BIOGEOCHEMISTRY OF BENTHIC BOUNDARY LAYER ZOOPLANKTON AND PARTICULATE ORGANIC MATTER ON THE BEAUFORT SEA SHELF

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By

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Abstract

Food webs of benthic boundary layer zooplankton and the biogeochemistry of near-bottom water on the Beaufort Sea shelf were studied during fall 2003 and summer 2004. The influence of the Mackenzie River on the source, quantity, and quality of organic matter in near-bottom waters across the Beaufort Sea shelf was investigated by integrating chlorophyll, fatty acid, C, N, and P concentration and ratio, and $\delta^{13}C$ data of particulate organic matter (POM). The Mackenzie River had a strong influence on the composition of POM in near-bottom waters across the entire Beaufort Sea shelf, including the Amundsen Gulf, with terrestrial markers, such as POM concentrations, fatty acid signatures and $\delta^{13}C$ values, strongest near the river. An enhanced microbial fingerprint on near-bottom waters near the river was also observed based on C:N ratios and bacterial fatty acid signatures. Fatty acids allowed detection of a phytoplankton sinking event during summer that would not have been apparent using only C:N ratios and chlorophyll *a*. In addition, elemental composition (C, N, and P content and stoichiometry), lipid classes, fatty acids, and stable isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) were used to study the diets and energy storage of 26 taxa of benthic boundary layer zooplankton. This is the first report of the biochemical composition and trophic ecology of many of the amphipods and mysids presented here. Almost all taxa had high levels of wax esters or triacylglycerol, suggesting that benthic boundary layer zooplankton on the Beaufort Sea shelf are directly linked to intense seasonal pulses of primary production characteristic of high latitude seas. $\delta^{15}N$ and fatty acid signatures indicate that there were diverse feeding modes among the taxa with trophic levels ranging from 2 - 4. Fatty acid profiles not only reflected diet but also phylogeny, with taxa of malacostracan crustaceans

having similar fatty acid profiles. Phytoplankton fatty acid markers in copepods and chaetognaths indicate that the conventional, phytoplankton-copepod-chaetognath food web was also present in the benthic boundary layer. Using multiple biomarkers and tracers allowed for increased understanding of zooplankton feeding ecology and the sources of organic matter in near-bottom waters.

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This thesis is dedicated to my parents.

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List of Abbreviations

ALC	Alcohol
AMPL	Acetone-mobile polar lipids
BBL	Benthic boundary layer
C	Carbon
CASES	Canadian Arctic Shelf Exchange Study
CF-IRMS	Continuous flow-ion ratio mass spectrometry
CTD	Conductivity, temperature, depth
CV	Coefficient of variation
DHA	Docosahexaenoic acid (22:6ω3)
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DON	Dissolved organic nitrogen
DOP	Dissolved organic phosphorus
DS	Discriminant score
DW	Dry weight
EPA	Eicosapentaenoic acid (20:5ω3)
FA	Fatty acid
FFA	Free fatty acid
FID	Flame ionization detector
GC	Gas chromatograph
HC	Hydrocarbon
KET	Ketone
Lg	Length
LOOCV	Leave-one-out cross validation

MS	Mass spectrometer
MUFA	Monounsaturated fatty acids
N	Nitrogen
ns	Not significant
OBFA	Odd-numbered and/or branched-chain fatty acids
P	Phosphorus
PH	Peak height
PL	Phospholipid
POC	Particulate organic carbon
POM	Particulate organic matter
PON	Particulate organic nitrogen
PP	Particulate phosphorus
PUFA	Polyunsaturated fatty acids
SE	Steryl ester
SFA	Saturated fatty acids
ST	Sterol
TDN	Total dissolved nitrogen
TDP	Total dissolved phosphorus
TG	Triacylglycerol
TL	Trophic level
TLip	Total lipid
WE	Wax ester

CHAPTER 1

INTRODUCTION

1.1. CARBON CYCLING AND THE ARCTIC OCEAN

Continental shelves are important in the cycling of organic carbon because they are sites of high biological production, they control the transfer of organic and inorganic matter from land to ocean, and they are important locations for the recycling and sequestering of organic carbon in the world's oceans. The Arctic Ocean is < 3% of the world's oceans by area but contributes about 20% to the world's continental shelves. Defining characteristics of the Arctic Ocean include the largest relative proportion of continental shelves (> 50% by area) of all oceans (Jakobsson et al. 2004), extensive seasonal and permanent ice cover (Parkinson et al. 1999), and extreme seasonal flux of freshwater and sediment from major Eurasian and North American rivers (Rachold et al. 2004). These factors have important consequences for food webs and biogeochemical cycles of organic matter in the Arctic Ocean.

Biological communities in Arctic seas are subject to extreme temporal variability, confounded by strong spatial variability. Seasonality is expressed locally in changing sea-ice coverage, day length, river input, and mixing of water masses by tides and winds. These physical forces have strong impacts on primary production through changing stratification, light, and nutrient availability, which influence organic matter fluxes and the function and structure of Arctic food webs. Longhurst (1998), recognizing the unique influence of sea ice on stratification and, therefore on primary production and community

structure, argues for the existence of a distinct polar biome, where low-salinity surface waters, following spring melt at the ice-margins, restrict vertical mixing.

Sea ice is a unique aspect of high latitude marine ecosystems that prevents a direct relationship between sunlight and biological productivity (Maykut and Grenfell 1975). Even within a seemingly uniform ice cap across polar seas, sea ice is not always continuous. Cracks, leads, and polynyas can open up, creating localized areas of open water that, along with conditions at the ice-margin, create different environmental regimes than those directly under ice (Eicken 1992). These areas of localized open water, particularly polynyas, often have enhanced biological activity (Stirling 1997). The extent of snow, melt ponds, and sediment on top of the ice can also impact the light levels below (Perovich et al. 1998). These spatial and temporal variations in sea ice coverage and degradation regulate the timing, location, and magnitude of primary production in the Arctic Ocean (Sakshaug 2004, Wassman et al. 2006).

A marine carbon source unique to ice-covered waters is ice algae. When ice melts, high concentrations of biogenic material (living and dead algal and bacterial cells, proto- and metazoan faecal pellets, dissolved organic matter) that have accumulated within the sea ice matrix are released into the water column (Legendre et al. 1992). The magnitude of this seasonal flux of organic material into the water column is not well known in the Arctic Ocean but is a large proportion of total ice algae production in other ice-covered waters (60% in Hudson Bay, Tremblay et al. 1989; 70% in McMurdo Sound, Knox 1990). Aggregates of cells and faecal pellets released during melting may become available to pelagic grazers (Tremblay et al. 1989, Michel et al. 1996) or eventually sink through the water column reaching the benthos (Legendre et al. 1992, Werner 2000, Ambrose et al. 2001). The timing and magnitude of this seasonal

pulse of organic material can have important consequences for organic carbon cycling and benthic-pelagic-ice coupling.

Increases in solar radiation and stratification during ice melt combine to produce potentially intense phytoplankton blooms at ice-margins. These blooms are highly variable and can track the receding ice-margin, persisting until nutrient concentrations decrease or grazing increases (Hegseth 1987, Sakshaug 2004). The intensity of phytoplankton production at ice-margins and on some Arctic shelves, together with decreased constancy of the timing and location of production due to dynamic physical forcing, often results in a mismatch between early-season phytoplankton blooms and grazers in Arctic seas (Wassmann 1998, Sakshaug 2004). This weakened interaction between phytoplankton and zooplankton is reflected in strong vertical fluxes of autotrophic biomass out of the euphotic zone in some Arctic seas. These vertical fluxes provide necessary food and nutrients to benthic communities (Grebmeier et al. 2006, Wassmann et al. 2006). The extreme spatial variability in phytoplankton production in high latitude seas is evident in the range of sedimentation rates of organic matter, fluxes being high near ice-margins, intermediate in open waters, and low under multiyear ice (Hebbeln and Wefer 1991, Klages et al. 2004).

In addition to phytoplankton and ice algae, terrestrial input can also supply organic carbon to marine ecosystems, especially on shelves highly influenced by rivers like those common in the Arctic Ocean (Dunton et al. 2006). One of the major uncertainties in organic carbon studies is the fate of terrestrial-organic carbon in the world's oceans (Hedges et al. 1997). The Arctic Ocean is heavily influenced by rivers, and understanding the production and utilization of terrestrial- *versus* marine-organic matter is therefore critical for constructing organic carbon budgets of the Arctic. Stein and Macdonald (2004) constructed a

carbon budget for the Arctic Ocean based on particulate organic carbon (POC) which differentiates between the fate of terrestrial and marine sources. In their model, about 1% POC from marine primary production on shelves (271×10^6 t y^{-1} for phytoplankton and 8×10^6 t y^{-1} for ice algae primary production; Sakshaug 2004) is buried on Arctic shelves, whereas about 28% of the terrestrial-organic carbon that enters the Arctic Ocean (11.5×10^6 t y^{-1} total for river discharge, coastal erosion, and eolian input to shelves) is buried on its shelves. They conclude that close to 95% of all marine source POC is respired; however, using a global average reported by Ittekkot (1988) they assume only 35% of terrestrial POC is labile and is remineralized in estuaries and in coastal regions. Using this value and disregarding dissolved organic carbon (DOC), there is a large gap between terrestrial POC input and POC sedimentation/burial, leaving about 25% terrestrial POC left for export out of the Arctic Ocean, which Stein and Macdonald (2004) assess as high but possible. According to this model, labile terrestrial POC is consumed before reaching Arctic shelves, leaving marine POC as the major fuel for marine communities on Arctic shelves. However, there is still much uncertainty about estimates and assumptions used in constructing Stein and Macdonald's (2004) Arctic carbon budget.

1.2. ARCTIC OCEAN AND CLIMATE CHANGE

Polar environments are very sensitive to anthropogenic increases in carbon dioxide and subsequent changes in the radiation balance of the Earth. Climate change models project a warmer Earth by the end of this century with more warming at high northern latitudes relative to the global average (Meehl et al. 2007). Sea ice dynamics will differ considerably from current conditions as a result of this warming, likely becoming the most dramatic and visible change in

the polar oceans. There is increasing evidence that sea ice dynamics in the Arctic are already responding to climate forcing resulting from increased levels of CO_2 (Dickson 1999, Johannessen et al. 2004, Lemke et al. 2007). Projected and observed changes in sea ice dynamics important for polar marine ecosystems include sea ice coverage, ice thickness, and the timing, magnitude and location of sea ice melt and formation (Lemke et al. 2007, Meehl et al. 2007). Overall, sea ice coverage will decrease, greater changes occurring in summer than in winter, extending the range of first-year ice and permanently ice-free waters while decreasing the range of multiyear ice (Meehl et al. 2007). Projections for the Arctic Ocean indicate an 80% loss of sea ice in summer and a 20% loss of sea ice in winter by the end of this century (Johannessen et al. 2004). These decreases in sea ice coverage will have direct impacts on Arctic ecosystems, as well as indirect impacts through increased human activity from increased shipping through Arctic waters, changes in traditional patterns of migration and hunting, and possible penetration of human communities further north.

Changes in sea ice dynamics will have a huge impact on factors that regulate primary production in the Arctic Ocean, including stratification, light, and nutrient availability (Priddle et al. 1992). Major changes in the production and cycling of organic matter and in the structure of food webs in the Arctic Ocean will result. Of relevance to climate change studies is whether biological systems can influence the fate of increased atmospheric CO_2 by responding to changes in ice coverage, temperature, freshwater inputs, and mixing of water masses (Denman et al. 1996, Sarmiento et al. 1998, Boyd and Doney 2003). The biological pump is an important regulator of CO_2 distribution within the ocean and thus is closely coupled with atmospheric CO_2 concentrations (Sarmiento and Orr 1991, Sigman and Boyle 2000). In the absence of a biological pump,

atmospheric carbon levels would be several times higher than they are today (Shaffer 1993). The input of inorganic nutrients, (thus the amount of new production), the level of export, the rate of remineralization, community composition, trophic dynamics, and the extent of utilization of inorganic nutrients in surface waters control the rate and efficiency of the biological pump (Eppley and Peterson 1979, Longhurst 1991, Sigman and Boyle 2000). Climate change as manifested in altered sea ice dynamics will affect many of these controls of the biological pump by altering nutrient input, increasing primary production, and changing community composition (Denman et al. 1996, Marchant et al. 2001). Changes in the amount, timing, and location of primary production in relation to heterotrophic activity will then dictate climate-forced flux-patterns of organic matter out of the euphotic zone.

1.3. BENTHIC BOUNDARY LAYER

The benthic boundary layer (BBL) is defined here as the portion of the sediment and the water column that is influenced by the sediment-water interface (Boudreau and Jørgensen 2001). There are strong vertical chemical and physical gradients within this dynamic near bottom zone (Thomsen 1999) that include gradients of flow, dissolved and particulate matter, heat, and energy. The BBL regulates the exchange and transport of organic matter between the water column and the sea floor and is also a reservoir for various consumer food resources resulting from sedimentation and resuspension. The quality and quantity of deposited organic matter strongly affects subsequent burial and sequestration into sediments and is heavily influenced by several processes occurring within the BBL, including decomposition during sedimentation, aggregation and disaggregation, resuspension and lateral transport, and

biological mediated activity near the sediment-water interface (Townsend et al. 1992, Auffret et al. 1994, Thomsen 1999, Rutgers van der Loeff et al. 2002). However, typical pelagic nets, box core devices, and CTC rosettes do not adequately sample this ocean realm, and therefore samples from the BBL are not often included in interdisciplinary oceanographic projects.

This ocean realm supports abundant and active microbial and invertebrate communities of pelagic and benthic origin (Ritzrau 1996, Mees and Jones 1997, Dauvin and Vallet 2006). Due to sampling difficulties little is known about the ecology of invertebrates living in the BBL, but it seems that these animals are able to exploit various food resources (Mees and Jones 1997) and can respond to seasonal pulses of phytoplankton input (Richoux et al. 2005). Still, the role of these organisms in energy flow and nutrient cycling in the Arctic and how they respond to the highly seasonal fluxes of organic matter is largely unknown.

1.4. STABLE ISOTOPES

Naturally occurring stable isotopes of carbon ($^{13}C/^{12}C$) and nitrogen ($^{15}N/^{14}N$) have been applied to Arctic marine ecosystem studies to investigate sources of organic matter, to trace primary production through food webs, and to determine trophic interactions in marine ecosystems (e.g., Hobson and Welch 1992, Goñi et al. 2000, Iken et al. 2005). The higher the value of the stable isotope signature represents a greater portion of the heavy isotope (^{13}C or ^{15}N) relative to the light isotope (^{12}C or ^{14}N) and is referred to as *heavier*, whereas a lower value is referred to as *lighter*. The basis of applying stable isotopes to ecosystems studies is that the stable isotope ratios of consumer tissue can be related to that of their diet in a predictable way. Stable isotopes also provide a time-integrated measure of diet, unlike gut content analysis which is a snapshot of the consumers latest

meal. The isotopic ratio in primary producers is lighter than that of inorganic nutrients due to fractionation against heavy isotopes during nutrient uptake, and it depends on many biotic and abiotic factors such as growth rate, taxonomy, inorganic nutrient supply, and temperature (Raven et al. 1993, Goericke et al. 1994). In addition, some autotrophs exhibit variations in their carbon-isotope signatures due to different fractionation patterns during photosynthesis (i.e. C_3 *vs* C_4 plants). Carbon typically shows little isotopic fractionation between primary producers and consumers, and can therefore be used to identify the sources of organic carbon in a consumer's diet (Fry and Sherr 1984, Hobson et al. 1995, Søreide et al. 2006). Trophic fractionation of nitrogen leads to a predictable increase in $^{15}N/^{14}N$ between adjacent trophic levels of 3 - 4‰ in ^{15}N (Hobson and Welch 1992, Post 2002, Søreide et al. 2006). Trophic position can therefore be estimated from the difference in the nitrogen isotope ratio between a consumer and the original primary producer. Carbon and nitrogen stable isotopes can provide valuable information on trophic interactions and the feeding ecology of organisms that are difficult to monitor, such as BBL zooplankton.

1.5. LIPIDS

One adaptation of polar zooplankton to the episodic food supply characteristic of high latitude seas is an ability to accumulate and store large amounts of energy as lipids when food becomes available (Lee et al. 2006). Herbivorous zooplankton probably use these energy reserves accumulated during intense phytoplankton blooms to survive periods of food shortage and to fuel gametogenesis (Conover and Siferd 1993, Hagen and Auel 2001). A lipid-driven flux of energy, characteristic of polar food webs, is associated with the efficient production and conservation of lipid by pelagic zooplankton, which is

then transferred through the food web to supply energy to higher trophic levels. In contrast to the rich lipid storage seen in many pelagic zooplankton, benthic invertebrates are generally poor in lipid storage (Graeve et al. 1997, 2001). However, compared with pelagic zooplankton, there are few studies on lipids in benthic communities in the Arctic.

Fatty acids are found in the membranes of all living organisms and are also important components of energy storage lipids and various biochemically active compounds. Certain fatty acids have known sources and are incorporated by consumers relatively unchanged. Although no single fatty acid is associated with any one species, the use of several fatty acid biomarkers in combination can strengthen interpretation of trophic interactions (Dalsgaard et al. 2003). In this way, fatty acids can be powerful tools in determining the diets of consumers and have been successfully applied in several Arctic food web studies (Stevens et al. 2004, Budge et al. 2007, Thiemann et al. 2008). Like stable isotopes, but unlike gut content analysis, fatty acids also provide a time-integrated measure of diet. Furthermore, a deficiency in polyunsaturated fatty acids (PUFA) can limit zooplankton productivity (Müller-Navarro et al. 2000), specifically the amounts of the ω3 fatty acids, 20:5ω3 and 22:6ω3, both of which are common in diatoms and dinoflagellates (Viso and Marty 1993). PUFA are important components of cell membranes of polar and benthic organisms because they may help to maintain membrane fluidity at low temperatures (Hall et al. 2002). The primary source of PUFA in marine ecosystems is phytoplankton (Dalsgaard et al. 2003), but most animals cannot synthesize PUFA *de novo*, making PUFA essential nutrients for many animals. Fatty acid signatures in water and sediments can also give important clues about the quality and source of organic carbon. Since

PUFA are more labile than saturated fatty acids, the PUFA content of water and sediments indicates the quality of organic matter available to consumers.

1.6. ELEMENTAL STOICHIOMETRY

Recently, there has been increased interest in how the elemental stoichiometries of inorganic nutrients, molecules, organisms, and ecosystems are connected with nutrient cycling, biological production, energy flow, and ecosystem function. This research has grown into the field of ecological stoichiometry (Sterner and Elser 2002). Redfield et al. (1963) found that the C:N:P (carbon:nitrogen:phosphorus) ratio of seston was fairly consistent across marine systems and resembled that of regenerated inorganic nutrients. Since then the Redfield ratio (C_{106}:N_{16}:P_1) and its successors have been used as a benchmark in biogeochemical models of various elements and for determining imbalances in nutrient uptake and regeneration (e.g. Anderson and Sarmiento 1994, Van Cappellen and Ingall 1994, Daly et al. 1999, Lenton and Watson 2000). At smaller temporal and spatial scales, deviations from the Redfield ratio do occur in phytoplankton in surface oceans and are usually the result of differences in growth rate, nutrient concentrations, taxonomy, light availability, or the loss or gain of nitrogen through denitrification and nitrogen fixation. In addition, nitrogen and phosphorus are preferentially regenerated over carbon, resulting in POM that is depleted in nitrogen and phosphorus relative to carbon as POM is exported to greater depths (Schneider et al. 2003). This variability in phytodetritus stoichiometry often means that the intraspecific variation in stoichiometry of consumers is generally more homeostatic than that of its food sources (Hessen 1992). Therefore, imbalances can occur between variable C:N:P ratios of primary producers and the static ratios of consumers. These imbalances

can have important consequences for consumer-driven nutrient cycling in various ecosystems (Sterner 1990, Elser and Urabe 1999).

1.7. BEAUFORT SEA SHELF AND CANADIAN ARCTIC SHELF EXCHANGE STUDY (CASES)

The Beaufort Sea shelf is the largest continental shelf of the North American side of the Arctic Ocean, and is composed of the Alaskan shelf (44 000 km^2), the Mackenzie shelf (65 000 km^2), and the Banks shelf (23 000 km^2) (Macdonald et al. 2004; Fig. 1.1). One of the main features of the Beaufort Sea shelf is input from the Mackenzie River directly onto the Mackenzie shelf. The Mackenzie River is the largest contributor of sediment and terrestrial-organic carbon to the Arctic Ocean and is the 4th largest contributor of freshwater input (Rachold et al. 2004). It is a highly seasonal river, discharging about 70% of its freshwater from May to September and > 90% of its sediment from June to August when the shelf is generally ice free (Macdonald et al. 1995). The Beaufort Sea shelf usually starts to freeze in mid-October. During freezing, a zone of landfast ice forms out to about the 20 m isobath. Seaward of the landfast ice, a persistent flaw lead forms where the immobile landfast ice is scoured by the Arctic pack ice circulating counterclockwise with the Beaufort Gyre. At the outer edge of the landfast ice, a stamukhi zone forms. The stamukhi zone is characterized by an ice ridge that can extend downward to the sea floor and limits outflow from the Mackenzie River during winter (Macdonald et al. 1995). Eastward of the Mackenzie shelf is the Amundsen Gulf, which is a site of a reoccurring polynya that forms a continuum between the flaw leads of the Mackenzie shelf and those of the Banks shelf. The seasonal and variable ice

coverage across the Beaufort Sea shelf is most likely important for biological production and organic carbon fluxes.

Research for this thesis was done as part of the Canadian Arctic Shelf Exchange Study (CASES) project. CASES was a year-long, interdisciplinary research project that investigated the impact of the Mackenzie River and sea-ice dynamics on carbon budgets of the Beaufort Sea shelf. The central hypothesis for CASES was that "the atmospheric, oceanic and hydrologic forcing of sea ice variability dictates the nature and magnitude of biogeochemical carbon fluxes on and at the edge of the Mackenzie Shelf." There were 9 subprojects addressing the physical, chemical, and biological interactions within the study area. The role of the current study in CASES was to investigate the BBL within the subproject *Pelagic food web: structure, function and contaminants*. The main CASES program took place from September 2003 - August 2004 aboard the CCGS *Amundsen*.

The CASES program compliments various other large research projects that have recently investigated other continental shelves in the Arctic, including the Chukchi Sea (Shelf-Basin-Interaction (SBI) program, Grebmeier and Harvey 2005), the Laptev Sea (Kassesns et al. 1999), and the Kara Sea (Siberian River Run-off (SIRRO) program, Stein et al. 2003). However, these programs did not include investigations into the BBL which highlights the lack of knowledge of processes that occur in the BBL on Arctic shelves.

1.8. OBJECTIVES

This thesis investigates the ecology of the BBL of the Beaufort Sea shelf. This was achieved by determining the biogeochemistry of suspended particulate matter in near-bottom waters (Chapter 2), the biochemical composition of BBL zooplankton (Chapter 3), and the trophic structure and carbon sources of these

zooplankton communities (Chapter 4). Specifically, Chapter 2 uses stable isotope ratios of carbon, fatty acids, and elemental content and ratios to determine the influence of the Mackenzie River on the biogeochemistry of suspended particulate matter in near-bottom water across the Beaufort Sea shelf. It was predicted that the Mackenzie shelf would be heavily influenced by Mackenzie River relative to the Amundsen Gulf and the Amundsen Gulf would have higher inputs of organic matter of marine origin relative to the Mackenzie Shelf. Chapters 3 and 4 report on biochemical analyses of zooplankton collected from the BBL. Chapter 3 uses lipid class and elemental composition of zooplankton in understanding energy storage capacities and biological stoichiometry. My hypothesis was that the zooplankton would have limited storage lipids if they reflected benthic adaptations and high storage lipids if they reflected pelagic adaptations. Chapter 4 presents data on the natural stable isotope ratios of carbon and nitrogen and fatty acid profiles of zooplankton to determine trophic interactions and carbon sources in BBL communities. I expected that if zooplankton were incorporating terrestrial it would be evident in animals collected near the Mackenzie River. However, I also predict that terrestrial organic matter is not a significant source of food for these zooplankton. I use the term *zooplankton* in the thesis to highlight that most of the taxa analyzed were mobile and absent from box core samples. However, a few taxa of benthic origin were included that allowed for an informative contrast between those taxa of pelagic to those of benthic origin. In meeting the above objectives, these results provide baseline data for comparison with future ecological studies on the Beaufort Sea shelf and with other Arctic shelves. This aspect is important for evaluating ecological change in light of recent and predicted perturbations to sea

ice coverage, sea ice thickness, and freshwater budgets in the Arctic due to global warming.

1.9. CO-AUTHORSHIP STATEMENT

I designed the research project, collected samples, performed data analyses, and wrote this document. My committee (Drs. Don Deibel, Chris Parrish, and Ray Thompson) contributed to the continued development of this research, gave valuable advice, and made instructive editorial comments that improved this thesis. Sources of complementary data kindly shared by scientist involved with CASES and those that assisted in the field and in the laboratory are acknowledged in the text.

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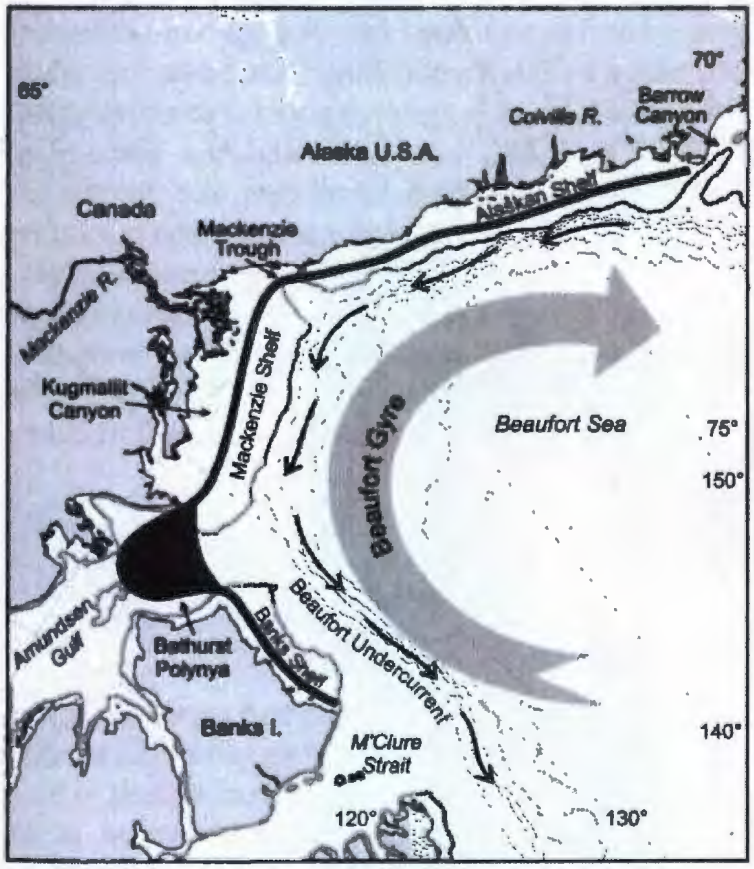

Figure 1.1. Map of the Beaufort Sea. The thick, black line over the Beaufort Sea shelves marks the flaw lead. Landfast ice is present shoreward of the flaw lead and the Arctic pack ice is seaward of the flaw lead. A reoccurring polynya in the Amundsen Gulf connects the flaw lead system across the Beaufort Sea shelf. (From Macdonald et al. 2004.)

CHAPTER 2

BIOGEOCHEMISTRY OF NEAR-BOTTOM SUSPENDED PARTICULATE MATTER OF THE BEAUFORT SEA SHELF: C, N, P, $\delta^{13}C$ AND FATTY ACIDS

2.1. ABSTRACT

The influence of the Mackenzie River on the source, composition, and distribution of particulate organic matter (POM) in near-bottom waters on the Beaufort Sea shelf was determined by measuring particulate organic carbon (POC), particulate organic nitrogen (PON), particulate phosphorus (PP), elemental ratios (C:N, C:P, N:P), $\delta^{13}C$, and fatty acids. The Mackenzie River had a strong influence on the composition of POM in near-bottom waters across the entire Beaufort Sea shelf, including the Amundsen Gulf. This influence was strongest at stations near the river mouth and decreased offshore and northeastward towards the Amundsen Gulf as seen in POM concentrations, $\delta^{13}C$, and terrestrial fatty acid markers. Low C:N ratios and high bacterial fatty acid markers indicate that bacteria were an important contributor to organic matter at stations near the river and on the Mackenzie shelf. Fatty acid analysis allowed detection of a phytoplankton sinking event in the Amundsen Gulf in which polyunsaturated fatty acid (PUFA) levels in near-bottom waters significantly increased from June to July. However, this change in PUFA was not associated with any temporal change in chlorophyll *a*, ^{13}C, or C:N ratios. These results emphasize that a multiple biomarker approach is necessary in ecosystem studies of dynamic environments such as near-bottom waters or river-influenced shelves.

2.2. INTRODUCTION

Continental shelves are of global significance owing to their high biological productivity and their control of the flux of inorganic and organic matter between land and ocean (Walsh 1991). Considering that 20% of the world's continental shelves are in the Arctic (Macdonald et al. 1998) and that the Arctic is sensitive to global change, much emphasis is being placed on determining carbon budgets for its shelves. Arctic shelves are characterized by intense, seasonal pulses of algal production (Sakshaug 2004) and are also highly influenced by rivers that supply large quantities of terrestrial matter (Holmes et al. 2002, Dittmar and Kattner 2003, Rachold et al. 2004). A major gap in our understanding of carbon cycling in coastal systems is the fate of terrestrial and marine organic matter. Of the North American terrestrial inputs into the Arctic Ocean, the Mackenzie River delivers the most organic matter annually (Holmes et al. 2002).

The Mackenzie River supplies the Beaufort Sea with 2.1×10^6 tons of particulate organic carbon (POC) annually (Macdonald et al. 1998), which is about 7% of the total organic carbon supplied to the Artic Ocean by rivers (Rachold et al. 2004). The transformation and fate of this terrigenous material *versus* the transformation and fate of marine organic matter is still unclear. Macdonald et al. (1998) estimate that 60% of terrestrial POC emptying from the Mackenzie River onto the Beaufort Sea shelf remains in the Mackenzie delta and on the shelf, < 30% leaves the shelf, and the remainder is remineralized. In contrast, most POC produced from marine primary production (3.0×10^6 tons yr^{-1}) is assumed to be remineralized on the shelf (Macdonald et al. 1998). Processes that occur near the sediment-water

interface are important in early stages of diagenesis and in determining whether organic matter is sequestered on the shelf, remineralized at the sediment-water interface, or swept off the shelf to the deep ocean (Thomsen et al. 2002, McKee et al. 2004). In addition, the quality of organic matter reaching the sea floor on the shelf has important consequences for the relative rates of these three fates. Generally, terrestrial-derived organic matter is more refractory than marine-derived organic matter (Macdonald et al. 1998, Amon et al. 2001, Dittmar and Kattner 2003).

Most of our knowledge of carbon cycling on Arctic shelves is based on investigations of the upper ocean and sediments. However, because of sampling difficulties little is known about the processes and mechanisms that control the transformation of organic matter within waters of the benthic boundary layer (i.e., near-bottom water; McKee et al. 2004). The benthic boundary layer is defined here as that portion of sea floor and water column that is influenced by the sediment-water interface. There are strong vertical chemical and physical gradients within this dynamic near-bottom zone (Thomsen 1999). The biogeochemisty of water near the sea floor is influenced by processes occurring in the upper ocean as well as by those occurring on the sea floor below. Deposition, aggregation, turbulence, waves, tides, resuspension, bioturbation, across shelf flow, and biological community composition may all affect the biochemical composition of near-bottom water and suspended particles (Thomsen 1999). Previous investigations of near-bottom waters in Arctic polynyas have shown higher microbial activity than in overlying waters (Ritzrau et al. 1997, Ritzrau and Thomsen 1997). However, the study of organic matter cycling in near-bottom waters is more

complex in a river-influenced environment like the Beaufort Sea shelf (Goñi et al. 2000, McKee et al. 2004).

One aim of the present study was to provide baseline data on the biogeochemistry of near-bottom waters of the Beaufort Sea shelf, because the impacts of climate change on Arctic ecosystems can only be assessed if we have historical data to compare with future observations. Here I present biogeochemical data for samples of near-bottom water collected with a bottom-tripping Niskin bottle at stations covering the eastern Beaufort Sea shelf during summer 2004. I examined the quantity and quality of particulate matter (i.e., concentration, elemental ratios, $\delta^{13}C$, and fatty acids) in near-bottom waters to infer the role of the Mackenzie River in the cycling of organic matter on the Beaufort Sea shelf. This is the first systematic investigation of the benthic boundary layer on the Beaufort Sea shelf, although near-bottom sediment traps have been used inshore of the 30 m isobath (O'Brien et al. 2006). This study is also one of few in the Arctic in which measurements of particulate phosphorus, carbon stable isotopes, and fatty acids have been made.

2.3. METHODS

2.3.1. Sample Collection

Samples were collected from 27 stations on the Beaufort Sea shelf aboard the CCGS *Amundsen* from 4 June to 1 August 2004 as part of the Canadian Arctic Shelf Exchange Study (CASES; Table 2.1, Fig. 2.1). These 27 stations were a subset of the total number of stations sampled in the CASES program, which varied depending on the research group. For examples, over

100 stations were sampled for dissolved nutrients (Simpson et al. in press). Stations were placed into one of three regions: river, shelf and gulf (Table 2.1). *Gulf* stations were those east of Tuktyuktuk Peninsula. Stations deeper than 10 m not in the gulf were labeled as *shelf* and all those < 10 m were labeled as *river*. Transects 700, 800, and 900 were on the Mackenzie shelf, with stations extending offshore from Kugmallit Bay on transect 700 and from Mackenzie Bay on transect 900 (Fig. 2.1). The Mackenzie shelf is only slightly effected by tides (Hill et al. 1991).

Near-bottom water was collected from approximately 0.5 m above the sea floor with two 12-L bottom-tripping Niskin bottles secured vertically in a frame (Fig. 2.2). The trigging mechanisms on the Niskin bottles was sufficiently sensitive and instantaneous to prevent contamination from stirred up material. Two casts were made at each station. Samples were collected from the first cast for determination of inorganic nutrients ($NO_3^- + NO_2^-$, PO_4^{3-}, $Si(OH)_4$, and NH_4^+), dissolved organic nutrients (dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP)), and particulate organic matter (POM) (particulate organic carbon (POC), particulate organic nitrogen (PON), particulate phosphorus (PP), chlorophyll *a*, carbon stable isotopes, and fatty acids). The second cast was used to collect water for duplicate samples of POC/PON, PP and chlorophyll *a*. River-influenced water (stations R7A, R7B, R9A, and R9B) was collected with a 5 L Go-Flo bottle deployed from a Zodiac, and samples from station 721 were collected 5 m above the sea floor with a 12 L Niskin bottle attached to a CTD rosette. Chlorophyll *a* data were not available at these 5 stations. Salinity, temperature, and turbidity from the greatest depth of corresponding CTD

(Seabird) casts, usually about 10 m above the sea floor, were recorded for each station.

2.3.2. *Dissolved Inorganic and Organic Nutrients*

Inorganic and dissolved organic nutrient samples were passed through 0.22 µm sterile-syringe filters directly from the Niskin bottle. The concentrations of all inorganic nutrients were determined using standard colorimetric methods (Hansen and Koroleff 1999), adapted for use on a Bran + Luebbe Auto-Analyzer 3 with an analytical detection limit of 0.9% at 15 µmol L^{-1} for nitrate, 1.5% at 1.0 µmol L^{-1} for phosphate, and 0.8% at 10 µmol L^{-1} for silicate. DON and DOP were calculated by subtracting nitrate + nitrite and ammonium from total dissolved nitrogen (TDN), and phosphate from total dissolved phosphorus (TDP). TDN and TDP were determined by persulphate oxidation (Valderrama 1981, Simpson et al. in press).

2.3.3. *Particulate Organic Matter*

For POM samples, each Niskin bottle was completely drained through a 300 µm mesh funnel into separate carboys, which were shaken gently before drawing samples through combusted 47 mm GF/F filters under gentle vacuum. Duplicates for POC/PON, PP, and chlorophyll *a* were taken from two consecutive bottom-tripping Niskin casts, except at station 398, where duplicates were obtained from the two different Niskin bottles from the same cast. Generally, 1- to 4-L of seawater were filtered for POC/PON and PP, 2- to 4-L for $\delta^{13}C$ and fatty acids, and 1- to 3-L for chlorophyll *a* measurements.

Filters for POC/PON and PP determinations were then immediately frozen and stored at -80°C until processed ashore. Two filters from each station, each from a different cast, were dried, acidified, and analyzed for POC/PON with a Perkin-Elmer 2400 CHN analyzer. PP content was determined from two additional filters, each from a different cast but from the same Niskin bottle as POC/PON. PP content was measured colorimetrically as soluble reactive phosphorus following high temperature hydrolysis according to the method of Solórzano and Sharp (1980). Precision in duplicate samples from different casts for POC, PON and PP was 8%. This precision estimate includes both analytical and environmental precision due to sampling and *in situ* variability. Ratios of POC, PON, and PP are reported as molar ratios.

Filtered samples for $\delta^{13}C$ were also immediately frozen and stored at -80°C until they were processed on land. Before analysis by continuous flow ion ratio mass spectrometry (CF-IRMS), filters were dried, acidified, divided in two, and each half analyzed for $\delta^{13}C$ (GV-Instruments® IsoPrime attached to a peripheral temperature controlled EuroVector® elemental analyzer, University of Winnipeg Isotope Laboratory). Isotopic values were expressed in the conventional δ notation following the equation:

$$\delta^{13}C = [(R_{sample}/R_{standard}) - 1] \times 1000$$

where R is $^{13}C/^{12}C$ and the standard reference material is Vienna Pee Dee Belemnite. Since 47 mm filters were too large to analyze whole, the stable isotope signature for the entire filter was calculated by averaging the

weighted isotopic composition of each filter half, which were weighted for their concentration of POC:

$$\delta^{13}C_{\text{Total Filter}} = [(\delta^{13}C_{\text{Filter A}} \times PH_{\text{Filter A}}) + (\delta^{13}C_{\text{Filter B}} \times PH_{\text{Filter B}})]/(PH_{\text{Filter A}} + PH_{\text{Filter B}})$$

where Filter A and Filter B are two halves of the same filter and PH is the respective peak height on the chromatogram. Analytical precision, expressed as the standard deviation of replicates of the internal standard, was 0.15‰.

For chlorophyll *a* analysis, pigments were extracted for 24 hours in 90% acetone while being refrigerated in the dark immediately following filtration. Chlorophyll concentrations were then determined fluorometrically (Strickland and Parsons 1972) with a Turner 10AU Fluorometer. The precision estimate based on replicate samples from different casts at the same station was 3%.

Filtered samples for fatty acid analysis were immediately put into 15 mL vials containing chloroform, sealed under N_2, and stored at -20°C for about 2 - 4 months until being processed. Lipids were extracted in chloroform:methanol:water (8:4:3) following Parrish (1999; modified from Folch et al. (1957)) and fatty acids were analyzed as methyl esters in a Varian 3400 gas chromatograph (GC; Omegawax 320 column, 60 min.) after transesterfication of total lipid samples with BF_3-methanol (85°C, 1 h; Budge and Parrish 1998). Peaks were identified by comparing sample retention times to those of known external standards and by using a Varian 2000 GC/MS. Fatty acids are reported as the percentage of total identified fatty acids. Mean error for all identified fatty acids on duplicate GC runs of certain samples was 5.4%.

The diatom fatty acid biomarker used here is the sum of C_{16} monounsaturates divided by C_{16} saturate ($\sum$16:1/16:0) (Claustre et al. 1988-89). The C_{16} PUFA index, used as an indicator of nutrient status of diatoms, is the ratio of 16:2ω4 + 16:3ω4 + 16:4ω3 + 16:4ω1 to 16:0 + 16:1ω7 + 16:1ω5 + 16:2ω4 + 16:3ω4 + 16:4ω3 + 16:4ω1 (Parrish et al. 2005). Bacterial fatty acid biomarkers were calculated by summing odd-carbon numbered and branched-chain fatty acids (Kaneda 1991) except 21:5ω3. Terrestrial fatty acid biomarkers were calculated first as the sum of long-chain even numbered saturates (C_{24}, C_{26}, C_{28}; Belicka et al. 2004), then as the sum of 18:3ω3 and 18:2ω6 (Budge and Parrish 1998).

Statistical analyses were carried out with the general linear model. Differences in mean values of POC, PON, PP, elemental ratios, chlorophyll a, fatty acid markers including PUFA, and $\delta^{13}C$ among regions (gulf, shelf, and river) were tested (ANOVA). Relationships between depth, salinity, or date to the above variables across the entire study area and within a region were also tested with a general linear model (ANCOVA). In addition, regression analysis were preformed to determine the presence of a relationship among C:N, chlorophyll a, $\delta^{13}C$, and fatty acid markers such as PUFA, bacterial markers, and diatom markers. A rejection criteria of $p \leq 0.05$ was used to determine statistical significance in all analyses. Contour plots were made using weighted averages of nearest points with Ocean Data View (Schlitzer 2008). Errors are reported as standard deviations unless stated otherwise.

