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Temporal and vertical distributions of IP25 and other lipid biomarkers in sea ice from Resolute Bay, Nunavut, Canada

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Temporal and vertical distributions of IP_{25} and other lipid biomarkers in sea ice from Resolute Bay, Nunavut, Canada.

By

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ABSTRACT

IP_{25} (Ice Proxy with 25 carbon atoms) is a highly branched isoprenoid biomarker, specifically produced by marine diatoms in Arctic sea ice. Temporal and vertical IP_{25} concentrations were measured in sea ice from a second location in the Canadian Arctic, Resolute Bay, Nunavut. Sea ice samples were collected as part of the Arctic ICE project in collaboration with scientists of the University of Manitoba from April to June 2011. Comparisons were made between other established lipid biomarkers of diatom origin and general organic production, along with previously established temporal and vertical distributions in sea ice collected from the Amundsen Gulf, from January to June 2008. IP_{25} was present in sea ice from a second location in the Canadian Arctic over the spring sea ice bloom period and concentrations correlated well with those of chlorophyll *a* ($r = 0.81$; $n = 10$; $P < 0.05$). IP_{25} and chlorophyll *a* were present throughout sea ice cores. Accumulation of IP_{25} and chlorophyll *a* were highest (89% - 99%) in the lower 3 cm, whereas vertical distributions of fatty acids were more distributed throughout the sea ice cores. Overall accumulation of IP_{25} in the lower section of the sea ice was found to be affected by snow cover.

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AUTHORS DECLARATION

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Ashleigh E. Ringrose

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PRESENTATIONS GIVEN, CONFERENCES AND COURSES ATTENDED

MOSJ cruise presentation series. RV Lance, Svalbard, Norway. July 2012. Oral presentation: “Highly branched isoprenoids: potential dietary source indicators in Arctic food webs”.

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LIST OF COMMON ABREVIATIONS

ANOVA – Analysis of variance

$DSIP_{25}$ – Dietary source indicator proxy with 25 carbon atoms

ESC – East Spitsbergen current

GC – Gas chromatography

GC/MS – Gas chromatography – mass spectrometry

HBI – Highly branched isoprenoid

IP_{25} – C_{25} highly branched isoprenoid monoene

IS – Internal standard

NSL – Non saponifiable lipids

RF – Response factor

SIM – Selective ion monitoring

SL – Saponifiable lipids

TIC – Total ion current

WSC – West Spitsbergen current

GLOSSARY OF TERMS

Cell lysis – The breakdown of a cell due to osmotic shock

Eukaryotes – Cells with a membrane-bound nucleus

Eutrophication – The ecosystem response to the addition of artificial or natural substances to an aquatic system

Lead – An area of open water within an ice field caused by movements of the ice due to winds and currents

Metazoan – All multicellular eukaryotes

Osmotic shock – The state a cell goes into when there is a rapid movement of water across the membrane, giving a sudden change in solute concentration

Paleo – A prefix meaning prehistoric

Polynya – An area of open water surrounded by sea ice which is due to topographic features

Protist – A single or multicellular eukaryotic celled organism that is not an animal, plant or fungi

CHAPTER ONE

1.0 INTRODUCTION

1.1 The Arctic Environment

1.1.1 Climate warming

Due to rapid climate change, the Arctic is currently one of the fastest warming regions in the world, warming on average 1.9 times faster than the global mean (Winton, 2006). The annual land-surface air temperature has risen by 0.09^{o}C per decade between 1900 and 2002 (McBean, 2005), whilst January sea surface temperatures in the Barents Sea have risen by 0.5-1.0 ^{o}C from 2005 to 2012 (NOAA, 2012). More evidence of Arctic warming is shown by the reduction in sea ice extent (Fig. 1.1) (NSIDC, 2012a). The extent of Arctic sea ice reduced at an average annual rate of approximately 45,100 km^2 (±4,600 km^2) per year from 1979 to 2006 (Parkinson and Cavalieri, 2008). In January 2012, the winter sea ice extent averaged 13.7 million km^2, 1.1 million km^2 below the 1979 to 2000 winter average and the summer 2012 sea ice extent reached a record low (3.41 million km^2) since satellite data was first recorded in 1979. Further studies have also shown that the thickness of multiyear ice has reduced by at least 40% over the past 30 years (Liu et al., 2004; Rothrock et al., 1999). Predictions using climate models simulate complete or nearly complete loss of multiyear sea ice in the Arctic as early as 2040 (Holland et al., 2006; Wang and Overland, 2009). Melting of sea ice and reduction in snow cover are related to greenhouse warming through the Albedo effect (Fig. 1.1). As snow and ice reflect more solar radiation than open water, soil or vegetation, it is postulated that sea ice depletion will amplify greenhouse warming by 10 to 20 % globally (Reuss and Poulsen, 2002). There are a number of mechanisms thought to affect the melting of sea ice and climate forcing in the Arctic, Barber *et al.*

(2012) provides an overview of these. For example an increase in sea surface temperature has been associated with a decline in the sea ice extent through changes in latent ocean heat (Zhang, 2005). Sea surface temperatures are also affected by an increase in first year ice and decrease in stable multiyear ice, as the increase in annual open water gives rise to solar radiation and absorption into the ocean, decreasing the Albedo effect (Lindsay and Zhang, 2005; Woodgate et al., 2006). This increase in fragile first year ice has made the ice cover more susceptible to regional atmospheric forcing. Large-scale atmospheric changes can also result in pole-ward retreat of sea ice (Barber et al., 2012) and an increase in the break-up, resulting in more mobile pack ice.

Melting of Arctic sea ice could also result in changes to the current food web structure and a reduction in biodiversity (Gill et al., 2011) as the sea ice is vital for providing a habitat for polar marine organisms. Retreat of the sea ice may also have implications for Inuit populations (ACIA 2005). Some communities from Arctic regions in Canada, Norway, the USA, Finland and Russia depend on hunting and fishing for their livelihoods. As food web dynamics in the Arctic marine ecosystem change, indigenous people, who depend on some of these animals for survival, may be affected by these changes first and most intensely (ACIA 2005). Changes in timing of freeze-up and breakup of the sea ice may affect the safety, transportation and annual food security of northern communities in the Arctic. Further investigation into the physical factors of climate change will lead to ensuring adaptability of northern communities to their currently changing environment in which they live. Reduction of sea ice may also have a significant impact on seasonal shipping and industrial development in the Arctic. As sea ice has an important role to play in the Arctic ecosystem, it is vital we increase our understanding of the possible impacts of climate change on the polar environments to ensure further understanding of environmental and socio-economic implications.

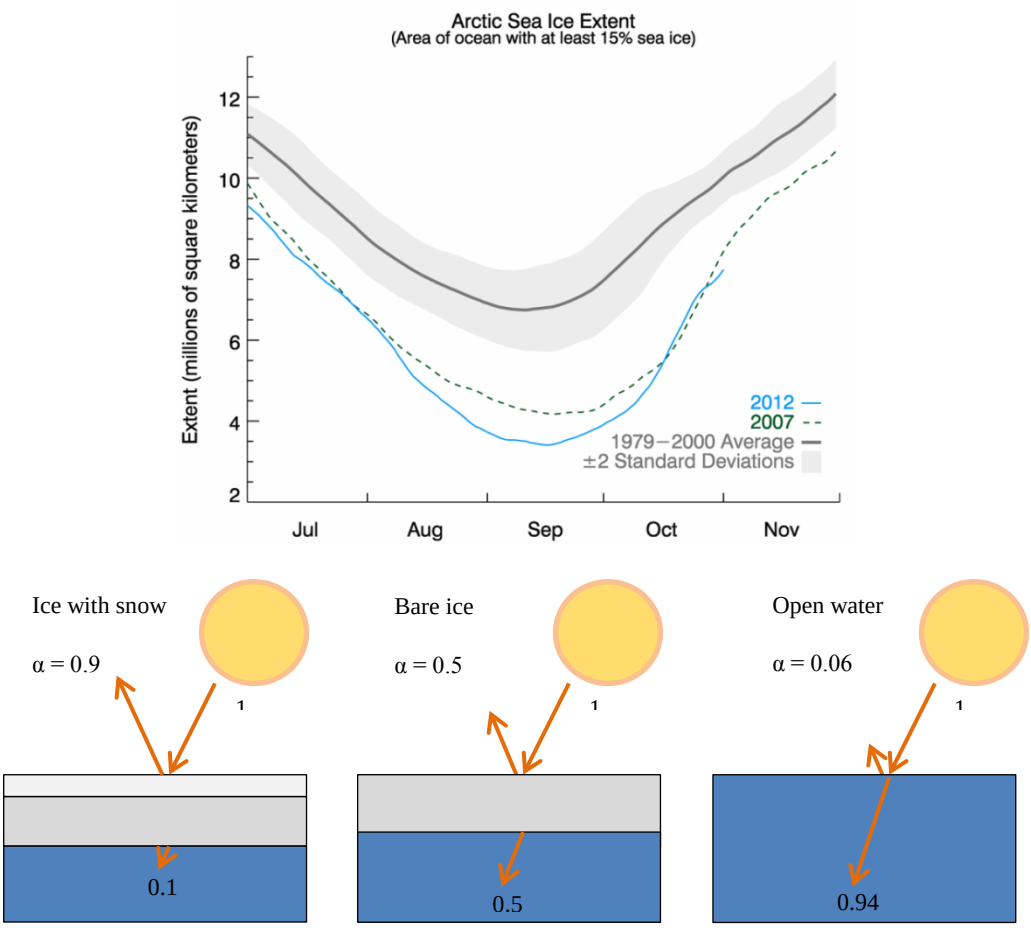


Figure 1.1 Arctic sea ice extent (NSIDC, 2012a) and schematic of the Albedo Effect (α) over ice/snow covered waters and open water (adapted from (NSIDC, 2012b)).

1.1.2 Arctic sea ice

As sea ice is frozen salty water, it forms, grows and melts over the oceans in the Polar regions. Icebergs and glaciers differ from sea ice in that they are formed from fresh water or compacted snow and originate on land. Sea ice in the Arctic is present in different forms with varying area, thickness and distribution.

Arctic sea ice varies with the season. Ice that remains during the summer season is known as multi year ice, this is thick ice that has built up over extended periods of time. In the summer months there are also usually large open areas of water or thin-ice. The water temperature in the summer is normally higher than the freezing point due to increased solar-radiation. The Arctic sea ice that melts during the summer and forms

during the winter is known as first year ice (Thomas and Dieckmann, 2010). In the winter months, the amount of Arctic sea ice increases as temperatures fall. Large areas of both multi-year and first-year ice form. Polynas in the winter can also form further ice as the openings, created by the topography of the ocean floor, create space for the ice crystals to aggritate together at the surface.

Sea ice classifications and types are mainly categorised by ice thickness and structure of the ice within a floe. Sea ice can range from a few centimetres to metres thick however generally multi year ice is thicker than first year ice.

Sea ice is formed from frazil crystals (typically 3-4 millimetres in diameter) floating to the surface, accumulating and aggregating together (NSIDC, 2012c). In calm conditions, such as those found in a fjord or bay close to land, ice forms a thin and smooth layer of ice called grease ice. Grease ice develops into a continuous thin sheet called nilas, which gradually thickens due to currents and winds pushing sheets of nilas on top of each other, in a process known as rafting. The resulting thick and more stable ice, with a smooth bottom surface, is known as congelation ice. This ice can further develop in thickness by formation of long congelation crystals on the bottom of the ice, advancing vertically downwards. In aggitated conditions, usually further out to sea, ice forms and breaks apart easily, resulting in smaller pieces called pancake ice (Rafferty, 2011). Rafting can then bring these pieces together to form large ice sheets with rough edges, resulting from movement as pieces collide with one another. If the ice is thick enough, ridging sometimes occurs when the sea ice sheets bend or fracture and pile on top of each other. In the Arctic, ridges can be up to 20 m thick. Eventually, a rough-bottomed ice sheet is formed when further pieces are aggregated together, a contrast to the smooth-bottomed ice sheets formed in calm conditions. Over the winter these ice sheets continue to grow, however if the ice is not thick enough when the warmer temperatures are reached in summer, the ice will melt (first year ice). If the ice is thick

enough, it will remain over summer until the next winter when it will grow and continue to thicken (multi year ice). A simple schematic of sea ice formation is shown in Figure 1.2.

As temperature and salinity measured in sea ice samples have a functional linear relationship (Thomas and Dieckmann, 2010) and temperature changes have a strong influence on the production of brine in sea ice (Petrich and Eicken, 2010), temperature and salinity are major influences of the structure of sea ice (Golden et al., 2007; Thomas and Dieckmann, 2010). Sea water contains many ions including Na^{+}, Mg^{2+}, K^{+}, Cl^{-}, SO_4^{2-}, CO_3^{2-} and Ca^{2-}. The crystal lattice structure of sea ice is resistant to the incorporation of these sea salt ions, therefore they are rejected from the structure when sea ice forms. These salt ions are rejected in the form of brine through channels that are formed by expulsion and gravity drainage of brine pockets in the sea ice (Eide and Martin, 1975). These micro and macroscopic channels allow organisms, including algae, to inhabit the sea ice. As the salt ions are rejected from the downward advancing ice, the salt builds up ahead of the advancing interface. This increases the salinity of a thin layer of ice at the bottom that is at the respective melting/freezing point and is of both solid and liquid properties. This increase in salt concentration then leads to diffusion into the ocean out of the brine channels (Thomas and Dieckmann, 2010).

Sea ice melt is partly dependent on the Albedo of the ice/snow and levels of solar radiation penetrating it during the summer months (NSIDC, 2012b). As snow and the surface of the ice start to melt, meltponds form ontop of the ice floes. As these deepen and the ice carries on melting the Albedo continues to decrease, thus increasing the absorption of solar radiation and increasing the rate of melt. Sea ice can also melt from underneath without direct solar radiation. If the underlying and surrounding surface sea water has a temperature above the freezing point, typically in leads or polynyas, this will begin to melt the bottom and side surfaces of the ice floe.

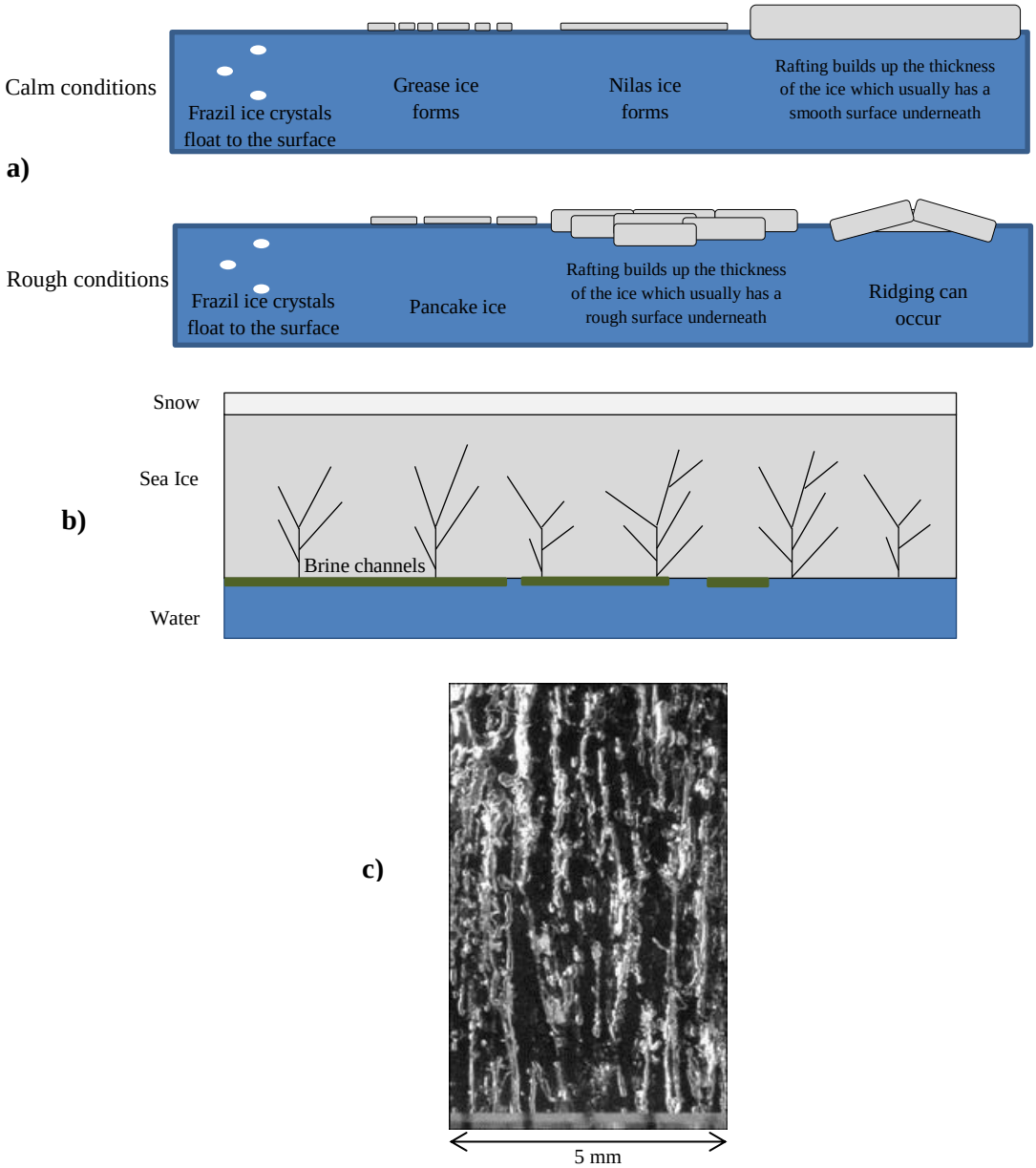


Figure 1.2. Simple schematics of **a**) sea ice formation in calm and rough conditions and **b)** brine channels in sea ice along with **c)** a photograph in natural light showing elongated brine channels between ice crystals (image taken from www.nsidc.org courtesy of Ted Maksym, United States Naval Academy).

1.2 The Arctic ecosystem

1.2.1 Marine primary production

There are two important habitats for Arctic marine primary production; sea ice and open water. In these two marine environments, different algal species grow; algae on the underside and within the seasonal sea ice (Syvertsen, 1991) and phytoplankton growing in the open waters (Round, 1981). Ice formation processes are important for the initial

incorporation of organisms into the developing sea ice, including bacteria, protists and metazoans. Mechanisms of incorporation include scavenging of frazil ice crystals (Ackley, 1982) and wave fields that pump water through grease ice, trapping organisms between the ice crystals (Ackley, 1987).

The amount of sunlight available, due to ice and snow cover (Palmisano et al., 1985) and seasonal variability of day light hours (Lee et al., 2008), are key factors affecting the amount of algal growth. Other important factors include salinity (Grant and Horner, 1976), temperature (Arrigo and Sullivan, 1992) and availability of nutrients (Lizotte and Sullivan, 1992). In ice covered regions, the bottom few centimetres of ice containing the algae is the main source of food for the ecosystems below (Gosselin et al., 1997; Thomas and Dieckmann, 2010). During spring, there is an enhancement in this ice-associated algae as it is the optimal period for growth (Brown et al., 2011; Smith et al., 1993). In summer, the algae and nutrients, previously within and attached to the underside of the ice, are released into the water column in pulses (Brown, 2011; Hegseth, 1998). The associated bloom is initiated by increased solar radiation, stratification induced ice melting and abundant winter-accumulated nutrients (Wassmann et al., 2006a). The rapid sinking of ice algae provides an early season food source for the benthic community (Morata et al., 2010; Renaud et al., 2007).

1.2.2 Diatoms

One of the most common primary sources of organic matter in the Arctic marine environment are the unicellular photosynthetic protists, diatoms. Diatoms are eukaryotic single celled colonial organisms found in marine and terrestrial environments and make up the majority of sea ice algae in the Arctic. They are responsible for around one fifth of the world's primary production (Falkowski et al., 1998) with annual average Arctic primary production estimates at approximately 26 g C m^{-2} y^{-1} (Sakshaug, 2004). Characterised by their silica cell walls called frustules (Rampen, 2009), marine diatoms

have two main types; pennate and centric. Pennate diatoms are thin, lenticular in shape and found attached to substrate, such as sea ice, these include *Nitzschia spp.* and *Haslea spp*. Centric diatoms, including *Chaetoceros spp.* and *Thalassiosira spp.*, are circular in shape, bouyant and found mostly in the water column (Booth and Horner, 1997; Falkowski et al., 1998; Gran, 1904).

Diatom assemblages can be used to monitor environmental changes and in some cases the implications of long-term human impacts on the environment. For example sedimentary diatom assemblages can give detailed information of eutrophication trends in lakes. For example Anderson (Anderson, 1989) studied the eutophication of the lake Lough Augher in Northern Ireland, due to untreated sewage effluent from a local manufacturer. This was determined through diatom assemblages identified within the sediment. Diatoms have also been used as indicators of pH and to measure surface-water acidification. In certain areas of the UK which are prone to low or high levels of acid deposition (acid rain), diatom assemblages along with other chemical and biological indicators, are monitored as part of national monitoring programmes (Battarbee et al., 2010).

Diatoms can also be used as paleo primary production indicators (Chmura et al., 2004) and variation in diatom species in sediment cores can provide information on paleo sea ice cover (Gersonde and Zielinski, 2000). For example, Gersonde and Zielinski found that abundance changes in the diatom taxa *Fragilariopsis curta* and *Fragilariopsis cylindrus*, within sediment cores collected in the Antarctic, was a robust identification tool for the winter sea ice extent.

1.2.3 Consumers

Sea ice in the Arctic has been established as a prime environment for primary consumers (Laurion et al., 1995; Sime-Ngando et al., 1997). Some of these species live

within the ice, such as copepods (Fig.1.3c) and nematodes (Fig.1.3f) and are known as in-ice fauna (Thomas and Dieckmann, 2010). Other larger metazoan species are known as under-ice macrofauna and include species such as amphipods and fish that live in close proximity to the under side of the ice (Gradinger and Bluhm, 2004) (Fig. 1.3). This densely packed food source of sea ice algae on the underside and within ice can be much more favourable to consumers when phytoplankton concentrations are low, especially in the spring season. For example, the nearshore amphipod *Onismus litoralis* feeds almost exclusively on sea ice algae in the spring time; feeding primarily on pennate sea ice diatoms (Carey and Boudrias, 1987).

1.2.4 Predators

Polar cod (*Boreogadus saida*) (Fig. 1.3a), is an important species in the Arctic food web as it feeds on sympagic fauna and directly on sea ice algae. Its predators include black guillemots (*Cepphus grylle*), Brünnich's guillemots (*Uria lomvia*) (Bradstreet, 1979) and ringed seals (*Phoca hispida*) (Finley et al., 1983). In ice-covered regions, polar cod rely on the ice for both protection against predators and as a feeding habitat (Gradinger and Bluhm, 2004; Welch et al., 1992). In winter they have also been observed in ice-covered regions near the bottom of the water column in shallow shelves (first suggested by Welch et al. in 1992), possibly avoiding predation by diving seals (Benoit et al., 2008) or following their prey such as amphipods (personal observations). Ringed seals depend on stable annual ice and sufficient snow coverage for lairs while seal pups rely on the ice for initial growth and development (Thomas and Dieckmann, 2010). Polar bears (*Ursus maritimus*) (Fig. 1.3k) are known to feed on ringed seals as their primary prey (Amstrup et al., 2001). They use the sea ice as a platform for travelling, mating and feeding, and so live out most of their lives on the sea ice (Derocher, 2012; Stirling et al., 1999). These populations of primary production, consumers and predators have great influence on Inuit sustainability as they contribute significantly to food sources of Inuit

communities (IPY-API, 2010). A few examples of polar species that rely on sea ice presence and the primary sources of food within are shown in Fig. 1.3.

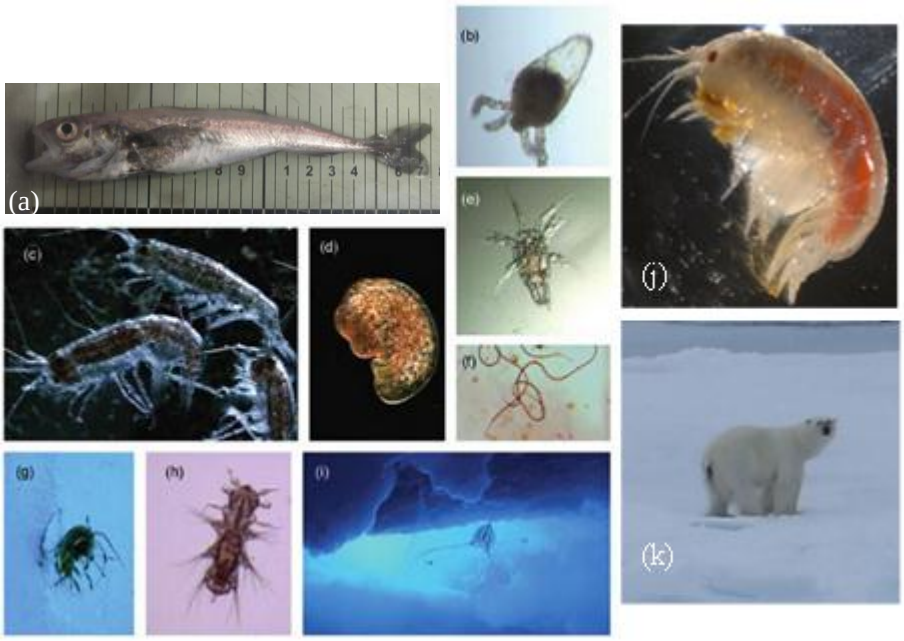


Figure 1.3. Examples of Arctic ice-associated fauna. **a)** Polar cod (Photograph by Thomas Brown), *Boreogadus saida*, **b)** *Sympagohydra tuuli*, **c)** *Apherusa glacialis*, **d)** turbellarian, **e)** Copepod nauplius, **f)** nematode, **g)** *Gammarus wilkitzkii*, **h)** Hesionidae juvenile, **i)** *Mertensia sp.* (Thomas and Dieckmann 2010), **j)** *Onisimus nanseni*, photograph by Mikko Vihtakari, MOSJ cruise and **k)** Polar Bear (*Ursus maritimus*), photograph by Ashleigh Ringrose.

1.2.5 The effects of climate change on Arctic food webs

Predictions of Arctic sea ice retreat and information of species reliance on the habitat and food source within, may allow effects of climate change on Arctic food webs to be anticipated in the future.

Prehistoric Heinrich events, have been widely studied to gain a wider understanding of possible future climate change effects. By analysing prehistoric, rapid and abrupt past climatic events, a better understanding of the environments response to a similar climatic event, currently predicted partly due to human-impact, may be provided. Heinrich events are climate transitions which are linked to discharges of ice-bergs from the Northern Hemisphere that melt in the North Atlantic. Using sediment analysis from these prehistoric events, Cermeño and co-workers have predicted that marine diatom

communities will respond to future, climate-induced environmental changes through variation in species abundance. However, they also suggested marine diatom communities will also be able to maintain the potential to shift back to previous states if the environmental conditions are re-established (Cermeño et al., 2013).

Phytoplankton, inlcuding sea ice algae (made up partly by marine diatoms), produce organic molecules such as polyunsaturated fatty acids (PUFAs) that are vital in animal diets (Søreide et al., 2010). Some animal species cannot synthesise these themselves (Nichols, 2003), resulting in malnutrition, stunted growth and death (Yongmanitchai and Ward, 1989). Shifts in animal populations that heavily rely on sea ice algae for their intake of PUFAs may be observed due to a reduction in accessibility to these vital compounds.

Alternative predictions of climate induced changes to the Arctic ecosystem show an overall increase of primary production of more than 30% (Wassmann et al., 2006b), however with a greater contribution from open water phytoplankton and less from sea ice algae (Horner and Schrader, 1982; Hsiao, 1992). This switch between the availability of primary production sources may induce feeding habbit changes of consumers that rely mainly on sea ice algae. This will add demand for vital compounds, such as PUFAs, from open water phytoplankton.

Changes in *Calanus* species dominance due to temperature shifts have also been predicted; a warmer Arctic with reduced ice cover and new phytoplanktonic bloom regimes would favour the smaller and less lipid rich *Calanus finmarchicus* (Falk-Petersen et al., 2007). This in turn, may reduce populations of the little auk (*Alcidae alle*) and minke whale (*Balaenoptera acutorostata*). Arctic ringed seals have long lactation periods, usually 36 to 41 days (Hammill et al., 1991). Pups obtain 93% of their first year growth during this suckling period (Smith, 1987). Absence of stable ice

throughout this period may make this species vulnerable. This could potentially result in slower growth and higher mortality rates of the ringed seal, with retreat of their vital habitat (Smith and Harwood, 2001). The effects of climate change on Arctic food webs are difficult to measure. Some methods of monitoring these effects include using satellite imagery to measure sea ice extent changes and animal population monitoring. Chemical biomarkers are also useful when monitoring the effects of climate change. For example, the unsaturation index U^K_{37} of long chain alkenones, produced by coccolithophores, provides information of past sea surface temperatures (Brassell et al., 1986). Another index to investigate past sea surface temperatures is TEX_{86}. This uses the number of cyclopentane moieties in glycerol dialkyl glycerol tetraethers (GDGTs) as an indicator of temperature, an increase in rings corresponds to an increase in production temperature.

1.3 Biomarkers found in the Arctic marine environment

A molecular biomarker is a chemical indicator of a process that cannot be measured and evaluated directly. Biomarkers can be chemical finger prints of the organism from which they are produced. They can indicate the existence, either past or present, of biological sources and environmental states or changes.

1.3.1 Fatty acids

Fatty acids are a set of common biomarkers used to study food webs in marine ecosystems (Nichols et al., 1986). Saturated and unsaturated fatty acids are important for storing energy and maintaining cell fluidity at low temperatures (Gillan et al., 1981; Sicko-Goad et al., 1988) and some, including $C_{18:0}$, are ubiquitous. Some fatty acids including C_{14}, $C_{16:1\omega7}$ and C_{16} (**FI**, **FII**, **FIII**; Fig. 1.4) are believed to be representative of marine diatoms (Dunstan et al., 1993; Opute, 1974; Volkman et al., 1998; Zhukova and Aizdaicher, 1995). Discriminating between a sea ice and/or phytoplanktic origin however is not possible. Despite the lack of clarity of fatty acid primary source origins,

their relative abundances can give information towards changes in the environment, such as algal blooms (Brown et al., 2011; Reuss and Poulsen, 2002) and overall primary productivity (Rampen et al., 2010).

1.3.2 HBIs

A third class of biomarkers are highly branched isoprenoids (HBIs) which, unlike fatty acids, are resticted in terms of their origin. HBIs are produced by some diatomaceous algae including; *Haslea spp.* (Allard et al., 2001; Johns et al., 1999; Volkman et al., 1994; Wraige et al., 1997), *Rhizosolenia sp.* (Sinninghe Damsté et al., 1999), and *Pleurosigma sp.* (Belt et al., 2000). HBIs are branched hydrocarbons with usually 20, 25 or 30 carbon atoms, with between at least 1 and 6 double bonds (Volkman et al., 1994; Wraige et al., 1997).

C_{25} HBIs were first found in sediment in 1976 (Gearing et al., 1976), later the structure and biological source were identified (Robson and Rowland, 1986; Volkman et al., 1994). The extent of unsaturation in *Haslea ostrearia* was found to be temperature dependent (Rowland et al., 2001). Therefore it was hypothesised that a monoene HBI would be present at temperatures lower than 5°C. IP_{25} (**I**; Fig. 1.4) is an HBI with one double bond and was identified in Arctic sea ice (Belt et al., 2007) and recognised to have a likely sea ice source, based on stable carbon isotope analysis (Belt et al., 2008).

