JOURNAL OF PLANKTON RESEARCH | VOLUME 34 | NUMBER 8 | PAGES 647–654 | 2012

Closely linked sea ice–pelagic coupling in the Amundsen Gulf revealed by the sea ice diatom biomarker IP_{25}

THOMAS A. BROWN* AND SIMON T. BELT

BIOGEOCHEMISTRY RESEARCH CENTRE, SCHOOL OF GEOGRAPHY, EARTH AND ENVIRONMENTAL SCIENCES, PLYMOUTH UNIVERSITY, DRAKE CIRCUS, PLYMOUTH, DEVON PL4 8AA, UK

*CORRESPONDING AUTHOR: thomas.brown@plymouth.ac.uk

Received April 5, 2012; accepted in principle May 10, 2012; accepted for publication May 15, 2012

Corresponding editor: Roger Harris

The sea ice diatom biomarker IP_{25} has been detected and quantified in bulk zooplankton obtained from the Amundsen Gulf (Canada) in 2008. This study represents the first example of the detection of this biomarker in the pelagic food web. Concentrations of IP_{25} ranged from ~5 to 15 ng g^{-1} dry weight with peak values occurring broadly at the same time as those found for this biomarker in sea ice samples determined previously from the same region; a 25–30 day lag between the sea ice bloom and zooplankton IP_{25} profiles is interpreted in terms of a predator–prey relationship. IP_{25} concentrations in zooplankton declined towards the end of the spring sea ice algal bloom and during the main period of ice melt. At this point, concentrations of *n*-$C_{21:6}$, a common biomarker of general marine diatoms, increased substantially in the zooplankton, indicative of a switch in feeding patterns. This detection of IP_{25} in one of the first trophic levels of the Arctic marine ecosystem has potentially important implications for the investigation of polar food webs and the impacts that changes to sea ice conditions will have on these.

KEYWORDS: diatoms; ice algae; zooplankton; IP_{25}; food web

INTRODUCTION

In addition to marine phytoplankton, Arctic sea ice diatoms form an important source of primary production in the Arctic ecosystem (Sakshaug, 2004; Falk-Petersen *et al.*, 2008; Arrigo *et al.*, 2010; Brown *et al.*, 2011). In particular, ice algae are considered crucial as a food source for first-order consumers such as zooplankton in areas with extensive sea ice cover (e.g. Werner, 1997; Søreide *et al.*, 2006). Sea ice algae derived lipids provide the necessary energy required for reproduction and growth of zooplankton (e.g. Graeve *et al.*, 2005; Falk-Petersen *et al.*, 2008; Søreide *et al.*, 2008, 2010; Leu *et al.*, 2011), while the timing and quality of the lipids produced can be responsible for defining the structure of biological communities and populations in Arctic ecosystems (Falk-Petersen *et al.*, 2008). Despite these clear roles, the period of sea ice algae production and its associated contribution to the Arctic food web is restricted largely to a few weeks during the spring period (e.g. Wassmann *et al.*, 2006; Różanska *et al.*, 2009; Brown *et al.*, 2011) and this will reduce if sea ice cover continues to decrease in the future (Søreide *et al.*, 2010). In an extreme case scenario, this component of the Arctic ecosystem may become removed completely.

Although Arctic-adapted primary producers such as sea ice diatoms can often provide the initial carbon and

doi:10.1093/plankt/fbs045, available online at www.plankt.oxfordjournals.org. Advance Access publication June 18, 2012

energy source that supplies the food web in the Arctic region (e.g. Wold *et al.*, 2011), the fate of this carbon is determined, in part, by the extent or efficiency of coupling that occurs between sea ice and the heterotrophic food web; however, this acute or pulsed contribution of organic carbon to the Arctic Ocean may not necessarily be utilized effectively by zooplankton given its rapid export to the benthos (e.g. Renaud *et al.*, 2008). To better understand the utilization of the short-term supply of organic carbon that usually occurs during the spring ice algal bloom (e.g. Brown *et al.*, 2011), it is important to first establish the initial steps within the marine food web that represent the sequestering of this energy source. Further, the ability to determine both how and when sea ice and phytoplanktonic origin carbon is transferred to the first trophic levels of the pelagic food web is crucial for better understanding the significance of sea ice algal blooms in the Arctic and, in particular, predicting the effects that reduced sea ice might have on such systems in the future.