2.4. RESULTS

2.4.1. Hydrography

Monthly mean discharge of the Mackenzie River for June and July 2004 was 19 100 and 12 700 $m^3 s^{-1}$, respectively, with peak discharge occurring in late May and early June (Archived Hydrometric Data, Environment Canada; Fig. 2.3). The point of half maximum discharge occurred about 1 July 2004 (Fig. 2.3). Although, the temporal coverage of this study was only two months, it coincided with maximum river discharge and the melting of the sea ice. Surface salinity ranged from brackish at the westernmost stations on the shelf (transect 900, < 20 psu) reflecting freshwater input from the Mackenzie River, to fully marine in the Amundsen Gulf (> 30 psu; Fig. 2.4a). On the Mackenzie shelf and near the river there was a continuous offshore gradient in bottom water salinity away from the Mackenzie River, ranging from fresh to marine (Fig. 2.4b). However, bottom water salinity values on the shelf and in the gulf were fully marine ranging from 31.2 to 34.8 psu, and increased with bottom depth (Fig. 2.5a). Shelf and gulf bottom water temperatures were generally low ranging from -1.4 to 0.4°C with a mean of -0.8 ± 0.1°C (Table 2.1). The highest temperatures occurred in the deeper, saltier waters of the Amundsen Gulf. Turbidity in bottom waters on the shelf and in the gulf was variable (60% to 90% transmittance) and significantly increased linearly with both bottom depth up to 100 m and with bottom salinity up to 33 psu (Fig. 2.5b,c). Spatial patterns of transmittance in bottom waters across the study region show similar patterns to those of bottom salinity with a continuous offshore increase in transmittance on the

Mackenzie Shelf (Fig. 2.4c) reflecting sediment input from the Mackenzie River and clearer waters in the Amundsen Gulf. Minimum transmittance (< 10%) was recorded nearshore in the eastern discharge channel of the Mackenzie River in Kugmallit Bay (Fig. 2.4c).

2.4.2. *Dissolved Inorganic and Organic Nutrients*

Nitrate + nitrite-N concentrations varied between < 1 and 16 μmol L^{-1} (mean 10.8 ± 5.5 μmol L^{-1}) with the lowest values at station 721 and stations near the river (R9a, R9b, R7a, R7b; Table 2.2), and the highest values at station 200 in the Amundsen Gulf. Phosphate varied between < 0.1 and 1.8 μmol L^{-1} (mean 1.3 ± 0.5 μmol L^{-1}), the lowest being at river stations (R9a, R9b, R7a, R7b; Table 2.2) and the highest at station 206 in the Amundsen Gulf. Ammonium-N varied from below 0.01 to 1.20 with a mean of 0.28 ± 0.29 μmol L^{-1}. Silicate was highly variable with low values of ca 9 μmol L^{-1} at stations in the gulf and the highest value (56 μmol L^{-1}) near the river. The mean silicate value was 25.7 ± 10.4 μmol L^{-1}. DON and DOP varied from 1.3 - 9.2 μmol L^{-1} (mean 4.2 ± 2.3 μmol L^{-1}) and 0.21 - 2.12 μmol L^{-1} (mean 0.87 ± 0.48 μmol L^{-1}), respectively.

2.4.3. *Particulate Organic Matter*

POC, PON, and PP concentrations were highly variable across the study region (27 - 1780 μg L^{-1} for POC; 2 - 201 μg L^{-1} for PON; < 1 - 32 μg L^{-1} for PP). The highest concentrations of POC, PON, and PP were found at the four stations closest to the Mackenzie River (R7a, R7b, R9a, R9b; Fig. 2.6). However, there was no significant difference in POC (mean 121 ± 45 μg L^{-1}) or

PON (mean 14 ± 5 μg L^{-1}; Table 2.2) between those stations on the Mackenzie Shelf and those in the Amundsen Gulf but there was a significant difference in PP (Mackenzie Shelf, mean 4.5 ± 2.0 μg L^{-1}; Amundsen Gulf, mean 2.9 ± 1.6 μg L^{-1}. There was a significant increase in POM with a decrease in depth (for log transformed POC, PON and PP; Fig. 2.7a-c).

Elemental ratios were also highly variable across the study region (ranges 3 - 22 for C:N; 34 - 185 for C:P; 2 - 24 for N:P), some of the lowest values being obtained near the Mackenzie River (Fig. 2.8). C:N ratios generally increased offshore on the Mackenzie Shelf with relatively low values (< 10) obtained for the stations closest to the Mackenzie River (Fig. 2.8a). Likewise, C:P and N:P were generally lower near the river than on the shelf break (Fig. 2.8b-c). However, a zone of higher C:P and N:P located at stations 721 and 909 interrupted the continuous increase of these two ratios from the river to the shelf break. There was no significant difference in mean C:N, C:P or N:P between the Mackenzie Shelf and the Amundsen Gulf. C:N ratios were significantly correlated with depth, higher values of C:N being found near the shelf break and in deeper waters of the Amundsen Gulf (Fig. 2.7d). However, there was no relationship between C:P and depth (Fig. 2.7e) but a significant inverse relationship between N:P and depth (Fig. 2.7f), generally due to low N:P ratios (< 6) at deeper stations (> 350 m) in the Amundsen Gulf (Fig. 2.8c).

Carbon stable isotope signatures were light across the sampling region, ranging from -29.9 to -24.8‰. Signatures were lowest near the Mackenzie River (< -28.8‰), where the source of organic carbon is predominately terrestrial (Table 2.2, Fig. 2.9). Higher $\delta^{13}C$ values in deeper waters of the

Amundsen Gulf (> -28‰ at > 100 m) suggest an increased contribution of organic carbon with marine origins. $\delta^{13}C$ was directly proportional to both C:N and depth (Fig. 2.10). However, C:N did not explain much of the variability in $\delta^{13}C$ ($r^2 = 0.05$).

Chlorophyll *a* in near-bottom waters was relatively low at all stations (< 0.80 μg L^{-1}) except in shallow waters near Banks Island (station 415), where the chlorophyll maximum occurred in bottom waters (10 μg L^{-1}). Chlorophyll *a* was not significantly related either to C:N or to PUFA levels (Fig. 2.11).

At most stations (14 of 24), the 2 predominant fatty acids were 16:0 and 16:1ω7 (range of 32 to 56% at stations where these are dominant; Table 2.3). At the remaining stations, either 16:0 or 16:1ω7 was one of the two most abundant fatty acids except at station 718 where 16:4ω1 and 18:4ω1 were highest and station R9a where 18:0 and 18:1ω9 were highest. In the Amundsen Gulf, 16:0 and 16:1ω7 were dominant at all stations sampled before June 20 (Table 2.3). Across the study area, the two most dominant fatty acids, on average, accounted for 38.8% of total fatty acids at a particular station.

PUFA, expressed as a percentage of total fatty acids, were highly variable across the study region (4 to 61%). The highest PUFA level (61%) was measured on the Mackenzie shelf at station 718. This high value is mostly due to the sum of four dominant PUFA, 20:2ω6, 18:4ω1, 16:4ω1, and 16:2ω4, each of which was > 10% of total fatty acids at this station. There was a significant temporal trend of increasing PUFA levels with date across the study region, especially in the Amundsen Gulf (Fig. 2.12). PUFA levels at station 406 increased from 4% on June 15 to 24% on July 24. In the Amundsen

Gulf, the C_{16} PUFA index and nine PUFA increased significantly between stations sampled before June 20 (PUFA levels ≤ 10%) and stations sampled after June 20 (PUFA levels > 24%: 16:2ω4, 16:4ω1, 18:3ω3, 18:4ω3, 18:4ω1, 20:2ω6, 20:3ω3, 20:5ω3, and 22:6ω3; Table 2.4). There was no relation between PUFA and depth.

Diatom fatty acid markers ranged from 0.1 to 3.5 across the Beaufort Sea shelf, indicating variable input of fresh diatom lipids in near bottom waters and significantly decreased with increasing bottom depth. Generally, stations with higher values for diatom markers were near the river or on the shelf (Fig. 2.13a). Fatty acids of bacterial origin ranged from 3 to 14% of total fatty acids. On the Mackenzie shelf percentages of bacterial fatty acids were highest at the westernmost stations (transect 900, > 9%) and usually lower at stations on transect 700 and 800 (Fig 2.13b). The highest value for bacterial fatty acids (14%) was obtained at the deepest station in the southeast of the Amundsen Gulf (station 108, 478 m). Terrestrial fatty acids markers (18:3ω3 + 18:2ω6) ranged from < 1 to 5% of total fatty acids. Highest proportions of terrestrial fatty acids were recorded from stations near the Mackenzie River (> 3%; Fig. 2.13c). On the Mackenzie shelf, there was a continuous decrease in terrestrial fatty acids offshore, away from the Mackenzie River on transect 900 (from 5 to 1%). The lowest terrestrial fatty acid signal in the Amundsen Gulf was at station 415, which also had the highest chlorophyll *a* value (10 μg L^{-1}). There was no relation between terrestrial fatty acid markers and $\delta^{13}C$. Long-chain even-number saturates (C_{24}, C_{26}, C_{28}), often used as indicators of terrestrial material, were low at all stations (< 1%).

2.5. DISCUSSION

2.5.1. POC, PON, and PP

The Mackenzie River has a strong influence on the distribution of organic matter in near-bottom water on the entire Beaufort Sea shelf. The highest POM values in near-bottom waters were found near the mouth of the river and lesser POM values towards the slope and in the Amundsen Gulf (Fig. 2.6). In general, the gradients of POC, PON, and PP northeastward from the mouth of the Mackenzie River were inversely related to bottom salinity, which has a crosshelf gradient, increasing from the mouth of the river (Fig. 2.4b). However, these patterns were not reflected in the surface salinity values, which seemed to have an along shelf gradient, increasing from west to east (Fig. 2.4a). Therefore, at the time of sampling, POM patterns reflected bottom salinity rather than surface salinity even though bottom salinity was not highly variable on the shelf and surface salinity should reflect the spatial extent of river outflow.

In addition to the northeastward gradient of POM on the Mackenzie shelf, near-bottom water concentrations of POC, PON, and PP were inversely correlated with bottom depth across the entire study area. The most plausible explanation for this observation is that organic matter is remineralized as it sinks through the water column and, therefore, at deeper stations less organic matter reaches the sediment-water interface. Bottom depth on the Mackenzie shelf is related to distance from the Mackenzie River outflow, so this depth relationship may also be explained by the dual processes of less supply of organic matter and more time for remineralization during sinking at deeper

stations. However, this depth related pattern was not limited to the Mackenzie shelf but was also seen in the Amundsen Gulf for POC and PON, which supports the former explanation.

The lack of a difference in POC and PON between the Mackenzie shelf and Amundsen Gulf suggests that depth is a more important regulator of distribution patterns of POC and PON in near-bottom waters than is the proximity of a given station to the Mackenzie River. Alternatively, small rivers emptying into the Amundsen Gulf, such as the Horton River in combination with greater authocthonous sources from a phytoplankton bloom in bottom waters at station 415, may supply enough POC and PON to shallower stations in the Gulf to balance the higher POC and PON loads from the Mackenzie River at inshore (shallower) stations on the shelf. However, PP was higher at the Mackenzie shelf stations than the Amundsen Gulf stations. Because I measured PP, which includes both particulate inorganic and organic phosphorus, a portion of the PP at the shelf stations may have derived from adsorption of inorganic and refractory phosphorus compounds onto the abundant sediments from the Mackenzie River (Rottenberg and Goñi 1997). Ruttenberg and Goñi (1997) found that Beaufort Sea sediments are enriched in inorganic phosphorus especially relative to other river-influenced shelves such as the Louisiana shelf (Mississippi River) and the Amazon shelf.

Although POM concentrations were highly variable across the study area, the precision of replicate casts at the same station was high, indicating that small-scale variability was smaller than large-scale spatial and temporal variability. Even in a dynamic environment such as near-bottom waters, patchiness in these variables was small in this data set. However, the gradient above the sea floor was not measured, and this is likely where small-

scale changes in organic chemistry would be encountered at cm or smaller scales (Thomsen and Graf 1994, Boetius et al. 2000).

2.5.2. *Elemental Ratios*

A surprising finding was the low C:N ratios near the Mackenzie River (Fig. 2.8a). It was predicted that C:N ratios would be higher near the mouth of the river since terrestrial sources of organic matter usually have C:N ratios > 20 (Goni and Hedges 1995; Emmerton et al. in press). Likewise, Emmerton et al. (in press) found that C:N ratios of samples taken further up stream during the same time period approach 20 and decrease to less than 7 in bottom waters around the 20 m isobath on the Mackenzie shelf. Low $\delta^{13}C$ and chlorophyll *a* values near the river suggest low input from marine phytoplankton and that POM near the river was likely terrigenous. However, since $\delta^{13}C$ data indicates the source of organic carbon, the flow and transformation of organic nitrogen in this region may be independent of organic carbon. For example, low C:N values (≤ 10) near the river could have resulted from a high contribution of organic matter from bacterial cells with relatively low C:N ratios (Luria 1960, Fagerbakke et al. 1996). Bacteria accumulate nitrogen during decomposition, which results in lower C:N ratios than in the original source material.

Coastal and estuarine bacteria can also have C:P ratios that are much lower (7 to 80) than the Redfield ratio (106:1) (Luria 1960, Gachter and Meyer 1993, Fagerbakke et al. 1996). In this study, many stations, both in the gulf and on the shelf, had C:P ratios well below the Redfield ratio, including some low ratios (< 80) near the river (Fig. 2.8b). Bacterial fatty acid signatures,

which were higher near the mouth of the river,suggest that bacterial biomass partially determined elemental ratios near the river. Likewise, higher concentrations of archaea have been found near the river mouth in waters 5 m above bottom (Wells et al. 2006). However, Vallières et al. (in press) found no difference in bacterial concentration from the Mackenzie River to the 20 m isobath on the shelf. In the Barents Sea, about 15% of POC in near bottom waters is composed of bacteria (Thomsen and Graf 1994). If indeed the ratios I observed largely reflect the elemental composition of bacteria found in near-bottom waters, then the low N:P ratios over much of the study region, including stations near the river, may indicate that bacteria are nitrogen rather than phosphorus limited. The proximity of these living bacteria to phosphorus-rich sediments (Ruttenberg and Goni 1997) could account for this observation.

Although there was no difference in mean elemental ratios between stations from the gulf and the shelf, as expected there was a direct relationship between C:N and bottom depth, which usually indicates that nitrogen is preferentially remineralized relative to carbon (Fig. 2.7d). The direct relation of C:N to bottom depth does not suggest anything about the change in C:N ratio at a specific station as the data in the figures are not depth profiles. Likewise, the absence of a relationship between C:P and bottom depth does not mean that at a particular station the ratios would not be related to water depth.

The correlation of depth and C:N across the study region and a lack of difference between C:N ratios on the shelf and in the gulf may indicate that depth related processes have a stronger influence on C:N ratios than does the Mackenzie River. The high C:N ratios at deeper stations indicate that the

quality of organic matter was relatively low. The inverse relationship of N:P with bottom depth also supports the hypothesis that in bottom waters nitrogen was more limiting than phosphorus (Carmack et al. 2004). It is unclear whether organisms living in near-bottom waters are nitrogen limited.

2.5.3. Carbon Stable Isotopes

Generally, it is assumed that terrestrial C_3 plants have $\delta^{13}C$ values of about -23 to -28‰ and marine phytoplankton have $\delta^{13}C$ values of about -18 to -25‰ (Fry and Sherr 1984, Parsons et al. 1989). According to these reference values, $\delta^{13}C$ signatures (< -24.8‰) in my study indicate that much of the organic carbon found in near-bottom waters on the Beaufort Sea shelf was highly terrestrial, even in the Amundsen Gulf, where values were surprisingly depleted (-27.3‰; Table 2.2). However, Amundsen Gulf values are heavier than those of the shelf, indicating an increase in marine-sourced organic matter relative to the shelf. However, the lighter than expected $\delta^{13}C$ fraction at deeper stations in the gulf could also be attributable to the tendency of isotopic signatures of relatively heavy POM in the upper-water column to become lighter with depth due to preferential decomposition of protein (Cowie and Hedges 1992, Lee et al. 2000) and carbohydrate (Cowie and Hedges 1984), which are enriched in ^{13}C relative to lipids (De Niro and Epstein 1977, Griffiths 1991).

Temperature also strongly affects the $\delta^{13}C$ signature of POM because it partially determines that of phytoplankton. Phytoplankton that grow at temperatures near 0°C often have $\delta^{13}C$ values approaching -30‰ due to kinetic fractionation (Rau et al. 1989). If these values apply to phytoplankton

growing in the Beaufort Sea, the interpretation of depleted $\delta^{13}C$ values in near-bottom waters may be ambiguous. $\delta^{13}C$ values for the chlorophyll maximum in the Amundsen Gulf are around -25‰ in summer and -27 to -28‰ in the autumn (Paul Renaud, personal communication), consistent with data that show $\delta^{13}C$ of phytoplankton in cold water can be depleted in ^{13}C (Wainright and Fry 1994, Rau et al. 1989). These values overlap directly with the assumed terrestrial $\delta^{13}C$ reference values and with most of my $\delta^{13}C$ observations, making it difficult to determine the source of organic matter based on isotopic signatures alone (Table 2.2). In this data set, station 415 had the highest chlorophyll *a* value (10 $\mu g\ L^{-1}$), and yet the $\delta^{13}C$ value was -26.6‰, heavier than the average gulf values but still relatively light, which again supports the idea that marine phytoplankton growing at high latitudes are more depleted in ^{13}C than the reference values usually used. Although temperature effects on $\delta^{13}C$ of phytoplankton may limit our ability to differentiate between terrestrial and marine inputs in high latitude seas such as the Beaufort Sea, conclusions based on the relative inputs of terrestrial and marine matter among regions and stations are still valid. For instance, we can conclude that station 117, with a $\delta^{13}C$ of -25.9‰, is more influenced by marine carbon inputs than is station 108 with -27.6‰. However, the extent to which the isotopic signature of either of these stations reflects mostly terrestrial or marine inputs cannot be easily determined from the $\delta^{13}C$ values alone.

Carbon signatures from near-bottom water did not necessarily reflect those of surface sediments. $\delta^{13}C$ values for surface sediment (-25.8 to -21.1‰) on the shelf were generally heavier or equal to the lightest values for near-bottom water in the gulf (-29.9 to -24.8‰; Cedric Magnen and Paul Renaud

personal communication). The $\delta^{13}C$ of surface sediments increased from ca -25‰ near the river (station 718) to ca -23‰ on the outer shelf, with some values > -23‰ in the Amundsen Gulf (P. Renaud, personal communication). In contrast, $\delta^{13}C$ values from near-bottom waters more closely resembled upper-water column values, including the chlorophyll maximum (P. Renaud, personal communication). Thus, sediments were generally $\delta^{13}C$ heavier than near-bottom water POM and chlorophyll maximum POM, indicating that there were processes occurring near the sediment-water interface that were enriching the sediment with ^{13}C.

Similar ^{13}C enrichment patterns in sediments relative to the overlying water have been documented off Spitsbergen in waters less than 200 m deep (Tamelander et al. 2006). Again, bacterial activity may account for this difference. One possible expanation is that consumers intercepting settling POM in near-bottom waters before it reaches the sediment preferentially select for compounds depleted in ^{13}C, such as lipids and cellulose. Generally, bacteria have higher affinities for protein and carbohydrates (Cowie and Hedges 1992), which are $\delta^{13}C$ heavy compared with lipids (De Niro and Epstein 1977). However, if zooplankton and bacteria collectively tend to metabolize light compounds, then heavy compounds are left to sink to the sediments. Likewise, bacteria in sediments preferentially respire ^{12}C rather than ^{13}C (Macko and Estep 1984), so there would be an increase in $\delta^{13}C$ values in sediments relative to the waters directly above.

2.5.4. *Fatty Acids*

Because certain fatty acids have known sources and can be used to understand the origins of organic matter (Sargent et al. 1987, Parrish et al. 2000), the determination of the lipid content of POM can provide insight into the quality of organic matter and its degree of lability (Parrish 1999, Parrish et al. 2005). Some fatty acids, specifically PUFA, are also essential dietary requirements for animals (Müller-Navarra et al. 2000). In marine systems, PUFA are usually synthesized by phytoplankton. Because PUFA are highly labile, their presence in deeper waters and on the sea floor can be used to detect the recent input of fresh, high quality algal matter (Parrish et al. 2005). However, deep-sea bacteria as well as psychrophilic bacteria also synthesize PUFA *de novo* (DeLong and Yayanos 1986, Nichols et al. 1997, Fang et al. 2004). The contribution of bacterial PUFA to the PUFA pool in the Arctic is unknown, although there is increasing evidence that the contribution of bacteria-synthesized PUFA in seas and sediments at high latitudes has been underestimated (Nichols 2003).

In general, PUFA levels in near-bottom POM were low throughout the study area, suggesting that much of the organic matter found in near-bottom waters had been consumed by zooplankton and degraded by bacteria before sinking, or had been processed shortly after reaching bottom waters, or both, as indicated by comparisons between upper-water column PUFA values and near-bottom water values. Average PUFA values in the upper-water column across the entire study area for June and July 2004 were 52% for surface water, 64% for the chlorophyll max, and 33% for water from the deepest depth of the CTD-rosette cast (Tara Businski, personal communication). On average the

bottom depth of the CTD-Niskin casts had over 10% more PUFA as a percent of total fatty acids than near-bottom water (mean 20%) even though the difference in depth was generally less than 10 m. The high PUFA levels in near-bottom water at station 718 (61%) primarily consisting of 20:2ω6, 18:4ω1, 16:4ω1, and 16:2ω4, may be of diatom origin since C_{16} fatty acids are usually from diatoms (Viso and Maty 1993). 18:4ω1 was probably an elongation of 16:4ω1, and 20:2ω6 is found in Prasinophyceae (Zhukova and Aizdaicher 1995) which is one of the dominant phytoplankton taxon on the Beaufort Sea shelf (Lovejoy et al. 2007). Low chlorophyll *a* values at this station and at all others except station 415 suggest that benthic algae do not contribute significantly to organic matter in near-bottom waters.

A temporal trend was detected in PUFA levels in the Amundsen Gulf, with increases in PUFA in near-bottom water in July compared with early June (Fig. 2.12). Significant increases in C_{16}, C_{18}, 20:5ω3 (eicosapentaenoic acid; EPA) and 22:6ω3 (docosahexaenoic acid; DHA) were seen in July, indicating a phytoplankton sinking event in the Amundsen Gulf sometime at the end of June. This timing is consistent with an apparent phytoplankton bloom that occurred during the month of June (Simpson et al. in press).

A comparison between samples taken at station 406 in June and July revealed that near-bottom waters can receive seasonal pulses of higher quality organic matter, with PUFA levels increasing from 4% to 24%. However, temporal changes in C:N, $\delta^{13}C$, and chlorophyll *a* were not observed. Therefore, if only chlorophyll or C:N had been used as an indicator of phytoplankton production reaching near-bottom waters, a different conclusion would have been reached. Commonly, C:N and chlorophyll *a* are

used to detect fresh phytoplankton inputs to the benthos, with fresh phytoplankton usually having low C:N rations and high chlorophyll *a* levels. C:N, $\delta^{13}C$, and chlorophyll *a* may not have changed because these are bulk measurements. Compound specific tools such as fatty acids may be more reliable indicators of the quality of organic matter reaching the benthos. Animals living near the sea floor probably depend on, and take advantage of, these sinking events to meet their dietary fatty acid requirement (Richoux et al. 2004).

Although C_{16} PUFA and the C_{16} PUFA index increased in July, there was no corresponding increase in the diatom marker $\sum$16:1/16:0, which was variable across the study region in near bottom waters but increased with decreasing depth. Excluding station 398, which had the highest value for this diatom marker (3.5), diatom markers at stations in the gulf sampled after June 20 were low (mean 0.7 ± 0.3). The relative lack of diatom fatty acids in near-bottom waters at these stations is consistent with the low chlorophyll values but inconsistent with the high PUFA levels and C_{16} PUFA index observed. One exception to low chlorophyll values was station 415, where the chlorophyll maximum was recorded from its bottom waters (10 μg L^{-1}). This station also had one of the highest 20:5ω3 levels (10%). However, 2 other stations had 20:5ω3 levels ≥ 10% but insignificant chlorophyll *a* (< 0.08 μg L^{-1}). Because 22:6ω3 levels were low at most stations in the gulf (≤ 3.2%, mean 1.6 ± 1.1%), the common dinoflagellate marker 22:6ω3/20:5ω3 (DHA/EPA; Budge and Parrish 1998) could not be used with confidence. 22:6ω3 values reported here are considerably lower than those used in 22:6ω3/20:5ω3

calculations for samples that have high proportions of dinoflagellates, as reported by Budge and Parrish (1998; 22:6ω3, > 10%).

Branched-chain and odd-numbered fatty acids are typically of bacterial origin (Kaneda 1991). In near-bottom waters on the Beaufort Sea shelf, these bacterial fatty acids ranged from 3% - 14%. High percentages of bacterial fatty acids on the shelf at stations nearest the river outflow are consistent with high bacteria and archaea abundance in inshore waters on the shelf (Garneau et al. 2006) as well as the low C:N ratios at stations closest to the Mackenzie River (Fig. 2.8). The highest levels of bacteria fatty acids were found at the deepest station in the Amundsen Gulf (station 108), probably due to a relative decrease in phytoplankton derived fatty acids, because bacterial abundance was shown to decrease with depth in the Amundsen Gulf (Wells et al. 2006).

The fatty acids that I used as terrestrial markers were long chain even numbered saturates (C_{24}, C_{26}, C_{28}) and 18:3ω3 and 18:2ω6 (Budge and Parrish 1998). Even-numbered long chain saturates, which are typical of vascular plants, accounted for < 1% of total fatty acids at all stations. This is surprising considering the depleted $\delta^{13}C$ values found in near-bottom water near the river and the amount of river and terrestrial based material which flows onto the Beaufort Sea shelf in summer (Macdonald et al. 1998, O'Brien et al. 2004). Perhaps organic carbon from plants makes a small contribution to the standing stock of organic carbon in near-bottom waters. However, the presence of the terrestrial fatty acids 18:3ω3 and 18:2ω6 indicated increased levels of terrestrial inputs near the river. These are two of the dominant fatty acids of sedge, willow, and spruce genera that are dominant in the Mackenzie River drainage basin (Cody 1965, Hietala et al. 1998, Ayaz and

Olgun 2000, Grigová et al. 2007). However, these fatty acids are also present in many species of diatoms (Viso and Marty 1993). The station with the highest chlorophyll *a* value (station 415, 10 μg L^{-1}) had the lowest levels of 18:3ω3 and 18:2ω6 (1%), probably because the high chlorophyll values (and associated lipids) diluted any terrestrial signal that may have been present. This pattern of a high terrestrial signal near the river and a low signal in chlorophyll rich waters indicate that these 2 fatty acids are more appropriate than even-numbered long chain saturates for determining the relative contribution of terrestrial lipids in this study area. The lack of a direct relationship between terrestrial fatty acid signatures and $\delta^{13}C$ on the Beaufort Sea shelf indicates that perhaps other lipid based terrestrial markers may be more reliable in detecting terrestrial contributions or that bulk organic carbon measurements such as $\delta^{13}C$ are not always reliable predictors of lipid distributions. Combining natural isotopes with lipid compounds (Drenzek et al. 2007), such as determining fatty acid specific $\delta^{13}C$ signatures, may be a more robust method for detecting the presence of terrigenous carbon in near-bottom waters.

2.6. CONCLUSIONS

Characterizing the POM in near-bottom waters is confounded by the dynamic nature of the benthic boundary layer. My observations resulted from the interaction of various physical and biological processes such as deposition, resuspension, and degradation. An environment with anomalous elemental ratios and poorly defined end-members makes interpretation of biogeochemical data difficult, but by including bacteria as an alternative end-

member to terrestial- and marine-signatures, and by using multiple biomarkers, I was able to provide insights into the distribution of organic matter in near-bottom waters across the Mackenzie shelf. I found that the Mackenzie River influences the organic chemistry of near-bottom waters across the entire Beaufort Sea shelf, including the Amundsen Gulf. However, terrestrial markers, such as POM concentrations, fatty acid biomarkers and $\delta^{13}C$ values, were strongest near the river mouth and decreased northeastward towards the Amundsen Gulf. There was an unexpected direct relationship between C:N and $\delta^{13}C$, which suggests that there is a strong microbial fingerprint in the biogeochemistry of near-bottom waters near the river and on the shelf. High levels of bacterial fatty acids near the river support this conclusion. Fatty acid analysis allowed detection of a sinking event in the Amundsen Gulf which would not have been observed from $\delta^{13}C$ and chlorophyll *a* data alone. This clearly suggests that multiple tracers are necessary to increase accuracy in ecosystems studies, especially in dynamic environments like the benthic boundary layer.

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2.9. TABLES

Table 2.1. Description and location of stations where near-bottom water was collected from the Beaufort Sea shelf with a bottom-tripping Niskin bottle. Turbidity is presented as % transmittance (% Trans). 'gulf' are stations east of Tuktyuktut Peninsula, 'shelf' are stations > 10 m not in the gulf, and 'river' are those < 10 m.

					Bottom Water			Surface	
Station	Date	Lat (°N)	Long (°W)	Depth (m)	Temp (°C)	%Trans	Salinity (psu)	Salinity (psu)	Region
206	04-06-04	70.32	124.85	99	-1.3	88.8	33.3	31.2	gulf
108	06-06-04	70.63	123.17	478	0.3	89.4	34.8	30.2	gulf
117	10-06-04	70.88	125.50	377	0.4	88.1	34.8	30.5	gulf
406	15-06-04	71.31	127.69	179	-0.6	88.1	34.2	30.4	gulf
303	19-06-04	70.80	127.04	246	0.1	88.1	34.6	30.8	gulf
398	21-06-04	70.79	129.36	24	-1.0	74.4	32.2	30.7	gulf
709	30-06-04	70.94	133.68	86	-1.4	88.2	32.6	26.5	shelf
906	04-07-04	70.02	138.60	281	-0.6	90.3	34.3	15.0	shelf
909	05-07-04	69.80	138.28	169	-1.2	88.5	33.6	17.7	shelf
912	06-07-04	69.49	137.94	56	-1.4	85.5	32.6	8.7	shelf
R9a	06-07-04	69.12	137.57	2	7.2	25.7	8.7	NA	river
R9b	06-07-04	69.19	137.57	3	7.2	25.7	8.7	NA	river
809	07-07-04	70.09	135.34	44	-1.4	76.6	32.0	21.4	shelf
803	08-07-04	70.64	135.87	242	-1.0	89.5	33.8	23.9	shelf
712	10-07-04	70.69	133.68	68	-1.4	76.7	32.3	25.1	shelf
718	11-07-04	70.17	133.52	45	-1.4	68.4	32.0	27.6	shelf
R7a	11-07-04	69.53	133.43	4	3.1	2.0	6.5	NA	river
R7b	11-07-04	69.66	133.43	7	3.0	4.1	4.0	NA	river
650	13-07-04	71.31	131.61	254	-1.1	88.6	33.6	28.7	shelf
200	16-07-04	70.04	126.30	235	-0.6	89.5	34.1	29.3	gulf
309	18-07-04	71.12	125.83	397	0.4	87.1	34.8	29.9	gulf
415	20-07-04	71.91	125.87	52	-1.1	76.9	31.7	29.4	gulf
409	23-07-04	71.50	127.09	380	0.3	86.7	34.8	27.1	gulf
406	24-07-04	71.30	127.69	176	-1.3	89.0	33.3	27.5	gulf
400	25-07-04	70.92	128.92	242	-1.0	71.0	32.1	29.9	gulf
721	26-07-04	69.86	133.29	14	-0.9	59.8	31.2	27.6	shelf
206	01-08-04	70.32	124.84	95	-1.3	84.5	32.4	28.6	gulf

Table 2.2. Mean (sd) dissolved and particulate matter in near-bottom water on the Beaufort Sea shelf. Units for inorganic nutrients, dissolved organic nitrogen (DON), and dissolved organic phosphorus (DOP) are μmol L^{-1}; units for particulate organic carbon (POC), particulate organic nitrogen (PON), and particulate phosphorus (PP) are μg L^{-1}; elemental ratios are mol:mol, and units for $\delta^{13}C$ are ‰.

		River		Shelf		Gulf	
Dissolved	$NO_3^-+NO_2^-$	3.3	(2.7)	12.5	(5.7)	11.6	(2.0)
	PO_4	0.3	(0.6)	1.5	(0.5)	1.3	(0.2)
	$Si(OH)_4$	33.0	(16.5)	26.5	(10.1)	18.9	(3.9)
	NH_4^+	0.3	(0.3)	0.2	(0.3)	0.2	(0.2)
	DON	4.2	(3.4)	3.3	(2.6)	1.8	(1.9)
	DOP	0.5	(0.6)	1.0	(0.4)	0.3	(0.6)
Particulate	POC	751	(605)	141	(119)	105	(90)
	PON	87	(66)	17	(16)	12	(14)
	PP	19	(7)	5	(2)	3	(2)
	POC:PON	10	(1)	12	(4)	13	(4)
	POC:PP	93	(37)	94	(35)	101	(37)
	PON:PP	9	(3)	9	(4)	9	(6)
	$\delta^{13}C$	-29.2	(0.5)	-27.5	(0.8)	-27.3	(1.5)

Table 2.3. The dominant fatty acids in near-bottom suspended particulate matter from the Beaufort Sea shelf. The two most abundant fatty acids at each station are in bold and the sum of these eight fatty acids are given. Fatty acid values are % of total fatty acids.

			Dominant Fatty Acids								Sum
Station	Region	Date	16:0	16:1ω7	16:4ω1	18:00	18:1ω9	18:4ω1	20:5ω3	14:0	Fatty Acids
R9a	river	06-07-04	10.1	11	-	**11.2**	**19.0**	-	tr	tr	51.3
R9b	river	06-07-04	11.6	**12.3**	1.5	10.1	**16.3**	-	7.4	1.8	61.0
R7a	river	11-07-04	**15.3**	**19.9**	3.2	4.1	4.5	tr	10.5	7.0	64.5
R7b	river	11-07-04	**18.7**	**29.8**	2.0	2.4	5.8	tr	7.0	7.8	73.5
709	shelf	30-06-04	**19.7**	**40.1**	tr	2.4	2.9	-	2.0	8.2	75.3
906	shelf	04-07-04	**11.1**	**22.6**	tr	5.4	6.3	-	6.5	5.5	57.4
909	shelf	05-07-04	**14.9**	**17.7**	tr	9.8	5.0	-	5.2	3.9	56.5
912	shelf	06-07-04	**13.0**	8.3	tr	**10.2**	10.1	-	3.5	4.7	49.8
809	shelf	07-07-04	**20.7**	**29.9**	tr	3.4	3.5	-	6.0	5.5	69.0
803	shelf	08-07-04	**26.7**	**20.8**	1.8	10.7	6.0	1.0	4.5	6.1	77.6
712	shelf	10-07-04	**14.5**	**29.1**	tr	3.3	3.4	-	2.8	9.4	62.5
718	shelf	11-07-04	6.7	tr	**15.4**	6.3	7.9	**14.0**	tr	1.0	51.3
650	shelf	13-07-04	**22.1**	**11.7**	1.1	9.9	11.7	1.2	2.7	6.5	66.9
206	gulf	04-06-04	**34.3**	**21.4**	-	11.4	6.9	-	tr	3.2	77.2
108	gulf	06-06-04	**25.5**	**21.3**	-	12.7	9.1	-	-	2.5	71.1
117	gulf	10-06-04	**23.6**	**20.2**	-	9.7	12.3	-	-	4.6	70.4
406	gulf	15-06-04	**24.7**	**21.7**	-	12.3	10.0	-	tr	5.1	73.8
303	gulf	19-06-04	**20.6**	**11.3**	-	9.4	9.3	tr	tr	4.4	55.0
398	gulf	21-06-04	11.0	**29.5**	3.9	tr	1.6	-	**13.2**	10.0	69.2
200	gulf	16-07-04	**16.6**	9.5	5.5	8.0	5.7	**9.8**	2.9	5.4	63.4
309	gulf	18-07-04	**19.0**	6.5	4.1	**12.0**	7.7	6.6	2.5	4.5	62.9
415	gulf	20-07-04	12.6	**13.3**	8.9	2.2	1.4	5.0	10.8	**15.4**	69.6
406	gulf	24-07-04	**20.8**	6.8	tr	**22.8**	6.1	1.4	2.4	4.9	65.2
400	gulf	25-07-04	**18.5**	14.2	tr	**19.9**	4.7	tr	4.5	6.4	68.2
										mean=	65.6

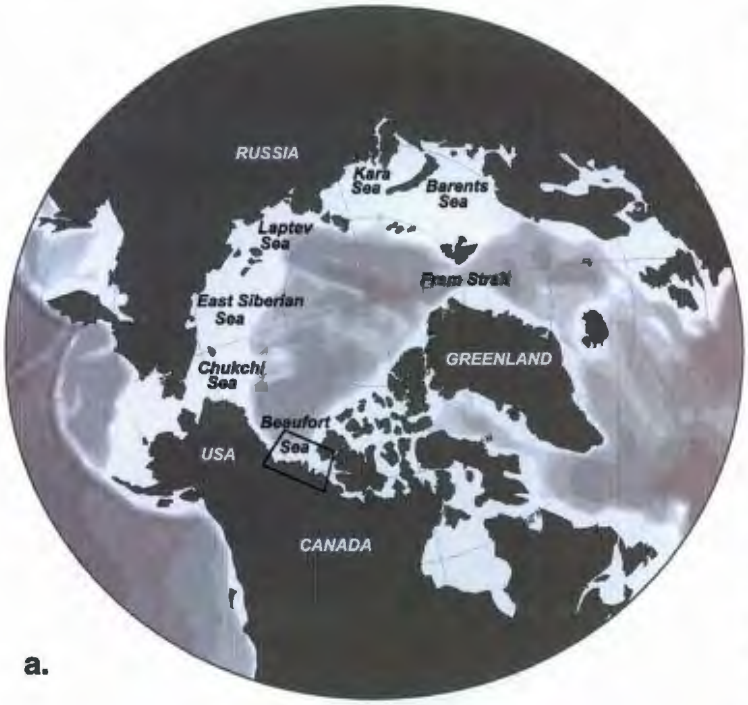
tr= < 1% of total fatty acids; '-' = below detection limit.

Table 2.4. Mean (sd) fatty acids (% of total FA) of suspended particulate matter in near-bottom waters of the Beaufort Sea shelf. 'n' equals the number of stations used to calculate mean values in the indicated areas of the study region.