The curent understanding of the role of HBIs and specifically IP_{25} in marine diatoms is unknown. However a broad hypothesis can be made to suggest the purpose of HBIs being similar to other lipids such as fatty acids and sterols, to store energy and to be constructural constituents in diatom cells. To date, the individual species of diatom responsible for producing IP_{25} have not been identified due to the absense of IP_{25} from laboratory culturing experiments. This was possibly due to a lack of facilities to accurately create minus temperatures, similar to the natural environment. However it is

likely that either *Haslea spp.* or *Navicula spp.* (or both) are the diatom sources, as these diatom genera are known to produce C_{25} HBIs in culture and both have been found in sea ice samples containing IP_{25} (Belt et al., 2007; Brown, 2011).

It is also hypothesised that temperature is the controling factor that localises the production of IP_{25} to the sea ice rather than the open water. For the past five years IP_{25} has been used to map former sea ice cover throughout the Holocene period and has provided information towards climate reconstruction and prediction models (Belt et al., 2010; Gregory et al., 2010; Müller et al., 2009; Vare et al., 2009).

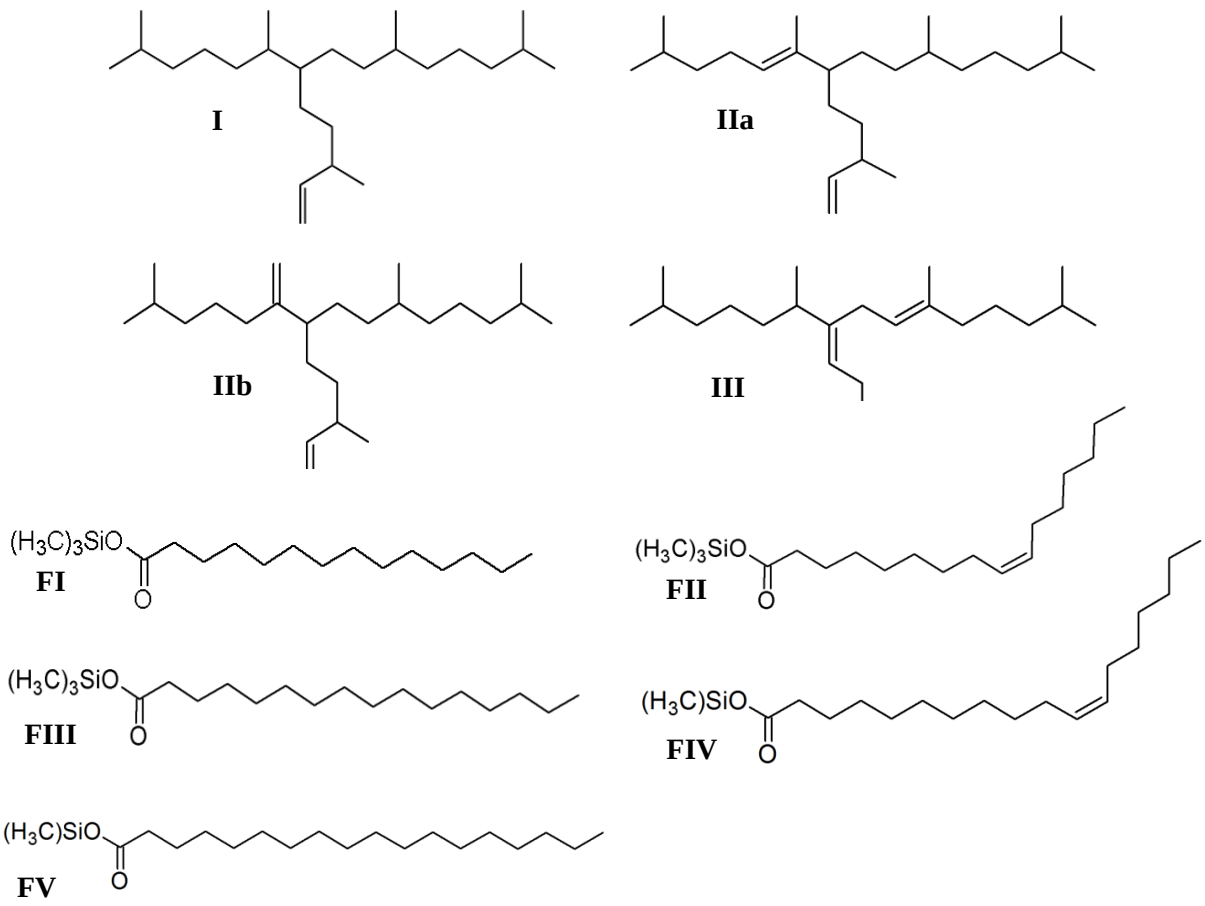


Figure 1.4 Molecular structures of analytes in the current study. IP_{25} (**I**), $C_{25:2(5/6)}$ (**IIa**), $C_{25:2(6/17)}$ (**IIb**), $C_{25:3(7/20)\ E}$ (**III**), silylated fatty acids C_{14} (**FI**), $C_{16:1\omega7}$ (**FII**), C_{16} (**FIII**), $C_{18:1\omega7}$ (**FIV**) and C_{18} (**FV**).

CHAPTER TWO

2.0 THE CURRENT STUDY

2.1 Previous work: IP_{25} in sea ice

IP_{25} was first identified in sea ice from three separate locations in the Canadian sub and high Arctic; Button Bay, McDougall Sound and Franklin Bay (Belt et al., 2007) (Fig. 2.1). To give further understanding of the production of IP_{25}, temporal and vertical distributions were investigated in sea ice collected from the Amundsen Gulf in 2008 (Brown et al., 2011) (Fig. 2.1). The majority of IP_{25} production (ca. 90%) in the Amundsen Gulf took place from mid-March to the end of May and peak concentrations reached 310 pg mL^{-1} in early May (Brown et al., 2011). As IP_{25} production paralleled the main production interval of other biomarkers (chlorophyll *a*, fatty acids, sterols and diatom cell abundances) and was not detected in sea ice samples from mid-winter to early spring, it was concluded that IP_{25} was synthesised during the spring bloom (Brown et al., 2011). In terms of vertical distributions, peak IP_{25} concentations occurred close to the ice-water interface (ca. 1-3 cm). The majority of IP_{25} production (>85%) was found within ice sections that had brine volume fractions >5% (Brown et al., 2011), which is required for diatom colonisation and growth (Brown et al., 2011 and references therein).

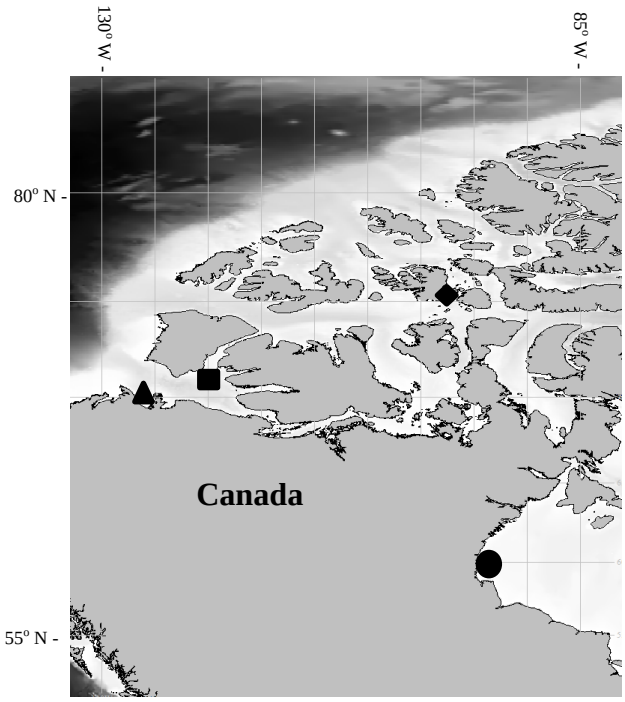


Figure 2.1. Previous sea ice sampling locations for IP_{25} analysis. Symbols denote the following; ● Button Bay, ♦ McDougall Sound, ▲ Franklin Bay, ■ Amundsen Gulf.

2.2 Aims and objectives of this study

Initial findings of the environmental influences affecting IP_{25} production in sea ice and its temporal and spatial distributions have been investigated in the Amundsen Gulf. To be able to use this specific biomarker in future studies across the Arctic, more temporal and spatial information needs to be provided. Therefore the main aim of this study was to give further understanding of the occurrence and accumulation of IP_{25} and other lipid biomarkers in Arctic sea ice. This was achieved by the following objectives:

i. To investigate concentration changes in IP_{25} and other lipid biomarkers in Arctic sea ice from Resolute Bay over the spring period

ii. To investigate relationships between concentrations of IP_{25} and other indicators of general sea ice primary production in sea ice from Resolute Bay

iii. To investigate concentration changes in IP_{25} and other lipid biomarkers vertically within Arctic sea ice from Resolute Bay

iv. To investigate the effect (if any) of snow cover on IP_{25} and other lipid concentrations in sea ice from Resolute Bay

v. To compare timing and concentrations of these lipid biomarkers in sea ice between Resolute Bay and previous data from the Amundsen Gulf in the Canadian Arctic

2.3 Study location

The Resolute Passage in the centre of the Canadian Arctic Archipelago (Fig. 2.2) has a maximum depth of 168 m and land-fast sea ice can be up to 2 m thick, persistent from November to July (Siferd and Conover, 1992). This area has been a popular study site for many multidisciplinary ice algal ecosystem and carbon flow studies (Fukuchi et al., 1997; Michel et al., 2006; Smith et al., 1988; Vézina et al., 1997; Welch et al., 1992). Located on the south coast of Cornwallis Island, Resolute Bay (74°41'N, 094°52'W) is a small inuit hamlet in Nunavut, Canada.

2.4 Sample collection

The process described here was carried out by scientists from the University of Manitoba, participating on the Arctic ICE project in 2011. Replicate ice cores (Table 2.1) were sampled with a Kovacs ice corer in an approximate 0.17 miles^2 (0.27 km^2) sampling area and sectioned into five sections, usually with the same or similar horizons. For simplicity of this study, these sections will be denoted as the following; section **A** (0-3 cm; zero being the ice/water interface), section **B** (3-10 cm), section **C** (approx.10-60 cm), section **D** (approx. 60-110 cm) and section **E** (approx. 110 to the top of the core). The same section from each core was then pooled together to take into account for environmental variability and added to filtered sea water (100 ml for every 1

cm of sea ice). This minimises cell lysis which is the breakdown of a cell, due to osmotic shock (Thomas and Dieckmann, 2010). The addition of filtered sea water ensures that little additional organic matter is added. Ice cores with filtered sea water were then left to melt in the dark at the room temperature of the vessel (24 h). The sealed container was swirled to make sure the mixture was homogeneous and a sub sample (100 – 3900 mL) was filtered under vacuum onto a glass fibre filter (GF/F; 0.7 µm), flash frozen at -80°C and then stored at -20°C until further analysis (Fig. 2.3).

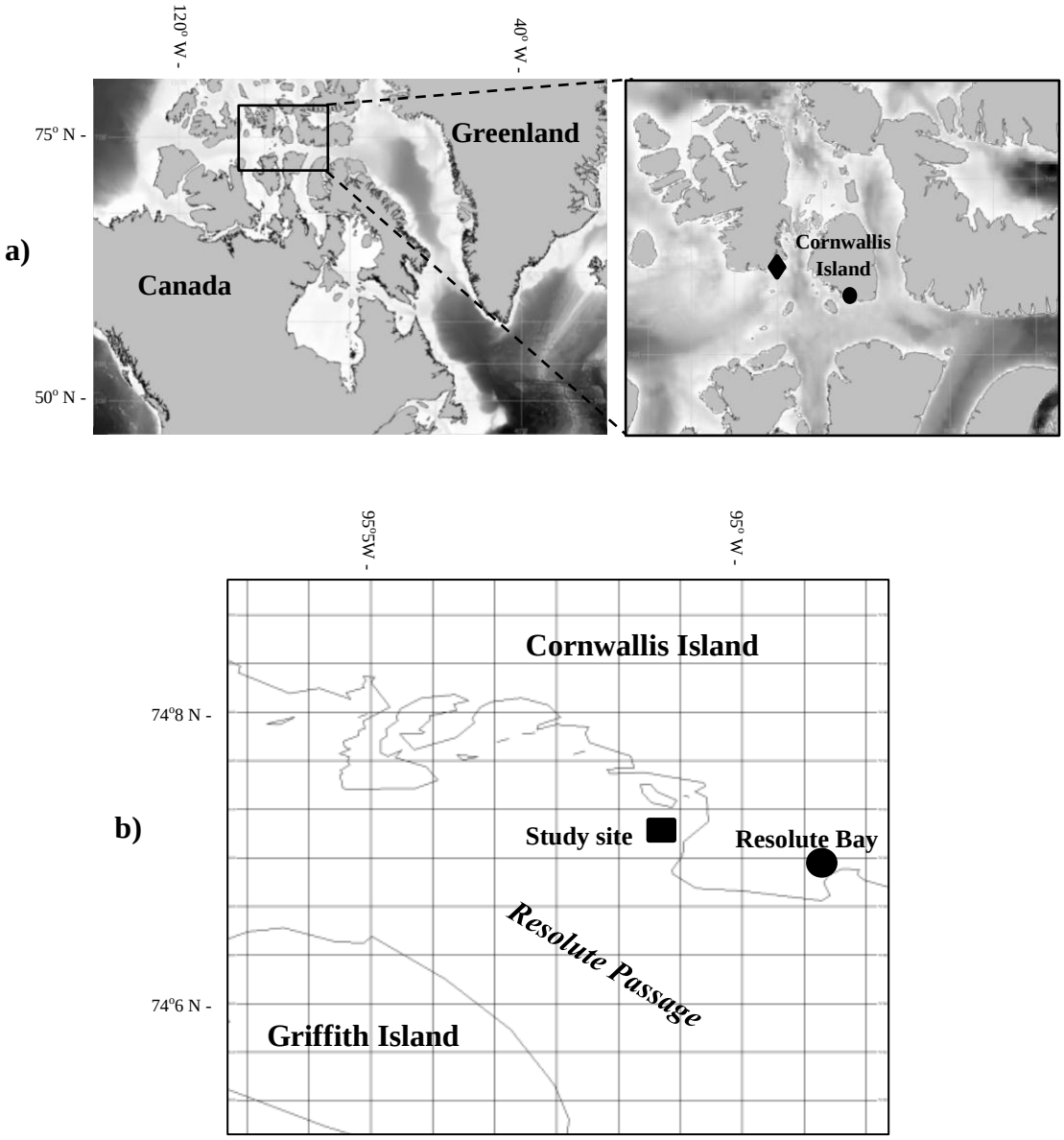


Figure 2.2. a) A map of the Canadian Arctic Archipelago region and Greenland. Resolute Bay is indicated by● and McDougall Sound is indicated by ♦. **b)** A map of the study site in comparison to Resolute Bay for the Arctic ICE project 2011.

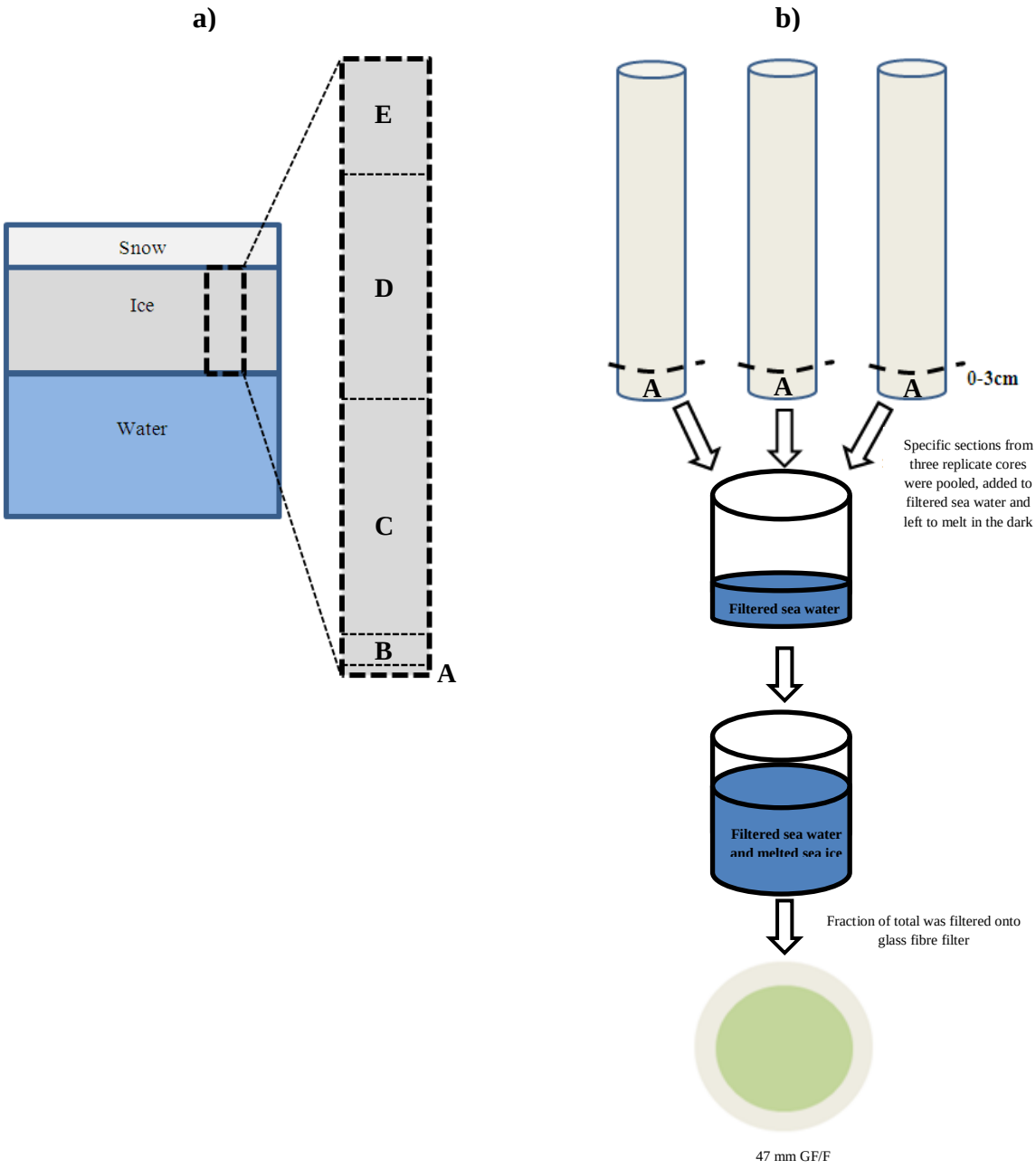


Figure 2.3. Schematics of **a)** sea ice core sectioning and **b)** sea ice core filtration method.

Table 2.1. Summary of the sea ice core sampling in Resolute Bay during the Arctic ICE project 2011. Low, medium and high snow cover represented by L, M and H.

Date	Station ID	Lat. (N)	Long. (W)	Averaged ice thickness of pooled cores (cm)	Horizon (cm)	Snow depth category	Average snow cover of pooled cores (cm)	Number of cores pooled
27/04/11	AI1	74°43.161	95°09.974	158.3	0-3	L	5.6	3
27/04/11	AI1	74°43.163	95°09.965	158.6	0-3	M	13	3
27/04/11	AI1	74°43.162	95°09.953	161	0-3	H	23.6	4
01/05/11	AI2	74°43.161	95°09.919	155.6	0-3	L	7.6	3
01/05/11	AI2	74°43.159	95°09.938	No data provided	0-3	M	17	3
01/05/11	AI2	74°43.157	95°09.947	181.6	0-3	H	29.3	3
01/05/11	AI2	74°43.159	95°09.938		3-10	M		3
01/05/11	AI2	74°43.159	95°09.938		10-57	M		1
01/05/11	AI2	74°43.159	95°09.938		57-107	M		1
01/05/11	AI2	74°43.159	95°09.938		107-157	M		1
05/05/11	AI3	74°43.165	95°09.868	160	0-3	L	7.6	3
05/05/11	AI3	74°43.164	95°09.982	137.6	0-3	M	22	3
05/05/11	AI3	74°43.158	95°09.911	142	0-3	H	20.3	3
10/05/11	AI4	74°43.166	95°09.864	159.6	0-3	L	12	3
10/05/11	AI4	74°43.167	95°09.851	161.5	0-3	M	14	3
10/05/11	AI4	74°43.168	95°09.827	134.6	0-3	H	23.2	3
10/05/11	AI4	74°43.167	95°09.851		3-10	M		3
10/05/11	AI4	74°43.167	95°09.851		10-50	M		1
10/05/11	AI4	74°43.167	95°09.851		50-110	M		1
10/05/11	AI4	74°43.167	95°09.851		110-150	M		1
15/05/11	AI5	74°43.162	95°09.740	154.8	0-3	L	7.8	3
15/05/11	AI5	74°43.160	95°09.750	142	0-3	M	18.6	3
15/05/11	AI5	74°43.161	95°09.769	139.8	0-3	H	27	3
19/05/11	AI6	74°43.171	95°09.665	155.2	0-3	L	8	3
19/05/11	AI6	74°43.171	95°09.653	150.8	0-3	M	13.7	3
19/05/11	AI6	74°43.168	95°09.678	153.2	0-3	H	24.3	3
19/05/11	AI6	74°43.171	95°09.653		3-10	M		3
19/05/11	AI6	74°43.171	95°09.653		10-60	M		1
19/05/11	AI6	74°43.171	95°09.653		60-110	M		1
19/05/11	AI6	74°43.171	95°09.653		110-164	M		1
23/05/11	AI7	74°43.144	95°09.699	154.8	0-3	L	8.5	3
23/05/11	AI7	74°43.150	95°09.659	152.6	0-3	M	12.2	3
27/05/11	AI8	74°43.138	95°09.655	156.2	0-3	L	8.5	3
27/05/11	AI8	74°43.136	95°09.631	147.6	0-3	M	13	3
27/05/11	AI8	74°43.132	95°09.609	142.6	0-3	H	21.2	3
27/05/11	AI8	74°43.136	95°09.631		3-10	M		3
27/05/11	AI8	74°43.136	95°09.631		10-60	M		1
27/05/11	AI8	74°43.136	95°09.631		60-110	M		1
27/05/11	AI8	74°43.136	95°09.631		110-150	M		1
31/05/11	AI9	74°43. 099	95°09.601	148.3	0-3	L	10.5	3
31/05/11	AI9	74°43.099	95°09.646	143.8	0-3	M	16.6	3

31/05/11	AI9	74°43.100	95°09.583	135.3	0-3	H	28.3	3
04/06/11	AI10	74°43.087	95°09.526	150.3	0-3	L	7.6	3
04/06/11	AI10	74°43.084	95°09.591	136	0-3	M	13.6	3
04/06/11	AI10	74°43.079	95°09.648	148.3	0-3	H	18.6	3
04/06/11	AI10	74°43.084	95°09.591		3-10	M		3
04/06/11	AI10	74°43.084	95°09.591		10-60	M		1
04/06/11	AI10	74°43.084	95°09.591		60-110	M		1
04/06/11	AI10	74°43.084	95°09.591		110-140	M		1
08/06/11	AI11	74°43.081	95°09.498	154.8	0-3	L	7.2	3
08/06/11	AI11	74°43.071	95°09.508	148	0-3	M	16	3
08/06/11	AI11	74°43.072	95°09.491	154.5	0-3	H	39.6	3
12/06/11	AI12	74°43.075	95°09.446	146.3	0-3	L	No data provided	3
12/06/11	AI12	74°43.074	95°09.467	145.5	0-3	H	9.3	3
16/06/11	AI13	74°43.063	95°09.495	154	0-3	H	3	3
20/06/11	AI14	74°43.042	95°09. 564	143	0-3	H	2.2	3

CHAPTER THREE

3.0 METHODOLOGY

3.1 Introduction

This chapter describes the experimental procedures undertaken in this study to separate the biomarkers of interest (HBIs including IP_{25}, fatty acids and chlorophyll *a*) from the filtered sea ice core samples to enable analysis. Samples were provided by colleagues at the University of Manitoba, Canada, and were collected during the Arctic ICE 2011 project. Samples were flash frozen (-80°C), stored (-20°C) and freeze dried before delivery to Plymouth University (UK). Each filtered sea ice sample was analysed either as a whole, in half or in quarters, in order to test the reproducibility of the data and analytical procedures. Figure 3.1 represents the portioning method of filtered samples. Replicates of the mass of analyte per mL of sea ice were calculated by calculating the means of the concentrations in each half/quarter).

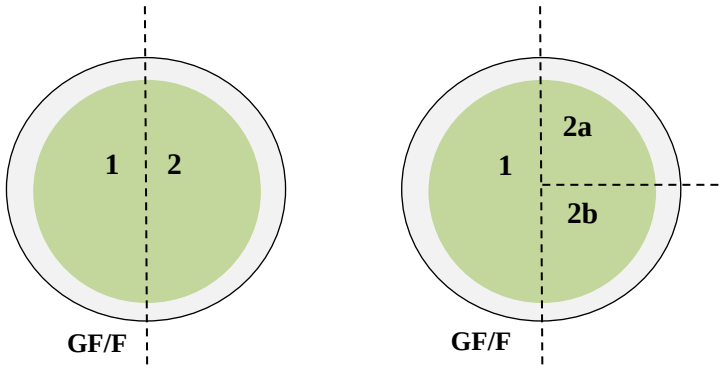


Figure 3.1. Schematic of filter portioning for samples collected on the Arctic ICE project 2011. **1** and **2** represent portioning in two halves whilst **2a** and **2b** represent portioning in quarters (Filter size 47mm).

3.2 Extraction and purification of lipid fractions

Whole or part filters were placed in clear glass 7 mL vials and four internal standards were added prior to extraction of lipids for later quantification (Table 3.1). These were; 9-octyl-8-heptadecene (**ISa**) and 7-hexylnonadecane (**ISb**) to quantify HBIs and

nonadecanoic acid (**ISc**) to quantify fatty acids. These standards were selected as they best represent the specific analytes in their structure and chemical behaviour and are not normally present in sea ice. For example **ISa** and **ISb** both have a molecular structure with 25 carbon atoms which behave similarly to **I** and the other HBIs during the extraction and purification process (Belt et al., 2012; Brown et al., 2011).

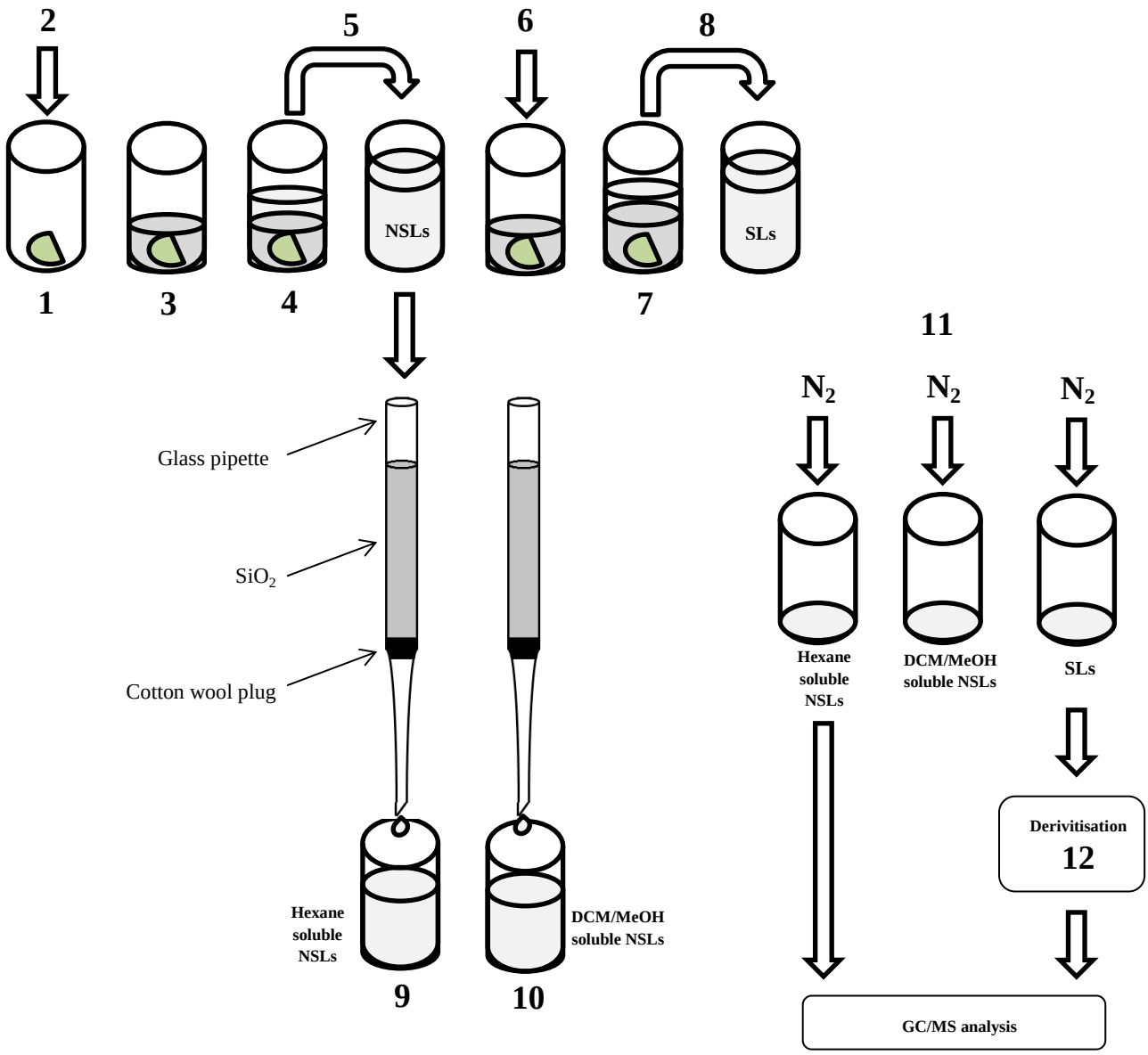
Samples were then saponified with a sufficient amount of methanolic potassium hydroxide (5% KOH; MeOH, H_2O; 80/20 v/v) to cover the filter (ca. 2-3 mL), capped, vortexed (10 sec), sonicated (5 min) and heated at 80°C for 60 min. Non-saponifiable lipids (NSLs) were extracted into clean vials with hexane using the following method; 1 mL of hexane was added, the vial was capped, vortexed (10 sec) and centrifuged (30 sec at 2500 rpm) and then transferred into an additional clean vial. This extraction was repeated twice more. Solutions containing potassium hydroxide were then protonated with concentrated HCl (1 mL), capped, vortexed (10 sec) and saponifiable lipids (SLs), including free fatty acids, were extracted into hexane (3 x 1 mL as before). NSLs were purified by open column silica chromatography (99:1 SiO_2: NSLs). Apolar lipids including HBIs were collected into clean vials with hexane (5 column volumes), followed by the more polar compounds with dichloromethane/methanol (50:50 v/v; 5 column volumes). Figure 3.2 shows a schematic of the extraction and purification procedures undertaken.

3.3 Derivatisation

Saponifiable polar lipids including free fatty acids were converted into trimethylsilyl derivatives (TMS), to reduce polarity and improve peak shape during analysis by GC/MS. After the derivatising agent, bis(trimethylsilyl)trifluoroacetamide (BSTFA) was added (50 µL), samples were capped and heated at 70°C for 20 min.

3.4 Gas chromatography-mass spectrometry (GC/MS)

All samples were diluted with hexane (non-polar extracts) or dichloromethane (polar extracts) to an appropriate concentration (0.001 mg mL^{-1}) for analysis by GC/MS. Analysis was carried out using an Agilent 7890A gas chromatograph (GC), coupled to an Agilent 5975 mass selective detector, fitted with an Agilent HP-5_{MS} (30 m x 0.25 mm x 0.25 µm) column with auto-splitless injection (300°C) and helium carrier gas (1 mL min^{-1} constant flow). Detectable compounds were determined by both total ion current (TIC; *m/z* 50-500 Daltons) and selective ion monitoring (SIM; -0.3 +0.7 *m/z* of interest) modes. TIC allowed the retention times and mass spectra of selected compounds to be elucidated, while SIM was used for compound quantification due to its higher selectivity and sensitivity. Analysis by GC involved a ramped temperature profile from 40-300°C at 10°C min^{-1}, with a 10 minute isothermal at 300°C. Data analysis and collection was achieved with Agilent Chemstation software, version C.03.00.



