Mercury and Stable Isotopes in the Pelagic Food Web of Hudson Bay.

By Monica Anne Pazerniuk

Submitted to:
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MASTER OF SCIENCE

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A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University of

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CHAPTER 1

Introduction

Climate change has been highlighted by the media, politicians, and economists around the world as the single most important issue to face the world in this century. The poles of our Earth are extremely sensitive to small changes in temperature, and from a contaminant prospective this means the difference between volatile or non-volatile properties as well as bioconcentration or biodilution. These changes may impact the physical and biological processes in the Arctic including humans (Macdonald et al. 2005). Hudson Bay is a sub-arctic zone which exists along transitional permafrost melt and tree line zones. Hudson Bay is a large inland sea that is shallow enough to behave similarly to continental shelves (Martini 1986). There is significant freshwater outflow into Hudson Bay, as its watershed extends to Minnesota, the Northwest Territories, Canadian Rockies and Quebec (Bajkov 1975). Contaminant loadings to the watershed will be transported to the aquatic ecosystem of Hudson Bay, including algae, zooplankton, fish, and marine mammals.

The following thesis was designed as two manuscripts sandwiched between an introduction and conclusion, otherwise known as a "sandwich thesis". The overall theme of this thesis was to investigate the biomagnification of mercury and methylmercury in the pelagic food web of Hudson Bay. There is an approximately one-million-times increase in Hg levels from water to top predators such as piscivorous fish (Watras and Bloom 1992). Biomagnification of methylmercury (MeHg) is of greater importance due to its toxicity at high levels. The lipophilic nature of MeHg may contribute to its

biomagnification, however studies show that $HgCl_2$ and CH_3HgCl have similar membrane transport tendencies and hydrophobic characteristics (Gutknect 1981, Mason et al. 1995). Inorganic Hg behaves in a similar manner to other cations; it accumulates in the cell membrane *via* passive diffusion compared to MeHg which accumulates in the cytoplasm (Mason et al. 1995). There is an effect on the accumulation of Hg species because zooplankton more effectively digest cytoplasm in comparison to cell membrane material. Mason (1995) used a model to describe how Hg is accumulated in zooplankton called the "eat-the-grapes-and-spit-the-skins" model. The bioaccumulation of different Hg species, namely the inorganic and organic complexes, is thus governed by the regions in which these two chemical forms of mercury become sequestered in cells and by the greater trophic level transfer of MeHg (Mason et al. 1995). It is also known that transfer of Hg between water and phytoplankton has the highest enrichment factors compared to other trophic levels, therefore contaminant levels in fish are strongly dependent upon the levels in the water and in phytoplankton at the base of the food web.

Part I of this thesis explores the different zooplankton genera in Hudson Bay, and the processes affecting their mercury contaminant levels and stable isotope signatures on a seasonal as well as a regional basis. We investigate different relationships that zooplankton have with each other with respect to contaminant levels. Stable isotope analysis ($\delta^{15}N$ and $\delta^{13}C$) is used to identify trophic levels in zooplankton as well as potential carbon sources. We expand these investigations to higher trophic level pelagic fish and marine mammals in Part II. We focus on samples from Southeast Hudson Bay, based on our diverse collections in this region, as well as our results from Part I. Simply

put, Part I focuses on the lower food web while Part II incorporates some of the top level predators in Hudson Bay. Both manuscripts utilized similar collection and analysis methods.

Our findings imply that the food web in Hudson Bay has regional variation. We calculated highest biomagnification factors for zooplankton in Hudson Strait compared to Hudson Bay. When the food web was extended in Part II to incorporate higher trophic level fish and marine mammals, we observed a trend of higher contaminant levels in western Hudson Bay fish compared to eastern Hudson Bay fish. We suspect that the higher trophic positioning of western Hudson Bay fish was related to this contaminant enrichment. Further implications from stomach contents analysis allowed us to design a simple food web for Hudson Bay in both Eastern and Western coastal regions. This is some of the first food web work developed for Hudson Bay, and may be used as reference material for future biological, environmental and chemical investigations of one of Canada's largest watersheds.

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CHAPTER 2

Part I:

Total, methyl mercury and stable isotope levels in Hudson Bay zooplankton; Spatial trends and processes.

By Monica Anne Pazerniuk

Abstract

The objective of this project was to investigate mercury and stable isotope relationships in common zooplankton from Hudson Bay. Zooplankton collected from stations along the MERICA 2003 and 2004 summer cruises as well as ArcticNet 2005 fall cruise transects were analyzed for HgT, MeHg, and stable isotopes in order to interpret any spatial and seasonal trends. Levels of HgT as well as stable isotopes had little seasonal variability, however some spatial trends with respect to stable isotopes were observed. Zooplankton collected in regions with high freshwater influence had isotopically depleted ^{13}C levels compared to regions with more marine influence.

Concentrations of HgT in *Cliona* sp. and *Limacina* sp. were 2-3 times higher compared to *Euchaeta sp.*, *Hyperia* sp., and *Themisto* sp., which were approximately double the levels seen in *Sagitta* sp., *Thysanoessa sp.*, *Calanus* sp. and Cnidarian. Levels of MeHg were lowest in *Calanus* sp., *Thysanoessa* sp., and *Sagitta* sp. compared to *Themisto* sp. and *Euchaeta* sp. High % MeHg was seen in carnivorous zooplankton such as *Themisto* sp. and *Sagitta* sp. The % MeHg in *Cliona* sp. doubled that of *Limacina* sp., which suggested that biomagnification of MeHg was occurring among zooplankton with monophagous diets.

We found that *Calanus* sp. and T*hysanoessa* sp. were ideal prey genera for *Themisto* sp. and *Euchaeta* sp. due to a significant correlation among these zooplankton in MeHg versus $\delta^{15}N$ ($r^2 > 0.90$, $P < 0.05$). This was confirmed by biomagnification factors (BMF's) for MeHg greater than 1 observed in *Euchaeta sp.* and *Themisto* sp. *Limacina*

sp. also displayed BMFs greater than one, however not enough samples were analyzed in order to make any firm conclusions as to the nature of this zooplankton. We suspect that biomagnification of MeHg in other carnivorous zooplanktons such as *Sagitta* sp. was inhibited due to biological factors. There was also a lot of regional variability, including highest BMFs for MeHg consistently in the FC and South Hudson Strait regions for different zooplankton.

Dedication

To all of the communities surrounding Hudson Bay, who lend helping hands and welcome scientists into their communities with warm smiles and friendly handshakes, and to Graham for his endless support and motivation.

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Introduction

High Mercury (Hg) levels are reported in marine mammals, as well as some pelagic fishes and zooplankton across the Canadian Arctic Ocean (Stern and MacDonald 2005). In some regions there has been a dramatic increase in Hg since the late 1980s and early 1990s (Stern and Lockhart 2006, Lockhart et al. 2005). Hg levels in beluga, narwhal and ringed seal range from 4 times (muscle and muktuk) to 2-3 orders of magnitude higher (liver) than is considered to be the safe limit for consumption (the Health Canada consumption guideline for methylmercury in commercial fish is 0.50 µg/g wet wt; CFIA, 2001) and may pose reproductive, immunosuppressive and neurobehavioral risks to marine mammals (AMAP 2005, Givelet et al., 2005). Recently, Hylander and Goodsite (2006) suggest that the Arctic is experiencing one of the most severe, large-scale Hg problems under our watch. This raises serious concerns over the health of the fragile Arctic ecosystem and of the local community people who consume marine mammal tissues as part of their traditional diets.

The cause of high Hg burdens and large variations in arctic marine mammals remains a mystery. Global anthropogenic emissions have shown decline in the past two decades (Pacyna and Pacyna 2002) and median atmospheric Hg concentrations in the Arctic have been constant for the past 10 years (Steffen et al. 2005). Nevertheless, atmospheric Hg deposition in the Arctic is receiving a lot of scientific attention, due mainly to the discovery of atmospheric mercury depletion events (MDEs) in the mid-1990s (Schroeder et al. 1998). After polar sunrise, the concentration of atmospheric elemental mercury (Hg^0) drops significantly with a corresponding increase in Hg concentrations in surface

snow, showing a potential mechanism of altering surface flux of Hg in the Arctic. It is apparent that photochemically driven MDEs remove Hg^0 from the lower km of the atmosphere after polar sunrise and deposit it to surfaces in a reactive, biologically available form (Lindberg et al. 2002, Steffen et al. 2005). Lu estimates that about 17 tonnes of Hg is deposited into snowpack of the High Arctic Ocean annually, 90% of which occurs during MDEs (Lu et al. 2001). Further studies suggest that much of the Hg deposited in snow during MDEs is photo-reduced to Hg^0, re-enters the atmosphere, and does not actually impinge on Arctic aquatic systems (Lalonde et al. 2002, Ferrari et al. 2005, Lahoutifard et al. 2005, St. Louis et al. 2005, Steffen et al. 2005). Therefore, MDEs, global emissions and atmospheric trends do not appear to provide an explanation for observed Hg increases and variation in Arctic aquatic ecosystems. We hypothesize that other processes play a more important role in Hg distribution and trends in Arctic ecosystems. Examples of such processes include riverine Hg discharge, direct freshwater Hg input from melted permafrost and coastal erosion, oceanic Hg transport, sea ice loss, and changes in marine mammal feeding habitats, food web structures and zooplankton biology, each of which is sensitive to climate variation and none of which has been studied in any detail.

Leitch et al. (2006) report that the Mackenzie River discharges approximately 2.2 ± 0.9 tonnes/yr of total Hg into the Beaufort Sea, a portion of which (7-22 kg) is in the form of MeHg. When compared with limited literature on other potential Hg sources, the Mackenzie River seems to be the largest source of Hg to the Beaufort Shelf and, potentially, the largest source of Hg to the upper ocean of the Beaufort Sea. Melting

permafrost/coastal erosion contributes approximately 609 kg of Hg annually to the Beaufort Sea (Leitch et. al. 2006).

It was previously thought that elements without biological function such as mercury would not accumulate in organisms simply because there was no use for them. We now acknowledge that this is not the case. Experiments have shown that photosynthesis decreases in phytoplankton when Hg levels exceed 1 μg/kg in cells, and MeHg causes a dramatic decrease in photosynthesis at even lower detection levels of 0.05 μg/kg in seawater (Knauer and Martin 1972). When levels of $HgCl_2$ become elevated, biological mechanisms activate enzymes in zooplankton to excrete $HgCl_2$ and avoid accumulation. No mechanism has evolved in cells to activate attack enzymes when MeHg levels become elevated, therefore MeHg is toxic at relatively low levels. (Knauer and Martin 1972).

Hudson Bay is one of the largest inland shelf seas with a vast coastal freshwater region. It drains soils east of Great Slave Lake (NWT, Nunavut), parts of Alberta, nearly all of Saskatchewan, all of Manitoba, parts of North Dakota, Minnesota, Ontario, and most of Quebec (Bajkov 1975). The mixing of waters from the Atlantic and Arctic Oceans coupled with the freshwater drainage basins and estuaries causes diverse organisms to thrive, including zooplankton found in areas of the high Arctic, as well as sub-Arctic zooplankton that are capable of adapting to the freshwater influence in Hudson Bay. Up-welling of marine waters and further displacement of sediments due to tides and currents

result in an increase of nutrient loads to the estuaries contributing freshwater to Hudson Bay.

Hudson Bay behaves more like a continental shelf than an ocean or sea due to its shallow nature. River tributaries are increasingly becoming altered due to hydro-electric development, permafrost melt, and climate warming trends. The annual water discharge rate from the Hudson Bay Basin is 22.6 x 10^3 m^3/s compared to half this amount for the Mackenzie and St. Lawrence Basins (Prinsenberg 1980). Dammed rivers are causing freshwater plumes to be larger in winter, which leads to decreasing vertical nutrient fluxes, increasing ice cover thickness, and increasing ice cover duration (Prinsenberg 1994). Water and ice properties in Hudson Bay are also influenced by atmospheric changes such as wind speed and direction as well as by climate change. Surface water currents (Figure 1 arrows) flow into and out of Hudson Bay by a cyclonic (anti-clockwise) pattern due to Earth's rotation and the position of Hudson Bay in the Northern Hemisphere (Martini 1986). The mean surface current velocity is 0.04 m/s, therefore surface water may take 2 years to circulate around the Bay, and up to 6 years due to wind re-circulation to finally exit Hudson Strait (Prinsenberg 1994). These water circulation patterns in Hudson Bay coincide with average zooplankton life cycles of 2-3 years.

In this study, total mercury (HgT), methylmercury (MeHg), stable isotopes of nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) are quantified in zooplankton. Water samples are collected for analysis of $\delta^{18}O$, dissolved organic carbon (DOC), salinity, HgT and MeHg (surface, 10m) during the 2003 and 2004 MERICA cruises and during the ArcticNet Leg 2 Hudson

Bay cruise aboard the *CCGS Amundsen* (Sept 14 – Oct 27, 2005). Sample stations shown in Figure 1 are divided up into 8 regions based on the physical oceanographic characteristics described in the Methods section below. The major objective of this study is to assess mercury and isotopic relationships, biomagnification in different regions of Hudson Bay, and to further investigate the physical and biological processes giving rise to any regional differences among the zooplankton genera. These results will also help to understand and model the potential effects of climate change on these processes. A second objective, although preliminary due to collection of only a limited number of collection years and seasons (summer zooplankton collected in 2003 and 2004, followed by fall collections in 2005), is to explore seasonal and annual trends.

Figure 1. Ship Tracks for MERICA 2003 and 2004, ArcticNet 2005 and corresponding regions to partition sample stations in Hudson Bay:

North Hudson Strait (NHS), Foxe Channel (FC), Roes Welcome Sound (RWS), West Hudson Bay (WHB), Central Hudson Bay (CHB), South East Hudson Bay (SEHB), East Hudson Bay (EHB), and South Hudson Strait (SHS). Surface anti-cyclonic currents are shown (arrows). Point of reference: station 25 latitude: 94°4' W, longitude: 58°45' N.

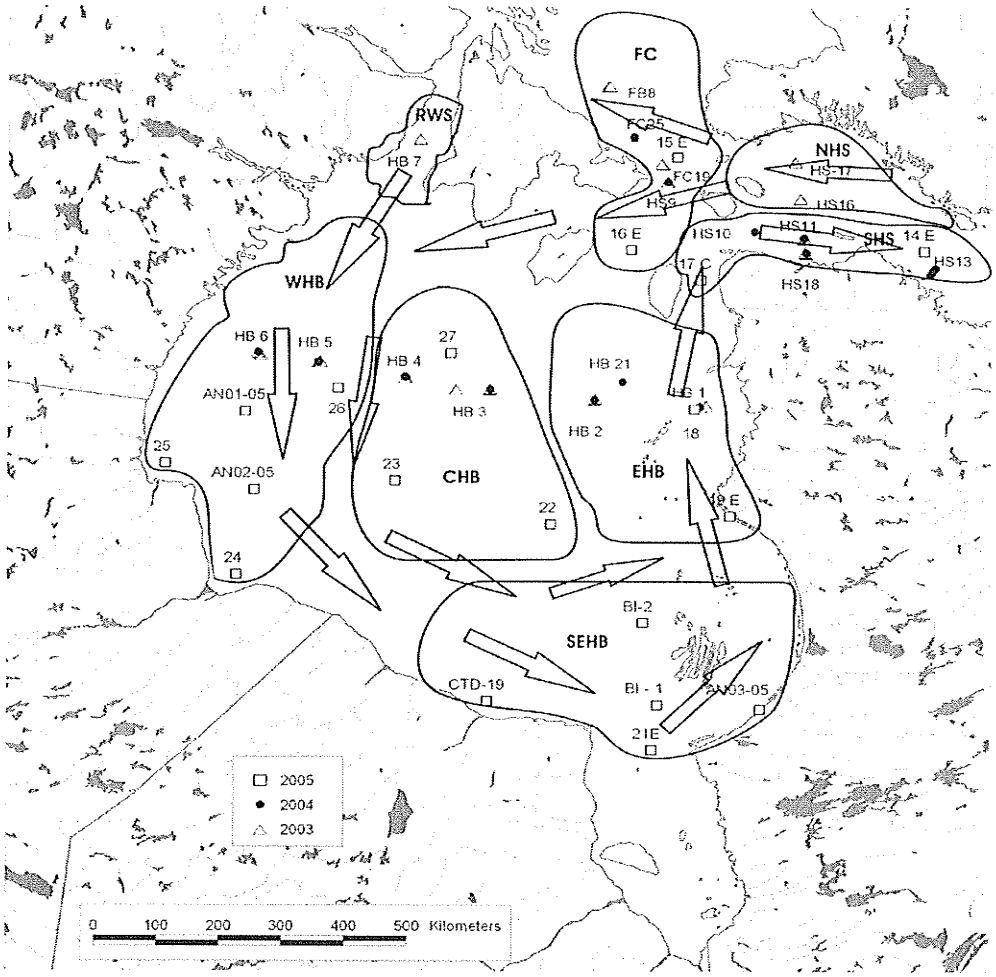

Figure 1.

Methods

Sample Collection.

Sample sites along the MERICA (*CCGS Radison* and *Des Groseillers*) cruise transect (August 2003, 2004) and the ArcticNet (*CCGS Amundsen*) leg 2 cruise transect (September – October 2005) are shown in Figure 1. Zooplankton were collected during MERICA using an oblique tow tucker net (d = 1 m^2, 333 μm). During the ArcticNet cruise, oblique (d = 1 m^2, 500 μm), vertical quadrupole (d = 1 m^2, 2 x 200 μm, 2 x 500 μm), and Rectangular Mid-water Trawl (RMT, d = 9 m^2, 1600 μm) nets were used. Zooplankton samples were collected in "live-catch" zooplankton tows. Zooplankton dead upon sampling were not kept for further analysis. Gut contents in zooplankton were not cleared before freezing the samples due to time constraints and logistics of sampling. Live catches were sorted into different genera and frozen as quickly as possible to avoid samples warming and the zooplankton perishing, which would compromise the sampling technique. There were no sufficient clean outdoor locations for sample sorting, which may have allowed some time for zooplankton to clear their guts in a suitable sub-arctic environment. This being the case, had guts been cleared, no literature to date has been published to our knowledge on the difference in stable isotopes this would have made, so we are confident that our sampling techniques were sufficient given the time constraints and sample logistics.

Bulk zooplankton were separated into genera: *Calanus* sp., *Themisto* sp., *Sagitta* sp., *Cliona* sp., *Euchaeta sp., Limacina* sp. (without the shell), Cnidarian (it was only possible to identify to the family level), *Hyperia* sp., and *Thysanoessa sp.* Samples were placed in

sterile plastic bags and shipped frozen (-20°C) to the Freshwater Institute where they were kept until mercury analysis. *Themisto* sp. was the most ubiquitous zooplankton collected. At select stations, *Themisto* sp. caught in the oblique tow were small enough to be separated by measurement underneath a microscope as juvenile ($Z < 15$ µm), or adult ($Z > 15$ µm). Studies on metal concentrations in *Themisto* sp. and *Calanus* sp. in relation to body length and life cycle suggests that only adult individuals should be used for biomonitoring of a contaminant (Ritterhoff and Zauke 1997). We refer to zooplankton that eat phytoplankton, particulate organic matter (POM), and ice algae as planktivores, those that eat predominantly other zooplankton as carnivores, and zooplankton that eat both plant material and other zooplankton as omnivores.

Water was collected from the rosette (Seabird, 24 X 12 L Niskin Bottles; PVC non-metallic material) for mercury and nutrient data. Depths were pre-determined based on maximum chlorophyll, pycnocline, and thermocline levels. The "clean hands dirty hands" 2 person sampling technique (Boutron et. al. 1993) was used to minimize contamination. Samples for MeHg and HgT were collected in acidified 1 L high density poly ethylene (HDPE) bottles and 50 mL falcon tubes (33-36 % ultrapure HCl). Salinity and $\delta^{18}O$ samples were collected in 125 ml and 50 ml HDPE bottles during MERICA, and 125 ml and 25 ml glass bottles during the ArcticNet cruise. DOC samples were filtered through baked (500°C for 12 hours) Whatman GFF filters (0.7 µm). The filtrate was poured into 5-ml glass storage vials with Teflon-lined caps previously cleaned and acidified to ~pH 2 with 25% v/v H_3PO_4 (10 µl ml^{-1}) (Burdige and Homstead 1994). All water samples were kept refrigerated until analysis.