Fatty Acid[a] (%)	River n=4		Shelf n=9		Gulf pre-June 20 n=5		Gulf post-June 20 n=6	
14:0	4.2	(3.2)	5.6	(2.3)	4.0	(1.0)	7.8	(4.3)
TMTD[b]	0.2	(0.2)	1.5	(1.1)	3.0	(0.7)	0.3	(0.4)
14:1	2.7	(2.4)	0.2	(0.5)	0.0	(0.0)	0.4	(0.4)
*i*15:0	1.4	(0.8)	0.8	(0.4)	1.4	(1.2)	1.0	(0.3)
*a*15:0	1.8	(1.0)	0.7	(0.3)	1.2	(0.9)	0.5	(0.3)
15:0	0.9	(0.5)	1.7	(0.8)	2.2	(1.6)	1.2	(0.6)
pristanic	0.0	(0.0)	1.1	(2.7)	0.0	(0.0)	0.4	(0.4)
16:0	14.1	(3.2)	16.6	(5.8)	25.7	(5.1)	16.4	(3.9)
16:1ω11	4.1	(4.3)	2.7	(3.3)	0.0	(0.0)	0.1	(0.1)
16:1ω9	0.3	(0.3)	1.1	(1.6)	0.0	(0.0)	1.1	(0.9)
16:1ω7	18.3	(7.5)	20.1	(11.4)	19.2	(4.5)	13.3	(8.5)
16:1ω5	3.9	(3.6)	4.0	(3.8)	1.8	(2.6)	2.1	(3.4)
*i*17:0	1.0	(0.6)	2.0	(2.1)	1.9	(1.2)	0.5	(0.5)
16:2ω4*	1.0	(0.9)	2.7	(3.9)	0.5	(0.6)	1.5	(1.1)
phytanic	0.6	(0.8)	0.6	(0.6)	0.1	(0.1)	1.5	(1.0)
17:0	0.1	(0.1)	0.7	(0.4)	1.4	(0.5)	0.5	(0.4)
16:3ω4	1.9	(1.4)	0.6	(0.6)	0.5	(0.5)	0.9	(0.6)
16:4ω1*	1.7	(1.1)	2.2	(4.7)	0.0	(0.0)	4.0	(3.1)
18:0	7.0	(3.8)	6.8	(3.2)	11.1	(1.5)	10.9	(9.1)
18:1ω9	11.4	(6.4)	6.3	(2.9)	9.5	(1.9)	4.5	(2.5)
18:1ω7	0.8	(0.9)	2.3	(1.4)	5.1	(5.4)	1.5	(0.7)
18:1ω6	0.0	(0.2)	0.3	(0.9)	1.9	(2.5)	0.0	(0.0)
18:1ω5	0.0	(0.0)	1.2	(1.8)	1.5	(3.3)	0.0	(0.1)
18:2ω6	1.6	(0.4)	2.2	(1.0)	2.3	(1.4)	1.5	(0.6)
18:3ω3*	2.2	(0.5)	0.2	(0.2)	0.1	(0.1)	0.4	(0.1)
18:4ω3*	2.9	(1.5)	0.9	(0.4)	0.2	(0.4)	1.6	(1.2)
18:4ω1*	0.1	(0.1)	1.8	(4.3)	0.0	(0.1)	3.9	(3.9)
20:2ω6*	0.1	(0.2)	1.5	(3.5)	0.0	(0.0)	3.8	(4.0)
20:3ω3*	0.4	(0.3)	0.3	(0.5)	0.0	(0.0)	2.8	(3.0)
20:4ω3	1.2	(1.0)	0.3	(0.3)	0.6	(0.4)	0.0	(0.1)
20:5ω3*	6.5	(3.5)	3.7	(1.9)	0.3	(0.4)	6.1	(4.7)
22:6ω3*	2.2	(1.3)	1.4	(0.4)	0.6	(0.9)	2.3	(0.6)
PUFA[c]	22.6	(8.5)	19.3	(15.8)	6.5	(2.5)	31.1	(7.0)
MUFA[c]	43.9	(9.3)	40.2	(12.6)	39.9	(4.8)	25.2	(9.8)
SFA[c]	32.7	(2.1)	39.6	(6.2)	52.8	(5.2)	43.0	(11.2)
Diatom[d]	1.0	(0.5)	1.7	(1.0)	0.8	(0.1)	1.2	(1.2)
Bacteria[e]	7.5	(3.5)	7.4	(3.5)	9.5	(3.5)	5.5	(1.1)
Terrestrial[e]	3.8	(0.6)	2.5	(1.1)	2.4	(1.4)	1.9	(0.7)
C_{16}PUFA[f]	11.1	(9.1)	14.0	(24.6)	2.1	(2.0)	18.8	(8.8)

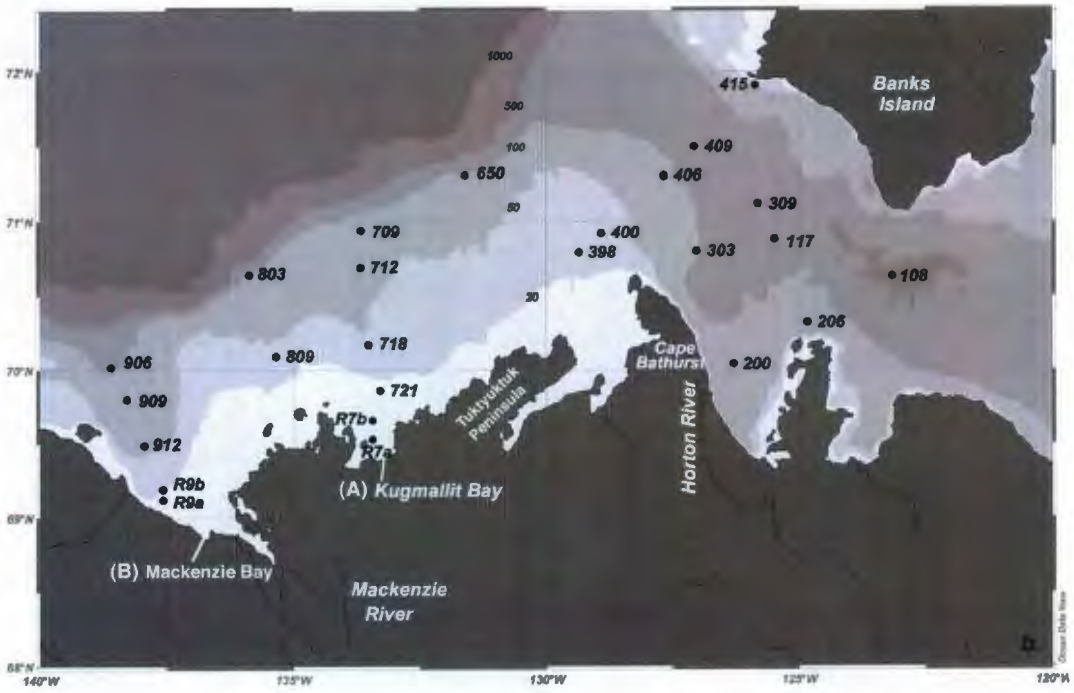
*PUFA that significantly increased from before June 20 to after June 20; [a]only FA with a mean of ≥ 1% in at least one region are listed; [b]TMTD is 4,8,12-trimethyltridecanoic acid; [c]sums of polyunsaturated FA (PUFA), monounsaturated FA (MUFA), and saturated FA (SFA); [d] unitless ratio of ∑16:1/16:0; [e] bacterial FA is the sum of odd and branched chain FA and terrestrial FA is 18:3ω3 + 18:2ω6; [f]unitless ratio (see Methods for calculation).

2.10. FIGURES



a.

Figure 2.1. (a) Location of the Canadian Arctic Shelf Exchange Study (CASES) site in the Arctic Ocean (box). (b) Station locations and labels of near-bottom water samples collected during summer 2004 from the Beaufort Sea shelf. (A) and (B) mark two of the major outflow channels from the Mackenzie River into Kugmallit Bay (A) and Mackenzie Bay (B). These outflow channels align with stations on transect 700 (A) and 900 (B). Depth contours are in meters.



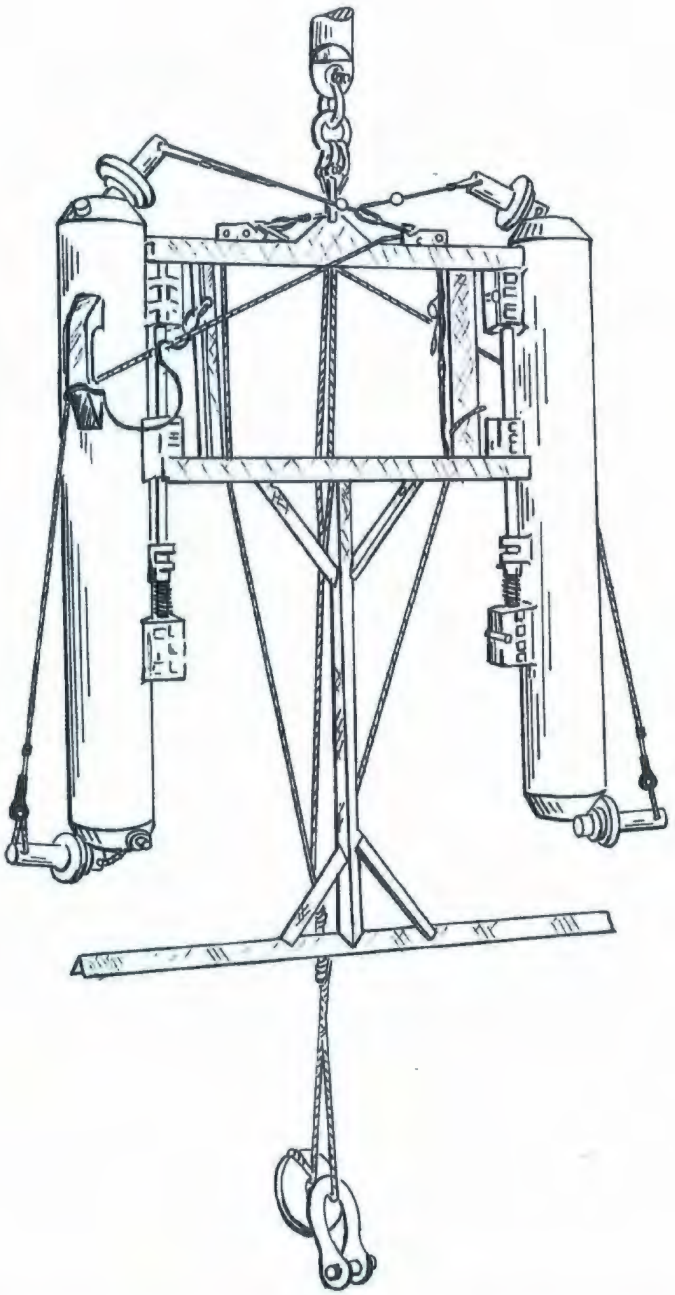


Figure 2.2. Line drawing of bottom-tripping Niskin bottles used to collect near-bottom water from the Beaufort Sea shelf. The hanging weights hitting the sea floor triggered the 12-L Niskin bottles to close. Line drawing courtesy of Charles Connelly.

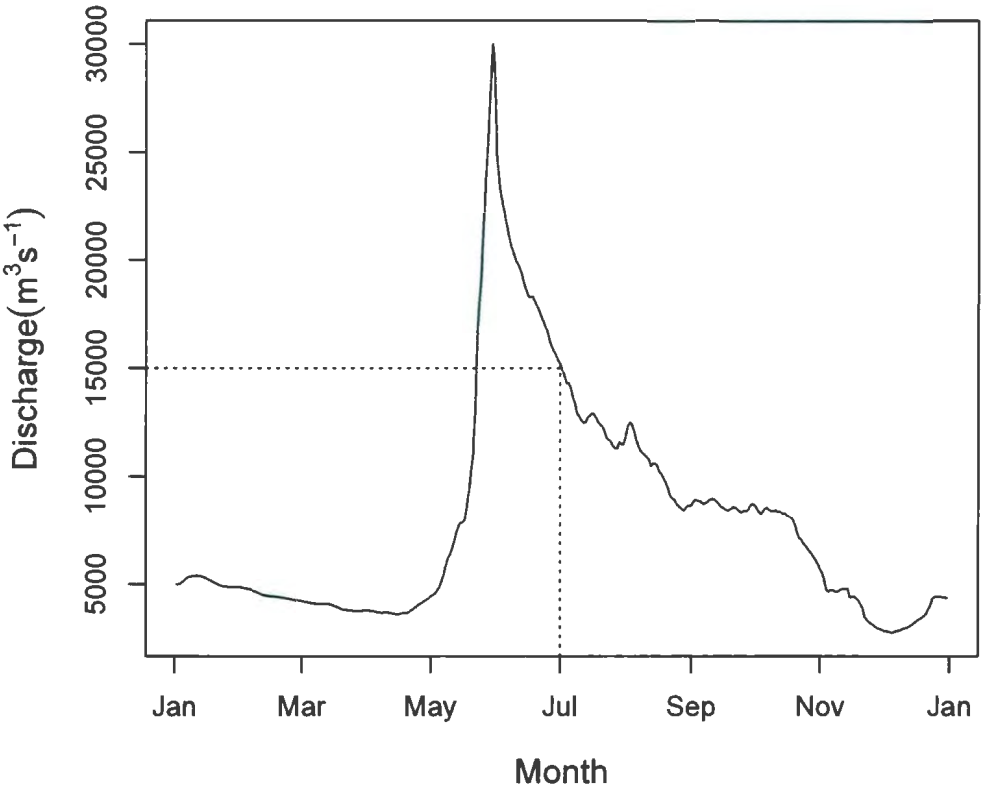


Figure 2.3. Average daily water discharge of the Mackenzie River for 2004. Dotted lines indicate date at half maximum discharge. Data courtesy of Archived Hydrometric Data, Environment Canada.

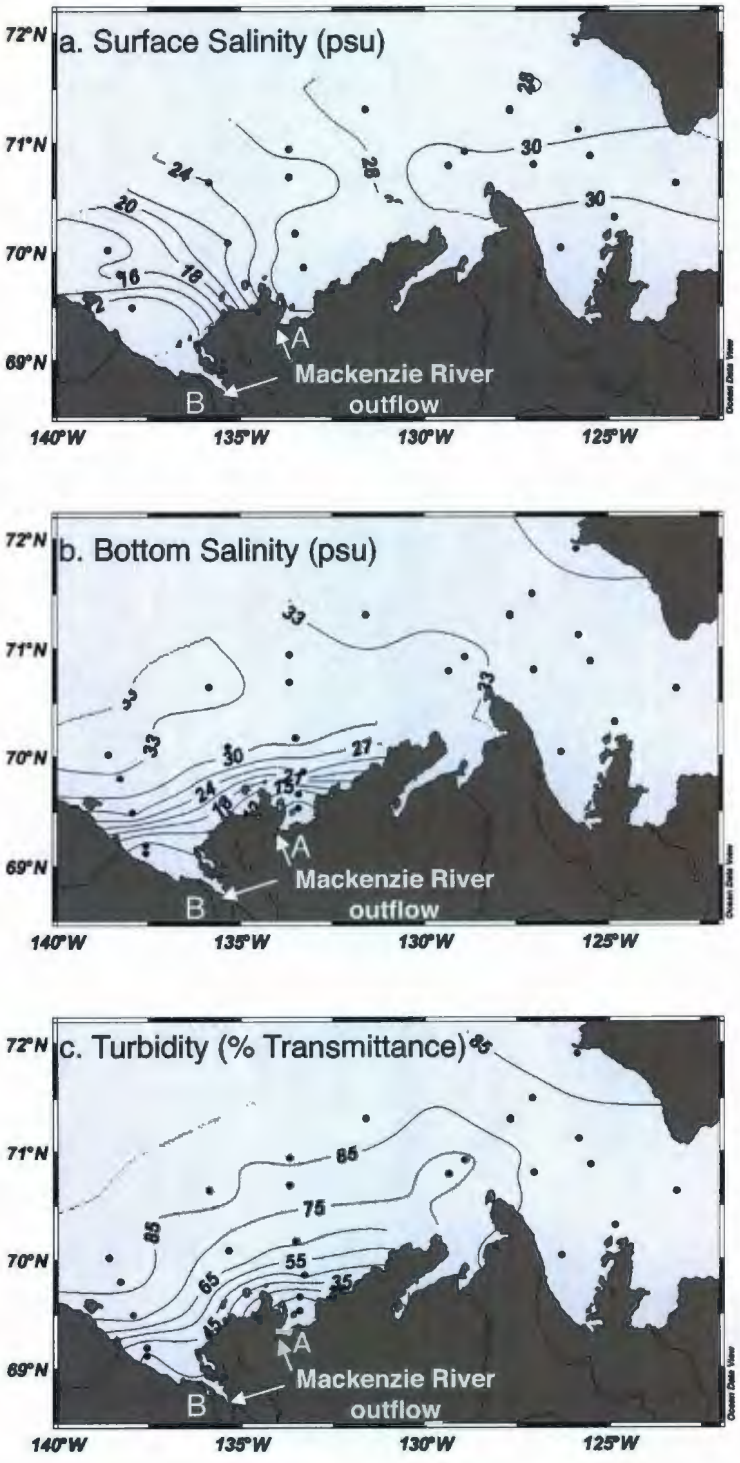


Figure 2.4. Contour plots of (a) surface salinity, (b) bottom salinity and (c) turbidity across the Beaufort Sea shelf. Data were collected from CTD casts about 10 m above the sea floor corresponding to stations where near-bottom water was collected.

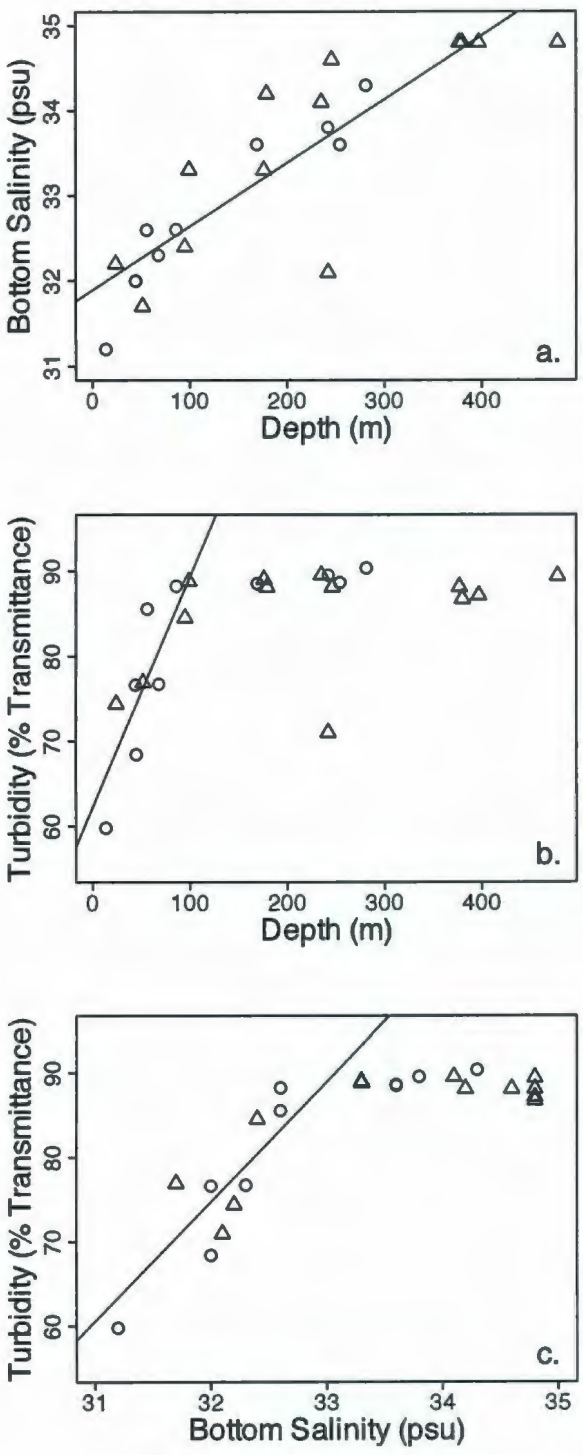


Figure 2.5. Bottom salinity, turbidity, and depth at which near-bottom water was collected at shelf (o) and gulf (△) stations on the Beaufort Sea shelf. Salinity and turbidity were measured with a CTD profiler about 10 m from the sea floor. Line in (a) indicates significant linear regression ($p < 0.05$, $df = 22$, $r^2 = 0.77$). Turbidity is positively related to bottom depth up to 100 m (b) and bottom salinity up to 33 psu (c; $p < 0.05$, $df = 9$).

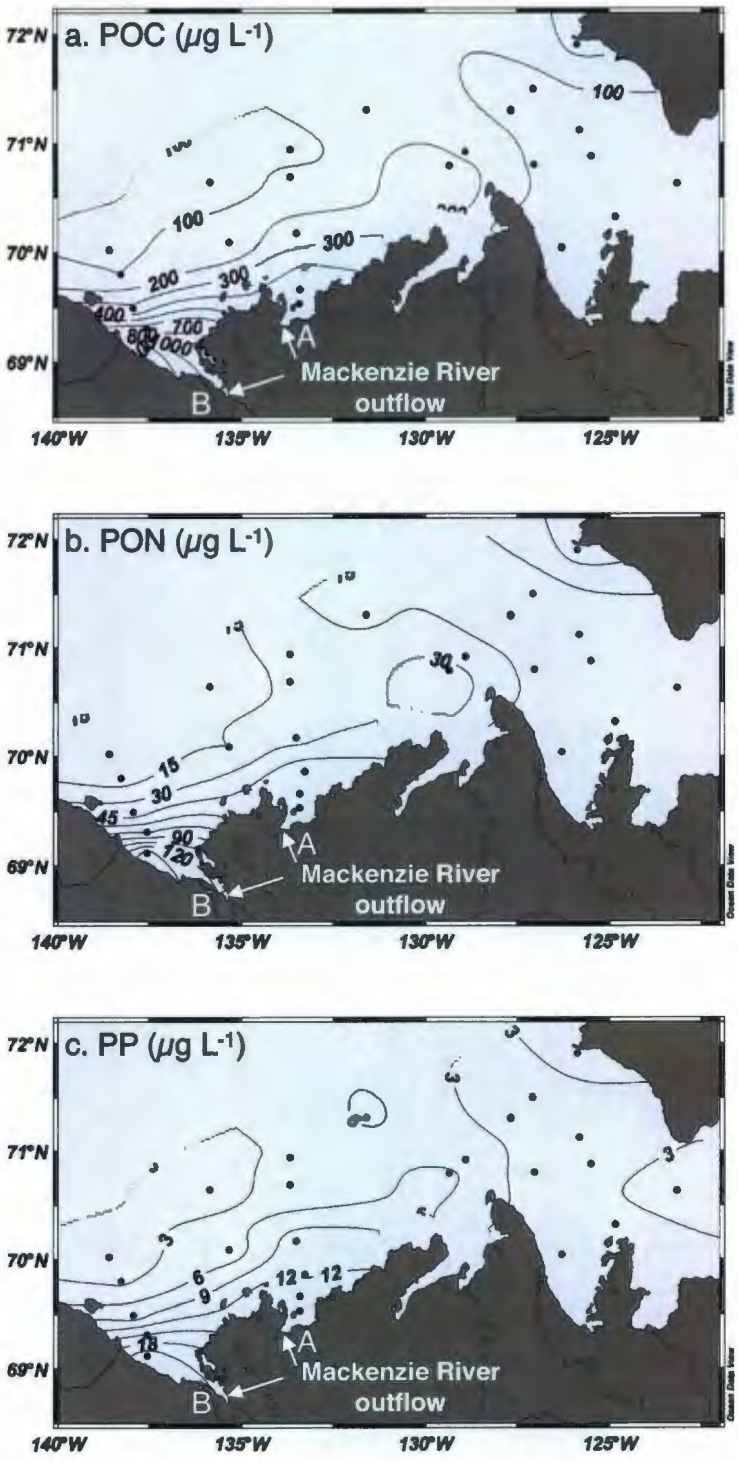


Figure 2.6. Contour plots of (a) particulate organic carbon (POC), (b) particulate organic nitrogen (PON), and (c) particulate phosphorus (PP) in near-bottom water across the Beaufort Sea shelf. Samples were collected with a bottom-tripping Niskin bottle.

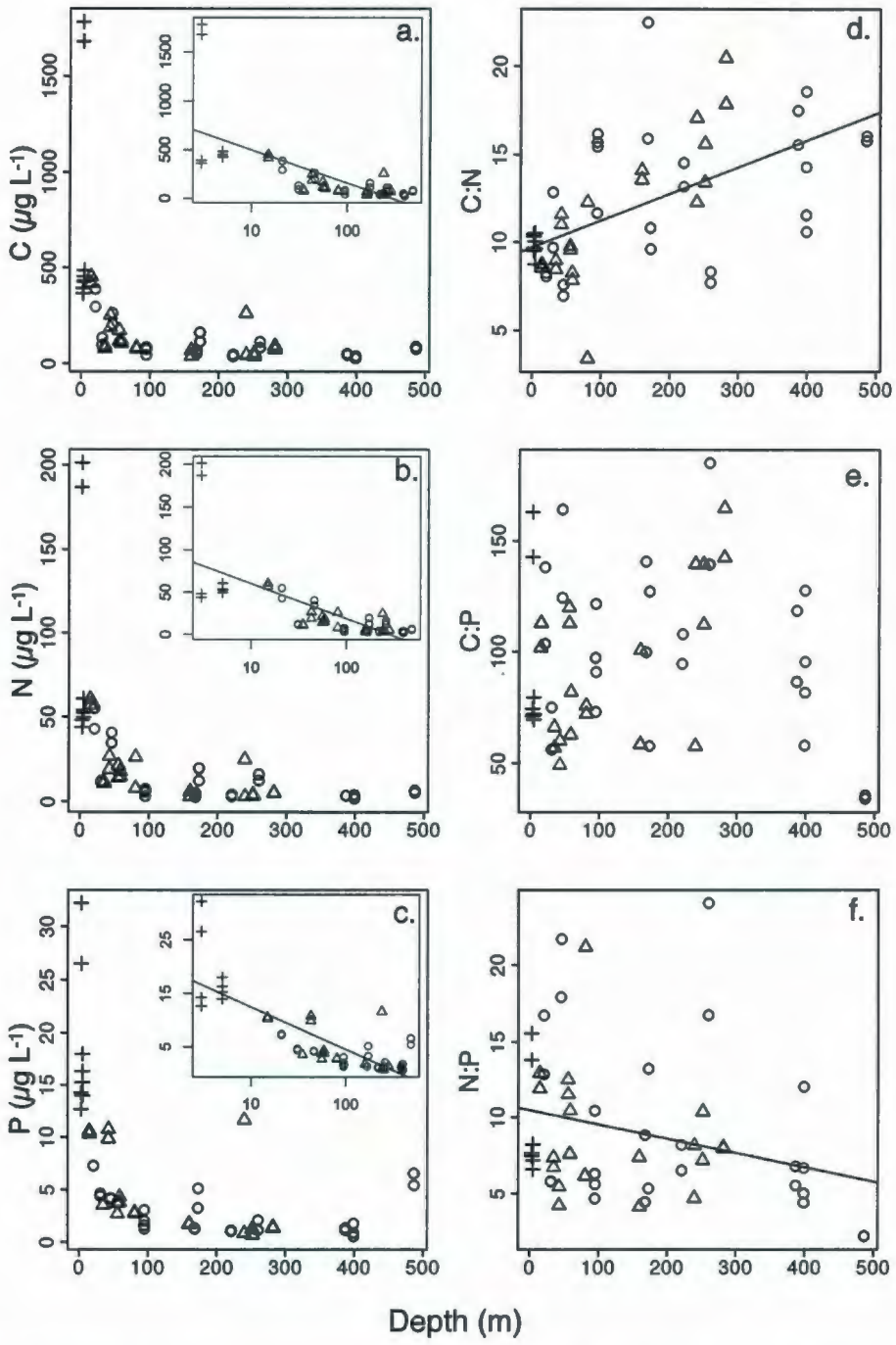


Figure 2.7. Bottom depth *versus* (a) carbon (C), (b) nitrogen (N), (c) phosphorus (P), (d) C:N, (e) C:P, and (f) N:P for particulate organic matter from near-bottom waters on the Beaufort Sea shelf. Inserts in (a)-(c) are with bottom depth on a $\log_{10}$ scale. Lines in (a)-(d) and (f) indicate significant regressions ($p < 0.05$, $df = 53$, $r^2 = 0.54$ (a.), 0.59 (b), 0.67 (c), .0.33 (d), and 0.11 (f). Elemental ratios are molar:molar. Symbols represent samples from river (+), shelf (o), and gulf (△) stations.

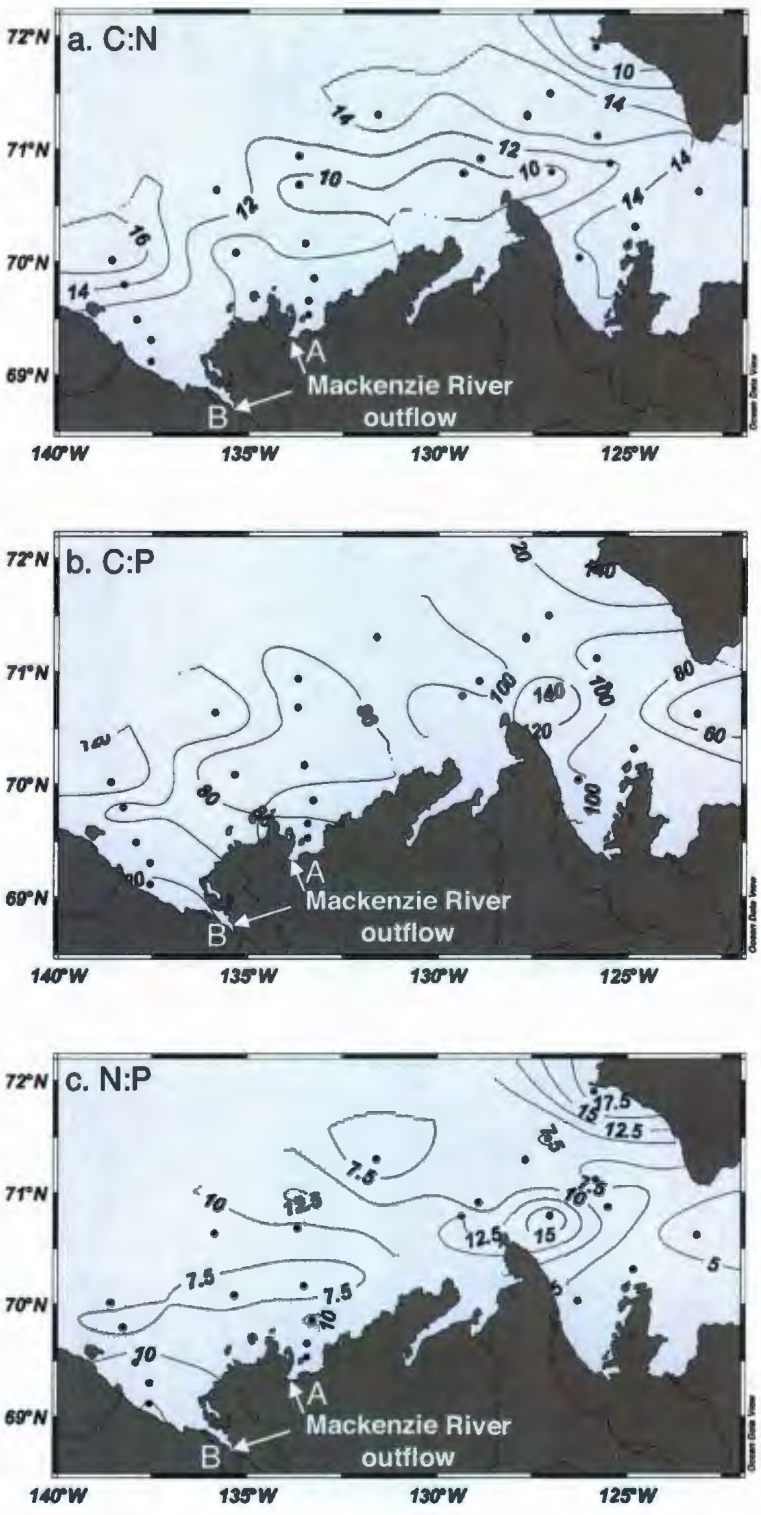


Figure 2.8. Contour plots of carbon (C), nitrogen (N), and phosphorus (P) ratios for near-bottom water across the Beaufort Sea shelf; (a) C:N, (b) C:P, and (c) N:P as mol:mol. Samples were collected with a bottom-tripping Niskin bottle.

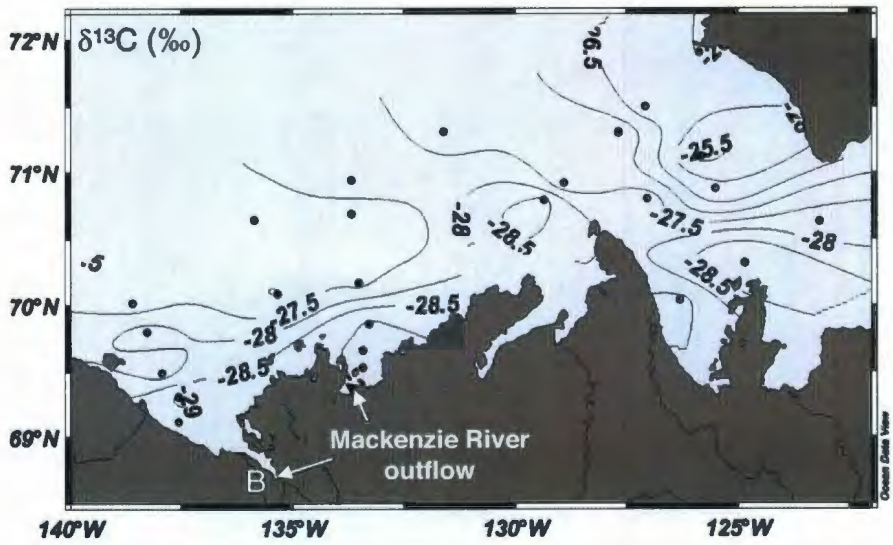


Figure 2.9. Contour plot of $\delta^{13}C$ (‰) in near-bottom water across the Beaufort Sea shelf. Samples were collected with a bottom-tripping Niskin bottle.

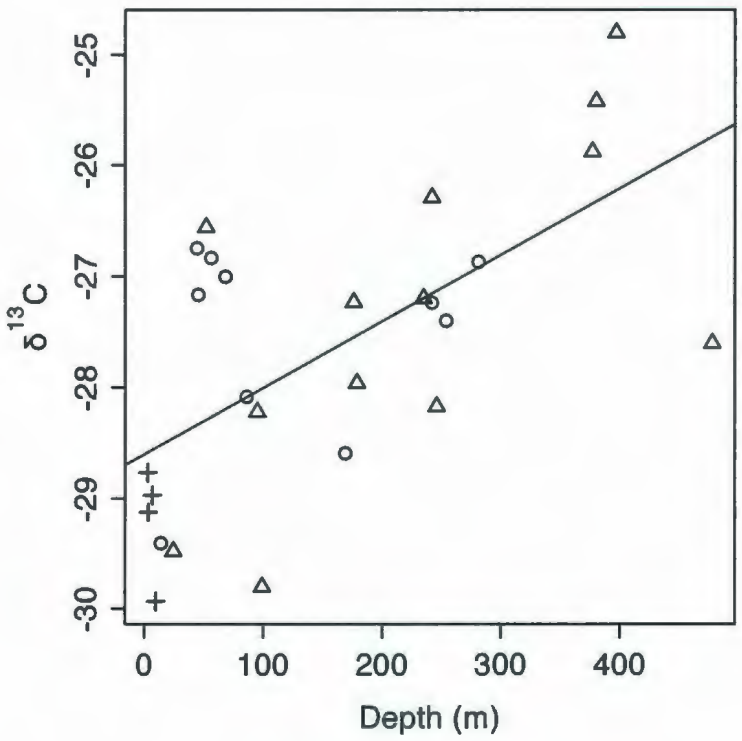


Figure 2.10. $\delta^{13}C$ (‰) *vs* depth for near-bottom water samples from the Beaufort Sea shelf. Symbols indicate samples from river (+), shelf (o), and gulf (△) stations. Line indicates significant linear regression ($p < 0.05$, $df = 26$, $r^2 = 0.40$).

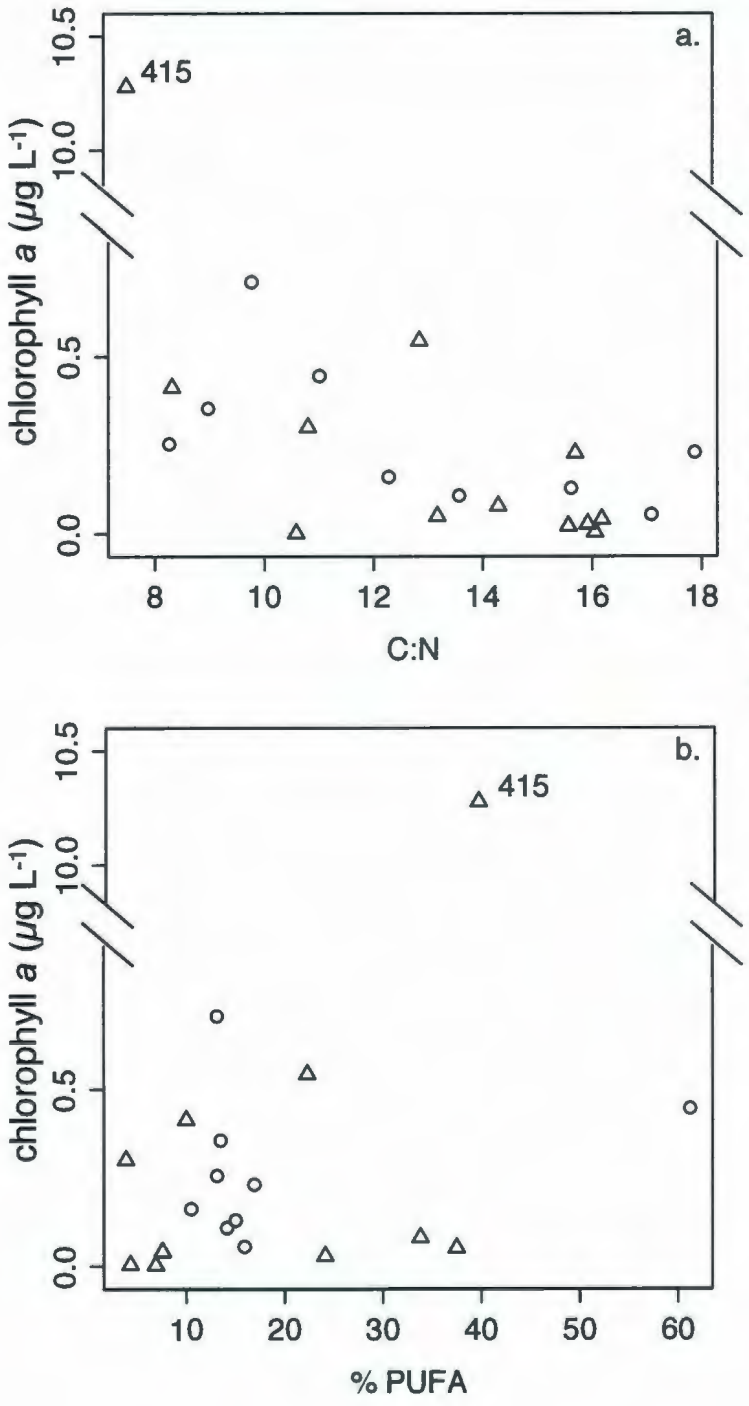


Figure 2.11. Chlorophyll *a vs* C:N (a) and polyunsaturated fatty acids (PUFA) as a % of total fatty acids (b) for near-bottom water collected from the Beaufort Sea shelf. Symbols represent samples taken from shelf (o) and gulf (△) stations. Chlorophyll *a* values were < 1 µg L^{-1}except at station 415. Note break in y-axis at 1 µg L^{-1}.

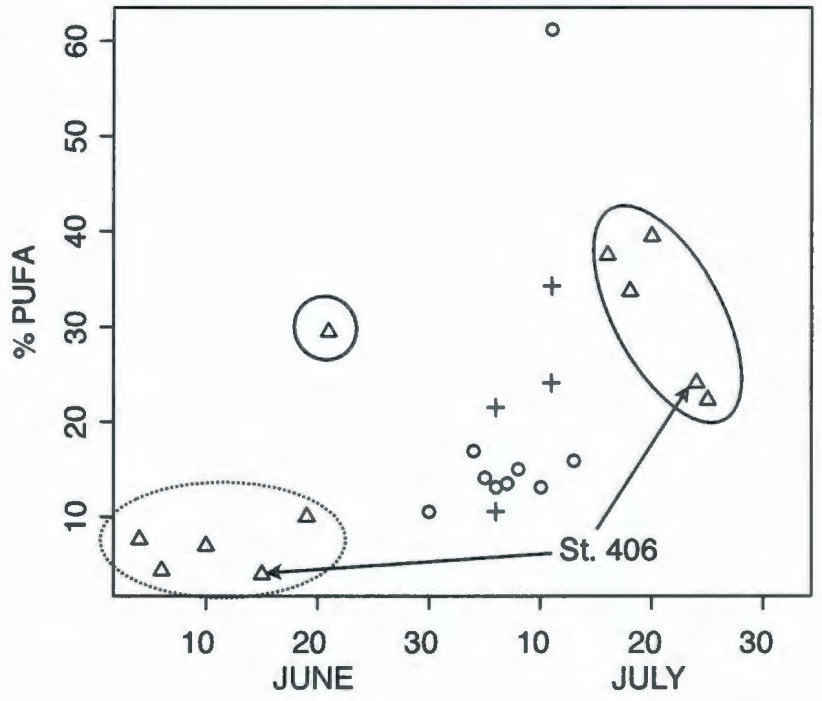


Figure 2.12. Temporal change in percentage of polyunsaturated fatty acids (PUFA) from June to July for near-bottom water samples collected from the Beaufort Sea shelf in 2004. Symbols represent samples collected from river (+), shelf (o), and gulf (△) stations. PUFA levels significantly increased from the beginning of June (stations in dotted oval) to the end of June and July (stations in solid ovals) in the Amundsen Gulf. Arrows point to station 406 in the Amundsen Gulf, where near-bottom water was collected once in mid-June and once in July.

