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

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Abstract

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

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

1. Introduction

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

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

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

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

primary production is enhanced. Although the use of HBI-III for calculating the PIP_{25} is thought to improve sea ice description, this proxy still requires further assessment. Finally, a di-unsaturated highly branched isoprenoid (HBI-II; Fig. 1) has been found in the surface sediments of polar and more temperate oceans (Belt and Müller, 2013) and has been used as a novel Antarctic sea ice proxy (Massé et al., 2011; Belt et al., 2016). The positive correlation between this compound and sea ice diatoms in Antarctic Ocean sediments has led to the suggestion of its potential application as a proxy for the duration of the sea ice season when combined to HBI-III (Collins et al., 2013).

In this study, we investigate the seasonal pattern of production and export of HBIs and phytosterols found in sinking particles collected during a one-year sediment trap experiment conducted in the Chukchi Sea in order to improve our understanding and use of these proxies to reconstruct past sea ice changes. We combine for the first time IP_{25} and HBI-III fluxes measured in the Arctic Ocean to provide a more accurate description of sea ice conditions. Surface sediments retrieved from across the western Arctic Ocean where sea ice ranges from perennial sea ice to ice-free conditions were also analysed to see how well they reflect sea ice distribution. Our approach is thus (i) to document the seasonal production and export mechanisms of HBIs over one year in parallel with sterols for PIP_{25} calculations and alkanes as a by-product and (ii) to assess the spatial distribution of sea ice and phytoplankton production over the recent years based on surface sediments from the western Arctic Ocean.

2. Regional setting

Our mooring site is located in the Chukchi Sea, one of the largest marginal seas in the Arctic Ocean covered by sea ice in winter. This area is influenced by the northward flowing Pacific Water (PW), which has an annual mean transport rate of 0.8 Sv ($1 \text{ Sv} = 10^6 \text{ m}^3/\text{s}$; Roach et al., 1995) and strong seasonal and interannual variability (Woodgate et al., 2005). The PW is primarily driven by salinity gradients between the Pacific and the Arctic oceans (Coachman et al., 1975). The surface circulation in the Chukchi Sea (Fig. 2) is described in detail by Overl and Roach (1987) and Woodgate et al. (2005). In brief, water masses flow across the Chukchi Sea along three main pathways: the saline (>32.5) and nutrient-rich ($\text{NO}_3^{-1} \geq 20 \mu\text{M}$) Anadyr Waters (AW; Grebmeier et al., 1988; Weingartner et al., 2005); the relatively warm, fresher (<31.8) and nutrient-poor Alaska Coastal Waters (ACW; Woodgate and Aagaard, 2005; Hunt et al., 2013); and the Bering Shelf Waters in the central channel with moderate nutrient and salinity values (31.8–32.5; Weingartner et al., 2005).

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

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

3. Material and Methods

3.1 Sediment trap material and sediment samples

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

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

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

3.2 Methods

3.2.1 Particulate organic carbon analysis

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

3.2.2 Biomarker analysis

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

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

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

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

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

3.2.3 Sea ice distributions

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

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

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

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

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

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

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

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

4. Results and discussion

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

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

(Fig. 3a).

At high latitudes, the seasonal variations in sea ice cover have a strong influence on marine production and thus on the vertical fluxes and characteristics of the sinking material (Hebbeln and Wefer, 1991). Indeed, total mass fluxes show a pronounced seasonal pattern that follows the temporal evolution of sea ice cover (Fig. 3a–c). 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 September 2009. Persistently lowest fluxes occurred from December 2008 to early July 2009 under the permanent sea ice cover of boreal winter (Fig. 3c; Table 1). From July to August–September 2009, fluxes increased by one order of magnitude with retreating sea ice and the concomitant penetration of sunlight into the upper ocean waters. These high fluxes indicate the rapid response of surface-water productivity to changing environmental conditions as sea ice melted (Hill and Cota, 2005).

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

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

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

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

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

4.2 Seasonal variations in terrigenous and marine biomarker fluxes

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

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

while dinosterol flux in September 2009 are ~6 times higher than during the previous summer. These results suggest that ice-free surface waters at the end of summer 2008 were less productive than those of the MIZ in summer 2009. Lowest values are consistently found in winter when darkness prevents phytoplankton growth. Flux of 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 higher values measured in August 2008 and August 2009 when primary production was also high.

4.3 Biomarker fluxes: sea ice algae and pelagic primary production

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

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

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

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

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

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

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

4.4 Assessment of the sea ice index

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

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

values retains and even improves the correlation ($R^2 = 0.88$). This relationship also holds true when using HBI-III and IP₂₅ relative abundances instead of fluxes, though weaker ($R^2 = 0.6$). The positive correlation shown here is consistent with HBI-III production being linked to the MIZ as discussed above (i.e. HBI-III increases with IP₂₅).

We first calculated the P_BIP₂₅ index values using $c = 0.00393$. From August to September 2008, P_BIP₂₅ declines from 0.87 to ~0.2 reflecting the transition from MIZ to ice-free conditions. High HBI-III fluxes at high P_BIP₂₅ are compatible with limited phytoplankton production at the sea ice edge as suggested by low sterol values (Fig. 5c, f). From October 2008 to July 2009, the P_BIP₂₅ index is highly variable with generally low values in winter, except between January and April 2009 (P_BIP₂₅>0.6). Minor export of IP₂₅ under high sea ice cover in the absence of phytoplankton production can account for these values. From August to September 2009, P_BIP₂₅ showed large variations (from 0.1 to 0.8) as sea ice rapid declines towards MIZ conditions.

Similar typical ice-edge P_BIP₂₅ values (0.5 – 0.8) were found in the shallow sediment trap material (150 m) at the southern Lomonosov Ridge site LOMO2 in July–August 1996 (Fahl and Stein, 2012; Fig. S1, Supplementary material). However, during winter (November 1995 – June 1996) P_BIP₂₅ values remained close to zero primarily because IP₂₅ was absent or present in minor amounts. The unexpectedly high P_BIP₂₅ values in winter at our site highlight the sensitivity and limitation of the use of P_BIP₂₅ under extreme situations of low winter IP₂₅ at low phytoplankton values.

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

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

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

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

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

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

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

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

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

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

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

5. Conclusions

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

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

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

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