Ice Camp – Churchill Manitoba, Canada

A polar ice camp near Churchill in Button Bay was set up for sample collection through the ice in the spring of 2005. Zooplankton biomass, water, sediments, as well as amphipods were collected. A 0.5 m diameter zooplankton net with nylon mesh of a 253 µm pore size was used to collect the biomass through the ice. The net was submerged and left to stream out at different depths over periods ranging between 24 and 48 hours. All of the biomass was rinsed into the cod end, transferred into a glass dish, and zooplankton families were picked out with forceps. Minnow traps baited with raw meat in small mesh bags were hung at depths ranging throughout the water column (0-15 m) to catch amphipods of the species *anonyx*. All biological samples were collected in Whirlpak® bags and stored in coolers at -20°C until shipment back to DFO where they were stored at -20°C until further analysis. Water sampling for mercury and salinity in Button Bay was performed using a Niskin (PVC non-metallic material) water sampler instead of a rosette, however sample bottles were prepared in a similar manner to those used on the MERICA and ArcticNet cruises.

It was time consuming and difficult to obtain zooplankton samples through the ice in Button Bay. Productivity was low, and at times even streaming the net underneath the ice for up to 12 hours was not effective in obtaining enough zooplanktons for stable isotope and mercury analysis. There was enough organic matter collected in the cod end to perform analyses at the base of the pelagic food web. We freeze dried these organic samples and analyzed them as bulk biomass. The bulk biomass contained some small

Cnidarian and *Sagitta* sp. as well as diatoms, phytoplankton, and microalgae. Particulate organic matter was collected and analyzed for $\delta^{15}N$ and $\delta^{13}C$ according to the methods of Kuzyk et al. (2005, pers. comm.) which provided an interesting comparison to the biomass collected in our study.

Hudson Bay regions.

Both MERICA and ArcticNet expeditions sampled at stations influenced by different water masses, which complemented the grouping of stations into eight regions as shown in Figure 1. Regions were represented in graphs and Figures in accordance with the known surface water cyclonic circulation patterns (Martini, 1986); i) North Hudson Strait (NHS), ii) Foxe Channel (FC), iii) Roes Welcome Sound (RWS), iv) West Hudson Bay (WHB), v) Central Hudson Bay (CHB), vi) South East Hudson Bay (SEHB), (vii) East Hudson Bay (EHB), and (viii) South Hudson Strait (SHS). Cluster analysis was used to group stations in Eastern Hudson Bay and Hudson Strait into 4 unique groups based on oceanographic, nutrient as well as biological data (Harvey et al. 1997, 2001), which provided merit for our grouping system.

Sample Analysis.

Methods of Armstrong and Uthe (1971) were used for mercury analysis. Replicate 0.1g samples of freeze dried zooplankton, Certified Reference Materials (CRMs), and blanks were acid digested with a HNO_3/H_2SO_4 solution at 180°C for 16 hours. Calibration standards were not acid digested at 180°C. Samples were cooled and a permanganate ($KMnO_4$) solution was added until the sample turned light pink. A solution of dilute

hydrogen peroxide (~ 6 drops 30% H_2O_2 in 30 ml distilled H_2O) was used to drive the equilibrium of the reaction back to light pink in case the oxidation reaction was taken too far from equilibrium (dark pink). Samples were cooled and brought to a final volume of 25 ml with distilled water. Cold Vapour Atomic Absorption (CVAA) was used for analysis of mercury (Armstrong and Uthe 1971). Reference standards TORT-1 and 2976 Mussel Tissue were run in duplicate for the analysis. Detection limits for HgT in zooplankton were 5.0 ng/g based on three standard deviations of the reagent blank readings, and 0.2 g zooplankton dw samples. Average HgT (± SE) concentrations for TORT-1 reference standard was 282 ± 9.4 ng/g dw (National Research Council of Canada value: 270 ± 60 ng/g, www.nrc-cnrc.gc.ca). Average HgT (± SE) concentrations for 2976 Mussel Tissue was 62.1 ± 2.2 ng/g dw (National Institute of Standards and Technology value: 61.0 ± 4.0 ng/g, www.nist.gov). Mean differences (± SE) in HgT between replicates for zooplankton was shown in Table 1a based on 2004-2005 results.

Freeze dried zooplankton from the ArcticNet 2005 expedition were analyzed for MeHg according to the methods of Uthe et. al. 1972, and Cai 1997. A 0.2 g sample of freeze dried zooplankton was placed in a 20 ml scintillation vial with a Teflon lid. A 5 ml aliquot of 6 N KOH was added to each vial, and the samples were placed on an orbital shaker to extract for 4 hours. Samples were acidified using a 6N HCl solution to a pH of less than 3.0. A 5 ml aliquot of a 3:1 KBr:Cu_2SO_4 was added to each sample, followed by 5 ml of dichloromethane (DCM). The samples were placed on the orbital shaker overnight. Samples were centrifuged until good separation (transparent top layer was observed) was reached between the aqueous and organic phases, and 2 ml DCM was

removed and placed in a 7 ml glass vial. A sodium thiosulfate solution was added (1 ml) and the samples were placed on the orbital shaker for 45 minutes. Samples were centrifuged, and a 0.5 ml aliquot of the aqueous layer was removed and placed into a micro-centrifuge tube. 300 µl of 3:1 KBr:Cu_2SO_4 and 200 µl DCM was added to each micro-centrifuge tube. Samples were placed on the orbital shaker for 15 minutes, and centrifuged for 2 minutes. A 150 µl sub-sample of DCM was extracted and placed in GC vials with glass inserts for Gas Chromatography Atomic Fluorescence Spectroscopy (GCAFS) at the University of Ottawa (Uthe et al. 1972, Cai 1997). Average MeHg (± SE) concentration for DORM-2 reference standard was 4.19 ± 0.16 ng/g based on 2005 sub-samples analyzed, which was comparable to the National Institute of Standards and Technology value for DORM-2 of 4.47 ± 0.32 ng/g (www.nist.gov). Average MeHg (± SE) recovered from a 200µl (5 ppb) spike was 4.61 ± 0.15 ppb, therefore MeHg recovery was 92.1%. Mean differences in MeHg between replicates for 2005 zooplankton was shown in Table 1b.

Table 1. Mean (± standard deviation) differences in (a) HgT (b) MeHg between replicates (n = 1-2) for zooplankton.*

a.

Year	Zooplankton	mean diff. (± SD) HgT (ng/g)
2003	*Calanus* sp.	5.6 ± 0.5
2004	*Calanus* sp.	1.3 ± 0.4
2005	*Calanus* sp.	1.5 ± 0.5
2004	*Thysanoessa sp.*	2.0 ± 1
2005	*Thysanoessa sp.*	6.2 ± 0.4
2003	*Themisto* sp.	5.0 ± 0.4
2004	*Themisto* sp.	4.5 ± 0.4
2005	*Themisto* sp.	3.4 ± 1
2004	*Euchaeta sp.*	5.8 ± 0.5
2005	*Euchaeta sp.*	3.3 ± 0.2
2003	*Sagitta* sp.	1.2 ± 0.7
2004	*Sagitta* sp.	2.5 ± 1
2005	*Sagitta* sp.	4.1 ± 0.2
2003	*Cliona* sp.	2.0 ± 0.2
2004	*Cliona* sp.	1.9 ± 0.8
2005	*Cliona* sp.	7.1 ± 0.5
2005	*Limacina* sp.	-
2005	*Hyperiid* sp.	-
2005	Cnidarian	6.0 ± 0.5
2005	*Cyanea* sp.	2.1 ± 0.5

b.

Year	Zooplankton	mean diff. (± SD) MeHg (ng/g)
2005	*Calanus* sp.	0.989 ± 0.61
2005	*Thysanoessa sp.*	2.55 ± 1.3
2005	*Themisto* sp.*	1.17
2005	*Sagitta* sp.	0.636 ± 0.69
2005	*Euchaeta sp.*	1.93 ± 0.62

*there was not enough biomass in these samples to prepare replicates.

Water samples for HgT were analyzed at the University of Manitoba Ultra Clean Trace Elements Laboratory (UCTEL, U.S. EPA Method 1631 (2002)). Water samples for MeHg were analyzed at the University of Ottawa (Cai et al. 1996). Salinity samples from MERICA were analyzed at the Institute of Ocean Sciences (IOS), and $\delta^{18}O$ samples were analyzed at the G.G. Hatch Isotope Laboratory[1]. During ArcticNet, salinity samples were analyzed on board the *Amundsen* using the salinometer (GuildLine Instruments Model 8400B). The measurement range was from 0.005 to 42 practical salinity units (psu) and the maximum resolution was better than ± 0.0002 psu at salinity 35 psu. A TOC-5000 analyzer (Shimadzu, Kyoto, Japan) was used for DOC analysis (Whitehead et al. 2000). Potassium hydrogen phthalate was used to standardize DOC measurements. Samples were further systematically checked every seven analyses against low-carbon water (2 µM DOC) and deep Sargasso Sea reference water (44-47 µM DOC). These seawater DOC reference standards were produced by the Hansell's Certified Reference Materials (CRM) program (http://www.rsmas.miami.edu/groups/organic-biogeochem/crm.html).

Stable Isotopes $\delta^{13}C$ and $\delta^{15}N$.

Stable isotopes were determined by Continuous Flow Ion Ratio Mass Spectroscopy (CFIR-MS) at the University of Winnipeg Stable Isotope Laboratory (UWIL). Stable isotopes of carbon ($\delta^{13}C$) were determined in an attempt to trace the source of carbon in each region for different zooplankton genera. An isotopically depleted carbon signature

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[1] University of Ottawa Faculty of Science
130 Louis Pasteur St.
Ottawa, OT
K1N6N5

was indicative of carbon influence from river runoff and erosion, and an isotopically enriched carbon signal was indicative of marine carbon sources.

Stable isotopes of nitrogen ($\delta^{15}N$) were determined for zooplankton genera collected during the MERICA and ArcticNet expeditions. The $\delta^{15}N$ values were used to assess diet and predict predator-prey relationships in each region. The abundance of $\delta^{15}N$ in zooplankton incorporates a continuum from which positioning in the trophic chain may be interpreted (Atwell et al. 1998). Trophic level (TL) was calculated from $\delta^{15}N$ values according to the following formula:

$$TL = 2 + (\delta^{15}N_{pred} - \delta^{15}N_{cal})/3.8 \quad \text{(Fisk et al. 2001)} \qquad (1)$$

Where $\delta^{15}N_{cal}$ and $\delta^{15}N_{pred}$ in (1) were average $\delta^{15}N$ values for *Calanus* sp. and predators in the region. *Calanus* sp. was considered the base of the pelagic food web in the high Arctic as well as in sub-Arctic Hudson Bay (Campbell et al. 2005). Values of $\delta^{15}N$ were established for food web members, and trophic transfer of methylmercury (MeHg) was interpreted in relation to carbon source. Further calculations of TL corrected Biomagnification Factors (BMF_{TLC}) for individuals within the food web provided a better indication of the biomagnification that was occurring at each trophic level:

$$BMF_{TLC} = [[MeHg]_{pred}/[MeHg]_{prey}]/[TL_{pred}/TL_{prey}] \quad \text{(Fisk et al. 2001)} \qquad (2a)$$

The TL's in (2a) were calculated from (1) and the $\delta^{15}N$ values for the predator and prey. For the Hudson Bay pelagic food web, the base of the food chain and the most ideal prey species was chosen to be *Calanus* sp. in accordance with previous studies (Fisk et al. 2001). The [MeHg] values in (2a) were concentrations of methylmercury in the predator and prey zooplankton (i.e. *Calanus* sp.). An alternative way to calculate BMFs and still correcting for differences in trophic levels based on $\delta^{15}N$ was given by the following formula:

$$BMF_{\delta^{15}N\ Corr.} = [[MeHg]_{pred}/[MeHg]_{prey}]/[\delta^{15}N_{pred}/\delta^{15}N_{prey}] \quad \text{(Dehn et al. 2006) (2b)}$$

Both equations 2a and 2b resulted in comparable BMF calculations. For simplicity, we used 2b based on $\delta^{15}N$ results in the different zooplankton. BMFs for plantivorous zooplankton such as *Calanus* sp., *Thysanoessa sp.*, and Juvenille *Themisto* sp. were estimated based on POM as the prey in equation 2b. Estimated $\delta^{15}N$ for POM (4.79 ± 1.7 ‰) collected from stations throughout Hudson Bay on the ArcticNet 2005 expedition was used (Kuzyk pers. comm.) in conjunction with HgT analyzed in biomass (7.55 ± 1.3 ng/g dw) collected from Churchill Manitoba in 2005. MeHg in POM was estimated from literature values as 15% of HgT in POM (Morel et al. 1998). We used our biomass HgT levels from Churchill as a rough estimate and calculated MeHg levels in Hudson Bay POM to be 1.13 ng/g dw.

Stable Isotope Analysis.

Representative sub-samples (1-2 mg dw) were placed in glass vials and shipped to the University of Winnipeg Isotope Laboratory (UWIL) for stable isotope analyses by Continuous Flow Ion Ratio Mass Spectrometry (CF-IRMS) that incorporated a GV-Instruments® IsoPrime connected to a EuroVector® EA (temperature controlled elemental analyzer). The CO_2 and N_2 gases produced were used to obtain δ values for carbon and nitrogen ratios, which deviated per million (‰) from the standards used:

$$\delta_{sample} = [(R_{sample}/R_{standard})-1]*1000 \quad (3)$$

where R represented the $^{13}C/^{12}C$ or $^{15}N/^{14}N$ ratio in the sample and standard. Values of δ displayed analytical precision of ± 0.16 ‰ and ± 0.18 ‰. Internally calibrated C/N standards were used intermittently with samples for accuracy and calibration throughout the entire analysis.

Statistics

A *t*-test difference in means at the 95% confidence interval was chosen in order to determine if there were any statistical differences among 2003-2004 summer and 2005 fall zooplankton samples. T-critical values ranged depending on the number of zooplankton samples in the dataset, from n-1=2 to n-1=8. T values calculated to be greater than t-critical values indicated a significant difference when comparing the 2003-2004 and 2005 datasets ($P<0.05$, n-1 d.o.f), which was suggestive of seasonal variability. The *t*-test was used to combine 2003-2004 and 2005 data in our defined Hudson Bay

regions (Fowler et al. 1998). There were no statistical differences in stable isotopes for the 6 zooplankton tested, which was indicative of low seasonal variability. The *t*-test was also used to interpret any regional differences in conjunction with station location and variance in the Hudson Bay dataset (Fowler et al. 1998). The following 2003-2004 and 2005 stable isotope zooplankton datasets could not be incorporated into the main dataset due to significant regional differences ($P<0.05$, t_{calc} dependent on n-1 d.o.f.): *Themisto* sp. in FC, as well as *Euchaeta sp.* and *Sagitta* sp. in EHB.

Results

Water chemistry, HgT and MeHg.

Salinity, $\delta^{18}O$, DOC, HgT, and MeHg water column values (10 meters below water surface) are shown in Figure 2 for the sampling sites in each of the eight designated regions. Not surprisingly, lowest salinity, light $\delta^{18}O$ and high DOC values were observed in the water samples from South Eastern Hudson Bay (SEHB) signifying greater freshwater influence. Highest MeHg (and %MeHg) were observed in water samples from Roes Welcome Sound (RWS) and Western Hudson Bay.

Zooplankton analyses.

Station specific levels of $\delta^{15}N$, $\delta^{13}C$, HgT, MeHg, and %MeHg for different zooplankton are shown in Table 2a-e, respectively, for individual stations from the Hudson Bay 2003-2004 and 2005 combined datasets. Mean values were reported (± standard error) where stations were sampled in multiple years. Stable isotope values and HgT were plotted for

individual stations in Figure 3a-d for the four most ubiquitous zooplankton collected. Sub-samples analyzed for MeHg as well as corresponding stable isotopes were plotted in Figure 4a-d.

Figure 2. Water chemistry profile for Hudson Bay regions.

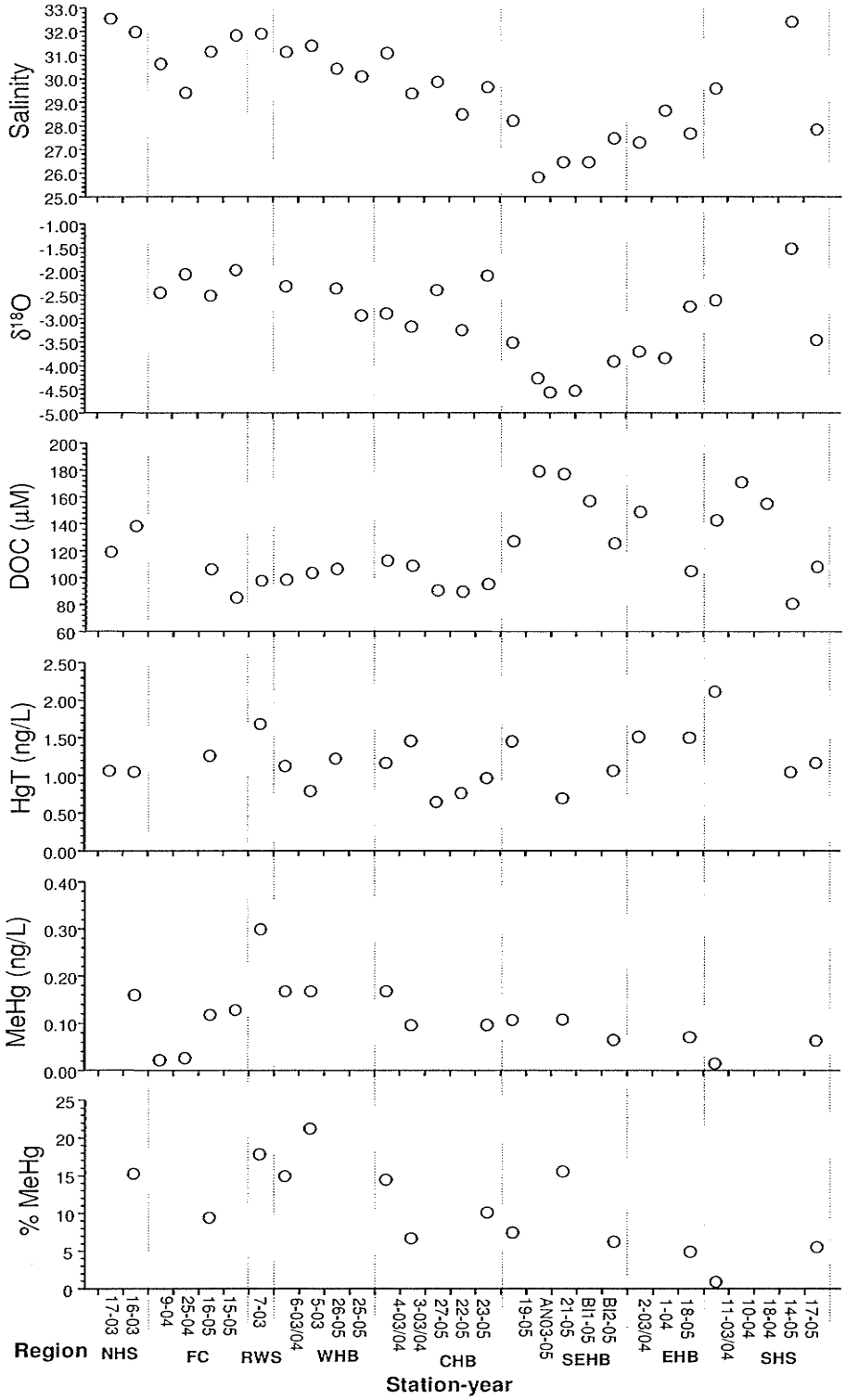


Table 2. Station specific levels of (a) $\delta^{15}N$ (b) $\delta^{13}C$ (c) HgT (d) MeHg (e) %MeHg for zooplankton in Hudson Bay during MERICA 2003, 2004 and ArcticNet 2005.