1. Place filtered sample (whole or part) into clean glass 7 mL vial
2. Add internal standards
3. Add enough 5% KOH; MeOH, H_2O; 80/20 v/v, to cover filter (ca. 2-3 mL). Cap, vortex (10 sec) and sonicate (5 min)
4. Add 1 mL of hexane, cap, vortex (10 sec) and centrifuge (30 sec at 2500 rpm)
5. Extract hexane layer with glass pipette into new vial to give the NSLs
   Repeat steps 4 and 5 twice more.
6. Add 1 mL of conc. HCl to the vial containing the filter and KOH solution, cap and vortex (10 sec)
7. Add 1 mL of hexane, cap, vortex (10 sec) and centrifuge (30 sec at 2500 rpm)
8. Extract top hexane layer with glass pipette into new vial to give the SLs
   Repeat steps 7 and 8 twice more.
9. Transfer NSL mixture to column, elute with hexane (5 column volumes) and collect hexane soluble NSLs in new vial
10. Elute DCM/MeOH soluble NSLs with DCM/MeOH (50:50 v/v; 5 column volumes) into new vial
11. Dry all extracts under N_2 (25°C)
12. Derivitise SLs (BSTFA; 50µL; 70°C; 20 min) before GCMS analysis of them and hexane soluble NSLs

Figure 3.2. Schematic diagram showing the extraction and purification process used on the filtered sea ice samples.

3.5 Quantification of HBIs

Quantification of HBIs and internal standards extracted from the filtered sea ice samples were first achieved by identification of individual isomers and internal standards from their mass spectra from the TIC chromatogram (for example Fig. 3.3) and manual integration of the SIM chromatograms. The integrated peak areas of the molecular ion (M^+) signal for each HBI (**I**: *m/z* 350.3 **II**: *m/z* 348.3 **III**: *m/z* 346.3 (Fig. 3.4)) and the respective internal standard from the SIM chromatograms were then used to calculate the concentration of each isomer according to equation 3.1. The detection limit for quantification of IP_{25} using the GC-MS system described is 10 ng mL^{-1} (S/N > 3) (Belt et al., 2012). It is presumed that this value is the same for the other analyte GC/MS detection limits.

Equation 3.1 $$Analyte\ \left(\frac{\mu g}{mL}\right) = \frac{(\frac{Pa}{Pis} \times RF \times Mis)}{Vice} \times \frac{Vtot}{Vfilt \times x}$$

There are many factors to consider when quantifying analytes using GC/MS, some of these include; detector sensitivity towards each analyte and internal standard (*RF*), mass of the internal standard added (*Mis*), volume of sea ice analysed (*Vice*), proportion of sea ice filtered for analysis (*Vtot/Vfilt*) and the proportion of filter analysed(x).

Equation 3.1 allows for quantification of all HBI analytes in this study. *Pa/Pis* denotes the ratio between the integrated peak area of the SIM M^+ HBI ion (Fig. 3.4) and the integrated peak area of the SIM M^+ internal standard ion, **ISa** (*m/z* 350.3) or **ISb** (*m/z* 99) depending on the analyte. This ratio is then multiplied by the corresponding GC/MS response factor (*RF*) to take account of the detector sensitivity towards each analyte and the internal standard. To convert this number into a mass unit, it is multiplied by the mass of the internal standard added (*Mis*). Equation 3.1 gives the abundance of the analyte in mass per unit volume of sea ice, therefore *Vice* denotes for the volume of sea ice analysed. To take into account for the proportion of the sea ice filtered, the value is

multiplied by the inversed proportion of ice filtered (*Vtot* (sea ice volume and filtered sea water volume) over the volume filtered (*Vfilt*). Finally, to take into account the proportion of the filter analysed (either a quarter, half or whole), the volume filtered is multiplied by x (0.25, 0.5 or 1).

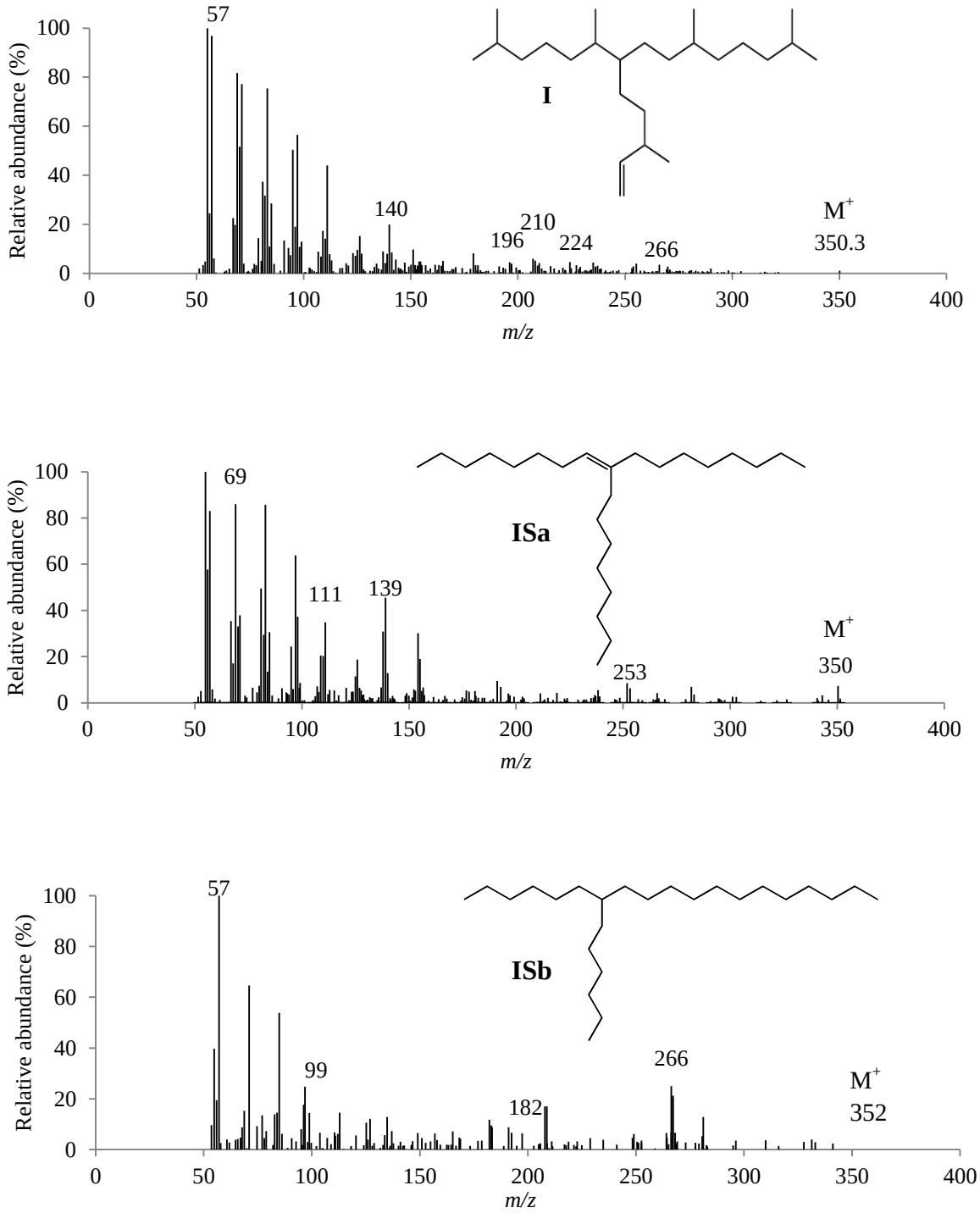


Figure 3.3. Background subtracted mass spectra and structure of **I** (M^+ = *m/z* 350.3), internal standards **ISa** (M^+ = *m/z* 350.3) and **ISb** (M^+ = *m/z* 352).

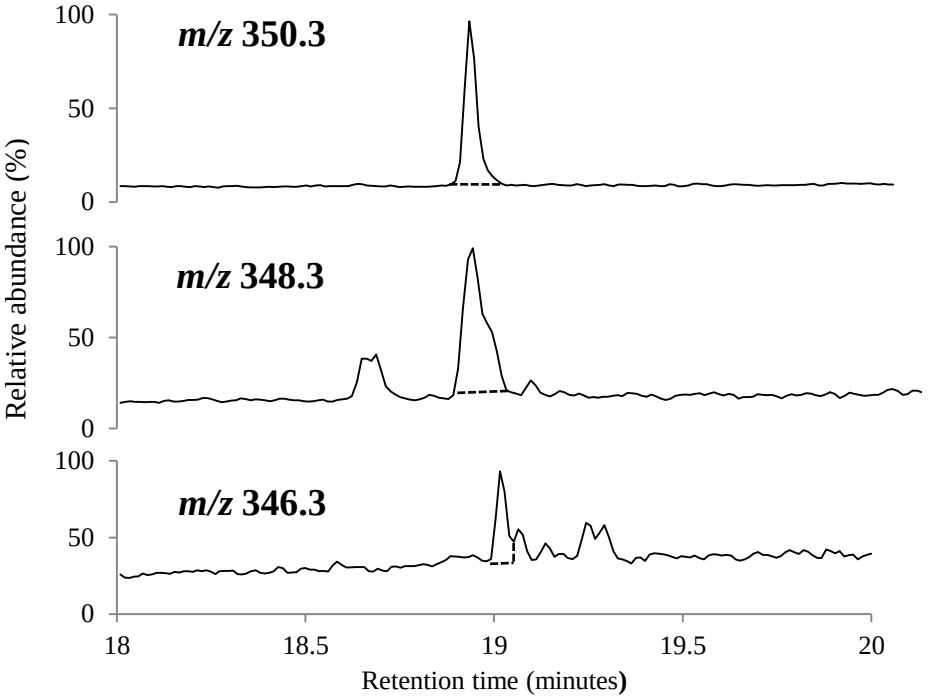


Figure 3.4. An example of partial SIM extracted chromatograms of the hexane soluble NSL extract of filtered sea ice samples. HBIs; **I** (*m/z* 350.3), **II** (*m/z* 348.3) and **III** (*m/z* 346.3) are shown along with the integration technique shown by dotted lines.

3.6 Quantification of fatty acid trimethylsilyl esters

Quantification of derivatised fatty acids extracted from filtered sea ice samples was first achieved by identification of individual isomers and internal standard from their mass spectra from the TIC chromatograms (Fig. 3.5) with comparison of the previous order of elution of individual analytes (Brown, 2011) and manual integration of the TMS fragment ion (*m/z* 117) in SIM mode. These peak area values were incorporated into equation 3.1 as *Pa*, along with individual *RF* values for each analyte (Table 3.1) to accurately calculate individual fatty acid concentrations.

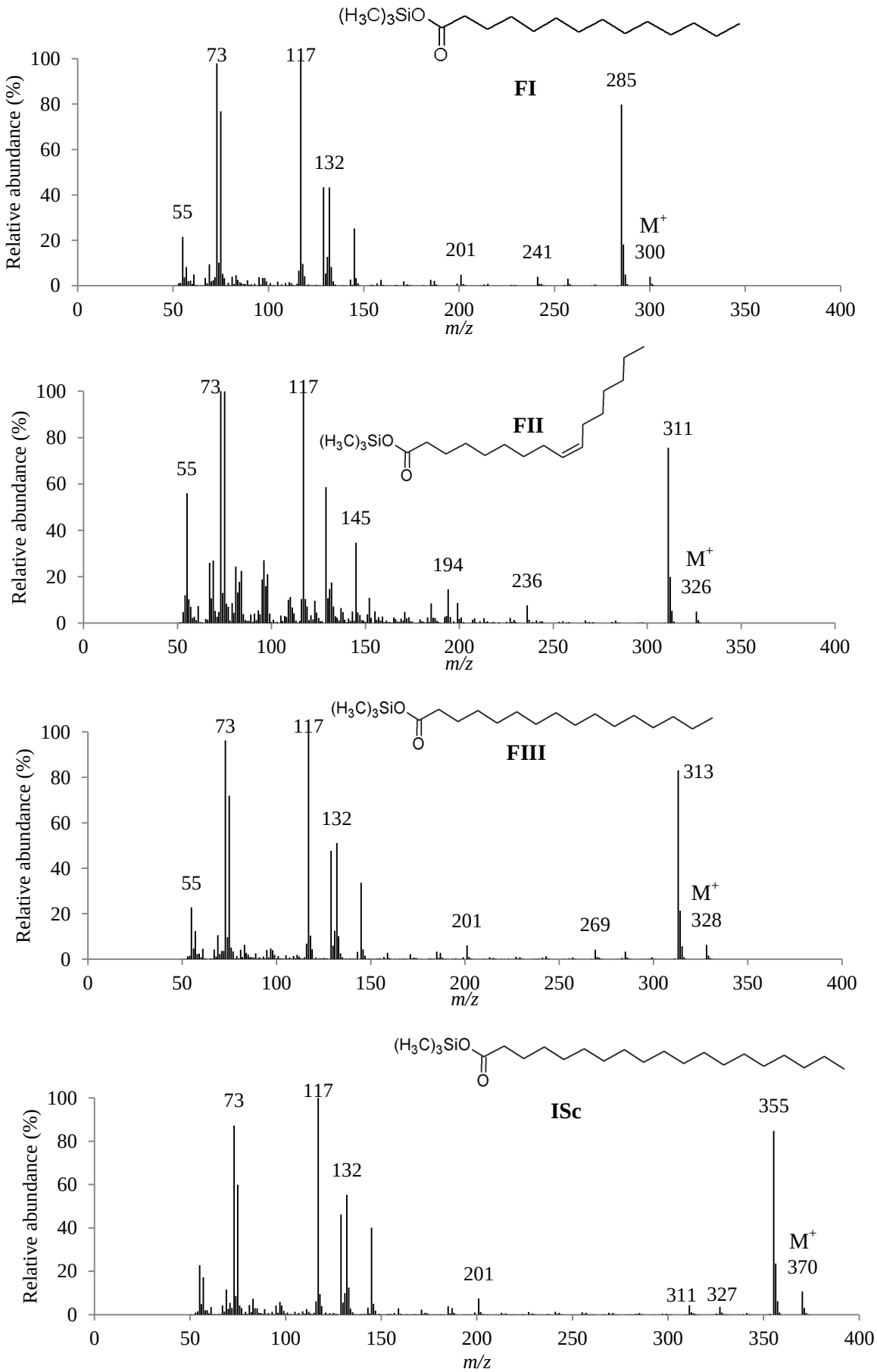


Figure 3.5. Background subtracted mass spectra and structures of fatty acid trimethylsilyl (TMS) esters Tetradecanoate **FI** (M^+ = *m/z* 300), cis-9-Hexadecanoate **FII** (M^+ = *m/z* 326), Hexadecanoate **FIII** (M^+ = *m/z* 328) and internal standard Nonadecanoate **ISc** (M^+ = *m/z* 370).

3.7 Quantification of chlorophyll *a*

Colleagues at the University of Manitoba melted and filtered sea ice sub-samples (section **A**; 0-3 cm) for the determination of chlorophyll *a*. Concentrations (mg m^{-2}) were calculated using equations (Holm-Hansen et al., 1965) after measuring fluorescence with a Turner Designs 10-005R fluorometer after 24 h extraction in 90% acetone at approximately 5°C in the dark (Parsons et al., 1984).

Table 3.1. All analytes with relative response factors, SIM m/z ions used for quantification and relative amounts of each used. Response factors were calculated from calibration curves produced by colleagues at Plymouth University. **I** was isolated from mass extraction of marine sediment. **II** and **III** were isolated from diatom laboratory cultures. Fatty acid response factors were also calculated by calibration curves, however from purchased standards.

Lipid			SIM *m/z* ion	Response factor (*RF*) and standard used to quantify		Concentrations and amount of standards added to sea ice samples	
						Section **A** (0-3 cm)	Sections **B-E**
HBIs	**I**	IP_{25}	350.3	5.0	**ISa**	10 µL; 10 µg mL^{-1}	20 µL; 0.1 µg mL^{-1}
	II	$C_{25:2(5/6)}$ and $C_{25:2(6/17)}$	348.3	11.3			
	III	$C_{25:3(7/20)\ E}$	346.3	10.0	**ISb**	10 µL; 10 µg mL^{-1}	20 µL; 0.1 µg mL^{-1}
Fatty acids	**FI**	C_{14}	117	1.2	**ISc**	10 µL; 4 $mgmL^{-1}$	20 µL; 0.04 mg mL^{-1}
	FII	$C_{16:1\omega7}$	117	0.9			
	FIII	C_{16}	117	1.3			
	FIV	$C_{18:1\omega7}$	117	0.5			
	FV	C_{18}	117	1.0			
Internal standards	**ISa**	9-octyl-8-heptadecene	350.3	-	-	-	-
	ISb	7-hexylnonadecane	99	-	-	-	-
	ISc	C_{19}	117	-	-	-	-

CHAPTER FOUR

4.0 RESULTS

4.1 Introduction

This chapter describes temporal concentrations of, and correlations between, **I** (IP_{25}) and other lipids in sea ice collected from Resolute Bay over the spring period between April 27th and June 8th 2011. Vertical lipid concentration profiles from sea ice cores collected from the same sampling site and time period are also described. This chapter also describes the investigation into the effect snow cover has on overall accumulation of the lipids present in the sea ice. Findings from this study in Resolute Bay are then compared to previous temporal and vertical findings from sea ice cores collected in the Amundsen Gulf in 2008.

4.2 Temporal distributions of lipids in sea ice over the spring period

Concentrations of **I** and other lipids were established by GC/MS analysis of the **A** section (lower 0-3 cm) of sea ice cores collected in Resolute Bay from mid-April to early June 2011. Figure 4.1 shows the analytical outcomes of the GC/MS analysis procedure. The TIC chromatograms show retention times for the individual analytes whilst the SIM chromatograms show signals used for quantification.

These example chromatograms are from sea ice samples collected on the 27th May with low snow cover (8.5 cm). These resulted in the following concentrations of each analyte; **I** (IP_{25}) 2.4 ng mL^{-1}, **II** ($C_{25:2(5/6)}$ and $C_{25:2(6/17)}$ 7.6 ng mL^{-1}, **III** ($C_{25:3(7/20)E}$) 0.33 ng mL^{-1}, **FI** (C_{14}) 1.3 µg mL^{-1}, **FII** ($C_{16:1\omega7}$) 1.8 µg mL^{-1}, **FIII** (C_{16}) 1.9 µg mL^{-1}, **FIV** ($C_{18:1\omega7}$) 0.044 µg mL^{-1} and **FV** (C_{18}) 0.082 µg mL^{-1}.

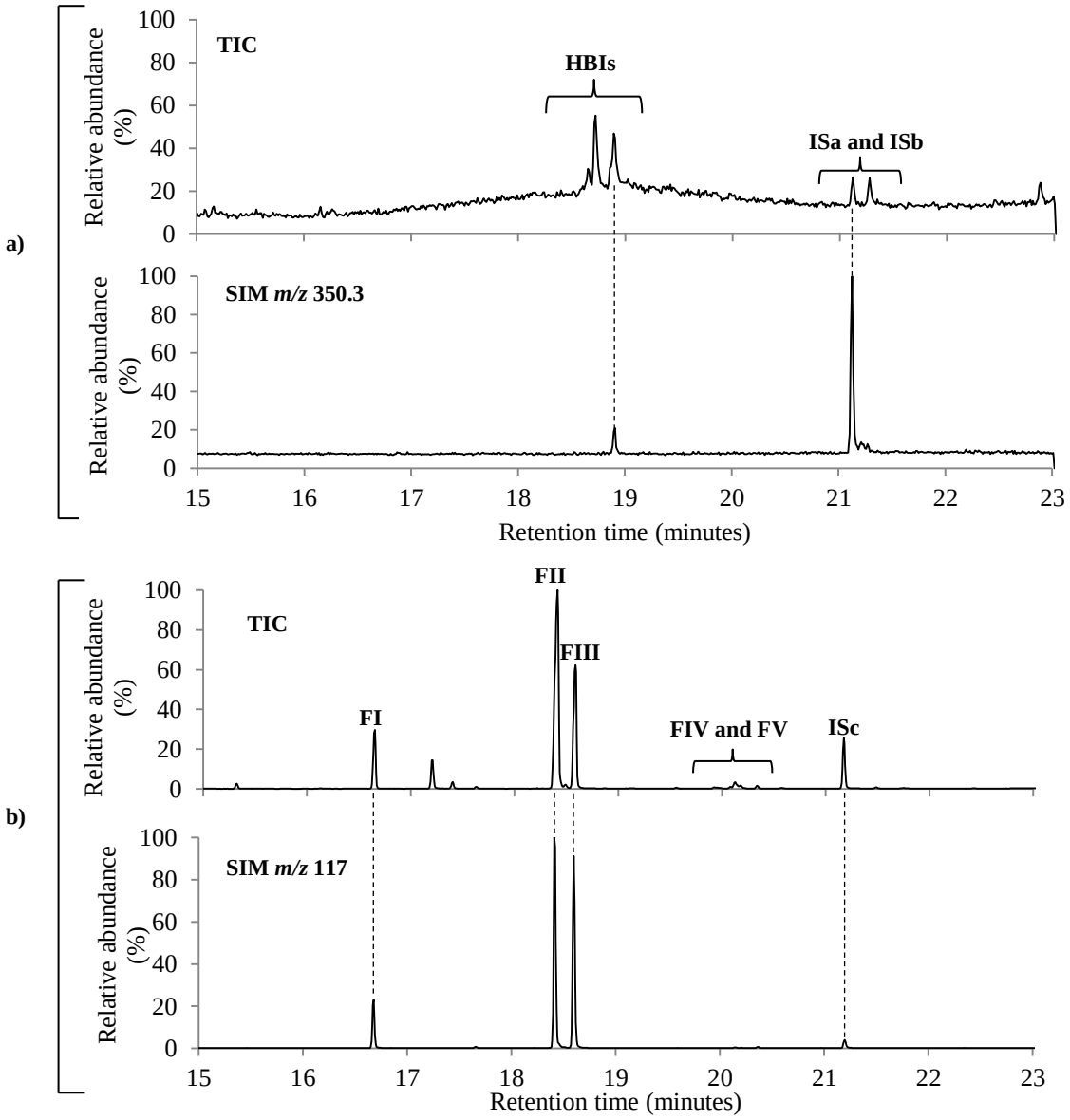


Figure 4.1. Partial TIC and SIM chromatograms of **a)** hexane soluble NSL and **b)** SL from filtered sea ice sample AI8 (27th May 2011) filter half 1 with low snow cover.

Analysis of the sea ice samples with medium snow cover (12.2 cm – 22 cm) allowed temporal concentrations of the analytes to be quantified. Samples with medium snow depth were chosen for the temporal analysis to be comparable to the vertical samples. Concentrations of HBIs (**I** (IP_{25}), **II** (combined dienes $C_{25:2(5/6)}$ and $C_{25:2(6/17)}$) and **III** (**(**$C_{25:3(7/20)\ E}$) were investigated in the **A** section of the sea ice samples over the temporal sampling period (27th April to the 8th June 2011). The mean concentration of **I** over the sampling period ranged from 0.23 ng mL^{-1} to 4.5 ng mL^{-1} and peaked on the 27th May (Fig. 4.2). The mean concentration of **II** ranged from 1.5 ng mL^{-1} to 14 ng mL^{-1}, which

peaked earlier on the 23rd May, whilst the mean concentration of **III** ranged from 0.28 ng mL^{-1} to 3.4 ng mL^{-1} and peaked on the 19th May. Determination of average relative contributions of individual HBI isomers to the total HBIs over the sampling period (Fig. 4.2), revealed **II** to be the most abundant, contributing ca. 70% of the total HBI concentration in the **A** section of the sea ice samples whereas **I** contributed ca. 20% and **III** ca. 10%.

Concentrations of fatty acids (**FI** (C_{14}), **FII** ($C_{16:1\omega7}$), **FIII** (C_{16}), **FIV** ($C_{18:1\omega7}$) and **FV** (C_{18})) were also investigated in the **A** section of the sea ice samples over the temporal sampling period. Figure 4.3 shows the mean concentrations of the fatty acids between the replicate filter sample halves. The mean concentration of **FI** ranged from 0.021 µg mL^{-1} to 1.9 µg mL^{-1}, which peaked on the 31st May. Mean concentrations of **FII** peaked on the 8th June and ranged from 0.0054 µg mL^{-1} to 3.1 µg mL^{-1}. **FIII** mean concentrations ranged from 0.062 µg mL^{-1} to 3.4 µg mL^{-1} but peaked slightly later on the 8th June, whereas mean concentrations of **FIV** peaked on the 31st May and ranged from 0.00039 µg mL^{-1} to 0.047 µg mL^{-1}. Lastly, **FV** mean concentrations ranged from 0.0033 µg mL^{-1} to 0.098 µg mL^{-1} and peaked on the 4th June. Determination of average relative contributions of individual fatty acids to the total fatty acid abundance over the temporal sampling period (Fig. 4.4), revealed **FIII** to be the most abundant, contributing ca. 50% of the total fatty acid concentration in the **A** section of the sea ice samples. **FI** and **FII** contributed ca. 22% and 26% respectively, whilst **FIV** and **FV** only contributed ca. 2% collectively. **FII** and **FIII** appear to have opposite trends in their contributions to the total fatty acids as accumulation of **FII** increases and **FIII** decreases over the sampling period. As **FI**, **FII** and **FIII** are known to be from a diatom origin, it can be stated that ca. 98% of the total fatty acids analysed in the **A** section of the sea ice samples over the temporal sampling period, were produced by diatomaceous algae.

Concentrations of chlorophyll *a* were also investigated in the **A** section of the sea ice samples over the temporal sampling period (Fig. 4.5). Two replicate measurements and quantification of chlorophyll *a* were carried out by other scientists at the University of Manitoba. Mean chlorophyll a concentrations ranged from 3.9 mg m^{-2} to 34 mg m^{-2} and peaked on the 10th May.

The reproducibility of this temporal data, for all measured analytes, is variable (Table 4.1.). The mass of analyte measured on each half of the GF/F was between 0 and 1.6 times greater than the corresponding half. Vacuum filtration onto a GF/F does not guarantee a homogeneously spread filtrate. However when portioning the filters, every effort was made to visually equally divide the amounts of filtrate on each half. The variability of the reproducibility may be due to inaccurate portioning of the filters. However, variability of the concentrations may also be due to the heterogeneous nature of sea ice in terms of both diatom abundances and varying species. Ice cores were pooled to try and to take into account for some of the natural variation however this could still be reflected in the variable replicate concentrations.

Table 4.1. Calculated mass of HBIs and fatty acids on each half of the filter for medium snow samples over the temporal sampling period.

Analyte	**I**		**II**		**III**		**FI**		**FII**		**FIII**		**FIV**		**FV**	
Mass of analyte in each half of the filter (µg)	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
27/04/11	0.035	0.045	0.27	0.26	0.01	0.01	6.8	7.8	5.6	5.8	22	24	0.17	0.24	0.82	0.88
01/05/11	0.047	0.045	0.28	0.27	0.024	0.021	9.4	9.2	8.2	7.8	23	22	0.16	0.16	0.43	0.43
05/05/11	0.033	0.033	0.13	0.15	0.007	0.01	4.7	4.5	2.5	3.7	12	12	0.06	0.094	0.26	0.28
10/05/11	0.050	0.053	0.31	0.29	0.004	0.01	6.3	7.2	8.0	8.3	18	20	0.15	0.16	0.98	1.09
15/05/11	0.044	0.06	0.18	0.20	0	0	8.9	12	24	31	40	52	0.44	0.59	1.7	2.2

19/05/11	0.023	0.039	0.15	0.21	0.0097	0.0071	14	20	49	58	62	71	0.46	0.64	0.80	1.05
23/05/11	0.103	0.19	0.63	0.95	0	0	61	63	99	100	104	109	1.2	1.2	2.4	2.4
27/05/11	0.095	0.13	0.303	0.36	0.013	0.019	51	54	70	78	78	83	1.8	2.7	3.3	4.4
31/05/11	0.16	0.18	0.62	0.71	0.013	0.021	62	65	98	97	97	100	2.2	2.0	2.9	3.04
04/06/11	0.15	0.17	1.15	1.44	0.013	0.016	73	69	110	103	113	108	2.4	2.4	3.5	3.3
08/06/11	0.071	0.086	0.68	0.78	0	0	59	48	97	72	115	84	1.4	1.4	2.0	2.0

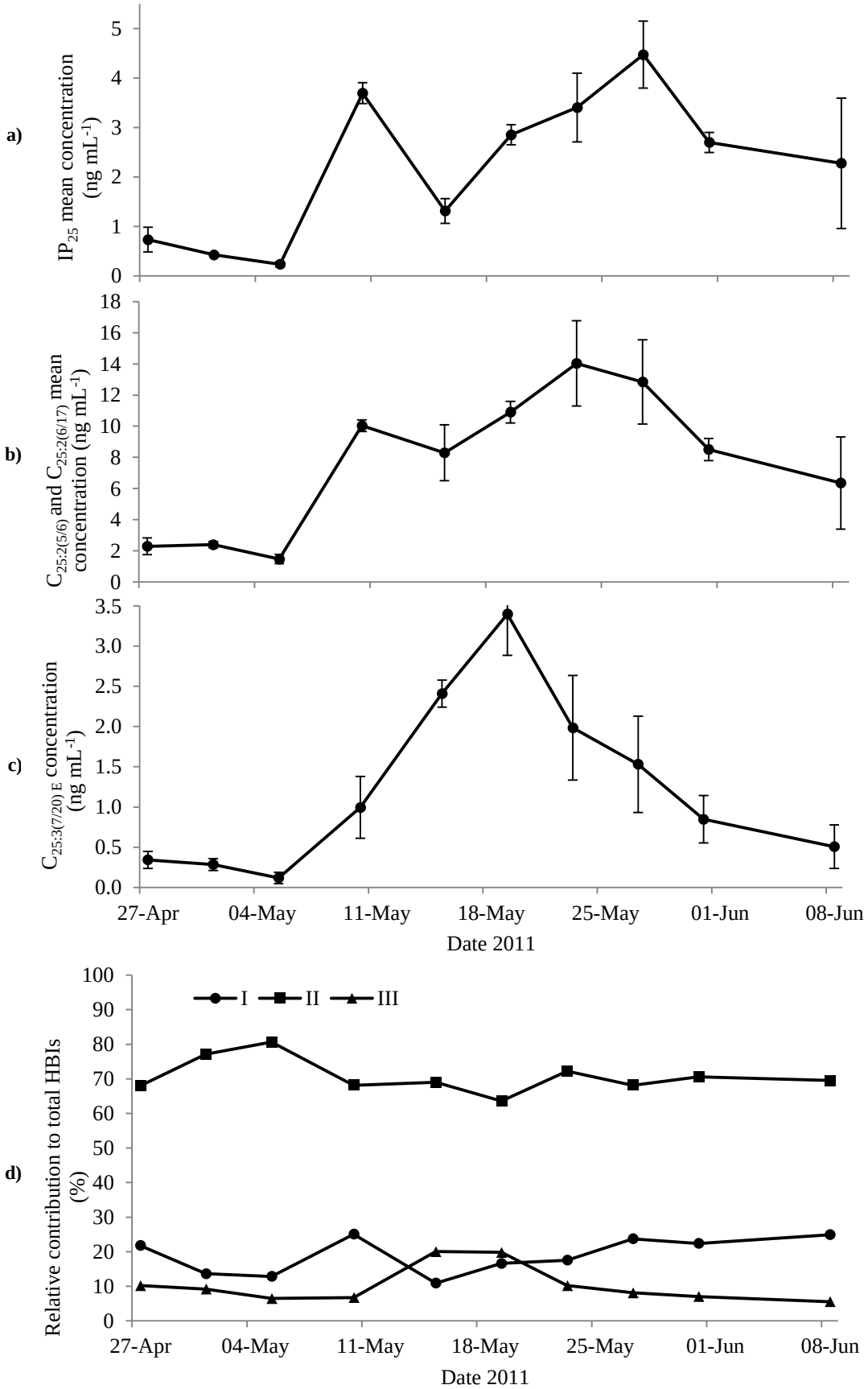


Figure 4.2. Temporal mean concentrations (±1 s.d. n = 2) of HBIs **a) I**, **b) II**, **c) III** and **d)** relative contributions of HBI isomers to the total HBIs, observed in the **A** section of sea ice with medium snow cover during the Arctic ICE project.