Currently, there is only a partial understanding of the importance of the seasonal primary production cycle and how the vertical export of organic carbon is used (Forest *et al.*, 2008). To provide more details on this, a recent study carried out in the central Amundsen Gulf (Canadian Arctic) in spring–summer 2008 aimed to both resolve and quantify the pathways of the biogenic carbon flow in the pelagic food web (Forest *et al.*, 2011a). This study established that the mesozooplankton communities of this region were dominated by the copepods *Calanus hyperboreus*, *Calanus glacialis* and *Mertridia longa* and that these and other heterotrophs were responsible for retaining up to 97% of the primary-produced carbon in the water column (Forest *et al.*, 2011a). While this study demonstrated clearly the importance of mesozooplankton as primary consumers in the food web, further investigations, including the identification of any dietary preferences of these organisms with respect to sea ice versus open water primary production, would be advantageous for constraining developing Arctic food web models (e.g. Slagstad *et al.*, 2011). Previous attempts to identify individual carbon sources in Arctic food webs have adopted biochemical and physico-chemical approaches based on the analysis of stable isotopes (e.g. Tamelander *et al.*, 2008; Forest *et al.*, 2011b), fatty acids (e.g. Cripps and Hill, 1998; Falk-Petersen *et al.*, 2008; Søreide *et al.*, 2010; Wold *et al.*, 2011) and algal pigments (e.g. Morata *et al.*, 2010). Although these approaches have improved our understanding of carbon assimilation in the Arctic, it is also recognized that such investigations have their limitations and would benefit, in particular, from improvements in the specificity of the approaches taken. For example, in their assessment of the diet of *Calanus* spp. in the high Arctic, Søreide *et al.* (Søreide *et al.*, 2008) noted that it was not possible to determine specific (sea ice/phytoplankton) carbon sources by the analysis of fatty acids alone, since both sea ice-diatoms and pelagic-diatoms were characterized by the same fatty acids. Similarly, although the use of $\delta^{13}C$ and $\delta^{15}N$ data may provide general information on an organism's major carbon source, more specific measures of individual carbon sources would enable more detailed assessments of the importance of sea ice to particular organisms in the Arctic. The lack of a strict association between isotopic composition and lipid sources through well-defined end member values is a further limitation to this approach.

Most recently, the detection of the sea ice diatom biomarker IP_{25} (Belt *et al.*, 2007), in a range of benthic macrofauna from the Canadian Arctic (Brown and Belt, 2012a) and in sea urchins from a number of different Arctic locations (Brown *et al.*, 2012b), has confirmed the contribution of sea ice algae to certain components of the Arctic marine food web. Therefore, it is proposed that the detection of IP_{25} in other components of the Arctic marine ecosystem has the potential to provide more compelling evidence for the utilization of sea ice-derived OM more generally into Arctic food webs.

For the current study, the use of IP_{25} as a tracer for sea ice diatom-derived organic matter has been extended to investigate the initial transfer of sea ice primary production as a result of zooplankton grazing. Specifically, the main objectives of the study were to (i) analyse for, and quantify, the sea ice diatom biomarker IP_{25} in Arctic zooplankton; (ii) compare temporal changes in IP_{25} concentrations in Arctic zooplankton to those previously reported in sea ice from the same location; (iii) use the data generated from (i) and (ii) to test the hypothesis that the analysis of IP_{25} in Arctic zooplankton could provide evidence for zooplankton grazing of sea ice algae during the winter–spring transition. These three objectives were addressed through the analysis of IP_{25} and n-$C_{21:6}$ (a common marine diatom biomarker) in bulk zooplankton samples collected from the Amundsen Gulf (Canada) during the transitional period February to June 2008 and comparison with IP_{25} concentration data in sea ice established previously (Brown *et al.*, 2011).

METHOD

Field investigation

Sampling of bulk zooplankton was carried out within the Amundsen Gulf, south-eastern Beaufort Sea,

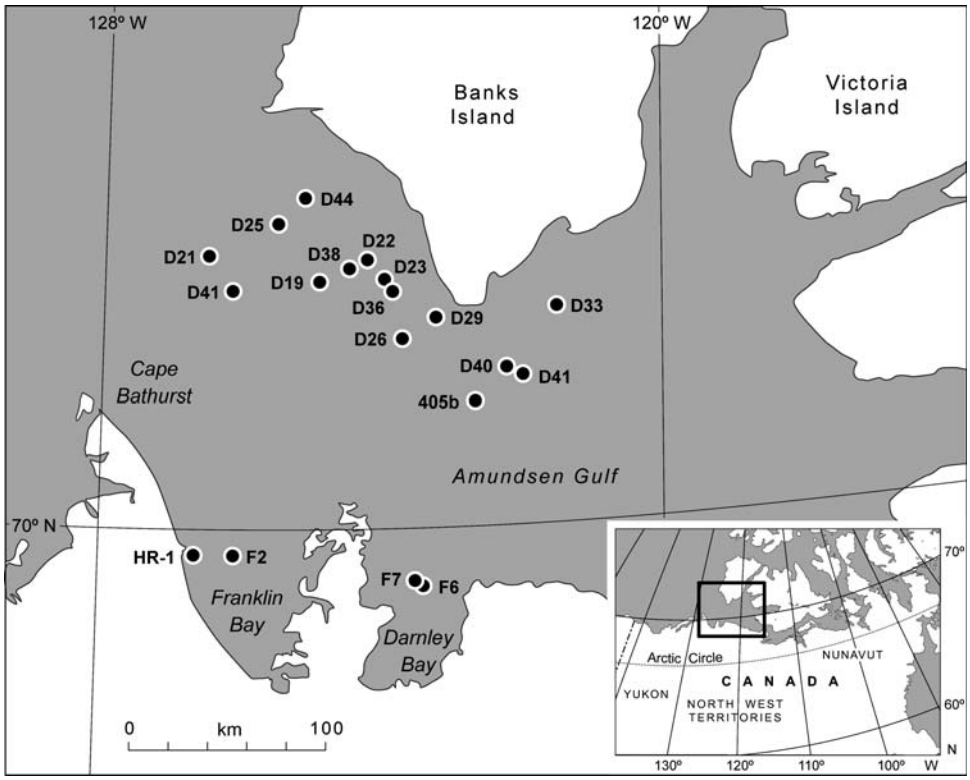

Fig. 1. Study region and location of the sampling stations listed in Table I.