Region	EHB				NHS		FC				WHB				
Year	03/04	03/04	05	05	03	03	03/04	04	05	05	03/04	03/04	05	05	05
Station	2	1	18	19	17	16	9	25	16	15	6	5	26	24	25
Calanus sp.	6.46	6.37	5.14	-	6.33	5.18	6.55	7.27	5.39	7.57	7.98	-	-	-	-
(n = 1-3)	± 0.38	± 0.20	-	-	± 0.14	± 0.13	-	± 1.0	± 0.19	-	-	-	-	-	-
Thysanoessa sp.	-	7.71	8.40	9.16	-		12.0	8.88	8.50	8.47	8.30	-	8.79	7.67	-
(n = 1-3)		-	-	-	-	-	-	-	-	-	-	-	-	-	-
Themisto sp.	8.18	8.80	9.55	8.81	7.10	8.57	8.35	8.29	9.04	11.1	8.67	9.25	11.4	-	9.62
(n = 2-3)	± 0.50	-	-	± 0.19	-	-	-	-	-	-	± 0.034	± 0.45	-	-	-
Sagitta sp.	Sig. diff.				-	-	11.7	11.8	9.49	13.3	12.2	9.38	12.0	-	-
(n = 2-3)					-	-	-	-	-	-	± 0.15	-	± 0.064	-	-
Euchaeta sp.	Sig. diff.				-	-	-	-	8.86	10.1	-	-	-	-	-
(n = 1-3)					-	-	-	-	-	-	-	-	-	-	-
Cliona sp.	-	-	5.98	9.51	-	-	-	-	-	8.77	7.20	9.27	-	-	-
(n = 1-3)	-	-	-	± 0.83	-	-	-	-	-	± 0.18	-	-	-	-	-
Limacina sp.	-	-	8.21	-	-	-	-	-	8.99	7.52	-	-	-	-	-
(n = 1-2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Hyperia sp.	-	-	-	-	-	-	-	-	13.4	13.9	-	-	11.0	-	11.8
(n = 1)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cnidarian	-	-	-	9.56	-	-	-	-	12.6	-	-	-	-	10.8	-
(n = 1-2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Region	SHS					RWS	CHB					SEHB			
Year	03/04	05	03/04	04	05	03	03/04	03/04	05	05	05	05	05	05	05
Station	18	17	11	10	14	7	4	3	27	22	23	AN03	21	BI1	BI2
Calanus sp.	7.17	7.55	6.28	7.46	7.86	-	7.17	7.79	9.38	8.84	9.41	-	9.39	9.32	9.93
(n = 1-3)	-	-	-	-	-	-	-	± 0.53	± 0.022	-	± 0.009	-	-	-	-
Thysanoessa sp.	6.56	8.51	6.79	8.74	7.63	-	9.42	8.52	-	7.67	-	7.71	7.48	-	7.55
(n = 1-3)	± 0.38	-	± 0.40	-	-	-	-	-	-	-	-	-	± 0.25	-	± 0.074
Themisto sp.	8.42	7.36	8.40	10.2	9.64	8.53	9.70	9.91	12.1	11.3	12.4	11.7	6.87	9.39	9.08
(n = 2-3)	-	-	± 2.3	-	-	-	± 0.66	± 0.33	± 0.048	± 0.60	± 0.73	-	-	-	-
Sagitta sp.	11.6	12.8	10.4	12.0	11.9	-	11.2	11.5	11.4	11.8	11.2	13.3	11.7	11.8	9.52
(n = 2-3)	-	-	± 0.033	-	-	-	± 0.32	± 0.40	± 0.28	-	± 0.47	-	-	± 0.19	-
Euchaeta sp.	10.7	11.9	-	10.3	10.7	-	-	-	10.7	-	-	-	-	-	10.6
(n = 1-3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	± 0.029
Cliona sp.	-	10.5	-	8.27	7.78	7.45	7.43	10.7	7.69	10.2	9.36	10.0	9.35	8.59	-
(n = 1-3)	-	-	-	-	-	-	± 1.3	-	-	-	± 0.44	-	-	-	-
Limacina sp.	-	8.02	-	-	8.56	-	-	-	10.2	8.74	9.83	-	-	-	-
(n = 1-2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Hyperia sp.	-	-	-	-	-	-	-	-	11.1	-	8.82	10.4	-	-	10.7
(n = 1)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cnidarian	-	10.8	-	-	9.36	-	-	-	11.9	10.7	10.1	-	10.7	12.3	9.10
(n = 1-2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

b. $\delta^{13}C$ (‰)

Region	EHB				NHS		FC				WHB				
Year	03/04	03/04	05	05	03	03	03/04	04	05	05	03/04	03/04	05	05	05
Station	2	1	18	19	17	16	9	25	16	15	6	5	26	24	25
Calanus sp.	-23.6	-23.3	-23.6	-	-23.7	-23.0	-20.8	-20.5	-22.5	-21.8	-24.2	-	-	-	-
(n = 1-3)	± 0.46	± 0.79	-	-	± 2.5	± 2.8	± 0.66	± 0.50	± 0.11	-	± 1.6	-	-	-	-
Thysanoessa sp.	-	-24.3	-24.5	-24.5	-	-	-21.2	-21.1	-21.5	-20.6	-22.4	-	-22.8	-25.4	-
(n = 1-3)	-	-	± 0.068	-	-	-	-	-	-	-	-	-	-	-	-
Themisto sp.	-22.4	-23.6	-22.8	-23.7	-18.9	-18.0	Sig diff.				-21.8	-22.4	-22.7	-	-21.9
(n = 2-3)	± 0.57	-	-	± 0.025	± 1.2	-					± 1.3	± 1.4	-	-	-
Sagitta sp.	Sig. diff.				-	-	-21.0	-20.7	-25.5	-21.4	-23.9	-25.3	-18.7	-	-
(n = 2-3)					-	-	± 0.33	± 0.11	-	-	± 1.4	± 1.2	± 0.25	-	-
Euchaeta sp.	-23.9	-23.1	-22.4	-	-	-	-	-	-22.9	-22.0	-	-	-	-	-
(n = 1-3)		-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cliona sp.	-	-	-26.0	-24.4	-	-	-	-	-	-23.1	-24.8	-24.3	-	-	-
(n = 1-3)	-	-	-	± 0.41	-	-	-	-	-	± 0.085	-	-	-	-	-
Limacina sp.	-	-	-24.1	-	-	-	-	-	-22.1	-20.5	-	-	-	-	-
(n = 1-2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Hyperia sp.	-	-	-	-	-	-	-	-	-19.7	-21.8	-	-	-23.2	-	-18.3
(n = 1)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cnidarian	-	-	-	-16.3	-	-	-	-	-23.1	-	-	-	-	-17.3	-
(n = 1-2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Region	SHS					RWS	CHB					SEHB			
Year	03/04	05	03/04	04	05	03	03/04	03/04	05	05	05	05	05	05	05
Station	18	17	11	10	14	7	4	3	27	22	23	AN03	21	BI1	BI2
Calanus sp.	-20.7	-22.2	-24.5	-21.3	-19.9	-	-23.8	-25.0	-25.1	-25.4	-21.4	-	-24.0	-22.9	-24.4
(n = 1-3)	-	-	± 0.86	± 0.86	-	-	± 3.5	± 2.7	± 0.50	± 0.030	± 0.22	-	± 0.086	± 0.19	± 0.36
Thysanoessa sp.	-21.0	-23.7	-21.3	-19.5	-18.4	-	-22.5	-24.6	-	-25.9	-	-20.8	-22.6	-	-24.5
(n = 1-3)	± 0.65	-	± 0.042	-	-	-	-	-	-	-	-	-	± 0.11	-	± 0.13
Themisto sp.	-19.4	-22.9	-21.1	-21.5	-20.2	-23.5	-22.9	-23.7	-22.7	-25.2	-23.5	-23.8	-23.0	-22.0	-22.8
(n = 2-3)	-	-	± 2.3	-	-	± 0.42	± 1.4	± 0.81	± 0.14	± 0.25	± 0.48	-	-	-	-
Sagitta sp.	-22.6	-20.9	-22.1	-21.6	-21.4	-	-23.4	-24.7	-20.2	-25.1	-21.9	-23.5	-23.21	-23.7	-23.3
(n = 2-3)	-	-	± 1.1	-	-	-	± 0.64	± 0.60	± 0.57	-	± 0.83	-	-	± 0.065	-
Euchaeta sp.	-22.2	-21.2	-	-22.2	-22.4	-	-	-	-25.7	-	-	-	-	-	-24.34
(n = 1-3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	± 0.10
Cliona sp.	-	-23.7	-	-25.6	-22.2	-22.0	-24.6	-24.1	-24.3	-24.8	-24.9	-26.4	-24.1	-26.5	-
(n = 1-3)	-	-	-	-	-	-	± 0.72	-	-	-	± 0.17	-	-	-	-
Limacina sp.	-	-23.0	-	-	-21.2	-	-	-	-21.4	-23.6	-22.7	-	-	-	-
(n = 1-2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Hyperia sp.	-	-	-	-	-	-	-	-	-22.4	-	-22.9	-23.1	-	-	-22.0
(n = 1)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cnidarian	-	-15.7	-	-	-13.4	-	-	-	-17.0	-19.8	-19.4	-	-16.5	-21.0	-18.0
(n = 1-2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

c. HgT (ng/g) dw

Region	EHB				NHS		FC				WHB				
Year	03/04	03/04	05	05	03	03	03/04	04	05	05	03/04	03/04	05	05	05
Station	2	1	18	19	17	16	9	25	16	15	6	5	26	24	25
Calanus sp.	14.2	14.9	6.28	-	6.24	5.67	14.1	9.60	7.04	6.27	10.6	-	-	-	-
(n = 1-3)	± 1.1	± 0.85	± 0.63	-	-	± 1.2	-	± 1.3	± 1.6	± 0.13	-	-	-	-	-
Thysanoessa sp.	-	11.7	9.31	8.22	-	-	6.93	13.7	36.9	8.10	13.1	-	10.9	81.2	-
(n = 1-3)	-	± 1.4	± 2.3	± 0.26	-	-	-	± 3.2	± 0.71	± 6.9	-	-	± 1.7	± 0.33	-
Themisto sp.	40.0	16.1	22.8	17.31	14.7	12.3	19.7	15.7	22.3	29.1	29.7	37.8	13.1	14.2	16.7
(n = 2-3)	± 7.8	± 1.4	± 6.4	± 2.2	± 2.1	± 0.58	± 0.53	± 4.2	± 6.1	± 10	± 8.5	± 7.4	± 0.18	± 0.59	± 0.47
Sagitta sp.	16.0	13.2	8.96	-	-	-	14.7	16.7	8.00	12.7	18.2	21.5	6.88	-	-
(n = 2-3)	± 2.3	± 0.14	± 2.7	-	-	-	± 2.0	± 2.7	± 0.46	± 1.1	± 3.0	± 2.1	± 3.1	-	-
Euchaeta sp.	142	74.5	30.4	-	-	-	-	-	25.4	16.6	-	-	-	-	-
(n = 1-3)	-	-	-	-	-	-	-	-	± 3.3	± 4.5	-	-	-	-	-
Cliona sp.	42.3	-	74.8	46.6	-	-	-	-	-	56.8	12.4	122	-	-	-
(n = 1-3)	± 4.0	-	-	± 4.4	-	-	-	-	-	± 5.4	± 35	-	-	-	-
Limacina sp.	-	-	68.3	-	-	-	-	-	80.3	64.4	-	-	-	-	-
(n = 1-2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Hyperia sp.	-	-	-	-	-	-	-	-	32.5	41.3	-	-	27.9	-	37.4
(n = 1)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cnidarian	-	-	-	3.25	-	-	-	-	10.7	-	-	-	-	4.10	3.40
(n = 1-2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Region	SHS					RWS	CHB					SEHB			
Year	03/04	05	03/04	04	05	03	03/04	03/04	05	05	05	05	05	05	05
Station	18	17	11	10	14	7	4	3	27	22	23	AN03	21	BI1	BI2
Calanus sp.	10.2	6.13	14.4	9.46	7.01	-	13.1	19.0	18.7	13.7	15.9	-	7.21	10.3	8.14
(n = 1-3)	± 0.69	± 0.47	± 12	± 1.4	± 1.3	-	± 3.0	± 6.5	± 3.1	± 0.054	± 0.38	-	± 0.69	± 1.2	± 0.99
Thysanoessa sp.	24.4	10.4	21.2	19.8	10.3	-	17.5	32.5	-	13.0	-	13.7	11.3	-	17.7
(n = 1-3)	± 2.5	± 0.13	± 0.56	± 0.38	± 9.8	-	-	-	-	± 0.089	-	± 2.8	± 8.3	-	± 9.4
Themisto sp.	13.7	18.6	18.4	27.7	18.9	29.0	31.9	43.5	24.8	24.3	22.2	15.5	18.6	18.3	17.8
(n = 2-3)	± 0.80	± 4.0	± 10	± 12	± 1.3	± 7.6	± 10	± 0.66	± 3.5	± 3.7	± 0.27	± 1.5	± 1.8	± 6.4	± 1.3
Sagitta sp.	18.8	8.73	13.6	23.1	4.58	-	20.4	21.5	11.0	17.5	15.0	6.14	5.47	9.42	5.32
(n = 2-3)	± 0.58	± 0.41	± 3.2	± 0.87	± 1.2	-	± 1.6	± 5.0	± 0.78	± 4.8	± 5.0	-	± 0.39	± 1.5	± 0.051
Euchaeta sp.	130	19.3	-	39.6	23.3	-	-	-	30.8	-	-	-	-	-	40.3
(n = 1-3)	-	± 0.071		± 4.5	± 0.59	-	-	-	-	-	-	-	-	-	-
Cliona sp.	-	63.3	-	63.0	55.7	88.0	132	61.3	51.6	45.8	63.4	43.9	72.3	48.4	-
(n = 1-3)	-	± 1.8	-	± 17	± 1.8	-	± 110	± 4.6	-	-	-	-	± 0.23	± 16	-
Limacina sp.	-	68.3	-	-	29.2	-	-	-	51.9	70.6	56.8	-	-	-	-
(n = 1-2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Hyperia sp.	-	-	-	-	-	-	-	-	40.2	-	32.5	15.9	-	-	52.3
(n = 1)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cnidarian	-	4.31	-	-	16.0	-	-	-	4.43	11.0	16.9	-	3.87	3.79	3.26
(n = 1-2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

d. MeHg (ng/g) dw

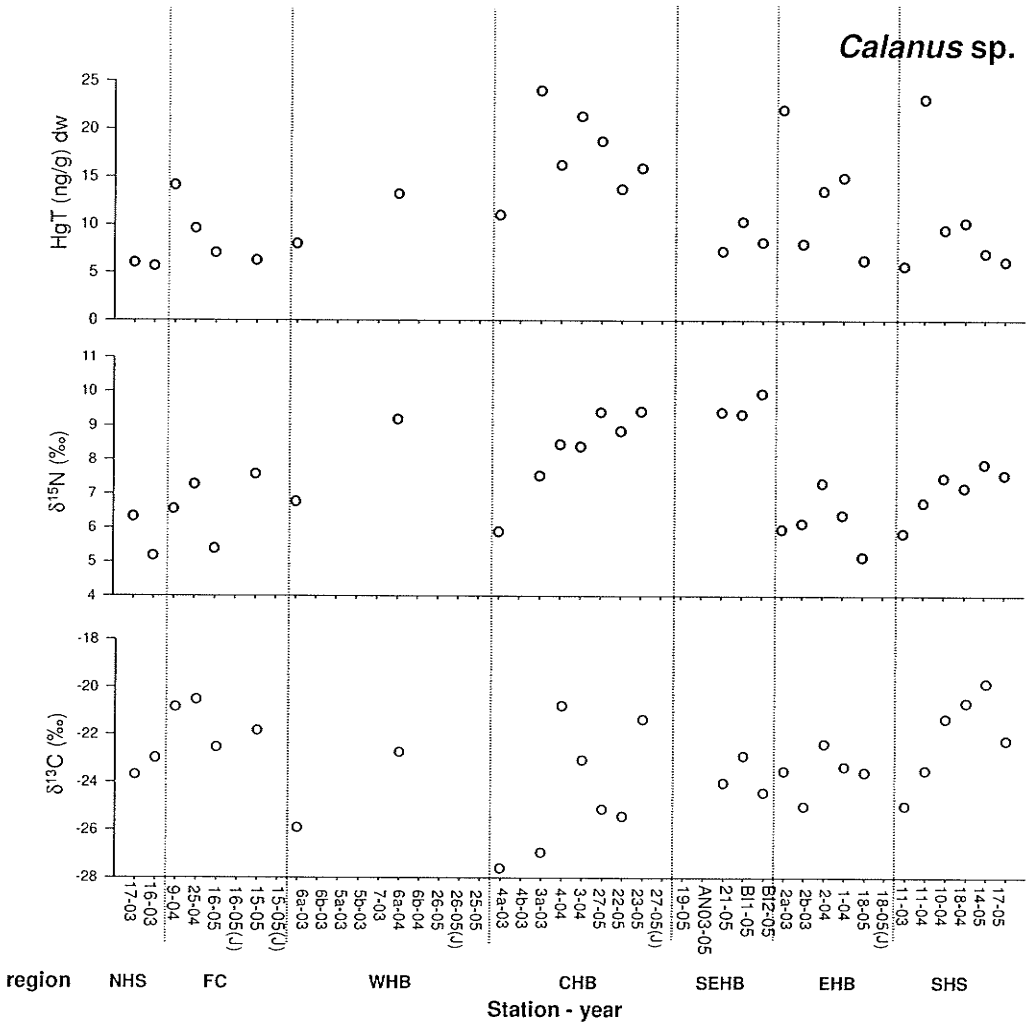
Region	EHB		FC		WHB				SHS		CHB			SEHB			
Year	05	05	05	05	05	05	05	05	05	05	05	05	05	05	05	05	05
Station	18	19	16	15	AN01	26	24	25	17	14	22	23	27	AN03	21	B11	B12
Calanus sp. (n = 1-3)	- -	- -	1.45 ± 1.6	0.737 ± 0.18	- -	- -	- -	- -	0.648 ± 0.34	1.59 ± 0.82	- -	9.49 -	3.92 ± 0.025	- -	- -	2.35 ± 0.57	- -
Thysanoessa sp. (n = 1-3)	0.529 ± 0.090	2.28 ± 0.47	11.1 ± 4.8	- -	1.70 ± 1.6	9.57 -	17.3 ± 2.5	- -	2.40 ± 2.4	4.57 -	1.72 ± 1.5	- -	6.65 -	1.16 ± 1.1	- -	- -	2.70 -
Themisto sp. (n = 2-3)	13.7 -	13.4 -	22.7 -	12.9 -	9.21 -	8.11 -	- -	15.7 -	11.8 -	16.1 -	22.0 -	29.0 -	28.1 -	4.10 ± 0.83	14.3 -	12.7 -	12.9 -
Sagitta sp. (n = 2-3)	6.82 ± 0.14	- -	5.95 ± 0.66	9.87 ± 0.75	2.49 -	9.04 ± 0.12	- -	- -	8.39 -	- -	- -	8.54 ± 0.79	8.95 -	0.986 -	5.98 ± 0.30	4.53 -	5.66 ± 0.38
Euchaeta sp. (n = 1-3)	- -	- -	22.0 ± 1.1	18.9 -	- -	- -	- -	- -	21.7 ± 1.6	- -	- -	- -	- -	- -	- -	- -	- -
Cliona sp. (n = 1-3)	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	34.6 -	- -	- -	- -	- -
Limacina sp. (n = 1-2)	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	14.2 -	- -	- -	- -	- -