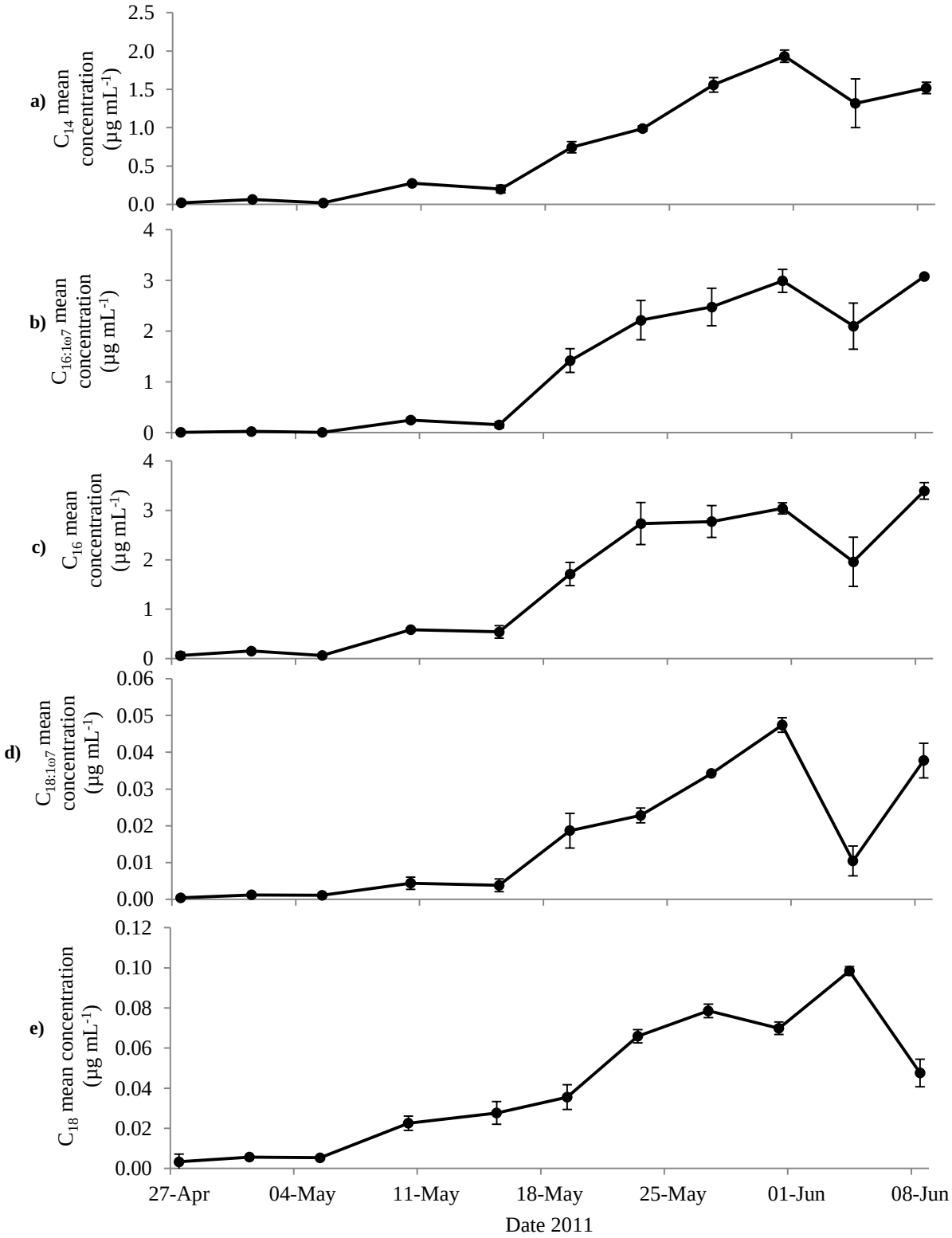


Figure 4.3. Temporal mean concentrations (±1 s.d. n = 2) of fatty acids **a) FI**, **b) FII**, **c) FIII** and **d) FIV** and **e) FV** observed in the **A** section of sea ice with medium snow cover during the Arctic ICE project.

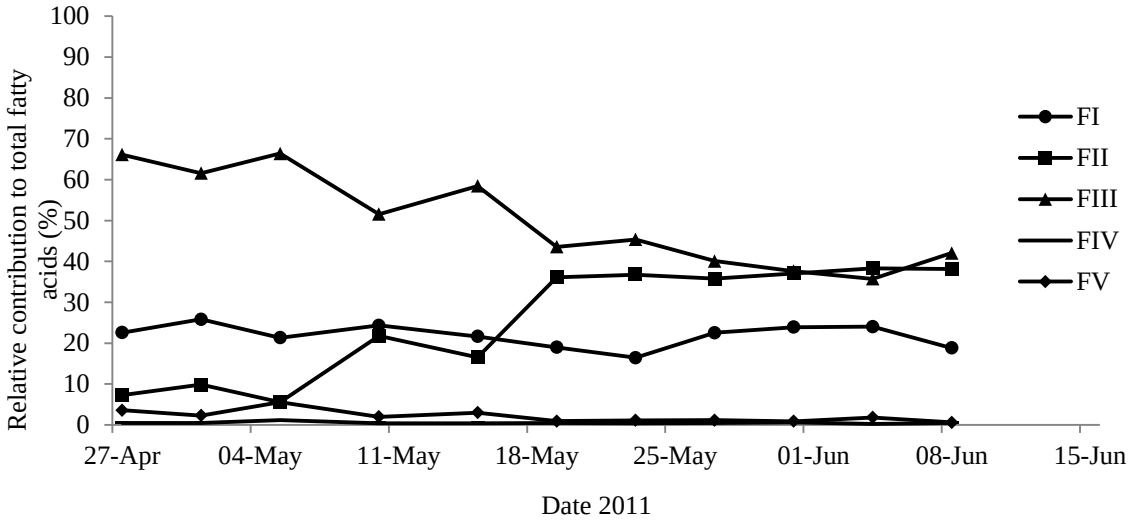


Figure 4.4. Relative contributions of individual fatty acids to the total fatty acids observed in the **A** section of sea ice with medium snow cover during the Arctic ICE project.

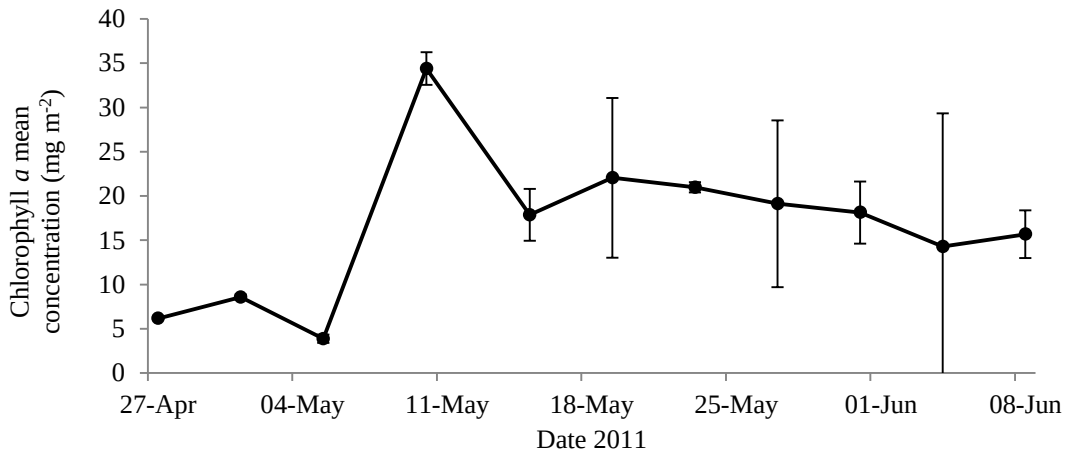


Figure 4.5. Temporal mean concentrations of chlorophyll *a* (±1 s.d. n = 2) observed in the **A** section of sea ice with medium snow cover during the Arctic ICE project.

4.3 Vertical distributions of lipids in sea ice over the spring period

Concentrations of HBIs including **I**, fatty acids and chlorophyll *a* were also investigated throughout sea ice cores on five dates over the sampling period of the Arctic ICE project in 2011. These cores were collected on the following dates, with the same or similar amount of snow cover (represented as medium snow cover) as the previous temporal distributions; 1st May, 10th May, 19th May, 27th May and 4th June. Figure 4.6

shows the distribution between these dates over the sampling period. As previously described in Chapter Two, the sea ice cores were sectioned into five; section **A** (0-3 cm), **B** (3-10 cm), **C** (approx. 10-60 cm), **D** (approx. 60-110 cm) and **E** (approx. 110 to the top of the core). Exact lengths of sections for each core are provided in Table 2.1.

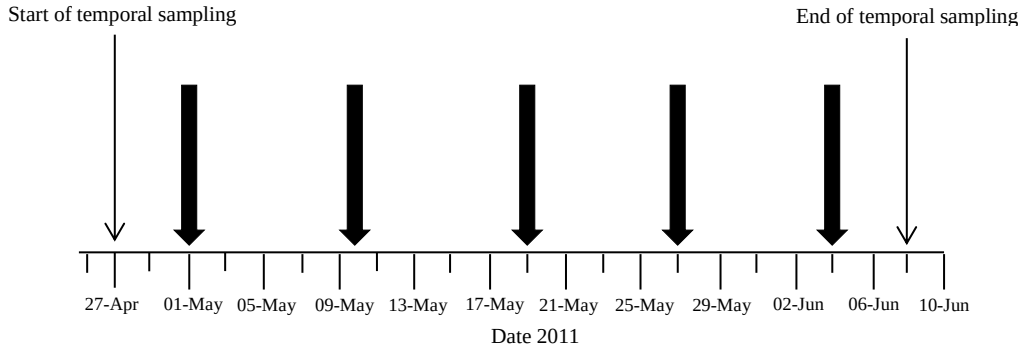
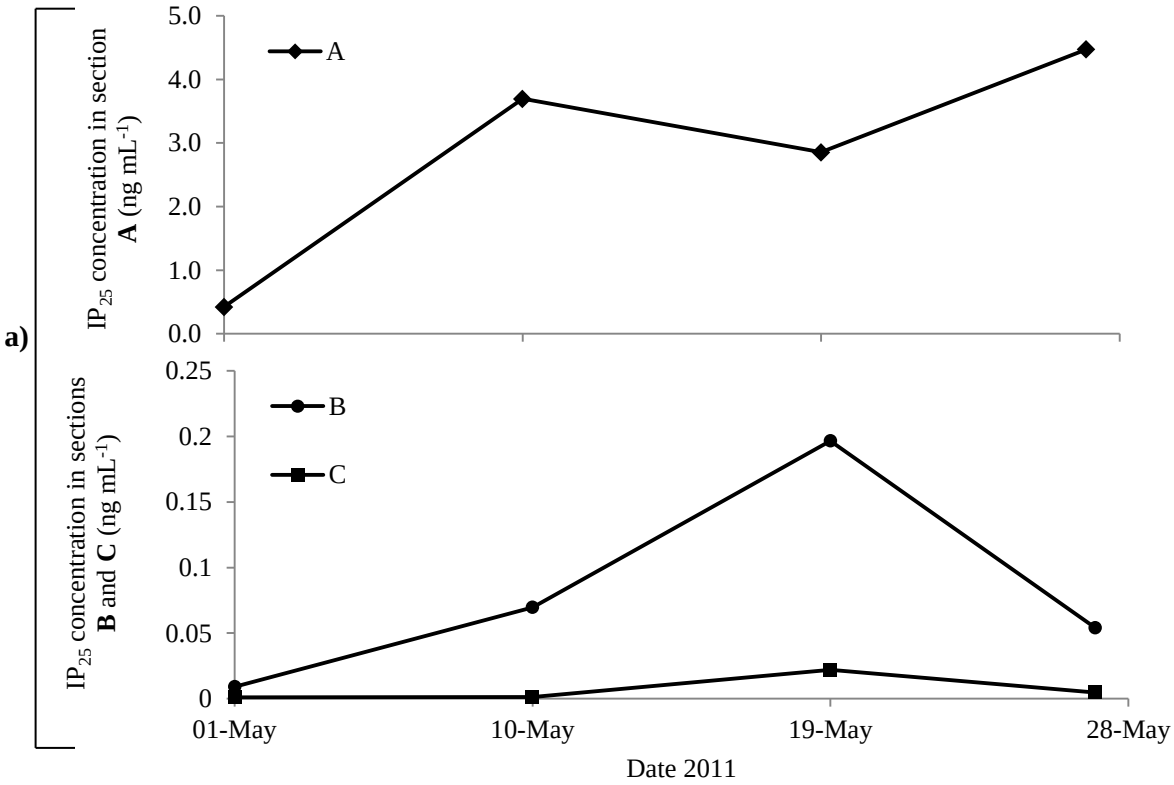


Figure 4.6. Distribution of full sea ice cores with medium snow cover collected for vertical lipid distribution analysis over the sampling period on the Arctic ICE project. Dates at which the full sea ice cores were collected for the vertical distribution analysis are represented by thick arrows. Temporal sampling begins on the 27th April and ends on the 8th June.

GC/MS analysis of sectioned sea ice cores enabled observations of vertical lipid concentrations over the spring sampling period to be made. All concentrations in sections above 3 cm from the ice/water interface (**B**, **C**, **D** and **E**) were calculated from analysing the filtered samples as a single sample and not divided into two as were the filters for the temporal study, so mean concentrations could not be calculated in the same way. Data of HBI concentrations are represented for only four out of the five cores sampled due to a procedural error. Concentrations of **I** were consistently highest in the **A** section of the five sea ice cores, these reached 4.5 ng mL^{-1} (27th May). Concentrations of **I** in the **A** section always contributed at least 86% of the total **I** in the core. The concentration of **I** then decreased rapidly above 3 cm from the ice/water interface. Highest **I** concentrations in the **B** section reached 0.20 ng mL^{-1} (19th May), which contributed at most 13% of the total **I** in the core. Concentrations of **I** in the **C** section only reached 0.02 ng mL^{-1} (19th May) and less than 0.003 ng mL^{-1} in both sections **D**

and **E** (both reached on the 4th June). Sections **C**, **D** and **E** consistently contributed as a whole at most 1% of the total **I** in the core.

Similarly, concentrations of **II** were consistently highest in the **A** section, these reached 13 ng mL^{-1} (27th May) and always contributed at least 94% of the total **II** in the core. Concentrations of **II** also decreased rapidly above 3 cm from the ice/water interface. Highest concentrations of **II** in section **B** reached 0.63 ng mL^{-1} (19th May) and contributed at most 5.4% of the total **II** in the core. Concentrations of **II** in section **C** only reached 0.1 ng mL^{-1} and less than 0.005 ng mL^{-1} in both sections **D** and **E** (all reached on the 19th May). Sections **C**, **D** and **E** did not consistently contribute to the total **II** in the core as concentrations of **II** in some of the sections were either too low to be detected or **II** was not present. **III** was only detected in sections **A** and **B** of the sea ice cores and not in any other sections above 10 cm from the ice/water interface (**C**, **D** and **E**). Concentrations of **III** reached 3.4 ng mL^{-1} (19th May) in the **A** section which always contributed at least 68% of the total **III** in the core. Highest concentrations of **III** in section **B** reached 0.46 ng mL^{-1} (10th May) however varied in contribution to the total **III** in the core (0% - 32%). For all HBIs, the contribution from sections **A** and **B** (the lower 0-10 cm) to the total of each was at least 99% for all cores analysed. Figures 4.7 to 4.9 show vertical concentrations of **I**, **II**, **III** and relative contributions of each section, to the total in the core.



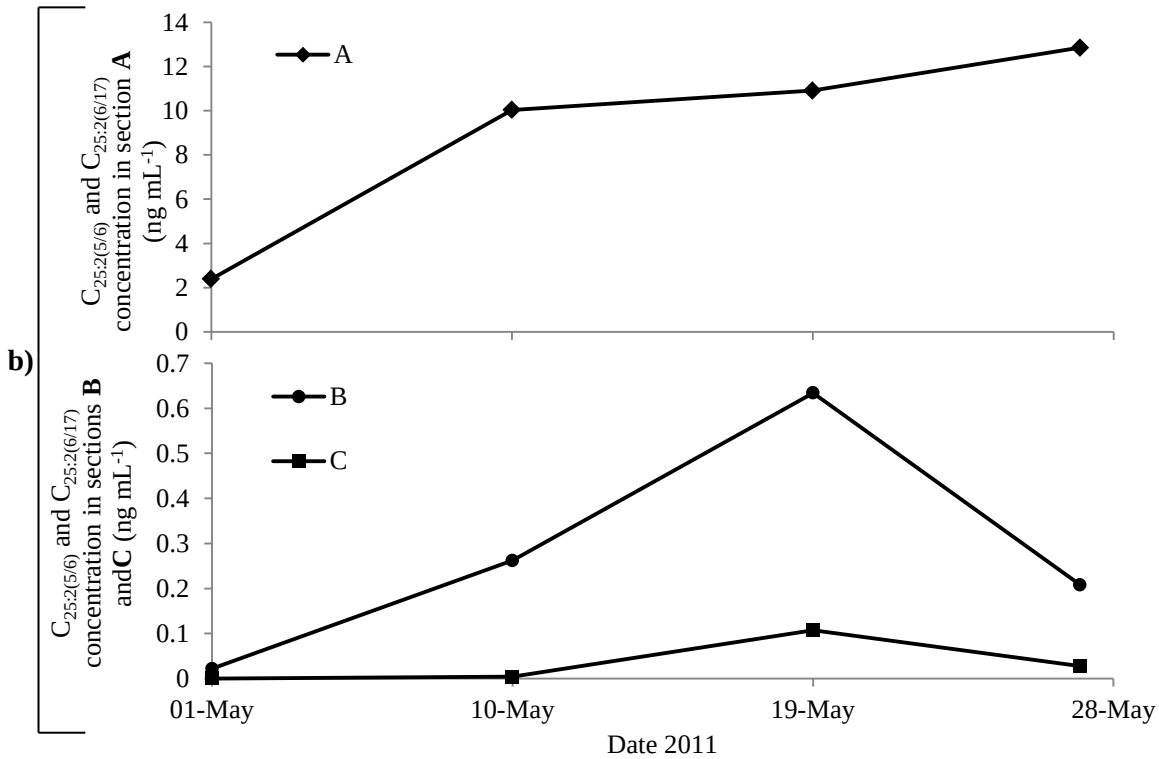


Figure 4.7. Vertical concentrations of **a) I** and **b) II** in samples collected on the Arctic ICE project with medium snow cover. Concentrations in sections **D** and **E** are not represented as they contributed less than 1% of the total.

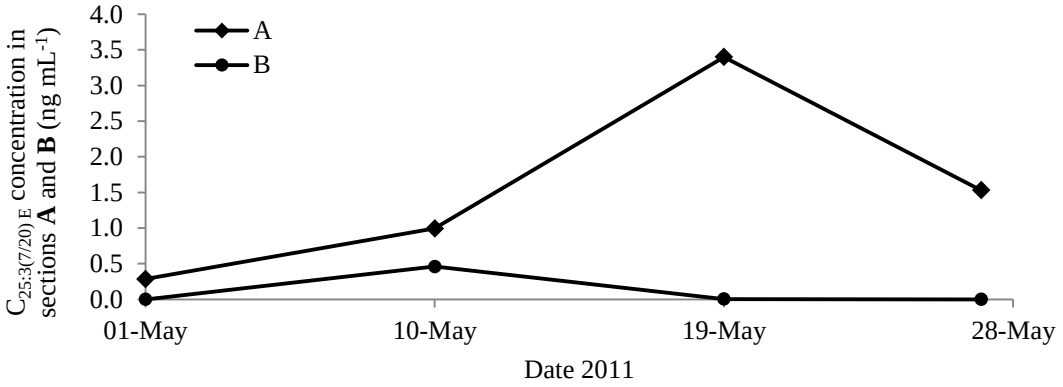


Figure 4.8. Vertical concentrations of **III** in sections A and B of the sea ice core samples collected on the Arctic ICE project with medium snow cover.

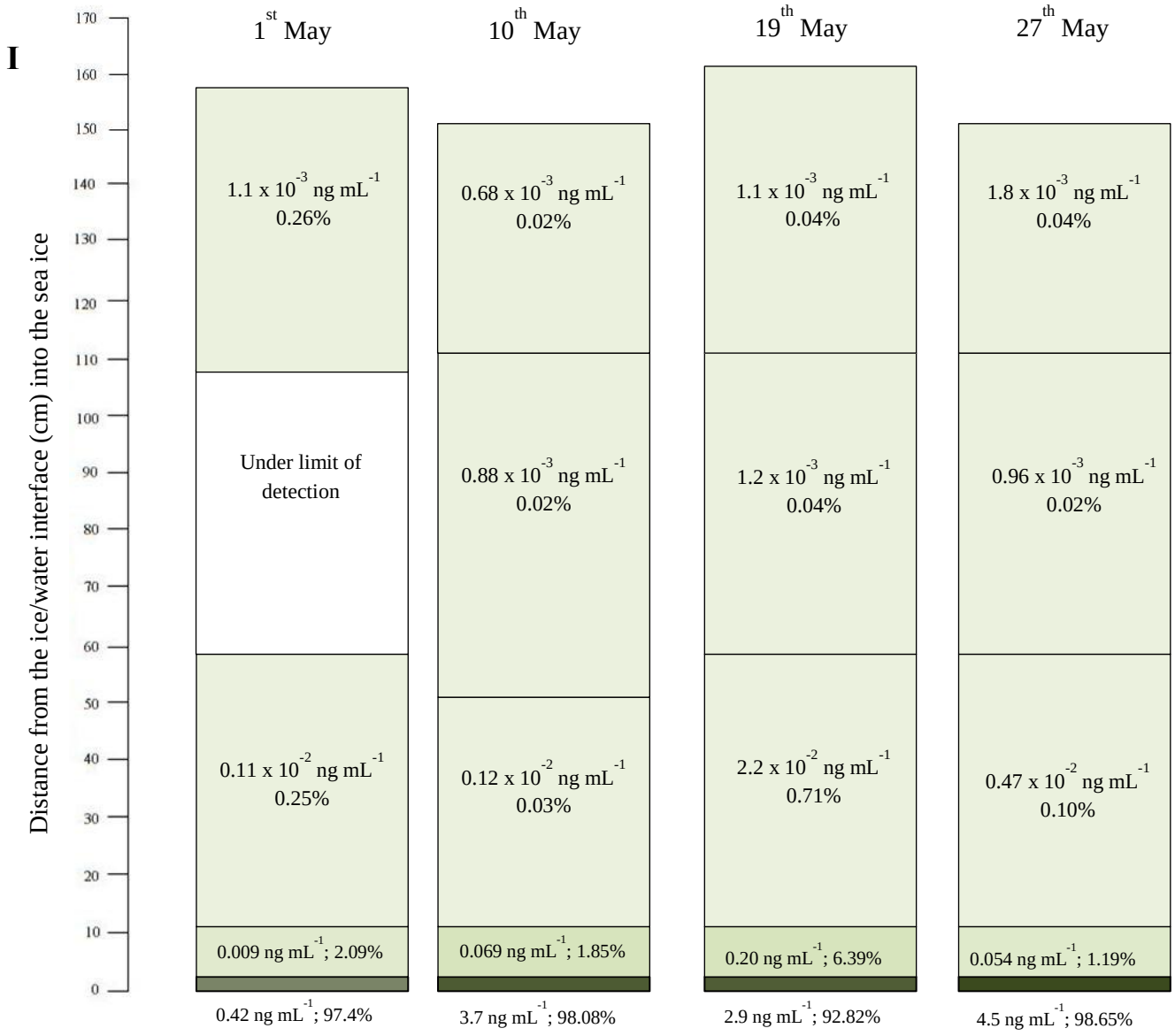


Figure 4.9. Schematic of vertical distributions of **I** and % of total **I**, throughout sea ice collected on the Arctic ICE project with medium snow cover.

Concentrations of fatty acids (**FI**, **FII**, **FIII**, **FIV** and **FV**) throughout sea ice cores were also investigated over the sampling period (Fig.4.10 to Fig. 4.13). Fatty acids were more evenly distributed through the cores, at the start of sampling, than the HBIs. The upper sections (**B**, **C**, **D** and **E**) that were slightly away from the ice/water interface, contributed higher proportions to the total fatty acids in the core. All fatty acids were present in all sections of the full sea ice cores with the exception of section **C** of the sample taken on the 1st May. Peak concentrations of **FI** in section **A** reached 1.6 µg mL^{-1} (27th May) and ranged in contribution of the total **FI** in the core from 60% to 93% (Fig. 4.10). Concentrations of **FI** in section **B** decreased rapidly and contributed between 4% and 29%, and peak concentrations reached 0.18 µg mL^{-1} (19th May). Section **C** contributed between 0% and 9.4% and peak concentrations reached 0.097 µg mL^{-1} (19th May). Highest concentrations of **FI** in sections **D** and **E** decreased again to 0.012 µg mL^{-1} (1st May) and 0.011 µg mL^{-1} (1st May) respectively. Both sections, **D** and **E**, always contributed between 0.2% and 13% to the total **FI** in the core.

Highest concentrations of **FII** in section **A** reached 2.5 µg mL^{-1} (27th May) and contributed between 52% and 90% of the total (Fig. 4.10). Concentrations in section **B** reached 0.53 µg mL^{-1} (19th May) and contributed between 7% and 38% of the total **FII** in the core. Section **C** contributed between 0% and 9.3% of the total **FII** and peak concentrations reached 0.14 µg mL^{-1} (19th May). Highest concentrations of **FII** in both sections **D** and **E** were less than 0.01 µg mL^{-1} (4th June and 1st May respectively). These sections contributed, as a whole, at most 25% of the total **FII** in the core.

Concentrations of **FIII** in section **A** reached 2.8 µg mL^{-1} (27th May) and always contributed between 36% and 71% of the total (Fig. 4.11). The **FIII** concentration in section **B** reached 1.3 µg mL^{-1} (4th June) and contributed between 16% and 38% of the total **FIII** in the core. Section **C** contributed between 0% and 30% of the total **FIII** as peak concentrations reached 1.2 µg mL^{-1} (19th May). Concentrations in sections **D** and

E reached 0.10 µg mL^{-1} (27th May) and 0.18 µg mL^{-1} (19th May) respectively and contributed at most 24% and 22% of the total **FIII** in the core.

Concentrations of **FIV** (Fig. 4.11) and **FV** (Fig. 4.12) throughout the sea ice samples were considerably less than the other fatty acids. Concentrations of **FIV** in section **A** reached 3.4 x 10^{-2} µg mL^{-1} (27th May) and contributed between 9.7% and 46% of the total **FIV** in the core. Concentrations of **FIV** in sections **B** and **C** reached 1.3 x 10^{-2} µg mL^{-1} (10th May) and 3.8 x 10^{-2} µg mL^{-1} (19th May) respectively and contributed at most 30% and 53% to the total **FIV**. Peak **FIV** concentrations in sections **D** and **E** reached 0.43 x 10^{-2} µg $mL^{-1}$and 0.34 x 10^{-2} µg mL^{-1} (both peak dates on the 1st May) respectively. Section **D** and **E** contributed at most 41% and 32% of the total **FIV** in the core. Concentrations of **FV** in section **A** reached 9.8 x 10^{-2} µg mL^{-1} (4th June) and contributed between 6.6% and 59% of the total **FV** in the core. Concentrations of **FV** in sections **B** and **C** reached 6.2 x 10^{-2} µg mL^{-1} (27th May) and 0.21 µg mL^{-1} (19th May) respectively and contributed at most 24% and 52% to the total **FV** in the core. Peak **FV** concentrations in sections **D** and **E** reached 9.1 x 10^{-2} µg mL^{-1} and 8.9 x 10^{-2} µg mL^{-1} (both peak dates on the 10th May). These sections contributed at most 36% and 33% to the total **FV** in the core. Figure 4.12 shows relative contributions of the total diatom fatty acids from each section of the sea ice cores over the sampling period. Figure 4.13 demonstrates the increase in contribution from section **A** over the sampling period.

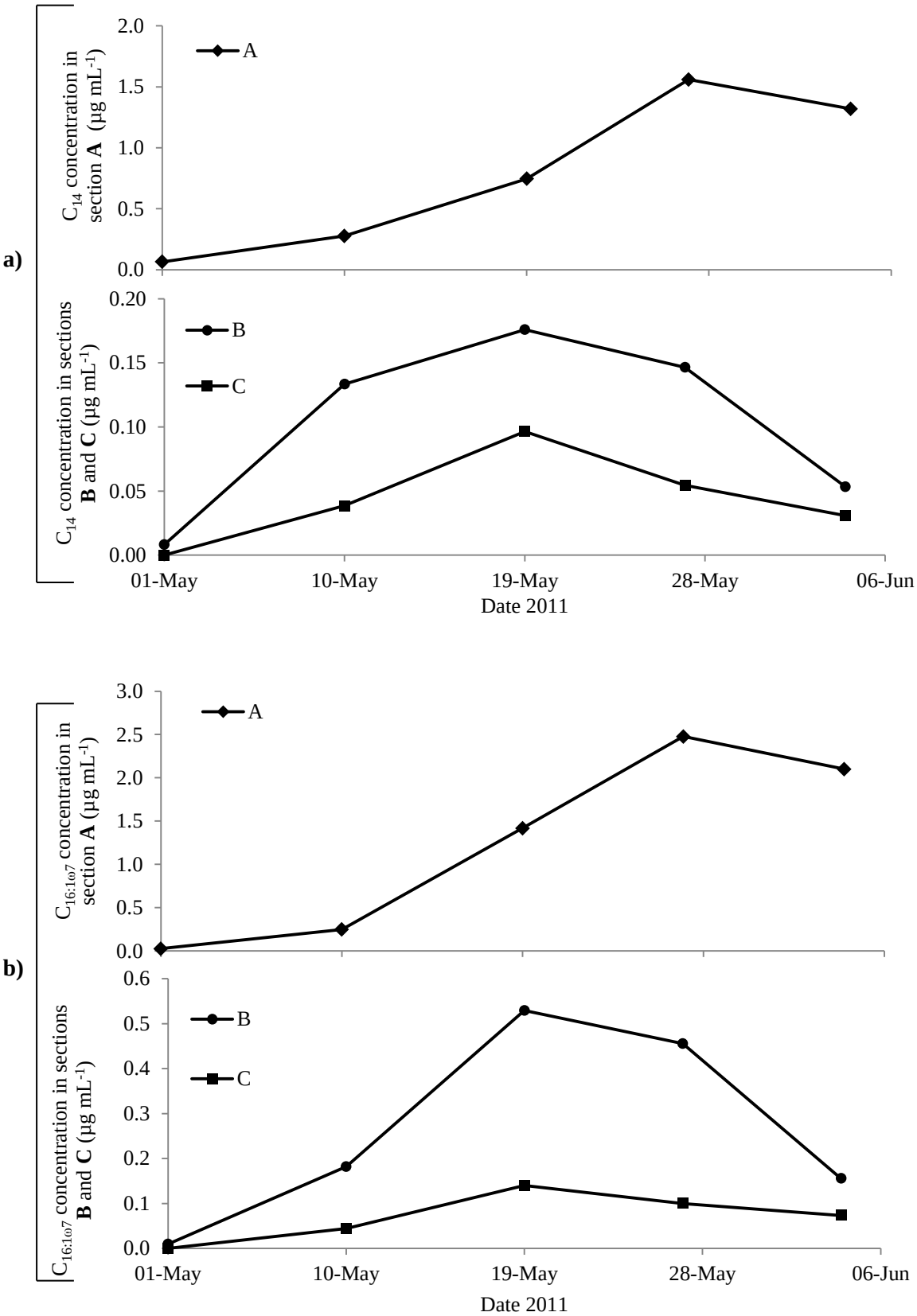
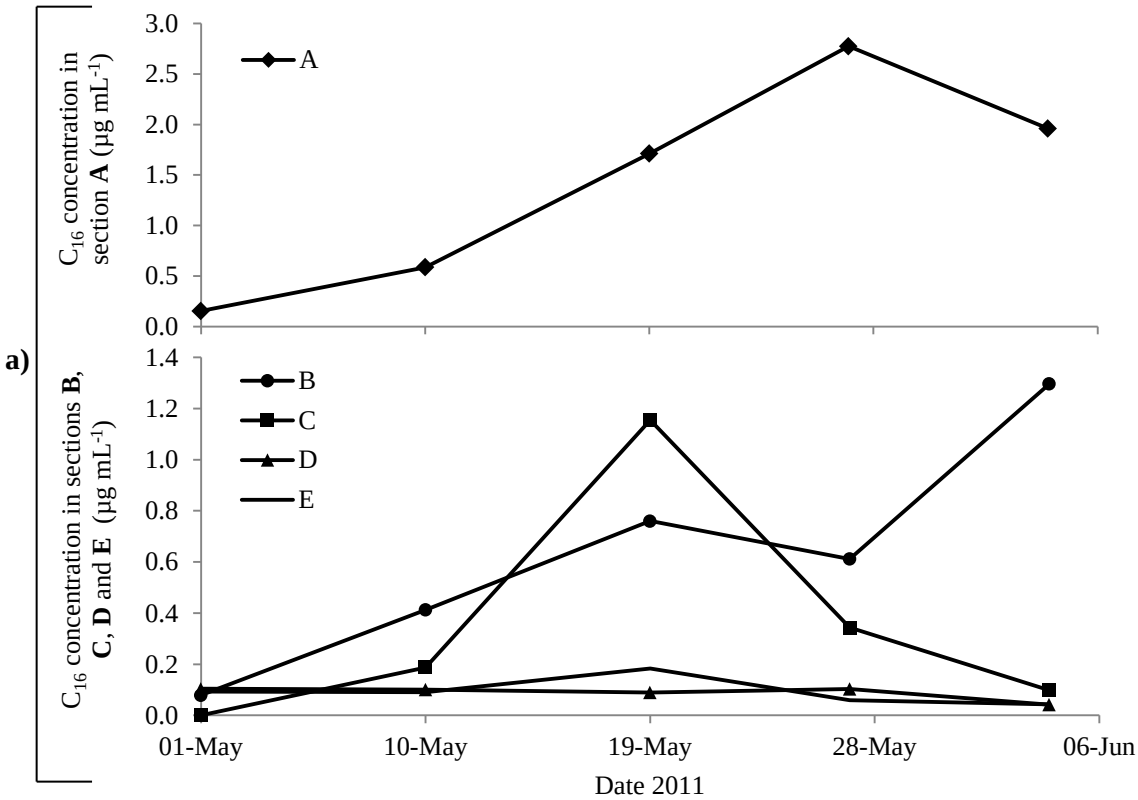


Figure 4.10. Vertical concentrations of **a) FI** and **b) FII** in sections A, B and C of sea ice samples collected on the Arctic ICE project with medium snow cover. Concentrations in sections **D** and **E** are not represented as they contributed less than 2% to the total (excluding on the 1st May, contributing 13% and 12% respectively in both **FI** and **FII**).