Northwest Territories, Canada (Fig. 1). Collection of bulk zooplankton took place between February and June 2008 as part of the International Polar Year–Circumpolar Flaw Lead system study (IPY-CFL) onboard the *CCGS Amundsen*. The initial aim of overwintering with the *CCGS Amundsen* was to obtain a time series of samples from a single location; however, due to the unusual sea ice conditions (Barber *et al.*, 2010), the ship was forced to relocate on several occasions to account for shifting ice and open leads, resulting in a broader sampling region than originally intended (Fig. 1). Nevertheless, all of the zooplankton samples collected and analysed were from the Amundsen Gulf and the time interval (February–June 2008) closely matched that of the sea ice sampling described previously (Brown *et al.*, 2011).

Zooplankton sample collection

Collection of bulk zooplankton samples was achieved via whole water column vertical net tows from 10 m above the seafloor to the sea surface using a large ring net (1 m^2 square metal frame; 200-μm mesh) deployed and retrieved through the ship's moonpool. Bulk zooplankton samples were then stored in the freezer (−20°C) before being shipped to the UK for the analysis of lipids.

Extraction and analysis of lipids

The general method of extraction and analysis of IP_{25} was adapted from Belt *et al.* (Belt *et al.*, 2012a). Briefly, bulk zooplankton samples (5–20 g wet weight) consisting mainly of *M. longa* (56%), *C. glacialis* (38%) and *C. hyperboreus* (6%) (Forest *et al.*, 2011b) were freeze-dried (−45°C; 0.2 mbar; 72 h), ground using a pestle and mortar and homogenized by thorough mixing in the sample bag before sub-sampling (~140 mg dry weight). Following addition of internal standards to facilitate lipid quantification (9-octyl-8-heptadecene and 7-hexylnonadecane; 10 μL; 10 μg mL^{-1} each), the dried and ground zooplankton sub-samples were extracted using dichloromethane/methanol (DCM/MeOH; 2:1 v/v; 5 mL) and ultrasonication (34 kHz; 5 min) to yield a total organic extract (TOE). The resulting TOE suspensions were transferred by pipette to glass columns and filtered through pre-extracted (DCM/MeOH) cotton wool to remove any remaining particulates before being dried (N_2 stream; 25°C) and weighed (typical mass 73 mg; 53 ± 9% dry weight; $n = 40$).

Table I: Sampling dates and station identification with coordinates (Fig. 1) for bulk zooplankton (ZP) and sea ice (SI; Brown et al., 2011) collected in spring 2008

Date (2008)	CFL Station ID	Lat. (°N)	Long. (°W)	Sea ice (SI) or Zooplankton (ZP) collected
16 Jan	D17	71°30′	124°55′	SI
19 Jan	D17			SI
26 Jan	D19	71°11′	125°03′	SI
4 Feb	D19			ZP
8 Feb	D19			SI/ZP
11 Feb	D19			ZP
12 Feb	D19			ZP
16 Feb	D21	71°17′	126°37′	ZP
18 Feb	D22	71°17′	124°25′	ZP
20 Feb	D23	71°09′	124°02′	ZP
23 Feb	D25	71°26′	125°39′	ZP
24 Feb	D25			ZP
25 Feb	D26	70°56′	123°55′	ZP
27 Feb	D26			SI/ZP
28 Feb	D26			ZP
29 Feb	D26			ZP
5 Mar	D29	71°02′	123°26′	ZP
7 Mar	D29			SI/ZP
8 Mar	D29			ZP
9 Mar	D29			ZP
17 Mar	D29			SI
19 Mar	D31	70°54′	123°01′	SI
22 Mar	D32	71°03′	121°47′	SI
24 Mar	D33	71°04′	121°47′	ZP
25 Mar	D33			SI
26 Mar	D33			ZP
28 Mar	D33			SI
30 Mar	D33			ZP
30 Mar	D33			ZP
31 Mar	D33			SI
1 Apr	D33			ZP
2 Apr	D33			ZP
3 Apr	D33			SI
6 Apr	D36	71°12′	124°09′	SI/ZP
7 Apr	D36			ZP
8 Apr	D36			SI
9 Apr	D36			ZP
11 Apr	D38	71°15′	124°37′	SI/ZP
15 Apr	D40	70°48′	122°27′	ZP
16 Apr	D41	70°46′	122°15′	ZP
21 Apr	D41			ZP
1 May	D43	71°08′	126°14′	SI
5 May	D43			SI/ZP
8 May	F1	70°10′	124°49′	SI
12 May	F2	69°56′	126°10′	SI
16 May	F2			SI
17 May	F2			ZP
19 May	405b	70°39′	122°54′	ZP
20 May	F3	71°34′	119°36′	SI
21 May	D45	70°43′	124°03′	SI
24 May	F4	72°36′	126°02′	SI
28 May	F5	74°30′	124°05′	SI
30 May	D44	71°34′	125°17′	SI/ZP
2 Jun	F6	69°51′	123°45′	SI/ZP
7 Jun	F7	69°49′	123°37′	SI
8 Jun	F7			ZP
9 Jun	F7			SI/ZP
11 Jun	F7			SI/ZP
12 Jun	F7			ZP
13 Jun	F7			SI
15 Jun	FB04	69°57′	125°52′	SI
17 Jun	HR-1	69°56′	126°41′	ZP
18 Jun	F7	69°49′	123°37′	SI