e. % MeHg

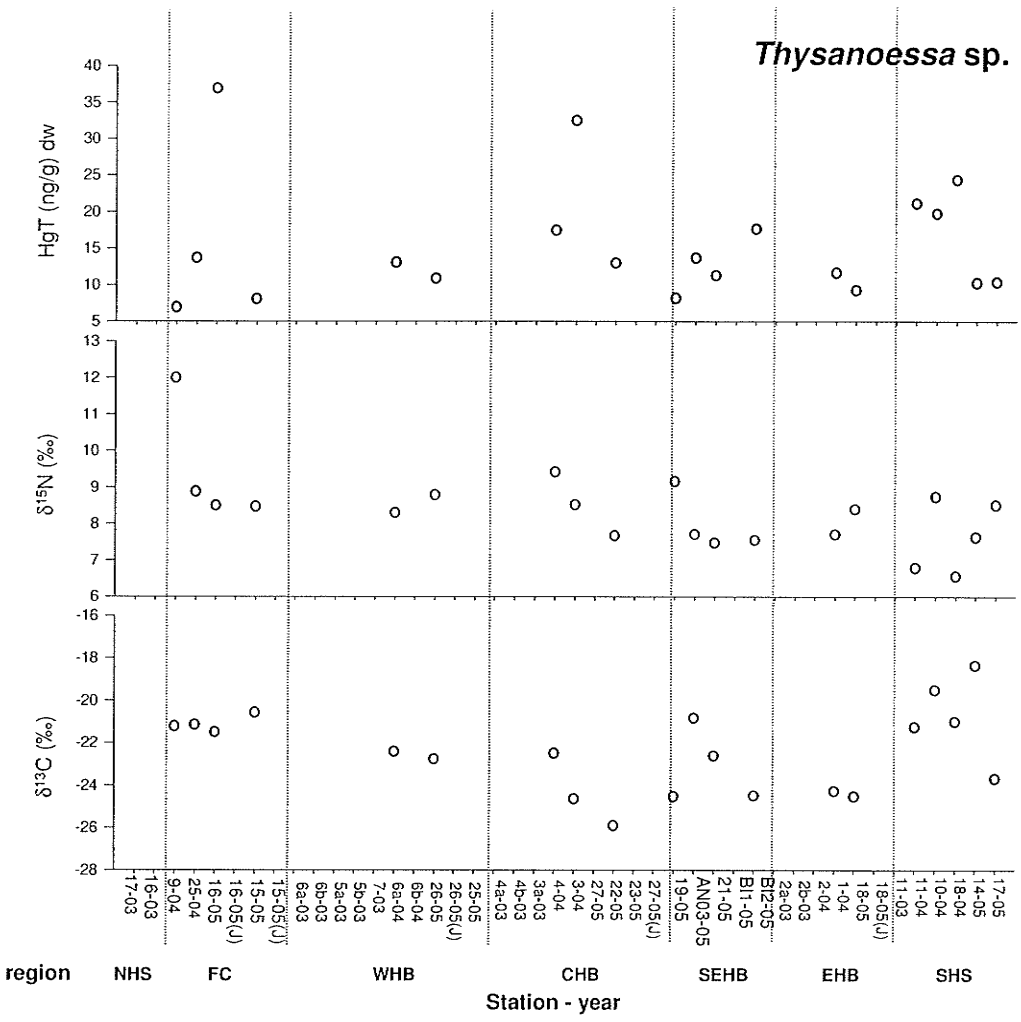
Region	EHB		FC		WHB				SHS		CHB			SEHB			
Year	05	05	05	05	05	05	05	05	05	05	05	05	05	05	05	05	05
Station	18	19	16	15	AN01	26	24	25	17	14	22	23	27	AN03	21	B11	B12
Calanus sp. (n = 1-3)	- -	- -	20.6 ± 23	11.8 ± 2.8	- -	- -	- -	- -	10.6 ± 5.6	22.7 ± 12	- -	59.8 -	20.9 ± 0.19	- -	- -	22.8 ± 5.5	- -
Thysanoessa sp. (n = 1-3)	5.68 ± 0.97	27.7 ± 5.7	30.0 ± 13	- -	19.8 ± 19	88.0 -	21.3 ± 3.1	- -	23.0 ± 23	44.2 -	13.2 ± 11	- -	- -	8.50 ± 8.2	- -	- -	15.2 -
Themisto sp. (n = 2-3)	60.2 -	77.6 -	100 -	44.4 -	54.4 -	62.0 -	- -	93.8 -	63.6 -	85.1 -	90.5 -	100 -	100 -	26.4 ± 5.4	76.6 -	69.4 -	72.1 -
Sagitta sp. (n = 2-3)	76.0 ± 1.6	- -	74.4 ± 8.2	77.9 ± 5.9	34.0 -	100 ± 1.8	- -	- -	96.1 -	- -	- -	56.9 ± 5.3	81.0 -	16.0 -	100 ± 5.5	48.1 -	100 ± 7.2
Euchaeta sp. (n = 1-3)	- -	- -	86.7 ± 4.4	100 -	- -	- -	- -	- -	100 ± 8.4	- -	- -	- -	- -	- -	- -	- -	- -
Cliona sp. (n = 1-3)	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	67.1 -	- -	- -	- -	- -
Limacina sp. (n = 1-2)	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	27.3 -	- -	- -	- -	- -

Figure 3. Stable isotopes and HgT for (a) *Calanus* sp. (b) *Thysanoessa* sp. (c) *Themisto* sp. (d) *Sagitta* sp. Shaded circles: significant differences were found in these regions using the t-test.

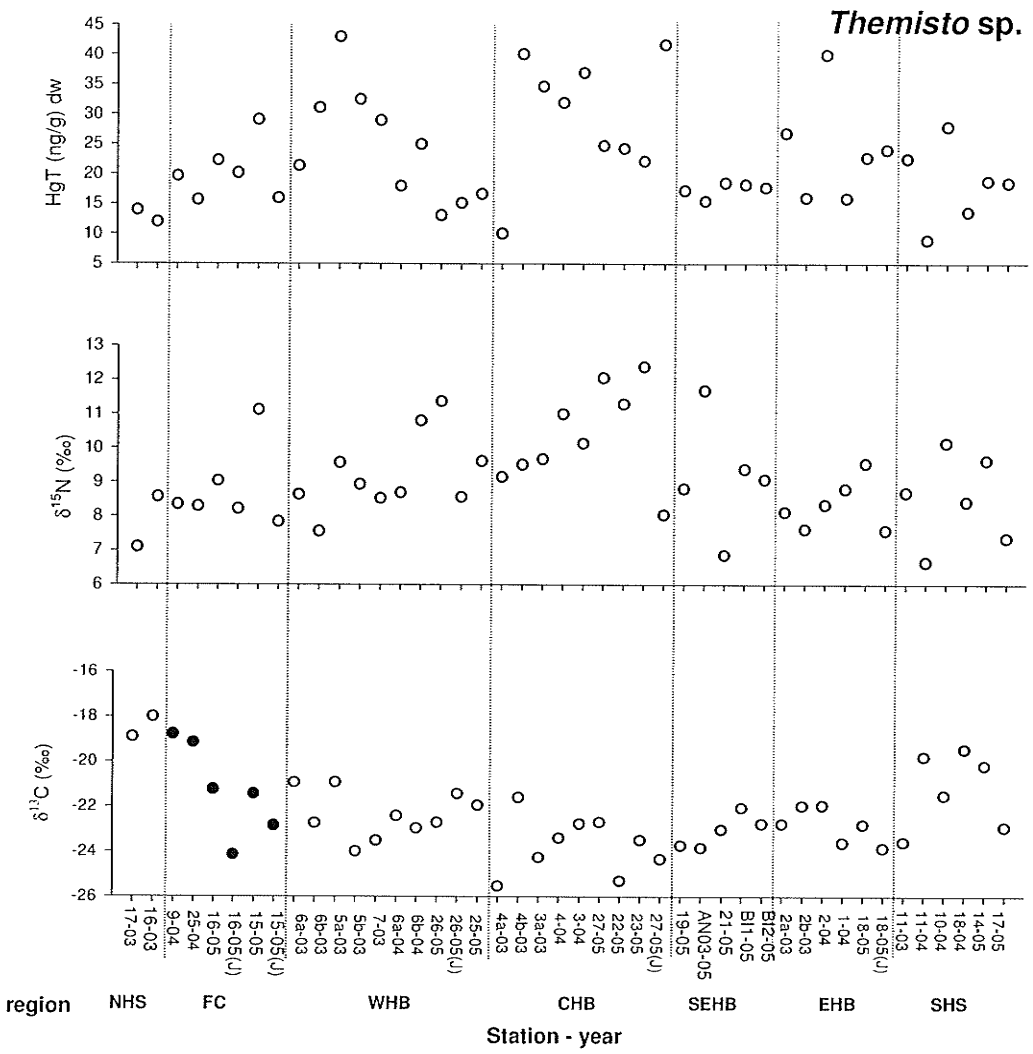
a.



b.


Thysanoessa sp.
HgT (ng/g) dw
δ15N (‰)
δ13C (‰)
region
NHS
FC
WHB
CHB
SEHB
EHB
SHS
Station - year

c.


Themisto sp.
HgT (ng/g) dw
δ15N (‰)
δ13C (‰)
region
NHS
FC
WHB
CHB
SEHB
EHB
SHS
Station - year

d.

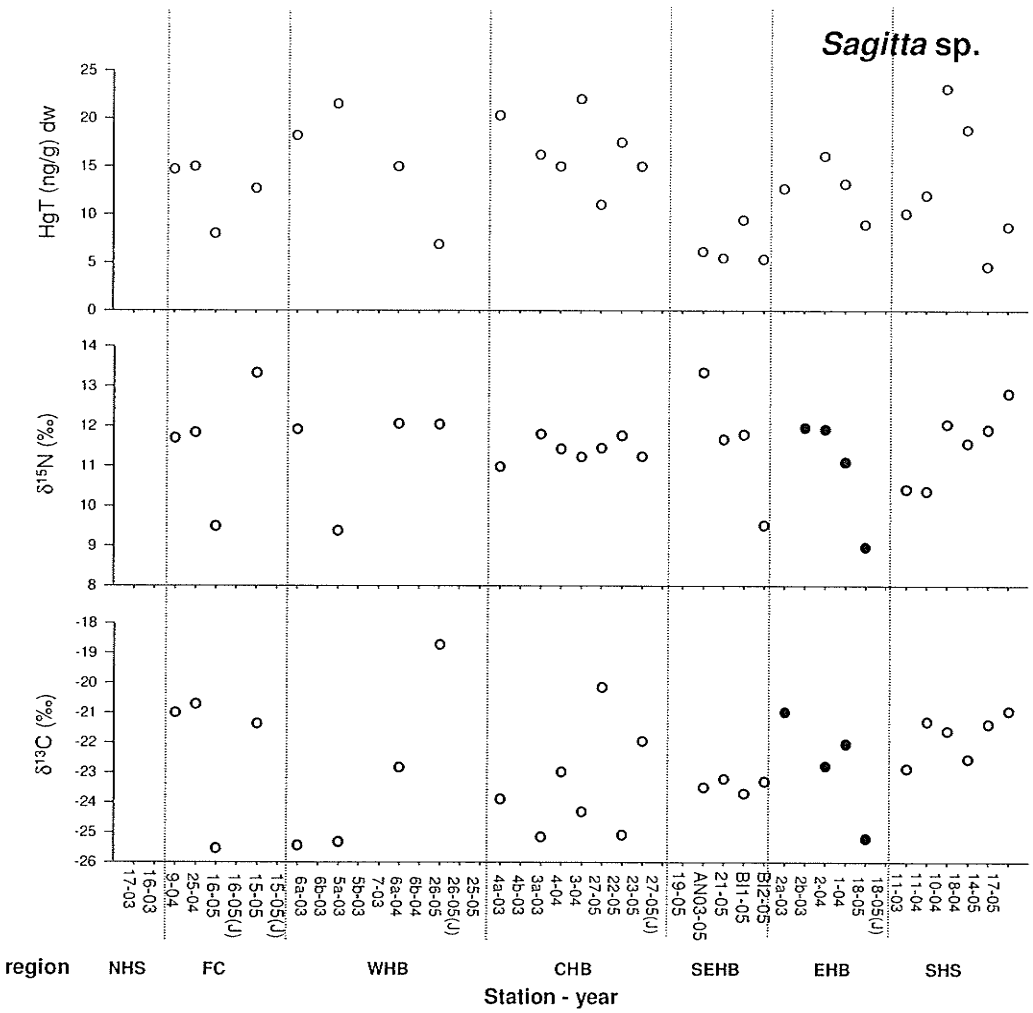
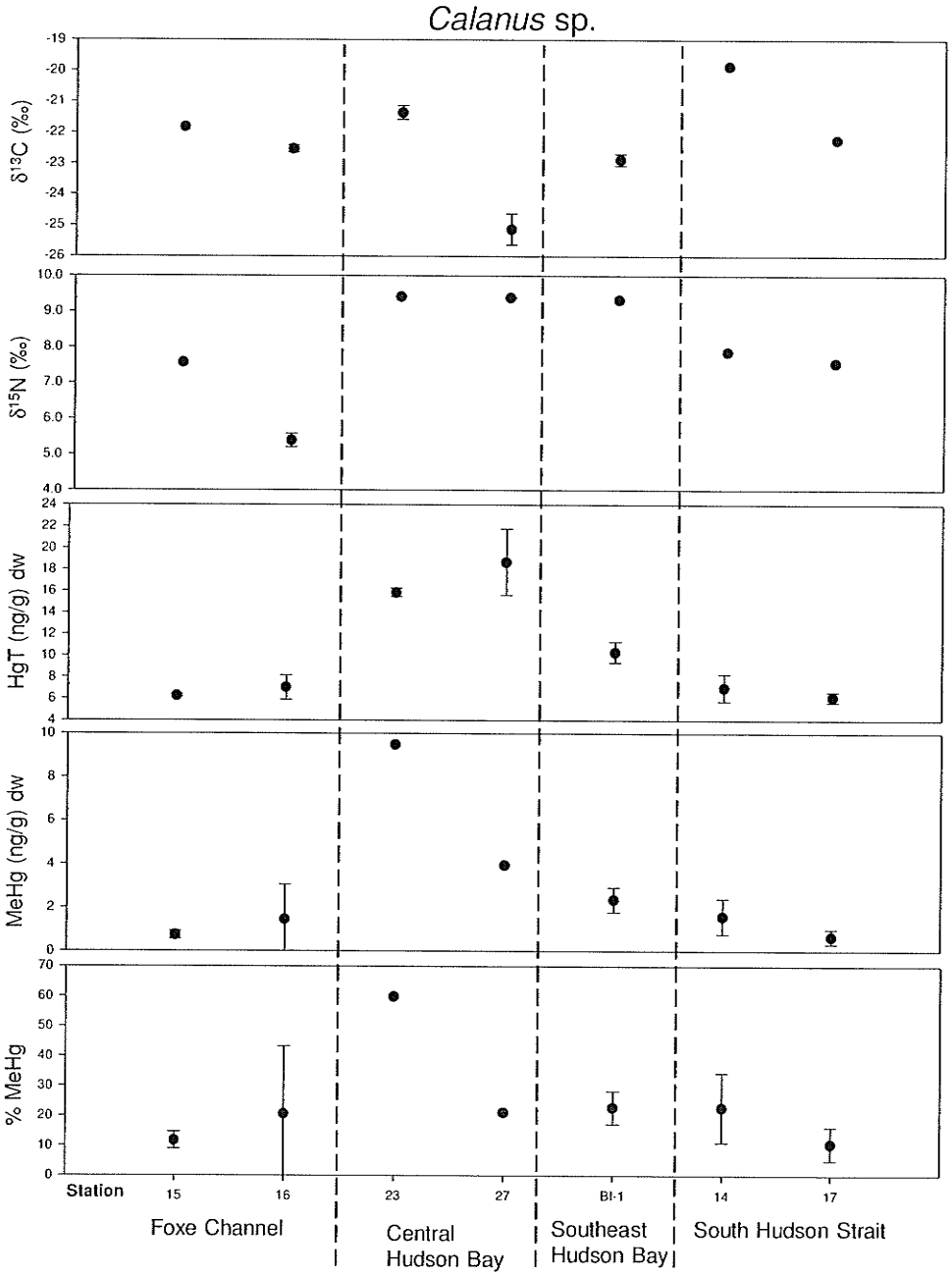

Sagitta sp.
HgT (ng/g) dw
δ15N (‰)
δ13C (‰)
region
NHS
FC
WHB
CHB
SEHB
EHB
SHS
Station - year

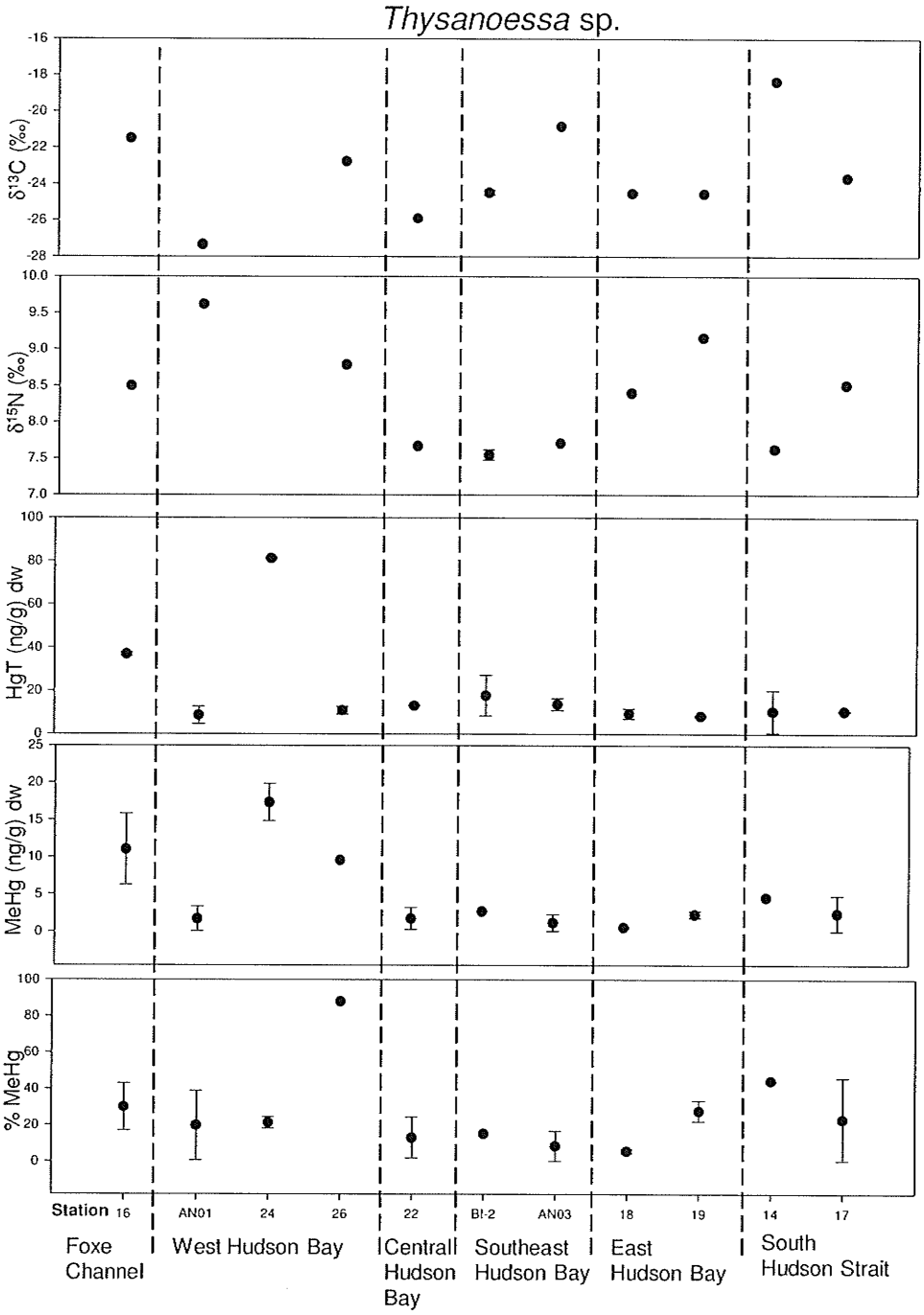
Figure 4. Stable isotopes and MeHg for (a) *Calanus* sp.(b) *Thysanoessa sp.* (c) *Themisto* sp. (d) *Sagitta* sp.

