBI\ TR_{25} = \frac{[III]}{([III] + [IV])} \quad (1)$$

214

$$HBI\ T_{25} = \frac{HBI\ TR_{25}}{0.62} \quad (2)$$

215

$$P_{III}IP_{25} = \frac{[IP_{25}]}{([IP_{25}] + [III] \times 0.63)} \quad (3)$$

216

$$SpSIC\ (\%) = \frac{(P_{III}IP_{25} - 0.0692)}{0.0107} \quad (4)$$

217

218 *3.4 Oceanographic data*

219 Sea ice concentration data were obtained from Nimbus-7 SMMR and DMSP
220 SSM/I-SSMIS databases on a 25×25km grid (Cavalieri et al., 1996). Data from the
221 Aqua satellite (NASA, <https://oceancolor.gsfc.nasa.gov/data/aqua/>) equipped with a
222 Moderate Resolution Imaging Spectroradiometer (MODIS) was used to retrieve
223 chlorophyll a (chl a; mg m⁻³), particulate inorganic carbon (PIC; mol m⁻³),

224 photosynthetically available radiation (PAR; E m⁻² d⁻¹), and sea surface temperatures
225 (SST; °C). Sea surface salinity (SSS; psu; 0–30m water depth) was obtained from
226 World Ocean Atlas 2013 (<https://www.nodc.noaa.gov/OC5/woa13/>) on a 25×25km
227 grid. Monthly aggregates throughout April–August were created (chl a only), as well
228 as those spanning April–June and July–September (all data). Daily-resolution chl a
229 time series spanning 2003–2017 were also created to showcase differences
230 between areas of contrasting spring (ca. April–June) phytoplankton productivity in
231 the Barents Sea. Temporally-averaged (2003–2017) annual maximum concentration
232 of chl a, and the timing of its occurrence (day of year), were also derived. The
233 percentage differences between successive 8-daily averaged chl a (mg m⁻³)
234 spanning years 2003–2017 were calculated using Eq. 5, where Δchl a is the relative
235 difference (in %) between an initial and subsequent 8-day chl a composite at the
236 same location, labelled chl a_{reference} and chl a_{current}, respectively.

$$237 \Delta\text{chl } a (\%) = \frac{(\text{chl } a_{\text{current}} - \text{chl } a_{\text{reference}})}{\text{chl } a_{\text{reference}}} \times 100 \quad (5)$$

238

239 3.6 Statistical analysis

240 To explore associations between the various datasets and between the HBI
241 distributions and satellite-derived chl a data, in particular, Principal Component
242 Analysis (PCA) and complete-linkage Agglomerative Hierarchical Clustering (AHC)
243 using squared Euclidean distance were carried out using XLSTAT (Addinsoft, 2018).
244 More specifically, PCA was used to reduce the high-dimensionality dataset of HBI
245 concentrations, P_{IIIP25}, TR₂₅, satellite-derived and other variables in surface
246 sediments for visualisation on a two-dimensional grid, where the proximity and
247 magnitude of variables indicated their degree of association. Thus, satellite-derived

248 parameters strongly associated with TR₂₅ according to PCA were chosen and
249 individually processed via AHC to determine the optimal number and composition of
250 clusters, as well as their similarity to those obtained using TR₂₅ data. The AHC
251 helped determine a single satellite-derived parameter most closely associated with
252 TR₂₅ in surface sediments.

253

254 **4. Results**

255

256 *4.1 Distribution of HBIs III and IV in surface sediments*

257 HBI IV could be quantified in virtually all surface sediments consistent with the
258 previous identification of near-ubiquity of HBI III in the same sediments (Köseoğlu et
259 al., 2018a) and their co-production by certain marine diatoms (Rowland et al., 2001;
260 Belt et al., 2000, 2017). The distributions of III and IV, when expressed as individual
261 biomarker concentrations, were both somewhat heterogeneous (Fig. 3a,b); however,
262 although spatial variability in the relative amounts of the two HBIs (i.e. HBI TR₂₅
263 (Eqn. 1)) was also evident, generally higher values were observed for sites in the
264 eastern region compared to those in the west (Fig. 3c).

265 Based on PCA (Fig. 4), we found no associations between the sedimentary
266 concentrations of HBIs III or IV with any of the oceanographic parameters
267 considered, including chl a. In contrast, HBI TR₂₅ exhibited a strong association with
268 chl a, but mainly during April and May (i.e. during the spring phytoplankton bloom).
269 AHC analysis between HBI TR₂₅ and chl a resulted in two clusters within areas of
270 well-defined spring bloom seasonality and less productive regions characterised by
271 strong Atlantic Water inflow and continuous upwelling (Fig. 5). Clustering was
272 dependent on the month(s) selected for chl a data (i.e. April, May, April–May, April–

273 June), with the April–May aggregate exhibiting the least mismatched cluster
274 memberships ($n = 28$) relative to those of HBI TR₂₅ (Fig. 5). In contrast, the number
275 of mis-matches for the other months ranged from 30 to 57 (Supplementary Fig. 1).
276 Averaging the AHC centroids using the April-May aggregated chl a data yielded an
277 approximate threshold value for HBI TR₂₅ of ca. 0.62 ± 0.02 to separate regions of
278 high (i.e. TR ≥ 0.62) and low (TR < 0.62) April–May chl a delineated by a 1.5 mg m^{-3}
279 boundary.

280

281 *4.2 HBI biomarkers in downcore records*

282 For cores representing recent centuries, the sea ice biomarker IP₂₅ was
283 absent (or below detection limits) in cores 1, 10 and 32 (Supplementary Fig. 2;
284 Köseoğlu et al., 2018a) as expected due to their ice-free settings in modern times
285 (Fig. 2a). Further, HBIs III and IV were present in virtually all horizons in each core,
286 (with the exception of the early part of the record in core 32; Supplementary Fig. 2),
287 consistent with our findings from proximal surface sediments described herein (Fig.
288 3a,b). In contrast, IP₂₅ was identified in the three cores from sites of seasonal sea ice
289 cover (i.e. cores 8, 43, 712; Vare et al., 2010; Cabedo-Sanz and Belt, 2016;
290 Koseoglu et al., 2018a), and HBIs III and IV were again present throughout, albeit in
291 variable concentrations (Supplementary Fig. 2). HBI TR₂₅ also exhibited some spatial
292 variability, with values broadly reflecting those found in nearby surface sediments
293 (Fig. 3c, 6a). Thus, relatively low (i.e. <0.62) HBI TR₂₅ values were observed
294 throughout each of cores 8, 10, 32 and 712, all of which are located in regions of low
295 spring chl a in modern times. Similarly, consistently high HBI TR₂₅ values (i.e. >0.62)
296 characterise core 43, located in a region of high spring chl a adjacent to the modern

297 winter sea ice margin (Fig. 2a). In contrast, HBI TR₂₅ values both above and below
298 0.62 were evident in core 1 (Fig. 6a).

299 In the longer timeframe records (i.e. cores 3, 11 and 70), individual biomarker
300 concentrations and HBI TR₂₅ values were also variable. For example, IP₂₅ was not
301 identified in core 3, although HBIs III and IV were present throughout the last ca. 3.0
302 cal kyr BP (Supplementary Fig. 3). Consistent with its low spring chl a setting in
303 modern times, HBI TR₂₅ was also <0.62 throughout (Fig. 7a). For core 11, IP₂₅ and
304 SpSIC were low during the early–mid Holocene, with increases in both to near-
305 modern values since ca. 1.1. cal kyr BP, as reported previously (Berben et al., 2014;
306 Belt et al., 2015) (Fig. 7b). HBI TR₂₅ was low (<0.62) in the early Holocene, before
307 increasing to ca. 0.62 around 6.0 cal. kyr BP, and then to values consistently >0.62
308 after ca. 1.1 cal. kyr BP, coincident with increases to IP₂₅ and SpSIC estimates (Fig.
309 7b). Finally, progressive increases to IP₂₅ and SpSIC from the early to late Holocene
310 characterise the core 70 site, as described previously (Belt et al., 2015; Berben et
311 al., 2017) (Fig. 7c). HBIs III and IV were also present throughout the Holocene
312 (Supplementary Fig. 3), with HBI TR₂₅ values mainly greater than 0.62; however,
313 slightly higher values were observed ca. 9.0–6.0 cal kyr BP, while some values close
314 to the 0.62 threshold were evident thereafter (Fig. 7c).