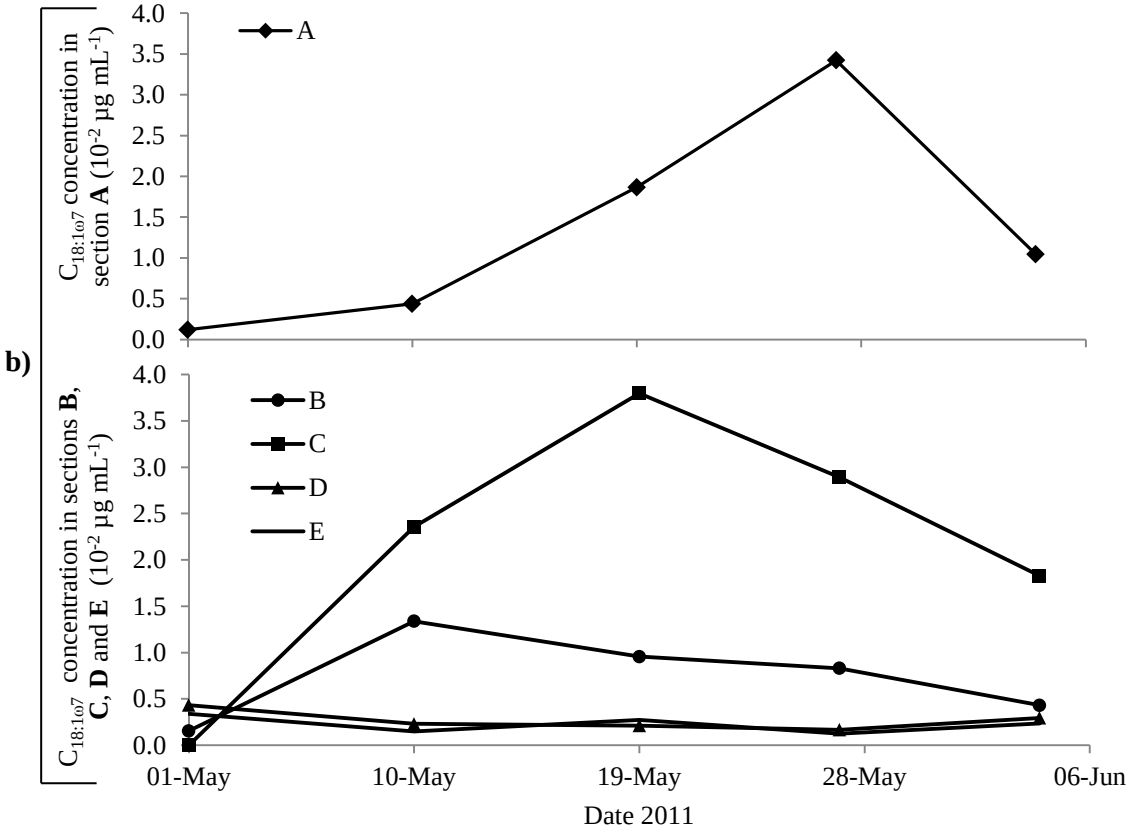
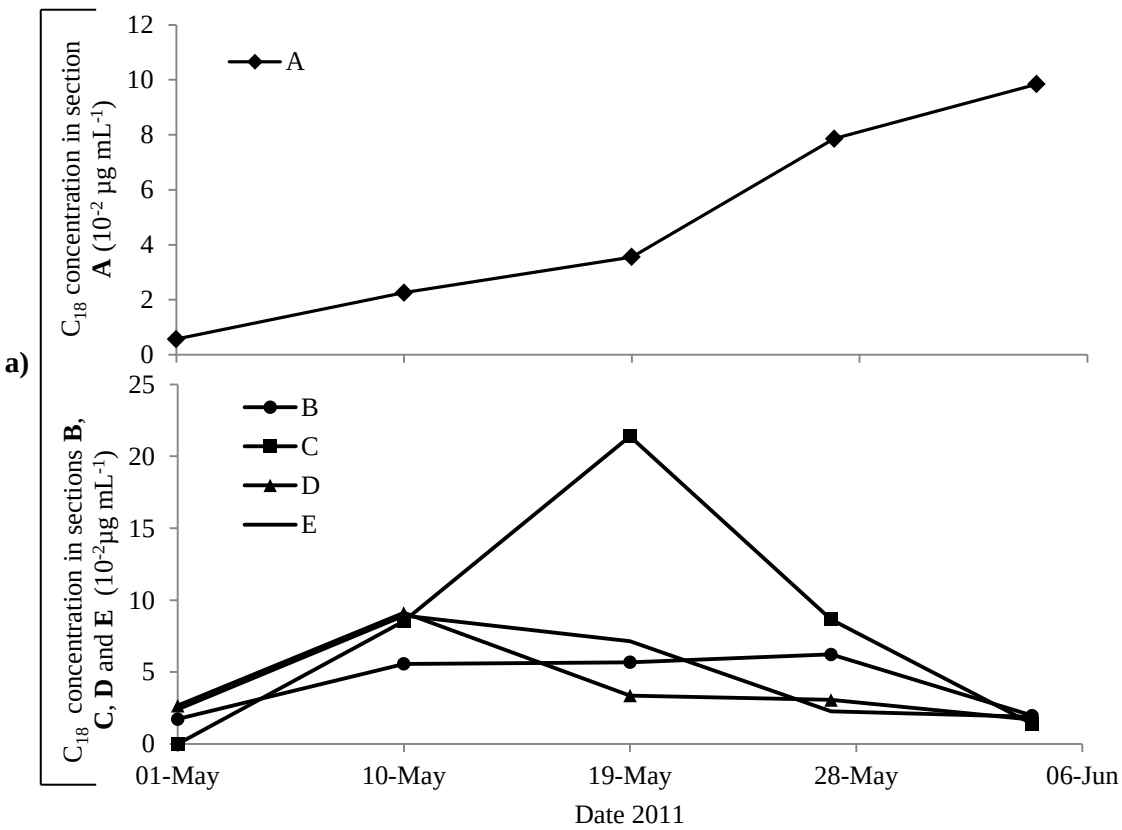


Figure 4.11. Vertical concentrations of **a) FIII** and **b) FIV** in sea ice samples collected on the Arctic ICE project with medium snow cover.



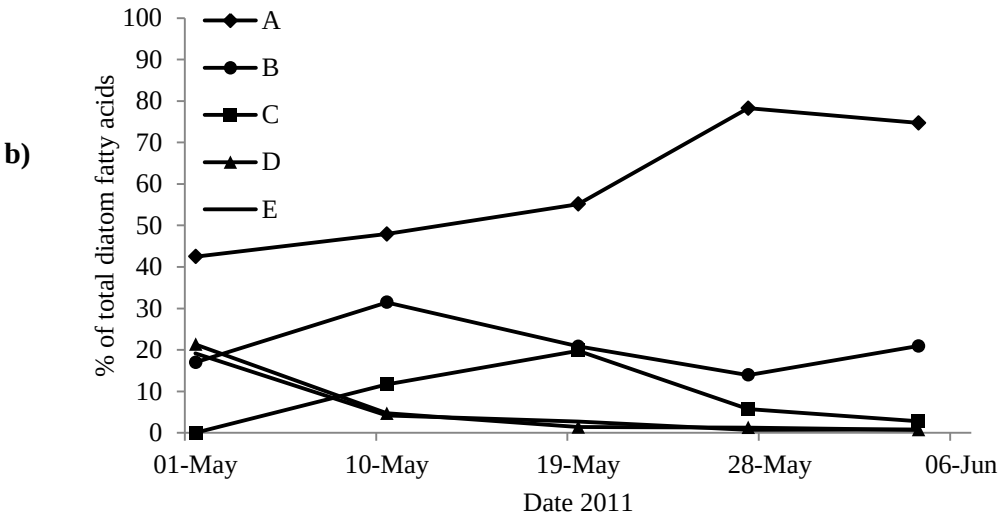


Figure 4.12. a) Vertical concentrations of **FV** and **b)** relative contributions from all sections of the diatom fatty acids (**FI**, **FII** and **FIII**) to the total in sea ice core samples collected on the Arctic ICE project with medium snow cover.

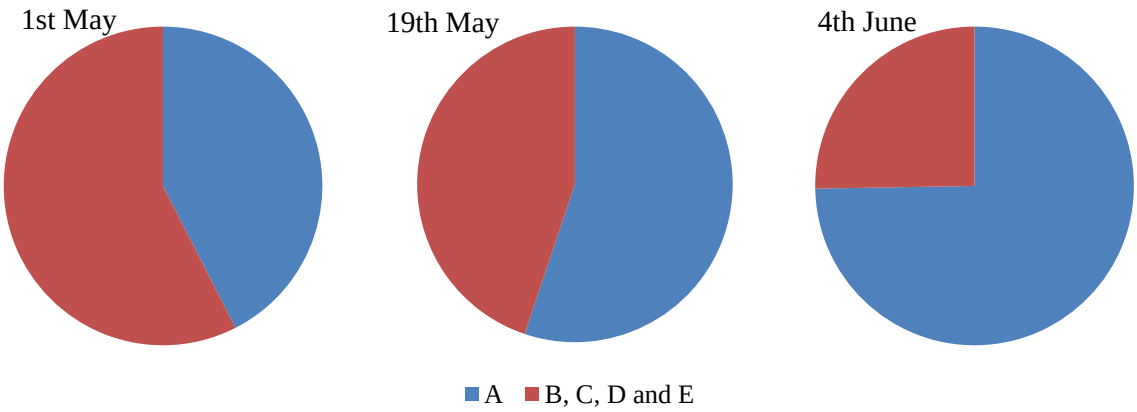


Figure 4.13. Relative contributions from section **A** and others of the diatom fatty acids (**FI**, **FII** and **FIII**) to the total in sea ice core samples collected on the Arctic ICE project with medium snow cover.

Concentrations of chlorophyll *a* were also investigated throughout the sea ice cores over the sampling period (Fig. 4.14). Two replicate measurements and quantification of chlorophyll *a* were carried out by other scientists at the University of Manitoba. Chlorophyll *a* showed similar trends to the other analytes, the majority of accumulation occurred in the **A** section of the sea ice cores. Highest concentrations of chlorophyll *a* in the **A** section reached 34 mg m^{-2} (10th May) and always contributed at least 89% of the total chlorophyll *a* in the core. Concentrations in sections **B** and **C** reached 0.36 mg m^{-2} (10th May) and 0.88 mg m^{-2} (4th June) respectively and contributed at most 1.7% and 5.4% of the total chlorophyll *a* in the core. Maximum concentrations of chlorophyll *a* in sections **D** and **E** reached 0.42 mg m^{-2} and 0.34 mg m^{-2} (both peak dates on the 4th June) and contributed at most 2.6% and 2.1% of the total.

Total fatty acid concentrations were also consistently higher (ca. x 80-500) than those of total HBIs. Vertical distributions of HBIs, diatom fatty acids (**FI**, **FII** and **FIII**) and chlorophyll *a* are summarised in Table 4.2.

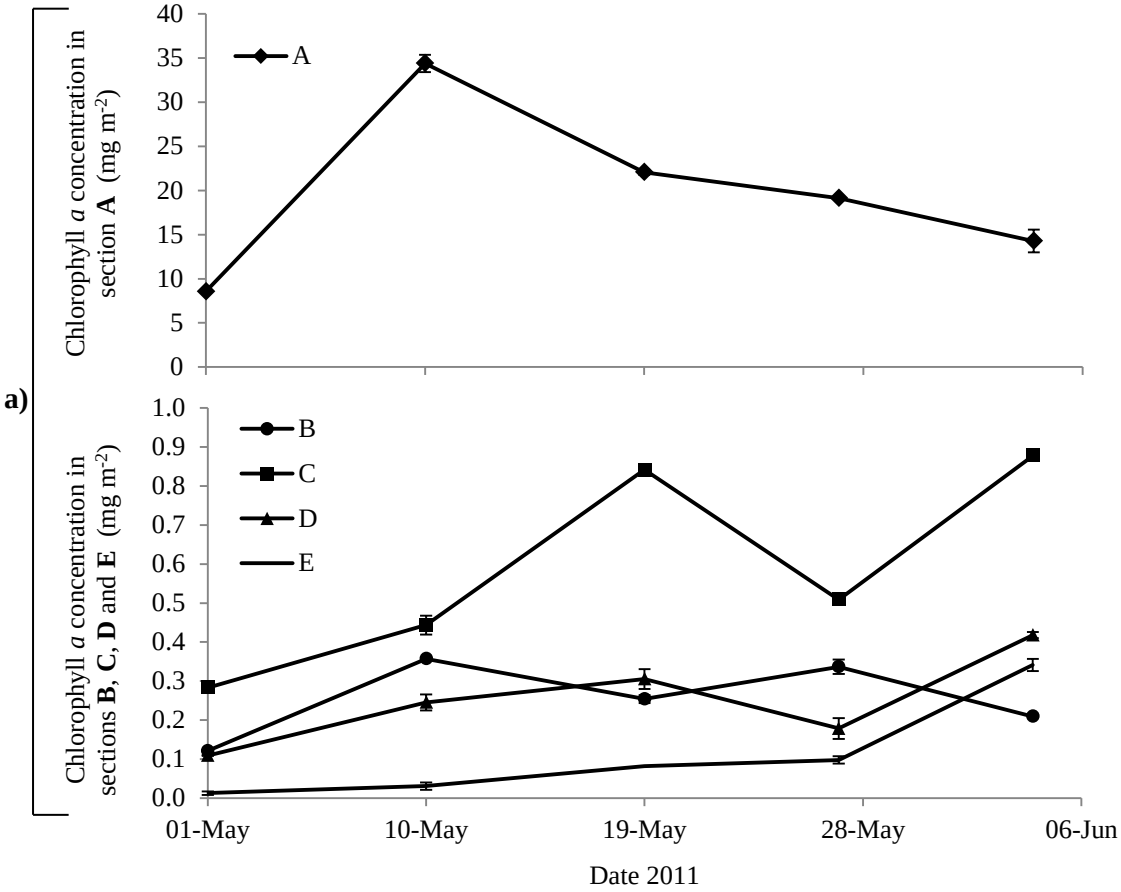


Figure 4.14. a) Mean vertical concentrations of chlorophyll *a* (±1 s.d. n =2) in each section of the sea ice core samples collected on the Arctic ICE project with medium snow cover.

Table 4.2. Vertical distributions of **a) I**, **b) II**, **c) III**, **d)** total HBIs, **e)** diatom fatty acids and **f)** chlorophyll *a* in sea ice cores collected on the Arctic ICE project with medium snow cover. * denotes analyte abundance under limits of detection or unavailability of data. Ice core sections are denoted by the following; **A** (0-3 cm), **B** (3-10 cm), **C** (approx. 10-60 cm), **D** (approx. 60-110 cm), **E** (approx. 110 to the top of the core).

a)	**I** concentration (ng mL^{-1}) and percentage of total in the ice core			
Ice core section	**1st May**	**10th May**	**19th May**	**27th May**
E	1.1 x 10^{-3} 0.26%	0.68 x 10^{-3} 0.02%	1.1 x 10^{-3} 0.04%	1.8 x 10^{-3} 0.04%
D	*	0.88 x 10^{-3} 0.02%	1.2 x 10^{-3} 0.04%	0.96 x 10^{-3} 0.02%
C	0.11 x 10^{-2} 0.25%	0.12 x 10^{-2} 0.03%	2.2 x 10^{-2} 0.71%	0.47 x 10^{-2} 0.10%
B	0.009 2.09%	0.069 1.85%	0.20 6.39%	0.054 1.19%
A	0.42 97.4%	3.7 98.08%	2.9 92.82%	4.5 98.65%

b)	**II** concentration (ng mL^{-1}) and percentage of total in the ice core			
Ice core section	**1st May**	**10th May**	**19th May**	**27th May**

E	*	*	0.45 x 10^{-2} 0.04%	*
D	*	0.30 x 10^{-2} 0.03%	0.33 x 10^{-2} 0.03%	*
C	*	0.40 x 10^{-2} 0.04%	0.107 0.92%	0.028 0.21%
B	2.2 x 10^{-2} 0.9%	0.26 2.54%	0.63 5.44%	0.21 1.59%
A	2.4 99.1%	10 97.39%	11 93.57%	13 98.20%

c)	**III** concentration (ng mL^{-1}) and percentage of total in the ice core			
Ice core section	**1st May**	**10th May**	**19th May**	**27th May**
E	*	*	*	*
D	*	*	*	*
C	*	*	*	*
B	*	0.46 31.69%	0.5 x 10^{-2} 0.15%	0.1 x 10^{-2} 0.08%
A	0.29 100%	1.0 68.31%	3.4 99.85%	1.5 99.92%

d)	Total HBI concentration (**I**, **II** and **III**) (ng mL^{-1}) and percentage of total in the ice core			
Ice core section	**1st May**	**10th May**	**19th May**	**27th May**
E	1.1 x 10^{-3} 0.03%	0.68 x 10^{-3} <0.01%	5.7 x 10^{-3} 0.04%	1.8 x 10^{-3} 0.01%
D	*	3.5 x 10^{-3} 0.02%	4.5 x 10^{-3} 0.02%	0.96 x 10^{-3} 0.01%
C	0.11 x 10^{-2} 0.04%	0.52 x 10^{-2} 0.03%	0.12 0.71%	3.2 x 10^{-2} 0.17%
B	0.031 0.98%	0.79 5.11%	0.84 4.61%	0.26 1.37%
A	3.09 98.95%	15 94.83%	17 94.62%	19 98.44%

e)	Total diatom fatty acid (**FI**, **FII** and **FIII**) concentration (µg mL^{-1}) and percentage of total in the ice core				
Ice core section	**1st May**	**10th May**	**19th May**	**27th May**	**4th June**
E	0.109 19.19%	0.098 4.23%	0.19 2.75%	0.065 0.75%	0.057 0.79%
D	0.12 21.34%	0.109 4.72%	0.10 1.42%	0.11 1.3%	0.054 0.75%
C	*	0.27 11.67%	1.39 19.81%	0.49 5.72%	0.202 2.81%
B	0.097 16.99%	0.73 31.46%	1.5 20.86%	1.2 13.95%	1.5 20.92%
A	0.24 42.48%	1.1 47.92%	3.9 55.16%	6.8 78.28%	5.4 74.73%

f)	Chlorophyll *a* concentration (mg m^{-2}) and percentage of total in the ice core				
Ice core section	**1st May**	**10th May**	**19th May**	**27th May**	**4th June**
E	0.013 0.14%	0.031 0.09%	0.082 0.35%	0.098 0.49%	0.34 2.12%
D	0.11 1.20%	0.25 0.69%	0.31 1.30%	0.18 0.88%	0.42 2.59%

C	0.28 3.12%	0.44 1.25%	0.84 3.57%	0.51 2.51%	0.88 5.44%
B	0.12 1.33%	0.36 1.01%	0.25 1.08%	0.34 1.66%	0.21 1.30%
A	8.6 94.21%	34 96.96%	22 93.70%	19 94.46%	14 88.55%

4.4 Effect of snow cover on lipid production

As diatoms are photosynthetic organisms, they rely on natural light for growth and production. The depth of snow cover on top of sea ice limits the amount of sunlight available to the organisms below and within the sea ice. Replicate sea ice cores were collected over the sampling period on the Arctic ICE project 2011 with low, medium and high snow cover (ranging from 2.2 cm to 39.6 cm). These allowed the effect (if any) of snow depth, and therefore light availability, on production of **I** and other lipids to be investigated. Temporal filtered sea ice samples with low and medium snow cover were portioned into two halves, giving two replicates to calculate means, whilst the majority of high snow samples were portioned into three (Fig. 3.1). Filters were portioned to create replicate samples to test the reproducibility of the experimental procedure. High snow samples on the 4th and 12th of June were only portioned into two.

Figure 4.15 shows mean concentrations of **I** in the **A** section of sea ice cores collected over the sampling period with low, medium and high snow cover. Mean concentrations of **I** in sea ice collected with low snow cover ranged from 0.25 ng mL^{-1} to 3.7 ng mL^{-1}, which peaked on the 31st May. Medium snow cover provided mean **I** concentrations ranging from 0.23 ng mL^{-1} to 4.5 ng mL^{-1} which peaked on the 27th May. **I** was absent or under the limits of detection in samples with high snow cover collected on the 27th April and 1st May, however reached 4.7 ng mL^{-1} on the 27th May. Mean concentrations of **II** in the **A** section of sea ice cores collected with low snow cover ranged from 0.42 ng mL^{-1} to 27 ng mL^{-1} and peaked on the 4th June (Fig. 4.16). Medium snow cover

provided mean **II** concentrations ranging from 1.0 ng mL^{-1} to 14 ng mL^{-1} which peaked on the 23rd May. **II** was absent or under the limits of detection in samples with high snow cover on the 27th April and 1st May, however reached 23 ng mL^{-1} (27th May). **III** was absent or under the limits of detection in samples collected with low snow cover on 15th and 23rd of May and the 8th of June. However mean concentrations of **III** with low snow cover did reach 0.48 ng mL^{-1} (1st May) (Fig. 4.17). Medium snow cover provided mean concentrations of **III** ranging from 0.12 ng mL^{-1} to 3.4 ng mL^{-1}, which peaked on the 19th May. **III** was absent or under the limits of detection in samples collected with high snow cover on the 27th April and the 1st May. However peak concentrations of **III** in sea ice with high snow cover reached 4.4 ng mL^{-1} on the 4th June.

The potential effect of snow cover on the production of diatom fatty acids (Fig. 4.18), and chlorophyll *a* (Fig. 4.19) were also investigated. Mean concentrations of combined fatty acids known to be from a diatom origin (**FI**, **FII** and **FIII**) reached 8.3 µg mL^{-1} in the **A** section of sea ice cores collected on the 8th of June with low snow cover. Medium snow cover provided a peak mean concentration of 8.0 µg mL^{-1} (31st May), whilst mean concentrations in the **A** section of sea ice with high snow cover reached 6.9 µg mL^{-1} (27th May). Mean concentrations of chlorophyll *a* collected with low snow cover reached 21 mg m^{-2} (15th May), 34 mg m^{-2} (10th May) with medium snow cover and 35 mg m^{-2} (4th June) with high snow cover.

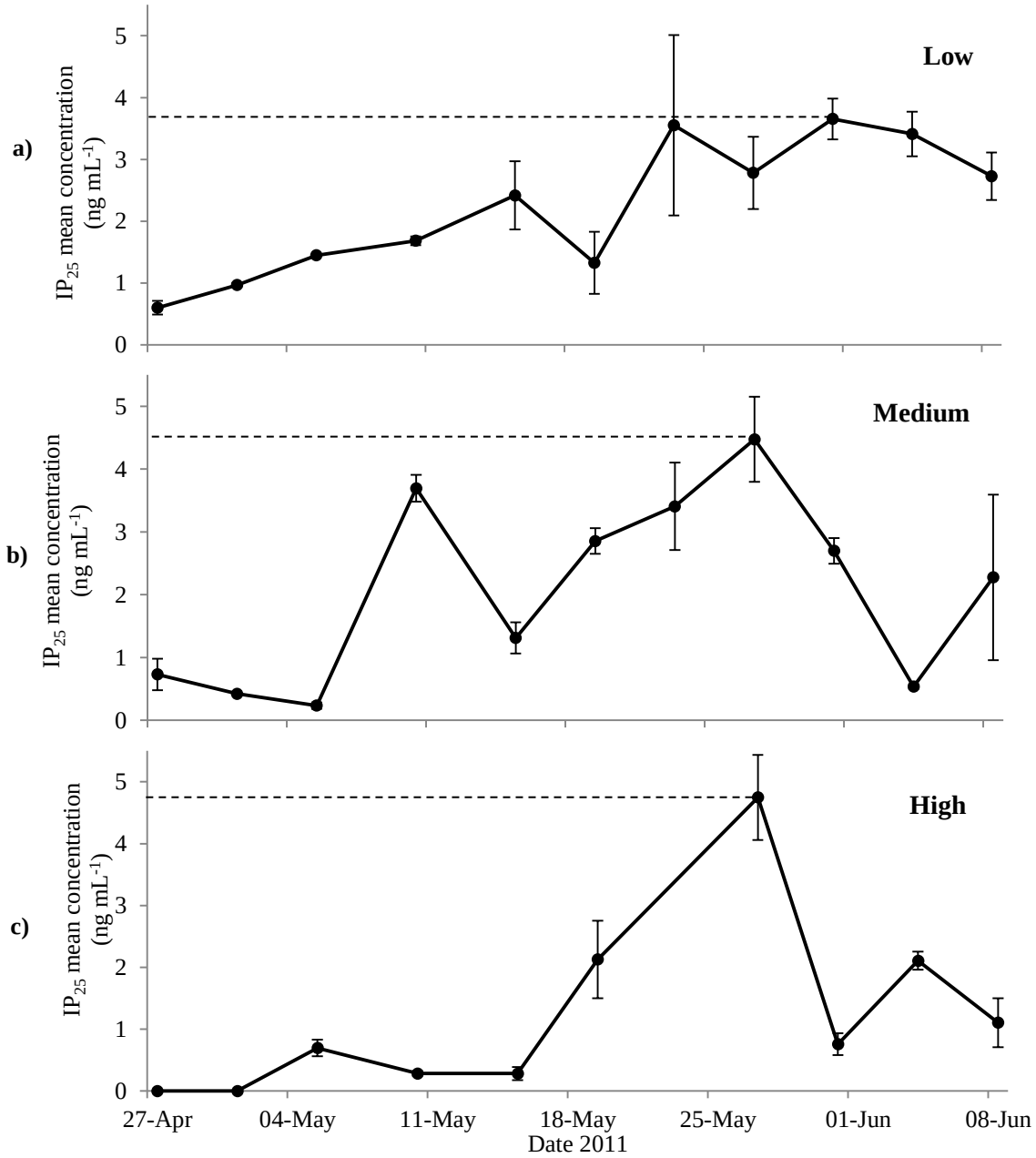


Figure 4.15. Temporal mean concentrations (±1 s.d. n = 2 or 3) of **I** observed in the **A** section of sea ice during the Arctic ICE project with **a)** low, **b)** medium and **c)** high snow cover. Absence of a data point on the 23rd May for high snow due to no sample being provided.

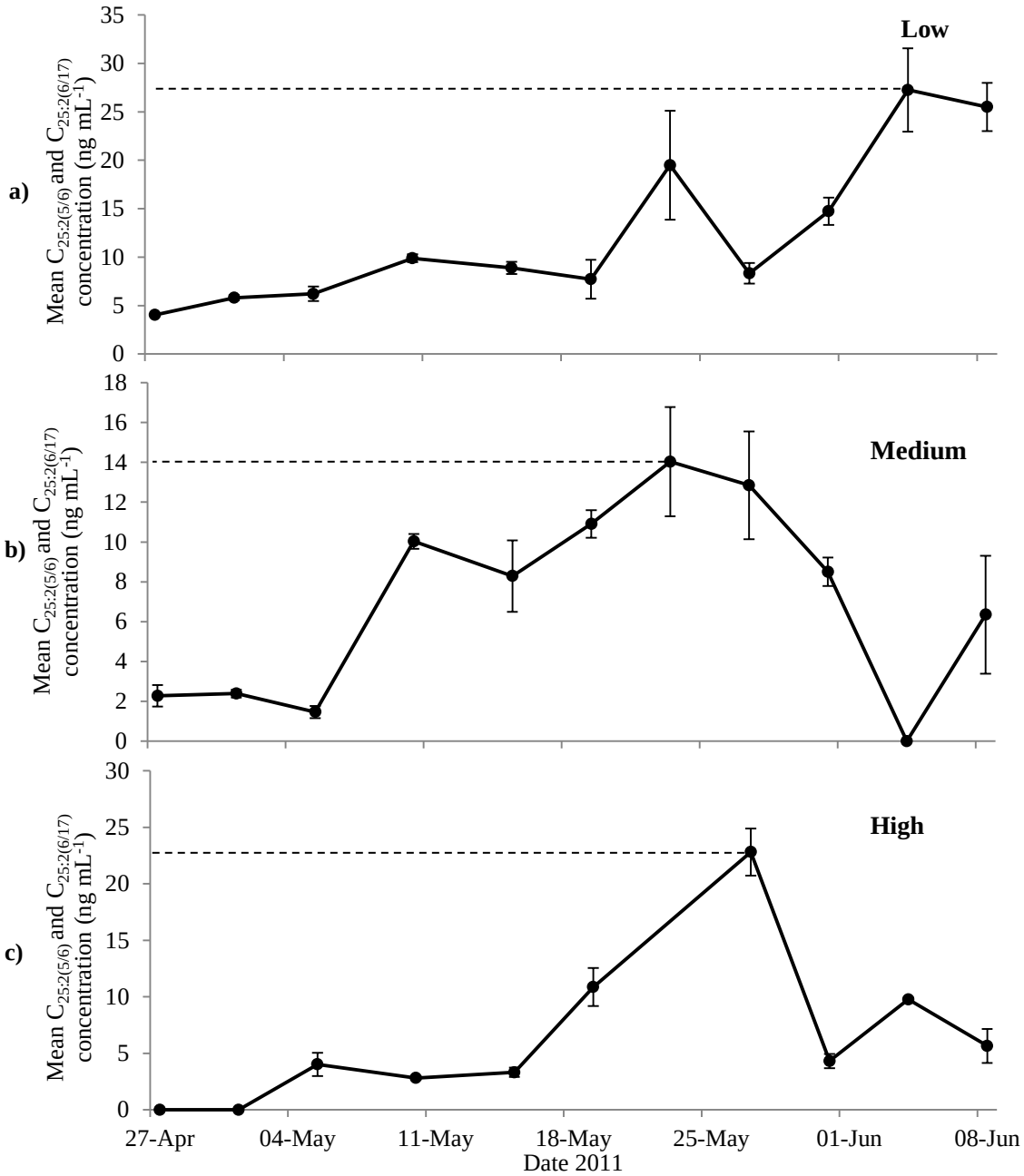


Figure 4.16. Temporal mean concentrations (±1 s.d. n = 2 or 3) of **II** observed in the **A** section of sea ice during the Arctic ICE project with **a)** low, **b)** medium and **c)** high snow cover. Absence of a data point on the 23rd May for high snow due to no sample being provided.