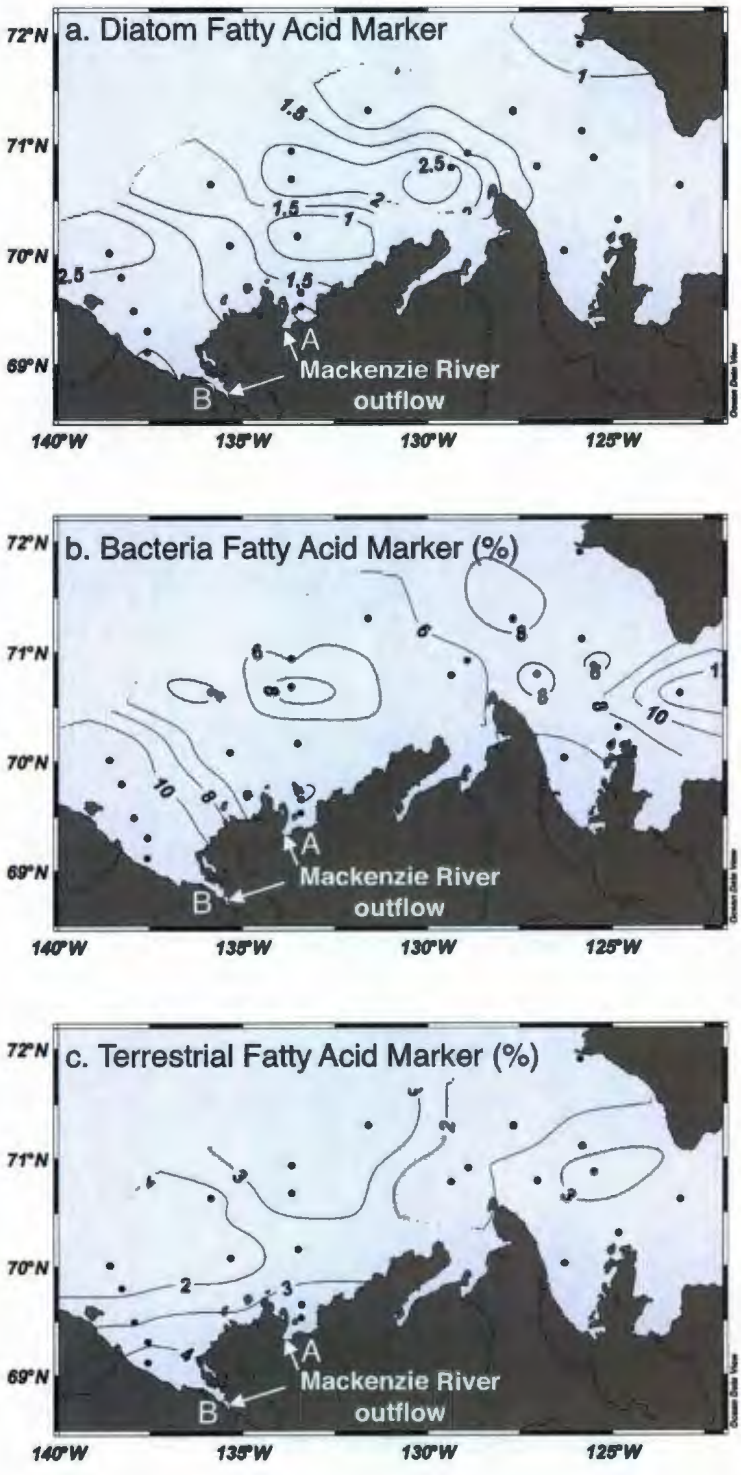


Figure 2.13. Contour plots of fatty acid biomarkers for near-bottom water across the Beaufort Sea shelf; (a) diatom (∑16:1/16:0), (b) bacteria (odd-chain and branched fatty acids), and (c) terrestrial (18:3ω3 + 18:2ω6) markers. Samples were collected with a bottom-tripping Niskin bottle. Bacterial and terrestrial markers are % of total fatty acids identified, diatom marker is unitless.

CHAPTER 3

ELEMENTAL COMPOSITION AND LIPID CLASSES OF ZOOPLANKTON FROM THE BENTHIC BOUNDARY LAYER OF THE BEAUFORT SEA SHELF

3.1. ABSTRACT

Elemental and lipid class compositions were determined for 26 taxa (genus and species) within 8 taxonomic groups (amphipod, mysid, decapod shrimp, euphausiid, chaetognath, copepod, holothurian, and polychaete) of benthic boundary layer zooplankton from the Beaufort Sea shelf. P content and N:P ratios for the entire data set were more variable than C, N or C:N ratios. P content was negatively correlated with body length, probably reflecting decreasing P content with growth. C content and C:N were positively correlated with storage lipids (triacylglycerols (TG) and wax ester-steryl esters (WE/SE)) and negatively correlated with membrane lipids (phospholipids and sterols). Most taxa had high levels of storage lipids, generally TG. High levels of WE/SE were found in the copepod *Calanus hyperboreus* (> 90% of total lipid) and the chaetognath *Eukrohnia hamata* (72%). In contrast, the chaetognath *Parasagitta elegans* had only minor proportions of both TG and WE/SE. The high levels of storage lipids in most taxa analyzed here indicate that feeding behavior of benthic boundary layer zooplankton on the Beaufort Sea shelf is tightly linked with seasonal pulses of epipelagic production. This is the first report on the biochemical composition of many of the amphipod and mysid taxa presented here.

3.2. INTRODUCTION

In the past decade, there has been an increase in our understanding of the diversity of invertebrates in the benthic boundary layer (BBL) in polar oceans (Brandt 1997, Brandt 2001, Linse et al. 2002, Brandt and Berge 2007, Brökeland et al. 2007). Zooplankton in the BBL have access to a variety of food resources resulting from sedimentation, resuspension, and active migration to epipelagic waters, and may therefore play a role in the trophic transfer of energy, in nutrient cycling, and in enhancing links between pelagic and benthic populations. However, because of sampling difficulties, the life histories, trophic dynamics, and role of BBL zooplankton in nutrient cycling remain poorly understood.

Insight into the role of a species in community energetics and nutrient cycling can be gained by biochemical analyses such as lipid class composition and elemental composition. The elemental content and stoichiometry of zooplankton are influenced by growth rate, reproduction, energy storage and usage, nutrient availability, and life history (Elser et al. 1996, Elser et al. 2000, Vrede et al. 2004, Ventura and Catalan 2005). Elemental composition reflects the molecular composition of organisms and can often be related to macromolecules such as lipid and protein (Ventura 2006). In addition, comparisons between the elemental stoichiometry of consumers and their food sources have provided insight into the cycling of nutrients in aquatic ecosystems (Sterner 1990, Elser and Urabe 1999). However, most of this work has been done on freshwater crustaceans and relatively little on marine zooplankton, particularly in relation to phosphorus. There is a need to increase our knowledge of the elemental compositions of marine species in order to determine whether hypotheses about ecosystem function (i.e. nutrient recycling, nutrient limitation, species

interactions, and primary production) based on C:N:P (carbon:nitrogen:phosphorus) ratios in lakes and rivers are applicable to continental shelf waters.

Herbivorous zooplankton living in areas with pronounced seasonal primary production are able to accumulate large stores of energy in the form of lipids. The two primary storage lipids of zooplankton are wax esters and triacylglycerols (Lee et al. 2006). They use these lipid reserves to survive during periods of low food supply and to reproduce (Hagen and Auel 2001, Lee et al. 2006). However, much of our knowledge of lipid storage dynamics in the Arctic relates to calanoid copepods (Scott et al. 2002, Hirche et al. 2003, Stevens et al. 2004, Graeve et al. 2005). Data from the few studies that have been carried out demonstrate that benthic invertebrates in the Arctic and Antarctic store less lipid than do pelagic herbivorous copepods (Graeve et al. 1997, Graeve et al. 2001) suggesting a more constant food supply. Whether this trend is generally true of polar invertebrates living in close association with the sea floor, including BBL zooplankton, remains to be seen.

The aim of this study was to examine the biochemical composition (lipid classes and C, N, and P composition) of BBL zooplankton from the Beaufort Sea shelf. The Beaufort Sea shelf, in the western Canadian Arctic, is an area of intense seasonality in pelagic production (Carmack et al. 2004), which is heavily influenced by the Mackenzie River (Chapter 2, Macdonald et al. 1998). This is the first report on the biochemical composition of many of the species analyzed here, using either elemental content or lipid classes.

3.3. METHODS

3.3.1. Sample Collection

BBL zooplankton were collected at 27 stations on the Beaufort Sea shelf from the Canadian CCGS *Amundsen* in fall 2003 and summer 2004 as part of the Canadian Arctic Shelf Exchange Study (CASES; Table 3.1, Fig. 3.1). Animals within 60 cm of the bottom were collected with an epibenthic sled equipped with a 500 μm net and open cod end (Choe and Deibel 2000). A door across the mouth was triggered to open only during those times when the sled was in contact with the bottom. As soon as the sled was retrieved, the contents of the cod end were gently rinsed into coolers with seawater. Cooler contents were then rinsed with surface water to remove mud. Four to five common species were selected at each station depending on size and abundance, but usually included amphipods, mysids, decapod shrimp and chaetognaths. At each station, two sets of up to 20 animals of each species were sized (body length) and pooled for either C/N and P, or lipid analyses. Samples for C/N and P analyses were frozen at -80°C to await transfer to the laboratory. Samples for lipid analysis were put in 15-mL vials prewashed with lipid solvents, covered with chloroform (2 - 4 mL) and stored at -20°C under N_2 until processing on land. Additional individuals were fixed in 4% buffered formaldehyde for species identification. A total of 109 pooled samples from 8 different taxonomic groups was analyzed during this study. 'n' was the number of stations a taxa was collected from.

3.3.2. C, N, and P Content and Lipid Analyses

Samples were freeze-dried, homogenized, and subsamples of known weight removed for C/N and P analyses. C and N were measured simultaneously with a Perkin-Elmer 2400 CHN analyzer, using acetanilide as a standard. P was measured colorimetrically as soluble reactive phosphorus following high temperature hydrolysis (Solórzano and Sharp 1980). Duplicate samples for C/N were analyzed when possible. Errors of duplicate samples for C and N were 5 and 6%, respectively. Coefficient of varation (CV) for P estimated from 4 replicate standards was 3%. C, N, and P content is reported as a percentage of dry weight and elemental ratios of C:N:P are reported as molar ratios.

Lipids were extracted in chloroform:methanol:water (2:1:0.5) following a modified version of Folch et al. (1957; Parrish 1999). Briefly, samples were ground, sonicated and centrifuged in the chloroform:methanol:water mixture three times. Lipid layers were removed and pooled following each of the three chloroform washes. Lipid classes were separated and quantified by spotting lipid extracts on silica gel coated rods (Chromarods-SIII) and passing rods through the flame ionization detector of an Iatroscan MK V (Parrish 1987). Lipid classes were identified and quantified by comparing peak position and peak area with the following standards: *n*-nonadecane (hydrocarbon; HC), cholesteryl palmitate (steryl ester; SE), 3-hexdecanone (ketone), tripalmitin (triacylglycerol; TG), palmitic acid (free fatty acid; FFA), 1-hexadecanol (alcohol; ALC), cholesterol (sterol; ST), 1-monopalmitoyl-rac-glycerol (acetone-mobile polar lipid; AMPL), and DL-α-phosphatidylcholine depalmitoyl (phospholipid; PL). Wax esters and steryl esters are not separable with this method and are referred to

here collectively as WE/SE. The relative amount of each lipid class was determined as a percent of total lipid and total lipid was calculated as the sum of the masses of all the lipid classes identified. A lipolysis index was calculated for all samples: (free fatty acids + free fatty alcohols) / (acyl lipids + alcohols) x 100.

3.3.3. *Statistical Analysis*

Differences in mean values of lipid classes and elemental content among and within taxonomic groups were tested with a general linear model using the statistical package R, where *taxonomic group* referred to a taxonomic level of order and higher, and divisions within taxonomic groups were referred to as *taxa* (i.e. at the genus or species level, usually the later). In 7 cases, species within the same genus were pooled (*Bythocaris* spp., *Erythrops* spp., *Rhachotropis* spp., *Anonyx* spp., *Hippomedon* spp., *Halirages* spp., and *Syrrhoe* spp.). Differences in mean values among taxa within a taxonomic group were also tested with a general linear model. When taxa were significantly different for a specific response variable a pairwise *t*-test with an adjusted p-value (Bonferroni correction) was used to determine which taxa accounted for the difference. Those taxonomic groups and taxa with only one sample were not included in the analyses. Relationships between lipid classes and elemental composition across all samples were explored using a Pearson product-moment correlation analysis. A rejection criterion of $p \leq 0.05$ was used to determine statistical significance in all analyses. Ketones were detected in only a few samples, but only at low levels and were therefore not included in statistical analyses. Errors are reported as standard deviations when $n > 2$ and as half the range when $n = 2$, unless otherwise noted. Samples were collected from across the Beaufort Sea shelf in

the months of June, July, and October. These spatial and temporal differences in sample collection could be a source of variability that cannot be tested.

3.4. RESULTS

3.4.1. Elemental and Lipid Class Content Among Taxonomic Groups

Twenty-six species and genera (collectively referred to here as 'taxa') from the following 8 taxonomic groups were collected for analysis: amphipod, chaetognath, copepod, decapod shrimp, euphausiid, holothurian, mysid, and polychaete (Table 3.2).

Taxonomic groups differed in both elemental and lipid composition (Fig. 3.2 - 3.4). Mean elemental content varied ~ 3-fold among taxonomic groups for C, N, and P (Fig. 3.2). Mean C content ranged from ~ 20% dry weight for holothurians to ~ 60% for copepods and euphausiids. Mean C content for the remaining 5 taxonomic groups was relatively constrained, ranging from ~ 37 - 47%. Mean N content ranged from 4% dry weight for holothurians to ~ 12% for euphausiids (Fig. 3.2). Unlike the case for C content, copepods had a mean N content (7.4%) close to the grand mean of 8.1% (Table 3.3). Mean P content ranged from ~ 0.4% dry weight for holothurians and chaetognaths to 1.1% for euphausiids (Fig. 3.2). Most notable was the greater within group variability in mean P content in comparison with mean C and N content (Fig. 3.2). This pattern of variability was also evident in the grand mean C, N and P content over all taxa and taxonomic groups, with a coefficient of variation of ca 20% for C and N and ~ 40% for P (Table 3.3).

Mean elemental ratios were conserved more than the individual C, N, and P values (Fig. 3.3). Mean C:N, C:P, and N:P ratios all varied ca 2-fold among

taxonomic groups. Decapod shrimp and the polychaete had the lowest mean C:N ratios (~ 4.8) and copepods the highest (~ 9; Fig. 3.3), suggesting high levels of energy stores in copepods (see lipid classes below). Mean C:P and N:P ratios were highest in chaetognaths (~ 40 and 7, respectively) and lowest in the holothurian (ca 17 and 3, respectively). As was the case for individual P values, the grand mean C:P and N:P values over all taxonomic groups were more variable than the grand mean C:N value (coefficient of variation ~ 43% and 17%, respectively)(Table 3.3). Mean values of all the above elemental covariates (content and ratios) were significantly different among taxonomic groups (Table 3.5).

There was evidence of highly diverse energy storage strategies among the BBL zooplankton of the Beaufort Sea shelf, as the dominant lipid class, either WE/SE, TG, or PL, varied among taxonomic groups (Fig. 3.4). TG was the predominant storage lipid in four of the taxonomic groups, whereas WE/SE was most important in copepods and chaetognaths. Euphausiids were remarkable for having essentially equal content of WE/SE and TG. Only the polychaete had very low lipid stores, containing predominantly PL (Fig. 3.4). The only two lipid classes with mean values that did not differ statistically among taxonomic groups were HC and ALC, which were only minor constituents of total lipid in most samples (Table 3.5). Note that the polychaete, which had a very high alcohol content, could not be included in this statistical analysis because there was a single sample. The mean lipolysis index for all samples was relatively low (2.6 ± 3.5%) suggesting minimal lipid degradation during transport and storage.

Information on lipid class content can often provide insight into the components of variability in bulk metrics such as C, N, and P content. The

storage lipids, WE/SE and TG, were positively correlated with C:N and C, respectively, strong evidence that variability in C:N and C content was due largely to variability in lipid storage (Table 3.6, Fig. 3.5). The membrane lipids ST and PL, on the other hand, were negatively correlated with C:N and C, respectively (Table 3.6, Fig. 3.5). PL was also negatively correlated with N. There was a strong inverse relationship between length and P content, perhaps accounting for some of the positive correlation between length and C:P and length and N:P (Table 3.6). In addition, P content was strongly positively correlated with WE/SE (Table 3.6).

3.4.2. Amphipods

The biochemical composition of amphipods varied within and among the 11 taxa analyzed in this study (Table 3.3 - 3.5, Fig. 3.6 - 3.8). This variability is not surprising given the taxonomic and size diversity within amphipods, with a 4-fold range in mean body length (i.e. 6 - 26 mm)(Table 3.2). There was a significant difference among amphipod taxa in elemental content and ratios, but not in total lipid per individual (Table 3.5, Fig. 3.6 - 3.7), most likely due to very high variability in total lipid content within *Anonyx* spp. and *Halirages* spp. (Table 3.4). Mean values of TG, AMPL, and PL differed significantly among amphipod taxa (Table 3.5), with TG generally the dominant lipid class (Table 3.4, Fig. 3.8). *Acanthostepheia malmgreni* was the only amphipod having PL as the dominant lipid class (Table 3.5, Fig. 3.8). However, a single sample of *A. malmgreni* collected in the fall indicated that this species was capable of storing lipids, with a TG level of 64% *versus* < 20% for the remaining samples. In addition, the single *Eusirus cuspidatus* sample had higher levels of WE/SE (23%) than other amphipods (Table 3.4, Fig. 3.8).

3.4.3. *Mysids*

The six mysid taxa were similar in biochemical composition (Table 3.5, Fig. 3.6 - 3.8). The only statistically significant differences were in mean total lipid content, C content, and WE/SE levels (Table 3.5). *Mysis litoralis* had the highest C content (50.0 ± 1.8%) and *Boreomysis arctica* the highest WE/SE levels (23.1 ± 1.6%), while *Michthyops theeli* had the lowest levels of both (Table 3.3, 3.4, Fig. 3.6, 3.8). TG was the dominant lipid class in all mysid samples except for one *Erythrops* spp. sample in which PL (~ 48%) was the dominant lipid class (data not shown).

3.4.4. *Decapod Shrimp*

The decapod shrimp *Eualus gaimardii* and *Bythocaris* spp. had similar elemental content and ratios (Fig. 3.6 - 3.8), with statistically significant differences only in mean WE/SE, FFA and PL levels (Table 3.5). While TG was the predominant storage lipid in both decapod species, *Bythocaris* spp. was the only taxon containing moderate levels of WE/SE and also had almost double the sum of storage lipids (i.e. TG + WE/SE) as did *E. gaimardii* (~ 70% *versus* 40%, respectively; Table 3.4, Fig. 3.8). Statistical comparisons including *Sclerocrangon ferox* could not be made (n = 1).

3.4.5. *Chaetognaths*

The two chaetognath species examined showed evidence of fundamentally different energy storage strategies, despite similarity in size with a pooled mean length of 30.1 ± 4.2 mm for pooled samples (Table 3.2). Mean C content, C:N ratios, and total lipid were higher in *Eukrohnia hamata* than in

Parasagitta elegans (Table 3.3, 3.4, Fig. 3.6 - 3.7). Mean values of HC, WE/SE, ST and PL also differed between the two species (Table 3.4 - 3.5, Fig. 3.8), likely due to much higher WE/SE levels in *E. hamata* (73 ± 10%) than in *P. elegans* (< 1%). As expected, given the low WE/SE and TG levels the dominant lipid class in *P. elegans* was PL (86 ± 5%; Fig. 3.8).

3.4.6. *Copepods, Holothurians, Euphausiids, and Polychaetes*

Adult female *Calanus hyperboreus* had relatively consistent C and N content but more variable P content (Table 3.3). The dominant lipid class was WE/SE (> 90% of total lipids) for both the fall and summer sample (Table 3.4, Fig. 3.8). Other lipid classes made only minor contributions.

The dominant lipid class of the euphausiid *Thysanoessa raschii* was PL (Fig. 3.8; note n = 1). However *T. raschii* did show evidence of considerable storage of both WE/SE and TG (Table 3.4, Fig. 3.8)

Two samples of an unidentified holothurian species were collected, one in the fall and one in the summer (Table 3.2). The dominant lipid classes were TG (58%) in the summer and PL (47%) in the fall.

PL dominated the lipid fraction in the single polychaete sample, possibly of the genus *Aglaophamus,* with WE/SE and TG found in lesser amounts (Table 3.4, Fig. 3.8). However, unlike any of the other taxa, ALC was over 20% of total lipid in this polychaete (Fig. 3.8).

3.5. DISCUSSION

3.5.1. C, N and P Content and Stoichiometry

The elemental composition of BBL zooplankton is poorly known. Generally, however, lipids contain high proportions of C and relatively little P and N, proteins high levels of C and N but little P, and carbohydrates insignificant amounts of either N and P (Ventura 2006, Table 3.7). C and N pools are primarily derived from protein and P pools from PL (Ventura 2006). Thus, the accumulation of lipid-rich energy stores can affect the elemental composition and stoichiometry of animal tissues because lipids and proteins differ in C, N and P content relative to one another and thus have different C:N:P ratios. Increased C content in relation to N and P may be amplified in zooplankton at higher latitudes due to increased seasonal lipid storage (Lee et al. 2006).

Direct comparison of my elemental composition data and published data for the same species is limited due to the general lack of physiological and ecological information on BBL zooplankton. However, the mean C, N, and P contents of BBL zooplankton in the present study were in the range typical for many non-gelatinous pelagic zooplankton from the Southern Ocean (33 – 47% C, 7 – 12% N, 0.3 – 1.2% P; Ikeda and Mitchell 1982). The high C content (56%) and C:N ratios (8.9) of *Calanus hyperboreus* from the Beaufort Sea shelf can probably be explained by its high levels of WE. C content > 50% has been observed in marine polar copepods (Ikeda and Skjoldal 1989, Donnelly et al. 1994) and is associated with the accumulation of lipid. The positive correlation of C content and C:N with storage lipids (i.e., WE/SE and TG) and the negative correlation with membrane lipid (i.e., PL and ST) in my data support the idea that C and

C:N ratios reflect lipid stores in polar zooplankton. Likewise, the higher C content and C:N ratios of *Eukrohnia hamata* compared with *Parasagitta elegans* are most likely related to the higher lipid content of the former species.

The mean C:N ratio of 5.0 for *Parasagitta elegans* in this study is higher than the maximum determined over an annual cycle of *P. elegans* samples from the BBL in Conception Bay, Newfoundland (< 4.7; Choe et al. 2003). Only one sample in my study had a C:N ratio ≤ 5.0, and was collected at the only station with high chlorophyll *a* levels (st. 415, Chapter 2). These high C:N ratios may be due to N limitation on the Beaufort Sea shelf, as the C content of *P. elegans* in my samples is similar to, but the N content lower than, that of *P. elegans* from the Barents Sea (Ikeda and Skjoldal 1989). For example, using mean C and N content from Ikeda and Skjoldal (1989) gives a C:N ratio for *P. elegans* of only 3.2, considerably lower than the value of 5.0 from my samples. Likewise, Donnelly et al. (1994) reported C:N ratios of 4.1 in the winter and 3.7 in the fall for *Eukrohnia hamata* collected in the Southern Ocean, lower than the minimum C:N ratio for *E. hamata* in the present study (5.4 – 8.0). In this case the C content of *E. hamata* from the Southern Ocean was much lower than in this study (19.7 – 37.5% *vs* 39.7 – 46.7%) while the N content was similar (Donnelly et al. 1994). An important difference among these studies (including this one) is that with the exception of Choe et al. (2003) published values come from pelagic chaetognaths. These comparisons of C content and C:N ratios suggest that Beaufort Sea chaetognaths are either N-limited or have a higher lipid content than those living in more temperate waters or in other seas at high latitudes (Båmstedt 1978, Percy and Fife 1981).

Amphipods were the only group that exhibited significant differences among taxa in mean values of all elemental composition variables. This probably

results from the greater diversity of amphipod species included in this study compared with the other taxonomic groups, and also the diverse physiology of the animals analyzed. Very little is known about the elemental composition of Arctic amphipods, including pelagic hyperiid species, sympagic gammarid species, and gammarid species living close to the sea floor.

Mysids were less variable in their elemental composition than amphipods. Again, there is a lack of published information on the mysid species analyzed here, so direct comparisons cannot be made, but comparisons with *Mysis mixta* from previous studies are possible. The C:N ratios of my species are higher than those of *M. mixta* from the Baltic Sea (Lehtiniemi et al. 2002). *M. littoralis* from the Beaufort Sea shelf has generally higher C and generally lower N content, and thus higher C:N ratios, than does *M. mixta* studied in the laboratory (*M. mixta:* 37 – 44% C, 10 – 13%N, Gorokhova and Hansson 2000). An important difference between these two studies is that Gorokhova and Hansson (2000) only used abdominal muscle while I used whole animal extracts. They also found that the elemental composition of *M. mixta* varies with growth and development, C content and C:N ratios generally decreasing with development, suggesting that lipids reserves represent an important energy source for developing mysids (Gorokhova and Hansson 2002). However, Richoux et al. (2004a) found that lipid levels of *M. mixta* from the BBL in Conception Bay, Newfoundland, increase with development which is generally the case for many marine invertebrates post-metamorphosis.

The inverse relationship between P content and body length is probably also related to developmental stage. This relationship can be seen most clearly in my data on decapod shrimp, since a wide range of body sizes of animals was analyzed. Also, the carapace of *Sclerocrangon ferox* was still soft and not fully

developed, suggesting recent molting of a juvenile stage. This species can grow to 140 mm length, yet the individual examined in my study was only 27 mm long (Table 3.2). A decrease in P concentration with age has also been observed in other crustacean zooplankton (Hessen 1990, Elser et al. 2000), perhaps reflecting decreases in the rRNA P-pool (Elser et al. 2000). A variety of organisms has a higher RNA content when actively growing due to up-regulated protein synthesis, and differences in P content and N:P ratios often reflect differences in RNA content and growth (Elser et al. 2000).

Few studies of marine zooplankton include P measurements; therefore, data on P content and N:P ratios are generally limited. However, the high variability in N:P compared with C:N across all taxonomic groups in the present study is consistent with published work (Walve and Larsson 1999, Ventura 2006). Even within a species the N:P ratio can be highly variable, which brings into question the assumption that animals have relatively constant elemental ratios compared with those of their food sources. In general, however, N:P ratios of zooplankton were higher than the those of seston throughout the study region (Chapter 2). This suggests high N retention and P recycling, and thus low N:P ratios of recycled matter for BBL zooplankton given similar turnover times for both N and P (Elser and Urabe 1999). Low N:P ratios of recycled matter on shelf bottom waters would result in greater N limitation for phytoplankton when these waters are cycled back into the photic zone by upwelling.

3.5.2. Lipid Classes

The three dominant lipid classes of the BBL zooplankton in this study were WE/SE, TG, and PL. Typically, zooplankton that need long-term energy stores accumulate WE, while those requiring shorter-term energy stores

accumulate TG (Lee et al. 2006). PL are primarily structural components of cell membranes, although some species also use PL for energy storage (Jeffs et al. 2001). Accumulation of storage lipids as energy reserves in polar zooplankton is an important adaptation to the pronounced seasonal and temporal variability of the food supply in high latitude seas (Lee et al. 2006). Although WE/SE are present in almost all taxonomic groups, *Calanus hyperboreus* had a much greater proportion of WE/SE in the present study than any other group (> 90% of total lipids), which is consistent with previous studies showing higher WE/SE levels in this species than in most copepods (Lee 1975, Stevens et al. 2004, Lee et al. 2006).

A surprising discovery was the high levels of WE/SE in the chaetognath *Eukrohnia hamata*. Previous studies have shown that this species can store moderate amounts of WE (12%, Lee 1975), unlike another chaetognath, *Parasagitta elegans* (< 1 - 8%, Sargent and Lee 1975, Falk-Petersen et al. 1987). An unidentified *Eukrohnia* species taken in a vertical plankton tow (2300 m to surface) in the South Pacific Ocean contained 26% WE (Lee and Hirota 1973). Similarly, two different unidentified chaetognaths from deep-water trawls in the North Pacific, most likely *Eukrohnia* spp., had high levels of WE (34% and 71%, Lee et al. 1971), comparable with values for my *E. hamata* samples. Lee and Hirota (1971) concluded that most deep-water chaetognaths store WE but epipelagic chaetognaths do not. The lipid class composition of *E. hamata* from the BBL in this study seems to support this conclusion. However, this generality may be species-specific, as *P. elegans* also from the BBL had insignificant levels of WE and low levels of TG.

Even for a predator such as *Eukrohnia hamata*, food availability may be limited in the winter, requiring the storage of energy reserves, especially if this

species is more omnivorous than *Parasagitta elegans*. Hop et al. (2006) proposed that in the Fram Strait, *E. hamata* feeds at a lower trophic level than *P. elegans*, according to stable isotope data for nitrogen. Stable isotope ratios of nitrogen for these two chaetognath species in the BBL of the Beaufort Sea shelf also place *E. hamata* at a lower trophic level than *P. elegans* (Chapter 4). In other studies of these two species, TG was often greater than 10% of total lipid. However, in this study it was a minor component of total lipids, *P. elegans* having slightly higher levels than *E. hamata*. High PL and low levels of TG and WE in *P. elegans* are in agreement with previous studies showing that *P. elegans* is a continuously feeding carnivore that depends on storage lipids to a limited degree (Sargent and Lee 1975, Falk-Petersen et al. 1987).

Four other taxa had mean WE/SE levels greater than 10%: the euphausiid *Thysanoessa raschii*, the mysids *Boreomysis arctica* and *Parerythrops obesa*, and the amphipod *Eusirus cuspidatus*. In addition to WE/SE, these species also contained significant amounts of TG. WE have previously been observed in *T. raschii* in waters off Norway with levels approaching 30% of total lipids in winter. However, TG was generally the major neutral lipid throughout the year (Falk-Petersen et al. 1981), as seen in this study. Falk-Petersen et al. (1981) suggested that high levels of PL in *T. raschii* might indicate that they have a purpose other than in cell membranes, e.g. gamete production or seasonal tissue renewal, as observed in cold water scallops (Thompson 1977). Specifically, the PL phosphatidylcholine may play a role in lipid storage of certain high latitude euphausiids (Hagen et al. 1996).

Although *Boreomysis arctica* and *Paraerythrops obsea* contained moderate levels of WE/SE, TG was the major lipid in both species. The diet of *B. arctica* in the Mediterranean Sea is mainly based on material of pelagic origin such as

phytodetritus and crustacean remains (Cartes and Sorbe 1998). The food supply of *B. arctica* in the Arctic may also vary with seasonal pelagic production, requiring WE and TG as energy reserves during periods of low food supply. *P. obesa* had a similar lipid class profile to *B. arctica* with slightly lower WE/SE, suggesting that *P. obesa* may also depend on seasonal pulses of food from the photic zone. The remaining mysid species had high levels of TG but lesser amounts of WE/SE. *Mysis litoralis* in this study had considerably more TG than *M. mixta* (90% *vs* ≤ 55%, respectively) from the BBL in Conception Bay, Newfoundland (Richoux et al. 2004a). However, seasonal changes in lipid content of *M. mixta* in Newfoundland resulted from changes in TG levels and it was therefore concluded that the feeding behavior of *M. mixta* is linked to epipelagic production. The even higher TG levels of *M. litoralis* in this study suggest that this species is well-suited to the intense seasonality of production at high latitudes. It appears that all mysid species on the Beaufort Sea shelf store TG when food is available.

Amphipods were generally more diverse in their lipid profiles than were mysids. TG was the dominant lipid class in all amphipod taxa except *Acanthostepheia malmgreni*. This contrasts with data from benthic amphipods from the Antarctic, where PL was the dominant lipid class in five of six species studied (Graeve et al. 2001). This contrast suggests that Arctic and/or BBL amphipod communities may be more tightly linked with seasonal production in the euphotic zone relative to benthic Antarctic communities and may rely on lipid reserves during periods of low food resources. This observation is consistent with data for pelagic zooplankton, Arctic species generally being lipid rich relative to Antarctic species, most likely due to greater seasonality in phytoplankton production in the Arctic than in the Antarctic (Kattner et al. 2007).

Generally, Arctic shelves are shallower than the narrow shelves found in the Antarctic, which allows for tighter benthic-pelagic coupling in the Arctic relative to the Antarctic. Likewise, the Arctic Ocean is at a higher latitude than the Southern Ocean, therefore the Arctic is subject to more intense seasonality in day length which is reflected in strong seasonal pulses of primary production relative to the Antarctic. In addition, *Eusirus cuspidatus* was the only amphipod taxon in which WE/SE were a major component of the lipid fraction. *Eusirus perdentatus* in the Southern Ocean, however, has no WE and only moderate levels of TG (Graeve et al. 2001).

Ancanthostepheia malmgreni was the only amphipod species with moderate levels of lipid storage. TG is the dominant lipid class in immature and mature *A. malmgreni* in Conception Bay, Newfoundland, while PL are the dominant class in juveniles and spent females (Richoux et al. 2004b). In general, TG levels of *A. malmgreni* in my study are consistent with those from juveniles in Conception Bay. Likewise, total lipid levels generally are most similar to those of juveniles and immature adults from Conception Bay. Based on size, however, most of my specimens were likely immature adults (Richoux et al. 2004b). Richoux et al. (2004b) observed that the lipid composition of *A. malmgreni* in Conception Bay is tightly linked to pelagic production. The high TG of the sample collected in October in my study indicates that *A. malmgreni* in the BBL of the Beaufort Sea shelf may also depend on pelagic production for food.

Decapod shrimp also had variable lipid composition and levels of storage lipids. The high levels of storage lipids in *Bythocaris* spp., including moderate levels of WE/SE and high levels of TG compared with *Eualus gaimardii,* indicate that *Bythocaris* spp. may be more tightly linked than is *E. gaimardii* to seasonal pulses of pelagic production. In a previous study, *E. gaimardii* from northeast

Greenland waters had undetectable levels of both WE and TG (Graeve et al. 1997). In my study TG was a major lipid class in *E. gaimardii,* in some cases the dominant lipid class. The differences in storage lipids between these two study sites indicate that food resources of *E. gaimardii* may be different or more constant near Greenland than in the Beaufort Sea. The Northeast Water Polynya, northeast of Greenland, is characterized by low primary productivity (Tremblay and Smith 2007). Therefore, BBL organisms such as *E. gaimardii* in northeast Greenland waters may be less coupled to epipelagic production than are organisms on the Beaufort Sea shelf. *Sclerocrangon ferox* had comparable levels of TG in the two studies, but in my study there were also detectable levels of WE/SE, whereas in Greenland *S. ferox* contained no WE/SE (Graeve et al. 1997).

The polychaete sample was the only one with a high proportion of ALC, which ranked second in relative abundance after PL. According to nitrogen stable isotope ratios, this species seems to be a predator (Chapter 4), and a high lipolysis index (20%) relative to the other taxa (mean 2.6 ± 3.5 %) indicates that high ALC levels could have resulted from the hydrolysis of copepod WE. Low levels of storage lipids have been found in other polychaete species (Clarke 1984, Graeve et al. 1997, Bühring and Christiansen 2001), but there are no reports in the literature on their ALC content.

3.6. CONCLUSIONS

The almost ubiquitous presence of high levels of WE and TG in these diverse taxa suggests that the BBL zooplankton on the Beaufort Sea shelf are directly linked to intense seasonal cycles of primary production characteristic of high latitude seas. Because of the relative absence of storage lipids, the unidentified polychaete and the chaetognath *Parasagitta elegans* seem to be the

only taxa with weak links to pelagic production. In order to appreciate better the function of different lipid classes and the role of storage lipids in BBL zooplankton of high latitude seas, there is a need for seasonal studies of the lipid dynamics in relation to benthic-pelagic coupling, life history, and reproduction.

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3.9. TABLES

Table 3.1. Station location and date of sampling for benthic boundary layer zooplankton collected from the Beaufort Sea shelf during fall 2003 and summer 2004.

Station	Lat (°N)	Long (°W)	Date	Depth (m)
718	70.17	133.52	30-Sep-03	45
CA10	69.93	138.58	7-Oct-03	238
CA06	70.59	127.23	11-Oct-03	255
500	72.00	127.57	25-Oct-03	396
118	70.95	125.83	27-Oct-03	401
206	70.32	124.85	1-Nov-03	99
206	70.32	124.85	4-Jun-04	99
256	70.25	123.50	5-Jun-04	342
108	70.63	123.17	7-Jun-04	478
117	70.88	125.50	10-Jun-04	377
406	71.31	127.69	15-Jun-04	179
400	70.92	128.92	17-Jun-04	242
303	70.80	127.04	20-Jun-04	256
398	70.79	129.36	21-Jun-04	24
609	70.92	130.53	27-Jun-04	40
709	70.94	133.68	1-Jul-04	86
803	70.64	135.87	2-Jul-04	242
906	70.02	138.60	4-Jul-04	281
909	69.80	138.28	5-Jul-04	169
912	69.49	137.94	5-Jul-04	56
809	70.09	135.34	7-Jul-04	44
712	70.69	133.68	10-Jul-04	712
718	70.17	133.52	11-Jul-04	45
200	70.04	126.30	16-Jul-04	235
309	71.12	125.83	19-Jul-04	235
415	71.91	125.87	20-Jul-04	52
409	71.50	127.09	22-Jul-04	380

Table 3.2. Species information and stations where animals were collected from the benthic boundary layer on the Beaufort Sea shelf. (F) refers to samples collected in fall 2003; all others were collected in June and July 2004. 'n' is number of samples per species and Indiv/sample is the range in the number of individuals that were pooled in each sample.

Species	Stations	n	Indiv/ sample	Length (mm)
Amphipoda				
Acanthostepheia malmgreni	200, 206, 406, 809, 909, 718(F)	6	1-4	26(5)
Anonyx sp.	206, 400, 609, 718(F)	4	1-3	22(7)
Anonyx nugax	909, 206(F)	2	2-3	19(4)
Arrhis phyllonyx	712, 718, 809	3	3-5	20(3)
Epimeria loricata	256, 309	2	3,5	11(4)
Eusirus cuspidatus	117	1	2	24(3)
Halirages sp.	118, 309, 409, 500	4	1-2	26(5)
Hippomedon sp.	398, 400, 912	3	1-10	9(3)
Melita formosa	609	1	1	25
Rhachotropis leucopthalma	108	1	1	24
R. acueata	400	1	3	25(1)
Rhachotropis sp.	303, 803, 906, 909, CA10(F)	5	5-10	14(3)
Syrrhoe crenulata	709, 712	2	5,10	7(1)
S. serrata	406	1	10	7(1)
Syrrhoe sp.	415	1	15	7(1)
Tmetonyx cicada	206(F)	1	4	6(1)
Mysidacea				
Boreomysis arctica	108, 256	2	4,10	19(6)
Erythrops spp.*	117, 200, 303, 309, 406, 609, 709, 712, 718, 803, 809, 906, 909, 912, CA06(F), CA10(F)	17	5-20	16(3)
Michthyops theeli	117, 409, 500	3	10	19(3)
Mysis litoralis	718, 809, 718(F)	3	5-10	25(3)
Parerythrops obesa	CA10(F)	1	10	
Pseudomma frigidum	108, 118, 256, 309, 309, 409	6	3-10	23(4)
Decapoda				
Bythocaris spp.	108, 117, 118, 309, 409, 500, CA10	7	1-3	37(10)
Eualus gaimardii	256, 400, 712, 718, 912, 206(F)	6	1-2	44(6)
Sclerocrangon ferox	906	1	1	27
Euphausiacea				
Thysanoessa raschii	912	1	4	20(2)
Copepoda				
Calanus hyperboreus	415, CA10(F)	2	20	
Chaetognatha				
Eukrohnia hamata	108, 117, 118, 200, 256, 303, 309, 409, 500, 709, CA06(F)	11	5-10	31(6)
Parasagitta elegans	415, 712, 718, 809, 206(F), 718(F)	6	10-20	27(6)
Holothuroidae				
Unidentified sp.	718, 718(F)	2	5,10	14(5)
Polychaeta				
Unidentified sp.	118	1	10	-

* *Erythrops erythrophthalma* was the most abundant species within the genus *Erythrops,* but *E. abyssorum, E. glacialis,* and *E. serrata* were all locally abundant.

Table 3.3. Elemental content (% dry weight) and elemental ratios (sd) of benthic boundary layer zooplankton from the Beaufort Sea shelf. Overall mean and sd are calculated from individual samples and % coefficient (% CV) is calculated from the overall mean and sd.