315

316 **5. Discussion**

317 *5.1 Use of HBI TR₂₅ and HBI T₂₅ as proxies for the spring phytoplankton bloom*

318 The spatially variable proportion of HBIs III and IV, albeit on a somewhat
319 smaller sample set, was previously suggested to possibly reflect the spatial
320 distribution of Atlantic Water (AW) and Arctic Water (ArW) in the region (Navarro-
321 Rodriguez, 2014). The defining characteristics of both water masses include

322 temperature and salinity (e.g. Loeng, 1991; Sakshaug et al., 2009). However, we
323 observed no association between any of the spring-summer satellite sea surface
324 temperature (SST), photoavailable radiation (PAR) or sea surface salinity (SSS)
325 records and HBI TR₂₅ in surface sediments presented herein (Fig. 4), which
326 suggests the influence of these is either absent or obscured by competing effects. In
327 contrast, chl a data, as an indicator of standing phytoplankton stocks, showed a
328 strong correlation with HBI TR₂₅, but only during the spring bloom (i.e. April–May).
329 This was further supported by similar clustering (AHC) of HBI TR₂₅ and chl a for
330 April–May and (to a lesser extent) May only, likely due to the high spatio-temporal
331 variability of phytoplankton bloom development in the Barents Sea.

332 Driven mainly by the spring phytoplankton bloom in April-May (Fig. 8a),
333 maximum annual chl a (Fig. 8c) is highest on the highly-productive south-eastern
334 and central shelves, reaching its maximum generally ca. 1–2 months earlier (Fig. 8d)
335 compared to the western and northern Barents Sea (Fig. 8c). The highest rates of
336 change in chl a, a further characteristic of a bloom event, are also most apparent
337 along the south-eastern and central shelves (Fig. 8b). Along the western margin,
338 slower (thermally-induced) vertical stratification and continuous AW upwelling hinder
339 phytoplankton accumulation, while insufficient light penetration through thick ice
340 cover lowers pelagic production at the northern margin (e.g. Dalpadado et al., 2014).
341 Thus, in April, only the ice-free south-eastern Barents Sea shows significant
342 increases in chl a (Supplementary Fig. 1a), followed by a propagation, north-
343 eastwards along the retreating sea ice edge, by early May (Supplementary Fig. 1b).
344 Phytoplankton biomass sharply declines by June (Fig. 8a) due to nutrient (e.g. nitrate
345 and silicate) depletion and limited replenishment through the meltwater-established
346 pycnocline in the marginal ice zone (MIZ) (e.g. Signorini and McClain, 2009; Leu et

347 al., 2011), with subsequent summer blooms dominated by coccolithophores
348 (Hopkins et al., 2015), which are not HBI-producers.

349 Thus, HBI TR₂₅ appears to be most representative of the pelagic spring bloom
350 throughout April–May. More specifically, HBI III is most prevalent (HBI TR₂₅ ≥ 0.62)
351 in the eastern/central Barents Sea, where chl a is mainly in excess of 1.5 mg m⁻³. In
352 contrast, relatively increased IV (HBI TR₂₅ = ca. 0.4–0.45) generally occurs in the
353 western Barents Sea, where chl a concentrations are generally in the range 0.5–1.5
354 mg m⁻³. Furthermore, bloom seasonality is not as pronounced in the western Barents
355 Sea compared to the eastern Barents Sea (Fig. 8a). Similarly, low HBI TR₂₅ is also
356 evident in extensively ice-covered areas north and east of Svalbard, where the
357 productive season is time- and nutrient-limited due to the late seasonal sea ice
358 retreat throughout July–August (Signorini and McClain, 2009). This further supports
359 our suggestion that HBI TR₂₅ is predominantly influenced by spring phytoplankton
360 bloom development in the Barents Sea.

361 Finally, we suggest that the HBI TR₂₅ threshold for the spring phytoplankton
362 bloom (i.e. HBI TR₂₅ ≥ 0.62) is most conveniently expressed as a simple binary
363 measure using a slightly modified ratio of the two HBI trienes. Thus, HBI T₂₅ ≥ 1
364 (Eqn. 2) provides a proxy measure for the spring phytoplankton bloom (Fig. 9).

5.2 HBI TR₂₅ and HBI T₂₅ in records covering recent centuries

365 The HBI TR₂₅ and HBI T₂₅ data for the six short cores (i.e. 1, 8, 10, 32, 43 and
366 712) representing recent centuries reflect their respective locations and the
367 occurrence of spring phytoplankton blooms (or otherwise) within the modern context
368 (Note: we refer only to HBI T₂₅ values from hereon). Thus, relatively low (<1) HBI T₂₅

369 values prevail throughout the 10 and 32 records, consistent with low chl a at these
370 ice-free locations (Fig. 2a,6a).

371 Similarly, HBI T₂₅ in core 712 was constantly below the threshold for a spring
372 phytoplankton bloom. The core site is characterised by low chl a in modern times,
373 and is located at the largely ice-free western Svalbard margin influenced by the
374 strongest inflow of AW with the North Atlantic Current (NAC; Fig. 2). The
375 contemporary ice edge duration at site 712 is limited, and stratification necessary for
376 rapid spring bloom development is weaker due to continuous AW overturning
377 (Smedsrød et al., 2013). However, instrumental records show that ice cover at the
378 Svalbard margin was more extensive prior to ca. 1850 AD (Divine and Dick, 2006),
379 supported by the P_{III}P₂₅-based estimates of SpSIC reported previously (Fig. 6b;
380 Cabedo-Sanz and Belt, 2016). Interestingly, a gradual decrease in HBI T₂₅ at site
381 712, possibly indicative of a lower frequency of spring phytoplankton blooms, also
382 coincides with the recent sea ice decline (Fig. 6a,b). Accordingly, increased
383 phytoplankton stocks at site 712 prior to 1850 AD could be attributable to longer
384 annual sea ice duration, when increased stratification potentially stabilised
385 phytoplankton in the photic zone, facilitating the type of rapid growth normally
386 associated with the contemporary MIZ in the central Barents Sea. Recent increases
387 in AW inflow and atmospheric temperatures (e.g. Årthun et al., 2012) subsequently
388 shifted the Barents Sea towards less productive, predominantly ice-free conditions
389 dominated by continuous upwelling, with lower HBI T₂₅ (Fig. 6a). Previously,
390 Pathirana et al. (2015) also linked reduced MIZ duration in the Barents Sea to
391 decreasing primary productivity over the last ca. 500 years.

392 Core 8 exhibits similar HBI T₂₅ values to core 712, but is located in a
393 significantly different setting of increased (>80%) SpSIC north of the central Barents

394 Sea MIZ, and influenced predominantly by colder ArW. HBI T_{25} values are, therefore,
395 potentially attributable to reduced productivity in areas of prolonged seasonal sea ice
396 duration, where the melt season is conversely shortened. Coupled with potential
397 nutrient depletion within the surrounding waters as a consequence of rapid spring
398 bloom development south of the core site (e.g. Wassmann et al., 2006; Signorini and
399 McClain, 2009), the extensive sea ice cover at site 8 over recent centuries (Fig. 6b)
400 likely prevented the development of spring phytoplankton blooms.

401 In contrast, cores 1 and 43 are characterised by consistently higher HBI T_{25}
402 relative to cores 8, 10, 32 and 712 (Fig. 6a). In fact, the highest HBI T_{25} values in the
403 current datasets are associated with core 43 (all $HBI\ T_{25} > 1$; Fig. 6a), a site located
404 firmly within the spring phytoplankton bloom zone, with chl a values $>2\ mg\ m^{-3}$.
405 Spring productivity was likely enhanced by the consistent presence of a proximal ice
406 edge with intermediate spring sea ice concentration (SpSIC) (Fig. 6b), which aided
407 stratification during the melt season. Conversely, the absence of seasonal sea ice at
408 site 1 may have reduced productivity somewhat, as indicated by slightly lower HBI
409 T_{25} values (Fig. 6a). In fact, the somewhat oscillatory (either side of 1) pattern of HBI
410 T_{25} likely reflects the close proximity of the core site to the recent (2003–2017) spring
411 phytoplankton bloom boundary, with short-term variability over decadal (or shorter)
412 timeframes during recent centuries. This possibly reflects the variable influence of
413 the North Cape Current (NCaC), since intensified AW upwelling could have reduced
414 the stability of the water column at the core site, resulting in lower productivity.