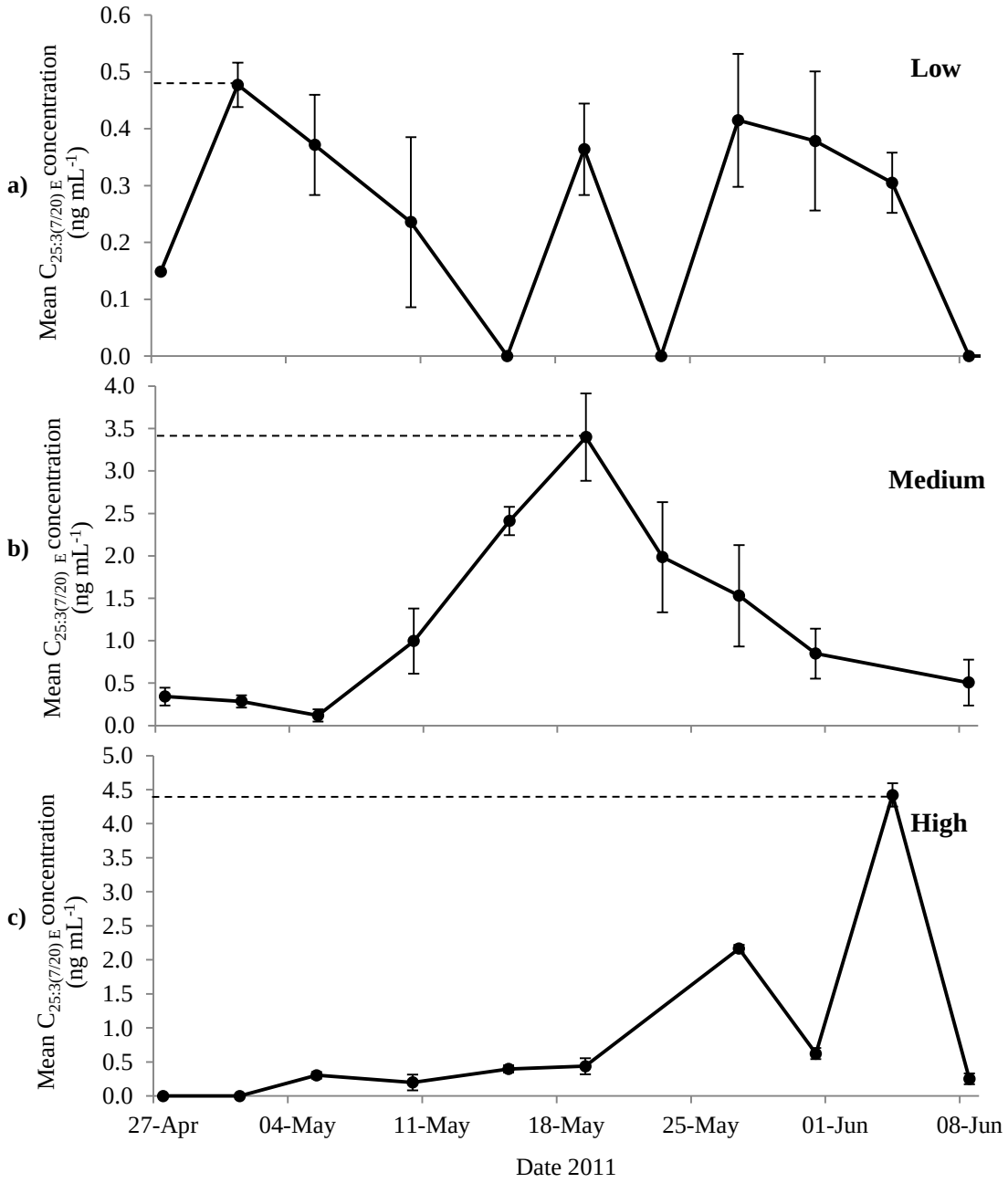


Figure 4.17. Temporal mean concentrations (±1 s.d. n = 2 or 3) of **III** observed in the **A** section of sea ice during the Arctic ICE project with **a)** low, **b)** medium and **c)** high snow cover. Absence of a data point on the 23rd May for high snow due to no sample being provided.

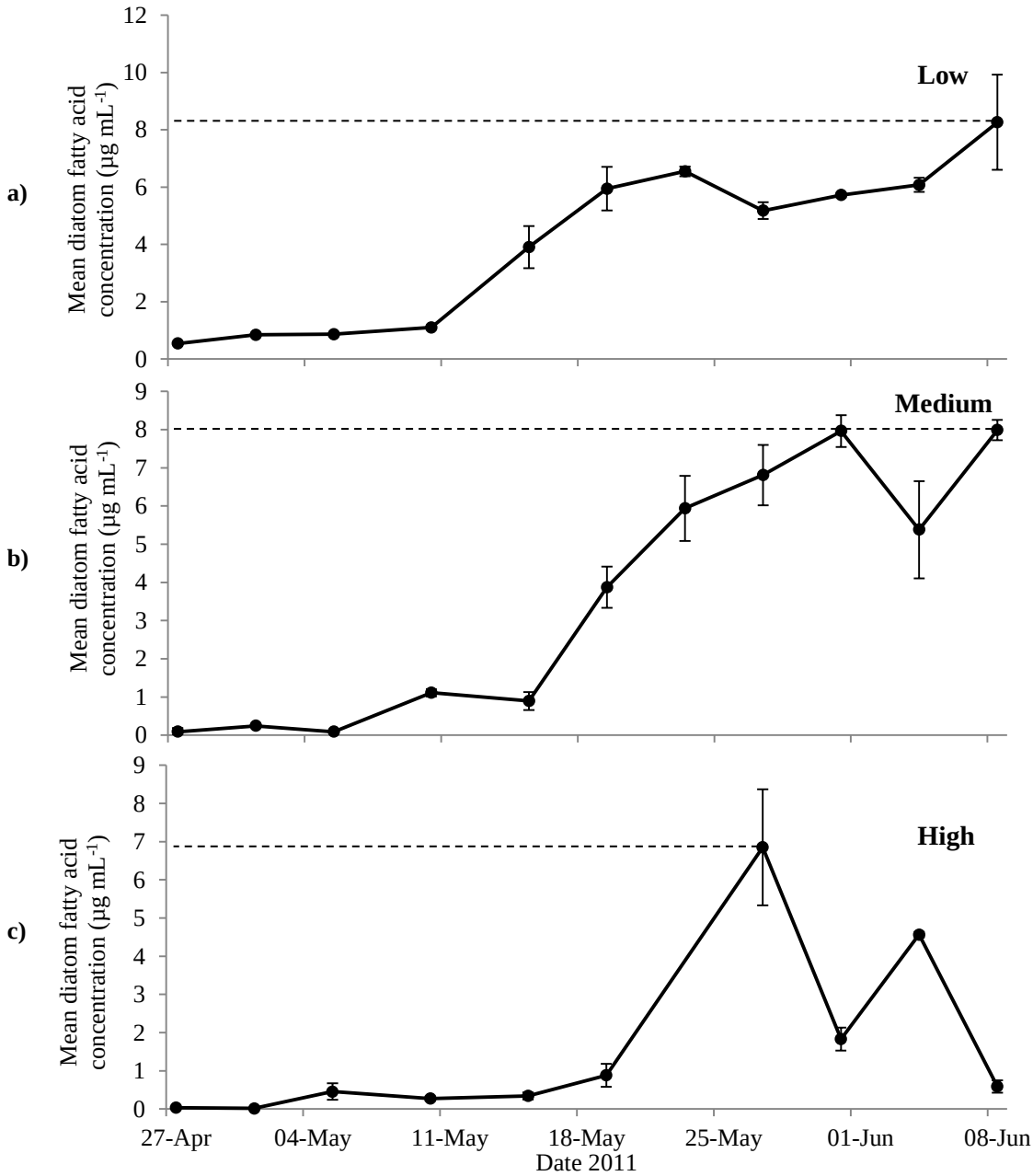


Figure 4.18. Temporal mean concentrations (±1 s.d. n = 2 or 3) of diatom fatty acids observed in the **A** section of sea ice during the Arctic ICE project with **a)** low, **b)** medium and **c)** high snow cover. Absence of a data point on the 23rd May for high snow due to no sample being provided.

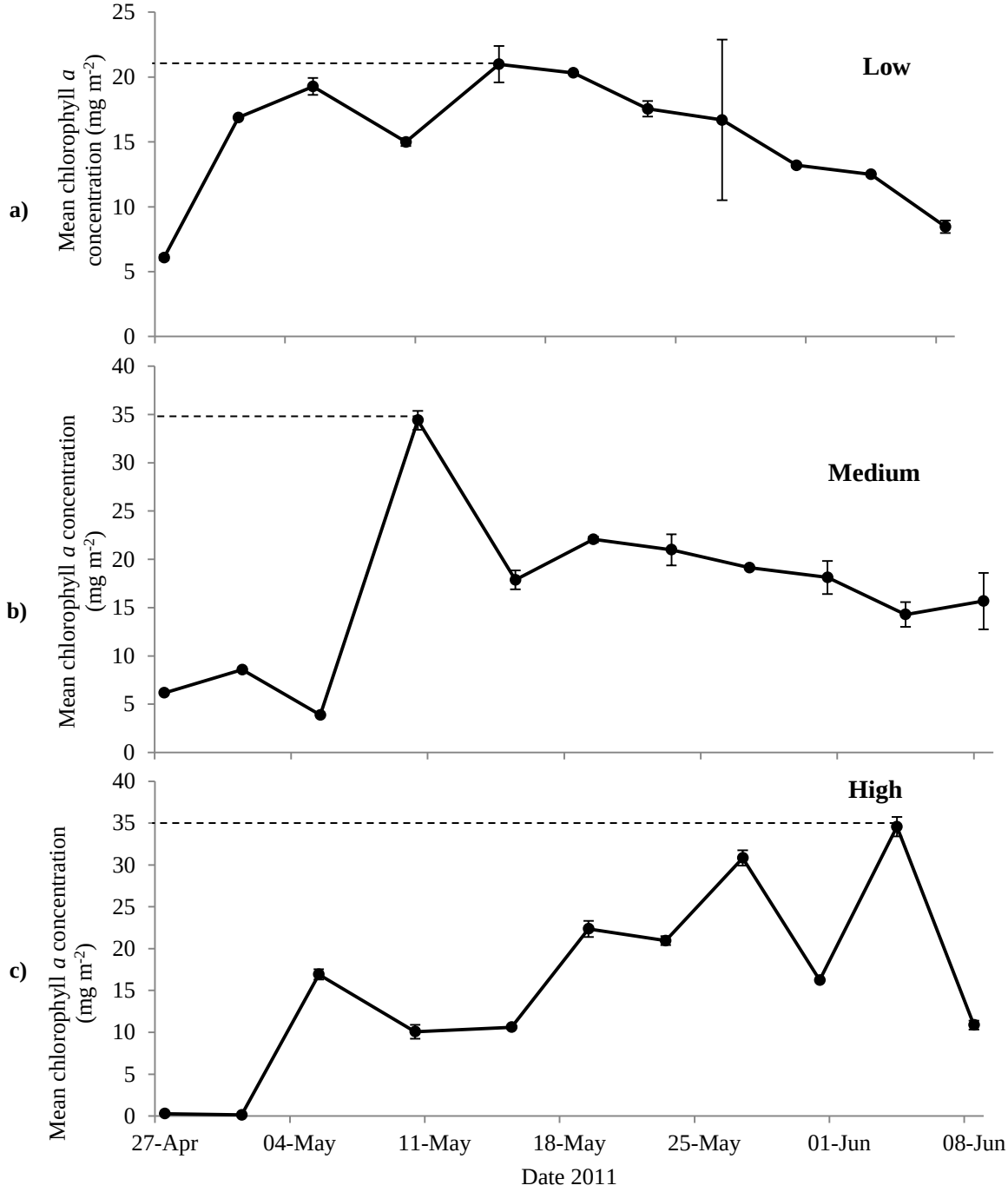


Figure 4.19. Temporal mean concentrations (±1 s.d. n = 2) of chlorophyll *a* observed in the **A** section of sea ice during the Arctic ICE project with **a)** low, **b)** medium and **c)** high snow cover.

CHAPTER FIVE

5.0 DISCUSSION

5.1 Introduction

Results presented in the previous chapter have established temporal and vertical distributions of **I** and other lipid biomarkers throughout sea ice collected over the spring period in Resolute Bay during 2011. The effects of snow cover on production of lipids over the temporal sampling period have also been investigated.

5.2 Temporal distributions of lipids in sea ice and correlations between them

The first and second aims of this study were to investigate concentration changes in and relationships between **I** and other lipid biomarkers in Arctic sea ice from Resolute Bay over the spring bloom from late April to early June 2011. The spring sea ice algal bloom in the Resolute Passage and the Canadian Arctic Archipelago, are well documented as a variety of studies have been carried out over the April to June period (Bergmann et al., 1991; Brown et al., 2011; Laurion et al., 1995). Blooms in primary production in the marine environment, phytoplanktic and sea ice-based, are typically identified by increased concentrations of chlorophyll *a*, photosynthetic cell abundances, nutrients and algal-specific lipids (Brown et al., 2011; Codispoti et al., 1991; Legendre, 1990; Mundy et al., 2009; Reuss and Poulsen, 2002; Rózanska et al., 2009). In this study, concentrations of different algal biomarkers including **I**, fatty acids and chlorophyll *a* were measured from the 27th April to the 8th June (Fig. 4.2 to 4.5). The specific sea ice diatom biomarker **I** contributed on average ca. 20% of the total HBIs over the sampling period, whilst **II** and **III** contributed on average ca. 70% and 10% respectively. **II** was consistently the most abundant throughout the sampling period. Accumulation of **I** in the sea ice over the first week of sampling (27th April to the 5th May) remained under

1.0 ng mL^{-1} until production rapidly increased on the 10th May to 3.7 ng mL^{-1}. This upward trend in accumulation over the five day period (5th May to the 10th May) is also observed in chlorophyll *a* concentrations and could be due to increases in natural light penetrating the ice. The downward solar flux in Resolute Bay on the 5th and 10th May increased from 448-480 W m^{-2} to 480-512 W m^{-2} (Fig. 5.1). This further supports the association between **I** and photosynthetic diatom production. It can also be noted that the average solar flux in Resolute Bay increased from 100 W m^{-2} to 237.5 W m^{-2} over the sampling period leading up to the summer sea ice melt (data provided by Physical Sciences Division, Earth System Research Laboratory).

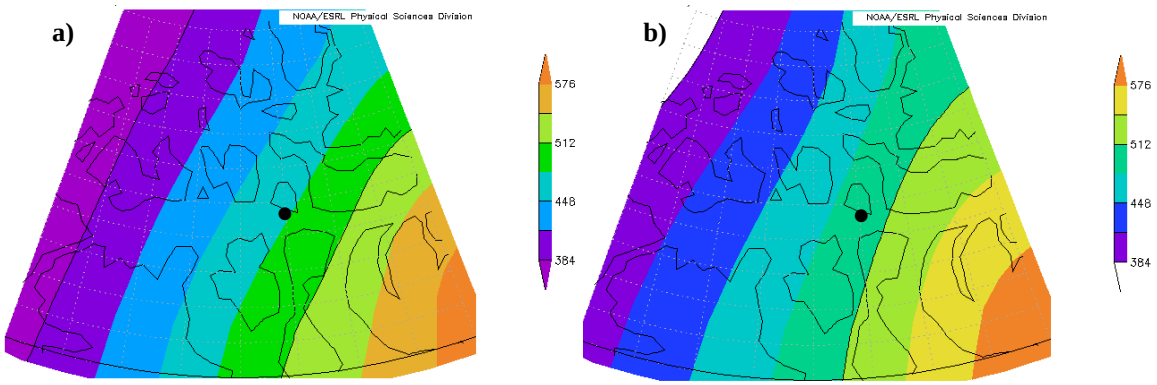


Figure 5.1. Downward solar flux over part of the Canadian Arctic Archipelago on **a)** 5th May 2011 and **b)** 10th May 2011, Resolute Bay denoted by ●. Image provided by Physical Sciences Division, Earth System Research Laboratory, NOAA, Boulder, Colorado, from their Web site at http://www.esrl.noaa.gov/psd/.

Along with local changes in solar radiation, changes in the accumulation of lipids may be attributed to an irregular underside of the sea ice and therefore local variation in algae abundances (Krembs et al., 2002). As there is difficulty in collecting samples in an extreme environment, especially with sea ice break-up imminent (27th June) (Campbell et al., 2011), all ice cores were collected in an approximate 0.17 $miles^2$ (0.27 km^2) area, this possibly leading to variations in algae biomass over a reasonably large area. Statistical determination of the extent of correlation between temporal concentration changes of **I** and chlorophyll *a* ($r = 0.81$; $n = 10$; $P < 0.05$) show the

temporal distribution of **I** effectively showed the spring sea ice bloom in Resolute Bay in 2011. HBIs **I** and **II** correlated well ($r = 0.91$; $n = 10$; $P = < 0.05$), providing further evidence for the co-production of **I** and $C_{25:2(6/17)}$ in sea ice diatoms (Belt et al., 2012; Belt et al., 2007; Brown, 2011) along with $C_{25:2(5/6)}$. On the contrary, the planktic origin of **III** ($C_{25:3(7/20)\ E}$) was reflected by no statistically significant correlation to **I** ($r = 0.46$; $n = 10$; $P > 0.05$). Incorporation of small amounts of **III**, in relation to **I** and **II**, into the sea ice may be due to the intermediate solid/liquid phase that the lower few centimetres of sea ice (closest to the water) normally naturally obtains. This part of the sea ice is a natural equilibrium between the sea ice and sea water that allows the transferal of nutrients and other material.

Fatty acids have typically been used as general biomarkers of primary production over the spring bloom period in marine environments. For example Reuss et al. (2002) used specific fatty acids and fatty acid ratios as general biomarkers of the plankton community in the spring bloom and post-spring bloom off west Greenland. Fatty acids were analysed in this study in Resolute Bay as biomarkers of general production, three of them (**FI**, **FII** and **FIII**) gave more information of diatom inputs. Along with diatom fatty acids, **FIV** and the saturated fatty acid **FV** were also present in sea ice samples. **FIV** is found in heterotrophic bacteria, as well as occurring from stereomutation resulting from photodegradation of *trans*-vaccenic acid (Christodoulou et al., 2010; Rontani et al., 2003), whilst **FV** is common to dinoflagellates (Reuss and Poulsen, 2002). Diatom fatty acids were observed as the majority (ca. 98%) of total fatty acid production; along with **FIV** and **FV** as the minority (Fig. 4.4), suggesting a predominately diatom-based sea ice algae bloom. This gives further evidence towards findings previously observed by Riedel et al. (2003) that show the spring bloom near Resolute Bay is comprised mainly of diatoms. Peak concentrations of pennate diatoms reached ca. 260×10^6 cells L^{-1} whilst dinoflagellates and flagellates only reached ca. 0.4

x 10^6 cells L^{-1} and ca. 18 x 10^6 cells L^{-1} respectively (Riedel et al., 2003). Total diatom fatty acid production over the temporal sampling period was significantly higher than total HBI production (ca. 50-400). Accumulation of diatom fatty acids showed different trends to those of HBIs.

Instead of a steady increase and decrease in concentrations over the sampling period, with a peak in mid to late May observed in HBI trends (Fig. 4.2), diatom fatty acid concentrations remained elevated until the end of sampling (Fig. 4.3). Temporal concentrations of **I** and fatty acids known to be from a diatom origin correlated poorly ($r = 0.66$; $n = 10$; $P = > 0.05$). Whilst **I** is believed to be produced specifically by some pennate sea ice diatoms, the fatty acids **FI**, **FII** and **FIII** are produced by many varieties of abundant diatoms including pennate and centric species, *Nitzschia palea*, *Navicula muralis*, *Thalassiosira fluviatilis* and *Skeletonema costatum* (Darley, 1977; Opute, 1974) along with other organisms. Therefore this prolonged elevation in diatom fatty acid concentrations may be due to other types of diatom contributing to the fatty acid content. Concentrations of chlorophyll *a* are typically used as a biomarker of general organic production as it is essential to all oxygenic photosynthetic organisms as a pigment to release chemical energy. In this study it has been used to represent the spring bloom, showing the production trend in organic matter from a wide variety of organisms (Fig. 4.5).

This temporal study has shown the presence of **I** in sea ice from Resolute Bay in the spring of 2011. Different temporal trends in the accumulation of fatty acids to the HBIs, demonstrate the wide production of fatty acids by a range of organisms.

5.3 Vertical distributions of lipids in sea ice

The third aim of this study was to investigate the vertical distributions of **I** and other lipid biomarkers throughout Arctic sea ice from Resolute Bay over the same spring sampling period as the temporal samples. In the majority of sea ice studies, lipid content is typically only investigated in the lower sections of sea ice cores (Brown et al., 2011; Lee et al., 2008; Nichols et al., 1993; Nichols et al., 1989) as it is commonly understood that the majority of accumulation of organic matter is closest to the ice-water interface, as the nutrients needed for growth and production are abundantly available. To the author's best knowledge, this is the first study to calculate concentrations of HBIs and fatty acids throughout sea ice cores from the ice/water interface to the ice/snow interface. The majority of accumulation of HBIs (Fig. 4.7 to 4.9) and chlorophyll *a* (Fig. 4.14) were in the **A** section (0-3cm from the ice/water interface).

Trends in distributions of **I**, **II** and **III** throughout the sea ice cores were similar as the majority of production appeared in the **A** section of all samples, averaging ca. 97%, 97% and 92% respectively. Accumulations of the HBIs were either under the limits of detection or contributed less than 1% in sections **C**, **D** and **E** (Table 4.2). The tri-unsaturated HBI **III** was not found in sections above 10 cm from the ice/water interface (sections **C**, **D** and **E**). This distribution of **III** is highly suggestive of its likely predominant planktonic origin. The distributions of the HBIs, fatty acids, and chlorophyll *a* are likely partly attributed to the brine volume (%). Brine volume, or the ice core permeability threshold (5%), indicates the threshold at which the connectivity of brine pores is sufficient to enable growth of organisms within the ice due to availability of nutrient replenishment during the bloom (Cox and Weeks, 1983; Golden et al., 2007).

In contrast to HBIs, fatty acid abundances in the sea ice cores collected in early and mid- bloom were much more evenly distributed and higher sections of the cores

contributed more to the total (Fig. 4.10 to 4.12). For example sections **C**, **D** and **E** each ice core contributed on average ca. 11%, 11% and 10% respectively in cores collected on the 1st, 10th and 19th of May in contrast to the less than 1% contributed in HBI production in those same sections. An increase in contribution to the accumulation of the diatom fatty acids in the **A** section is observed in samples collected in the later bloom, clearly represented in Figure 4.13. Over the five sampling dates the contribution from the **A** section to the diatom fatty acid abundance increases from ca. 42% to 78%. Possible reasons for this distribution change over the spring bloom may be attributed to contributions from other (non-IP_{25} producing) sea ice algae or from non-algal organic matter such as bacteria (Maranger et al., 1994) and increases in production of these organisms over the bloom period. As fatty acids are used for energy by cells and some are essential to animals' diets, they are produced in high abundances from a range of organisms in the marine environment (Arts et al., 2009). The organisms that undergo a spring sea ice bloom, for example algae (Brown, 2011) and bacteria (Maranger et al., 1994), will rapidly increase in abundance and therefore increase in fatty acid productivity, contributing to the content in the lower section of the sea ice.

The majority of chlorophyll *a* production (average ca. 94%) was also in the **A** section of the sea ice cores (Fig. 4.14). As with the HBIs, the contribution to the total vastly decreased above 3 cm from the ice/water interface. Section **B** contributed on average 1.3% whilst section **C** contributed ca. 3.2% and sections **D** and **E** contributed ca. 1.3% and 0.64% of the total chlorophyll *a* in the cores.

This study has also demonstrated that lipids of diatom and other organism production are present throughout sea ice from the ice/water interface to the ice/snow interface, however in small abundances compared to the lower sections. HBI, and chlorophyll *a* accumulation is highest in the lower 3 cm closest to the ice/water interface, whereas fatty acid accumulation is more distributed through the core. Two possible explanations

for the presence of these compounds throughout the ice are suggested; a) entrapment with ice formation and growth and b) extension of brine channels and migration. Mechanisms of the incorporation of organic matter and organisms into sea ice include harvesting/scavenging, nucleation and wave fields (Ackley, 1982). Harvesting/scavenging occurs when frazil ice crystals form around suspended algae cells in the water column, when they rise to the surface they are incorporated and harvested into the ice. Nucleation is a similar process when ice crystals form around any nucleus, a solid particle of any organic matter or mineral and a wave field is when water is pumped up through grease ice, trapping organic matter. As sea ice mainly grows from the underside vertically downwards, it can be hypothesised that small abundances of organisms such as diatoms that are temporarily suspended in the water column during the winter months, may be incorporated into the ice as it forms. This would continue as the ice thickens until the spring sea ice bloom occurs and enhances the abundance of the organisms in the lower section of sea ice where nutrients are ready available for growth (Nomura et al., 2009).

As the extent of brine channels in sea ice depend on different variables such as temperature, salinity, density and pH (Kutschan et al., 2010; Petrich and Eicken, 2010), the microstructure of sea ice, the brine channels, may be able to extend vertically (and horizontally) as these variables change naturally. As the ice warms, the walls of brine channels, along with the bottom of the ice, melt and brine channels enlarge, often connecting to each other creating larger cavities throughout the ice (Gow and Tucker III, 1990; Niedrauer and Martin, 1979). This is demonstrated by a rapid sea-water infiltration into the ice and demonstrates possible vertical exchanges through the ice (Hudier and Ingram, 1994). With previous investigations having already demonstrated vertical migration of benthic diatoms in the water column and sediments (Heckman, 1985; Pinckney and Zingmark, 1991), there is potential for this to occur in sea ice, as

the diatoms may naturally migrate towards the light. The vertical distributions of fatty acids established in this study (Fig. 4.10 to 4.13) provide evidence towards both suggested explanations.

Sea ice is a natural system with no clear cut boundaries or regimental and repetitive structures; therefore natural variation in the microstructure of sea ice is always clear. However, this study has shown that the majority of lipid accumulation occurs within the lower 3 cm of sea ice, closest to the ice/water interface, potentially a result of brine volumes greater than 5%. A rapid decrease in concentration of all the lipids occurs in sections above 3 cm from the ice/water interface. As fatty acid accumulation is however more distributed through the sea ice, it demonstrates a wider range of sources that go through a spring bloom, than of those who produce HBIs. Two possible preliminary explanations for the occurrence of these lipids throughout sea ice are proposed; a) entrapment with ice formation and growth and b) extension of brine channels and migration, however further investigation is needed to fully test these hypotheses.

5.4 The effect of snow cover on lipid production

The fourth aim of this study was to investigate the effects (if any) of snow cover on lipid concentrations in sea ice. GC/MS analysis of the **A** section of sea ice cores with low, medium and high depths of snow cover (Fig. 5.2) enabled observations of lipid content with varying snow depth, to be made. As diatoms are photosynthetic organisms, they rely on natural light for growth and production. The depth of snow cover on top of sea ice limits the amount of sunlight available to the organisms below and within the sea ice (Mackenthun, 1973).

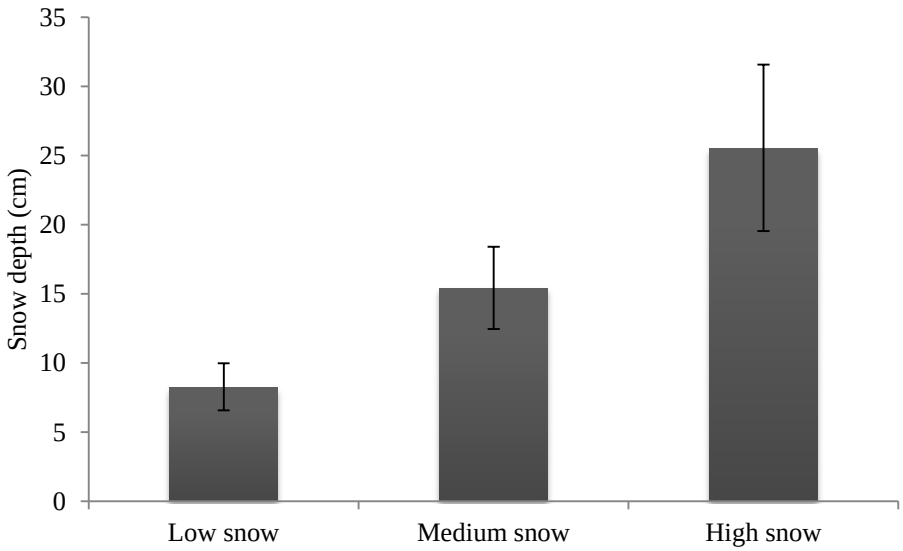


Figure 5.2. Mean snow cover (± 1s.d. n = 11) of sea ice collected on the Arctic ICE project over the temporal sampling period that were categorised as low, medium and high.

No particular level of snow depth (low, medium or high) gave consistently higher concentrations of any of the analytes in the sea ice over the spring sampling period. This being said, there is a visible difference in trends between high snow and the other snow depths (Fig. 4.15 to Fig. 4.18) with a delay in accumulation of HBIs and fatty acids over the temporal sampling period. High levels of snow cover seem to delay the accumulation of these lipids in the ice as concentrations remain low at the start of sampling (27th April to approximately the 11th May) and rapidly increase later in the sampling period. This delay may be due to lower levels of sunlight available to the diatoms and therefore limiting the production of organic chemicals produced before peak summer radiation levels are reached. Peak concentrations of chlorophyll *a* in samples with high snow cover occurred between 20 and 24 days after peak concentrations in the low and medium snow samples. This apparent difference in accumulation trends of chlorophyll *a* with higher snow cover is consistent with previous findings (Mundy et al., 2007).

This study has been the first to investigate the effect of snow cover on concentrations of HBIs **I**, **II** and **III** in sea ice. This is a preliminary study and further investigation into the effect of snow depth on HBI accumulation in the ice is needed.

5.5 Comparison of data to previous findings in the Amundsen Gulf

The fifth aim of this study was to compare the temporal and vertical distributions of **I** and other lipid biomarkers found in this study to previous findings in the Amundsen Gulf in 2008 (Brown, 2011). It has already been demonstrated that in the Amundsen Gulf, **I** is produced by diatoms during the spring ice algal bloom in significant correlation to fatty acid and chlorophyll *a* production (Brown et al., 2011). To be able to fully understand the production and distributions of **I** in Arctic sea ice, other regions needed to be investigated.