TOEs were then re-suspended in hexane (0.5 mL) and fractionated into non-polar (5 mL hexane) and polar (5 mL DCM/MeOH; 0.5:2 v/v) lipids by column chromatography (SiO_2).

The analysis of purified non-polar lipid extracts containing IP_{25} was carried out using an Agilent 7890A gas chromatograph (GC), coupled to an Agilent 5975 mass selective detector, fitted with an Agilent HP-5ms (30 m × 0.25 mm × 0.25 μm) column with auto-splitless injection (300°C) and helium carrier gas (1 mL min^{-1} constant flow). Detection of individual compounds was determined by both total ion current (TIC; m/z 50–500) and selective ion monitoring (SIM; m/z 350.3) techniques (70 eV) using a ramped temperature programme of 10°C min^{-1} from 40 to 300°C followed by a 10 min isothermal at 300°C. Data were collected and analysed with Agilent Chemstation software. TIC chromatograms were used to identify IP_{25} and n-$C_{21:6}$ via their respective retention indices (IP_{25} RI 2086; n-$C_{21:6}$ RI 2062) and mass spectra (Belt *et al.*, 2007, 2012b; Blumer *et al.*, 1970; Lee and Loeblich, 1971). Quantification of IP_{25} and n-$C_{21:6}$ was achieved by first calculating the ratios of the intensities of mass spectral responses of IP_{25} (SIM mode; m/z 350.3) and n-$C_{21:6}$ (TIC mode; m/z 50–500) to the corresponding intensities of the internal standards. These ratios were then normalized according to GC-MS response factors (Belt *et al.*, 2012a) and individual specimen masses so that final concentrations of IP_{25} could be expressed as dry weight equivalents. The limit of detection for IP_{25} was ~10 ng mL^{-1}; s/n 3.

RESULTS

In total, zooplankton samples from 40 sampling dates between February and mid-June 2008 were analysed

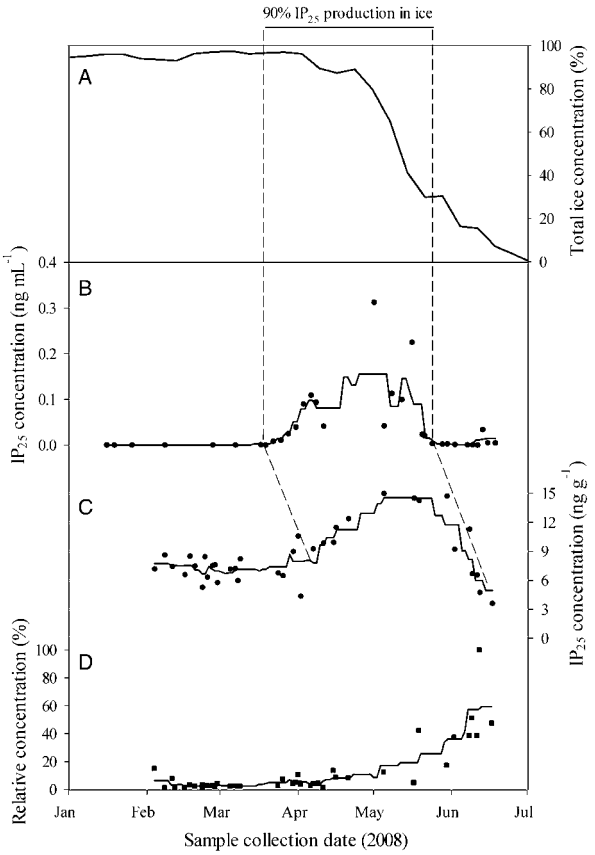

Fig. 2. Amundsen Gulf time series of (**A**) weekly total sea ice cover (%) from Forest *et al.* (Forest *et al.*, 2011b) (**B**) IP_{25} concentrations measured in sea ice from Brown *et al.* (Brown *et al.*, 2011) (**C**) IP_{25} concentrations measured in bulk zooplankton in this study (**D**) relative concentration (%) of *n*-$C_{21:6}$ in bulk zooplankton. The running average of concentration data was calculated using local smoothing of neighbouring points (sampling proportion−0.1). Dashed lines indicate a cross correlation lag of 25−30 days ($r^2 = 0.91$; $P \leq 0.0001$).