415 5.3 HBI T_{25} in Holocene records

416 In order to make a first assessment of the reliability of the HBI T_{25} proxy
417 measure of the spring phytoplankton bloom over longer timeframes, we measured it
418 in three early-late Holocene records from regions of contrasting sea ice and

419 phytoplankton bloom occurrence in modern times, and for which evidence for
420 temporal changes in oceanography had already been established from previous
421 proxy-based investigations. The shortest of these records, obtained from core 3,
422 located in the SW Barents Sea, adds to the findings presented earlier for sites 3 and
423 10 spanning recent centuries (Fig. 2a). Thus, consistently low HBI T₂₅ in core 3
424 characterises this perennially ice-free region with low spring chl a over the last ca.
425 3.0 cal. kyr BP (Fig. 7a).

426 The core 11 site is proximal to the modern maximum winter sea ice margin
427 (Fig. 2a). During the Holocene, HBI T₂₅ gradually increased since ca. 9.5 cal kyr BP,
428 with values generally exceeding the spring bloom threshold since the onset of the
429 Neoglacial at ca. 6.0 cal kyr BP (Fig. 7b). According to previous investigations, the
430 core 11 site was relatively ice-free during the Holocene (Berben et al., 2014; Belt et
431 al., 2015); however, a highly-productive ice edge likely remained close to the
432 Kveithola Trough following the Neoglacial ice advance, as previously suggested for
433 Storfjorden (Knies et al., 2017), located slightly further north. High productivity fuelled
434 by seasonal sea ice-induced stratification and AW upwelling could have propagated
435 towards the core 11 site at ca. 6.0 cal kyr BP, thus promoting the occurrence of
436 spring phytoplankton blooms as a more frequent feature. Finally, high (>1) HBI T₂₅ in
437 the late Holocene is consistent with spring phytoplankton blooms associated with the
438 productive ice edge having reached the core site at ca. 1.1 cal kyr BP (Fig. 6b;
439 Berben et al., 2014; Belt et al., 2015), a conclusion supported further by a
440 productivity increase inferred from higher benthic foraminiferal content (Berben et al.,
441 2014).

442 In contrast to cores 3 and 11, core 70 is situated at a site of extensive winter
443 sea ice cover in modern times. However, conditions during the early Holocene were

444 less severe, such that the site was proximal to the winter ice margin until ca. 6.0 cal
445 kyr BP (SpSIC ca. 20–50%; Fig. 7c) followed by a further progressive southward sea
446 ice expansion and increase in SpSIC (Fig. 7c; Belt et al., 2015; Berben et al., 2017).
447 Consistent with these changes, HBI T_{25} values are highest during the early–mid
448 Holocene (up to ca. 6.0 cal. kyr BP), likely as a result of the favourable MIZ
449 conditions, after which they undergo a slight decrease, possibly due to a reduction in
450 the length of the open water season due to delayed sea ice retreat (c.f. core 8).
451 However, on the basis of HBI T_{25} values generally higher than 1 across the record,
452 spring phytoplankton blooms would appear to have been an important feature of the
453 core site throughout the record.

454 *5.4 Rationalising the relationship between HBI T_{25} and spring phytoplankton blooms*

455 Our surface sediment outcomes (PCA and cluster analyses), together with
456 those from various downcore records suggest that the biomarker-based HBI T_{25}
457 parameter described herein provides a qualitative proxy indicator for the occurrence
458 of spring phytoplankton blooms across the study region from recent to Holocene
459 timeframes. Intuitively, this association is perhaps not surprising given that HBIs are
460 produced by the main constituents of the spring phytoplankton bloom (i.e. diatoms),
461 although this alone does not provide adequate explanation for the observed
462 relationship. For example, HBIs III and IV are present at virtually all study sites,
463 irrespective of the occurrence (or not) of a spring phytoplankton bloom. Further,
464 while absolute sedimentary concentrations of HBIs III and IV show a significant
465 enhancement within the MIZ, they are relatively low in some other regions of high chl
466 a (e.g. in the ice-free SE Barents Sea; Fig. 3) and are poorly associated with chl a
467 (Fig. 4), more generally. The latter is potentially attributable to the increased
468 prevalence of diatoms relative to other microalgae closer to the well-stratified waters

469 near the ice edge (e.g. Wassmann et al., 2006; Sakshaug et al., 2009). Absolute
470 biomarker concentrations are also influenced by sediment accumulation rates and
471 export efficiency from the water column, both of which can be variable, spatially, and
472 thus may not accurately reflect production, more generally. On the other hand, such
473 influences are often much less important with ratio-based measures.

474 In any case, in order to rationalise the association between HBI T_{25} and the
475 spring phytoplankton bloom, we briefly consider three possible contributing factors:
476 (i) different sources of HBIs III and IV; (ii) differential biomarker degradation; (iii)
477 variable phytoplankton growth rates.

478 First, HBIs III and IV are amongst the most common HBIs found in marine
479 sediments (Belt et al., 2000), yet very few sources have been identified. Of these,
480 *Rhizosolenia setigera* and related species are by far the most cosmopolitan and
481 abundant, and HBIs III and IV have indeed been identified in such species from the
482 current study region (Belt et al., 2017). In contrast, although HBIs III and IV have
483 been reported in the benthic diatom *Pleurosigma intermedium* (Belt et al., 2000),
484 they have not been identified in other marine *Pleurosigma* spp., which are, in any
485 case, generally very low or absent in taxonomic inventories. The more common
486 *Berkeleya rutilans* (Brown et al., 2014 and references cited therein) has been shown
487 to produce HBI IV (but not HBI III) in culture, although we are not aware of any
488 reports to indicate that the spatial distribution of *B. rutilans* (or *Rhizosolenia* spp.)
489 would result in the variability of HBI T_{25} described herein. Likewise, additional
490 contribution to sedimentary HBI IV may potentially also occur in ice covered regions
491 since *B. rutilans* has been reported in sea ice (von Quillfeldt, 2000); however, this
492 would result in a reduction in HBI T_{25} in such settings, which is not the case (Fig.

493 3,9). Thus, we suggest that *R. setigera* and related species are likely to be the main
494 sources of HBIs III and IV in the Barents Sea and neighbouring regions.

495 Of course, as yet unidentified sources of HBIs III and IV may also contribute
496 to the observed sedimentary variability in HBI T₂₅, although some of the most
497 common species characteristic of colder, nutrient-replete waters in the Barents Sea,
498 such as *Thalassiosira* or *Fragilariaopsis* spp. (von Quillfeldt, 2000), are not known to
499 be HBI-producers.

500 Second, changes to HBI T₂₅ may result from differential degradation of HBIs
501 III and IV in the water column or sediments, or by selective removal through grazing.
502 However, previous food web studies have shown no significant change to HBI
503 composition prior to, and after, consumption (e.g. Brown and Belt, 2017; Schmidt et
504 al., 2018). In some laboratory experiments, HBI IV was shown to be slightly more
505 reactive than HBI III towards photo-oxidation and autoxidation (Rontani et al., 2014),
506 although whether this is true under in situ environmental conditions is as yet
507 unknown. In the meantime, we note that a higher rate of degradation of HBI IV would
508 result in higher HBI T₂₅ values for regions of increased water depth, yet the opposite
509 is true in most cases. Further, we observe no significant association between HBI T₂₅
510 and water depth in the PCA (Fig. 4).

511 Third, we consider whether variable HBI T₂₅ is controlled by changes in
512 growth rates of *R. setigera* (and potentially related *Rhizosolenia* spp.), with higher
513 relative production of HBI III under conditions of more rapid growth (Fig. 8b). In
514 support of this suggestion, Rowland et al. (2001) demonstrated a systematic
515 increase in the amount of HBI III relative to HBI IV with increasing growth rate of *R.*
516 *setigera* cultured at different temperatures. Since we observe no relationship
517 between HBI T₂₅ and SST in the current dataset, we therefore suggest that the

518 variability described herein results from regional differences in phytoplankton growth
519 rates (Fig. 8b). Such a working hypothesis will, of course, require testing through
520 further investigations into the controls over HBI production by *R. setigera* and other
521 HBI-producing diatoms, including laboratory-based studies and time-series
522 monitoring of their production in the Barents Sea and other areas of well-defined
523 primary productivity.