Species	% C	% N	% P	C:N	C:P	N:P
Amphipoda						
Epimeria loricata	51.1 (26.8)	8.0 (5.3)	0.5 (0.2)	5.7 (0.1)	55.1 (45.1)	9.6 (7.8)
Rhachotropis spp.	38.2 (3.4)	6.0 (0.6)	0.8 (0.2)	5.5 (0.4)	26.0 (5.8)	4.7 (1.0)
Halirages spp.	38.0 (4.1)	8.0 (0.5)	0.9 (0.2)	6.3 (0.5)	22.5 (2.8)	3.5 (0.6)
Anonyx spp.	37.8 (4.0)	7.0 (0.4)	0.7 (0.1)	7.1 (0.0)	36.3 (0.9)	5.1 (5.5)
Melita formosa	35.8	6.3	0.9	7.0	26.3	3.6
Hippomedon spp.	35.0 (1.0)	7.1 (0.5)	0.8 (0.2)	6.5 (0.4)	21.4 (4.4)	3.2 (0.5)
Eusirus cuspidatus	34.4	10.5	0.6	5.0	26.9	5.4
Arrhis phyllonyx	34.1 (3.0)	6.2 (0.5)	0.8 (0.2)	5.0 (0.1)	20.8 (8.6)	4.0 (1.3)
*A. malmgreni**	32.6 (5.5)	8.6 (0.7)	0.4 (0.2)	5.5 (1.0)	23.8 (8.9)	4.3 (1.2)
Tmetonyx cicada	32.5	5.9	0.1	6.4	23.2	3.6
Syrrhoe spp.	32.0 (1.3)	5.9 (0.3)	1.1 (0.6)	6.3 (0.6)	15.6 (5.8)	2.5 (0.8)
Mysidacea						
Mysis litoralis	50.0 (1.8)	8.6 (0.9)	0.9 (0.1)	6.8 (0.9)	26.3 (2.5)	3.9 (0.3)
Boreomysis arctica	48.5 (3.5)	8.4 (1.8)	0.6 (0.1)	6.9 (1.9)	40.9 (12.2)	5.9 (0.1)
Pseudomma frigidum	45.2 (1.5)	9.3 (0.8)	0.8 (0.2)	5.7 (0.6)	27.5 (6.8)	4.8 (1.2)
Erythrops spp.	45.0 (2.8)	8.7 (0.8)	0.7 (0.2)	6.1 (0.8)	33.7 (21.1)	5.6 (3.2)
Michthyops theeli	43.0 (2.6)	8.6 (0.7)	0.6 (0.2)	5.9 (0.8)	34.5 (13.9)	6.0 (1.5)
Parerythrops obesa	-	-	-	-	-	-
Decapoda						
Bythocaris spp.	42.5 (3.6)	10.0 (0.7)	0.6 (0.2)	5.0 (0.4)	37.6 (13.8)	7.7 (3.1)
Eualus gaimardii	40.5 (3.0)	9.9 (0.9)	0.6 (0.5)	4.8 (4.8)	36.7 (36.8)	7.7 (7.7)
Sclerocrangon ferox	28.8	6.0	0.8	5.6	16.6	3.0
Copepoda						
Calanus hyperboreus	56.1 (0.2)	7.4 (0.3)	0.9 (0.3)	8.9 (0.4)	28.2 (8.4)	3.2 (0.8)
Euphausiacea						
Thysanoessa raschii	54.8	11.0	1.1	5.8	23.2	4.1
Chaetognatha						
Eukrohnia hamata	42.9 (2.6)	7.7 (0.9)	0.5 (0.2)	6.6 (0.8)	45.3 (18.7)	6.9 (3.1)
Parasagitta elegans	38.4 (2.9)	8.7 (1.3)	0.6 (0.2)	5.2 (0.7)	34.5 (14.9)	6.6 (2.3)
Holothuroidae						
Unidentified sp.	20.7 (1.7)	4.0 (0.5)	0.4 (0.5)	6.0 (0.2)	139.2 (178.5)	22.6 (28.8)
Polychaeta						
Unidentified sp.	38.1	9.7	0.6	4.6	30.4	6.6
overall mean (sd)=	40.6 (7.2)	8.1 (1.6)	0.7 (0.3)	5.9 (1.0)	30.6 (12.9)	5.3 (2.4)
% CV =	17.7	19.8	39.7	16.9	42.2	44.4

* full species name = *Acanthostepheia malmgreni*

Table 3.4. Mean (sd) total lipid per individual (TLip; mg ind^{-1}) and lipid classes (% total lipid) for benthic boundary layer zooplankton from the Beaufort Sea shelf. Overall mean and sd are calculated from individual samples and % coefficient of variation (% CV) is calculated from the overall mean and sd.

Species	Tlip	HC	WE/SE	TG	FFA	ALC	ST	AMPL	PL	LI
Amphipoda										
*A. malmgreni**	3.0 (2.2)	tr	3.0 (6.7)	20.5^{b} (22.0)	4.4 (6.3)	2.1 (4.2)	6.0^{a} (4.8)	2.0 (1.0)	61.7^{a} (18.0)	6.9 (7.8)
Anonyx sp.	22.2 (33.7)	tr	1.6 (2.6)	76.4^{a} (10.1)	tr	tr	1.5^{a} (0.7)	1.6 (1.0)	16.7^{b} (6.3)	1.3 (10.1)
Arrhis phyllonyx	2.5 (1.6)	tr	tr	49.9^{ab} (30.0)	tr	-	3.5^{ab} (2.2)	2.6 (2.5)	42.5^{ab} (31.1)	0.5 (0.0)
Epimeria loricata	2.4 (0.6)	tr	3.0 (4.2)	63.0^{ab} (22.6)	3.4 (4.8)	-	1.8^{ab} (2.5)	2.5 (1.6)	25.8^{ab} (31.4)	3.4 (3.4)
Eusirus cuspidatus	5.4	-	23.5	50.5	3.1	-	2.7	1.6	18.7	3.1
Halirages spp.	18.5 (11.7)	tr	6.3 (4.1)	71.8^{a} (5.1)	tr	-	2.3^{a} (1.4)	1.4 (0.6)	17.4^{b} (3.9)	0.8 (0.5)
Hippomedon spp.	1.3 (0.0)	1.4 (1.9)	3.2 (2.2)	64.8^{ab} (10.9)	1.4 (2.1)	-	2.0^{b} (1.9)	9.0 (6.4)	17.4^{b} (6.0)	1.5 (2.2)
Melita formosa	13.2	-	-	85.5	-	-	tr	1.6	12.0	0.0
Rhachotropis spp.	4.9 (4.4)	tr	4.8 (4.7)	62.3^{a} (20.4)	2.6 (2.0)	tr	2.2^{a} (1.6)	2.9 (2.5)	24.1^{b} (12.2)	2.9 (2.2)
Syrrhoe spp.	0.3 (0.1)	4.8 (5.9)	-	48.3^{ab} (19.5)	tr	tr	2.0^{a} (1.4)	3.9 (2.6)	39.5^{ab} (14.8)	1.2 (0.9)
Tmetonyx cicada	13.6	tr	tr	92.5	tr	-	tr	tr	5.1	0.9
Mysidacea										
Boreomysis arctica	12.2^{a} (15.5)	tr	23.1^{a} (1.6)	63.6 (7.8)	tr	-	1.1 (1.0)	tr	9.8 (6.5)	0.9 (0.9)
Erythrops spp.	2.4^{b} (1.7)	tr	1.8^{c} (2.3)	78.2 (11.6)	1.5 (2.2)	tr	2.0 (2.0)	1.8 (2.0)	13.3 (10.1)	2.6 (2.7)
Michthyops theeli	4.0^{ab} (1.3)	tr	tr	87.6 (4.1)	1.0 (0.6)	tr	tr	tr	9.2 (3.5)	1.1 (0.6)
Mysis litoralis	14.2^{a} (6.0)	tr	2.0^{bc} (1.2)	89.5 (4.0)	tr	tr	tr	tr	6.2 (1.9)	0.7 (0.9)
Parerythrops obesa	3.5	tr	13.2	70.4	1.3	-	tr	tr	13.8	1.3
Pseudomma frigidum	6.2^{ab} (4.0)	tr	6.2^{b} (4.0)	71.5 (17.8)	1.1 (1.7)	-	2.2 (1.7)	2.0 (2.0)	16.8 (11.0)	1.1 (1.7)
Decapoda										
Bythocaris spp.	14.1 (7.8)	tr	9.8 (5.6)	59.9 (15.8)	1.7 (0.9)	1.8 (3.1)	2.1 (1.0)	1.1 (0.6)	23.5 (8.3)	3.6 (3.8)
Eualus gaimardii	19.5 (19.7)	1.2 (2.6)	tr	39.9 (27.2)	5.0 (3.7)	1.2 (2.9)	9.2 (10.7)	1.0 (0.9)	42.3 (17.2)	7.1 (5.4)
Sclerocrangon ferox	0.9	-	4.3	24.3	2.7	-	6.4	2.7	59.7	2.8
Copepoda										
Calanus hyperboreus	1.6 (0.1)	1.3 (0.3)	93.4 (1.1)	-	tr	-	tr	tr	2.1 (2.2)	0.2 (0.2)
Euphausiacea										
Thysanoessa raschii	7.0	tr	18.8	21.5	3.2	-	3.7	1.2	50.4	3.3
Chaetognatha										
Eukronia hamata	1.7 (0.8)	2.4 (1.6)	72.3 (9.4)	1.9 (2.1)	2.1 (1.9)	tr	1.0 (1.0)	2.5 (2.3)	17.7 (7.5)	2.1 (1.9)
Parasagitta elegans	0.6 (0.6)	tr	tr	2.8 (2.8)	1.5 (2.7)	-	5.2 (2.2)	4.3 (2.4)	85.6 (4.6)	1.7 (3.0)
Holothuroidae										
Unidentified sp.	0.6 (0.3)	1.2 (0.5)	4.7 (6.6)	46.8 (16.0)	7.4 (5.7)	-	tr	5.0 (1.1)	34.4 (17.6)	7.5 (4.2)
Polychaeta										
Unidentified sp.		-	3.4	4.7	1.5	20.7	1.1	4.1	64.5	22.1
overall mean (sd) =	6.6 (11.6)	0.8 (1.7)	11.8 (23.5)	52.1 (31.9)	1.9 (2.7)	0.7 (2.6)	2.7 (3.6)	2.2 (2.4)	27.7 (23.6)	3.1 (4.4)
% CV =	103		199	61	139		134	106	85	

HC-hydrocarbons, WE/SE-wax esters-steryl esters, TG-triacylglycerols, FFA-free fatty acids, ALC-fatty alcohols, ST-sterols, AMPL-acetone mobile polar lipids, PL-phospholipids, LI-lipolysis index; ^{abc}differences among species from the results of a pariwise *t*-test with an adjusted p-value (Bonferroni correction); * full name = *Acanthostepheia malmgreni*

Table 3.5. Statistical analyses testing for significant differences in response variables (lipid and elemental composition) among taxonomic groups, and among taxa of amphipods, mysids, decapod shrimp, and chaetognaths.

Response Variable	Taxonomic Group	Amphipoda	Mysidacea	Decapoda	Chaetognatha
HC	ns	ns	ns	ns	**
WE/SE	***	ns	***	**	***
TG	***	***	ns	ns	ns
FFA	**	ns	ns	*	ns
ALC	ns	ns	ns	ns	ns
ST	*	ns	ns	ns	***
AMPL	**	**	ns	ns	ns
PL	***	***	ns	*	***
Tlip	**	ns	***	ns	**
C	***	**	*	ns	**
N	***	*	ns	ns	ns
P	**	*	ns	ns	ns
C:N	***	***	ns	ns	**
C:P	**	**	ns	ns	ns
N:P	***	**	ns	ns	ns

HC-hydrocarbons, WE/SE-wax esters-steryl esters, TG-triacylglycerols, FFA-free fatty acids, ALC-fatty alcohols, ST-sterols, AMPL-acetone mobile polar lipids, PL-phospholipids, Tlip-total lipid.

* $0.05 \geq p > 0.01$

** $0.01 \geq p > 0.001$

*** $0.001 \geq p$

Table 3.6. Matrix of Pearson correlation coefficients between lipid and elemental composition variables across all samples of benthic boundary layer zooplankton. $p < 0.05$ for correlation coefficients in bold. HC and ALC were not significantly correlated with any element content, ratio, or lipid class and are therefore not shown.

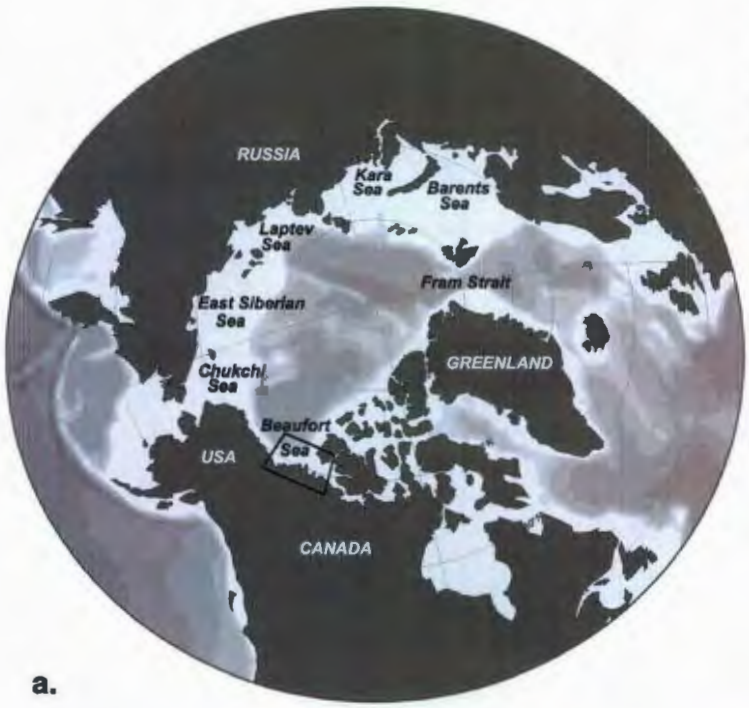
	Lg	WE/SE	TG	FFA	ST	AMPL	PL	Tlip
Lg		**-0.71**	ns	ns	ns	**0.10**	ns	**0.65**
C	ns	ns	**0.62**	ns	ns	**-0.23**	**-0.74**	ns
N	ns	ns	ns	ns	ns	**-0.04**	**-0.54**	ns
P	**-0.92**	**0.57**	ns	ns	ns	**-0.37**	ns	ns
C:N	**-0.72**	**0.60**	ns	ns	**-0.52**	**-0.27**	ns	ns
C:P	**0.82**	ns	ns	ns	ns	**0.48**	ns	ns
N:P	**0.84**	ns	ns	ns	ns	**0.48**	ns	ns

HC-hydrocarbon, WE/SE-wax ester-steryl esters, TG-triacylglycerol, FFA-free fatty acids, ALC-fatty alcohol, ST-sterols, AMPL-acetone mobile polar lipids, PL-phospholipids, Lg-body length. Tlip-total lipid.

Table 3.7. Carbon (C), nitrogen (N), and phosphorus (P) composition of biochemical compounds in marine and freshwater crustacean zooplankton as a percentage of total mass of each compound. Adapted from Ventura 2006.

	% C	% N	% P
Wax ester	81	0	0
Triacylglycerol	77	0	0
Phospholipid	61	2	4
Protein	53	16	0
Amino acids	46	22	0

3.10. FIGURES



a.

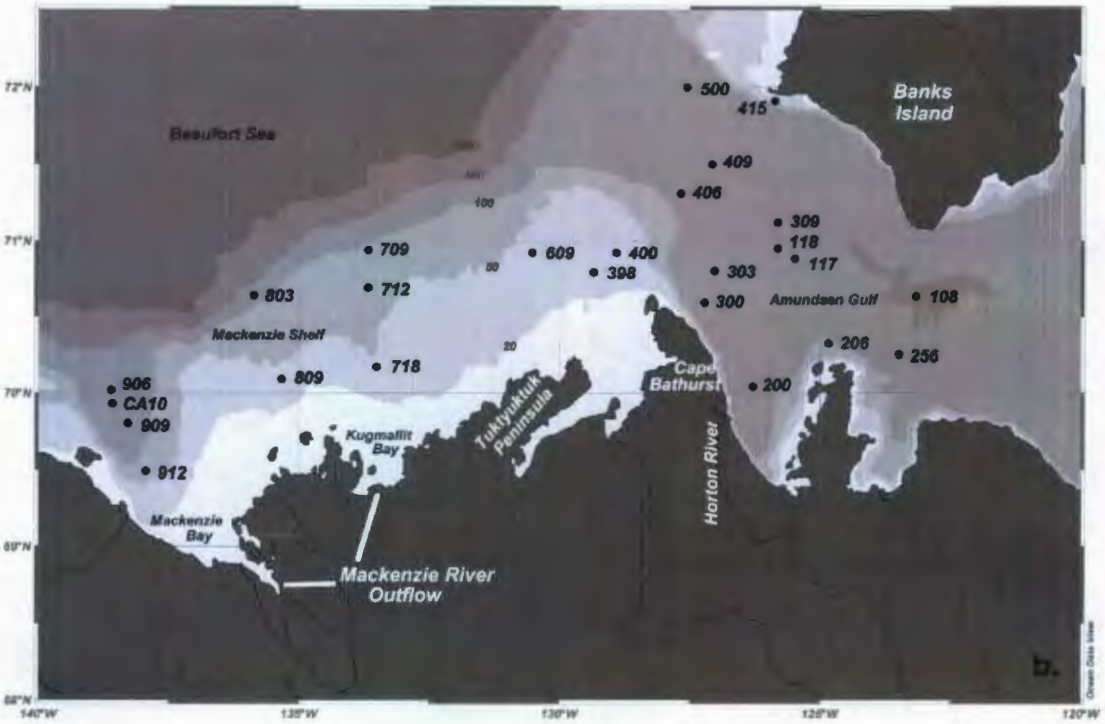


Figure 3.1. (a) Location of the Canadian Arctic Shelf Exchange Study (CASES) in the Arctic Ocean (box). (b) Station locations and labels for benthic boundary layer zooplankton collected during fall 2003 and summer 2004 from the Beaufort Sea Shelf. Depth contours are in meters.

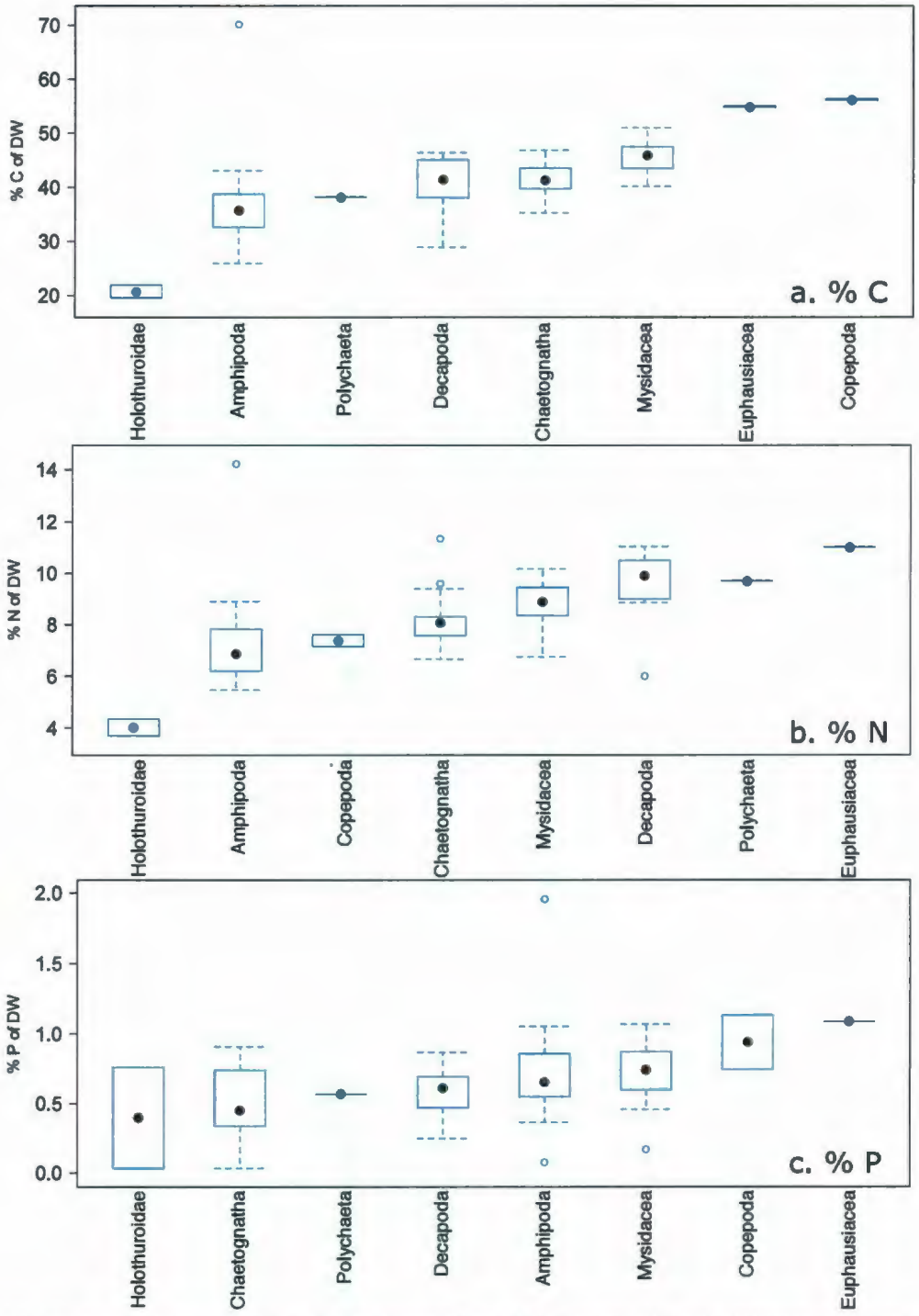


Figure 3.2. Carbon (C), nitrogen (N), and phosphorus (P) as % dry weight (DW) for different taxonomic groups of benthic boundary layer zooplankton collected from the Beaufort Sea shelf. The dark circle shows the median, the bottom and top of the box show the 25th and 75th percentiles. The dashed horizontal line is 1.5 times the interquartile range of data and values that are not within this range (outliers) are drawn as individual points.

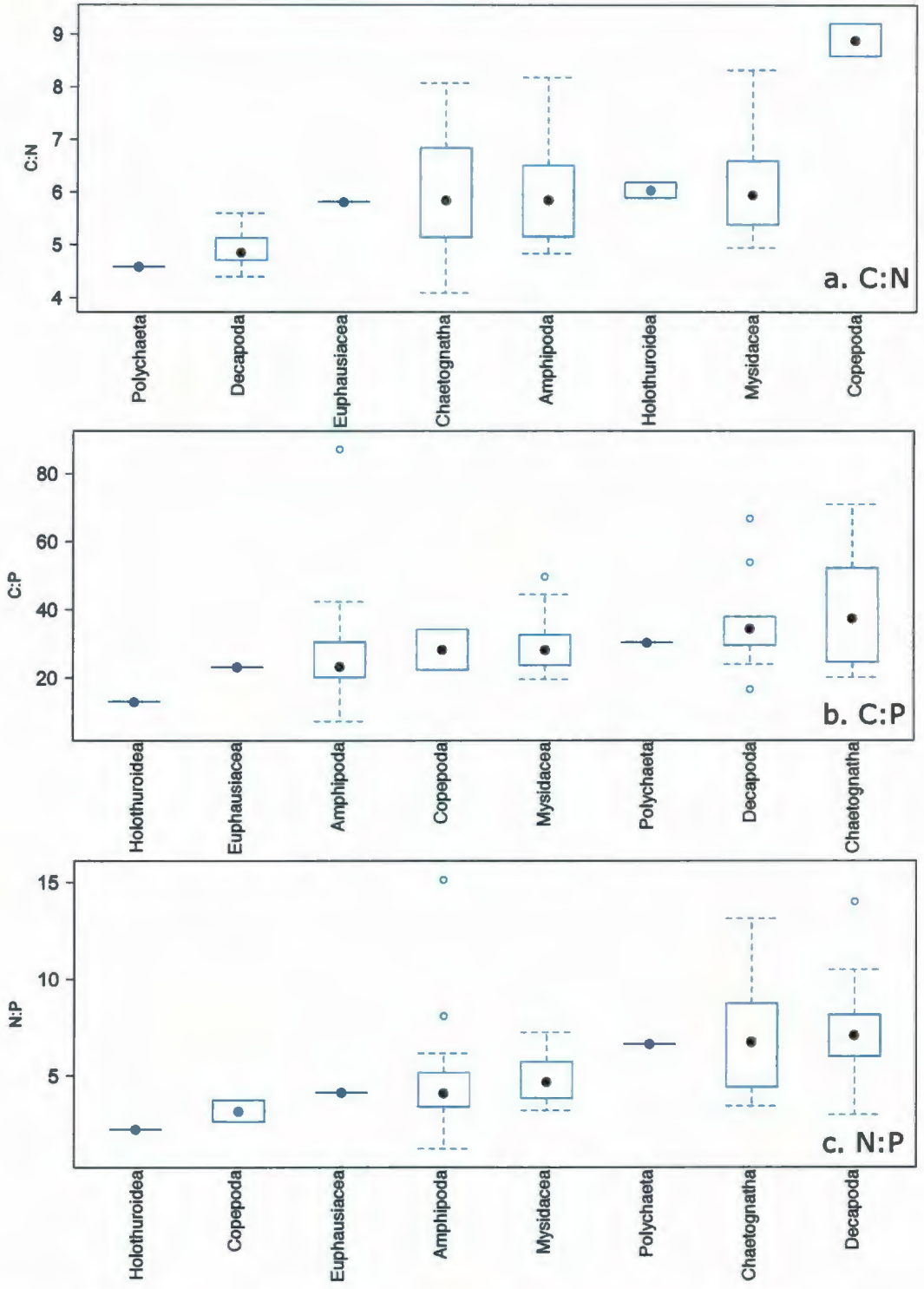


Figure 3.3. Elemental ratios of carbon (C), nitrogen (N), and phosphorus (P) for different taxonomic groups of benthic boundary layer zooplankton collected from the Beaufort Sea shelf. See Figure 3.2 for definitions of box and whiskers.

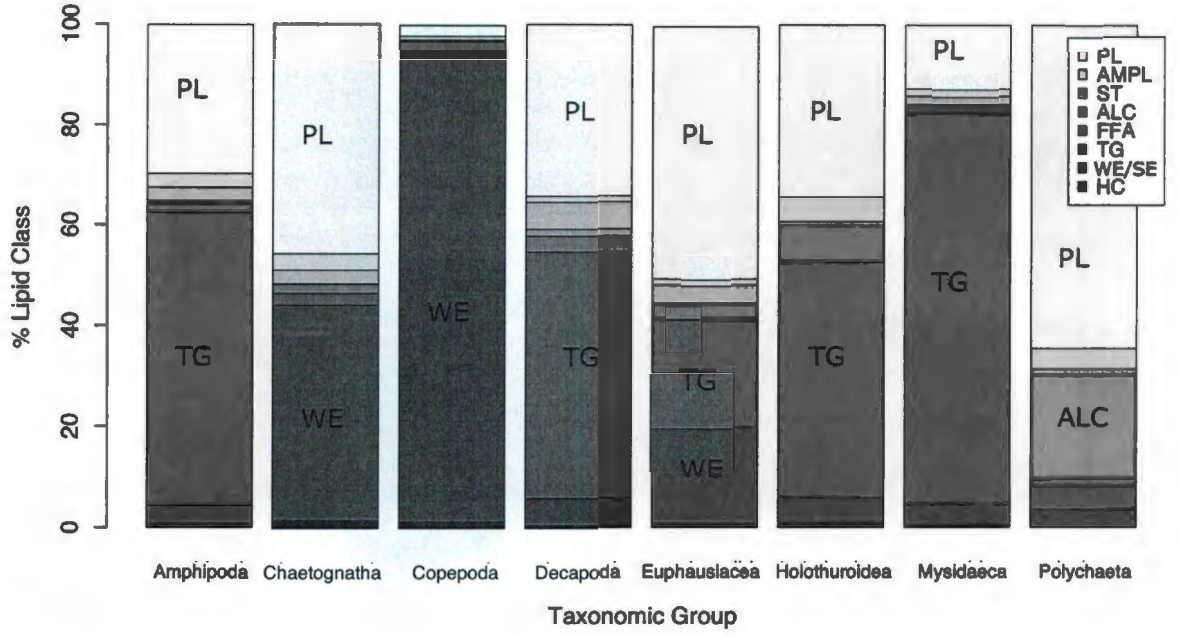


Figure 3.4. Relative lipid composition (% total lipid) of different taxonomic groups of benthic boundary layer zooplankton collected from the Beaufort Sea shelf. (PL-phospholipids, AMPL-acetone-mobile polar lipids, ST-sterols, ALC-alcohols, FFA-free fatty acids, TG-triacylglycerols, WE/SE-wax esters-steryl esters, HC-hydrocarbons)

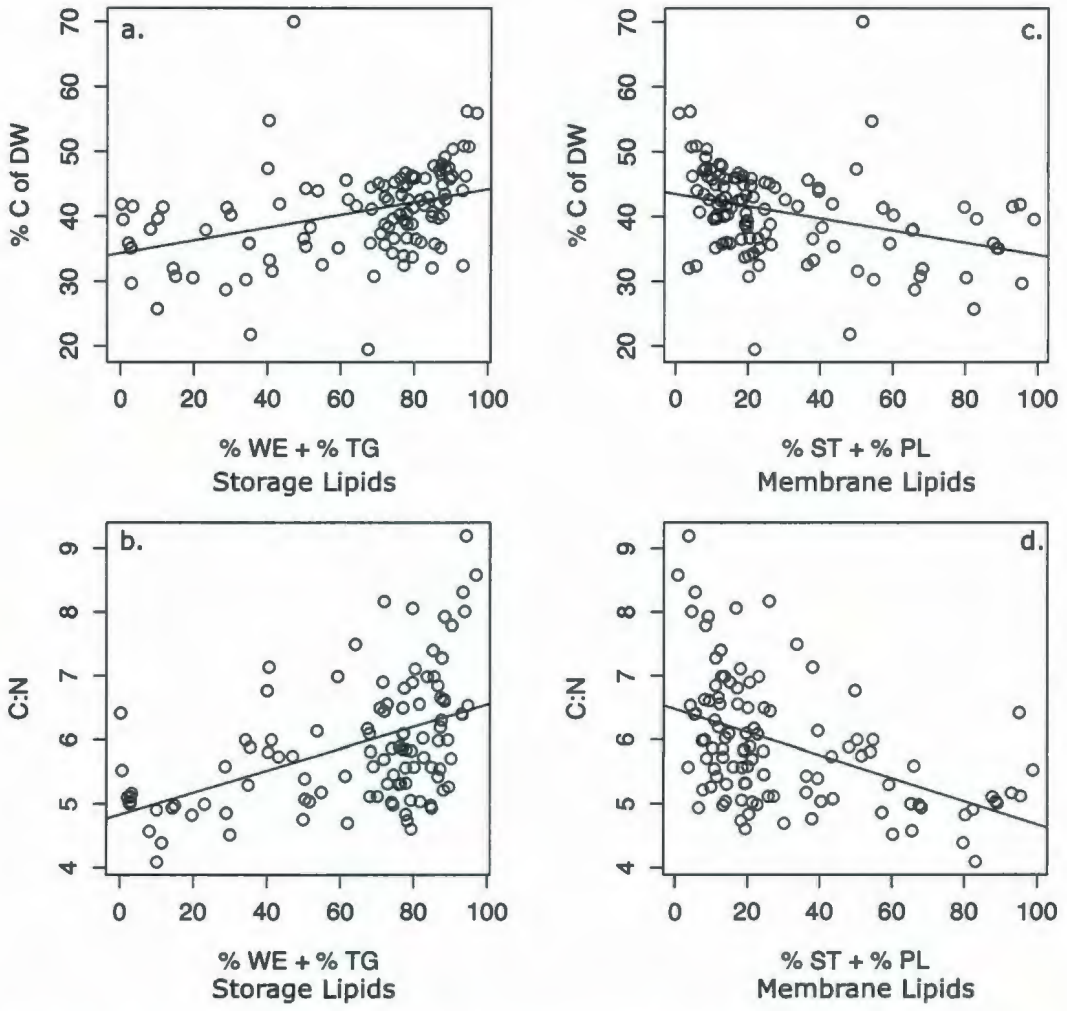


Figure 3.5. Relationship of storage lipids (triacylglycerols (TG) and wax esters-steryl esters (WE)) and membrane lipids (sterols (ST) and phospholipids (PL)) to carbon (% dry weight (DW)) and C:N ratios for all samples of benthic boundary layer zooplankton. Lipid classes are percent of total lipid. Line is added to aid in viewing correlation between variables and is significant at $p \leq 0.05$, df = 106. (r^2: a. = 0.14, b. = 0.23, c. = 0.11, and d. = 0.21.)

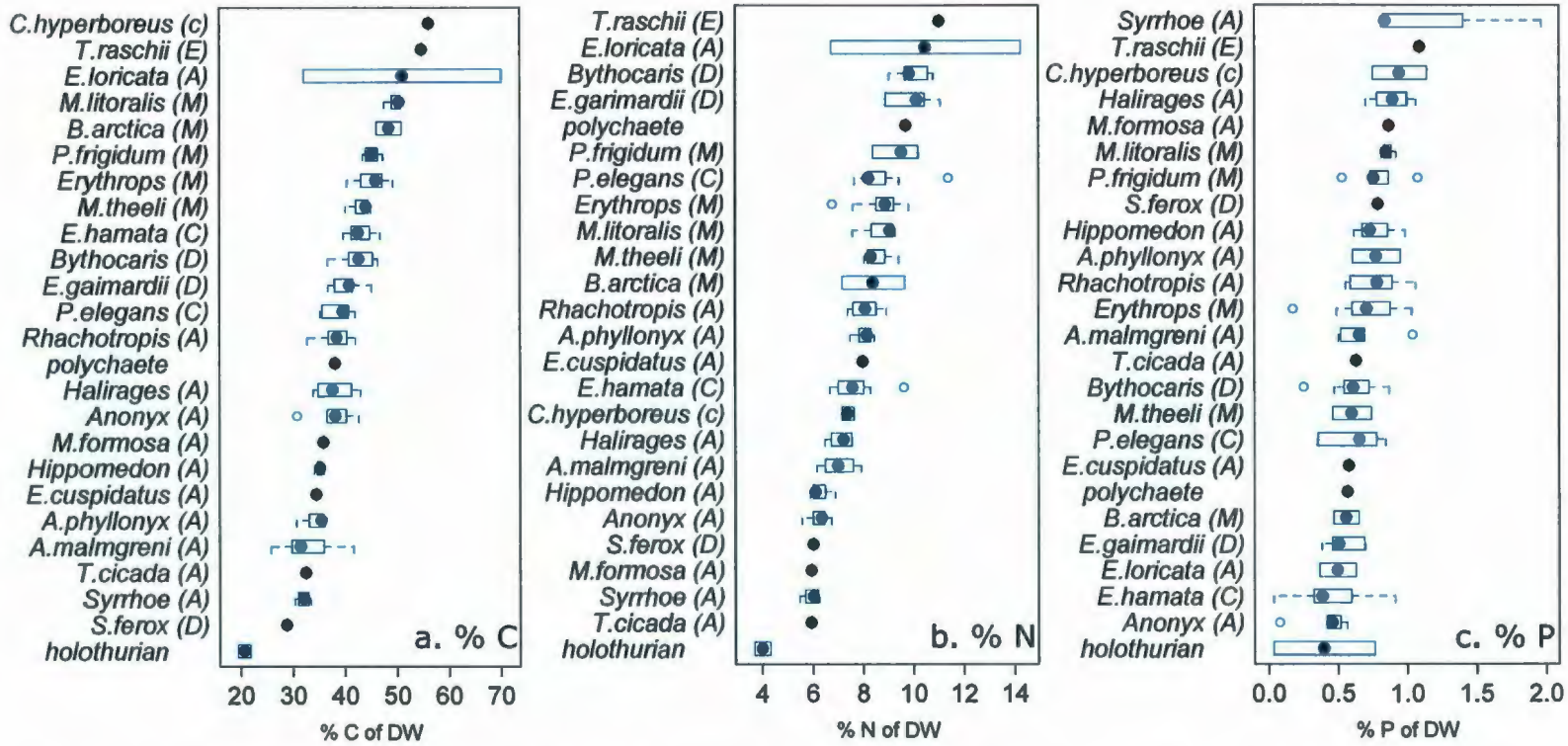


Figure. 3.6. Elemental composition (% dry weight (DW), (a) carbon (C), (b) nitrogen (N), and (c) phosphorus (P) for benthic boundary layer zooplankton from the Beaufort Sea shelf. See Fig. 3.2 for definitions of box and whiskers. A=amphipod, C=chaetognath, c=copepod, D=decapod shrimp, E=euphausiid, M=mysid. See Table 3.3 for full species names.

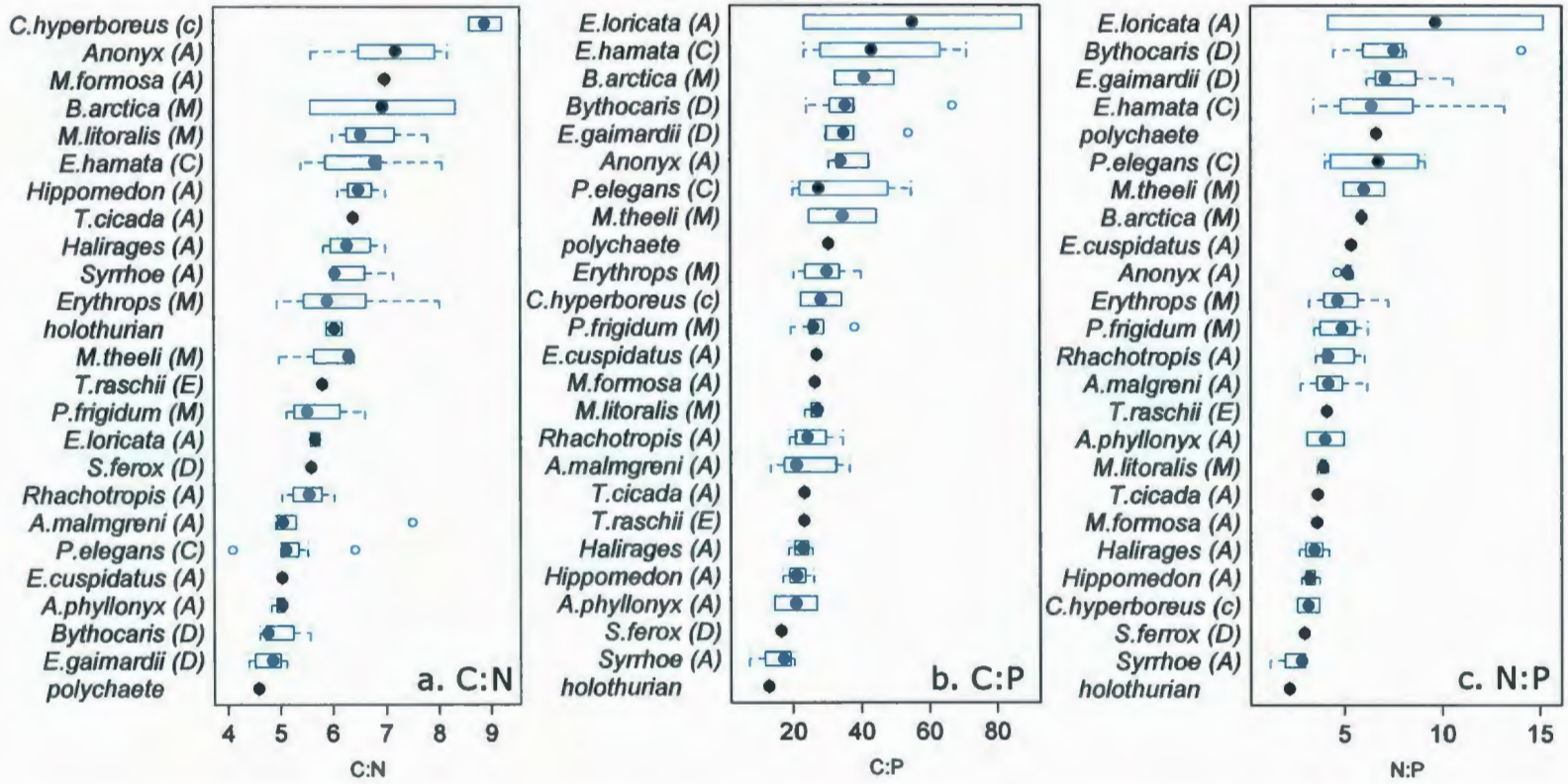


Figure 3.7. Elemental stoichiometry, (a) C:N, (b) C:P, and (c) N:P for benthic boundary layer zooplankton from the Beaufort Sea shelf. Ratios are mol:mol of carbon (C), nitrogen (N), and phosphorus (P). See Figure 3.2 for definitions of box and whiskers. Full species names are in Table 3.3.