Sub-samples analyzed for HgT were analyzed for MeHg due to limited sample quantities at some stations.

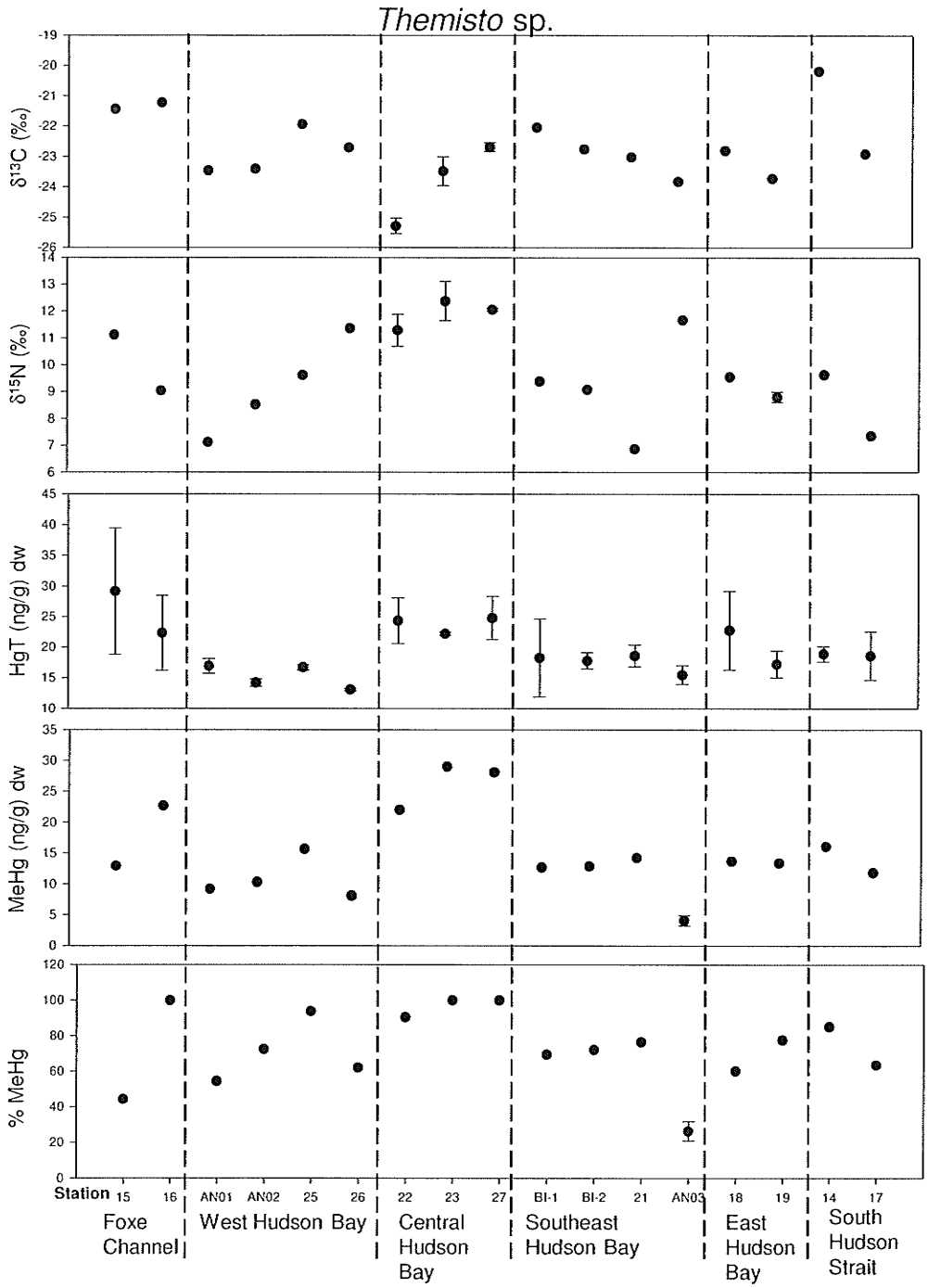
a.



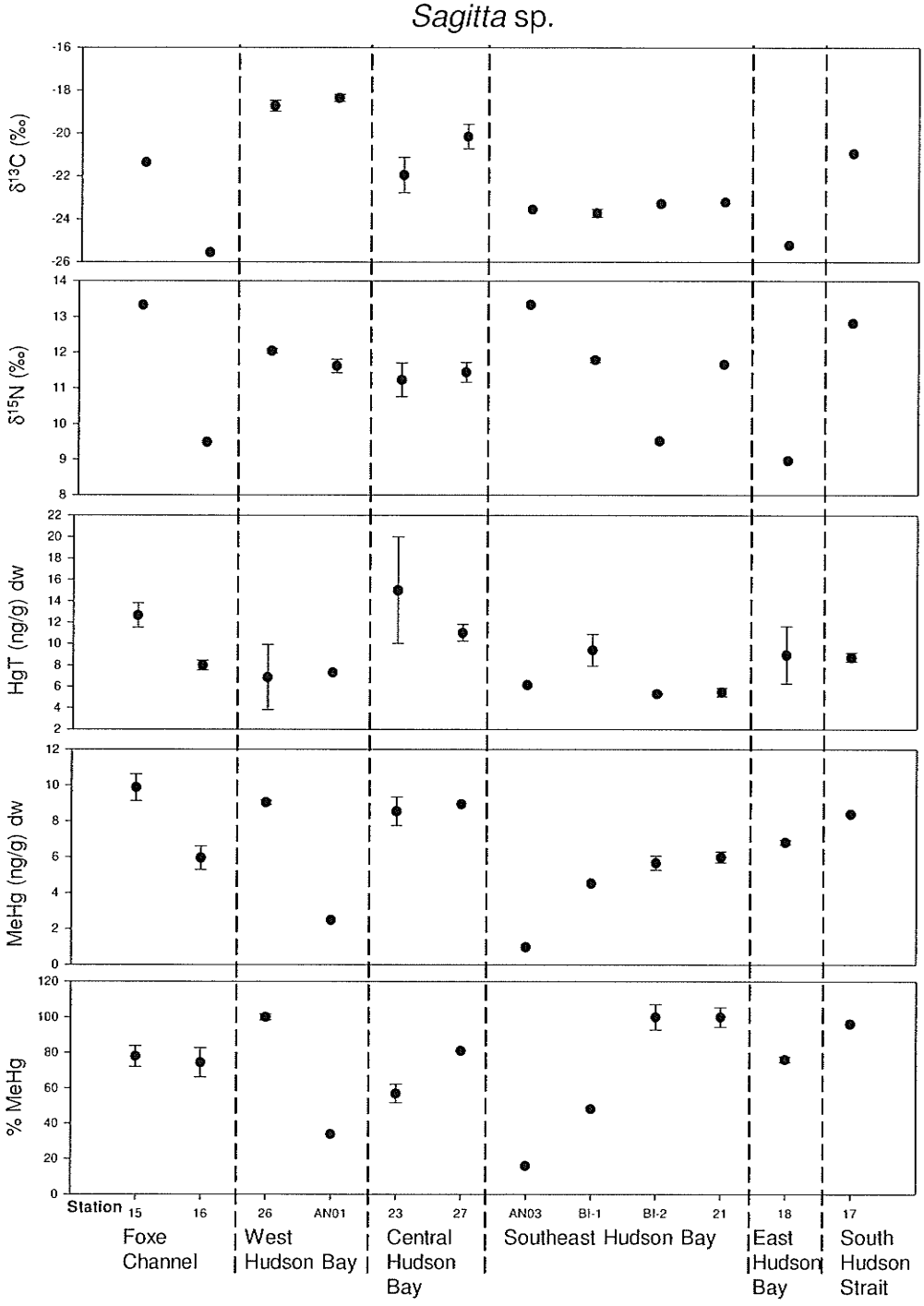
b.


Thysanoessa sp.
δ13C (‰)
δ15N (‰)
HgT (ng/g) dw
MeHg (ng/g) dw
% MeHg
Station 16 AN01 24 26 22 BI-2 AN03 18 19 14 17
Foxe Channel
West Hudson Bay
Central Hudson Bay
Southeast Hudson Bay
East Hudson Bay
South Hudson Strait

c.

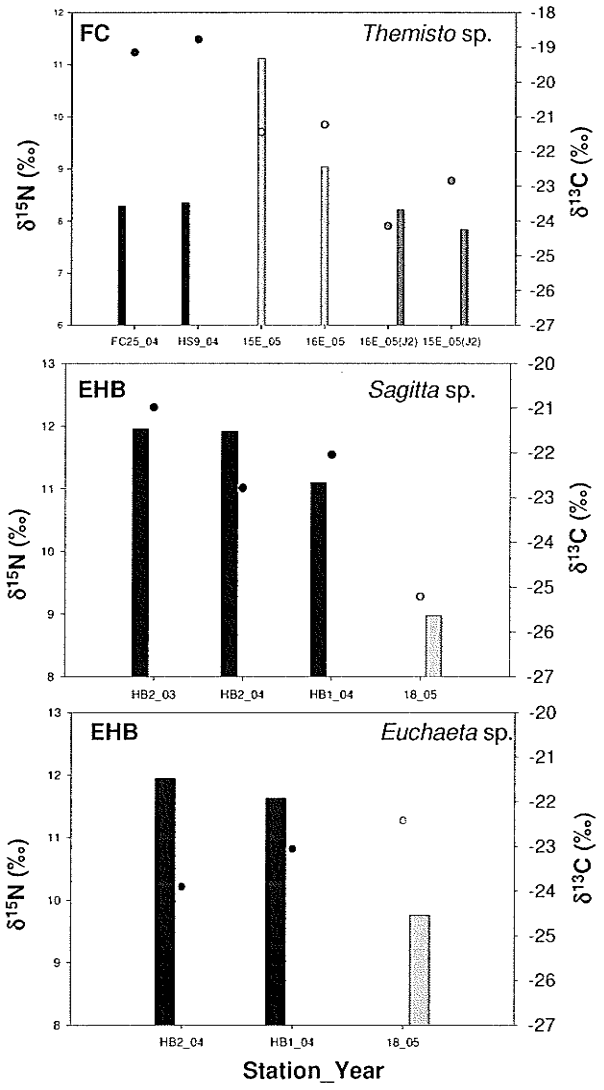

Themisto sp.
δ13C (‰)
δ15N (‰)
HgT (ng/g) dw
MeHg (ng/g) dw
% MeHg
Station 15 16 AN01 AN02 25 26 22 23 27 BI-1 BI-2 21 AN03 18 19 14 17
Foxe Channel
West Hudson Bay
Central Hudson Bay
Southeast Hudson Bay
East Hudson Bay
South Hudson Strait

d.


Sagitta sp.
δ13C (‰)
δ15N (‰)
HgT (ng/g) dw
MeHg (ng/g) dw
% MeHg
Station
15
16
26
AN01
23
27
AN03
BI-1
BI-2
21
18
17
Foxe Channel
West Hudson Bay
Central Hudson Bay
Southeast Hudson Bay
East Hudson Bay
South Hudson Strait

Values of $\delta^{15}N$ calculated to be significantly different by the *t*-test were shown for zooplankton genera collected in multiple years at individual stations in selected regions of Hudson Bay (Figure 5, bars). Values of $\delta^{15}N$ for *Sagitta* sp. ($t = 9.60$, $p<0.05$) and *Euchaeta sp.* ($t = 12.7$, $p<0.05$) in EHB were significantly higher by almost one trophic level in the 2004 dataset compared to 2005.

Figure 5. Stable Isotope data for specific stations and zooplankton genera with significant differences calculated by the *t*-test. Bars: $\delta^{15}N$ (‰), Points: $\delta^{13}C$ (‰)



Stable Isotopes 2003-2005.

$\delta^{15}N$ values for individual zooplankton species ranged broadly over the eight designated regions (Figure 6a). For example, in *Thysanoessa sp.* values varied from a low of 6.56 ‰ (station 18, SHS) to as high as 12.47 ‰ (station 9, FC). Minimum variation was observed for *Limacina* sp. with $\delta^{15}N$ values ranging from 7.52 ‰ (station 15, FC) to 10.20 ‰ (station 27, CHB). Figure 6a results indicated that *Calanus* sp., *Thysanoessa sp.*, *Themisto* sp., *Cliona* sp. and *Hyperia* sp. could vary regionally by up to one trophic level ($\delta^{15}N$ increased by 3.4‰, Atwell et al. 1998)). Figure 6a and $\delta^{15}N$ values shown in Table 2a indicated that *Euchaeta sp.*, Cnidarian, *Hyperia* sp., and *Sagitta* sp. were for the most part eating at a higher trophic level compared to *Calanus* sp. and *Thysanoessa sp.* At the seven stations where *Cliona* sp. and *Limacina* sp. were simultaneously collected in 2005, an increase in $\delta^{15}N$ from prey (*Limacina* sp.) to predator (*Cliona* sp.) was observed in three stations, including 17 SHS, 15 FC, and 22 CHB (Table 2a). Three stations displayed the opposite trend including 18 EHB, 14 SHS, and 27 CHB. Station 23 CHB displayed similar $\delta^{15}N$ for *Cliona* sp. and *Limacina* sp.

Values of $\delta^{13}C$ calculated to be significantly different by the *t*-test are shown for 2003, 2004 and 2005 zooplankton collected at specific stations (Figure 5, circles). $\delta^{13}C$ values in Juvenile *Themisto* sp. were 2-5 ‰ depleted in ^{13}C compared to adult *Themisto* sp. from 2004 and 2005 in the FC region ($t = 4.90$, $p<0.05$ n-1 = 5). Further depleted in ^{13}C (3-4 ‰) values were reported in *Sagitta* sp. from 2005 compared to 2004 in EHB ($t = 6.27$, $p<0.05$, n-1 = 3). $\delta^{13}C$ ranges for individual zooplankton species are shown in Figure 6b.

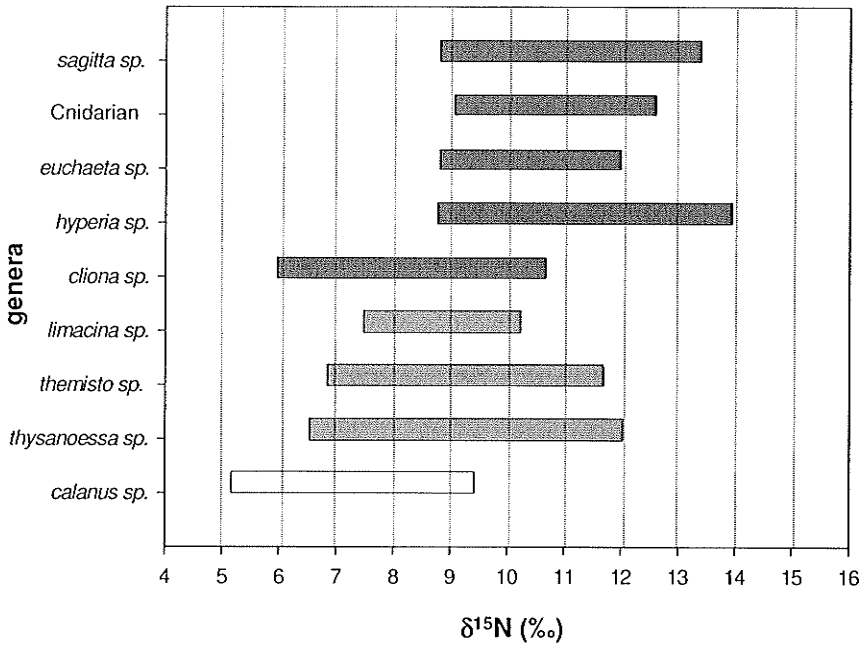
Cliona sp. had the most depleted range of $\delta^{13}C$ and Cnidarian had the most enriched (marine) range. Most zooplankton collected showed $\delta^{13}C$ values of marine character.

Values of $\delta^{13}C$ are shown for combined zooplankton genera from each region at individual stations in Table 2b. Values varied based on the carbon input in the different regions of Hudson Bay. $\delta^{13}C$ in Hudson Bay zooplankton was expected to reflect isotoically depleted signals in regions with greater freshwater influences, including WHB, SEHB, and EHB compared to isotopically enriched signals in NHS, FC, CHB and SHS due to marine character. Figure 3a shows values enriched in ^{13}C for *Calanus* sp. in FC and some stations in SHS, however values in NHS and at SHS station 11 (2003-2004 mean: -24.5 ± 0.865 ‰, Table 2b) are relatively depleted. *Thysanoessa sp.* displayed a similar trend enriched in ^{13}C (FC) and for most stations in SHS, however station 17 (2005 mean: -23.7 ‰, Table 2b) was depleted. Values depleted in ^{13}C were observed in WHB, SEHB, and EHB except for station AN03 (2005 mean: -20.8 ‰, Table 2b). In *Themisto* sp. (Figure 3c), high $\delta^{13}C$ was observed in NHS as well as in SHS compared to WHB, SEHB, and EHB. $\delta^{13}C$ for FC from different years was calculated significantly different by the *t*-test, however results show values enriched in ^{13}C for adult *Themisto* sp. and depleted ^{13}C signals only in juvenile *Themisto* sp. from the 2005 dataset (Figure 5, FC *Themisto* sp.). *Sagitta* sp. has values enriched in ^{13}C in FC and SHS compared to other regions except for FC station 16 (2005 mean: -25.5 ‰, Table 2b). $\delta^{13}C$ appeared to be influenced by region in Hudson Bay. $\delta^{13}C$ in zooplankton from CHB were low compared to values observed in zooplankton from stations in NHS, FC, and SHS. This was an unexpected result considering the marine character of CHB including low DOC, high

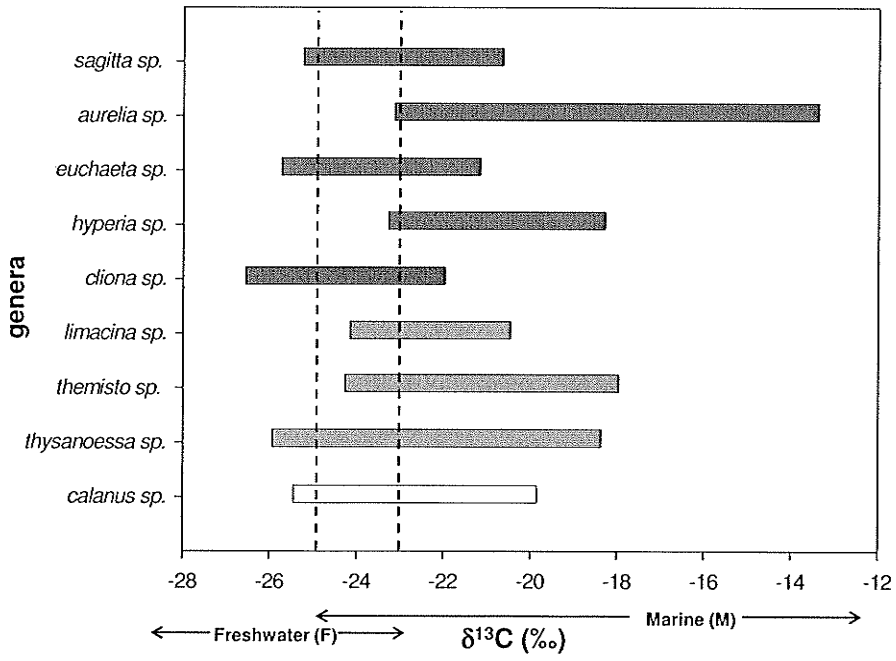
salinity and high $\delta^{18}O$ (Figure 2). An anomaly was seen in Cnidarian which displayed values enriched in ^{13}C (WHB, CHB, SEHB, SHS and EHB) compared to all other zooplankton in these regions (Table 2b).