524 Increased growth rates of *R. setigera*, in particular, may also help explain
525 some of the anomalies in our surface sediment data. For example, a number of
526 mismatches in AHC cluster memberships of chl a and HBI T₂₅ occurred along the
527 south-western Barents and Norwegian Sea coastlines (Fig. 5), which could be a
528 consequence of local effects associated with coastal water masses flowing inshore
529 of the NAC and within the NCC. In such settings *R. setigera* has the potential to
530 overtake other species under strong upwelling and nutrient-replete conditions, as
531 seen at the western Svalbard shelf (Belt et al., 2017). Moreover, the NCC (Fig. 2a)
532 carries brackish coastal waters from the Baltic Sea, where increasing dominance of
533 *R. setigera* and other cold-water species during spring and early summer blooms
534 has been reported (e.g. Wasmund et al., 2008). Interestingly, several of the higher
535 HBI T₂₅ values from near-coastal locations are also proximal to some chl a hotspots,
536 despite the generally lower chl a for this region (Fig. 9).

537 Apart from the binary division between spring phytoplankton bloom (HBI
538 T₂₅>1) versus bloom-free (HBI T₂₅<1) conditions (Fig. 9), we note some further
539 variability in HBI T₂₅ in both the surface sediment and downcore datasets (Fig. 6,7)
540 either side of this threshold. Such variability might potentially reflect the mean
541 frequency (or intensity) of spring phytoplankton bloom occurrence at each
542 site/timeslice, especially since the sediment horizons investigated herein (1-cm)

543 typically represent ca. 20–50 years of accumulation (e.g. Dylmer, 2013; Berben et
544 al., 2014,2017; Belt et al., 2015; Köseoğlu et al., 2018a). Such an interpretation
545 would likely improve the value of the HBI T₂₅ proxy in palaeo records, beyond a
546 simple binary measure, including the identification of temporal shifts in the frequency
547 of spring phytoplankton blooms, more generally; however, this aspect also requires
548 further investigation.

549 Finally, when used alongside IP₂₅ as a binary measure of seasonal sea ice
550 (Belt, 2018) and PIP₂₅ as a semi-quantitative tool for spring sea ice concentration,
551 the newly proposed HBI T₂₅ proxy for the spring phytoplankton bloom has the
552 potential to provide a more robust indicator of the MIZ in northern high latitude
553 locations, and its spatial and temporal variation within the palaeo record.

554

555 **6. Conclusions**

556 Based on their distribution in surface sediments from across the Barents Sea and
557 neighbouring regions, the relative amounts of two tri-unsaturated HBI (III and IV; Fig.
558 1) lipids (HBI TR₂₅) appears to provide proxy evidence for the spring phytoplankton
559 bloom. Further, by re-expressing the HBI TR₂₅ ratio in a simplified binary format, a
560 threshold for the spring bloom is proposed (i.e. HBI T₂₅ ≥ 1). HBI T₂₅ values in short
561 (decadal-centennial) and long (Holocene) records from the region are consistent with
562 the surface sediment calibration dataset, with some changes to the
563 occurrence/frequency of the spring bloom linked to temporal changes in sea ice
564 concentration identified previously. The identification of a novel proxy for the spring
565 phytoplankton bloom for northern high latitudes (at least), could potentially provide
566 important insights into characterising the marginal ice zone, especially when used
567 alongside established sea ice proxies such as IP₂₅ and PIP₂₅.

568

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578 **Figure Legends**

579
580

581 Figure 1. Structures of highly branched isoprenoid (HBI) biomarkers investigated in
582 the current study.

583 Figure 2. Maps of the Barents Sea showing: (a) Labelled centennial (black
584 diamonds) and millennial (white squares) downcore records, as well as a simplified
585 representation of Atlantic Water, Arctic Water, and Coastal Water surface currents
586 shown by red, blue, and white arrows, respectively. Abbreviations denote: WSC –
587 West Spitsbergen Current; NAC – North Atlantic Current; NCAC – North Cape
588 Current; NCC – Norwegian Coastal Current; ESC – East Spitsbergen Current; PC –
589 Persey Current; (b) Surface sediment locations. For both maps, the solid black line

590 illustrates the averaged (1988–2017) April–June sea ice extent, defined by a 15%
591 SpSIC threshold. Maps were generated with Ocean Data View (<http://odv.awi.de/>).

592 Figure 3. Distributions of absolute and relative HBI biomarker concentrations in
593 Barents Sea surface sediments: (a) HBI III; (b) HBI IV; (c) HBI TR₂₅. The 15% SpSIC
594 contour (1988–2017) is shown by a black line. Maps were generated with Ocean
595 Data View (<http://odv.awi.de/>).

596 Figure 4. Scaled factor loadings of primary (green markers) and secondary (blue
597 markers) variables with HBI TR₂₅ at surface sediment locations (Fig. 2b). Green
598 labels denote months of averaged (2003–2017) satellite-derived chl a (mg m⁻³). Blue
599 labels represent surface sediment water depths (m), average (2003–2017) sea
600 surface temperature (SST; °C), photoavailable radiation (PAR; E m⁻² d⁻¹), particulate
601 inorganic carbon (PIC; mol m⁻³), 1955–2012 sea surface salinity (SSS; psu), as well
602 as 1988–2017 sea ice concentration (SIC; %); prefixes “Su” and “Sp” denote
603 summer (July–September) and spring (April–June). Absolute concentrations of III
604 and IV (Fig. 1) and HBI TR₂₅ are highlighted in red.

605 **Figure 5:** Map of average chl a during April–May (2003–2017). Black and white
606 circle markers represent the two AHC clusters of TR₂₅ in surface sediments.
607 Diagonal crosses denote HBI TR₂₅ cluster memberships which mis-match those of
608 the chl a data (n = 28). The 1.5 mg m⁻³ contour for chl a (2003–2017) is shown as a
609 white line, and the 15% April–May sea ice concentration contour (1988–2017) is
610 indicated by a black line. Maps were generated with Ocean Data View
611 (<http://odv.awi.de/>).

612 Figure 6. HBI-derived proxy data from six short-core records within the study region,
613 spanning recent centuries and experiencing contrasting sea ice and phytoplankton

614 bloom occurrence in modern times: (a) HBI T₂₅ and HBI TR₂₅. The binary threshold
615 for the modern-day spring phytoplankton bloom (i.e. HBI T₂₅ >1) (Fig. 5,9), is
616 represented by a solid horizontal line. The shaded area represents the estimated
617 error in this threshold (HBI TR₂₅ ca. ±0.02; HBI T₂₅ ca. ±0.03). The colours of each
618 data point represent the proposed occurrence of a spring phytoplankton bloom
619 (orange) versus no bloom (blue) at each core site/timeslice; (b) spring sea ice
620 concentration estimates (% SpSIC).

621 Figure 7. HBI-derived proxy data for Holocene records: (a) 3; (b) 11; (c) 70. Left-
622 hand axes: HBI TR₂₅ and HBI T₂₅ represented by solid line profiles with coloured
623 markers. The solid horizontal line indicates the thresholds for the spring
624 phytoplankton bloom (Fig 5,9), while the shaded area represents the estimated error
625 in this threshold (HBI TR₂₅ ca. ±0.02; HBI T₂₅ ca. ±0.03). The colour of each data
626 point represents the proposed occurrence of a spring phytoplankton bloom (orange)
627 versus no bloom (blue) at each core site/timeslice. Right-hand axes: %SpSIC
628 estimates represented by a dash-dotted line together with RMSE estimates (ca.
629 ±11%; Smik et al., 2016).

630 Figure 8. Average (2003–2017) satellite-derived chl a data within the study area.
631 Upper panel shows the temporal evolution of mean chl a for regions where there is a
632 presence (green diamonds) or absence (red circles) of significant, diatom-dominated
633 spring blooms according to a 1.5 mg m⁻³ April–May chl a threshold: (a) daily chl a
634 concentration; (b) relative changes in chl a. Lower panel shows the temporally-
635 averaged (2003–2017) annual chl a maximum (c) and the day of its maximum
636 occurrence within the annual cycle (d). Maps were generated with Ocean Data View
637 (<http://odv.awi.de/>).

638 Figure 9. Distribution of HBI T₂₅ in surface sediments overlaid onto remotely-sensed
639 April–May (2003–2017) chl a. The white line represents a 1.5 mg m⁻³ chl a contour
640 and delimits zones of high and lower pelagic phytoplankton productivity during the
641 spring bloom (Fig. 5c). Map was generated with Ocean Data View
642 (<http://odv.awi.de/>).