and the sea ice diatom biomarker IP_{25} was detected in lipid extracts in each case (Table I; Fig. 2). IP_{25} concentrations ranged from ∼5 to 15 ng g^{-1} dry weight during the sampling period (Fig. 2C). Following an interval of relatively low, but consistent IP_{25} concentrations during February and March, abundances increased during April before reaching their maximum values in May. Following this peak period IP_{25} concentrations dropped relatively rapidly in late May-early June and, at the end of the sampling interval, IP_{25} concentrations were slightly lower than during February and March. When the temporal IP_{25} concentration profile was compared with that reported previously for this biomarker in sea ice cores from the same region (Fig. 2B), a similar trend in changes in relative concentrations could be seen, although the period of peak IP_{25} abundance in zooplankton was ∼25 days later than that found for the sea ice cores (Fig. 2).

In addition to the measurement of IP_{25} abundances, the quantification of *n*-$C_{21:6}$, a common constituent lipid of marine diatoms (e.g. Blumer *et al.*, 1970; Lee and Loeblich, 1971; Cripps and Hill, 1998; Sinninghe Damsté *et al.*, 2000), was also carried out across the entire sampling interval. This lipid was also present in all zooplankton samples, but the concentrations exhibited a different temporal trend to that of IP_{25} (Fig. 2). Concentrations of *n*-$C_{21:6}$ were at their lowest during February and March, remained low during the period of the sea ice algal bloom (April−May), before increasing rapidly towards the end of May and into June. This period of rapid increase in *n*-$C_{21:6}$ concentrations aligned closely with the decline in IP_{25} concentrations described earlier and with the main period of ice melt (Fig. 2).

DISCUSSION

At the outset of this study, we aimed to address three key objectives relating to the use of the sea ice diatom biomarker IP_{25} to investigate trophic transfer in Arctic food webs and so the structure of this discussion is based around these three objectives. Firstly, the identification of IP_{25} in the lipid extracts from all of the zooplankton samples provides clear evidence for the transfer of this biomarker into first-order consumers of sea ice algae, although this observation alone cannot necessarily be interpreted in terms of direct grazing of ice algae by zooplankton.

Secondly, the temporal concentration profiles of IP_{25} in both sea ice and zooplankton both show peak values during the period of the spring algal bloom (April−May), providing more compelling evidence than the presence of IP_{25} alone, that zooplankton undergo direct feeding on ice algae during the spring consistent with previous findings (Forest *et al.*, 2011a, b).

Thirdly, more detailed comparisons of the IP_{25} concentration profiles with those of a further biomarker and of the seasonal sea ice reveal some additional insights into the grazing of sea ice algae by zooplankton (Objective 3). For example, IP_{25} was observed in zooplankton as early as 4 February, albeit at lower levels compared with the bloom period, despite the absence of this biomarker in sea ice samples until March (Brown *et al.*, 2011). This apparent anomaly between the two profiles may potentially be explained by the bioaccumulation of relatively low concentrations of ice algae prior to the main spring bloom during which time IP_{25} may have been below the limit of detection in sea ice; although this period is generally considered as having low productivity (Forest *et al.*, 2011a; Leu *et al.*, 2011) and

what production does occur is dominated by flagellates rather than sea ice diatoms during this time (Różanska *et al.*, 2009). Alternatively, the pre-bloom occurrence of IP_{25} in zooplankton may either reflect retention from previous ice algal blooms or ingestion following resuspension of previously deposited material in sediments during winter, especially as IP_{25} has been detected in surface sediments from this region (Brown, 2011). Previously, Sargent and Falk-Petersen (Sargent and Falk-Petersen, 1981) provided precedent for the latter through the observation of phytol, a general diatom lipid produced during the breakdown of chlorophyll, in the tissue of zooplankton during winter (November–December) in a Norwegian fjord, concluding that this indicated a detrital diet. Further, Forest *et al.* (Forest *et al.*, 2011b) used relationships between carbon content and lipid contribution (fatty acids) to show that *M. longa*, which comprised 56% of the bulk zooplankton assemblage in the Amundsen Gulf during the field programme of the current study, grazed mainly on detrital material, although it is not known if this occurred near to the sediment surface. In any case, further investigations will be required in order to fully explain the pre-bloom occurrence of IP_{25} in zooplankton observed here.