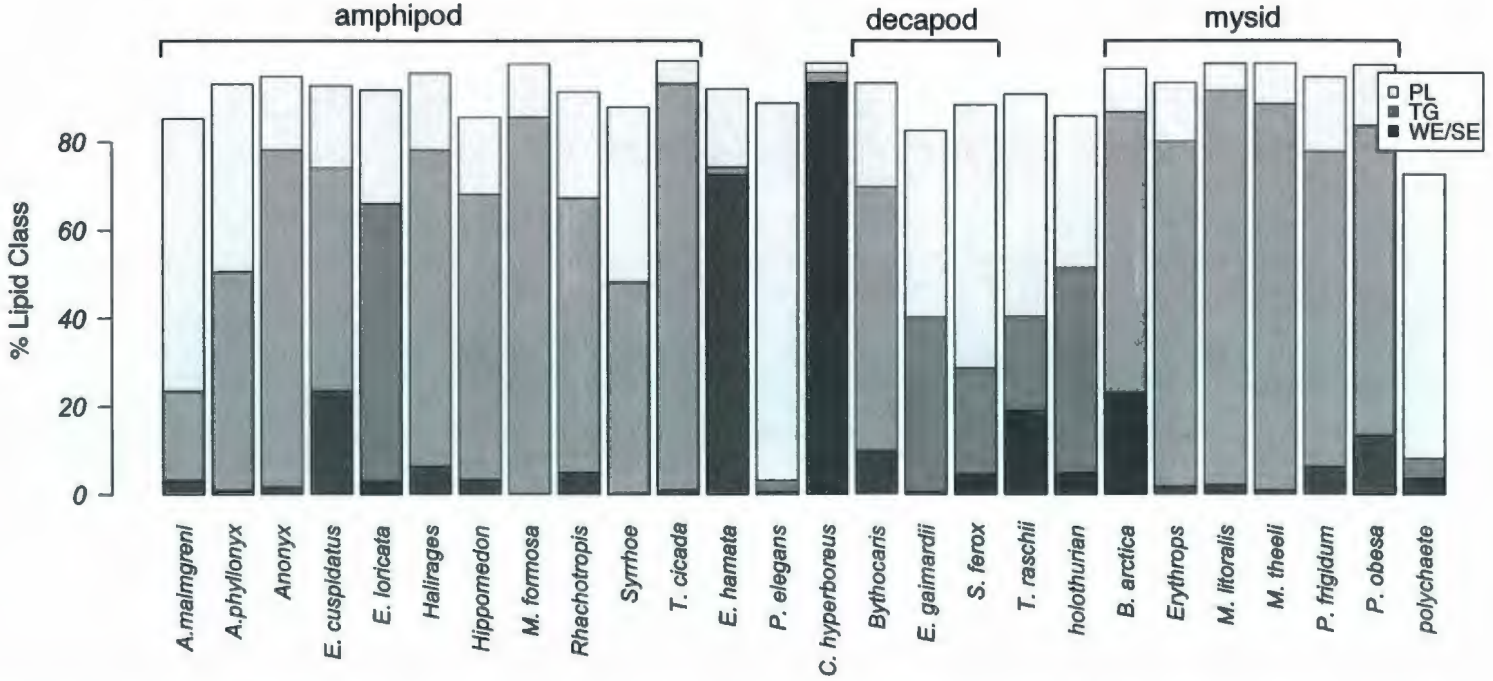


Figure 3.8. Phopholipids (PL), triacylglycerols (TG), and wax esters-steryl esters (WE/SE) of benthic boundary layer zooplankton from the Beaufort Sea shelf. Lipid classes are reported as precentage of total lipids.

CHAPTER 4

TROPHIC INTERACTIONS IN THE BENTHIC BOUNDARY LAYER OF THE BEAUFORT SEA SHELF: COMBINING BULK STABLE ISOTOPE AND FATTY ACID SIGNATURES

4.1. ABSTRACT

The food web structure and diets of 26 taxa of benthic boundary layer zooplankton from 8 taxonomic groups on the Beaufort Sea Shelf were studied using carbon and nitrogen stable isotopes and fatty acids. Mean $\delta^{15}N$ values ranged from 7.3‰ for the amphipod *Melita formosa* to 14.9‰ for an unidentified polychaete, suggesting that taxa sampled came from 3 trophic levels (TL). *M. formosa*, the mysid *Mysis litoralis*, the copepod *Calanus hyperboreus*, and an unidentified holothurian had the lowest mean $\delta^{15}N$ values and were primarily herbivores (TL 2). The amphipod *Epimeria loricata*, the decapod shrimp *Bythocaris* spp., and an unidentified polychaete had the highest $\delta^{15}N$ values and were predominantly secondary predators (TL 4). All other taxa were feeding omnivorously or carnivorously at TL 3. Mean $\delta^{13}C$ values ranged from -25.8‰ for an unidentified holothurian to -20.4 ± 0.3‰ for *E. loricata*. For 8 taxa, the lightest carbon signature occurred near the mouth of the Mackenzie River. Stable isotope ratios helped clarify the origin of signature fatty acids. Levels of certain polyunsaturated fatty acids (PUFA) were negatively correlated with $\delta^{15}N$, with the exception of 22:6ω3, which was positively correlated with $\delta^{15}N$, suggesting that this essential PUFA was highly conserved through the food web and was not used as an energy source. Discriminant analysis proved to be a powerful tool, predicting both taxonomic groups and taxa from fatty acid profiles with 84% and

61% accuracy respectively, and revealing strong phylogenetic trends in fatty acid profiles. The amphipod *Arrhis phyllonyx* had higher levels of ω6 PUFA, especially 20:4ω6, than other peracarid crustaceans. The holothurian had high levels of odd numbered and branched chain fatty acids, indicative of bacterial consumption, while fatty acids of phytoplankton origin were important discriminants for *C. hyperboreus* and the chaetognaths *Eukrohnia hamata* and *Parasagitta elegans*. This relationship indicates that the conventional phytoplankton-copepod-chaetognath food web found in the water column also exists in the benthic boundary layer. This observation, as well as low $\delta^{15}N$ and high levels of certain PUFA in samples with low $\delta^{15}N$, strongly suggests that benthic boundary layer zooplankton on the Beaufort Sea shelf have access to fresh material of phytoplankton origin either by feeding on sedimenting matter, resuspended sediments, or by active migration to surface waters.

4.2. INTRODUCTION

Trophic interactions and energy flow within biological communities in the benthic boundary layer (BBL) are poorly understood, primarily due to sampling difficulties, yet these communities have the potential to play a major role in mediating the flux of organic matter from the upper water column to the sea floor. Trophic interactions and benthic-pelagic coupling have been well studied in many Arctic seas, the focus being on sympagic (ice-associated), pelagic and benthic organisms, as well as marine mammals and birds (i.e. Ambrose and Renaud 1995, Hobson et al. 2002, Dunton et al. 2005, Schmid et al. 2006, Tamelander et al. 2006, Wassmann et al. 2006, Renaud et al. 2007a). However, there is limited understanding of how zooplankton near the sea floor influence

benthic-pelagic coupling and impact carbon flux to sediments in Arctic ecosystems.

Stable isotopes and fatty acid profiles are commonly used to study ecosystem structure and processes, and have been useful in determining energetics and the transfer of organic matter through marine food webs in the Arctic (Hobson et al. 1995, Hobson et al. 2002, Dahl et al. 2003, Iken et al. 2005, Werner and Auel 2005, Hop et al. 2006). Unlike gut content analysis, which provides information on recently ingested food, stable isotopes and fatty acids provide a time-integrated measure of energy sources. Sources of carbon can be traced through food webs using carbon stable isotope ratios, and diets and trophic levels can be inferred using nitrogen stable isotopes and signature fatty acids. These tools are particularly useful for studying the food webs of communities that are difficult to sample, such as those in the Arctic and specifically in the BBL. Although there have been few stable isotope studies of BBL zooplankton, several isotope studies have included a broad range of Arctic benthic organisms (i.e. Hobson and Welch 1992, Iken et al. 2005, Hobson et al. 1995, Tamelander et al. 2006). In contrast, very little is known about lipids and fatty acids of both BBL and benthic organisms in the Arctic, in contrast to sympagic and pelagic taxa (i.e. Auel et al. 2002, Scott et al. 2002, Kattner et al. 2003, Stevens et al. 2004, Werner and Auel 2005).

Trophic interactions and feeding behaviors of BBL zooplankton in the Arctic are not well characterized. Diets are often assumed based on morphology and phylogeny. The aim of this study was to combine bulk stable isotope and fatty acid analyses to investigate trophic interactions and food sources for communities of BBL zooplankton on the Beaufort Sea shelf. For many of the species considered in this study, this is the first investigation into their feeding

ecology using biochemical composition. This is also the first examination of a BBL community in the Arctic using either stable isotopes or fatty acids.

The Beaufort Sea shelf, in the western Canadian Arctic, is heavily influenced by terrestrial input from the Mackenzie River (Chapter 2, Macdonald et al. 1998). The Amundsen Gulf, between Cape Bathurst and Banks Island, is characterized by a seasonal polynya that may support increased biological activity (Carmack and Macdonald 2002). Pelagic production and trophic interactions strongly influence the quantity and quality of sedimenting material and therefore the patterns of benthic production and metabolism (Wassmann 1998, Klages et al. 2004). It is likely that terrestrial material from the Mackenzie River and seasonal algal production in the Amundsen Gulf both influence the feeding ecology and nutrition of BBL zooplankton.

4.3. METHODS

4.3.1. Sample Collection

BBL zooplankton were collected from 27 stations on the Beaufort Sea shelf aboard the CCGS *Amundsen* in fall 2003 and summer 2004 as part of the Canadian Arctic Shelf Exchange Study (CASES; Table 4.1, Fig. 4.1). Animals within 60 cm of the bottom were collected with an epibenthic sled equipped with a 500 µm net and an open cod end (Choe and Deibel 2000). The sled was towed at about 1 knot with about 10 min of contact on the bottom. As soon as the sled was retrieved, the contents of the cod end were gently rinsed into coolers with seawater. Cooler contents were then rinsed with surface water to remove mud. Four to five common species were selected at each station depending on size and abundance, but usually included amphipods, mysids, decapod shrimp and

chaetognaths. At each station, two sets of up to 20 animals of each species were sized (body length) and pooled for either stable isotope or fatty acid analyses. Samples for stable isotope analysis were frozen at -80°C until being processed on land. Samples for fatty acid analysis were put in 15-mL vials prewashed with lipid solvents, covered with chloroform (2- 4 mL), and stored at -20°C in N_2 until processed on land. Additional individuals were fixed in 4% formaldehyde for species identification. A total of 106 pooled samples from 8 different taxonomic groups (i.e. taxonomic classification level of order or higher) was analyzed during this study. 'n' is the number of stations where a taxa was collected.

Samples for $\delta^{15}N$ of near-bottom suspended particulate matter were collected with a bottom-tripping Niskin bottle at three stations. Samples were filtered through a 300 μm mesh before being filtered onto GFF filters (see Chapter 2 for details on particulate organic matter sampling methods).

4.3.2. *Fatty Acid Analysis*

Lipids were extracted in chloroform:methanol:water (2:1:0.5) following Folch et al. (1957; as modified by Parrish 1999). Briefly, samples were ground, sonicated and centrifuged in the chloroform:methanol:water mixture three times. Lipid layers were removed and pooled following each of the three chloroform washes. Fatty acids were quantified as methyl esters by FID using a Varian 3400 gas chromatrograph (GC, 30 min), following derivatization of samples with BF_3-methanol (85°C, 1.5hr). Methyl esters were analyzed on an Omegawax column following Budge and Parrish (1998). Peaks were identified by comparing sample retention times to those of known external standards and by using a Varian 2000 GC/mass spectrometer. Fatty acids are reported as a percent of total identified fatty acids.

The diatom fatty acid biomarker used here was the sum of C_{16} monounsaturates divided by C_{16} saturates ($\sum$16:1/16:0) (Claustre et al. 1988-89). Bacterial fatty acid biomarkers were calculated by summing odd-numbered carbon chains (except 21:5ω3) and branched-chain fatty acids (*iso* or *anteiso* branches; Kaneda 1991), while the sum of 22:1 and 20:1 was used as a copepod indicator (Falk-Petersen et al. 1987).

4.3.3. Stable Isotope Analysis

Each stable isotope sample was freeze-dried, homogenized, and acidified (acid fumes) for 24 hours in 5% HCl. Aliquots of homogenized tissue were analyzed for both $\delta^{15}N$ and $\delta^{13}C$ by continuous flow ion ratio mass spectrometry (CF-IRMS). Most samples were run on a GV-Instruments Isoprime® attached to a peripheral EuroVector elemental analyzer, University of Winnipeg Isotope Laboratory, while a few samples from the fall were run on a Micromass Optima mass spectrometer with a Carlo Erba NC 2500 elemental analyzer, Georgia Institute of Technology. Lipids were not extracted because the interest of this data set is in relating lipids (fatty acids) to stable isotope values. In addition, carbon in lipids stores can also be an important form of diet carbon (Chapter 3), and that is not considered when lipids are extracted. Isotope values are expressed in the conventional δ notation following the equation:

$$\delta^{13}C \text{ or } \delta^{15}N\ (‰) = [(R_{sample}/R_{standard}) - 1] \times 1000$$

where R is $^{13}C/^{12}C$ or $^{15}N/^{14}N$ and the standard reference material is Vienna Pee Dee Belemnite and atmospheric nitrogen N_2, respectively. Selected samples were run in duplicate or triplicate for both $\delta^{13}C$ and $\delta^{15}N$. Trophic level was calculated

using a ^{15}N enrichment factor of +3.8‰ (Hobson and Welch 1992, Hobson et al. 1995) using the following equation:

$$\text{Trophic Level (TL)} = (\delta^{15}N_{sample} - \delta^{15}N_{POM})/3.8 + 1$$

where $\delta^{15}N_{POM}$ is 3.75‰ and is the mean $\delta^{15}N$ of particulate organic matter from 3 stations across the study area. TL is reported as whole numbers because of the uncertainty in both the conversion factor (3.8‰) and the $\delta^{15}N$ value at the base of the food web.

4.3.4. Statistical Analysis

All bivariate data analyses were done with a general linear model and errors tested for normality. Discriminant analyses were carried out on normalized fatty acid proportions; observations were transformed to discriminant functions so that the within-group correlation matrix was spherical. Only fatty acids found in > 70% of samples were included in discriminant analyses. A general linear model (MANOVA) using Wilks' lambda was used to evaluate the relevance of the discriminant analysis by testing whether fatty acids were sufficiently variable to distinguish different taxonomic groups or taxa, where *taxonomic group* was based on a taxonomic classification level of order or higher, and divisions within taxonomic group were based on *taxa.* In most cases taxa were defined at the species level. In seven cases, however, species of the same genus were pooled (*Bythocaris* spp., *Erythrops* spp., *Rhachotropis* spp., *Anonyx* spp., *Hippomedon* spp., *Halirages* spp., and *Syrrhoe* spp.). Accuracy of predictions of taxonomic groups and taxa based on discriminant functions was calculated using leave-one-out cross validation (LOOCV). In LOOCV, n - 1

samples were used to define the model and the remaining sample was tested. This was repeated n times until all samples were excluded once from the model and subsequently tested. Taxonomic groups or taxa with only one sample were not used in these analyses, but were plotted *ad hoc*. Errors are reported as standard deviations when $n \geq 3$ and as half the range when $n = 2$, unless otherwise stated. All analyses were done using R statistical software.

4.4. RESULTS

4.4.1. Species collected and analyzed

Animals from the following taxonomic groups were selected at sea and analyzed in the lab (Table 4.2): amphipods (n = 39), chaetognaths (n = 17), copepods (n = 2), decapod shrimp (n = 14), euphausiids (n = 1), holothurians (n = 2), mysids (n = 33), and polychaetes (n = 1).

4.4.2. Stable Isotopes

Mean $\delta^{15}N$ values ranged from 7.3‰ for the amphipod *Melita formosa* to 14.9‰ in the polychaete sample suggesting that I sampled taxa from 3 trophic levels in the BBL (Table 4.3, Fig. 4.2). The copepod *Calanus hyperboreus* had a mean $\delta^{15}N$ value of 8.1 ± 0.8‰, which corresponds to a trophic level (TL) of 2 (Table 4.3). The chaetognath *Eukrohnia hamata* was significantly depleted in ^{15}N relative to *Parasagitta elegans*, both of which were feeding primarily at TL 3 (Table 4.3, Fig. 4.2). Among mysids, *Mysis litoralis* had the lightest mean $\delta^{15}N$ value and *Michthyops theeli* and *Parerythrops frigidum* the heaviest (Table 4.3). Based on these $\delta^{15}N$ values, trophic levels were TL 2 for *M. litoralis* and TL 3 for the remaining mysid taxa (Table 4.3). The decapod shrimp *Bythocaris* spp. had a high

mean $\delta^{15}N$ value, corresponding to a trophic level of 4 (Table 4.3, Fig. 4.2). *Eulalus gaimardii* was significantly less enriched in ^{15}N and was feeding at the same trophic level as *Sclerocragnon ferox* (TL 3). In amphipods, there was considerable variability with $\delta^{15}N$ values, which ranged from 7.3‰ in *M. formosa* to 13.4 ± 0.6‰ in *Epimeria loricata*. These $\delta^{15}N$ signatures correspond to trophic levels of TL 2 for *M. formosa*, TL 4 for *E. loricata*, and TL 3 for the remaining amphipod taxa (Table 4.3).

The overall relationship between $\delta^{15}N$ and $\delta^{13}C$ in my data indicates a general trophic enrichment factor of 1.3‰ for $\delta^{13}C$ (Fig. 4.3), assuming a trophic enrichment factor of 3.8‰ per trophic level for $\delta^{15}N$. This estimate is slightly higher than the conventionally assumed value of ≤ 1% per trophic level (DeNiro and Epstein 1978, Hobson and Welch 1992, McCutchan et al. 2003). Thus, taxa that were enriched in ^{15}N were often also enriched in ^{13}C. While samples from a given taxonomic group varied in both $\delta^{15}N$ and $\delta^{13}C$ (Fig. 4.3), fractionation patterns within a taxonomic group could not be determined due to insufficient sample numbers. Mean $\delta^{13}C$ values ranged from -25.8‰ for an unidentified holothurian feeding at TL 2 to -20.4 ± 0.3‰ for the amphipod *Epimeria loricata*, which was one of the few taxa feeding at TL 4 (Table 4.3). There was no relationship between $\delta^{13}C$ for samples of a given species from the Mackenzie shelf *vs* the same species from the Amundsen Gulf. However, for 8 taxa the lightest carbon signature occurred at station 718 near the mouth of the Mackenzie River (Fig. 4.2).

Significant relationships between bulk stable isotope signatures and certain fatty acids important for the interpretation of fatty acid data are presented in Table 4.4.

4.4.3. *Fatty Acids*

Although fatty acid composition varied considerably among taxa and taxonomic groups, some general patterns emerged. Across all taxa, 16:0, 16:1ω7, 18:1ω9, 20:5ω3, and 22:6ω3 were generally the most abundant fatty acids (Tables 4.5 - 4.8). However, in some cases, 18:1ω7 (*Arrhis phyllonyx, Eulalus gaimardii* and *Sclerocragnon ferox*) or 20:1ω9 (*Eusirus cuspidatus, Boreomysis arctica,* and the polychaete) was greater than 10% of total fatty acids. Furthermore, the amphipods *A. phyllonyx* and *Epimeria loricata* and the holothurian had high levels of 20:4ω6 (Fig. 4.6).

Diatom fatty acid signatures (∑16:1/16:0) and copepod fatty acid markers ($\sum C_{20}$ and C_{22} monounsaturated fatty acids) were variable among taxonomic groups and taxa. Diatom fatty acid markers ranged from 0.5 in the polychaete and in the amphipod *Epimeria loricata* to 5.1 in the chaetognath *Eukrohnia hamata,* while copepod markers ranged from 2.3% in the euphausiid *Thysanoessa raschii* to 33.1 ± 4.3% in the mysid *Boreomysis arctica* (Fig. 4.5). Mean percentages of bacterial fatty acids were highest in the holothurian (9.1 ± 2.0%) and less than 5% in all other species (mean 2.6 ± 1.3%; Fig. 4.5).

Discriminant analysis using fatty acids as classifiers and LOOCV had an 84% accuracy in predicting taxonomic group. Such predictions would be < 1% accurate by chance alone. The major inaccuracies in this model were that both *Calanus hyperboreus* samples were mis-classified as chaetognaths and peracarid crustaceans (amphipods and mysids) were mis-classified as each other (Table 4.9). The first two discriminant scores explained 49% and 24% of the variation in fatty acids among taxonomic groups. The first discriminant score, with strong positive coefficients for fatty acids of phytoplankton origin (15:0, 21:5ω3, and

22:5ω3) and of terrestrial origin (24:1) differentiated chaetognaths and copepods from all other taxonomic groups (Fig. 4.7). The second discriminant score separated the holothurian and polychaete from all other taxonomic groups, with strong positive loading coefficients for those fatty acids normally associated with bacteria (*i*15:0, *i*17:0, 17:1 and 18:0) and 22:1ω7 (Fig. 4.7). Although the third and fourth discriminant scores only explained 10 and 6% of the variance in fatty acid profiles among taxonomic groups, a combination of these two axes allowed separation of decapod shrimp, mysids and amphipods from each other (data not shown). Fatty acids that were important in this differentiation were both fatty acids of phytoplankton origin (16:4ω1, 20:2α, 22:5ω6, 21:5ω3, 18:3ω6, and 18:2ω4) and bacterial origin (15:1, i15:0, *ai*17:0, and 17:0).

Although discriminant analysis using fatty acids as predictors was not as accurate in defining individual taxa as it was for defining taxonomic groups, it was still 61% accurate by LOOCV, considerably better than chance alone (< 1%). Most of the prediction error stemmed from mis-classifying taxa within the same taxonomic group (Table 4.10). Because taxa were not often confused with taxa of other taxonomic groups, the plots of taxa based on the first two discriminant scores are similar to the taxonomic group plots (Fig. 4.7, 4.8). There were three major differences between the taxonomic group pattern and the taxa pattern for the first two discriminant scores. First, the amphipod *Arrhis phyllonyx* was separate from the rest of the amphipods, lying near the holothurian on the first and second axis (Fig. 4.8). Fatty acids important for this separation were the ω6 fatty acids, 20:2ω6, 22:5ω6, and 18:3ω6, as well as 22:1ω7, 18:3ω3, and 18:0 (Fig. 4.8). Furthermore, the decapod shrimp *Eualus gaimardii* separated from mysids, amphipods, and the other decapod shrimp, *Bythocaris* spp. (Fig. 4.8). This separation was not seen in the taxonomic group plots by the first two

discriminant scores, where both decapod shrimp grouped together (Fig. 4.7). Lastly, there was a slight but defined separation between the two chaetognaths, *Eukrohnia hamata* and *Parasagitta elegans*, by the first discriminant score, with *Calanus hyperboreus* grouping more strongly with *P. elegans* (Fig. 4.8). The first two discriminant scores in the taxa model accounted for 44 and 18% of the among-taxa variation in fatty acids.

4.5. DISCUSSION

4.5.1. $\delta^{15}N$ and Trophic Levels

The stable isotope ratio of nitrogen is a useful tool for determining the trophic levels of consumers, higher $\delta^{15}N$ indicating higher trophic levels as there is predictable enrichment in $\delta^{15}N$ between prey and consumers of 3.4 - 3.8‰ (Hobson and Welsh 1992, Søreide et al. 2006a). The taxa of BBL zooplankton examined in this study spanned trophic levels (TL) 2 - 4, assuming a trophic enrichment factor of 3.8‰ (Table 4.3). A similar range (1.8 - 3.8) was found by Søreide et al. (2006a) for pelagic zooplankton collected near Svalbard. In the present study, the copepod *Calanus hyperboreus* was estimated to have been feeding at TL 2, in accordance with published work on pelagic populations of this Arctic species (Hobson and Welch 1992, Søreide et al. 2006a, Tamelander et al. 2006). Thus, it seems that BBL and pelagic *C. hyperboreus* feed at a similar trophic level.

The amphipod *Melita formosa* had the lowest $\delta^{15}N$ values and was feeding at TL 2, like the herbivorous copepod *Calanus hyperboreus* (Table 4.3, Fig. 4.2). High levels of 16:1ω7 (24%) and 20:5ω3 (22%) in *M. formosa* are further evidence of a phytoplankton diet with a large diatom component (Table 4.5, Viso and

Marty 1993). There is no information in the literature on the diet of *M. formosa* from studies of $\delta^{15}N$ or fatty acids.

Likewise, the holothurian, the euphausiid *Thysanoessa raschii*, and the mysid *Mysis litoralis* all occupied relatively lower trophic levels than other taxa in this study, suggesting tighter links with epipelagic production in the former groups (Fig. 4.2). Some species of holothurians and *T. raschii* consume phytodetritus (Falk-Petersen 1981, Roberts et al. 2000). However, the fatty acid data suggest that the holothurian was feeding on bacteria rather than phytoplankton (Fig. 4.5).

Both chaetognath species, *Parasagitta elegans* and *Eukrohnia hamata*, were a full trophic level higher (TL 3) than *Calanus hyperboreus* (Table 4.3). However, $\delta^{15}N$ of *P. elegans* was significantly higher than that of *E. hamata*. *P. elegans* near Svalbard also feeds at a higher trophic level than *E. hamata* based on $\delta^{15}N$ (Hop et al. 2006, Søreide et al. 2006a). Hop et al. (2006) suggested that *E. hamata* may feed more omnivorously than *P. elegans*. However, *P. elegans* near Svalbard occupied a trophic level ≥ 3.7, higher than the BBL chaetognaths in this study even after adjusting the trophic enrichment factor to match theirs (3.4‰; Hop et al. 2006, Søreide et al. 2006a). In other reports of $\delta^{15}N$ for chaetognaths in the Arctic, both *E. hamata* and *P. elegans* were predominately feeding at a trophic level similar to conspecifics in the BBL of the Beaufort Sea shelf (Hobson et al. 2002, Iken et al. 2005).

Mysids are primarily omnivores, feeding on a wide variety of food sources, depending on their life history stage and on food availability (Viherluoto et al. 2000). Adults of some species are opportunistic predators able to select preferred prey (Viitasalo and Rautio 1995, Viherluoto and Viitasalo 2001). My $\delta^{15}N$ results suggest that *Mysis litoralis* was feeding more herbivorously than

other mysid taxa (Table. 4.3). There is a paucity of data on the feeding ecology of the mysid taxa considered in this study. However, a previous study of *Boreomysis arctica* from the Mediterranean Sea indicates that both Crustacea and phytodetritus are important components of the diet and that in general mysids living in deeper waters are less selective feeders than are those living in shallower waters (Cartes and Sorbe 1998).

Most amphipod taxa in this study occupied TL 3 (Table 4.3). However, as discussed previously, *Melita formosa* was primarily feeding at TL 2 and *Eusirus loricata* occupied the highest trophic level (TL 4) of the amphipod taxa, which was equivalent to trophic levels for the decapod shrimp, *Bythocaris* spp. and the polychaete. Research on trophic interactions of Arctic amphipods has primarily focused on sympagic and pelagic amphipods (Hobson and Welch 1992, Iken et al. 2005, Tamalander et al. 2006). In contrast, not much is known about the feeding behavior or ecology of the BBL amphipods investigated here. A few comprehensive studies of Antarctic benthic amphipod communities have related mouthpart morphology, gut content, stable isotopes, and fatty acids (Dauby et al. 2001, Graeve et al. 2001, Nyssen et al. 2002, Nyssen et al. 2005). While studies like these are generally lacking for benthic Arctic amphipods, species of the family Lysianassidae are the most studied (Sainte-Marie 1984, Legeżyńska 2008).

Lysianassid amphipods, which include *Tmetonyx cicada, Anonyx* spp., and *Hippomedon* spp., are generally scavengers, and *T. cicada, A. sarsi* and *A. nugax* have been caught in baited traps near Spitsbergen and Ellesmere Island (Legeżyńska et al. 2000, Legeżyńska 2008). Unfortunately, we did not collect enough specimans of *T. cicada* to permit analysis of stable isotopes, but the high levels of 18:1ω9/18:1ω7 suggest a scavenging feeding modality (Graeve et al.

1997). Likewise, both *Anonyx* spp. and *Hippomedon* spp. were feeding primarily at TL 3. Gut content analysis in both *A. sarsi* and *A. nugax* near Spitsbergen confirm a predominately scavenger lifestyle for both species, the former being the more predatory, relying heavily on polychaetes (Legeżyńska 2008). However, there were important differences in gut contents, depending on developmental stage, immature individuals of both species consuming more detritus than did mature individuals (Legeżyńska 2008).

Gut content analysis and morphological evidence suggest that *Rhachotropis* and *Acanthostepheia malmgreni* feed on both calanoid and harpacticoid copepods (Sainte-Marie and Brunel 1985). Our $\delta^{15}N$ data place both species about one trophic level above *C. hyperboreus*, which suggests that these Arctic amphipods may indeed feed directly on copepods. Our trophic level for *A. malmgreni* was equivalent to that of unidentified species of *Acanthostepheia* in the North Water polynya (TL 2.6; Hobson et al. 2002).

The variety of trophic levels among taxa highlights the diversity of feeding modes found in BBL invertebrates on the Beaufort Sea shelf and their ability to use various food resources. The low trophic levels of *Melita formosa, Calanus hyperboreus, Thysanoessa raschii, Mysis litoralis,* and the holothurian also indicate that (1) fresh phytoplankton reaches the BBL on the Beaufort Sea shelf and can be exploited by suspension feeders living in near-bottom waters and/or (2) zooplankton living in this ocean region actively contribute to the vertical flux of organic matter through vertical migration.

4.5.2. $\delta^{13}C$ *and Carbon Source*

The stable isotope ratio of carbon provides information on the original source of carbon in a consumer's diet. On the Beaufort Sea shelf the 3 main sources of carbon are ice algae, marine phytoplankton, and terrestrial matter from the Mackenzie River (Macdonald et al. 1998, Carmack et al. 2004, Renaud et al. 2007b). Generally, the $\delta^{13}C$ of animal tissue was heavier than particulate organic matter (POM) in near-bottom water (Chapter 2). Large enrichments of ^{13}C in invertebrates compared with POM have been reported in other studies of Arctic epipelagic zooplankton and benthic invertebrates (Dunton 1989, Hobson et al. 1995, Hobson et al. 2002). It is unclear why this pattern exists, but it has been attributed to increased microbial degradation of POM in the upper water column in the Arctic (Hobson et al. 1995) and to inconsistent analytical methods between animals and POM (Søreide et al. 2006a). For example, removal of lipids from animals but not from POM before isotope analysis is common in ecosystem studies in the Arctic, yet lipids are generally more depleted in ^{13}C than protein (DeNiro and Epstein 1977, Sotiropoulos et al. 2004). Different lipid storage capacities among species and seasonal differences within a species can complicate interspecific and intraspecific comparisons based on stable isotope data (Søreide et al. 2006b). Søreide et al. (2006a) and Tamelander et al. (2006), removed lipid from both animal tissue and POM, which resulted in more uniform $\delta^{13}C$ values between POM and grazers. However, in the present study, lipids were not removed from either animals or POM. Presumably animals have a higher lipid fraction than POM in near-bottom waters and therefore would probably be more depleted in ^{13}C if lipids were the major factor contributing to this trend. Although differential lipid removal may account for these patterns in

other Arctic ecosystems, this is unlikely in BBL zooplankton on the Beaufort Sea shelf. Another possibility for a river-influenced shelf, such as the Beaufort Sea shelf, is that zooplankton are selectively feeding on more ^{13}C enriched autochthonous carbon sources of marine origin, rather than more depleted allochthonous, terrigenous carbon. In combination with an active microbial loop, zooplankton incorporating phytoplankton-derived carbon preferentially over terrestrial carbon would account for higher $\delta^{13}C$ values in zooplankton compared with POM.

Carbon from terrestrial sources is depleted in ^{13}C relative to carbon fixed by marine phytoplankton. These source-specific differences in $\delta^{13}C$ signatures often result in $\delta^{13}C$ signatures of consumers that reflect the origin of carbon (Parsons et al. 1989, Dunton et al. 2006). A terrestrial influence on the $\delta^{13}C$ signature in zooplankton was only seen for animals from station 718 on the Mackenzie shelf, likely due to its nearshore location close to the eastern outflow into Kugmallit Bay (Fig. 4.2). Elsewhere, within a given taxon there was no clear difference in $\delta^{13}C$ between samples from the shelf and those from the Amundsen Gulf. However, analysis of spatial patterns in $\delta^{13}C$ of animals in relation to river outflow was limited in this study due to the relatively low numbers of individuals of various taxa collected from both the Mackenzie shelf and Amundsen Gulf.

4.5.3. Integrating Bulk Stable Isotopes with Fatty Acids

Combining bulk stable isotope data with fatty acid data can facilitate the interpretation of both data sets. The inverse relationship between $\delta^{13}C$ and the fatty acid 24:1 (Table 4.4) suggests that this fatty acid may be a more useful

indicator of terrestrial input in BBL zooplankton than are 18:3ω3 and 18:2ω6 (see Chapter 2). High proportions of 24:1 have been found in some terrestrial plant seeds (> 20%; Wilson et al. 1962, Litchfield 1970) and small quantities have been noted in sedges from the Canadian Arctic (> 1%; Dugan et al. 2007). In contrast, the direct relationship between $\delta^{13}C$ and the fatty acid 15:0 indicates that the latter may be a useful marine phytoplankton marker in these samples (Table 4.4). Parrish et al. (1992) also suggested that 15:0 may be a useful marker for phytoplankton blooms because it is commonly found in marine algae (Volkman et al. 1989). Likewise, 18:1ω7, which also had a direct relationship with $\delta^{13}C$ (Table. 4.4) is often a product of chain elongation of 16:1ω7, another common phytoplankton marker (Viso and Marty 1990).

The inverse relationship between $\delta^{15}N$ and various fatty acids of phytoplankton origin, especially PUFA (16:2ω4, 16:4ω1, 18:3ω6, 18:4ω3, 21:5ω3, and 20:5ω3 (eicosapentaenoic acid; EPA)), the fatty acids 14:0 and 16:1ω7, and the diatom marker (∑16:1/16:0) (Table 4.4) suggests that these fatty acids are not magnified through trophic levels, and therefore not conserved. They were most abundant in lower level consumers, which feed directly on phytodetritus. 22:6ω3 (docosahexaenoic acid; DHA) was the only PUFA positively correlated with $\delta^{15}N$. The positive relationship between $\delta^{15}N$ and the essential fatty acid 22:6ω3 and the ratio of 22:6ω3/20:5ω3 (DHA/EPA; Fig. 4.13) suggests that 22:6ω3 is a highly conserved fatty acid and is not catabolized for energy. Although both 22:6ω3 and 20:5ω3 are essential fatty acids, the greater nutritional value of 22:6ω3 relative to 20:5ω3 is well known in aquaculture research (Copeman et al. 2002). The trophic magnification of 22:6ω3 and a decrease in 20:5ω6 with trophic level suggests that 22:6ω3 is also a more important essential fatty acid than 20:5ω3 in BBL

zooplankton. An interesting result is the low value of 22:6ω3/20:5ω3 ratios across all taxa (< 2.0, mean 0.8 ± 0.3). Since a ratio > 2 is required for optimal fish growth and development (Copeman et al. 2002), demersal fish on the Beaufort Sea shelf may suffer an imbalance in the 22:6ω3 supply.

The positive relationship between $\delta^{15}N$ and fatty acids of copepod origin (20:1, 22:1), could have also resulted from trophic magnification. These fatty acids are often used as energy sources because they are generally too long to be useful as membrane components and therefore less likely to be conserved and magnified through trophic levels . However, in animals with rich lipid stores, such as the taxa analyzed here (Chapter 3), these fatty acids can be stored for use as an energy source. Alternatively, this trend may result from a higher contribution of copepods or copepod-derived lipids to the diets of species from higher trophic levels. This trend has also been observed in amphipods from the Southern Ocean (Nyssen et al. 2005).

4.5.4. Fatty Acids

Taxonomic groups were well defined by both the taxonomic group and the taxa discriminant models while individual taxa were less well defined. The most remarkable result of these analyses was the accuracy obtained in defining taxonomic groups in the taxa model when taxonomic groups were not specified (Table 4.10). This strongly suggests that there is a phylogenetic basis for fatty acid profiles, which are highly conserved among closely related taxa despite differing trophic levels and sampling seasons and locations.

The fatty acid data also suggested a clearly defined food web for copepods and chaetognaths and for the holothurian, and a very tight relationship within

the malacostrans, in which amphipods, mysids, and decapod shrimp grouped tightly together (Fig. 4.7 - 4.8). In the taxonomic group model, the third and fourth discriminant scores were required to differentiate the malacostracans from each other, whereas the peracarids (amphipods and mysids) were more similar to each other than to decapod shrimp. The tight grouping of malacostracans and the even tighter grouping of peracarids again strongly suggest that phylogeny is reflected in the fatty acid profiles.

Calanus hyperboreus was the only crustacean taxon that did not group with the other crustaceans. *C. hyperboreus* consistently grouped with chaetognaths and was always identified as a chaetognath in LOOCV (Fig. 4.7 - 4.8, Table 4.9 - 4.10). The most likely explanation is that the chaetognaths were feeding heavily on copepods. Additionally, in the taxa model in which the two chaetognaths were weakly defined by the second score (Fig. 4.8), *C. hyperboreus* grouped more tightly with *Parasagitta elegans* than with *Eukrohnia hamata,* which is consistent with the conclusion from the $\delta^{15}N$ data suggesting that *P. elegans* was more carnivorous than *E. hamata* (Fig. 4.2). Fatty acids of phytoplankton origin were strongly linked with chaetognaths and copepods by the first discriminant score (Fig. 4.5). The above evidence suggests that the conventional, 'linear' pelagic food web from phytoplankton to copepods to chaetognaths, also exists in the BBL. However, levels of the fatty acid 24:1 indicate that this simple food web model is modified on the Beaufort Sea shelf, with significant inputs of terrestrial carbon to *C. hyperboreus* which are transferred to the chaetognaths (Fig. 4.5).

In contrast, bacterial fatty acids (*i*15:0, 15:1, *i*17:0, and 17:1) strongly defined the holothurian samples by the second discriminant score (Fig. 4.7), suggesting a high contribution of bacterial carbon to the holothurian relative to the other taxa (Fig. 4.5). Bacterial fatty acids were found in the holothurian at

levels comparable with literature reports of for other echinoderms (Howell et al. 2003; Table 4.7), consistent with their surface deposit feeding behavior. The other strong fatty acid predictor for the holothurian was 22:1ω7. In contrast, when C_{22} monounsaturates were present in other taxa in this study, 22:1ω11(13) was dominant over 22:1ω7. High levels of 22:1ω7 have also been found in deep-sea holothurians, contributing up to 4.0% of total fatty acids (Hudson et al. 2004) Although 22:1ω11(13) is usually associated with copepods, the origin of 22:1ω7 is not clear, but it could result from chain elongation from 16:1ω7 and 18:1ω7 precursors. 16:1ω7 has been attributed to phytoplankton sources (Viso and Marty 1993) and 18:1ω7 to chain elongation of phytoplankton-derived 16:1ω7 and to bacterial sources (Desvilettes et al. 1997, Pond et al. 1998). The high levels of bacterial fatty acids in the holothurian indicate that 22:1ω7 may result from chain elongation of 18:1ω7 from bacteria. If this is the case, holothurians may have different requirements for 22:1ω7 than other benthic and BBL invertebrates.

Because malacostracans had similar fatty acid profiles, it is more difficult to differentiate among them. However, in the taxa model, the amphipod *Arrhis phyllonyx* largely separated from other amphipod taxa and from other malacostracans generally (Fig. 4.8). In the discriminant plot, *A. phyllonyx* samples are plotted opposite to chaetognaths and copepods by the first discriminant score, occurring in the same quadrant as the holothurian. Some of the most important fatty acid predictors for this grouping are ω6 PUFA (Fig. 4.8).

Certain PUFA are essential fatty acids for consumers, and marine invertebrates living at higher latitudes may have higher proportions of PUFA to compensate for reduced membrane fluidity at low temperatures. While PUFA generally come from phytoplankton sources, it is increasingly recognized that

some deep-sea and psychrophilic bacteria, as well as endosymbiotic bacteria, are capable of synthesizing PUFA *de novo*. Zooplankton contain primarily ω3 PUFA, which accounted for over 80% of total PUFA in our taxa (Fig. 4.6). However, *Arrhis phyllonyx* contained higher levels of ω6 PUFA (> 15% of PUFA) than other amphipod taxa, 20:4ω6 being dominant (Table 4.5, Fig. 4.6). The source of 20:4ω6 in marine systems is unclear but has been attributed to macroalgae, diatoms, microbial eukaryotes, and freshwater/terrestrial origins (Sargent et al. 1987, Scribe et al. 1991, Howell et al. 2003). This fatty acid was less than 1% of total fatty acids in suspended particles in near-bottom waters across the entire Beaufort Sea shelf (Chapter 2). Although zooplankton usually have low levels of 20:4ω6, benthic invertebrates such as echinoderms, mollusks and some crustaceans have high levels of 20:4ω6, exceeding 20% of total fatty acids in some species (Graeve et al. 2001, Howell et al. 2003, Hudson et al. 2004, Nyssen et al. 2005). The lower ω3:PUFA ratio of *A. phyllonyx, Epimerica loricata,* and the holothurian relative to other taxa was due to higher levels of 20:4ω6 (Table 4.5, 4.8).