At higher latitudes, spring blooms occur later in the year due to a delay in both thermal stratification and an increase in natural light. However annual variations in the timing of production must be taken into account when comparing results from the two sampling locations. The spring bloom in the Amundsen Gulf in 2008 ranged from late March to mid-May, whilst in Resolute Bay in 2011 the bloom occurred approximately 1-3 weeks later and ranged from early May to early June. Differences in the types of sea ice collected from each study site also need to be taken into account. Land-fast first-year ice was collected on the Arctic ICE project in Resolute Bay 2011whilst both land-fast and drift first-year ice were collected on the Circumpolar Flaw Lead system study in the Amundsen Gulf 2008 due to necessary ship mobility. Differences in salinity and microstructures of the different types of sea ice may affect the algal content within (Krembs et al., 2002; Mundy et al., 2007).

To allow the comparison of analyte concentrations between the two studies, concentrations in sections **A** and **B** of the vertical sea ice samples from Resolute Bay were converted into concentrations in the lower 10 cm (Table 5.1). The lower 10 cm was chosen to be appropriate as temporal sea ice samples from the Amundsen Gulf study were measured in the lower 10 cm. This was completed using Equation 5.1. To be able to make comparisons, it must be assumed that variability in snow cover from either location did not affect concentrations of the analytes in the sea ice.

Equation 5.1. $$[0 - 10\ cm] = (0.3[0 - 3\ cm]) + (0.7[3 - 10\ cm])$$

I contributed smaller proportions to the total HBI content in the lower sections of sea ice from Resolute Bay than from the Amundsen Gulf, maximum percentages reached 24% and 44% respectively. Peak production of **I** in the lower 10 cm of sea ice was approximately 4.5 times greater in Resolute Bay (1.38 ng mL^{-1}; 27th May 2011) than the Amundsen Gulf (0.31 ng mL^{-1}; 1st May 2008), indicating an increase in IP_{25}-producing sea ice diatoms.

In addition to HBIs, fatty acids and chlorophyll were also present in sea ice cores from both Resolute Bay and the Amundsen Gulf. The mean total fatty acids commonly associated with marine diatoms were consistently higher than production of **I** in both Resolute Bay (ca. x1,080-2,070) and the Amundsen Gulf (ca. x3,600-35,000). The peak concentration of diatom fatty acids in the lower 10 cm of the sea ice from Resolute Bay was approximately 2.6 times greater than the Amundsen Gulf (2.89 µg mL^{-1} and 1.12 µg mL^{-1} respectively). Peak production of **I** and diatom fatty acids in Resolute Bay are approximately 3 weeks later than peak production in the Amundsen Gulf between 2011

and 2008. This shift in production may be due to latitudinal differences of the sampling sites and so different algal bloom timings, or annual changes in production over a three year period.

The peak concentration of chlorophyll *a* in the lower 10 cm of sea ice was approximately 0.7 times lower in Resolute Bay (11 mg m^{-2}; 10th May 2011) than the Amundsen Gulf (16 mg m^{-2}, 8th May 2008).

Table 5.1. Peak abundances and ratios of analytes over the temporal sampling period in the Amundsen Gulf (2008) and Resolute Bay (2011). Values calculated for the concentrations in the lower 10 cm of sea ice from Resolute Bay (2011) are manipulated from original concentrations of the 0-3 cm and 3-10 cm sections.

Peak concentrations of analytes		Amundsen Gulf 2008 0-10cm	Resolute Bay 2011 0-10 cm	Ratio Resolute Bay/ Amundsen Gulf)
I	ng mL^{-1}	0.31	1.38	4.5
Total HBIs (**I**, **II** and **III**)		0.71	5.84	8.2
Diatom fatty acids (**FI**, **FII** and **FIII**)	µg mL^{-1}	1.12	2.89	2.6
Chlorophyll *a*	mg m^{-2}	16	11	0.7

Only general vertical distributions of the lipids in sea ice can be compared between Resolute Bay and the Amundsen Gulf as different sectioning methods were adopted. Whole sea ice cores (from the ice/water to the ice/snow interfaces) were analysed in Resolute Bay, whereas only two high resolution cores, one early and one mid-bloom, (1 cm horizons) of only the lower 10 cm were analysed in the Amundsen Gulf (Fig. 5.3). Vertical distributions of **I**, diatom fatty acids and chlorophyll *a* in sea ice from both Resolute Bay and the Amundsen Gulf provided further evidence to show the majority of accumulation of the lipids to reside within the lower sections of sea ice close to the ice/water interface. Brine volumes in sea ice were not calculated in this study in Resolute Bay. However, it can be hypothesised that the 5% brine volume threshold is an

influential factor on the distribution of **I** and the other lipids as distributions of **I** were found to be consistent with the threshold in the lower sections in sea ice from the Amundsen Gulf (Brown et al., 2011).

This study has allowed for the comparison of temporal and vertical distributions of **I** and other lipid biomarkers in Arctic sea ice over a spring sampling period. **I** has been shown to be accumulated in sea ice over the spring sea ice bloom in a second spatially distant location in the Canadian high Arctic to the Amundsen Gulf. In both Resolute Bay and the Amundsen Gulf, **I** has been shown to accumulate mainly in the lower sections of sea ice, close to the ice/water interface. A 3 week later peak in accumulation of **I** in the sea ice was also observed in Resolute Bay in 2011 to the Amundsen Gulf in 2008. Greater production of **I** and diatom fatty acids in Resolute Bay show an increase in IP_{25}-producing diatoms. However greater chlorophyll *a* production in the Amundsen Gulf shows more contribution from other photosynthetic organisms other than diatoms.

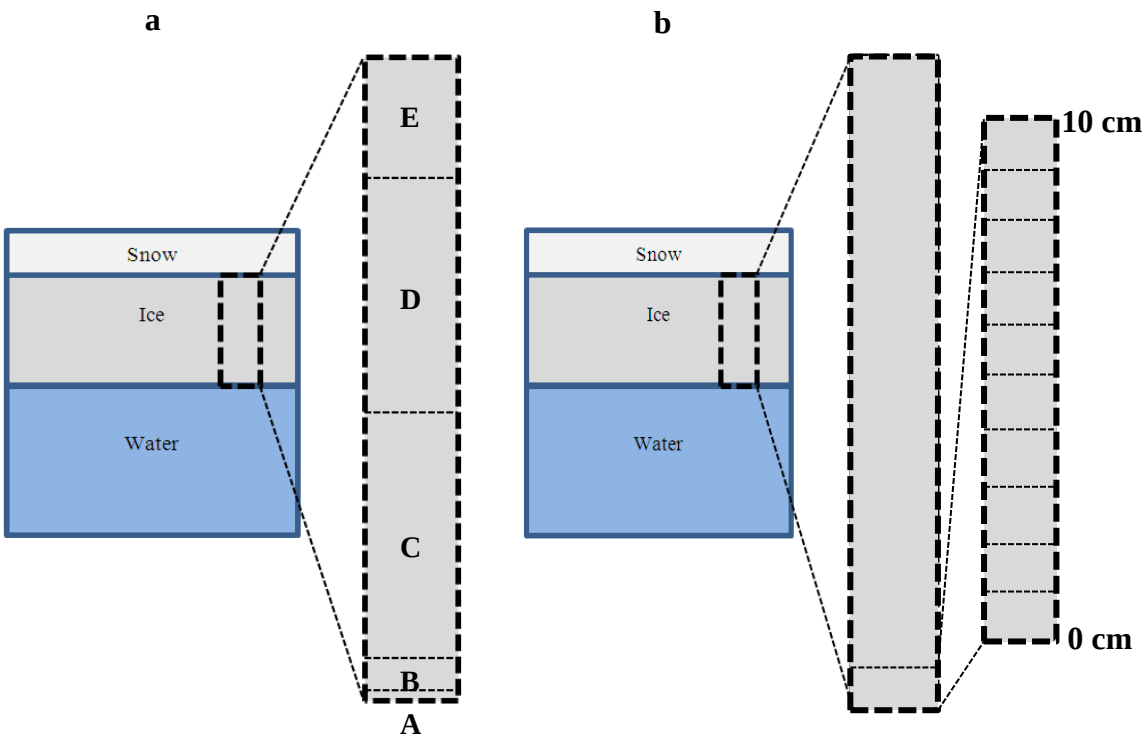


Figure 5.3. Schematics of sea ice core sectioning in **a)** Resolute Bay on the Arctic ICE project 2011 and **b)** the Amundsen Gulf on the Circum Polar Flaw Lead system study 2008.

5.6 Relating this study to other research

Climate change in the Arctic is currently of great concern of both the general public and scientific community, as recent observations of record low sea ice extents (NSIDC, 2012c) and predictions of rapid sea ice loss have been made (Holland et al., 2006; Wang and Overland, 2009). This provokes the need for more scientific research into the environmental changes currently taking place in the Arctic and predicted to take place in the future, some of which provided by both current and historical sea ice condition records. With this in mind, the HBI biomarker IP_{25} has proven to be beneficial in providing further information of past sea ice records in the Norwegian and Canadian Arctic from sediment samples (Belt et al., 2007; Belt et al., 2010; Müller et al., 2009; Vare et al., 2009). As this biomarker is becoming more commonly referred to in paleo-sea ice reconstruction research (Massé et al., 2008; Max et al., 2012; Müller et al., 2009; Müller et al., 2011; Müller et al., 2012), details of the accumulation and distributions of IP_{25} in sea ice across the Arctic first need to be understood.

Temporal and vertical distributions of IP_{25} (along with other lipid biomarkers) have previously only been investigated in the Amundsen Gulf. Findings from this study in Resolute Bay have provided further evidence towards the spring accumulation of IP_{25} in Arctic sea ice and its localisation mainly in the lower sections of sea ice close to the ice/water interface. These findings give evidence towards using IP_{25} on a pan-Arctic level, as its majority of production has been identified over the spring sea ice algal bloom in a second location in the Canadian Arctic Archipelago. However to be able to use IP_{25} all over the Arctic, further sampling sites need to be analysed for the distribution of IP_{25} in the sea ice and sediment.

Considerations into the best way to express IP_{25} concentrations in sediment to represent a semi-quantitative analysis of past sea ice conditions, rather than a presence/absence measurement, resulted in the PIP_{25} index (Müller et al., 2011). This incorporates both

the sea ice (IP_{25}) and a supposed open water sterol biomarker (brassicasterol), along with a regional specific balance factor, to provide a more detailed assessment of sea ice conditions that could be used in climate reconstruction models. This study however demonstrated regional differences in cell types of IP_{25}-producing diatoms and other single-celled protists and their relative abundances. In a situation of the same or similar ice thickness in two Arctic locations, however with different algal biomass and differing IP_{25}-producing diatom contribution to that algal content, different PIP_{25} values may be calculated from sediment samples. This questions the use of the PIP_{25} index to make semi-quantitative measurements of paleo-sea ice.

Another use of IP_{25} as a biomarker of sea ice derived organic matter has been demonstrated to have high potential in Arctic climate research as a dietary source indicator (Brown and Belt, 2012a; Brown and Belt, 2012b; Brown et al., 2012). Being able to trace sea ice derived primary production through an Arctic food web is needed for understanding the reliance of the sea ice as a vital food source for Arctic animals. This study further supports the use of IP_{25} in Arctic food webs as it has been shown that the localisation of IP_{25} mainly in the lower sections of sea ice in Resolute Bay, means IP_{25} (and the other lipids) are readily accessible for consumption. However key questions of the metabolic role of IP_{25} (if any) in Arctic animal species is still unknown and requires further investigation. This study has contributed to the current understanding of the accumulation and distribution of IP_{25} in Arctic sea ice, further enhancing the use of it in Arctic climate research.

5.7 Conclusions

The main aim of this study was to provide a better understanding of IP_{25} and other lipid biomarkers in Arctic sea ice. This has been achieved by completion of the proposed objectives. The combined experimental outcomes have provided a comparison to previous findings of IP_{25}, and other biomarker, temporal and vertical distributions in

Arctic sea ice, further elucidating the use of these paleo-climate indicators. Analysis of replicate sea ice samples from Resolute bay collected from late April to early June 2011, provided further information regarding the distribution of biomarkers, including IP_{25}. The definitive outcomes of this study can be summarised as follows:

i. IP_{25} and other lipid biomarkers were present in sea ice from Resolute Bay over the spring period in 2011
ii. HBI and chlorophyll *a* concentrations increase, peak and decrease, whereas fatty acid concentrations steadily increase over the temporal sampling period
iii. IP_{25}, fatty acids and chlorophyll *a* were present throughout sea ice from the ice/water to the ice/snow interfaces
iv. Peak IP_{25} and chlorophyll *a* concentrations occurred in the **A** section (lower 0-3 cm) of sea ice, closest to the ice/water interface
v. Fatty acid accumulation in sea ice was more distributed than HBIs, however contribution from the **A** section increased as the bloom progressed
vi. Overall accumulation of IP_{25}, HBI dienes, diatom fatty acids and chlorophyll *a* were not dependent on snow cover
vii. In both Resolute Bay and the Amundsen Gulf, IP_{25} was accumulated in sea ice over the relative spring periods and highest concentrations were in the lower sections of sea ice, close to the ice/water interface

5.8 Future work

Further investigation into the specific species of diatom that produce HBIs including IP_{25} is needed to progress the understanding of these chemicals and the use and reliability of IP_{25} as a spring sea ice biomarker. Further research into the biological role of HBIs in diatoms is also needed to give further understanding of the occurrence of

these biomarkers. As this study only provides preliminary findings of the effect of snow depth on the accumulation of IP_{25} and other lipids in sea ice, further investigation are needed.

CHAPTER SIX

6.0 FUTURE WORK: DIETARY SOURCE INDICATORS

6.1 Introduction

As IP_{25} is a specific indicator of Arctic sea ice diatom primary production, it is hypothesised that it can be used to trace sea ice derived organic matter through an Arctic food web. As other HBIs have also been identified to be from a phytoplanktonic origin, a suite of dietary source indicators, containing IP_{25}, is proposed ($DSIP_{25}$; Fig. 6.1). The hypothesis of the future study is that this suite of chemicals, including IP_{25}, can provide information towards dietary sources, tracing sea ice and open water derived organic matter through an Arctic food web. Presence of other lipid biomarkers, stable isotope data and pigment levels will also provide information towards dietary sources in animal species. This is the first biomarker suite to contain a specific sea ice origin proxy to access dietary sources in Arctic animal species and recent preliminary research has already demonstrated its potential (Brown and Belt, 2012a; Brown and Belt, 2012b; Brown et al., 2012). A future study involving a seasonal and spatial, two-part comparison study in the Norwegian Arctic will give critical information of species dependence on sea ice and effects that sea ice depletion may have on biodiverisity in the Arctic.

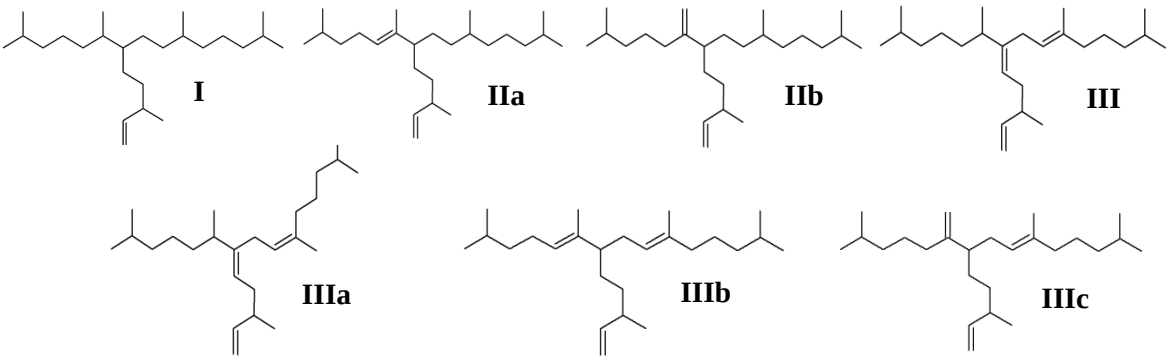


Figure 6.1. $DSIP_{25}$ biomarker suite. **I** comes from a sea ice origin only. **IIa** ($C_{25:2(5/6)}$) and **IIb** ($C_{25:2(6/17)}$) come from sea ice and phytoplanktic origins. **III** ($C_{25:3(7/20)\ E}$), **IIIa** ($C_{25:3(7/20)\ Z}$) , **IIIb** ($C_{25:3(5/6)}$), and **IIIc** ($C_{25:3(6/17)}$) are known to be from a phytoplanktic origin.

The contribution of sea ice algae and phytoplanktonic primary production in the Arctic marine ecosystem is unclear, therefore the effects from one of these primary sources diminishing drastically are unknown. On route to finding out what dependence each primary source has on the Arctic food web, being able to distinguish between the two is vital to understanding an animals major primary source of food.

6.1.1 Distinguishing between sources of primary production and energy transfer

6.1.1.2 Pigments

Pigment levels have been used to distinguish between marine primary sources (Bridoux, 2008). As sea ice algae can adapt to changes in light levels, it can show severe photoinhibition (Thomas and Dieckmann, 2010). Phytoplankton does not have this adaption and enhanced UV-B can decrease its productivitity (Behrenfeld et al., 1995; Häder and Liu, 1990; Karentz et al., 1991; Lesser et al., 1994; Schofield et al., 1995). Phytoplankton therefore contains more photoprotective pigments such as β-carotene (Thomas and Dieckmann, 2010) as they need to protect themselves against high levels of light.

6.1.1.3 Stable isotopes

Stable isotopes are also used to distinguish between these two food sources in grazers (Hobson and Welch, 1992; Post, 2002). Particulate organic matter from open water (pelagic-POM) and sea ice algae (ice-POM) were found to be isotopically different, ice-POM generally more enriched in ^{13}C than pelagic-POM ($\delta^{13}C$= -20‰ vs. -24‰) and less enriched in ^{15}N ($\delta^{15}N$=1.8‰ vs. 4.0‰) when dominated by typical ice diatoms *Nitzchia frigida* and *Melosira arctica* (Hobson et al., 1995; Søreide et al., 2006). ^{12}C is preferable to organisms as it is metabolised faster and is the smaller and lighter isotope. After an organism has metabolised ^{12}C, ^{13}C values are enriched and can then be transfered through the foodweb. Making it possible to follow sea ice algae pathways in

an Arctic food web and distinguishing trophic positions. Nitrogen stable isotopes are also used to evaluate trophic position (Søreide et al., 2006). ^{14}N is preferentially catabolised and excreted so enrichment of ^{15}N occurs through each trophic level. After each trophic transfer this value increases by approximately 3-5‰, (3.4‰ in the lower food web (Søreide et al., 2006)) relative to the standard (Cabana and Rasmussen, 1994; Peterson and Fry, 1987). Possition of an animals trophic level in a food web can give information towards food web models.

6.1.1.4 Gut analysis

Gut anaysis is also used to investigate food webs and predator-prey relationships (Michener and Lajtha, 2007), by disecting the gut the animals recent prey can be identified. This involves the collection and dissection of a wide range of individuals to compile general prey knowledge of a species. Some organisms also digest their prey rapidly, making identification difficult (Feller et al., 1979). This technique requires a high level of taxanomic skills and does not give great detail into overall species prey information. It is best used as a snap shot of what the individual ate recently, not always a good reflection of the species regular diet, giving only preliminary information of predator-prey relationships.

There are a number of techniques used to investigate predator-prey relationships however none are highly specific on their own to give detailed and precise information on major sources of primary production. Using the $DSIP_{25}$ suite alongside these other techniques will enable a more precise understanding of Arctic animals primary dietary sources.

6.2 Aims and objectives

To be able to further enhance preliminary studies using the $DSIP_{25}$ biomarker suite (Brown and Belt, 2012a; Brown and Belt, 2012b; Brown et al., 2012) and to make predictions of possible animal population changes, resulting from a warming Arctic, a sampling strategy first needs to be made and adhered to for collection of samples. The following objectives of this study are:

i. To design a comprehensive sampling strategy enabling analysis of lipid biomarkers in an Arctic food web

ii. To collect samples representing a full Arctic food web on the Polar Night and MOSJ cruises in the Norwegian Arctic, adhereing to the sampling strategy

6.3 Study location

Svalbard is a set of archipelago islands in the Norwegian Arctic located in a border area of Arctic and North Atlantic climatic and biogeographic zones (Strömberg 1989). The Barents sea surrounding Svalbard is influenced by warm Atlantic water coming up in the Gulf Stream through the Fram Strait between Svalbard and Greenland and is approximately 230 m deep (Loeng 1990; Daase 2012). The main currents around Svalbard are the East Spitsbergen current (ESC) which brings colder waters from the north down to the Atlantic, and the West Spitsbergen current (WSC) which brings up warmer waters from the Atlantic oceans (Harland, Anderson et al. 1997). The WSC runs up the western coast of Svalbard and has high inter-annual variability in its strength and the amount of Atlantic water being inputted into the Arctic (Saloranta and Haugan 2001). This colder water influences the temperature and therefore ecosystems of some of the western fjords around Svalbard (Overrein 2008).

6.3.1 Isfjorden

Isfjorden (78°20'N, 15°00'E) is the largest western fjord on Spitsbergen (Nilsen, Cottier et al. 2008), the largest island of Svalbard. The mouth of Isfjorden is approximately 10 km wide and the deepest point is 455 m (Svensksunddypet). Isfjorden is mostly open water year-round with frazil ice and thin ice. The Isfjorden system contains a number of smaller side-fjords, the more nothern based side-fjords, Tempelfjorden, Nordfjorden and the inner part of Billefjorden can contain fast-ice, up to 1m thick (Nilsen, Cottier et al. 2008).

6.3.2 Kongsfjorden

Kongsfjorden (78°57'N, 11°57'E) is another western fjord on Svalbard with an approximate maximum depth of 400 m (Svendsen, Beszczynska-Møller et al. 2002). Its outer parts are influenced by warmer waters from the WSC whilst its inner parts are highly influenced by glacial inputs. These glacial inputs of low salinity water reduce biomass, diversity and primary production in the inner fjord (Haakon Hop, Tom Pearson et al. 2002). Fast ice can form in the inner, northern part of Kongsfjorden between December and early February and glacial ice bergs are sometimes present (Gerland, Haas et al. 2004). The area becomes completely ice free during spring and complete ice cover is an exceptional event (Svendsen, Beszczynska-Møller et al. 2002).

6.3.3 Rijpfjorden

Rijpfjorden (80°10'N, 22°15'E) is a high-Arctic north facing fjord dominated by cold Arctic water, a comparable difference to Isfjorden. The fjord is predominately ice covered from October to June (Ambrose, Carroll et al. 2006) however in the summer months strong winds can push drifting pack-ice into the fjord. Bottom depths range from 200 – 250 m, opening out onto a broad shallow shelf approximately 200m deep (Ambrose, Carroll et al. 2006).

6.3.4 Ice station

The ice station (Polar Night cruise 81°44'N, 14°02'E and MOSJ cruise 81°23'N, 15°13'E) on both sampling cruises was at the ice edge north of Svalbard. Exact sampling locations were dependent on mooring and available access through the ice by the individual ships (note neither had ice-breaker classification).

6.4 Research cruises and sampling equipment available

Both Norwegian research cruises which allowed collection of the samples, were organised and funded by the Norwegian Polar Institute (NPI), University of Tromsø (UoT) and the University Centre in Svalbard (UNIS). The Polar Night cruise ran from the 8th January 2012 to the 21st January 2012 (RV Helmer Hanssen) and the MOSJ cruise ran from the 12th July 2012 to the 21st July 2012 (RV Lance). Figure 6.2 provides sample station details and maps. Available sampling equipment on board the vessels included trawls, dredges, nets, grabs and corers. Ice divers also collected fauna and algal samples by hand or with suction pumps from shallow sampling sights on the MOSJ cruise.

6.5 Sampling strategy

To represent a full Arctic food web, animal samples from a large range of trophic levels needed to be collected. These trophic levels included primary producers such as sea ice algae, consumers such as ice fauna and predators such as sea birds. To be able to make a comprehensive seasonal and spatial comparison of lipid content and other dietary indicators throughout an Arctic food web, samples collected at each comparable location needed to be as consistent as possible on each cruise. Table 6.1 shows basic details of the planned sampling depending on sampling equipment available and time scheduled on each research cruise.

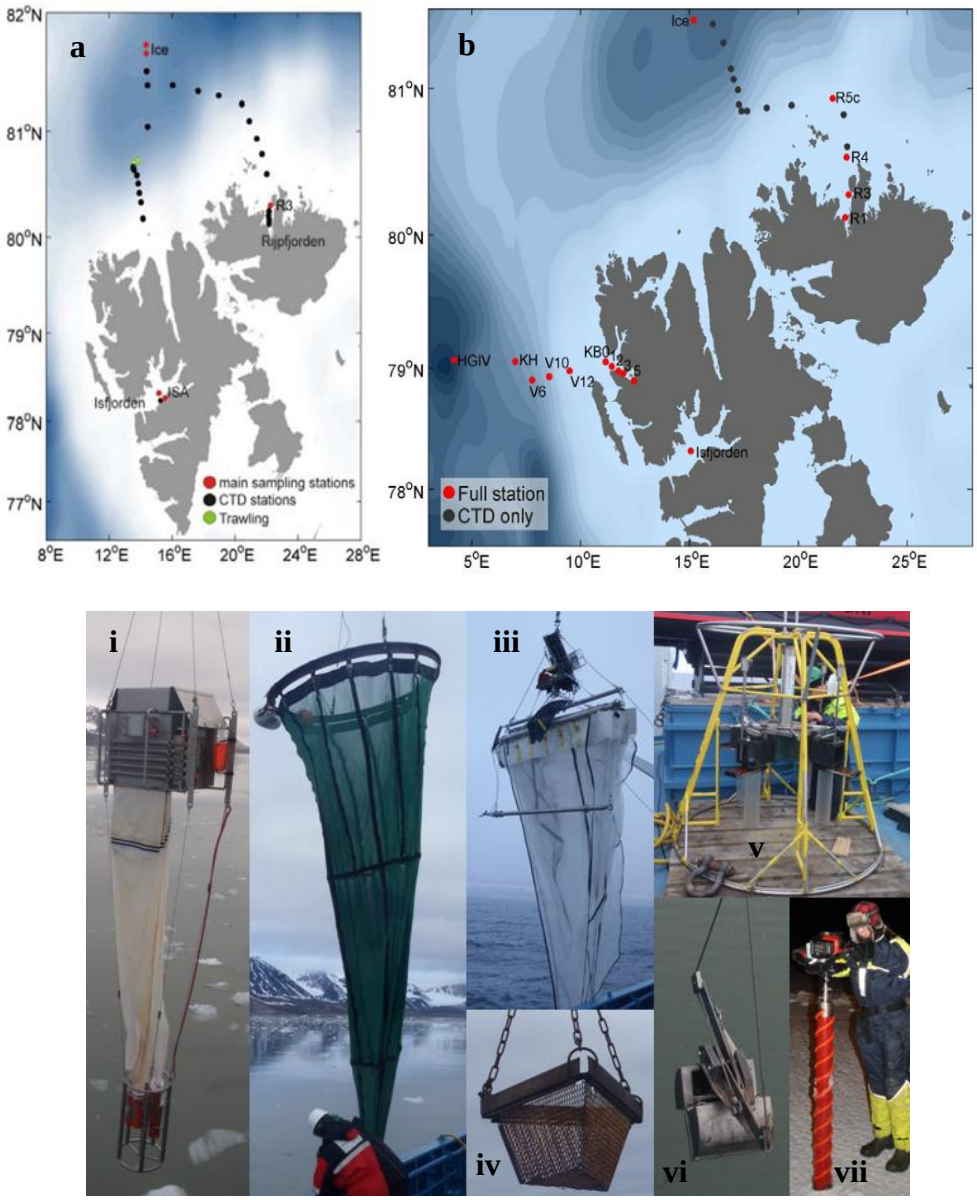


Figure 6.2. Maps of stations sampled on the **a)** Polar Night cruise (8th January 2012 to 21st January 2012) and **b)** MOSJ cruise (12th July 2012 to 21st July 2012) and sampling instruments used on the Polar Night and MOSJ cruises. **i)** Multinet, **ii)** MIK net, **iii)** Tucker Trawl, **iv)** Triangle dredge, **v)** Multicore, **vi)** Van Veen Grab, **vii)** Kovacs Ice corer. Photographs by Ashleigh Ringrose and Angelina Kraft.

Table 6.1. Sampling strategy for the Polar Night and MOSJ cruises, all samples include atleast 3 replicates of each species.

		Winter (Polar Night Cruise; January 2012)			**Summer** (MOSJ cruise; July 2012)		
Sample type	**Sample details**	**Rijpfjorden**	**West coast fjord**	**Ice edge**	**Rijpfjorden**	**West coast fjord**	**Ice edge**
Higher predators	Sea birds		x				
	Sea ice	x		x			x
	Filtered sea water	x	x	x	x	x	x
Pelagic fauna	Bulk zooplankton	x	x		x	x	
	Ice fauna						x
	Copepod	x	x		x	x	
	Chaetognath	x	x		x	x	
	Amphipod	x	x		x	x	
	Jellyfish				x	x	
	Pteropod				x	x	
	Shrimp	x	x		x	x	
	Fish including; Polar Cod, Greenland Halibut, Haddock and American Plaice.	x	x				
Epifauna	Crab	x	x		x	x	
	Bivalve	x	x		x	x	
	Starfish	x	x		x	x	
	Brittle star	x	x		x	x	
	Anemone	x	x		x	x	
Infauna	Polychaete worm	x	x		x	x	
	Sediment	x	x		x	x	

6.6 Samples obtained

The author had the opportunity to participate on the research cruises in January and July 2012 which allowed the collection of samples in accordance to the sampling strategy. Due to natural availability when sampling at some of the sampling stations, some animal species were not collected. However, the overall sample set accurately represents a basic food web with primary production, consumers and predators, from winter and summer in the Norwegian Arctic. Some extra animal samples, which were not included in the sampling strategy, were also collected, including some from locations other than the main three mentioned in the sampling strategy; Rijpfjorden, western fjords and the ice edge. Appendix 1 and Appendix 2 give full details of all samples collected on both cruises from all sampling locations.

6.7 Conclusions

The main aims of this future study are to further enhance preliminary studies using the $DSIP_{25}$ biomarker suite in Arctic food webs and to enable more established predictions to be made of possible animal population changes, due to a warming Arctic. The following outcomes have been achieved so far in preparation for the future study:

i. To design a comprehensive sampling strategy enabling analysis of lipid biomarkers in an Arctic food web
ii. To collect samples representing a full Arctic food web on the Polar Night and MOSJ cruises in the Norwegian Arctic, adhering to the sampling strategy

This future study will further elucidate the use of IP_{25} and other HBI biomarkers to follow organic matter through Arctic food webs. It may be able to provide information of the dependence of certain Arctic species on sea ice and/or open water primary production and therefore contribute to Arctic ecosystem and climate prediction models.