In mid-March, an increase in IP_{25} concentrations in sea ice reflected the onset of the spring sea ice algal bloom, before reaching a maximum in early May (Brown *et al.*, 2011). In contrast, concentrations of IP_{25} in bulk zooplankton assemblages did not increase significantly above winter levels until at least 3 weeks later at the beginning of April (Fig. 2). This lag response by zooplankton to the algal bloom has also been inferred through stable isotope ($\delta^{13}C$) measurements of bulk organic carbon in zooplankton (Forest *et al.*, 2011b) and is further constrained here by cross correlation of IP_{25} concentrations which indicates a lag of 25–30 days (cross correlation $r^2 = 0.91$; $P \leq 0.0001$). Maximum concentrations of IP_{25} in zooplankton also occurred later than in sea ice, reaching a peak in early June. Although the exact reason for this offset in peak IP_{25} levels between sea ice and zooplankton is not fully clear at this stage, it is hypothesized that it likely reflects the time lag associated with predator–prey relationships commonly observed in food web interactions (e.g. Matveev, 1995) and also the supply of sufficient quantities of sea ice algae for assimilation by a greater number of pelagic zooplankton. Whatever the exact explanation for this offset in IP_{25} concentrations, the increase in IP_{25} concentrations in zooplankton during the spring ice algal bloom clearly indicates that this sea ice-specific biomarker is transferred across an early trophic level which, in turn, potentially makes IP_{25} available to higher trophic level pelagic consumers (e.g. Benoit *et al.*, 2010). The short (~25–30 day) offset between changes in IP_{25} concentrations in sea ice and zooplankton also remained evident during the period of sea ice melt (Fig. 2) and IP_{25} remained detectable in the zooplankton samples in June, even though IP_{25} concentrations in sea ice diminished rapidly following peak values in mid-May and following the onset of ice melt. Since zooplankton sampling did not continue beyond mid-June it was not possible to determine whether these concentrations represented true lower limits. However, IP_{25} concentrations in zooplankton started to decline most noticeably during the last stages of ice melt and final concentrations were at least as low as pre-bloom values, albeit ~25–30 days later than in sea ice.

At the same time as the reduction in IP_{25} concentrations in zooplankton between the end of May and into June, there was a clear increase in the abundance of the marine diatom biomarker *n*-$C_{21:6}$, common to both ice and phytoplanktonic algae and a +4‰ increase in the stable isotopic composition ($\delta^{13}C$) of bulk POM (Forest *et al.*, 2011b). All of these observations indicate the introduction of an alternative and far more abundant dietary source for the zooplankton ~1–2 months after the sea ice algae bloom, most likely indicating the marginal ice phytoplankton bloom (Søreide *et al.*, 2008; Forest *et al.*, 2011b) that results during the final reduction in sea ice cover from 20 to 0%. Since this phytoplankton bloom can be significantly more productive than the preceding sea ice bloom (~94 and ~6%, respectively; Forest *et al.*, 2011a), it is possible that declining assimilation efficiencies of some lipids could result from superfluous feeding (Beklemishev, 1962; Urabe, 1991; Straile, 1997) leading to shorter gut retention of primary ingested material (Santer and Van den Bosch, 1994). Such a mechanism could be responsible for the effective displacement of ice algal-derived lipids like IP_{25} by phytoplankton lipids such as *n*-$C_{21:6}$ with net attenuation of IP_{25} concentrations in zooplankton during the period of ice melt (Fig. 2). As such, the data presented here suggest that although IP_{25} may be ingested and/or accumulated by heterotrophs, this effect may be somewhat ephemeral, in zooplankton, at least. Whether the reduction in IP_{25} concentrations in zooplankton is a result of a displacement process or some other mode of metabolism, excretion, or a combination, thereof (e.g. Graeve *et al.*, 2005), could not be established in the current study, partly due to the absence of sampling beyond mid-June. Nevertheless, this relatively rapid decline in IP_{25} concentrations has potentially important implications for the interpretation of IP_{25} and other lipid concentration data determined for other species and trophic levels in Arctic marine food webs and these warrant further investigation in the future. In a similar

vein, it will be important in future studies to determine whether IP_{25} concentrations in zooplankton decrease to zero beyond the latest time interval examined here (June) and identify the source of IP_{25} in zooplankton during the pre-bloom period (e.g. February/March samples here).

CONCLUSION

The identification of the sea ice diatom biomarker IP_{25} in bulk zooplankton samples from the Amundsen Gulf represents the first observation of this biomarker in the pelagic food web. The IP_{25} data are consistent with observations made previously on sea ice algal production and grazing by zooplankton from this (e.g. Forest *et al.*, 2011a, b; Wold *et al.*, 2011) and other regions (e.g. Leu *et al.*, 2011; Søreide *et al.*, 2006, 2008, 2010) and verify that sea ice primary production is likely to be a key contributor to the pelagic food web. Likewise, the identification of IP_{25} in zooplankton (this study) and benthic macrofauna (Brown and Belt, 2012a) collected from the same region over an equivalent spring sampling period suggests that sea ice origin carbon is distributed between both the pelagic and benthic food webs at this time of year. Finally, these data illustrate how the measurement of source-specific biomarkers can potentially provide valuable information pertaining to the responses of primary consumers to different dietary sources and to re-cycling mechanisms of primary produced organic matter. This, in turn, may be particularly useful for measuring or predicting sea ice-related changes in the diet of zooplankton through seasonal cycles, for tracing the fate of sea ice algal blooms in the Arctic and for evaluating the impacts of reduced sea ice cover on Arctic marine ecosystems. In order to realize this potential, it will be important to carry out more quantitative assessments of accumulation and retention of IP_{25} than the qualitative observations described here. Such quantitative measurements may include the determination of the relationship between IP_{25} and ice algal biomass, temporal abundances of IP_{25} in the water column, turnover rates within zooplankton and any species-specific dependence in terms of IP_{25} presence.