Figure 6. Ranges in (a) $\delta^{15}N$ (b) $\delta^{13}C$ for zooplankton in Hudson Bay.
Yellow bars: planktivores, Red bars: omnivores, Blue bars: carnivores

a.



b.



HgT and MeHg in zooplankton 2003-2005.

Levels of HgT for all zooplankton are shown in Table 2c. Regional differences in HgT are shown for *Calanus* sp., *Themisto* sp., *Thysanoessa sp.* and *Sagitta* sp. in Figure 3a-d. In general, concentrations in *Cliona* sp. and *Limacina* sp. were 2-3 times higher compared to *Euchaeta sp.*, *Hyperia* sp., and *Themisto* sp., which were approximately double the levels seen in *Sagitta* sp., *Thysanoessa sp.*, *Calanus* sp. and Cnidarian. HgT levels reflected different zooplankton eating habits for some genera. High HgT levels discovered in *Cliona* sp. and *Euchaeta sp.* were expected based on their carnivorous nature, however high levels in *Limacina* sp. was not expected (Table 2c) because it is an ideal prey genera for carnivores. Given the fact that *Themisto* sp., Cnidarian and *Sagitta* sp. are also carnivorous, it was expected that they would have higher HgT levels compared to the strictly planktivorous *Thysanoessa sp.* and *Calanus* sp. However, this was only observed for *Themisto* sp.

Levels of MeHg and % MeHg in zooplankton are shown in Figure 4a-d and Table 2d-e for 4 common zooplankton genera at selected stations. Levels were lowest in *Calanus* sp., *Thysanoessa* sp., and *Sagitta* sp. compared to *Themisto* sp. and *Euchaeta* sp. Highest levels of MeHg were seen in CHB stations for *Calanus* sp., *Themisto* sp., and *Sagitta* sp. compared to WHB for *Thysanoessa* sp.. Highest % MeHg was seen in carnivorous zooplankton such as *Themisto* sp. and *Sagitta* sp., and % MeHg in *Cliona* sp. was double to that seen in *Limacina* sp. It appears as though FC, WHB, and CHB had higher MeHg levels in *Thysanoessa* sp., *Themisto* sp., and *Sagitta* sp. when compared to levels in the eastern regions of Hudson Bay. *Calanus* sp. had comparatively high levels in CHB,

however low levels in FC. Overall, a trend of higher MeHg in zooplankton harvested from the western Hudson Bay stations was observed.

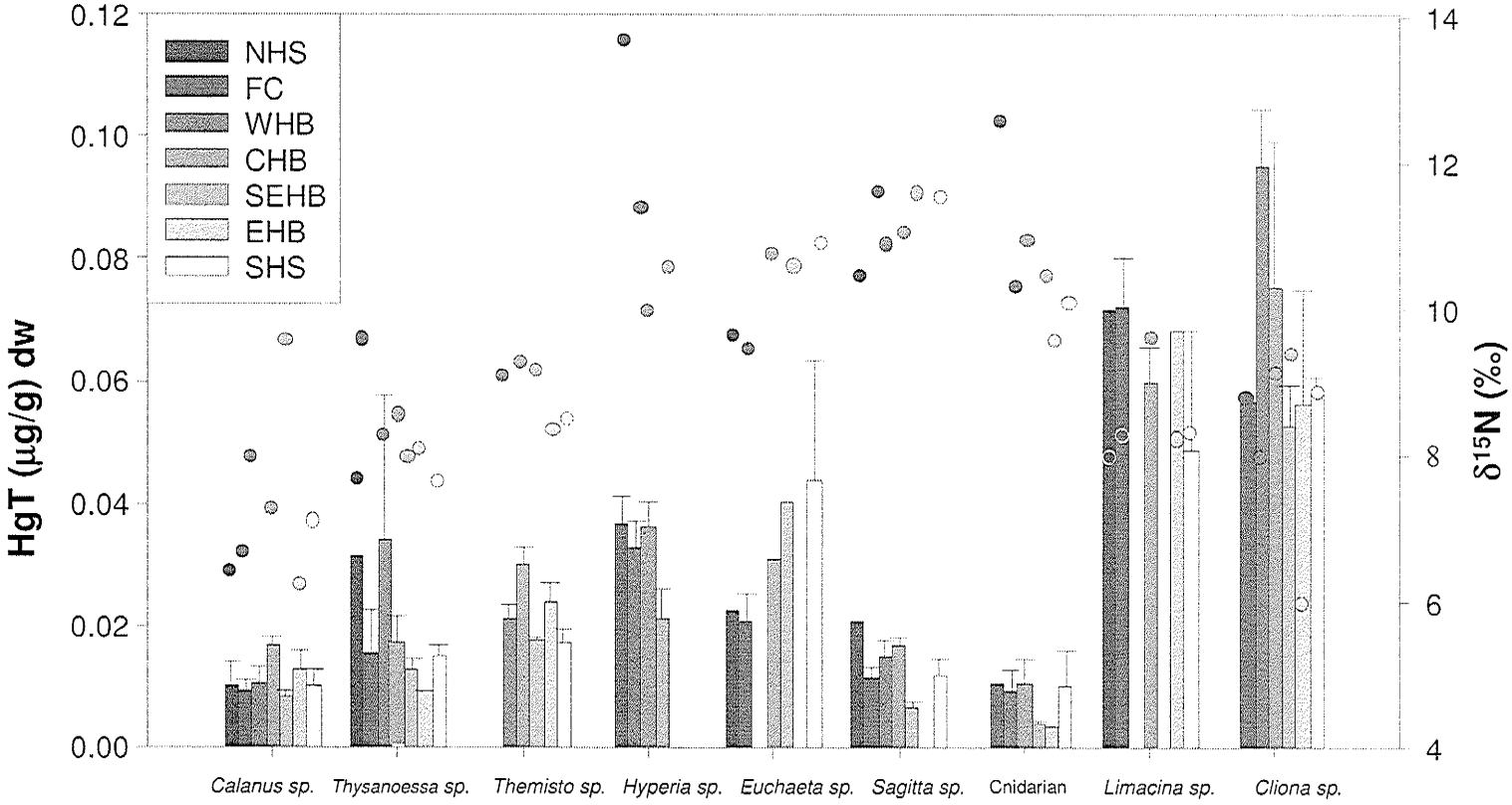
HgT, MeHg and stable isotope relationships.

Figure 7 shows the interspecies differences in HgT and $\delta^{15}N$ levels. Low values of $\delta^{15}N$ for *Calanus* sp. corresponded to low levels in HgT for the dataset (Figure 7). $\delta^{15}N$ values for Cnidarian, *Thysanoessa sp.*, and *Themisto* sp. were 1-3 ‰ higher compared to *Calanus* sp. in all regions of Hudson Bay excluding SEHB for the latter two zooplankton (Table 2a). Corresponding HgT values were the lowest in Cnidarian, and slightly higher in *Thysanoessa sp.* compared to *Calanus* sp. (Table 2c). Values of $\delta^{15}N$ for *Sagitta* sp., *Hyperia* sp., Cnidarian, and *Euchaeta sp.* were between one and two trophic levels ($\delta^{15}N$ 3-6 ‰) higher compared to *Calanus* sp. as shown in Figure 6. HgT concentrations for *Sagitta* sp. and Cnidarian were 2-3 times lower compared to *Euchaeta sp.*, and were further comparable to those of *Calanus* sp. in the dataset, which was an unexpected result. Furthermore, *Cliona* sp. and *Limacina* sp. displayed a unique trend, with high levels of HgT and intermediate $\delta^{15}N$ signatures, which was also unexpected. Regional variations in $\delta^{15}N$ such as high values in WHB, CHB and SEHB *Calanus* sp. as well as high $\delta^{15}N$ for FC *Thysanoessa sp.* (Table 2a) did not reflect a trend in HgT, which remained relatively consistent within species.

Figure 7. HgT (± standard error) levels and $\delta^{15}N$ of zooplankton genera in different regions of Hudson Bay 2003-2005 Merica / ArcticNet data.

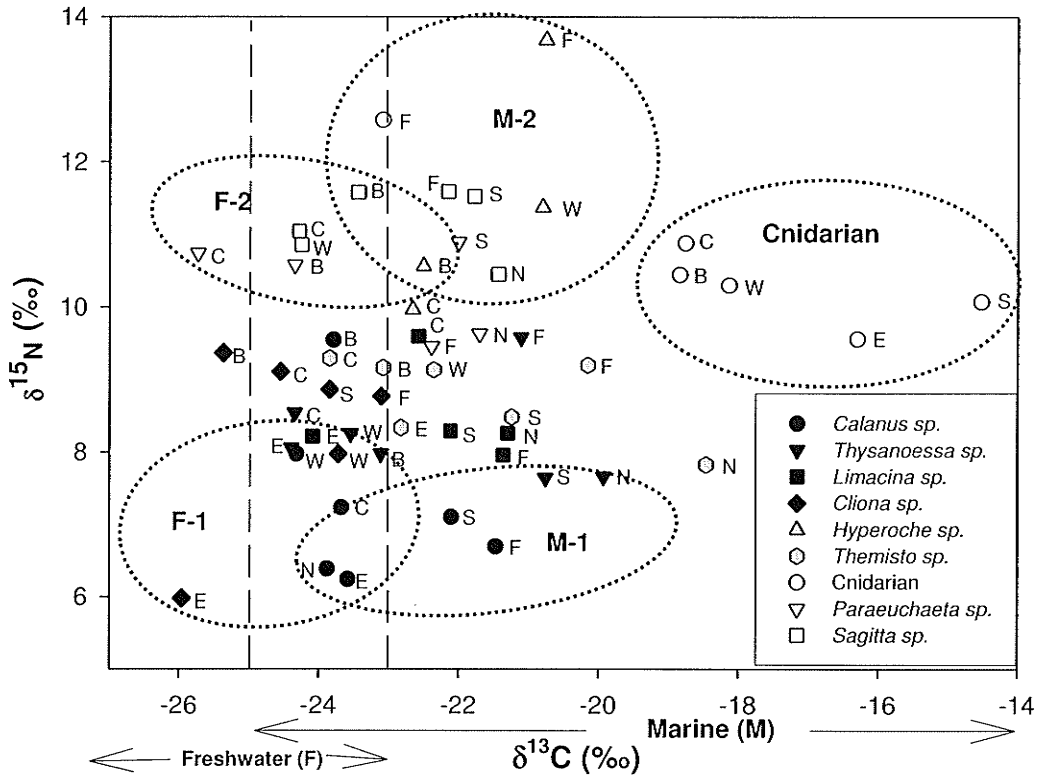
North Hudson Strait (NHS), Foxe Channel (FC), West Hudson Bay (WHB), Central Hudson Bay (CHB), South East Hudson Bay (SEHB), East Hudson Bay (EHB), and South Hudson Strait (SHS); shaded circles: $\delta^{15}N$, bars: HgT

Calanus sp. n = 31, *Thysanoessa sp.* n = 19, *Themisto* sp. n = 42, *Euchaeta sp.* n = 9, *Cliona* sp. n = 19, *Sagitta* sp. n = 26.



Regional predator-prey relationships are shown for zooplankton in Figure 8. Freshwater influence from river runoff was evident by the ^{13}C depleted signatures in WHB (W), EHB (E), and SEHB (B) regions of Hudson Bay. Values enriched in ^{13}C indicated a marine signal coming from NHS (N), SHS (S), and FC (F). *Sagitta* sp., *Hyperia* sp. and *Euchaeta sp.* were the top predators among zooplankton in Hudson Bay (M-1 and F-1), and its prey appeared to be mainly *Calanus* sp. and *Thysanoessa sp.* (M-2 and F-2), whereas *Themisto* sp. appeared to be an intermediate predator that preyed on *Calanus* sp. and *Thysanoessa sp.* however it may have also been prey for *Sagitta* sp. and *Euchaeta sp.* as interpreted by $\delta^{15}N$ (Figure 8). Predator-prey relationships between *Cliona* sp. and *Limacina* sp. showed ^{13}C depleted signals in *Cliona* sp. compared to its exclusive dietary source *Limacina* sp. Both *Cliona* sp. and *Limacina* sp. had intermediate $\delta^{15}N$ values therefore they may also have been prey for *Sagitta* sp. and *Euchaeta sp.* The opportunistic predator Cnidarian occupied a niche of high $\delta^{15}N$ and $\delta^{13}C$.

Figure 8. Relationship between $\delta^{13}C$ and $\delta^{15}N$ for zooplankton in different regions of Hudson Bay 2003-2004 and 2005 combined datasets.
N = North Hudson Strait, F = Foxe Channel, W = West Hudson Bay, C = Central Hudson Bay, B = Belcher Islands (Southeast) Hudson Bay, E = East Hudson Bay, S = South Hudson Strait
M = marine, F = freshwater, 1 = prey, 2 = predator. ($r^2 = 0.0465$, $P > 0.1$)



Average HgT (± s.e.) and average $\delta^{15}N$ (± s.e.) relationships are shown in Figure 9a. Strong correlations were observed between planktivorous zooplankton and their carnivorous predators ($r^2 = 0.999$, $P < 0.001$, $r^2 = 0.767$, $P = 0.052$, respectively). *Hyperia* sp. fit into the high end of one food chain, even though it has been found to exist in a parasitic relationship with Cnidarian. A negative slope in the *Calanus* sp.→*Thysanoessa* sp.→Cnidarian→*Sagitta* sp. food chain was seen. Although the P value was insignificant, the negative slope indicated that no biomagnification was occurring in this food chain. The significant correlation in the *Calanus* sp.→*Thysanoessa* sp.→*Cliona* sp.→*Limacina* sp. food chain was somewhat misleading due to exceptionally high HgT in *Limacina* sp. Average MeHg (± s.e.) versus average $\delta^{15}N$ (± s.e.) for 2005 zooplankton are plotted (Figure 9b). As seen with HgT, strong linear relationships were observed ($r^2 = 0.996$, $P = 0.002$, $r^2 = 0.824$, $P = 0.092$, $r^2 = 0.679$, $P = 0.383$, respectively). Evidence in support of MeHg biomagnification was observed in Figure 9b, where MeHg levels in *Limacina* sp. were approximately half of that seen in *Cliona* sp. Note that the small sample size ($n = 1$) for each of these zooplanktons poses the need for more sampling in order to confirm this result. A plot of [HgT-MeHg] versus $\delta^{15}N$ is shown in Figure 9c. Here we observe that the difference between total Hg and MeHg shows negative slopes, indicating biodilution of all HgT that isn't MeHg (i.e. inorganic mercury) in the organisms. These correlations were not significant (i.e. $P>0.05$), therefore showing that biodilution in the pelagic food chain is not occruing in Hudson Bay, and the lack of positive slopes confirms that biomagnification of the inorganic Hg species is not occuring either. One exception in Figure 9c was seen in the *Calanus* sp. → *Thysanoessa* sp. → *Limacina* sp. → *Cliona* sp. food chain. A positive (although

insignificant) slope (dotted line Figure 9c) was observed. We suspect that biological factors are driving *Limacina* sp. to have a high HgT and lower MeHg, which may be impeding a negative slope in this food chain.

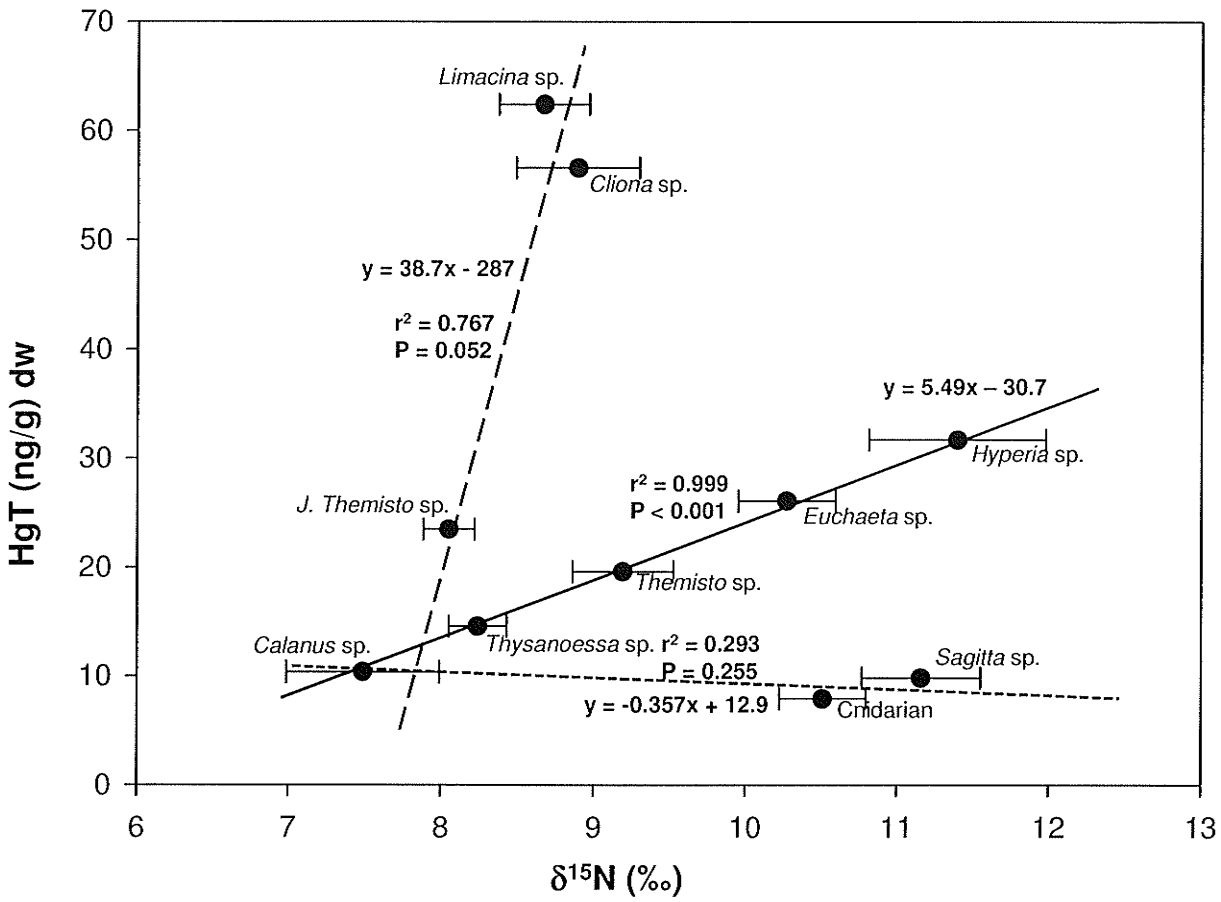
Regional HgT as a function of $\delta^{13}C$ are shown for the dataset in Figure 10a. The highest HgT levels were found in *Cliona* sp. coupled with some of the lowest $\delta^{13}C$ values in all regions. Cnidarian had the lowest HgT levels and the highest $\delta^{13}C$. Other zooplankton had lower HgT levels and a wider range of $\delta^{13}C$. Figure 10b displays similar relationships for MeHg values as a function of $\delta^{13}C$. There was a wide range of $\delta^{13}C$ signals for different zooplankton, especially in CHB.

Churchill Polar Ice Camp 2005.