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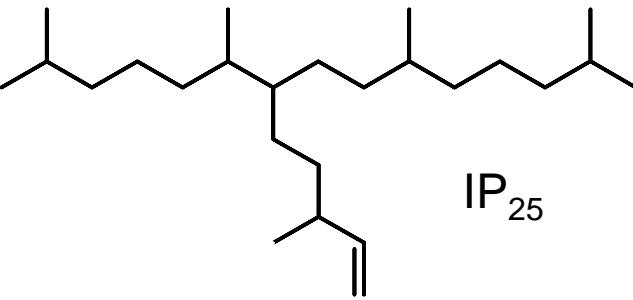
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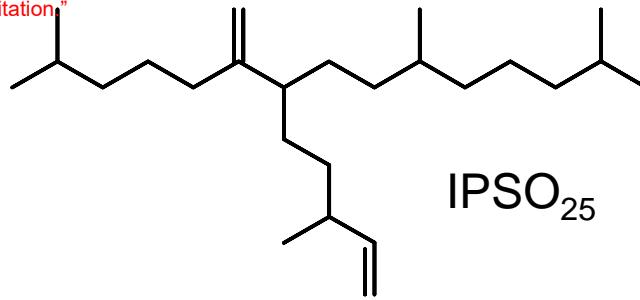
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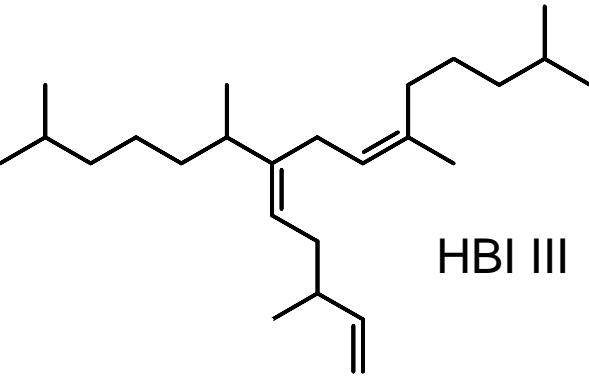
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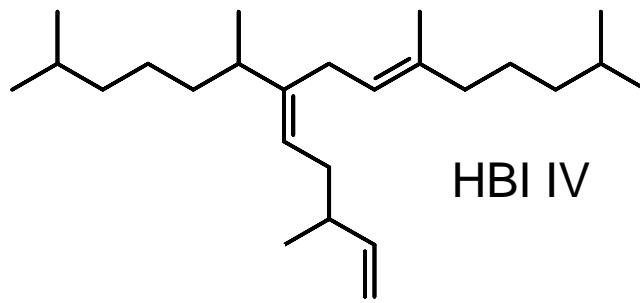
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HBI III