ACKNOWLEDGMENTS

The authors would like to thank the Natural Environment Research Council (NERC, UK) for providing a PhD studentship to T.B. (NE/F007043/1). We would like to extend our gratitude to the officers and crew of the *CCGS Amundsen* for their invaluable support during the expedition. We are also particularly grateful to Alexis Burt and other colleagues for providing us with zooplankton sub-samples and to two anonymous reviewers for helpful suggestions to improve this manuscript. This work is a contribution to the International Polar Year-Circumpolar Flaw Lead system study (IPY-CFL).

FUNDING

Partial operating funds for the *CCGS Amundsen* were provided by the International Joint Ventures Fund of the Canada Foundation for Innovation. Further funding for sample analysis was provided by the Seale Hayne Educational Trust (Plymouth University).

REFERENCES

Arrigo, K. R., Mock, T. and Lizotte, M. P. (2010) Primary producers and sea ice. In Thomas, D. N. and Dieckmann, G. S. (eds), *Sea Ice, 2nd edn*. Blackwell Publishing Ltd, Oxford, pp. 283–325.

Barber, D. G., Asplin, M. G., Gratton, Y. *et al.* (2010) The international polar year (IPY) circumpolar flaw lead (CFL) system study: overview and the physical system. *Atmos. Ocean*, **48**, 225–243.

Beklemishev, C. W. (1962) Superfluous feeding of marine herbivorous zooplankton *Rapp P.-V. Reun. Cons. Int. Explor. Mer.*, **153**, 108–113.

Belt, S., Brown, T., Cabedo Sanz, P. *et al.* (2012b) Structural confirmation of the sea ice biomarker IP_{25} found in Arctic marine sediments. *Environ. Chem. Lett.*, **10**, 189–192.

Belt, S. T., Brown, T. A., Navarro-Rodriguez, A. *et al.* (2012a) A reproducible method for the extraction, identification and quantification of the Arctic sea ice proxy IP_{25} from marine sediments. *Anal. Methods*, **4**, 705–713.

Belt, S. T., Massé, G., Rowland, S. J. *et al.* (2007) A novel chemical fossil of palaeo sea ice: IP_{25}. *Org. Geochem.*, **38**, 16–27.

Benoit, D., Simard, Y., Gagné, J. *et al.* (2010) From polar night to midnight sun: photoperiod, seal predation, and the diel vertical migrations of polar cod (*Boreogadus saida*) under landfast ice in the arctic ocean. *Polar Biol.*, **33**, 1505–1520.

Blumer, M., Mullin, M. M. and Guillard, R. R. L. (1970) A polyunsaturated hydrocarbon (3, 6, 9, 12, 15, 18-heneicosahexaene) in the marine food web. *Mar. Biol.*, **6**, 226–235.

Brown, T. A. (2011) Production and preservation of the Arctic sea ice diatom biomarker IP_{25}. *PhD Thesis*, University of Plymouth.

Brown, T. A. and Belt, S. T. (2012a) Identification of the sea ice diatom biomarker IP_{25} in Arctic benthic macrofauna: direct evidence for a sea ice diatom diet in Arctic heterotrophs. *Polar Biol.*, **35**, 131–137.

Brown, T. A., Belt, S. T. and Piepenburg, D. (2012b) Evidence for a pan-Arctic sea-ice diatom diet in *Strongylocentrotus* spp. *Polar Biol.*, doi:10.1007/s00300-012-1164-9.

Brown, T. A., Belt, S. T., Philippe, B. *et al.* (2011) Temporal and vertical variations of lipid biomarkers during a bottom ice diatom bloom in the Canadian Beaufort Sea: further evidence for the use

of the IP_{25} biomarker as a proxy for spring Arctic sea ice. *Polar Biol.*, **34**, 1857–1868.

Cripps, G. C. and Hill, H. J. (1998) Changes in lipid composition of copepods and *Euphausia superba* associated with diet and environmental conditions in the marginal ice zone, Bellingshausen Sea, Antarctica. *Deep Sea Res. Part I*, **45**, 1357–1381.

Falk-Petersen, S., Mayzaud, P., Kattner, G. *et al.* (2008) Lipids and life strategy of Arctic Calanus. *Mar. Biol. Res.*, **5**, 18–39.

Forest, A., Galindo, V., Darnis, G. *et al.* (2011b) Carbon biomass, elemental ratios (C:N) and stable isotopic composition (^{13}C, ^{15}N) of dominant calanoid copepods during the winter-to-summer transition in the Amundsen Gulf (Arctic Ocean). *J. Plankton Res.*, **33**, 161–178.

Forest, A., Sampei, M., Makabe, R. *et al.* (2008) The annual cycle of particulate organic carbon export in Franklin Bay (Canadian Arctic): environmental control and food web implications. *J. Geophysical Res.*, **113**, C03S05.