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APPENDIX 1. Sampling log from the Polar Night Cruise (January 2012)

Sampling station	Date	Time	GPS N	GPS E	Sampling instrument	Bottom water depth (m)	Trawled depth (m)	Co-samplers	Replicates	Type of sample	Genus	Species	Whole or sub sample
Bjornoya	11/01/12	03:30	74°44	19°15	TD	94.9	94.9	JB, JN	12	Lyre Crab	*Hyas*	*arameus*	Whole
Bjornoya	11/01/12	03:30	74°44	19°15	TD	94.9	94.9	JB, JN	5	Hermet Crab	*Pagurus*	*pubescens*	Whole
Bjornoya	11/01/12	03:30	74°44	19°15	TD	94.9	94.9	JB, JN	4	Snail	*Buccinum*	*sp.*	Whole
Bjornoya	11/01/12	03:30	74°44	19°15	TD	94.9	94.9	JB, JN	1	Spounge			Whole
Bjornoya	11/01/12	03:30	74°44	19°15	TD	94.9	94.9	JB, JN	1	Starfish	*Strongylocentrotus*	*arameus*	Whole
Bjornoya	11/01/12	03:30	74°44	19°15	TD	94.9	94.9	JB, JN	1	Starfish	*Urasterias*	*linckii*	Whole
Bjornoya	11/01/12	03:30	74°44	19°15	TD	94.9	94.9	JB, JN	1	Shrimp	*Lebbeus*	*polaris*	Whole
Bjornoya	11/01/12	03:30	74°44	19°15	TD	94.9	94.9	JB, JN	1	Starfish	*Henricia*	*sp.*	Whole
Bjornoya	11/01/12	03:30	74°44	19°15	TD	94.9	94.9	JB, JN	1	Ragworm	*Nereis*	*sp.*	Whole
Bjornoya	11/01/12	03:30	74°44	19°15	TD	94.9	94.9	JB, JN	5	Shrimp	*Lebbeus*	*polaris*	Whole
Bjornoya	11/01/12	03:30	74°44	19°15	TD	94.9	94.9	JB, JN	1	Shrimp	*Spironthocaris*	*spinus*	Whole
Bjornoya	11/01/12	03:30	74°44	19°15	TD	94.9	94.9	JB, JN	1	Bracciopod	*Hemithiris*	*psittica*	Whole
Bjornoya	11/01/12	03:30	74°44	19°15	TD	94.9	94.9	JB, JN	4	Holathurian	*Cucumaraia*	*fromdosa*	Whole
Bjornoya	11/01/12	03:30	74°44	19°15	TD	94.9	94.9	JB, JN	44	Sea Urchin	*Strongylocentrotus*	*sp.*	Whole
Rijpfjorden	12/01/12	03:30	80°19	22°15	BC	273	273	NM, EM	1	Surface sediment (0-1 cm)			
Rijpfjorden	12/01/12	09:17	80°18	22°13	BNT	268	268	ES, JB, JN	10	Atlantic Cod	*Gadus*	*morhua*	Whole
Rijpfjorden	12/01/12	09:17	80°18	22°13	BNT	268	268	ES, JB, JN	17	Polar Cod	*Boreogadus*	*saida*	Whole
Rijpfjorden	12/01/12	09:17	80°18	22°13	BNT	268	268	ES, JB, JN	4	Benthic fauna	*Liparis*	*bathyarcticus*	Whole
Rijpfjorden	12/01/12	09:17	80°18	22°13	BNT	268	268	ES, JB, JN	5	Benthic fauna	*Liparis*	*fabriai*	Whole
Rijpfjorden	12/01/12	09:17	80°18	22°13	BNT	268	268	ES, JB, JN	22	Amphipod	*Anonyx*	*nugax*	Whole
Rijpfjorden	12/01/12	09:17	80°18	22°13	BNT	268	268	ES, JB, JN	2	Fish	*Sebastes ef.*	*mentella*	Whole
Rijpfjorden	12/01/12	10:25	80°18	22°13	PNT	255	175	ES, JB, JN	3	Greenland Halibut	*Reinhardtius*	*hippoglossoides*	Whole
Rijpfjorden	12/01/12	10:25	80°18	22°13	PNT	255	175	ES, JB, JN	5	Haddock	*Helanogrammus*	*acglefinus*	Whole
Rijpfjorden	12/01/12	10:25	80°18	22°13	PNT	255	175	ES, JB, JN	1	Pelagic fauna	*Hallatus*	*villosus*	Whole
Rijpfjorden	12/01/12	10:25	80°18	22°13	PNT	255	175	ES, JB, JN	5	Fish	*Sebastes*	*sp.*	Whole
Rijpfjorden	12/01/12	10:25	80°18	22°13	PNT	255	175	ES, JB, JN	3	Unknown Shrimp			Whole
Rijpfjorden	12/01/12	10:25	80°18	22°13	PNT	255	175	ES, JB, JN	4	Fish	*Leptoclinus*	*sp.*	Whole
Rijpfjorden	12/01/12	11:46	80°19	22°11	MIK	211	75	JG, CW, AK, AW DP	3	Mass zooplankton			
Rijpfjorden	12/01/12	11:46	80°19	22°11	Deck hose	211	6		1	Sea water filtration			
Rijpfjorden	13/07/12	08:00	80°07	22°09	IC			EH, MC, TG	3	Sea ice algae (0-3cm)			
Rijpfjorden	13/07/12	08:00	80°07	22°09	IC			EH, MC, TG	3	Sea ice algae (3-10cm)			
Rijpfjorden	12/01/12	03:30	80°19	22°15	BC	273	273	NM, EM	1	Sediment infauna bulk			Whole
Rijpfjorden	13/01/12	14:40	80°18	22°14	RP	270	270		11	Starfish	*Asteris*	*sp.*	Whole

Rijpfjorden	13/01/12	14:40	80°18	22°14	RP	270	270		9	Ananome Type 1 + Mollusc	*Allantacis*	*sp.*	Whole
Rijpfjorden	13/01/12	14:40	80°18	22°14	RP	270	270		4	Scale Worm			Whole
Rijpfjorden	13/01/12	14:40	80°18	22°14	RP	270	270		1	Spider Crab with ananome			Whole
Rijpfjorden	13/01/12	14:40	80°18	22°14	RP	270	270		5	Brittlestar	*Ophiura*	*sp.*	Whole
Rijpfjorden	13/01/12	14:40	80°18	22°14	RP	270	270		19	Rag worms			Whole
Rijpfjorden	13/01/12	14:40	80°18	22°14	RP	270	270		1	Atlantic Poacher			Whole
Rijpfjorden	13/01/12	14:40	80°18	22°14	RP	270	270		1	Eel pout	*Lycodes*	*Esmarki*	Whole
Rijpfjorden	13/01/12	14:40	80°18	22°14	RP	270	270		1	Icelus bicornis			Whole
Rijpfjorden	12/01/12	10:25	80°18	22°13	PNT	255	175	AK	5	Amphipod	*Themisto*	*libellula*	Whole
Rijpfjorden	12/01/12	03:30	80°19	22°15	BC	273	273	NM, EM	9	Sediment cores (1 cm horizons)			
Rijpfjorden	12/01/12	03:30	80°19	22°15	BC	273	273	NM, EM		Sediment Food			
Rijpfjorden	12/01/12	03:30	80°19	22°15	BC	273	273	NM, EM		Fluorescent Beads			
Ice station	14/01/12	15:00			Deck hose		6			Filtered sea water			
Ice station	15/01/12	02:00	81°44	14°02	IC			EH, TG	3	Filtered sea ice (0-3cm)			
Ice station	15/01/12	02:00	81°44	14°02	IC			EH, TG	3	Filtered sea ice (3-10cm)			
Shelf Break	16/01/12	03:12	80°34	13°48	BNT	685	685	JN, CW, AK, ES	4	Greenland Hallibut Full stomach	*Reinhardtius*	*hippoglossoides*	Sub
Shelf Break	16/01/12	03:12	80°34	13°48	BNT	685	685	JN, CW, AK, ES	4	Greenland Hallibut Muscle tissue	*Reinhardtius*	*hippoglossoides*	Sub
Shelf Break	16/01/12	03:12	80°34	13°48	BNT	685	685	JN, CW, AK, ES	7	Atlantic Cod liver	*Gadus*	*morhua*	Sub
Shelf Break	16/01/12	03:12	80°34	13°48	BNT	685	685	JN, CW, AK, ES	7	Atlantic Cod Muscle	*Gadus*	*morhua*	Sub
Shelf Break	16/01/12	03:12	80°34	13°48	BNT	685	685	JN, CW, AK, ES	5	American Plaice	*Hippoglassoides*	*platessoides*	Whole
Shelf Break	16/01/12	03:12	80°34	13°48	BNT	685	685	JN, CW, AK, ES	4	Red Fish Full stomach	*Sebastes*	*sp.*	Sub
Shelf Break	16/01/12	03:12	80°34	13°48	BNT	685	685	JN, CW, AK, ES	4	Red Fish Muscle Tissue	*Sebastes*	*sp.*	Sub
Shelf Break	16/01/12	03:12	80°34	13°48	BNT	685	685	JN, CW, AK, ES	1	Shrimp Eggs			Whole
Shelf Break	16/01/12	03:12	80°34	13°48	BNT	685	685	JN, CW, AK, ES	5	Shrimp			Whole
Shelf Break	16/01/12	03:12	80°34	13°48	BNT	685	685	JN, CW, AK, ES	1	Octopus			Whole
Shelf Break	16/01/12	03:12	80°34	13°48	BNT	685	685	JN, CW, AK, ES	2	Squid	*Gonadus*	*fabricii*	Whole
Shelf Break	16/01/12	03:12	80°34	13°48	BNT	685	685	JN, CW, AK, ES	3	Polar Cod	*Boreogadus*	*saida*	Whole
Shelf Break	16/01/12	03:12	80°34	13°48	BNT	685	685	JN, CW, AK, ES	1	Starfish	*Grossaster*	*papposus*	Whole
Shelf Break	16/01/12	03:12	80°34	13°48	BNT	685	685	JN, CW, AK, ES	2	Sea Urchin	*Strongylocyntrotus*	*droebranchiensis*	Whole
Isfjorden	17/01/12	19:57	78°19	15°05	MIK	269	250	AK, JG, CW	2	Bulk zooplankton			Whole
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	4	Sea Tadpole Full Stomach	*Careproctus*	*reinhardti*	Sub
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW,	4	Sea Tadpole	*Careproctus*	*reinhardti*	Sub

								ES		Muscle			
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	4	Atlantic Cod Full Stomach	*Gadus*	*morhua*	Sub
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	4	Atlantic Cod Muscle	*Gadus*	*morhua*	Sub
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	3	American Plaice Full Stomach	*Hippoglassoides*	*platessoides*	Sub
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	3	American Plaice Full Muscle	*Hippoglassoides*	*platessoides*	Sub
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES		Parasites			Whole
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	3	Red Fish Full Stomach	*Sebastes*	*sp.*	Sub
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	3	Red Fish Full Muscle	*Sebastes*	*sp.*	Sub
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	2	Haddock	*Helanogrammus*	*acglefinus*	Whole
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	4	Atlantic Poacher	*Agonus*	*decagonus*	Whole
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	1	Crab	*Hyas*	*areneaus*	Whole
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	1	Atlantic Spiny lumpsucker	*Eumicrotremus*	*spinosus*	Whole
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	1	Bivalve	*Giliatocasdinin*	*ciliatum*	Whole
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	2	Snail	*Bucciunum*	*sp.*	Whole
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	1	Brittlestar	*Ophiosolpx*	*glacialis*	Whole
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	2	Amphipod	*Stegocephalus*	*inflatus*	Whole
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	3	Snakeblenny	*Lumpenus*	*lampretaeformis*	Whole
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	3	Shrimp	*Pandullus*	*borealis*	Whole
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	5	Polar Cod Liver	*Boreogadus*	*saida*	Sub
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK, JB, CW, ES	1	Bulk shrimp eggs			Whole
Isfjorden	17/01/12	17:45	78°18	15°12	BNT	274	274	AK	5	Amphipod	*Anonyx*	*nugax*	Whole
Adventfjorden	17/01/12	22:08	78°16	15°31	MIK	98	35	JG	1	Bulk chaetognaths			Whole
Adventfjorden	17/01/12		78°16	15°31	Shot gun			JB	2	Brunnich's Guillemot	*Uria*	*lomvia*	Whole
Isfjorden	18/01/12	01:29	78°20	15°08	BC	268	268	NM, EM	1	Sediment core (1 cm horizons)			

APPENDIX 2. Sampling log from the MOSJ cruise (July 2012)

Sampling station	Date	Time	GPS N	GPS E	Sampling instrument	Bottom water depth (m)	Trawled depth (m)	Co-samplers	Replicates	Type of sample	Genus	Species	Whole or sub sample
KB5	13/07/12	01:45	78°53	12°26	TD	49	49	WA, NM	1	Surface sediment (0-1 cm)			
KB5	13/07/12	01:45	78°53	12°26	TD	49	49	WA, NM	2	Starfish	*Henricia*	*sp.*	Whole
KB5	13/07/12	01:45	78°53	12°26	TD	49	49	WA, NM	1	Worm - Siponculide			Whole
KB5	13/07/12	01:45	78°53	12°26	TD	49	49	WA, NM	1	Clam	*Macoma*	*calcarea*	Whole
KB5	13/07/12	01:45	78°53	12°26	TD	49	49	WA, NM	2	Fish - Spotted sname blenny	*Leptoclinus*	*maculatus*	Whole
KB3	13/07/12	09:30	78°57	11°57	MN	336	20-0	JS, DF	33	Jellyfish	*Mertensia*	*ovum*	Whole
KB3	13/07/12	10:30	78°57	11°57	MIK	336	336-0	MD, AW	105	Amphipod	*Themisto*	*libellua*	Whole
KB3	13/07/12	10:30	78°57	11°57	MIK	336	336-0	MD, AW	97	Krill	*Thysanoessa*	*sp.*	Whole
KB3	13/07/12	10:30	78°57	11°57	MIK	336	336-0	MD, AW	80	Chaetognaths	*Sagilta*	*sp.*	Whole
KB3	13/07/12	10:30	78°57	11°57	MIK	336	336-0	MD, AW	1	Bulk zooplankton			Whole
KB3	13/07/12	10:30	78°57	11°57	MIK	336	336-0	MD, AW	2	Bulk Calanus	*Calanus*	*hyperboreus, glacialis and finmarchicus*	Whole
KB3	13/07/12	10:30	78°57	11°57	BR	336	1		1	Filtered sea water			
KB3	13/07/12	AM	78°57	11°57	SP	336	0-3cm	MM	1	Surface sediment (0-1 cm)			
KB3	13/07/12	AM	78°57	11°57	WP3	336	50-0	JS, DF	36	Jellyfish	*Mertensia*	*ovum*	Whole
Gludneset	13/07/12	AM	78°54	12°07	ID	22	22	HH, WA, MV, JR, PL, CW	6	Adductor Muscle	*Serripes*	*groenlandicus*	Sub
Gludneset	13/07/12	AM	78°54	12°07	ID	22	22	HH, WA, MV, JR, PL, CW	6	Foot	*Serripes*	*groenlandicus*	Sub
Gludneset	13/07/12	AM	78°54	12°07	ID	22	22	HH, WA, MV, JR, PL, CW	6	Digestive gland inc stomach	*Serripes*	*groenlandicus*	Sub
Gludneset	13/07/12	AM	78°54	12°07	ID	22	22	HH, WA, MV, JR, PL, CW	6	Intestines	*Serripes*	*groenlandicus*	Sub
Gludneset	13/07/12	AM	78°54	12°07	ID	22	22	HH, WA, MV, JR, PL, CW	2	Foot	*Mya*	*trancata*	Sub
Gludneset	13/07/12	AM	78°54	12°07	ID	22	22	HH, WA, MV, JR, PL, CW	5	Adductor Muscle	*Mya*	*trancata*	Sub
Gludneset	13/07/12	AM	78°54	12°07	ID	22	22	HH, WA, MV, JR, PL, CW	6	Digestive gland inc stomach	*Mya*	*trancata*	Sub
KB0	14/07/12	AM	79°02	11°07	BR	322	1		1	Filtered sea water			
KB0	14/07/12	AM	79°02	11°07	MIK	322	322-0	MD, AW	9	Jellyfish	*Beroe*	*Cucumis*	Whole
KB0	14/07/12	AM	79°02	11°07	MIK	322	322-0	MD, AW	79	Chaetognaths	*Sagritta and Ehkrohnia*	*elegans and hamata*	Whole
KB0	14/07/12	AM	79°02	11°07	MIK	322	322-0	MD, AW	6	Jellyfish	*Mertensia*	*ovum*	Whole
KB0	14/07/12	AM	79°02	11°07	MIK	322	322-0	MD, AW	90	Amphipods	*Themisto*	*Abyssorum*	Whole
KB0	14/07/12	AM	79°02	11°07	MIK	322	322-0	MD, AW	54	Amphipods	*Themisto*	*libellua*	Whole
KB0	14/07/12	AM	79°02	11°07	MIK	322	322-0	MD, AW	110	Calanus	*Calanus*	*hyperboreus*	Whole
KB0	14/07/12	AM	79°02	11°07	MIK	322	322-0	MD, AW	4	Krill	*Meganycthiphanes*	*norvegica*	Whole
KB0	14/07/12	AM	79°02	11°07	MIK	322	322-0	MD, AW	2	Krill	*Thysanoessa*	*inermis*	Whole
KB0	14/07/12	AM	79°02	11°07	MIK	322	322-0	MD, AW	2	Krill	*Thysanoessa*	*longicaudata*	Whole
KB0	14/07/12	AM	79°02	11°07	MIK	322	322-0	MD, AW	1	Bulk Calanus	*Calanus*	*finmarchicus, glacialis and few hyperboreus*	Whole
Princecarles Forlandet	14/07/12	PM	78°47	11°01	ID	10	10	HH, WA, MV, JR, PL, CW	6	Foot	*Serripes*	*groenlandicus*	Sub
Princecarles	14/07/12	PM	78°47	11°01	ID	10	10	HH, WA, MV,	6	Digestive gland inc	*Serripes*	*groenlandicus*	Sub

Forlandet								JR, PL, CW		stomach			
Princecarles Forlandet	14/07/12	PM	78°47	11°01	ID	10	10	HH, WA, MV, JR, PL, CW	6	Intestines	*Serripes*	*groenlandicus*	Sub
Princecarles Forlandet	14/07/12	PM	78°47	11°01	ID	10	10	HH, WA, MV, JR, PL, CW	6	Adductor muscle	*Serripes*	*groenlandicus*	Sub
Princecarles Forlandet	14/07/12	PM	78°47	11°01	ID	10	10	HH, WA, MV, JR, PL, CW	2	Whole clam	*Mya*	*trancata*	Whole
Princecarles Forlandet	14/07/12	PM	78°47	11°01	ID	10	10	HH, WA, MV, JR, PL, CW	5	Whole clam	*Serripes*	*groenlandicus*	Whole
Brardalspynten	13/07/12	PM	78°56	11°51	ID	15	15	HH, WA, MV, JR, PL, CW	5	Foot	*Serripes*	*groenlandicus*	Sub
Brardalspynten	13/07/12	PM	78°56	11°51	ID	15	15	HH, WA, MV, JR, PL, CW	5	Digestive gland inc stomach	*Serripes*	*groenlandicus*	Sub
Brardalspynten	13/07/12	PM	78°56	11°51	ID	15	15	HH, WA, MV, JR, PL, CW	5	Intestines	*Serripes*	*groenlandicus*	Sub
Brardalspynten	13/07/12	PM	78°56	11°51	ID	15	15	HH, WA, MV, JR, PL, CW	5	Adductor muscle	*Serripes*	*groenlandicus*	Sub
V6	14/07/12	01:45	78°54	07°45	MIK	1132	1000-0	MD	60	Chaetognaths	*Sagilta and Eukrohnia*	*sp. and hamata*	Whole
V6	14/07/12	01:45	78°54	07°45	MIK	1132	1000-0	MD	76	Calanus	*Calanus*	*hyperboreus*	Whole
V6	14/07/12	01:45	78°54	07°45	MIK	1132	1000-0	MD	56	Amphipods	*Themisto*	*abyssorum*	Whole
V6	14/07/12	01:45	78°54	07°45	MIK	1132	1000-0	MD	76	Amphipods	*Themisto*	*libellua*	Whole
V6	14/07/12	01:45	78°54	07°45	MIK	1132	1000-0	MD	1	Bulk zooplankton			Whole
V6	14/07/12	01:45	78°54	07°45	MIK	1132	1000-0	MD	2	Jellyfish	*Beroê*	*cucumis*	Whole
V6	14/07/12	01:45	78°54	07°45	MIK	1132	1000-0	MD	8	Krill	*Meganycthiphanes*	*norvegica*	Whole
V6	14/07/12	01:45	78°54	07°45	MIK	1132	1000-0	MD	50	Copepod	*Euchacta*	*norvegica*	Whole
V6	14/07/12	01:45	78°54	07°45	MIK	1132	1000-0	MD	9	Copepod	*Euchacta*	*barbarta*	Whole
V6	14/07/12	01:45	78°54	07°45	MIK	1132	1000-0	MD	1	Zooplankton	*Cyclocaris*	*guilelmi*	Whole
R3(a)	16/07/12	00:00	80°17	22°17	BR	244	1		1	Filtered sea water			
R3(a)	16/07/12	00:00	80°17	22°17	TT	244	225-0	CW	2	Ice fauna	*Apherusa*	*glacialis*	Whole
R3(a)	16/07/12	00:00	80°17	22°17	TT	244	225-0	CW	22	Ice fauna	*Gammerus*	*witziki*	Whole
R3(a)	16/07/12	00:00	80°17	22°17	TT	244	225-0	CW	7	Jellyfish	*Beroë*	*cucumis*	Whole
R3(a)	16/07/12	00:00	80°17	22°17	TT	244	225-0	CW	42	Jellyfish	*Euphysia*	*flammae*	Whole
R3(a)	16/07/12	00:00	80°17	22°17	TT	244	225-0	CW	5	Jellyfish	*Beroë*	*cucumis*	Whole
R3(a)	16/07/12	00:00	80°17	22°17	TT	244	225-0	CW	5	Fish larvae			Whole
R3(a)	16/07/12	02:30	80°17	22°17	MIK	244	220	CW	3	Bulk zooplankton			Whole
R3(a)	16/07/12	02:30	80°17	22°17	MIK	244	220	CW	2	Bulk calanus			Whole
R3(a)	16/07/12	02:30	80°17	22°17	MIK	244	75	CW	14	Pterrepod	*Clione*	*limacina*	Whole
R3(a)	16/07/12	00:00	80°17	22°17	TT	244	225-0	CW	96	Krill	*Thysanoessa*	*inermis*	Whole
R3(a)	16/07/12	12:30	80°17	22°17	MIK	272	20	CW	8	Jellyfish	*Mertensia*	*ovum*	Whole
R3(a)	16/07/12	12:30	80°17	22°17	MIK	272	20	CW	55	Jellyfish	*Euphysia*	*flammae*	Whole
R3(a)	16/07/12	12:30	80°17	22°17	MIK	272	20	CW	12	Krill	*Thysanoessa*	*inermis*	Whole
R3(a)	16/07/12	12:30	80°17	22°17	MIK	272	20	CW	62	Pterrepod	*Limacina*	*helincina*	Whole
R3(a)	16/07/12	12:30	80°17	22°17	MIK	272	75	CW	44	Jellyfish	*Euphysia*	*flammae*	Whole
R3(b)	15/07/12	08:47	80°25	22°02	VVG	208	208	WA, NM	1	Brittlestar	*Ophiura*	*bidentata*	Whole
R3(b)	15/07/12	08:47	80°25	22°02	VVG	208	208	WA, NM	4	Brittlestar	*Ophiura*	*satsi*	Whole
R3(b)	15/07/12	08:47	80°25	22°02	VVG	208	208	WA, NM	2	Clam	*Astarte*	*sulcata*	Whole
R3(c)	17/07/12	02:20	80°19	22°15	VVG	265	265	WA, NM, JR	1	Surface sediment (0-1 cm)			
R3(c)	17/07/12	02:20	80°19	22°15	VVG	265	265	WA, NM, JR	3	Polycheate worm			Whole
R3(c)	17/07/12	02:20	80°19	22°15	MC	265	265	WA, NM, JR	2	Sediment core (1 cm horizons)			
Vinbukta	16/07/12	11:00	80°17	22°32	ID	20	20	HH, WA, MV, JR, PL, CW	9	Brittlestar	*Ophiopholis*	*aculeata*	Whole
Vinbukta	16/07/12	11:00	80°17	22°32	ID	20	20	HH, WA, MV, JR, PL, CW	6	Foot	*Serripes*	*groenlandicus*	Sub

Vinbukta	16/07/12	11:00	80°17	22°32	ID	20	20	HH, WA, MV, JR, PL, CW	6	Digestive gland inc stomach	*Serripes*	*groenlandicus*	Sub
Vinbukta	16/07/12	11:00	80°17	22°32	ID	20	20	HH, WA, MV, JR, PL, CW	6	Intestines	*Serripes*	*groenlandicus*	Sub
Vinbukta	16/07/12	11:00	80°17	22°32	ID	20	20	HH, WA, MV, JR, PL, CW	6	Adductor muscle	*Serripes*	*groenlandicus*	Sub
Vinbukta	16/07/12	11:00	80°17	22°32	ID	20	20	HH, WA, MV, JR, PL, CW	2	Whole clam	*Serripes*	*groenlandicus*	Whole
R1	16/07/12	20:15	80°07	22°09	VVG	190	1		1	Surface sediment (0-1 cm)			
R1	16/07/12	20:15	80°07	22°09	BR	190	1		1	Filtered sea water			
R1(b)	16/07/12	16:45	80°13	22°22	BR		1		1	Filtered sea water			
Erkna Island	16/07/12	21:00	80°09	22°18	ID	23	23	HH, WA, MV, JR, PL, CW	8	Sea Urchin	*Strongylocentrotus*	*sp.*	Whole
Erkna Island	16/07/12	21:00	80°09	22°18	ID	23	23	HH, WA, MV, JR, PL, CW	2	Spider Crab			Whole
Erkna Island	16/07/12	21:00	80°09	22°18	ID	23	23	HH, WA, MV, JR, PL, CW	6	Digestive gland inc stomach	*Serripes*	*groenlandicus*	Sub
Erkna Island	16/07/12	21:00	80°09	22°18	ID	23	23	HH, WA, MV, JR, PL, CW	6	Intestines	*Serripes*	*groenlandicus*	Sub
Erkna Island	16/07/12	21:00	80°09	22°18	ID	23	23	HH, WA, MV, JR, PL, CW	6	Adductors Muscle	*Serripes*	*groenlandicus*	Sub
Erkna Island	16/07/12	21:00	80°09	22°18	ID	23	23	HH, WA, MV, JR, PL, CW	4	Whole clam	*Serripes*	*groenlandicus*	Whole
Parry Island	17/07/12	13:00	80°38	20°47	ID	20	20	HH, WA, MV, JR, PL, CW	1	Crab	*Hyas*	*sp.*	Whole
Parry Island	17/07/12	13:00	80°38	20°47	ID	20	20	HH, WA, MV, JR, PL, CW	6	Sea Urchin insides	*Strongylocentrotus*	*sp.*	Sub
Parry Island	17/07/12	13:00	80°38	20°47	ID	20	20	HH, WA, MV, JR, PL, CW	1	Starfish	*Henricia*	*sp.*	Whole
Parry Island	17/07/12	13:00	80°38	20°47	ID	20	20	HH, WA, MV, JR, PL, CW	1	Welk			Whole
Parry Island	17/07/12	13:00	80°38	20°47	ID	20	20	HH, WA, MV, JR, PL, CW	2	Clam	*Mya*	*trancata*	Whole
Parry Island	17/07/12	13:00	80°38	20°47	ID	20	20	HH, WA, MV, JR, PL, CW	2	Clam	*Hiatella*	*arctica*	Whole
Parry Island	17/07/12	13:00	80°38	20°47	ID	20	20	HH, WA, MV, JR, PL, CW	1	Anamone			Whole
Parry Island	17/07/12	13:00	80°38	20°47	ID	20	20	HH, WA, MV, JR, PL, CW	6	Clam Insides (except foot)	*Mya*	*trancata*	Sub
R4	17/07/12	09:30	80°32	22°12	MIK	220	200-0	AW, MD	1	Ice fauna	*Gammaruz*	*wilkitzki*	Whole
R4	17/07/12	09:30	80°32	22°12	MIK	220	200-0	AW, MD	2	Ice fauna	*Onisimus*	*glacialis*	Whole
R4	17/07/12	09:30	80°32	22°12	VVG	220	220	WA	1	Surface sediment (0-1 cm)			
R5	17/07/12	11:00	80°55	21°26	VVG	220	220	WA, NM, JR	1	Surface sediment (0-1 cm)			
R5	17/07/12	11:00	80°55	21°26	VVG	220	220	WA, NM, JR	1	Brittlestar	*Ophiopholis*	*aculeata*	Whole
Ice station	18/07/2012	17:00	81°23	15°13	IC	2200		JW, AnK MM	3	Filtered sea ice (0-3cm)			
Ice station	18/07/2012	17:00	81°23	15°13	IC	2200		JW, AnK MM	3	Filtered sea ice (3-10cm)			
Ice station	18/07/2012	19:00	81°23	15°13	MIK	2200	1300-0	AW, MD	51	Copepod	*Calanus*	*hyperboreus*	Whole
Ice station	18/07/2012	19:00	81°23	15°13	MIK	2200	1300-0	AW, MD	8	Amphipod	*Themisto*	*libellua*	Whole

Ice station	18/07/2012	19:00	81°23	15°13	MIK	2200	1300-0	AW, MD	16	Amphipod	*Themisto*	*abyssorum*	Whole
Ice station	18/07/2012	19:00	81°23	15°13	MIK	2200	1300-0	AW, MD	20	Chaetognaths	*Sagilta*	*sp.*	Whole
Ice station	18/07/2012	19:00	81°23	15°13	MIK	2200	1300-0	AW, MD	5	Amphipods	*Cyclocaris*	*guilelmi*	Whole
Ice station	18/07/2012	22:00	81°23	15°13	ID - SP	2200	6-7	HH, MV, CW, PL, JR	4	Ice fauna	*Onisimis*	*nanseni*	Whole
Ice station	18/07/2012	22:00	81°23	15°13	ID - SP	2200	6-7	HH, MV, CW, PL, JR	7	Ice fauna	*Onisimis*	*glacialis*	Whole
Ice station	18/07/2012	22:00	81°23	15°13	ID - SP	2200	6-7	HH, MV, CW, PL, JR	186	Ice fauna	*Apherosa*	*glacialis*	Whole
Ice station	18/07/2012	22:00	81°23	15°13	ID - SP	2200	6-7	HH, MV, CW, PL, JR	5	Ice fauna	*Gammarus*	*wilkitzkii*	Whole
Ice station	18/07/2012	22:00	81°23	15°13	ID - SP	2200	6-7	HH, MV, CW, PL, JR	1	Ice algae			Sub
Ice station	18/07/2012	22:00	81°23	15°13	ID - SP	2200	6-7	HH, MV, CW, PL, JR	1	Polar Cod	*Boreogadus*	*saida*	Whole
Isfjorden	21/07/12	09:45	78°19	15°08	SC	262	262	WA, NM, JR	2	Sediment cores (1 cm horizons)			

Sampling instrument	
BC	Box core
BNT	Bottom net trawl
BR	Bucket and rope
IC	Ice corer
ID	Ice divers
ID-SP	Ice divers – suction pump
MC	Multi-core
MIK	MIK net
PNT	Pelagic net trawl
RP	RP sledge
SC	Single core
SP	Sediment probe
TD	Triangle dredge
TT	Tucker trawl
VVG	Van Veen Grab
WP3	WP3 net

Co-samplers		
AK	Angelina Kraft	AWI
AnK	Anna Kubiszyn	IOPAS
AW	Annette Wold	NPI
CW	Claire Webster	University of St Andrews
DF	Daniella Freese	UNIS/AWI
DP	David Pond	BAS
EH	Else Hegseth	UiT
EM	Emma Michaud	LEMAR
ES	Eike Stubbner	UNIS
HH	Haakon Hop	NPI
JB	Jorgen Berge	UNIS
JG	Jordan Grigor	Universite Laval
JN	Jasmine Nahrgang	UNIS
JR	Joellë Richard	LEMAR
JS	Janne Søreide	UNIS
JW	Jozef Wictor	IOPAS
MC	Maria Calleja	CSIC
MD	Malin Daase	NPI
MM	Miriam Marquardt	UNIS
MV	Mikko Vihtakari	NPI
NM	Nathalie Morata	LEMAR
PL	Peter Leopold	NPI
TG	Tove Gabrielsen	UNIS
WA	William Ambrose	APN

Blank