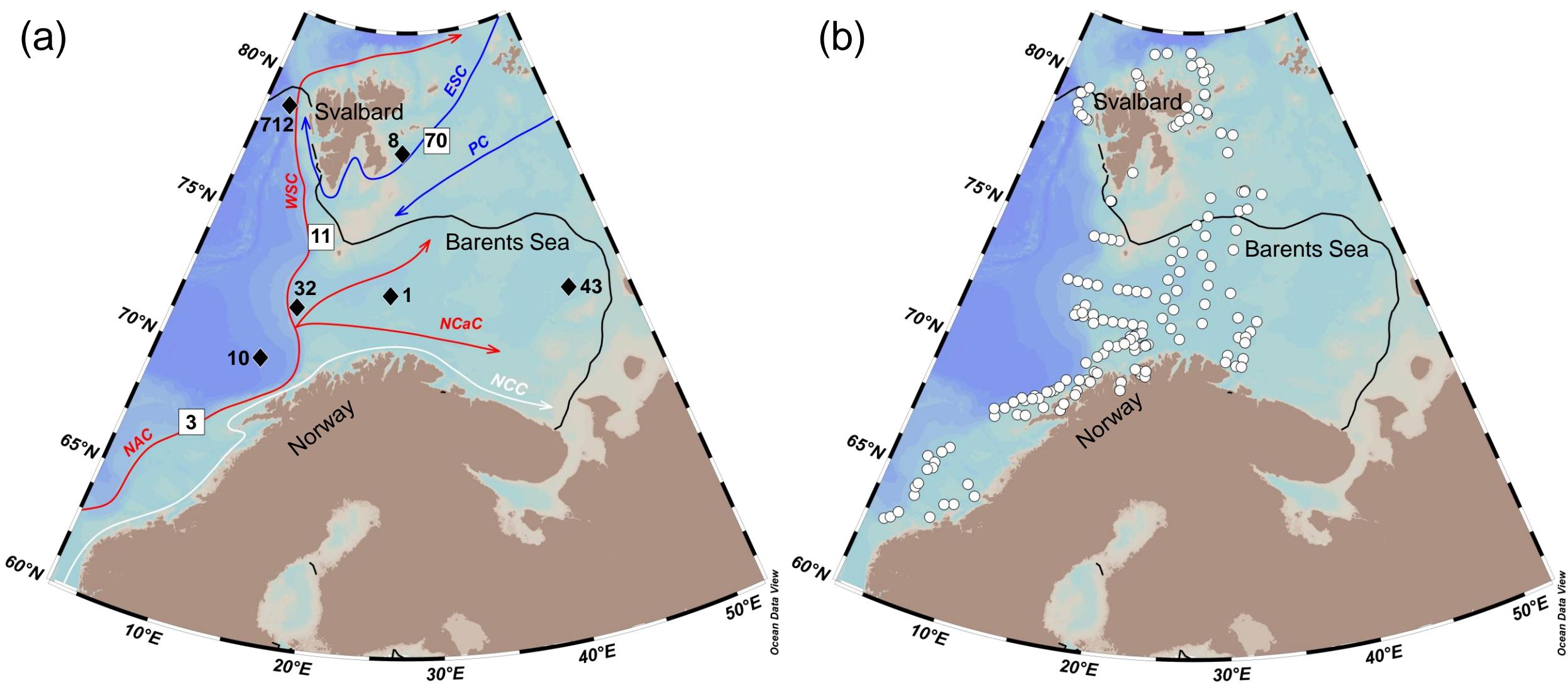


HBI IV

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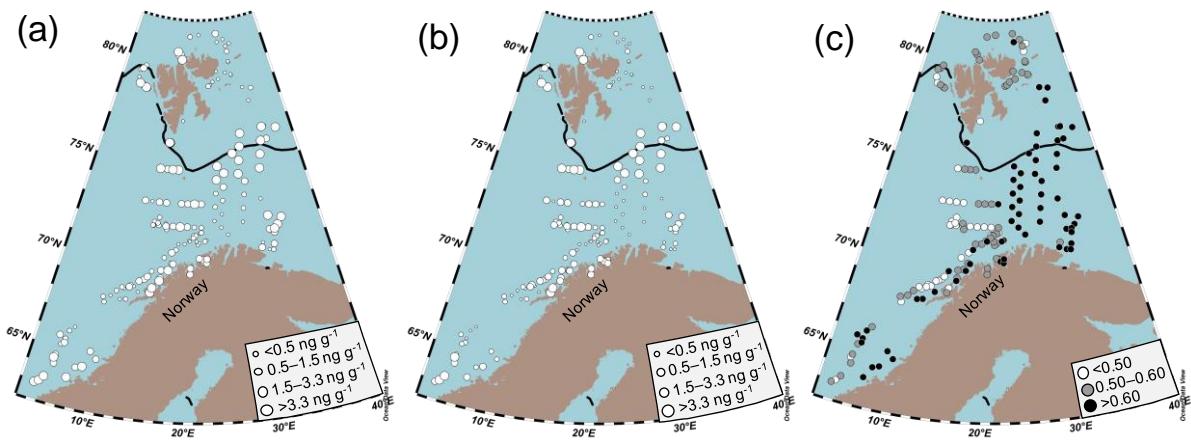
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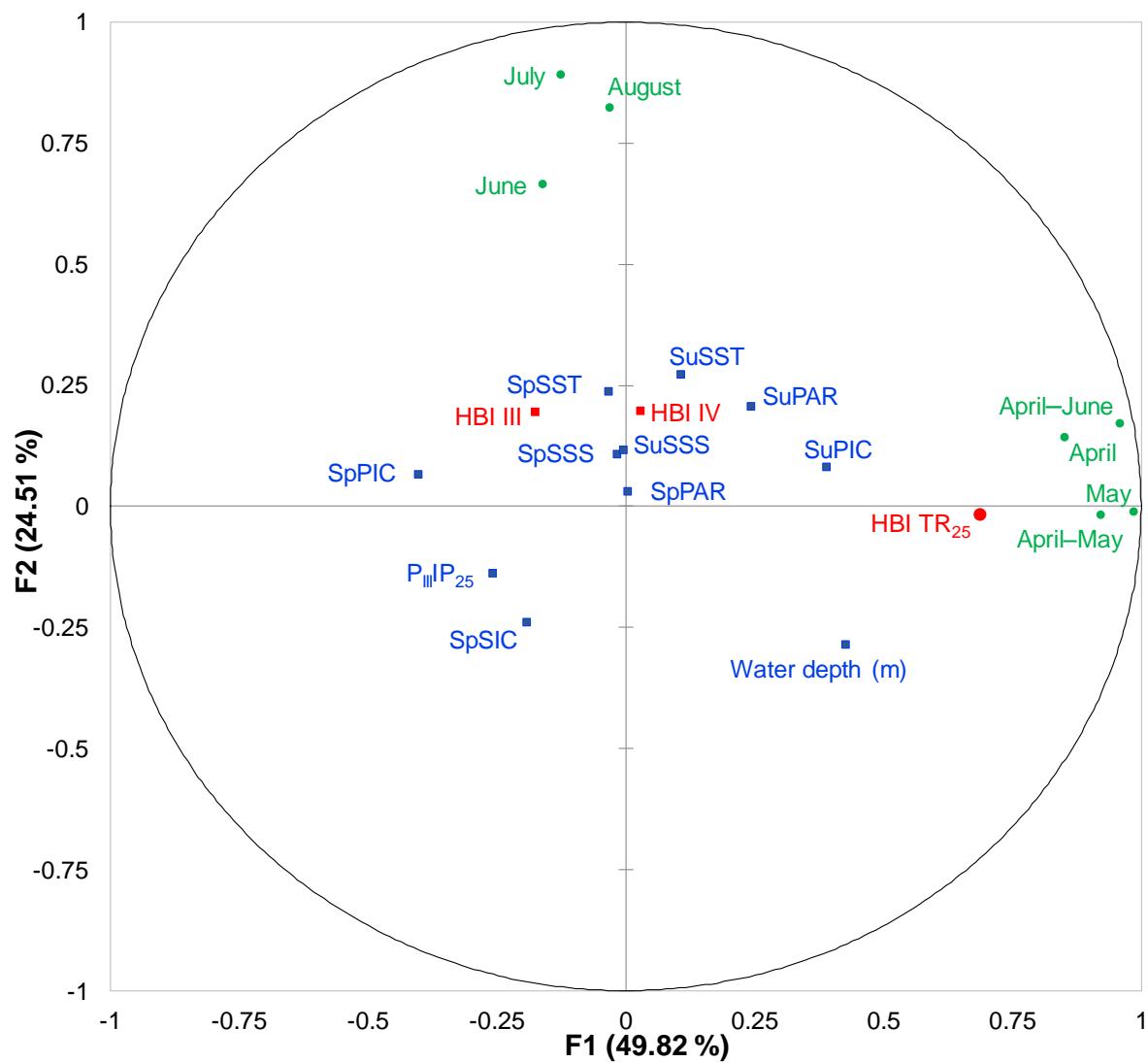
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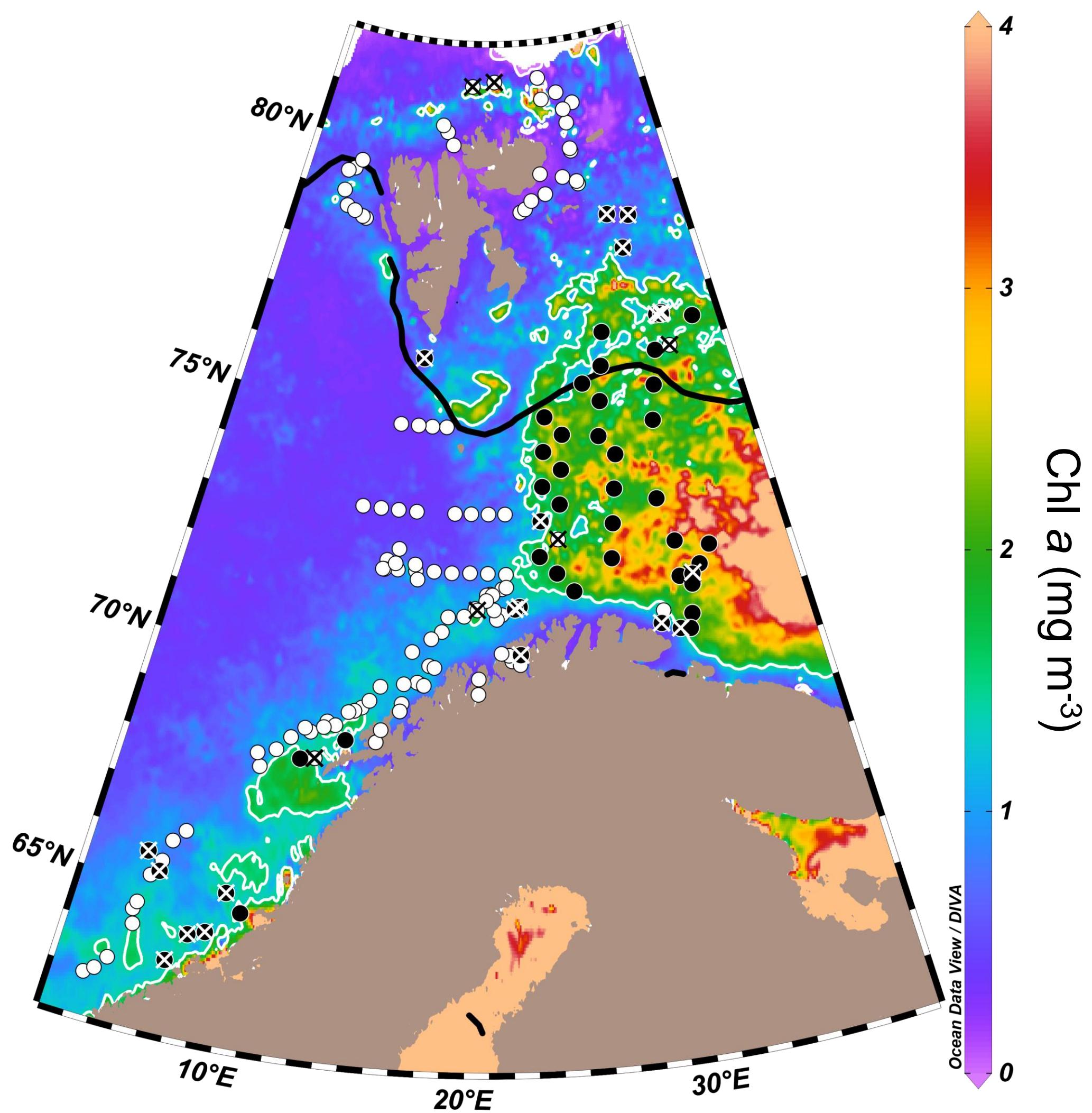