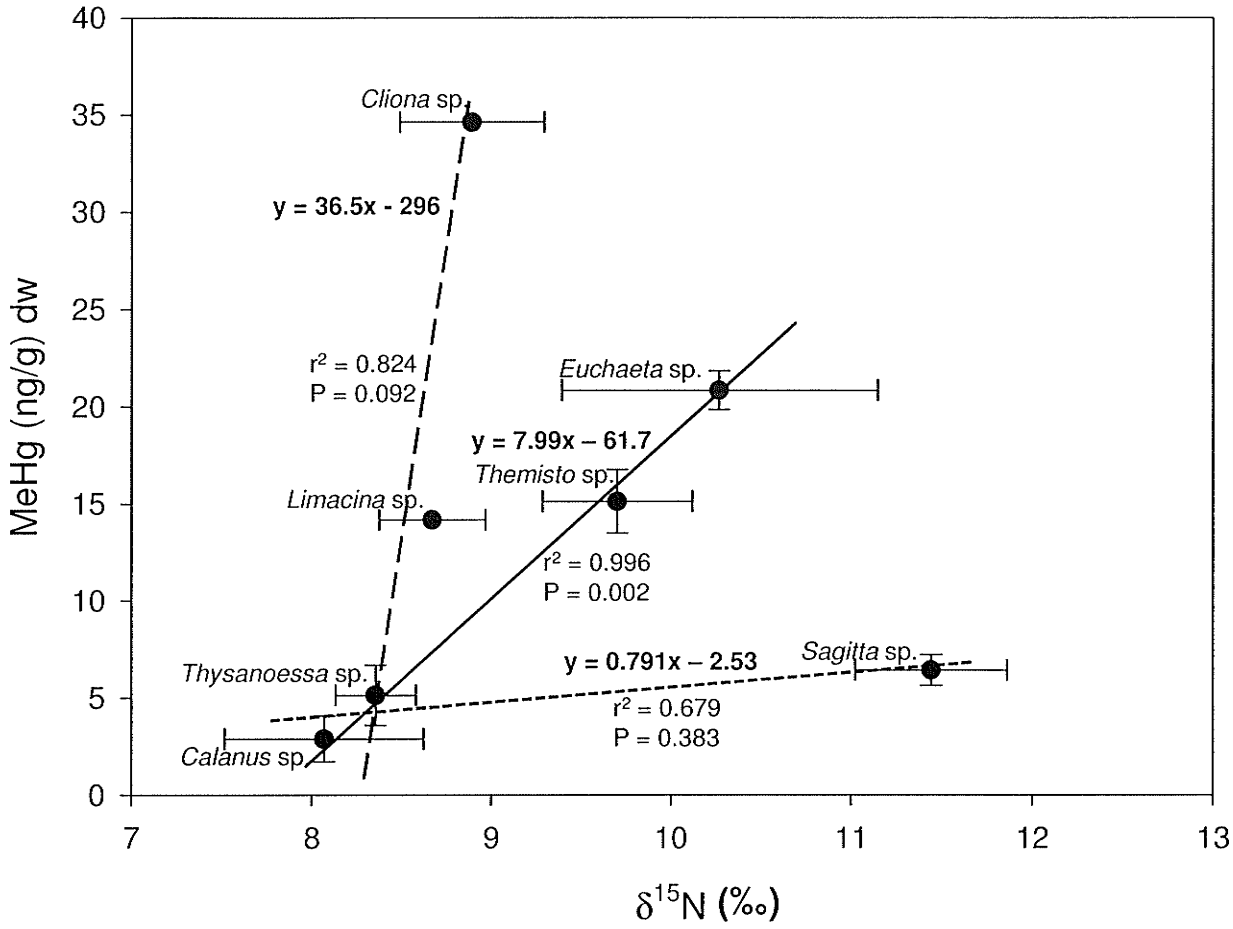
Stable isotope values for POM from the 2005 Button Bay sample site were 6.67 ‰ and -24.49 ‰, n = 12 for $\delta^{15}N$ and $\delta^{13}C$ (Kuzyk et al. 2006). Values for bulk biomass collected from the Button Bay sample site were high in $\delta^{15}N$ (9.79 ± 0.50 ‰, n = 8) and $\delta^{13}C$ (-22.85 ± 0.23 ‰, n = 8) compared to the POM analyzed by Kuzyk's research team. Isotope values for *Anonyx* sp. were 11.62 ± 0.25 ‰ and -19.64 ± 0.14 ‰ for $\delta^{15}N$ and $\delta^{13}C$, respectably. HgT values for bulk biomass and *Anonyx* sp. were 7.55 ± 1.3 and 56.5 ± 5.0 ng/g dw sample.

Figure 9. (a)HgT (b) MeHg (c) [HgT-MeHg] versus $\delta^{15}N$ (± standard error) relationships among zooplankton genera in Hudson Bay 2005 dataset.

a.



b.


MeHg (ng/g) dw
δ15N (‰)
Cliona sp.
y = 36.5x - 296
r2 = 0.824
P = 0.092
Euchaeta sp.
y = 7.99x – 61.7
Themisto sp.
Limacina sp.
r2 = 0.996
P = 0.002
Sagitta sp.
y = 0.791x – 2.53
r2 = 0.679
P = 0.383
Thysanoessa sp.
Calanus sp.

c.

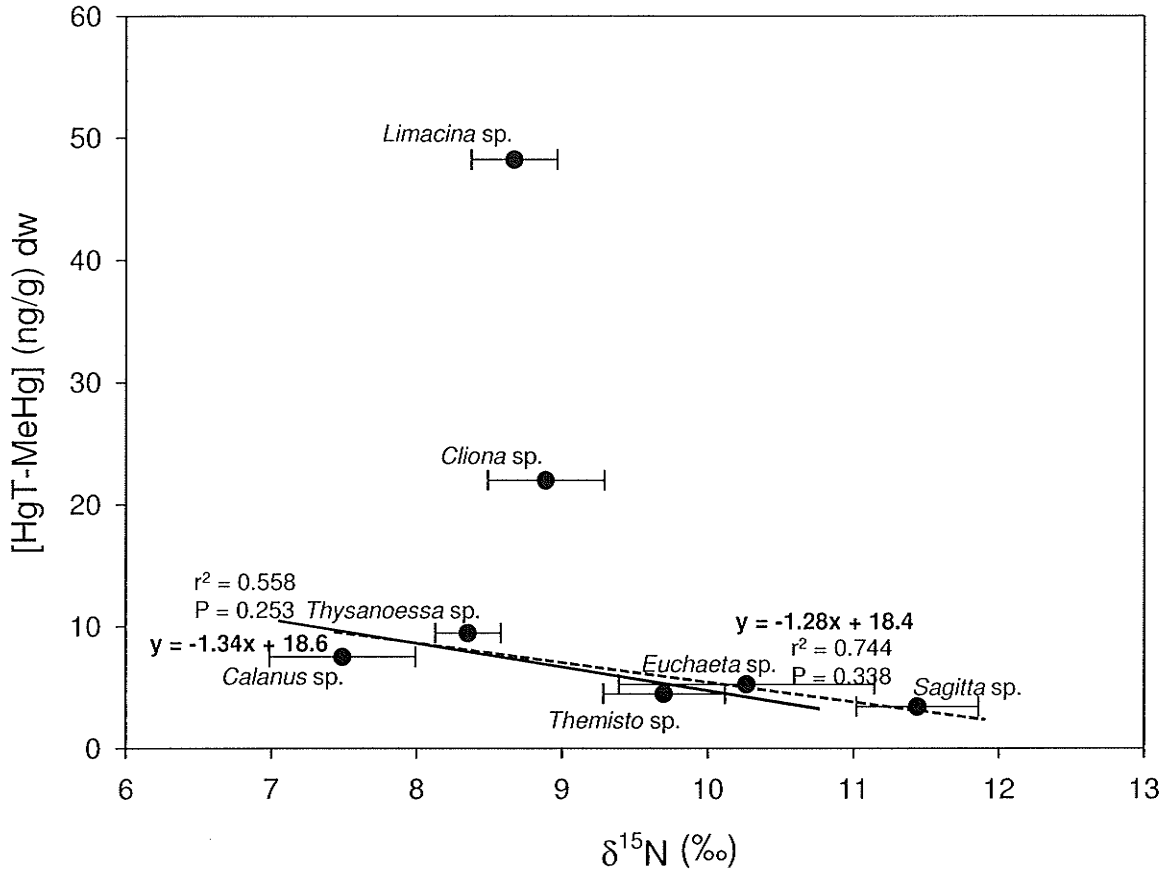
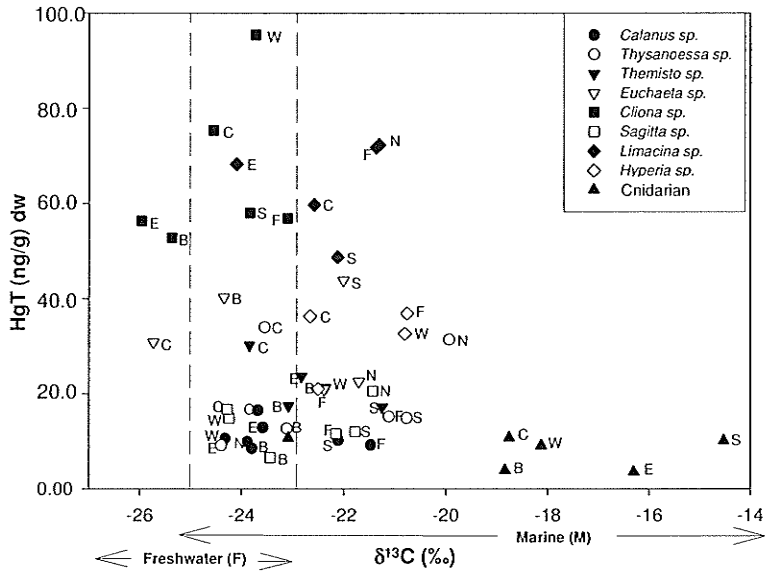
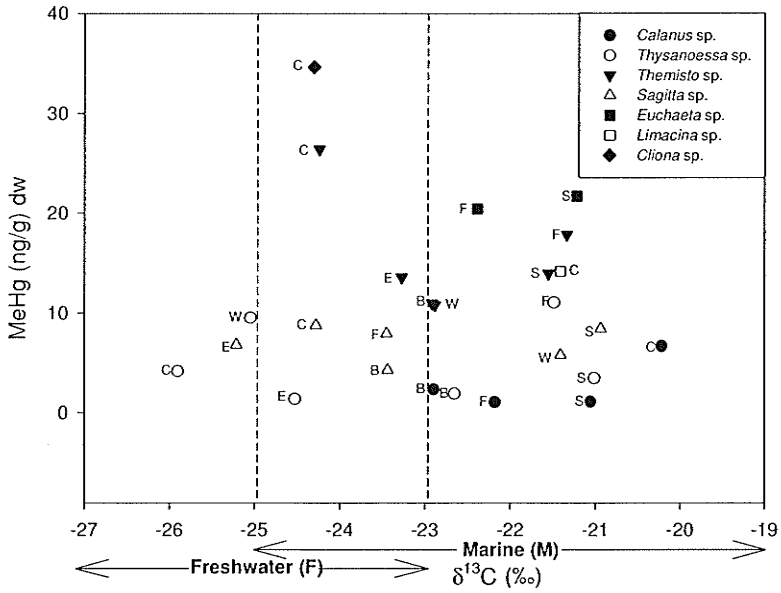

60
50
40
30
20
10
0
[HgT-MeHg] (ng/g) dw
6
7
8
9
10
11
12
13
δ15N (‰)
Limacina sp.
Cliona sp.
r2 = 0.558
P = 0.253
Thysanoessa sp.
y = -1.34x + 18.6
Calanus sp.
y = -1.28x + 18.4
r2 = 0.744
P = 0.338
Euchaeta sp.
Sagitta sp.
Themisto sp.

Figure 10. Relationship between $\delta^{13}C$ and (a) HgT (b) MeHg for zooplankton in different regions of Hudson Bay 2003-2004 and 2005 combined datasets.
N = North Hudson Strait, F = Foxe Channel, W = West Hudson Bay, C = Central Hudson Bay, B = Belcher Islands (Southeast) Hudson Bay, E = East Hudson Bay, S = South Hudson Strait

a.



b.



Biomagnification factors 2003-2005.

Mean (± standard error) Biomagnification factors (BMFs) for MeHg in zooplankton is shown in Figure 11 and Table 3. BMFs were calculated using equation 2b. We estimated BMFs for planktivorous zooplankton including *Calanus* sp. and *Thysanoessa sp.* based on POM as the prey species. *Thysanoessa sp.* was shown to have a wide range of $\delta^{15}N$ (Figure 6) which indicated a potential mixture of species analyzed including planktivores and omnivores, however for simplicity we assumed planktivorous feeding behaviour for BMF calculations in agreement with feeding experiments on Antarctic *Thysanoessa sp.* (Ikeda and Dixon 1984) as well as feeding behaviour of some neritic *Thysanoessa sp.* in the Arctic (Falk-Petersen et al. 2000). We consider our findings in Figure 11 rough estimates of BMF's for planktivorous zooplankton. Regional BMFs for *Limacina* sp. were estimated based on the percentage of HgT that was measured as MeHg in the sample from station 27 (23.7%), which was applied to other stations that had HgT values for *Limacina* sp. and *Calanus* sp. Similarly, regional BMFs for *Euchaeta* sp. were estimated based on approximately 100% HgT as MeHg, as seen in our results (Table 2d). BMFs were greater than 1 for *Cliona* sp., *Themisto* sp., *Limacina* sp., *Thysanoessa* sp. (some regions) and *Euchaeta* sp. BMFs were less than or closer to 1 for *Calanus* sp. *Thysanoessa* sp. (some regions) and *Sagitta* sp. Regional variability was observed, including highest BMFs consistently in the FC and SHS regions for different zooplankton (Figure 11). Furthermore, the slope of the *Calanus* sp.→*Thysanoessa* sp.→*Themisto* sp.→*Euchaeta* sp. food chain was steeper with respect to MeHg compared to HgT

(Figure 9a-b, $m_{HgT} = 5.492$, $m_{MeHg} = 7.986$). This indicated that biomagnification was accelerated for MeHg species compared to HgT.

Figure 11. BMFs (± standard error) for MeHg in Hudson Bay zooplankton for different regions based on equation 2b calculations.*

POM = Particulate Organic Matter, cal = *Calanus* sp., thys = *Thysanoessa* sp., them = *Themisto* sp., clion = *Cliona* sp., lima = *Limacina* sp., sag = *Sagitta* sp., euch = *Euchaeta* sp.
* MeHg levels in POM are an estimate from Morel et al. 1998. *Limacina* sp. estimate based on 27.3% MeHg from n = 1 sample analyzed in our results; *Euchaeta* sp. estimate based on 100% MeHg from n = 3 samples analyzed in our results.

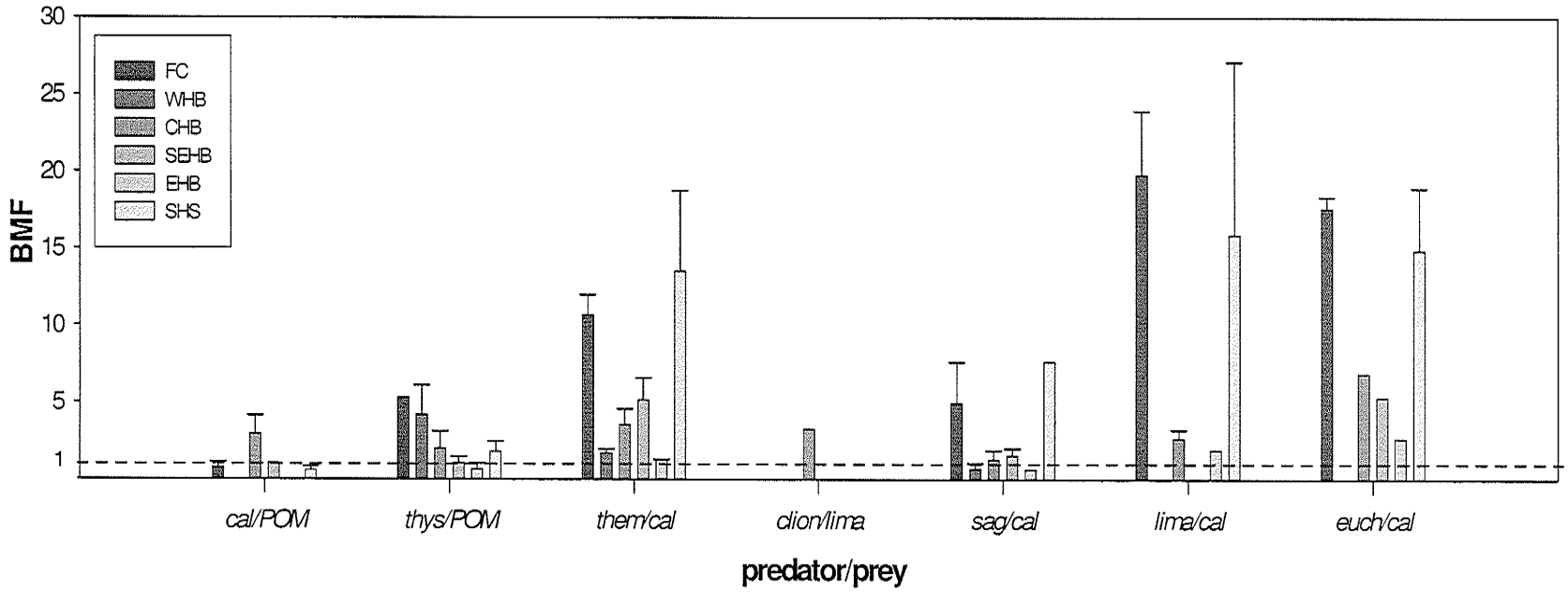


Table 3. BMFs (± standard error) for MeHg in Hudson Bay zooplankton for different regions*.

* POM from HB ($\delta^{15}N$ = 4.61 ± 0.84, Kuzyk pers. comm.) and biomass from Churchill (HgT = 7.55 ng/g) provided an estimate for planktivorous zooplankton BMFs.. MeHg levels in POM are an estimate from Morel et al. 1998, *Limacina* sp. estimate based on 27.3% MeHg from n = 1 sample analyzed in our results; *Euchaeta* sp. estimate based on 100% MeHg from n = 3 samples analyzed in our results.

Predator/Prey	Region	BMF predator	n
Calanus sp. / POM	FC	0.748	2
Calanus sp. / POM	CHB	2.91	2
Calanus sp. / POM	SEHB	1.03	1
Calanus sp. / POM	SHS	0.587	2
Thysanoessa sp. / POM	FC	5.31	1
Thysanoessa sp. / POM	WHB	4.17 ± 1.9	3
Thysanoessa sp. / POM	CHB	2.00	2
Thysanoessa sp. / POM	SEHB	1.04	2
Thysanoessa sp. / POM	EHB	0.635	2
Thysanoessa sp. / POM	SHS	1.80	2
Cliona sp. / *Limacina* sp.	CHB	3.24	1
Themisto sp. / *Calanus* sp.	FC	10.6	2
Themisto sp. / *Calanus* sp.	WHB	1.70 ± 0.26	4
Themisto sp. / *Calanus* sp.	CHB	3.54 ± 1.0	3
Themisto sp. / *Calanus* sp.	SEHB	5.15 ± 1.4	4
Themisto sp. / *Calanus* sp.	EHB	1.26	2
Themisto sp. / *Calanus* sp.	SHS	13.5	2
Euchaeta sp. / *Calanus* sp.	FC	17.6	2
Euchaeta sp. / *Calanus* sp.	CHB	6.85	1
Euchaeta sp. / *Calanus* sp.	SEHB	5.33	1
Euchaeta sp. / *Calanus* sp.	EHB	2.65	1
Euchaeta sp. / *Calanus* sp.	SHS	14.9	2
Sagitta sp. / *Calanus* sp.	FC	4.97	2
Sagitta sp. / *Calanus* sp.	WHB	0.675	2
Sagitta sp. / *Calanus* sp.	CHB	1.31	2
Sagitta sp. / *Calanus* sp.	SEHB	1.55 ± 0.45	4
Sagitta sp. / *Calanus* sp.	EHB	0.645	1
Sagitta sp. / *Calanus* sp.	SHS	7.63	1
Limacina sp. / *Calanus* sp.	FC	19.8	2
Limacina sp. / *Calanus* sp.	CHB	2.65 ± 0.55	3
Limacina sp. / *Calanus* sp.	EHB	1.93	1
Limacina sp. / *Calanus* sp.	SHS	15.9	2

Discussion

Water chemistry, HgT, and MeHg.