Although the fatty acid profiles of the chaetognaths *Eukrohnia hamata* and *Parasagitta elegans* were very similar (Fig. 4.8), important differences emerged on closer inspection of their fatty acid compositions, which were consistent within each species among stations (Fig. 4.9). Some important differences include higher 16:1ω7/16:0 ratios and higher levels of 22:1, 20:1, and 20:4ω3 in *E. hamata* and higher levels of 16:0, 18:1, 20:5ω3, 22:6ω3, and 24:1 in *P. elegans*. Some of these differences can be attributed to lower levels of storage lipids in *P. elegans* and higher levels of wax ester stores in *E. hamata* (Chapter 3). The higher levels of 20:5ω3 and 22:6ω3 in *P. elegans* are directly related to lipid class composition,

as these fatty acids are major components of cell membrane phospholipids, the dominant lipid class in *P. elegans* (see Chapter 3). In contrast, the high 20:1 and 22:1 levels in *E. hamata* are directly related to storage of wax esters (72% of total lipids, Chapter 3), which is usually composed of 20:1 and 22:1 fatty alcohols and fatty acids. Higher levels of 24:1 in *P. elegans* than in *E. hamata* suggests that *P. elegans* accumulated higher amounts of terrestrial carbon. This is not surprising, considering that all but one of the *P. elegans* samples came from the stations closest to the Mackenzie River. As the above comparison indicates, a detailed examination of the fatty acid profiles of individual samples can provide a better insight than using multivariate statistical analyses alone.

4.6. CONCLUSION

A large gap in our knowledge of Arctic food webs includes communities of BBL zooplankton. Natural stable isotope ratios and fatty acids are useful tools for examining the ecology of communities that are difficult to sample, and allowed investigation of trophic interactions of BBL zooplankton on a seasonally ice-covered Arctic shelf. The community in this study included taxa at three trophic levels and with different fatty acid profiles. Fatty acids not only provided information on diet but also reflected phylogeny. The wide range in trophic levels and the variation in fatty acid biomarkers, indicate that the trophic ecology of these communities may indeed be important for food web models and carbon budgets, but the role of these communities in carbon cycling is often overlooked. More research is needed in order to quantify elemental and nutrient fluxes through this poorly understood zooplankton community.

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4.9. TABLES

Table 4.1. Station locations for zooplankton collections from the benthic boundary layer of the Beaufort Sea shelf during fall 2003 and summer 2004.

Station	Lat (°N)	Long (°W)	Date	Depth (m)
718	70.17	133.52	30-Sep-03	45
CA10	69.93	138.58	7-Oct-03	238
CA06	70.59	127.23	11-Oct-03	255
500	72.00	127.57	25-Oct-03	396
118	70.95	125.83	27-Oct-03	401
206	70.32	124.85	1-Nov-03	99
206	70.32	124.85	4-Jun-04	99
256	70.25	123.50	5-Jun-04	342
108	70.63	123.17	7-Jun-04	478
117	70.88	125.50	10-Jun-04	377
406	71.31	127.69	15-Jun-04	179
400	70.92	128.92	17-Jun-04	242
303	70.80	127.04	20-Jun-04	256
398	70.79	129.36	21-Jun-04	24
609	70.92	130.53	27-Jun-04	40
709	70.94	133.68	1-Jul-04	86
803	70.64	135.87	2-Jul-04	242
906	70.02	138.60	4-Jul-04	281
909	69.80	138.28	5-Jul-04	169
912	69.49	137.94	5-Jul-04	56
809	70.09	135.34	7-Jul-04	44
712	70.69	133.68	10-Jul-04	712
718	70.17	133.52	11-Jul-04	45
200	70.04	126.30	16-Jul-04	235
309	71.12	125.83	19-Jul-04	235
415	71.91	125.87	20-Jul-04	52
409	71.50	127.09	22-Jul-04	380

Table 4.2. Species information and stations for collections from the benthic boundary layer on the Beaufort Sea shelf. (F) refers to samples collected in fall 2003; all others were collected in June and July 2004. 'n' is the number of samples per species and Indiv/sample is the range in the number of individuals pooled in each sample.

Species	Stations	n	Indiv/sample
Amphipoda			
Acanthostepheia malmgreni	200, 206, 406, 809, 909, 718(F)	6	1-4
Anonyx spp.	206, 400, 609, 718(F)	4	1-3
Anonyx nugax	909, 206(F)	2	2-3
Arrhis phyllonyx	712, 718, 809	3	3-5
Epimeria loricata	256, 309	2	3,5
Eusirus cuspidatus	117	1	2
Halirages spp.	118, 309, 409, 500	4	1-2
Hippomedon spp.	398, 400, 912	3	1-10
Melita formosa	609	1	1
Rhachotropis leucopthalma	108	1	1
Rhachotropis acueata	400	1	3
Rhachotropis sp.	303, 803, 906, 909, CA10(F)	5	5-10
Syrrhoe crenulata	709, 712	2	5,10
Syrrhoe serrata	406	1	10
Syrrhoe sp.	415	1	15
Tmetonyx cicada	206(F)	1	4
Mysidacea			
Boreomysis arctica	108, 256	2	4,10
Erythrops spp.*	117, 200, 303, 309, 406, 609, 709, 712, 718, 803, 809, 906, 909, 912, CA06(F), CA10(F)	16	5-20
Michthyops theeli	117, 409, 500	3	10
Mysis litoralis	718, 809, 718(F)	3	5-10
Parerythrops obesa	CA10(F)	1	10
Pseudomma frigidum	108, 118, 256, 309, 309, 409	6	3-10
Decapoda			
Bythocaris spp.	108, 117, 118, 309, 409, 500, CA10	7	1-3
Eualus gaimardii	256, 400, 712, 718, 912, 206(F)	6	1-2
Sclerograngon ferox	906	1	1
Euphausiacea			
Thysanoessa raschii	912	1	4
Copepoda			
Calanus hyperboreus	415, CA10(F)	2	20
Chaetognatha			
Eukrohnia hamata	108, 117, 118, 200, 256, 303, 309, 409, 500, 709, CA06(F)	11	5-10
Parasagitta elegans	415, 712, 718, 809, 206(F), 718(F)	6	10-20
Holothuroidea			
Unidentified sp.	718, 718(F)	2	5,10
Polychaeta			
Unidentified sp.	118	1	10

* *Erythrops erythrophthalma* was the most abundant species within the genus *Erythrops*, but *E. abyssorum, E. glacialis,* and *E. serrata* were locally abundant.

Table 4.3. Mean stable isotope ratios for nitrogen and carbon, and derived trophic levels (TL) using a trophic enrichment factor of 3.8‰ for taxa collected from the benthic boundary layer of the Beaufort Sea shelf. 'n' is the number of samples per taxa and error is reported as standard deviation, except when n =2 and is reported as half the range.

Species	n	$\delta^{15}N$	$\delta^{13}C$	TL
Amphipoda				
Acanthostepheia malmgreni	6	11.0 (1.7)	-22.1 (1.3)	3
Arrhis phyllonyx	3	11.5 (0.4)	-22.3 (0.6)	3
Anonyx spp.	6	10.9 (1.6)	-21.9 (1.3)	3
Eusirus cuspidatus	1	12.6	-23.2	3
Epimeria loricata	2	13.4 (0.6)	-20.4 (0.3)	4
Halirages spp.	4	11.7 (1.1)	-23.4 (0.6)	3
Hippomedon spp.	3	12.0 (2.1)	-21.8 (0.4)	3
Melita formosa	1	7.3	-22.0	2
Rachotropis spp.	7	11.5 (3.2)	-21.8 (1.0)	3
Syrrhoe spp.	3	9.5 (1.2)	-21.7 (1.4)	3
Mysidacea				
Boreomysis arctica	2	11.7 (0.0)	-22.9 (0.6)	3
Erythrops spp.	18	10.4 (1.3)	-22.7 (1.4)	3
Mysis litoralis	3	8.4 (0.3)	-25.4 (1.0)	2
Michthyops theeli	3	12.1 (1.5)	-21.9 (0.8)	3
Pseudomma frigidum	6	12.0 (1.3)	-23.4 (0.8)	3
Decapoda				
Bythocaris spp.	7	14.1 (0.7)	-21.8 (1.1)	4
Eualus gaimardii	6	12.3 (1.2)	-21.1 (0.7)	3
Sclerograngon ferox	1	11.0	-21.0	3
Euphausiacea				
Thysanoessa raschii	1	8.8	-23.8	2
Copepoda				
Calanus hyperboreus	2	8.1 (0.8)	-24.0 (0.7)	2
Chaetognatha				
Eukrohnia hamata	11	10.7 (0.8)	-24.8 (0.5)	3
Parasagitta elegans	5	12.4 (1.3)	-25.4 (1.4)	3
Holothuroidea				
Unidentified sp.	1	9.0	-25.8	2
Poychaeta				
Unidentified sp.	1	14.9	-20.5	4

Table 4.4. Pearson correlation coefficients between bulk stable isotope ratios and fatty acids. All correlation coefficients (corr coef) shown here were significant at $p \leq 0.05$. DHA/EPA is 22:6ω3/20:5ω3, 'Diatom' is the ratio ∑16:1/16:0, 'Copepod' is ∑20:1 + 22:1, SFA is saturated fatty acids, and MUFA is monounsaturated fatty acids.

Fatty acid	corr coef
$\delta^{15}N$	
14:0	-0.31
16:1ω7	-0.46
16:2ω4	-0.51
16:4ω1	-0.20
18:0	0.21
18:1ω5	0.22
18:3ω6	-0.37
18:4ω3	-0.26
20:1ω11	0.42
20:1ω9	0.30
20:1ω7	0.28
20:5ω3	-0.23
22:1ω11(13)	0.26
22:1ω7	0.29
21:5ω3	-0.22
22:6ω3	0.20
DHA/EPA	0.37
Diatom	-0.26
Copepod	0.32
$\delta^{13}C$	
15:0	0.20
phytanic	0.21
18:0	0.22
18:1ω9	0.39
18:1ω7	0.47
20:4ω6	0.32
22:5ω3	0.25
24:1	-0.45
SFA	0.21
MUFA	-0.23

Table 4.5. Relative fatty acid (FA) composition (% total FA) of amphipod taxa collected from the benthic boundary layer on the Beaufort Sea shelf. Errors are reported as standard deviations, except when n =2 where errors are half the range.

Fatty acid*	*Acanthostepeia malmgreni* (n = 6)	*Arrhis phyllonyx* (n = 3)	*Anonyx* spp. (n = 6)	*Eusirus cuspidatus* (n = 1)	*Epimeria loricata* (n = 2)	*Halirages* spp. (n = 4)	*Hippomedan* spp. (n = 3)	*Melita formosa* (n = 1)	*Rhachotropis* spp. (n = 7)	*Syrrhoe* spp. (n = 4)	*Tmetonyx cicada* (n = 1)
14:0	1.2 (0.7)	0.6 (0.2)	1.4 (1.0)	0.6	0.2 (0.02)	3.0 (1.1)	1.3 (1.0)	1.0	1.4 (0.6)	2.3 (0.8)	2.0
TMTD	0.2 (0.4)	0.3 (0.3)	0.3 (0.4)	0.8	0.3 (0.04)	0.5 (0.9)	0.7 (0.7)	1.3	0.7 (0.5)	1.1 (1.3)	-
15:0	0.4 (0.1)	0.3 (0.1)	0.3 (0.1)	0.2	0.4 (0.1)	0.3 (0.2)	0.6 (0.4)	0.6	0.2 (0.04)	0.2 (0.04)	0.4
16:0	13.1 (1.3)	11.5 (2.1)	12.1 (1.1)	9.9	9.8 (1.1)	10.9 (1.5)	12.2 (1.6)	10.6	10.9 (0.9)	14.0 (1.8)	11.2
16:1ω7	8.6 (3.7)	10.4 (3.0)	13.5 (6.5)	9.5	3.7 (0.2)	20.2 (8.0)	16.4 (8.1)	24.2	13.7 (2.8)	24.2 (9.4)	15.5
16:1ω5	0.5 (0.5)	1.3 (0.1)	1.1 (1.2)	1.3	1.0 (0.02)	0.8 (1.2)	0.8 (1.2)	-	0.7 (0.7)	0.7 (1.1)	0.3
*i*17:0	0.4 (0.3)	0.4 (0.4)	0.5 (0.5)	0.6	1.4 (0.2)	0.4 (0.5)	0.8 (0.5)	0.7	0.5 (0.2)	0.6 (0.5)	0.4
*a*i17:0	0.3 (0.1)	0.2 (0.2)	0.2 (0.1)	0.2	0.9 (0.4)	0.3 (0.1)	0.3 (0.2)	0.3	0.2 (0.05)	0.4 (0.2)	-
16:2ω4	0.2 (0.1)	0.2 (0.2)	0.4 (0.2)	0.2	-	0.5 (0.3)	0.3 (0.2)	0.8	0.4 (0.2)	0.6 (0.4)	0.4
phytanic	0.4 (0.4)	0.2 (0.3)	0.3 (0.2)	0.3	0.6 (0.02)	0.2 (0.2)	0.5 (0.7)	0.3	0.3 (0.2)	-	0.2
17:0	0.4 (0.2)	0.4 (0.1)	0.2 (0.1)	-	0.5 (0.04)	0.2 (0.1)	0.7 (0.9)	0.4	0.2 (0.1)	0.2 (0.05)	0.2
16:3ω4	-	0.3 (0.2)	0.2 (0.2)	-	0.3 (0.3)	0.2 (0.1)	0.4 (0.1)	1.0	0.2 (0.1)	0.4 (0.6)	0.4
17:1	-	0.2 (0.03)	0.3 (0.1)	-	0.3 (0.2)	0.3 (0.2)	0.2 (0.2)	0.5	0.3 (0.1)	0.2 (0.1)	-
16:4ω1	0.2 (0.2)	0.2 (0.1)	0.3 (0.2)	-	0.2 (0.02)	0.5 (0.2)	0.4 (0.2)	0.5	0.2 (0.3)	0.4 (0.3)	0.2
18:0	1.3 (1.0)	1.1 (0.1)	0.8 (0.3)	0.6	1.1 (0.1)	1.1 (0.8)	0.8 (0.3)	0.6	0.6 (0.1)	1.0 (0.3)	0.6
18:1ω9	10.2 (1.1)	7.3 (1.2)	16.5 (3.3)	11.1	10.6 (0.2)	12.1 (3.1)	15.8 (2.2)	6.7	13.8 (1.1)	8.3 (1.3)	18.9
18:1ω7	6.7 (3.5)	11.7 (1.0)	7.7 (2.8)	4.9	7.6 (0.5)	4.7 (1.7)	7.0 (1.7)	8.5	6.9 (1.0)	6.0 (1.0)	4.5
18:1ω5	1.1 (0.4)	1.1 (0.2)	0.8 (0.5)	1.6	1.9 (0.5)	0.9 (0.4)	1.1 (0.8)	0.5	1.2 (0.4)	0.6 (0.2)	0.8
18:2ω6	1.2 (0.1)	2.0 (0.3)	1.1 (0.4)	0.9	0.6 (0.2)	0.9 (0.2)	1.2 (0.3)	0.6	1.5 (0.3)	1.4 (1.2)	1.1
18:3ω3	0.4 (0.3)	0.3 (0.1)	0.4 (0.2)	0.5	-	0.3 (0.1)	0.4 (0.1)	0.3	0.5 (0.2)	0.5 (0.2)	0.3
18:4ω3	0.8 (0.6)	0.8 (0.2)	1.2 (0.5)	0.4	0.5 (0.1)	1.1 (0.3)	1.1 (0.6)	2.0	0.9 (0.6)	1.2 (0.5)	0.7
20:1ω11	0.6 (0.2)	0.2 (0.1)	0.6 (0.5)	2.7	1.8 (0.3)	0.5 (0.5)	0.7 (0.3)	-	0.8 (0.7)	0.2 (0.05)	2.2
20:1ω9	1.6 (1.5)	0.5 (0.2)	2.1 (2.5)	13.1	3.3 (1.0)	4.9 (2.0)	2.0 (0.6)	0.4	4.8 (3.3)	0.9 (0.5)	4.2
20:1ω7	1.0 (0.6)	1.1 (0.1)	1.7 (1.0)	2.6	2.6 (0.1)	1.4 (0.8)	2.5 (0.8)	1.1	1.5 (0.5)	0.7 (0.2)	2.3
20:2$^{\alpha}$	-	-	0.3 (0.3)	0.2	0.6 (0.3)	-	0.2 (0.3)	-	0.2 (0.1)	-	1.1
20:2ω6	0.3 (0.03)	1.0 (0.2)	0.2 (0.1)	0.2	0.4 (0.04)	0.2 (0.1)	0.2 (0.2)	0.2	0.2 (0.1)	0.2 (0.04)	0.2
20:4ω6	3.2 (1.1)	9.5 (0.3)	2.7 (1.6)	1.0	8.5 (1.1)	0.9 (0.2)	1.8 (1.0)	3.4	1.7 (0.6)	1.3 (0.5)	2.6
20:4ω3	0.2 (0.1)	0.3 (0.04)	0.4 (0.3)	0.2	-	0.2 (0.2)	0.4 (0.2)	0.6	0.3 (0.2)	0.3 (0.1)	0.4
20:5ω3	20.8 (3.3)	17.4 (1.3)	16.8 (2.4)	11.5	16.6 (0.2)	14.7 (2.4)	14.2 (3.9)	21.6	15.0 (4.3)	16.3 (6.6)	13.3
22:1ω11(13)	0.9 (1.3)	0.2 (0.1)	0.9 (1.2)	6.7	2.3 (1.3)	4.2 (1.7)	1.5 (0.8)	0.2	3.0 (2.9)	0.5 (0.3)	1.9
22:1ω9	0.3 (0.4)	0.2 (0.2)	0.5 (0.9)	1.6	1.0 (0.2)	0.9 (0.3)	0.7 (0.3)	0.5	0.9 (0.7)	0.2 (0.1)	0.8
22:1ω7	0.2 (0.1)	0.2 (0.1)	0.2 (0.2)	0.4	0.4 (0.1)	0.2 (0.1)	0.5 (0.3)	0.3	0.3 (0.1)	0.3 (0.4)	0.3
22:5ω6	0.8 (0.3)	1.4 (0.6)	0.2 (0.1)	0.2	0.7 (0.2)	-	0.4 (0.2)	1.2	0.2 (0.1)	0.2 (0.1)	0.2
22:5ω3	1.2 (0.2)	2.5 (0.9)	0.6 (0.2)	0.5	1.6 (0.6)	0.6 (0.1)	0.7 (0.4)	0.6	0.6 (0.1)	0.6 (0.2)	0.7
22:6ω3	17.8 (3.6)	11.3 (1.9)	10.4 (4.8)	12.3	14.7 (1.8)	8.9 (1.2)	7.9 (2.0)	4.2	12.5 (2.5)	11.1 (4.2)	9.0

*data not shown for fatty acids not detected or < 0.5% in all amphipod taxa (14:1, *i*15:0, *ai*15:0, 15:1, *i*16:0, *ai*16:0, pristanic, 16:1ω11, 16:1ω9, 16:4ω3, 18:1ω11, 18:1W6, 18:2ω4, 18:3ω6, 19:0, 18:3ω4, 18:4ω1, 20:0, 18:5ω3, 20:3ω6, 21:0, 22:0, 22:2(NMID), 21:5ω3, 23:0, 22:4ω6, 22:4ω3, 24:0, and 24:1); dash = not detected or ≤ 0.1%.

Table 4.6. Mean relative fatty acid (FA) composition (% total FA) of mysid taxa from the benthic boundary layer on the Beaufort Sea shelf. Errors is reported as standard deviation, except when n =2, where it is reported as half the range.

Fatty acid* (%)	*Boreomysis arctica* (n = 2)	*Erythrops* spp. (n = 16)	*Mysis litoralis* (n = 3)	*Michthyops theeli* (n = 3)	*Parerythrops obesa* (n = 1)	*Pseudomma frigidum* (n = 6)
14:0	1.9 (0.8)	3.3 (1.2)	3.8 (1.0)	4.5 (0.9)	2.3	2.8 (1.6)
TMTD	1.2 (0.05)	1.7 (1.3)	1.7 (1.5)	0.7 (1.1)	-	0.3 (0.5)
16:0	9.3 (1.0)	12.7 (0.9)	13.7 (0.6)	13.5 (0.3)	12.5	13.0 (1.1)
16:1ω7	12.8 (0.3)	27.7 (5.6)	33.0 (5.3)	27.2 (7.7)	17.2	16.6 (6.3)
16:1ω5	1.6 (0.4)	0.9 (1.6)	1.3 (2.0)	1.3 (1.7)	0.4	0.7 (0.7)
*i*17:0	0.7 (0.1)	0.4 (0.4)	0.2 (0.2)	0.3 (0.1)	-	0.3 (0.2)
16:2ω4	0.3 (0.1)	0.6 (0.1)	0.7 (0.1)	0.6 (0.2)	0.3	0.3 (0.1)
16:4ω1	0.2 (0.01)	0.5 (0.1)	0.8 (0.2)	0.7 (0.03)	0.5	0.2 (0.2)
18:0	0.4 (0.1)	0.7 (0.2)	0.5 (0.1)	0.7 (0.1)	0.5	0.6 (0.1)
18:1ω9	8.4 (1.9)	9.2 (1.6)	8.6 (1.8)	12.3 (5.5)	9.9	9.7 (1.0)
18:1ω7	4.1 (0.5)	6.3 (1.4)	3.5 (0.3)	3.6 (0.4)	3.8	4.3 (0.8)
18:1ω5	1.2 (0.1)	0.7 (0.6)	0.4 (0.1)	0.3 (0.2)	0.7	0.7 (0.4)
18:2ω6	0.5 (0.2)	0.7 (0.3)	1.0 (0.1)	0.8 (0.2)	0.7	0.7 (0.1)
18:3ω6	-	0.5 (0.1)	0.5 (0.2)	0.6 (0.2)	0.3	0.3 (0.2)
18:3ω3	0.5 (0.3)	0.2 (0.1)	0.5 (0.3)	0.2 (0.1)	0.5	0.3 (0.1)
18:4ω3	0.8 (0.01)	1.3 (0.6)	1.9 (0.1)	1.1 (0.4)	1.3	0.6 (0.3)
20:1ω11	1.5 (0.3)	0.4 (0.3)	0.2 (0.1)	0.6 (0.3)	0.3	1.6 (0.9)
20:1ω9	13.4 (1.1)	2.7 (2.0)	1.1 (0.4)	2.3 (0.6)	6.6	7.9 (3.2)
20:1ω7	2.5 (0.6)	0.8 (0.4)	0.5 (0.3)	0.5 (0.3)	0.9	1.5 (0.7)
20:4ω6	0.6 (0.1)	0.7 (0.2)	0.8 (0.1)	1.0 (0.04)	0.5	0.7 (0.2)
20:4ω3	0.3 (0.1)	0.3 (0.1)	0.5 (0.4)	0.3 (0.1)	1.7	0.3 (0.04)
20:5ω3	8.7 (0.7)	13.1 (2.5)	14.2 (1.4)	13.0 (2.3)	17.3	10.6 (0.5)
22:1$^{\alpha}$11(13)	9.9 (3.9)	2.0 (2.2)	0.4 (0.2)	2.0 (0.7)	2.3	7.5 (2.0)
22:1ω9	5.1 (1.3)	0.4 (0.5)	0.2 (0.03)	0.5 (0.1)	0.6	1.4 (0.4)
22:1ω7	0.7 (0.3)	-	-	-	0.2	0.4 (0.1)
22:5ω3	0.4 (0.01)	0.4 (0.1)	0.3 (0.1)	0.3 (0.1)	0.5	0.6 (0.2)
22:6ω3	8.9 (0.1)	7.9 (2.4)	6.1 (2.5)	6.7 (1.1)	15.5	12.3 (3.0)
24:1	0.5 (0.02)	0.3 (0.2)	0.2 (0.04)	0.2 (0.1)	0.4	0.5 (0.3)

*data not shown for fatty acids not detected or < 0.5% in all mysid taxa (14:1, 15:0, *i*15:0, *ai*15:0, 15:1, *i*16:0, *ai*16:0, pristanic, 16:1ω11, 16:1ω9, *ai*17:0, phytanic, 17:1, 16:3ω4, 16:4ω3, 18:1ω11, 18:1ω6, 18:2ω4, 19:0, 18:3ω4, 18:4ω1, 20:0, 18:5ω3, 20:2ω6, 20:3ω6, 21:0, 22:0, 22:2(NMID), 21:5ω3, 23:0, 22:4ω6, 22:4ω3, 22:5ω6, and 24:0); dash = not detected or ≤ 0.1%.

Table 4.7. Mean relative fatty acid (FA) composition (% total FA) of decapod shrimp and euphausiid taxa from the benthic boundary layer on the Beaufort Sea shelf. Errors are reported as standard deviations.

Fatty acid* (%)	*Bythocaris* spp. (n = 7)	*Eualus gaimardii* (n = 6)	*Sclerograngon ferox* (n = 1)	*Thysanoessa raschii* (n = 1)
14:0	1.1 (0.9)	2.1 (1.1)	1.8	4.1
TMTD	0.5 (0.5)	0.2 (0.3)	-	-
15:0	-	0.3 (0.1)	0.5	0.2
16:0	8.3 (2.7)	13.2 (1.0)	13.1	20.6
16:1ω7	8.8 (4.4)	14.5 (4.8)	16.0	14.1
16:1ω5	1.2 (1.2)	-	1.0	0.4
*i*17:0	0.5 (0.4)	0.6 (0.3)	-	-
*ai*17:0	0.2 (0.2)	0.4 (0.3)	0.6	0.2
16:2ω4	-	0.3 (0.1)	-	0.9
16:3ω4	3.4 (8.1)	0.2 (0.1)	-	0.5
16:4ω1	0.7 (0.9)	0.3 (0.1)	-	0.4
18:0	1.7 (1.5)	2.2 (0.5)	2.1	2.0
18:1ω9	8.1 (1.5)	8.2 (2.1)	5.5	7.3
18:1ω7	6.1 (3.5)	10.8 (3.0)	12.1	8.2
18:1ω5	1.9 (1.2)	1.0 (0.4)	1.5	0.4
18:2ω6	0.6 (0.2)	1.3 (0.9)	0.9	0.6
18:3ω3	0.2 (0.1)	0.5 (0.6)	0.2	0.2
18:4ω3	0.7 (0.7)	0.8 (0.5)	0.8	1.4
20:1ω11	1.1 (0.8)	0.4 (0.2)	0.4	-
20:1ω9	8.6 (2.8)	2.3 (2.4)	0.9	0.4
20:1ω7	2.0 (1.0)	1.0 (0.3)	1.8	0.4
20:2α	1.0 (1.8)	0.2 (0.2)	0.3	-
20:2ω6	0.7 (1.6)	0.2 (0.1)	0.2	0.2
20:4ω6	0.9 (0.3)	2.5 (1.5)	3.2	0.7
20:4ω3	0.7 (0.9)	0.3 (0.1)	0.2	0.3
20:5ω3	12.1 (3.7)	17.2 (3.0)	18.6	23.7
22:1ω11(13)	5.6 (3.0)	1.5 (2.0)	0.4	0.4
22:1ω9	1.7 (0.9)	0.5 (0.5)	-	0.6
22:1ω7	0.8 (0.5)	0.5 (0.2)	0.8	0.6
22:5ω3	0.7 (0.5)	1.2 (0.6)	2.8	0.4
22:6ω3	10.6 (2.9)	10.6 (3.1)	10.3	8.0
24:1	0.5 (0.4)	0.5 (0.2)	0.2	0.5

*data not shown for fatty acids not detected or < 0.5% in all mysid taxa (14:1, *i*15:0, *ai*15:0, 15:1, *i*16:0, *ai*16:0, pristanic, 16:1ω11, 16:1ω9, phytanic, 17:1, 16:4ω3, 18:1ω11, 18:1ω6, 18:2ω4, 19:0, 18:3ω4, 18:4ω1, 20:0, 18:5ω3, 20:3ω6, 21:0, 22:0, 22:2(NMID), 23:0, 22:4ω6, 22:4ω3, 22:5ω6, and 24:0); dash = not detected or ≤ 0.1%.

Table 4.8. Mean relative fatty acid (FA) composition (% total FA) of chaetognath, copepod, polychaete, and holothurian taxa collected from the benthic boundary layer on the Beaufort Sea shelf. Errors are reported as standard deviation, except when n = 2, where it is reported as half the range.

Fatty acid* (%)	*Eukrohnia hamata* (n = 11)	*Parasagitta elegans* (n = 6)	*Calanus hyperboreus* (n = 2)	polychaete (n = 1)	holothurian (n = 2)
14:0	0.9 (0.7)	1.8 (0.6)	2.8 (0.02)	0.7	2.9 (0.1)
TMTD	0.5 (0.3)	0.7 (0.5)	-	-	-
*i*15:0	0.2 (0.1)	0.2 (0.03)	-	-	1.5 (0.5)
15:1	0.6 (0.3)	0.3 (0.1)	-	-	0.5 (0.2)
16:0	5.7 (2.0)	12.9 (0.7)	8.7 (3.4)	8.6	8.4 (0.6)
16:1ω7	24.4 (4.9)	14.5 (2.6)	21.0 (8.3)	4.1	23.9 (0.9)
16:1ω5	2.1 (2.0)	2.6 (0.5)	0.9 (0.9)	0.3	2.5 (0.6)
*i*17:0	0.4 (0.4)	0.5 (0.2)	0.2 (0.2)	0.5	1.5 (0.2)
*ai*17:0	0.3 (0.1)	0.2 (0.03)	0.2 (0.03)	0.2	0.5 (0.2)
16:2ω4	0.8 (0.3)	0.3 (0.1)	0.8 (0.5)	0.4	1.1 (0.3)
phytanic	-	0.3 (0.3)	0.2 (0.3)	1.0	0.4 (0.4)
17:0	0.4 (0.3)	0.3 (0.2)	0.6 (0.5)	-	0.7 (0.2)
17:1	-	-	0.8 (0.6)	0.7	1.8 (0.5)
16:4ω1	0.7 (0.4)	0.4 (0.2)	1.4 (1.2)	0.4	0.2 (0.04)
18:0	0.8 (0.3)	0.6 (0.3)	0.6 (0.4)	3.3	2.1 (0.01)
18:1ω9	3.8 (0.7)	6.6 (1.8)	3.4 (1.7)	4.8	3.5 (2.3)
18:1ω7	3.1 (1.4)	4.2 (0.7)	2.7 (0.6)	6.0	2.7 (0.1)
18:1ω5	2.2 (1.2)	3.9 (0.6)	2.3 (1.1)	1.1	0.2 (0.04)
18:2ω6	0.7 (0.3)	1.0 (0.4)	0.6 (0.2)	2.7	0.9 (0.3)
18:2ω4	-	0.3 (0.2)	0.5 (0.3)	0.2	0.2 (0.04)
18:3ω3	0.5 (0.4)	0.6 (0.1)	0.4 (0.1)	2.1	0.5 (0.3)
18:4ω3	1.0 (0.4)	1.2 (0.2)	1.3 (0.3)	2.9	1.2 (0.5)
20:1ω9	9.0 (1.7)	3.1 (1.2)	4.7 (1.0)	9.8	1.0 (0.3)
20:1ω7	1.4 (0.6)	0.7 (0.1)	1.6 (0.9)	1.7	0.7 (0.1)
20:2?	1.0 (0.5)	0.8 (0.2)	0.4 (0.4)	-	0.2 (0.2)
20:2ω6	0.2 (0.1)	-	-	0.7	0.3 (0.3)
20:4ω6	0.3 (0.05)	0.4 (0.3)	0.3 (0.02)	1.2	5.4 (1.5)
20:4ω3	0.9 (0.9)	0.7 (0.3)	0.6 (0.1)	0.3	0.3 (0.1)
20:5ω3	12.3 (1.6)	16.6 (2.8)	20.2 (1.8)	18.71	19.2 (1.3)
22:1ω11(13)	6.3 (2.7)	1.7 (1.0)	2.9 (0.01)	1.4	0.2 (0.2)
22:1ω9	1.7 (0.8)	0.5 (0.2)	1.0 (0.4)	-	1.0 (0.1)
22:1ω7	0.4 (0.2)	0.4 (0.1)	0.3 (0.03)	1.0	2.5 (0.8)
22:5ω6	-	-	-	0.5	0.8 (0.2)
22:5ω3	0.9 (0.3)	0.6 (0.1)	0.8 (0.1)	3.7	0.5 (0.1)
22:6ω3	12.2 (3.6)	15.9 (1.5)	13.6 (2.2)	15.75	3.8 (0.3)
24:1	1.1 (0.8)	2.2 (0.4)	1.6 (0.4)	-	1.0 (0.1)

*data not shown for fatty acids not detected or < 0.5% in all mysid taxa (14:1, 15:0, *ai*15:0, *i*16:0, *ai*16:0, pristanic, 16:1ω11, 16:1ω9, phytanic, 16:3ω4, 16:4ω3, 18:1ω11, 18:1ω6, 19:0, 18:3ω4, 18:4ω1, 20:0, 18:5ω3, 20:3ω6, 21:0, 22:0, 22:2(NMID), 21:5ω3, 23:0, 22:4ω6, 22:4ω3, and 24:0); dash = not detected or ≤ 0.1%.

Table 4.9. Accuracy of fatty acid profiles in predicting taxonomic group using discriminant analysis (DA; taxonomic group model). Values indicate the number of samples predicted (either correctly or incorrectly) for each observed row. '-' indicates no samples were identified as that taxonomic group. Numbers in bold are the number of samples identified correctly and non-bold as those identified incorrectly.

Observed by microscope \ Predicted by DA	Amphipoda	Mysidacea	Decapoda	Chaetognatha	Copepoda	Holothuroidea
Amphipoda	**32**	5	2	-	-	-
Mysidacea	4	**27**	1	-	-	-
Decapoda	1	-	**12**	-	-	-
Chaetognatha	-	-	-	**16**	1	-
Copepoda	-	-	-	2	-	-
Holothuroidea	-	-	1	-	-	**1**

Table 4.10. Accuracy of fatty acid profiles in predicting taxa* using discriminant analysis (DA; taxa model) for benthic boundary layer zooplankton. Values indicate the number of samples predicted for each observed row. '-' indicates no samples were identified as that taxon. Numbers in bold are the number of samples identified correctly and non-bold as those identified incorrectly.

Observed by microscope \ Predicted by DA	*A. malmgreni*	*A. phyllonyx*	*Anonyx* spp.	*E. loricata*	*Halirages* spp.	*Hippomedan* spp.	*Rhachotropis* spp.	*Syrrhoe* spp.	*Bythocarisi* spp.	*E. gaimardii*	*B. arctica*	*Erythrops* spp.	*M. litoralis*	*M. theeli*	*P. frigidum*	*C. hyperboreus*	*E. hamata*	*P. elegans*	holothurian
A. malmgreni	**5**	-	-	-	-	-	1	-	-	-	-	-	-	-	-	-	-	-	-
A. phyllonyx	-	**3**	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Anonyx spp.	-	-	**4**	-	-	-	2	-	-	-	-	-	-	-	-	-	-	-	-
E. loricata	-	-	1	**1**	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Halirages spp.	-	-	-	-	-	-	2	-	-	-	-	1	-	1	-	-	-	-	-
Hippomedan spp.	1	-	1	-	-	-	1	-	-	-	-	-	-	-	-	-	-	-	-
Rhachotropis spp.	-	-	1	-	-	-	**6**	-	-	-	-	-	-	-	-	-	-	-	-
Syrrhoe spp.	1	-	-	-	1	-	-	**1**	-	-	-	-	1	-	-	-	-	-	-
Bythocaris spp.	-	-	1	-	-	-	-	-	**2**	-	-	2	-	-	1	-	-	-	-
E. gaimardii	-	-	-	-	-	-	-	-	-	**6**	-	-	-	-		-	-	-	-
B. arctica	-	-	-	-	-	-	-	-	1	-	**1**	-	-	-	-	-	-	-	-
Erythrops spp.	-	-	-	-	-	-	-	-	-	-	-	**10**	4	2	-	-	-	-	-
M. litoralis	-	-	-	-	-	-	-	-	-	-	-	2	-	1	-	-	-	-	-
M. theeli	-	-	-	-	1	-	-	-	-	-	-	2	-	-	-	-	-	-	-
P. frigidum	-	-	-	-	-	-	-	-	-	-	-	-	-	1	**5**	-	-	-	-
C. hyperboreus	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1	1	-
E. hamata	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	**10**	1	-
P. elegans	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1	-	**5**	-
holothurian	-	-	-	-	-	-	-	-	-	1	-	-	-	-	-	-	-	-	**1**

*Full species names are: *Acanthostepheia malmgreni, Arrhis phyllonyx, Epimeria loricata, Eualus gaimardii, Boreomysis arctica, Mysis litoralis, Michthyops theeli, Pseudomma frigidum, Calanus hyperboreus, Eukrohnia hamata,* and *Parasagitta elegans.*

4.10. FIGURES

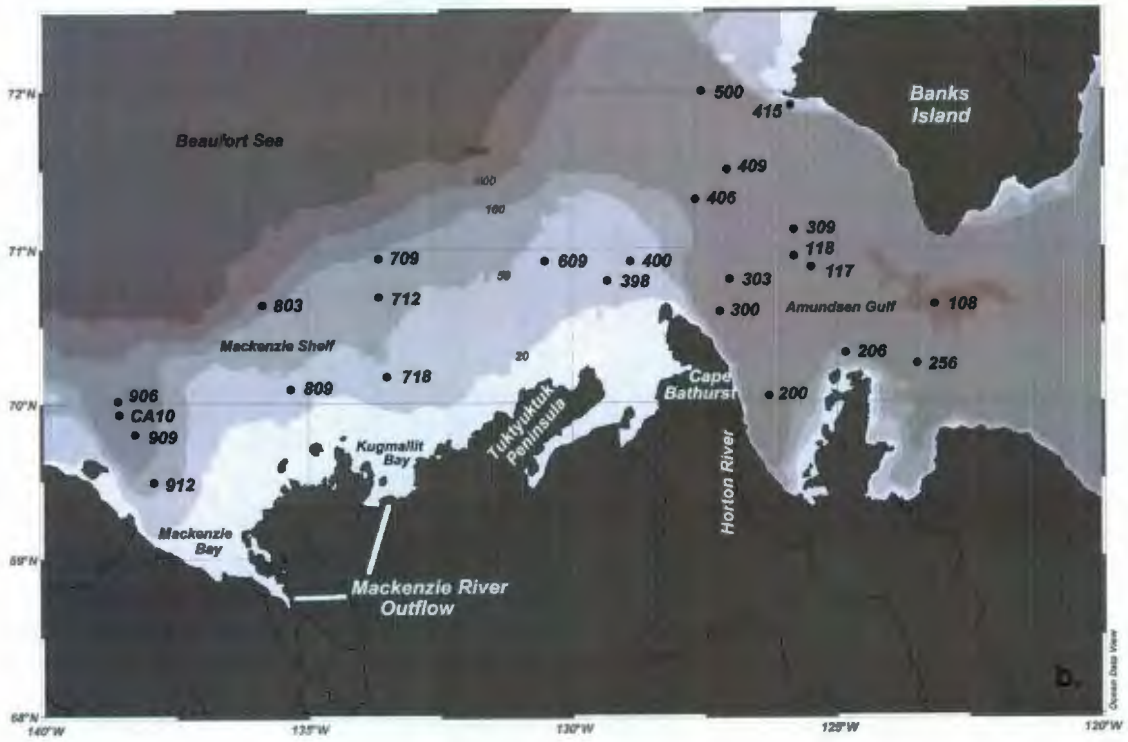


Figure 4.1. (a) Location of the Canadian Arctic Shelf Exchange Study (CASES) in the Arctic Ocean (box). (b) Station locations and labels for benthic boundary layer zooplankton collected during fall 2003 and summer 2004 from the Beaufort Sea Shelf. Depth contours are in meters.