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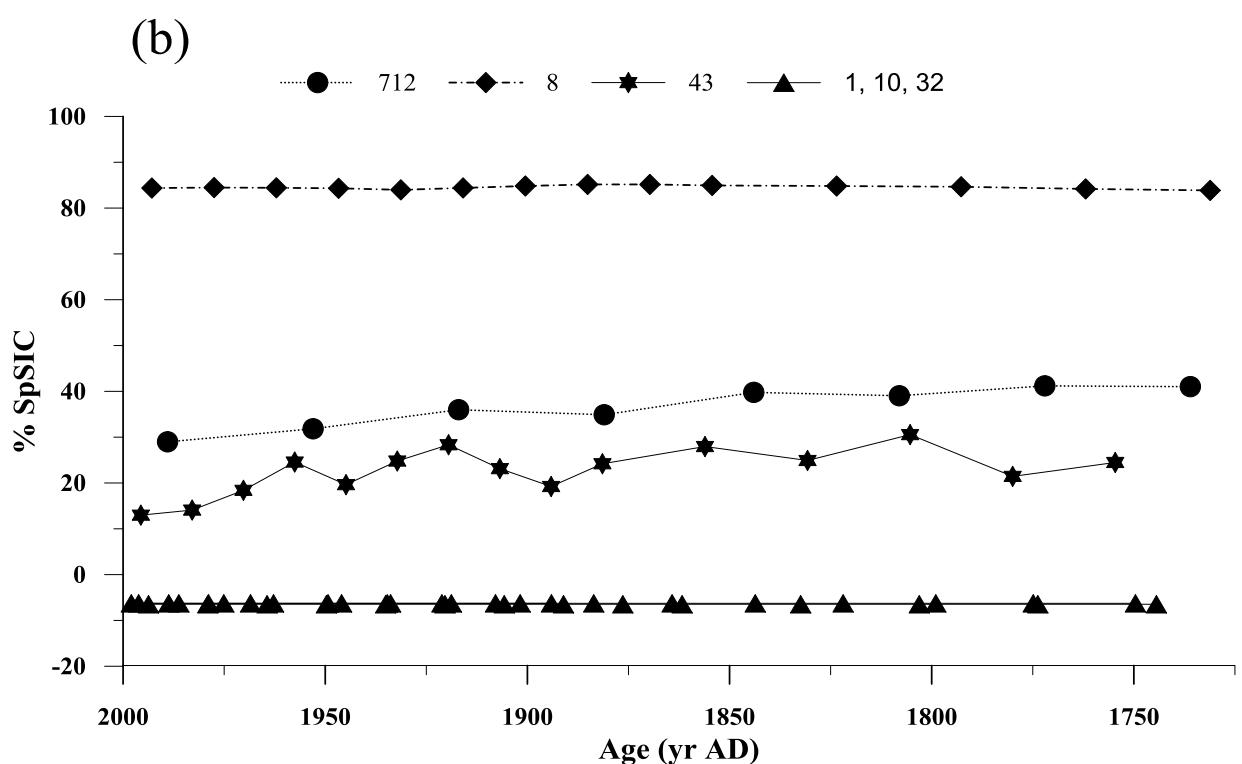
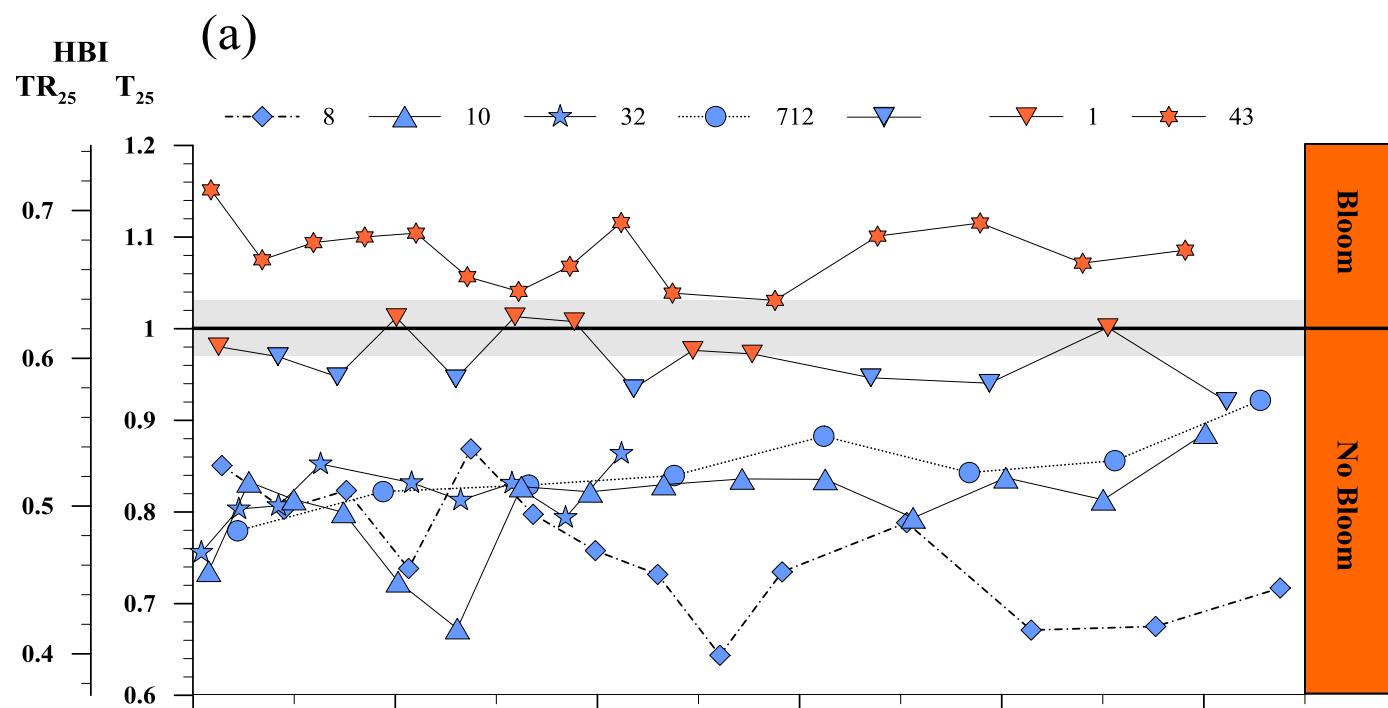
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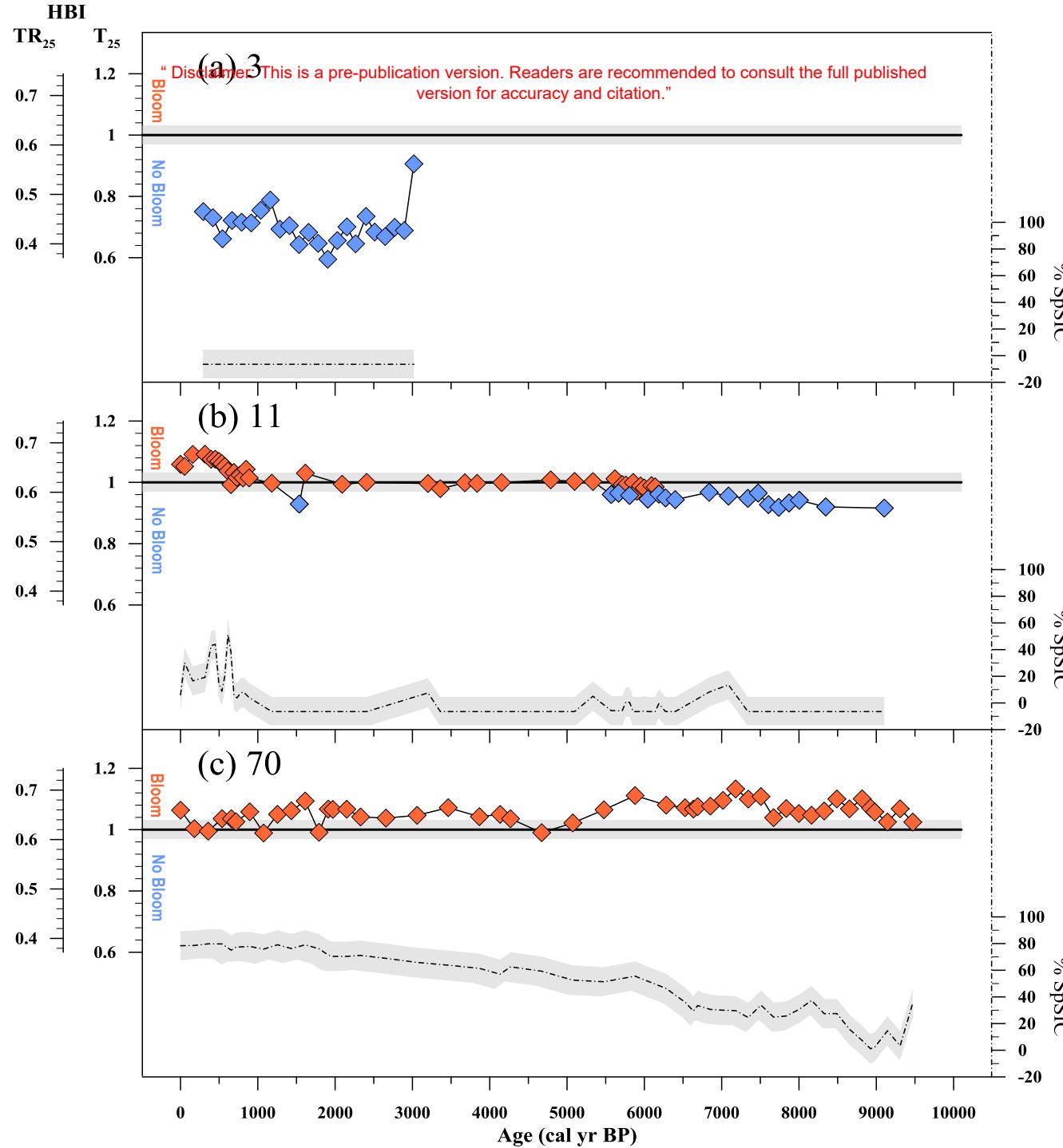
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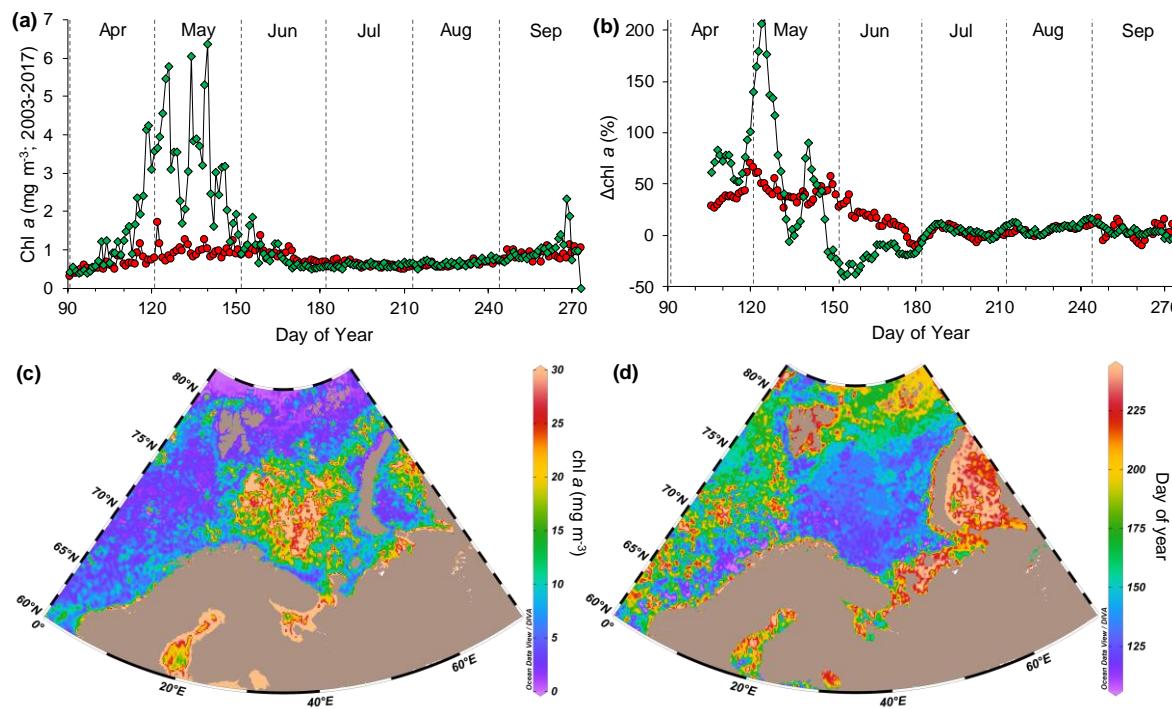
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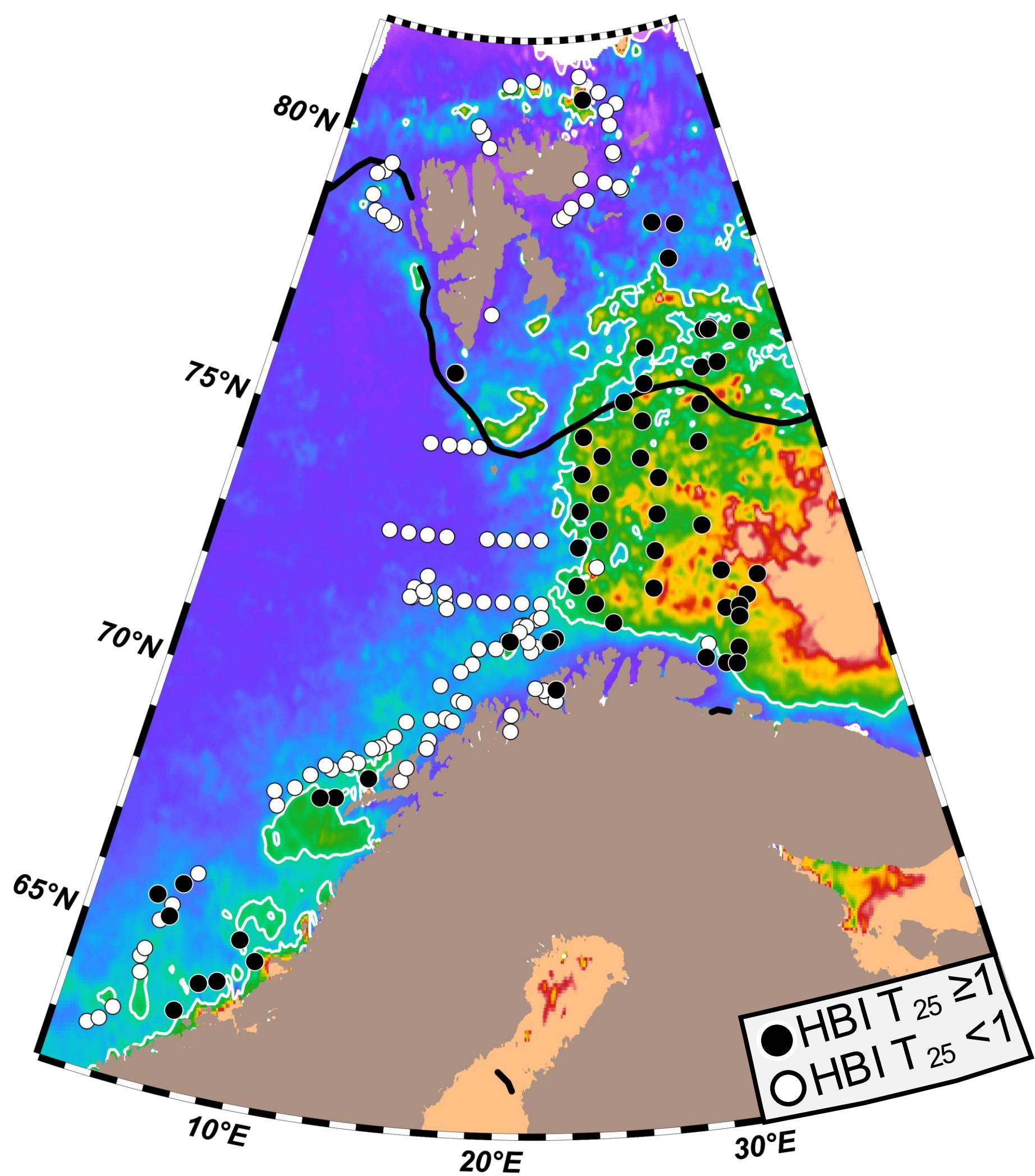