Forest, A., Tremblay, J.-É., Gratton, Y. *et al.* (2011a) Biogenic carbon flows through the planktonic food web of the Amundsen Gulf (Arctic Ocean): a synthesis of field measurements and inverse modelling analyses. *Prog. Oceanogr.*, **91**, 410–436.

Graeve, M., Albers, C. and Kattner, G. (2005) Assimilation and biosynthesis of lipids in Arctic Calanus species based on feeding experiments with a ^{13}C labelled diatom. *J. Exp. Mar. Biol. Ecol.*, **317**, 109–125.

Lee, R. F. and Loeblich III, A. R. (1971) Distribution of 21:6 hydrocarbon and its relationship to 22:6 fatty acid in algae. *Phytochemistry*, **10**, 593–602.

Leu, E., Søreide, J. E., Hessen, D. O. *et al.* (2011) Consequences of changing sea-ice cover for primary and secondary producers in the European Arctic shelf seas: Timing, quantity, and quality. *Prog. Oceanogr.*, **90**, 18–32.

Matveev, V. (1995) The dynamics and relative strength of bottom-up vs top-down impacts in a community of subtropical lake plankton. *Oikos*, **73**, 104–108.

Morata, N., Poulin, M. and Renaud, P. E. (2010) A multiple biomarker approach to tracking the fate of an ice algal bloom to the sea floor. *Polar Biol.*, **34**, 101–112.

Renaud, P. E., Morata, N., Carroll, M. L. *et al.* (2008) Pelagic-benthic coupling in the western Barents Sea: processes and time scales. *Deep Sea Res. Part II*, **55**, 2372–2380.

Różanska, M., Gosselin, M., Poulin, M. *et al.* (2009) Influence of environmental factors on the development of bottom ice protist communities during the winter-spring transition. *Mar. Ecol. Prog Ser.*, **386**, 43–59.

Sakshaug, E. (2004) Primary and secondary production in the Arctic Seas. In Stein, R. and Macdonald, R. W. (eds), *The Organic Carbon Cycle in the Arctic Ocean*. Springer, London.

Santer, B. and Van Den Bosch, F. (1994) Herbivorous nutrition of *Cyclops vicinus*: the effect of a pure algal diet on feeding, development, reproduction and life cycle. *J. Plankton Res.*, **16**, 171–195.

Sargent, J. R. and Falk-Petersen, S. (1981) Ecological investigation on the zooplankton community of Balsfjorden, Northern Norway: lipids and fatty acids in *Thysanoessa inermis* (Krøyer), *Thysanoessa raschii* (M.Sars) and *Meganytiphanes norvegica* (M.Sars) during midwinter. *Mar. Biol.*, **62**, 131–137.

Sinninghe Damsté, J. S., Schouten, S., Rijpstra, W. I. C. *et al.* (2000) Novel polyunsaturated *n*-alkenes in the marine diatom *Rhizosolenia setigera*. *Eur J Biochem*, **267**, 5727–5732.

Slagstad, D., Ellingsen, I. H. and Wassmann, P. (2011) Evaluating primary and secondary production in an Arctic Ocean void of summer sea ice: an experimental simulation approach. *Prog. Oceanogr.*, **90**, 117–131.

Søreide, J. E., Falk-Petersen, S., Hegseth, E. N. *et al.* (2008) Seasonal feeding strategies of Calanus in the high-Arctic Svalbard region. *Deep Sea Res., Part II*, **55**, 2225–2244.

Søreide, J. E., Hop, H., Carroll, M. L. *et al.* (2006) Seasonal food web structures and sympagic-pelagic coupling in the European Arctic revealed by stable isotopes and a two-source food web model. *Prog Oceanogr.*, **71**, 59–87.

Søreide, J. E., Leu, E. V. A., Berge, J. *et al.* (2010) Timing of blooms, algal food quality and *Calanus glacialis* reproduction and growth in a changing Arctic. *Glob Change Biol*, **16**, 3154–3163.

Straile, D. (1997) Gross growth efficiencies of protozoan and metazoan zooplankton and their dependence on food concentration, predator-prey weight ratio, and taxonomic group. *Limnol. Oceanogr.*, **42**, 1375–1385.

Tamelander, T., Reigstad, M., Hop, H. *et al.* (2008) Pelagic and sympagic contribution of organic matter to zooplankton and vertical export in the Barents Sea marginal ice zone. *Deep Sea Res., Part II*, **55**, 2330–2339.

Urabe, J. (1991) Effect of food concentration on the carbon balance of *Bosmina longirostris* (Crustacea: Cladocera). *Freshwater Biol*, **26**, 57–68.

Wassmann, P., Reigstad, M., Haug, T. *et al.* (2006) Food webs and carbon flux in the Barents Sea. *Prog Oceanogr.*, **71**, 232–287.

Werner, I. (1997) Grazing of Arctic under-ice amphipods on sea-ice algae. *Mar. Ecol. Prog Ser.*, **160**, 93–99.

Wold, A., Darnis, G., Søreide, J. *et al.* (2011) Life strategy and diet of *Calanus glacialis* during the winter–spring transition in Amundsen Gulf, south-eastern Beaufort Sea. *Polar Biol.*, **34**, 1929–1946.