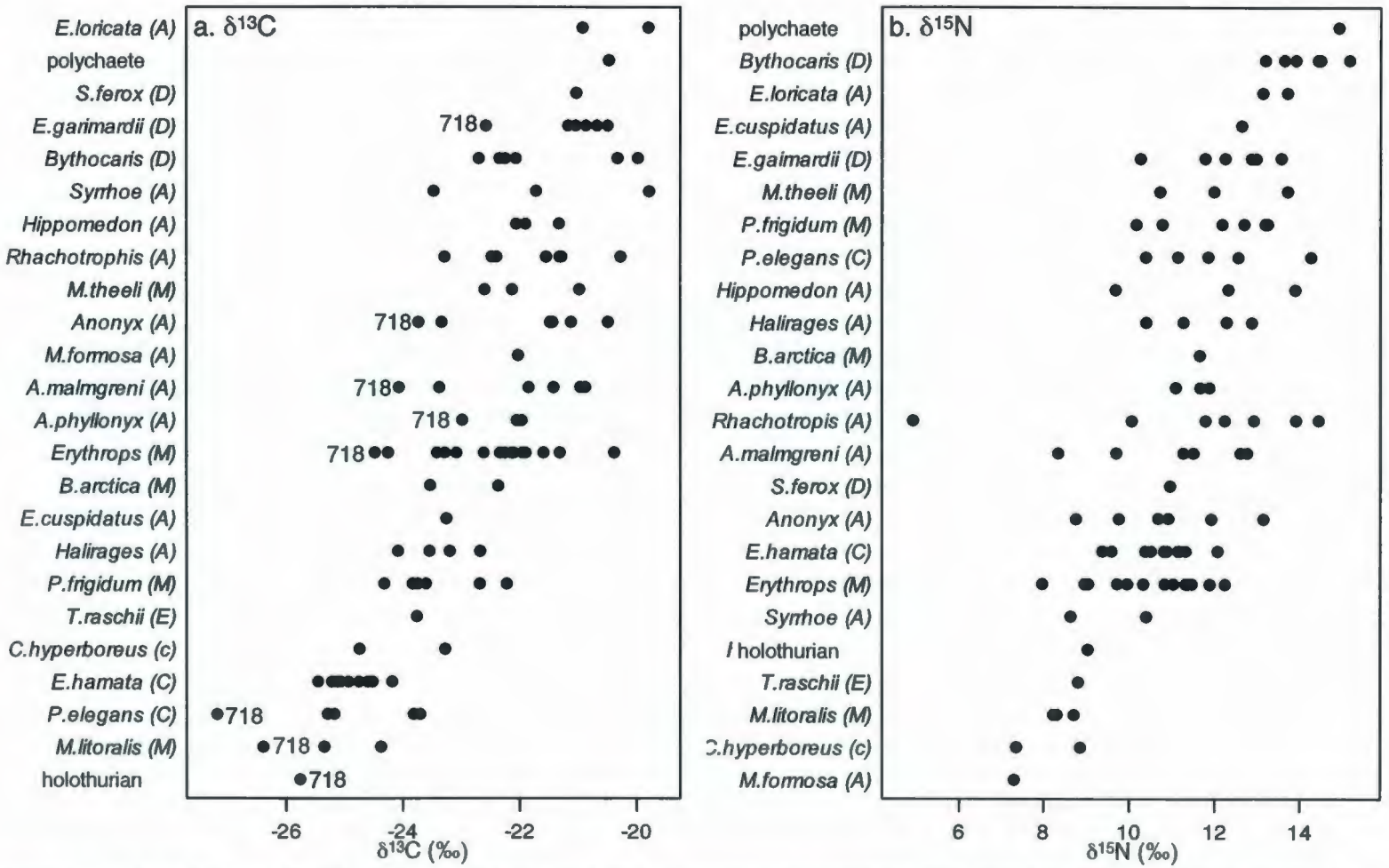


Figure 4.2. $\delta^{13}C$ (a) and $\delta^{15}N$ (b) values (‰) of benthic boundary layer zooplankton taxa collected from the Beaufort Sea shelf ordered by taxa mean from lowest (bottom) to highest (top). Lightest $\delta^{13}C$ sample for a taxa collected from st. 718 are labeled. Letters beside taxa denote taxonomic group, A = amphipod, C = chaetognath, c = copepod, D = decapod shrimp, E = euphausiid, and M = mysid. Full species names can be found in Table 4.3.

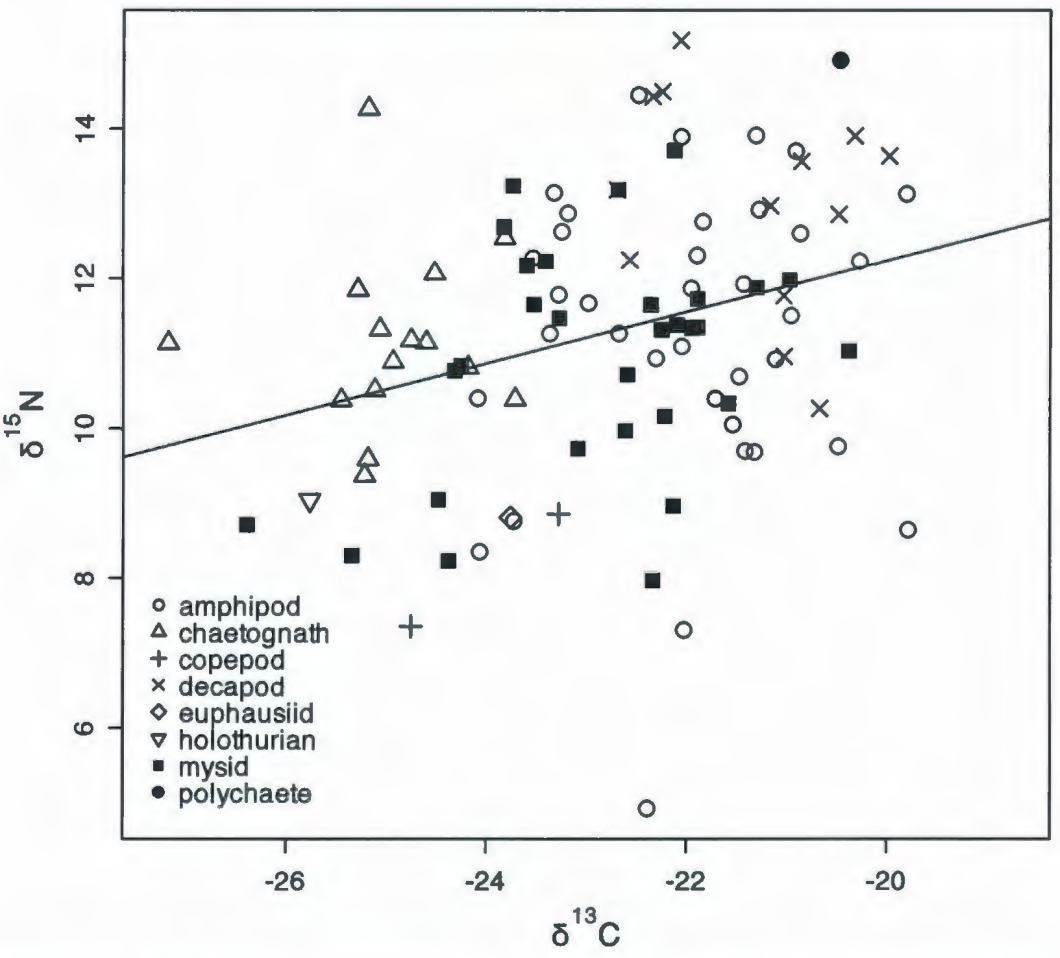


Figure 4.3. Relationship between $\delta^{13}C$ (‰) and $\delta^{15}N$ (‰) in benthic boundary layer zooplankton taxa from the Beaufort Sea shelf. ■ = mysid, ◇ = euphausiid, o = amphipod, ● = polychaete, △ = chaetognath, ▽ = holothurian, + = copepod, and x = decapod. Regression line is $y = 0.3x + 19.1$ ($p = 0.003$, $R^2 = 0.10$) and indicates a 1.3‰ increase in $\delta^{13}C$ per trophic level assuming a 3.8‰ increase in $\delta^{15}N$ per trophic level.

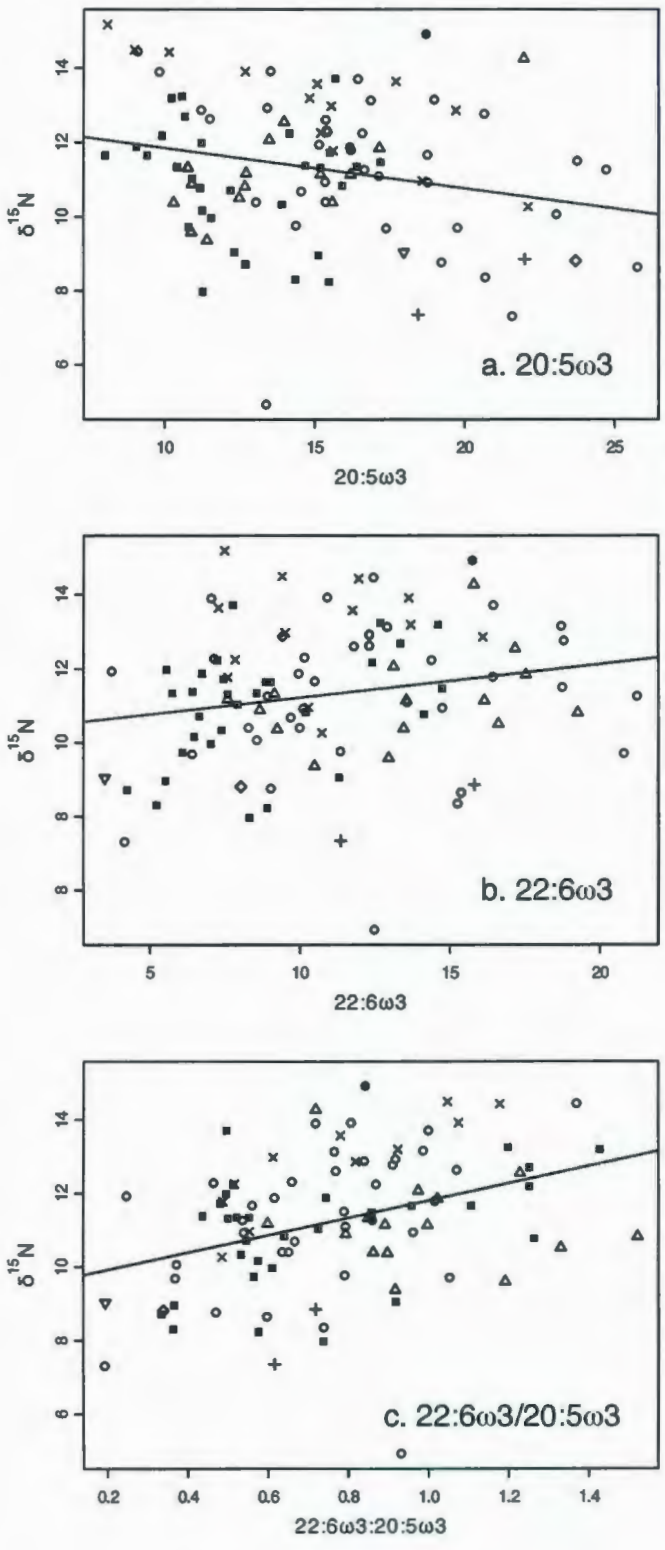


Figure 4.4. $\delta^{15}N$ (‰) and (a) 20:5ω3,(b) 22:6ω3 (% total fatty acids), and (c) 22:6ω3/20:5ω3 for benthic boundary layer zooplankton from the Beaufort Sea shelf. Trend line is added to aid in visualization of the significant correlation between ^{15}N and these fatty acid markers ($p \leq 0.05$). Symbols represent different taxonomic groups, ■ = mysid, ◇ = euphausiid, o = amphipod, ● = polychaete, △ = chaetognath, ▽ = holothurian, + = copepod, and x = decapod.

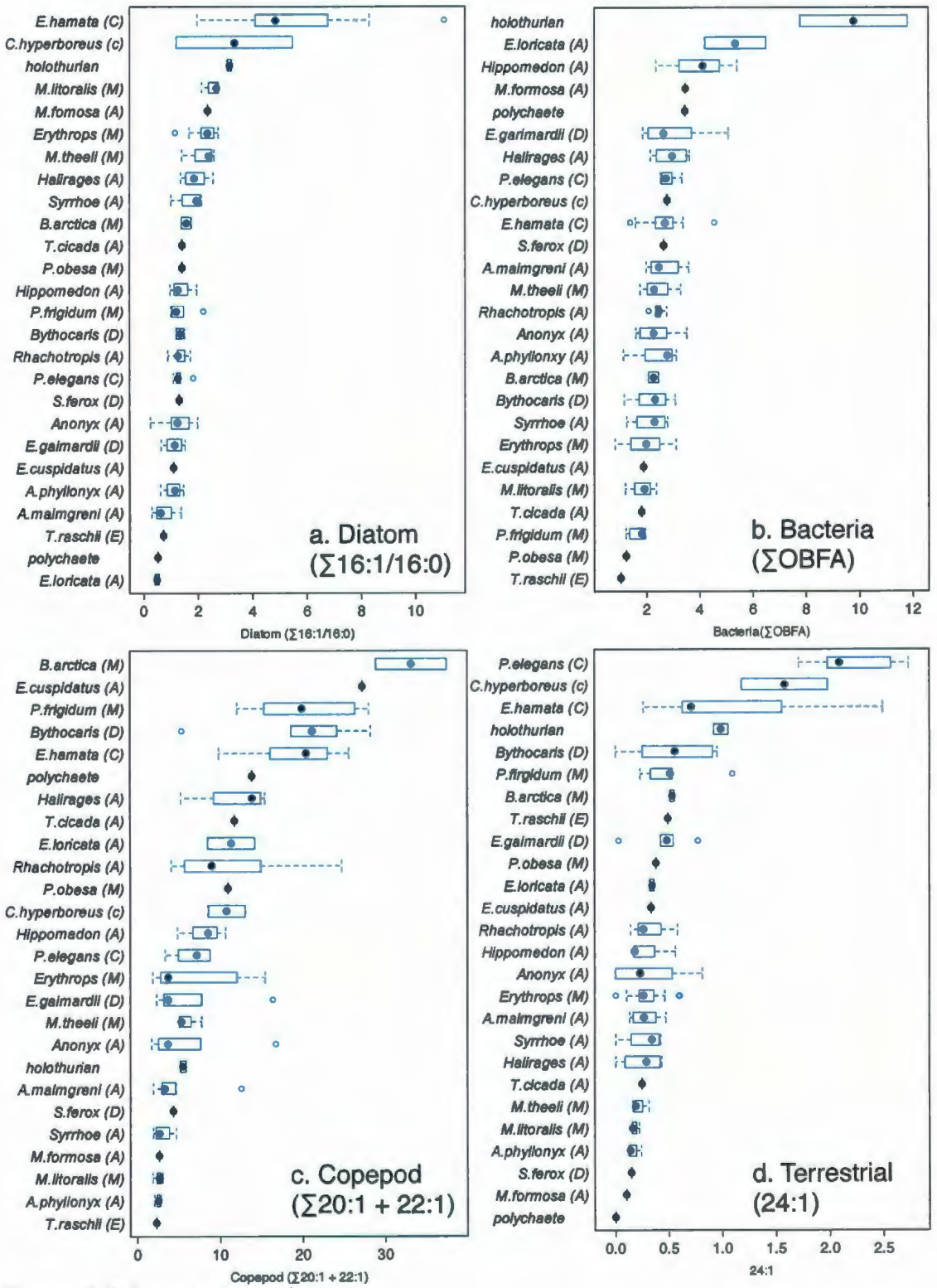


Figure 4.5. (see next page)

Figure 4.5. (a) Diatom fatty acid marker, (b) bacteria fatty acid marker, (c) copepod fatty acid marker, and (d) 24:1 values for benthic boundary layer zooplankton taxa from the Beaufort Sea shelf. Taxa are ordered by mean values from lowest (bottom) to highest (top). Black circle is the median and the left and right of the box show the 25th and 75th percentiles. The dotted vertical line is 1.5 times the interquartile range of data. Outliers are drawn as individual open circles. Letters beside taxa denote taxonomic group, A = amphipod, C = chaetognath, c = copepod, D = decapod shrimp, E = euphausiid, and M = mysid. Full names of taxa are given in Tables 4.4 - 4.7. Units are % of total fatty acids, except for the diatom fatty acid marker which is unitless. OBFA = odd-carbon and branched chain fatty acids.

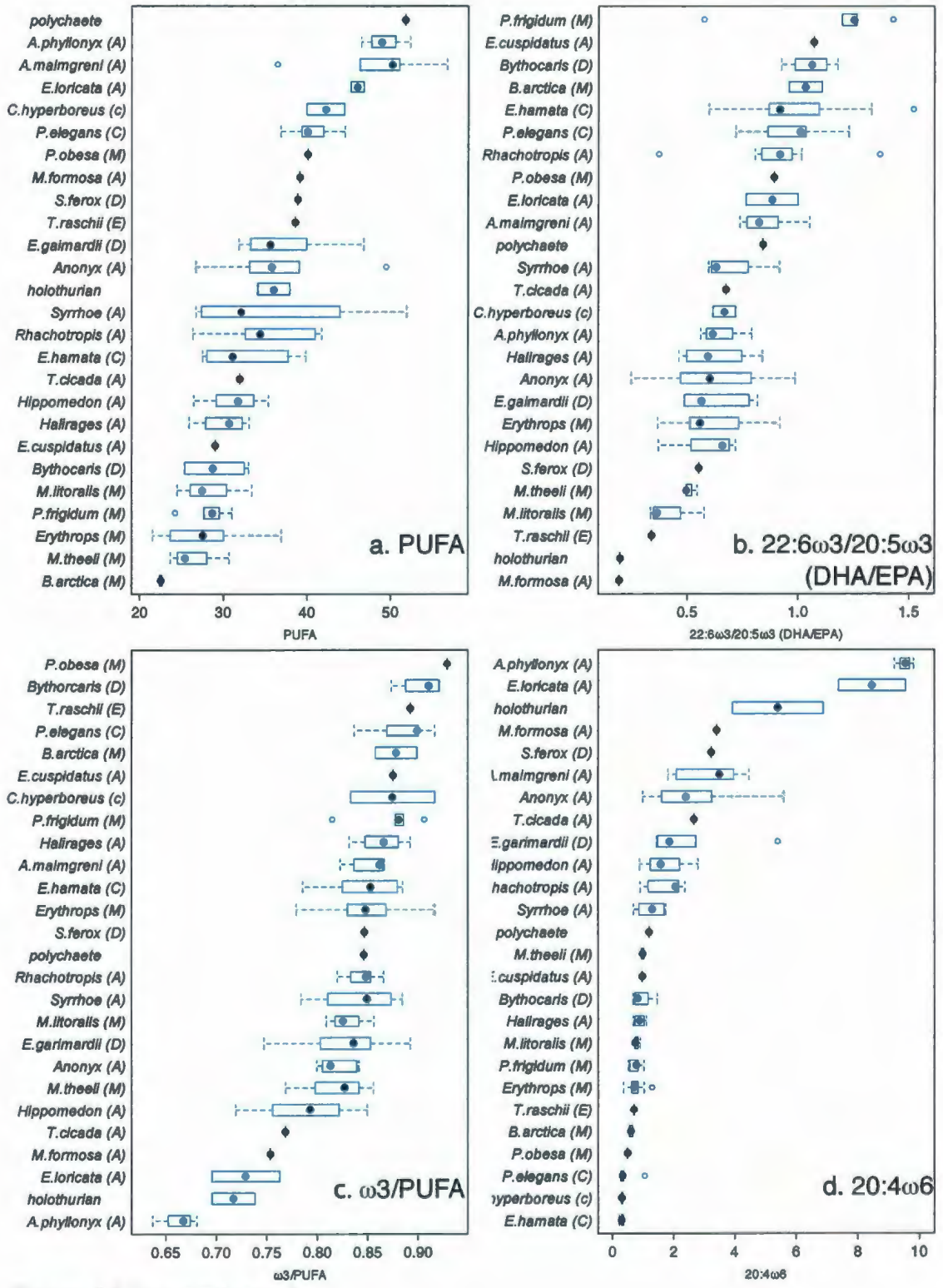


Figure 4.6 (see next page)

Figure 4.6. (a) Polyunsaturated fatty acids (PUFA), (b) 22:6ω3/20:5ω6 ratio, (c) ω3/PUFA ratio, and (d) 20:4ω6 levels for benthic boundary layer zooplankton taxa from the Beaufort Sea shelf. Taxa are ordered by mean from lowest (bottom) to highest (top). Black circle is the median and the left and right of the box show the 25th and 75th percentiles. The dotted vertical line is 1.5 times the interquartile range of data. Outliers are drawn as individual open circles. Letters beside taxa denote taxonomic group, A = amphipod, C = chaetognath, c = copepod, D = decapod shrimp, E = euphausiid, and M = mysid. Full names of taxa are given in Tables 4.4 - 4.7. PUFA and 20:4ω6 are % of total fatty acids and 22:6ω3/20:5ω6 and ω3/PUFA are unitless.

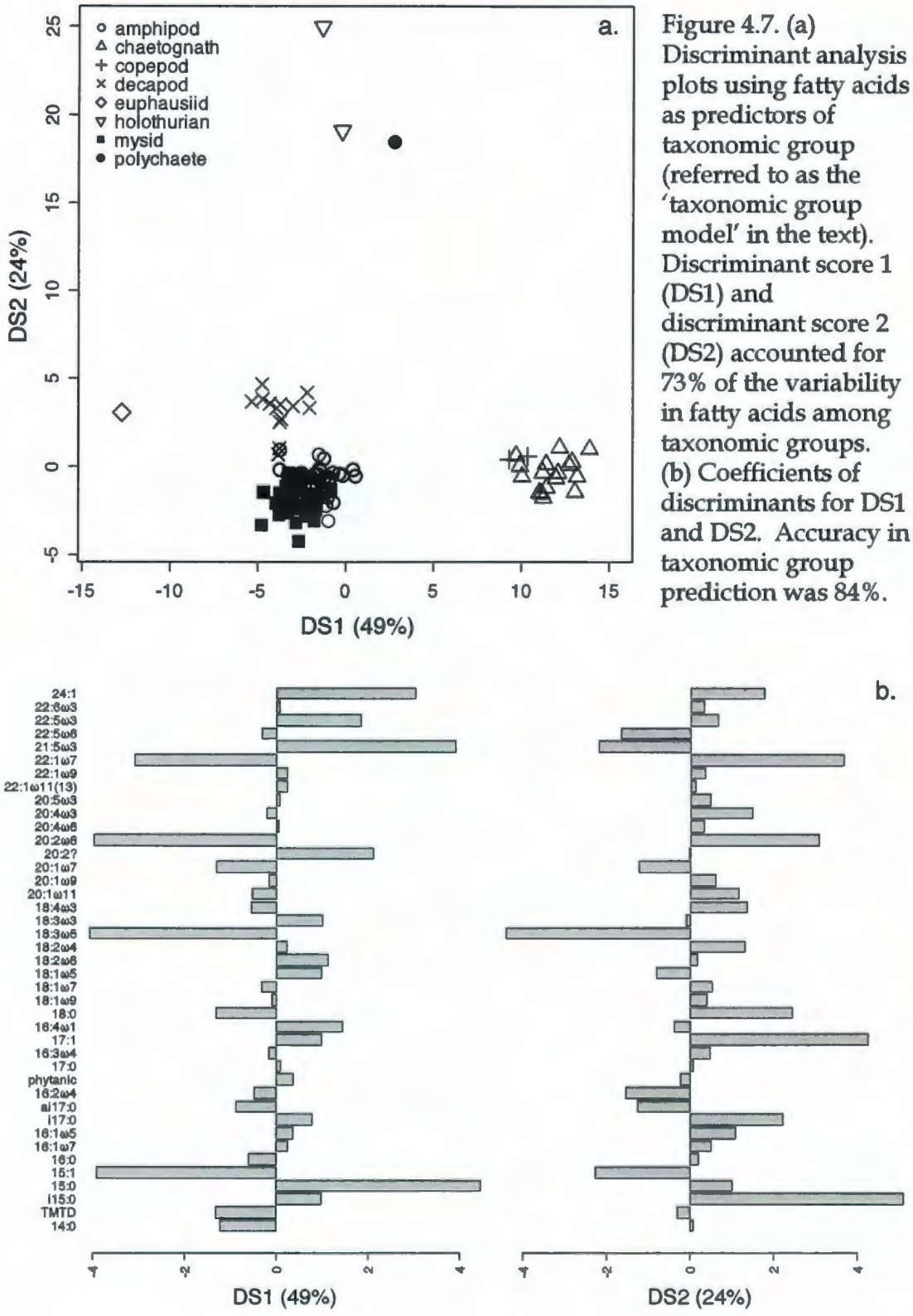


Figure 4.7. (a) Discriminant analysis plots using fatty acids as predictors of taxonomic group (referred to as the 'taxonomic group model' in the text). Discriminant score 1 (DS1) and discriminant score 2 (DS2) accounted for 73% of the variability in fatty acids among taxonomic groups. (b) Coefficients of discriminants for DS1 and DS2. Accuracy in taxonomic group prediction was 84%.

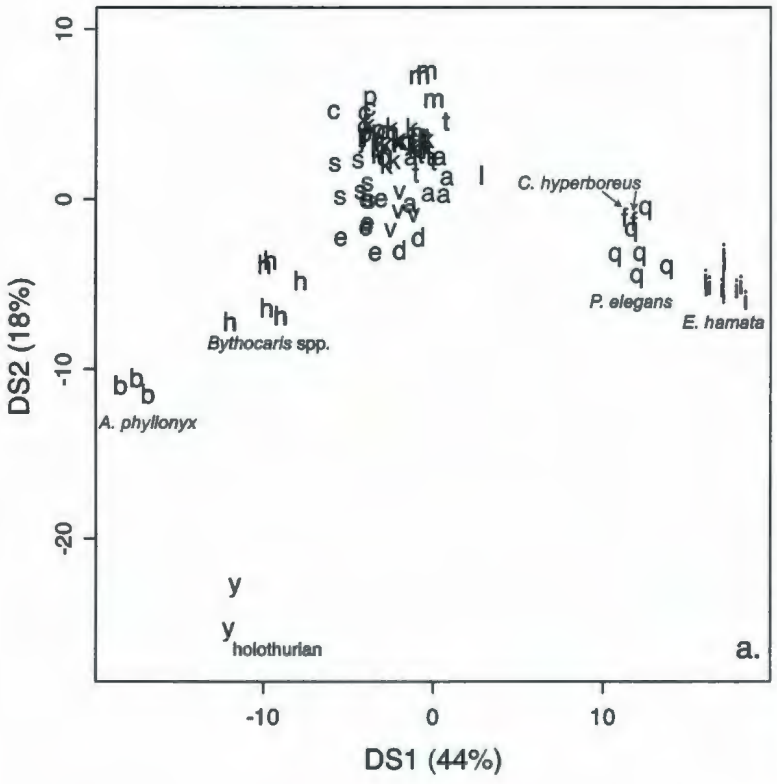
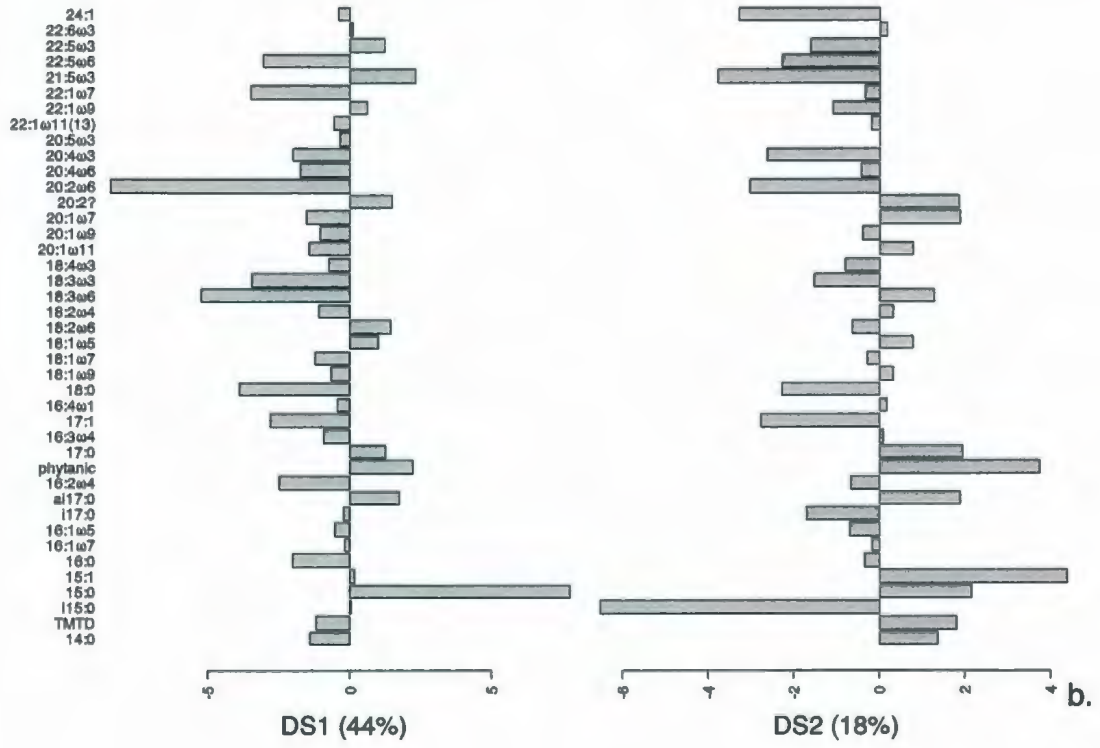


Figure 4.8. (a) Discriminant analysis plots using fatty acids as predictors of taxa (referred to as the 'taxa model' in the text). Discriminant score 1 (DS1) and discriminant score 2 (DS2) accounted for 62% of the variability in fatty acids among taxa. Accuracy in taxa prediction was 61%. b = *Arrhis phyllonyx*, f = *Calanus hyperboreus*, h = *Bythocaris* spp., i = *Eukrohnia hamata*, q = *Parasagitta elegans*, y = holothurian. Other letters represent remaining malacostra taxa that were not differentiated from each other on DS1 and DS2, (b) Coefficients of discriminants for DS1 and DS2.



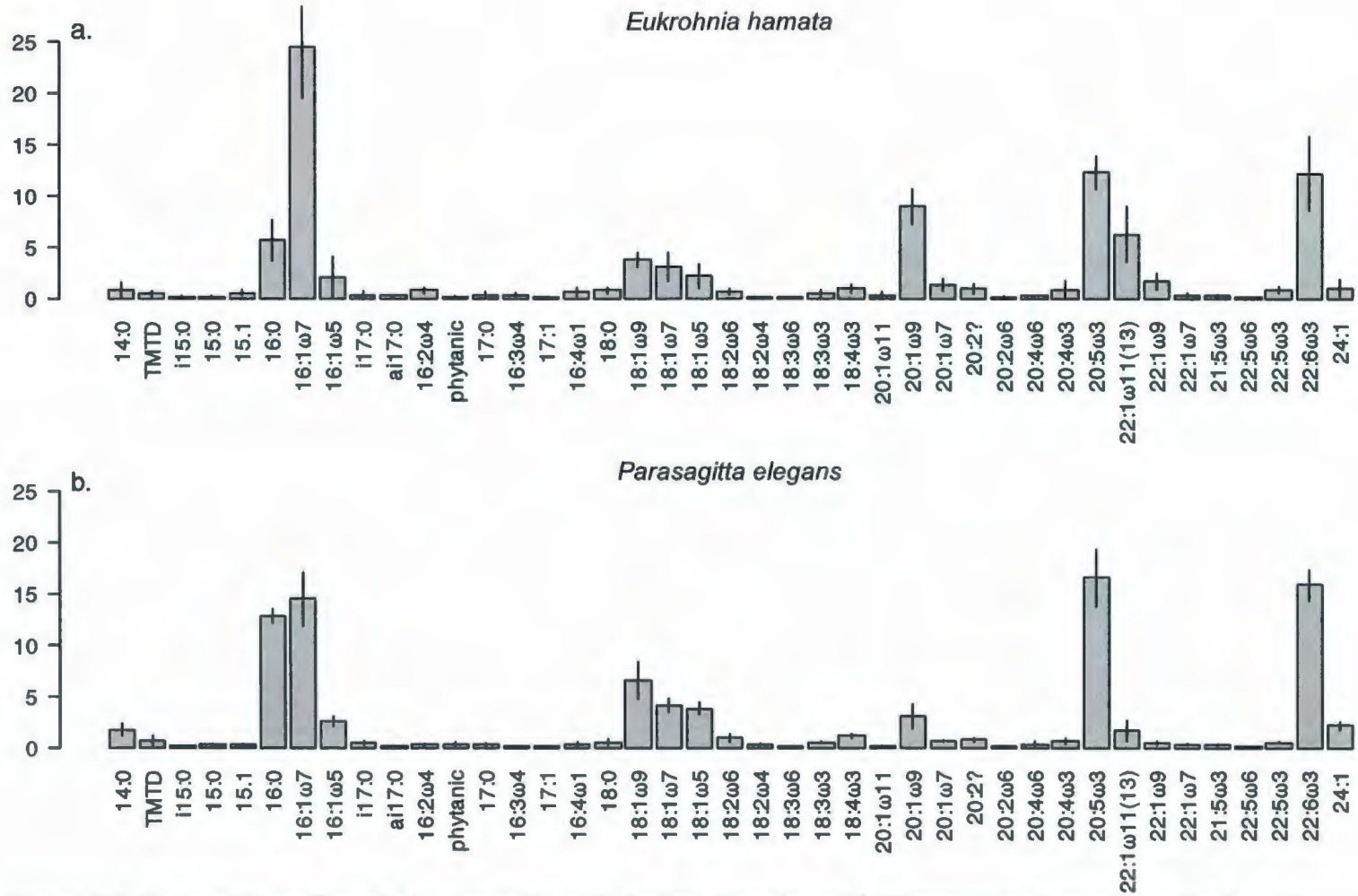


Figure 4.9. Fatty acid profiles of chaetognaths a) *Eukrohnia hamata* and b) *Parasagitta elegans* from the benthic boundary layer of the Beaufort Sea shelf. Mean (± sd) fatty acid proportions of total identified fatty acids are shown for each species.

CHAPTER 5

CONCLUSIONS

5.1. SUMMARY

This thesis presents the first comprehensive description of the chemical composition of benthic boundary layer (BBL) zooplankton and particulate organic matter (POM) in near-bottom waters on the Beaufort Sea shelf. A multiple biomarker and tracer approach including elemental ratios, natural stable isotope ratios, and lipids was employed to determine the sources of organic matter in near-bottom waters and to investigate the trophic ecology of BBL zooplankton. Determinations of the biochemical composition of both near-bottom POM and BBL zooplankton showed that the BBL is a very dynamic region supporting zooplankton with various feeding modes and life histories.

POM in near-bottom waters was heavily influenced by the Mackenzie River across the entire Beaufort Sea shelf, including the Amundsen Gulf. However, this dynamic environment with highly variable elemental ratios and poorly defined end-members made interpretation of biogeochemical data difficult. By including bacteria as an alternative end-member to terrestrial- and marine-signatures and by using several biomarkers, patterns in the distribution of organic matter in near-bottom waters were resolved. Low C:N ratios and high bacterial fatty acid markers indicated that bacteria are an important contributor to organic matter near the river. Fatty acid analyses allowed detection of a phytoplankton sinking event in the Amundsen Gulf in which polyunsaturated fatty acid (PUFA) levels in near-bottom waters significantly increased during

summer. However, there was no observed temporal change in the C:N ratio, chlorophyll *a*, or $\delta^{13}C$, emphasizing the need to use several biomarkers in ecosystem studies of dynamic environments such as near-bottom waters or river-influenced shelves.

The BBL zooplankton considered in this study occupy 3 trophic levels, and generally have high levels of either triacyglycerol (TG) or wax esters (WE), variable C:N:P ratios, and diverse fatty acid profiles. High levels of storage lipids and PUFA indicate that these BBL zooplankton depend on seasonal pulses of phytoplankton, suggesting that they may have important roles in the transformation of organic matter in near-bottom waters. The positive correlation of C and C:N with storage lipids and the high levels of C and C:N compared with similar taxa in other study areas also emphasize the enhanced energy stores of these taxa on the Beaufort Sea shelf. Fatty acid data not only provided information on diet but also reflected phylogeny, e.g. malacostracan crustaceans possessed similar fatty acid profiles. The amphipod *Arrhis phyllonyx,* however, had higher levels of ω6 PUFA, especially 20:4ω6, than all other taxa. The holothurian was rich in odd numbered and branched chain fatty acids, indicative of consumption of bacteria. Fatty acids of phytoplankton origin were important in defining the trophic position of *Calanus hyperboreus* and the chaetognaths *Eukrohnia hamata* and *Parasagitta elegans,* which suggests that the conventional phytoplankton-copepod-chaetognath food web also exists in the BBL. There were interesting differences between the two chaetognath taxa, including high levels of WE in *E. hamata,* negligible levels of both WE and TG in *P. elegans,* high levels of the 16:1ω7/16:0 ratio and of 22:1 and 20:1 in *E. hamata* relative to *P. elegans,* and high levels of 16:0 and the essential fatty acids 20:5ω3 and 22:6ω3 in *P. elegans.* The differences in fatty acid profiles between these two chaetognaths

reflect the differences in lipid class composition, highlighting the need to consider lipid classes when interpreting fatty acid profiles.

The diversity of trophic levels, fatty acid profiles, and energy storage suggests that BBL zooplankton on the Beaufort Sea shelf as a community are able to collectively exploit available food resources, and therefore probably have an important, but often overlooked, role in organic matter cycling. However, biomass and production estimates for BBL zooplankton are necessary to quantify the importance of this community in the organic matter cycling in near-bottom waters.

5.2. FUTURE RELATIONSHIPS BETWEEN CLIMATE CHANGE, ARCTIC MARINE FOOD WEBS, AND THE BENTHIC BOUNDARY LAYER

The relationship between climate and marine food webs is complex, involving numerous interactions and feedbacks, many of which are poorly understood. In the polar oceans, this relationship is highly dependent on how climate is manifested in sea ice dynamics (Anisimov and Fitzharris 2001). Climate projections indicate that sea ice dynamics will be profoundly different in the next few decades (Meehl et al. 2007), undoubtedly influencing the structure and function of marine food webs (Bluhm and Gradinger 2008). To understand organic carbon cycling and Arctic marine food webs in relation to long-term global warming, defined relationships between biological variables, sea ice, and climate in the context of natural climate variability are crucial. The shortage of long term climate and sea ice dynamic records, the variability of climate forcing on sea ice and hydrology, the incomplete historical baseline for biological systems, and the coarse spatial and temporal resolution of biological studies in the polar seas combine to limit our ability to detect past and future trends in

biological processes with respect to climate change and sea ice dynamics. This may be especially true in the Arctic Ocean, where biological processes have presumably already responded to dramatic changes in sea ice during the last few decades (Melkinov et al. 2002). Therefore, data from recent studies, including this one, may not accurately represent the biology and biogeochemistry of a pre-perturbed environment but may reflect a dynamic biological response to observed environmental changes from anthropogenic forcing.

Two facets of climate change in the Arctic important for the biogeochemistry in the BBL on the Beaufort Sea shelf include increases in freshwater input from river runoff and changes in primary production, and thus benthic-pelagic coupling, due to reduced ice coverage. Increases in freshwater input from rivers onto Arctic shelves will affect biological communities and organic carbon cycling by having an impact on primary production. Increased nutrient input from rivers may enhance primary production, while increased sediment load may decrease light levels, thereby limiting primary production (Sakshaug 2004). Furthermore, expansion of permanently and seasonally ice-free waters will increase photosynthetically active radiation and promote greater nutrient input from wind-induced mixing, resulting in increased primary production (Arrigo and Thomas 2004). Likewise, increases in the extent of first-year ice with its associated marginal ice zones are also predicted to have a positive effect on primary production. However, phytoplankton production may be more prolonged throughout the Arctic summer, in contrast to the intense, seasonal pulses of primary production that currently characterize many Arctic shelves (Sakshaug 2004). The results of this thesis show that the diets of BBL zooplankton on the Beaufort Sea shelf are generally tightly linked with pelagic production. Hence, changes in the timing and magnitude of primary production

on Arctic shelves will likely have important consequences for benthic-pelagic coupling and therefore, for BBL zooplankton.

There are two possibilities for the impact of the projected increases in pelagic production on benthic-pelagic coupling. First, an increase in the extent of the marginal ice zone and the high phytoplankton production often associated with it may increase carbon flux to the benthos (Grebmeier and Barry 2007), with consequences for the biogeochemistry of near-bottom waters and the production and abundance of BBL zooplankton. Increases in pelagic production may also benefit those BBL zooplankton species that actively migrate to surface waters to feed. Alternatively, less variable and less intense phytoplankton blooms resulting from increased pelagic zooplankton grazing and increased bacteria metabolism may limit export (Bluhm and Gradinger 2008), thus weakening benthic-pelagic coupling and inhibiting production of BBL zooplankton. Although the importance of ice algae to the diets of BBL zooplankton were not determined in this study, reduced ice cover could have a negative effect on this community if it depends on a seasonal flux of ice algae to the benthos (Renaud et al. 2007). Less intense and more prolonged phytoplankton production may also reduce the necessity for large lipid stores that are common in many Arctic zooplankton (Kattener et al. 2007), therefore lowering the lipid-driven flux of energy through trophic levels with potentially negative impacts on those populations of sea birds and marine mammals that depend upon a lipid-rich diet. The high levels of storage lipids, including wax esters, in BBL zooplankton presented in this thesis also indicate that changes in magnitude and timing of primary production may affect the life cycles and energy stores of this community.

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