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Table 1. Summary of core locations, water depths and age model methods for all the cores described in the study. Further information about the individual age models can be found in Supplementary Table 2.

Core ID	Short ID	Time interval	Latitude (°N)	Longitude (°E)	Water depth (m)	Age model method
R248MC010	10	Recent centuries	70.31	12.88	1254	^{210}Pb (Dylmer, 2013)
R406MC032	32	Recent centuries	72.32	15.38	1035	^{210}Pb (Dylmer, 2013)
BASICC 1	1	Recent centuries	73.10	25.63	425	^{210}Pb (Vare et al., 2010)
BASICC 8	8	Recent centuries	77.98	26.79	135	^{210}Pb (Vare et al., 2010)
BASICC 43	43	Recent centuries	72.54	45.74	285	^{210}Pb (Vare et al., 2010)
MSM5/5-712-1	712	Recent centuries	78.92	6.77	1491	^{14}C AMS (Spielhagen et al. 2011)
WOO/SC-3	3	Last ca. 3.0 kyr BP	67.40	8.52	1184	^{14}C AMS (Dylmer, 2013)
JM09-KA11-GC	11	Last ca. 9.5 kyr BP	74.87	16.48	345	^{14}C AMS (Belt et al., 2015)
NP05-11-70GC	70	Last ca. 9.5 kyr BP	78.40	32.42	293	^{14}C AMS (Berben et al., 2017)

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