MeHg is assimilated easily in organisms whereas other forms of Hg are not as easily assimilated (Campbell et al. 2003). This is due to microorganisms that catalyze the reaction that forms covalent bonds between Hg and Methane (CH_4). Chloride, sulphur and other organic compounds influence the types of microorganisms available to methylate Hg. Hudson Bay is considered "nutrient poor" (Bajkov 1975, Harvey 2006) and lacks many of these influences compared to more tropical oceans, therefore it's not surprising that % MeHg levels in Hudson Bay water are low (Figure 2).

$\delta^{15}N$ in zooplankton.

There were no significant seasonal differences in mean $\delta^{15}N$ when comparing zooplankton from 2003-2004 to the samples collected from 2005 as shown in Table 4 ($t_{calc} < 2.306$, $p<0.05$, n-1 d.o.f ≥ 8). This implies that zooplankton in Hudson Bay did not significantly change their diet between late summer and early fall. Analysis of $\delta^{15}N$ allows for assimilated as well as injested food in an organism's diet over multiple meals to be interpreted by trophic level (Atwell et al. 1998). Even though the 2003-2004 cruises occurred in August and the 2005 cruise occurred in late September – October, it is possible that there still wasn't a significant amount of time between seasons to measure any substantial dietary change. Another explanation is that zooplankton switched their diets to other sources with similar values of $\delta^{15}N$ (R. Macdonald, pers. comm.) The *t*-test for significance also showed no regional $\delta^{15}N$ differences for *Cliona* sp., *Euchaeta sp.*,

Thysanoessa sp., *Themisto* sp. and *Sagitta* sp. ($t_{calc} < 2.306$, data not shown) with the one exception being *Calanus* sp. *Calanus* sp. had mean $\delta^{15}N$ almost one trophic level higher at 9.54 in SEHB (Figures 3a and 6a, Table 2a). This may be explained by zooplankton excreting the lighter isotope (i.e. ^{14}N) and this light isotope lowers the true nitrogen isotope ratio ($\delta^{15}N$) in euphotic zone phytoplankton. High $\delta^{15}N$ in nitrate exists after denitrification processes in the euphotic zone of marine systems acting as a $\delta^{15}N$ source for phytoplankton. This source ^{15}N is readily available, therefore fluctuations of $\delta^{15}N$ in phytoplankton may transfer to marine organisms that prey primarily on phytoplankton such as *Calanus* sp. (Altabet 1988, Lajtha and Michener 1994). This significant variation in regional $\delta^{15}N$ was not seen in other zooplankton simply because they don't primarily feed on phytoplankton. *Calanus* sp. are abundant planktivorous zooplankton that feed on diatoms, phytoplankton, and microalgae (Skarra and Kaartvedt 2003). Spawning and reproduction of *Calanus* sp. has been shown to correspond to algal blooms in early spring (April – May) and summer (Tourangeau and Runge 1991). *Calanus* sp. migrate in the water column to feed nocturnally on the under-ice algae in spring, in order to lengthen their feeding season in the Arctic, which may also have contributed to the high $\delta^{15}N$ values observed in SEHB stations. This nocturnal feeding pattern is also an adaptation in order to avoid predation. The population in the Southeast corner of Hudson Bay is predominantly adult females during the spring algal bloom (Runge and Ingram 1988, Ingram and Prinsenberg 1998).

Table 4. Test of significant difference for seasonal changes, *t*-test at the 95% confidence interval ($P<0.05$, $t_{critical} = 2.306$ d.o.f ≥ 8).

Zooplankton	d.o.f.	t_{calc} HgT	t_{calc} $\delta^{15}N$	t_{calc} $\delta^{13}C$
Calanus sp.	11	1.350	0.955	1.33
Thysanoessa sp.	8	0.256	0.782	0.841
Themisto sp.	15	1.277	0.598	1.833
Sagitta sp.	15	3.644	0.594	0.852
Euchaeta sp.	8	2.671	1.756	0.038
Cliona sp.	8	1.392	0.528	0.482

High $\delta^{15}N$ in *Calanus* sp. may also have regional influence. South East Hudson Bay (SEHB) encompasses the Belcher Islands, and is marked by sharp drop-offs along the coastal regions to defining deeper waters, irregular bottom patterns, and islands scattering the shoreline (Leslie 1965). The bottom sediments consist of a fine silt material much different than the coarse sands along the Western Hudson Bay shore. South East Hudson Bay is further influenced by James Bay, which is a major tributary less than 50 m deep that contributes approximately half of the freshwater input (10.1×10^3 m^3/s) to Hudson Bay (Prinsenberg 1980). This was verified by the comparatively low salinity and high DOC values as shown for SEHB in Figure 2. Further influence from the Great Whale and Little Whale Rivers may be influencing the nutrient load to SEHB and causing increased $\delta^{15}N$ in phytoplankton which was reflected in *Calanus* sp. of the region, as well as the nutrient loads from the Churchill, Nelson and Hayes River due to the cyclonic surface currents moving these water masses into SEHB. Kuzyk (pers. comm.) reported spring $\delta^{15}N$ values in POM to be 6.67 ‰ in the Churchill region (WHB), however bulk biomass $\delta^{15}N$ from the same region was reported to be 9.79 ± 0.50 ‰ from this study. This discrepancy may be explained by the techniques used to collect POM that filtered out a lot of the biomass that was suspected of driving up the trophic enrichment of the bulk isotope sample. Due to surface anti-cyclonic currents, bulk biomass as well as POM from

the spring Churchill collection may have made its way to SEHB as food for copepods by the fall of the same year during the ArcticNet 2005 expedition.

The Chaetognath *Sagitta* sp. had one of the highest values of $\delta^{15}N$ (Figures 3d, 6a, Table 2a). A study by Falk-Petersen (1987) found that *Sagitta* sp. has trace amounts of wax esters in its composition compared to *Calanus* sp. and *Themisto* sp. which has significantly higher levels. This may contribute to high $\delta^{15}N$ values in *Sagitta* sp. because low levels of wax ester are indicative of low energy reserves (Falk-Petersen et al. 1987). *Sagitta* sp. therefore may be feeding year round to make up for its lack of wax ester, which in turn drives up its $\delta^{15}N$ values. The copepods family incorporates a wide range of primary consumers including *Calanus* sp. as previously described and *Euchaeta sp.*, which is a type of carnivorous copepod that feeds on smaller planktivorous copepods such as *Calanus* sp. (Skarra and Kaartvedt 2003). The euphausiids family incorporates *Thysanoessa sp.*, which is a primary source of food for pelagic fishes and marine mammals. Copepods and euphausiids are capable of in situ synthesis of wax esters because they contain essential fatty acids and fatty alcohols, which subsequently provide carnivorous zooplankton such as *Sagitta* sp. with a year-round lipid rich diet. *Sagitta* sp. is not dependent on reserve lipids during periods of low productivity; rather it is able to catch copepods and euphausiids year round in order to harvest lipids and catabolize them into energy. The absence of wax esters in *Sagitta* sp. may also be an adaptation to deter large prey such as pelagic fish from preying upon them, due to their inability to provide the necessary energy reserves for the long winter (Falk-Petersen et al. 1987). Recent studies report that high $\delta^{15}N$ values may be due to the cannibalistic nature of *Sagitta* sp.

upon periods of low productivity (Terazaki 1996, Giesecke et al. 2004, Tönnesson and Tiselius 2005). A third possible reason for the high $\delta^{15}N$ in *Sagitta* sp. (and a possible explanation for *Euchaeta sp.*) may be attributed to an enrichment of the heavy isotope (^{15}N) caused by food deprivation i.e. lack of source ^{14}N (Lajtha and Michener 1994). Based on the sample collections occurring in late August and in early fall when food is in abundance, low levels of wax esters and its year-round feeding behaviour seem like a probable explanation for the high $\delta^{15}N$ values in *Sagitta* sp.

The pteropod family consists of a wide variety of pelagic snails and "sea slugs", including *Cliona* sp. and *Limacina* sp. More commonly known as the sea butterfly, *Cliona* sp. exclusively feeds on *Limacina* sp. (Lalli and Gilmer 1989). It can grow to a maximum length of 25 mm. The life cycle of *Cliona* sp. is a minimum of 2 years (Böer et al. 2005). *Limacina* sp. is also prey for ctenophores, sea birds, as well as polar cod (Gannefors et al. 2005). *Limacina* sp. feeds on other zooplankton and juveniles of its own kind, and relies on this food source for nutrients and growth upon hatching. This is different compared to *Calanus* sp., which uses reserve lipids in the early life stages in order to sustain itself (Gannefors et al. 2005). The $\delta^{15}N$ levels in *Cliona* sp. were almost one trophic level lower compared to *Sagitta* sp. and comparable to *Limacina* sp. This may be due to the presence of alkyldiacylglycerol ethers (DAGE), which is a type of lipid biosynthesized in *Cliona* sp. in high amounts. It is further absent from most other arctic zooplankton (Kattner et al. 1998, Hagen and Auel 2001). The presence of DAGE increases the lipid component of *Cliona* sp., which may be used as an energy reserve when food is scarce. This is contrary to *Sagitta* sp., which isn't able to synthesize any

energy reserves. DAGE production by *Cliona* sp. is similar to the use of wax esters by *Themisto* sp, *Calanus* sp. and *Thysanoessa sp.* as noted earlier. One would expect a lower $\delta^{15}N$ in *Limacina* sp. due to its predation by *Cliona* sp., however these zooplankton are known to have similar $\delta^{15}N$ signatures (Kattner et al. 1998). This finding agreed with our results from Hudson Bay (Figure 9a-b). The diet of *Limacina* sp. consists of small pelagic zooplankton, and cannibalism of its own offspring (Gannefors et al. 2005), therefore driving its $\delta^{15}N$ signature to levels higher than originally expected. Studies show that *Limacina* sp. has a "trapper" mechanism of feeding, in which it secretes a sticky sheath which can trap prey larger than itself (Gilmer and Harbison 1991), which may also have contributed to its higher $\delta^{15}N$ and HgT levels. We propose that there may be a link between lower than expected $\delta^{15}N$ in *Cliona* sp. and DAGE production. Furthermore, as an adaptation to its selective diet, *Cliona* sp. is able to biosynthesize DAGE and use this fatty acid as storage energy during periods of low productivity of *Limacina* sp. and during periods of reproduction (Böer et al. 2005).

Calanus sp. and *Thysanoessa sp.* had the lowest $\delta^{15}N$ values, which is due to their planktivorous feeding pattern (Falk-Petersen et al. 2000). *Calanus* sp. feeds predominantly on diatoms, phytoplankton, and microalgae, whereas *Thysanoessa sp.* are filter feeders that eat phytoplankton, detritus, and small zooplankton, therefore the $\delta^{15}N$ values of *Thysanoessa sp.* were slightly higher and of a wider range due to its opportunistic omnivorous feeding behaviour. In summary, high $\delta^{15}N$ in *Euchaeta sp.* Cnidarian, *Hyperia* sp., and *Sagitta* sp. indicated predators, whereas *Calanus* sp. and at

some stations *Thysanoessa sp.* appeared to be ideal prey in agreement with studies based on Hobson and Welch 1992, as well as Giesecke and Gonzalez 2004.

The family hyperiidae consists of a variety of amphipods and carnivorous zooplankton such as *Themisto* sp. and *Hyperia* sp. Hyperiidae are intermediates in the food web between the primary consumers and higher trophic level pelagic fishes and marine mammals (Auel et al. 2002). *Hyperia* sp. is a type of hyperiid amphipod that forms symbiotic relationships with cnidarians, ctenophores and other gelatinous zooplankton (Gasca and Roo 2005). *Hyperia* sp. acts as a marine parasite that latches onto cnidarians while in the juvenile phase and may maintain this association through to the adult phase (Towanda and Thuesen 2006). They are also known to over-winter in a symbiotic relationship with cnidarians which suggests a life cycle longer than 1 year. *Hyperia* sp. benefits from the mobility of cnidarians in order to adopt an opportunistic pelagic life style. The high levels of $\delta^{15}N$ reported in *Hyperia* sp. is proposed to be due to its parasitic nature and ability to feed off of its host tissue, namely cnidarians such as *Cyanea* sp. (Arai 1997). The cnidarian family also displayed high levels of $\delta^{15}N$ due to its natural predation on fish larvae, fish eggs, and copepods. The hyperidae *Themisto* sp. is similar to *Sagitta* sp. in its carnivorous feeding habits, however its lipid composition is analogous to *Calanus* sp. and *Thysanoessa sp.* as well as other copepods consisting of a high percentage of wax ester in late fall and low percentage in early spring (Falk-Petersen et al. 1987). It has been reported that *Themisto* sp. synthesize wax esters for reserve lipids during periods of low productivity similar to *Calanus* sp., which caused its $\delta^{15}N$ signature to be lower than that of *Sagitta* sp. as we have seen in our results even though both were

carnivorous (Figures 2, 6, 7). The wide range of $\delta^{15}N$ signals reported in Hudson Bay zooplankton may also be due to different zooplankton having different $\delta^{15}N$ amino acid signatures. Small changes in $\delta^{15}N$ from prey to predator reflect large increases of $\delta^{15}N$ in certain amino acids from prey to predator (McClelland and Montoya 2002). With the case of *Cliona* sp. and *Limacina* sp., we propose that *Cliona* sp. may be lacking in these certain amino acids, therefore upon ingestion of *Limacina* sp., its trophic level didn't increase accordingly due to the lack of the appropriate amino acid composition.

Significantly different values of $\delta^{15}N$ for zooplankton at individual stations were shown (Figure 5 bars). The higher trophic positioning of adult *Themisto* sp. compared to juveniles in 2005 (Figure 5, FC) confirmed their carnivorous feeding behaviour upon maturity. Both *Sagitta* sp. and *Euchaeta sp.* in Figure 5 EHB displayed higher $\delta^{15}N$ signatures in the 2004 dataset compared to 2005, which may reflect a seasonal trend due to different sampling times in 2005 compared to 2004.

$\delta^{13}C$ in zooplankton.

There were no significant seasonal differences in mean $\delta^{13}C$ among zooplankton when comparing the samples from all of Hudson Bay in 2003-2004 to the samples from 2005 as shown in Table 4 ($t_{calc}<2.306$, $p<0.05$, n-1 d.o.f ≥ 8). There were significant differences for $\delta^{13}C$ between the coastal and marine regions ($t_{calc}>2.306$, $p<0.05$, n-1 d.o.f ≥ 8, data not shown). In general, coastal regions (WHB, SEHB, EHB) with higher river influence displayed depleted ^{13}C signals compared to marine regions (NHS, FC, SHS) as

seen in Figure 8. The cnidarian family displayed high $\delta^{13}C$ in all regions of Hudson Bay. We propose that lack of Dissolved Organic Matter (DOM) uptake as a food source by cnidarians in the medusae stage caused enriched ^{13}C when compared to its prey zooplankton. Our results were similar to enriched ^{13}C observed in jellyfish from the Adriatic Sea (Malej et al. 1993). The CHB region contained marine stations however $\delta^{13}C$ values (Table 2b, Figure 8) were low compared to FC and SHS, which was indicative of a carbon influence from river runoff. The CHB region consists of a shoal region in the centre of the Bay (50 m deep) surrounded by 150 m depressions, most likely due to pre-glacial land surface that has since eroded away (Leslie 1965). We propose that the shoal region combined with upwelling from the cyclonic surface currents may have contributed to relatively low $\delta^{13}C$ values in CHB. This was observed in 6 out of 9 zooplankton sampled from CHB (Figure 8 *Calanus* sp., *Thysanoessa sp. Euchaeta sp.*, *Themisto* sp., *Cliona* sp., *Sagitta* sp., Table 2b).

High $\delta^{13}C$ was observed in NHS and FC regions. The NHS region incorporates stations and water that flows along Baffin Island from the North Atlantic Ocean, therefore this surface water has the highest surface salinity (Figure 2) and lowest temperature of all defined regions (Martini 1986). This water flows into FC where the bathymetry indicates depths less than 100 m as well as deep crevices (Dunbar 1951). Water from FC continues its anti-clockwise surface flow around Hudson Bay. As the North Atlantic (surface) Current flows through the WHB region, it mixes with the freshwater influences from the Churchill, Nelson, Chesterfield, and other small contributing rivers (Martini, 1986). Western Hudson Bay (WHB) supports these 3 major estuaries that contribute the majority

of the freshwater to this region. The Nelson River Estuary is the largest of the three tributaries, after the Churchill River Diversion Project channelled approximately 85% of the flow from the Churchill River into the larger Nelson River for eventual hydrological use (Hertlein 1999). The amount of freshwater draining from the Nelson River into Hudson Bay is as high as 3,200 m^3/sec, which is a similar discharge to La Grande River Complex (Baker 1993).

The WHB region consists of very shallow depths, sand bars, and coarse sediment structure due to river runoff from the Nelson and Churchill, as well as strong tidal currents. Surface currents flow southeast towards the Belcher Islands from the WHB region (Martini 1986). The shallow depths and river influences caused ^{13}C depleted carbon throughout WHB stations as seen in most of our zooplankton results (Figures 3a-d, 10, Table 2b) with the exception of a few stations. Further river influence in the SEHB region as previously discussed mixes with the surface water flowing from the western shore, and $\delta^{13}C$ was shown to be depleted for zooplankton in this region as well as in EHB. SEHB and EHB was also characterized by low salinity (Figure 2) due to the increased freshwater influence, and is studded with three groups of islands, namely the Sleepers, Ottawa, and Nastapoka Islands. Most of the coastal shores in Hudson Bay are low, however high bluffs along the East Coast are a unique feature of this region (Martini 1986). Sediments are similar to those found in the SEHB region. The $\delta^{13}C$ for *Sagitta* sp. in FC showed an isotopically depleted signal at station 16 in 2005 (Figure 3a-d). We suspect that this may have been due to incorrectly grouping station 16 with stations further north in FC, whereas in reality station 16 had comparatively low $\delta^{13}C$ for many of

the zooplankton sampled in relation to other stations in the FC region. Station 16 in 2005 was in the mouth of Hudson Bay between two islands (Figure 1), and could easily have been incorporated into the EHB region.

Lowest $\delta^{13}C$ was found in *Cliona* sp. compared to other zooplankton (Table 2b), which may be due to the high (90%) efficiency in assimilating carbon from its prey as an adaptive strategy based on its monophagous diet (Lalli and Gilmer 1989). We noticed higher $\delta^{13}C$ in *Limacina* sp. compared to *Cliona* sp. *Limacina* sp. has a calcium carbonate shell similar to other marine molluscs, which causes expression of heavy ^{13}C isotope reflective of bicarbonate values in seawater (Perry et al. 1999). We analyzed *Limacina* sp. without the carbonate shell, therefore $\delta^{13}C$ was higher than expected.

Significantly different values of $\delta^{13}C$ for zooplankton in select regions were shown in the results (Figure 5, points). Depleted ^{13}C in Juvenile *Themisto* sp. (Figure 5) may be reflective of its planktivorous diet compared to mature carnivorous *Themisto* sp. The significant difference in $\delta^{13}C$ EHB *Sagitta* sp. may be indicative of the different feeding patterns during different seasons, namely summer (2003-2004) and fall (2005) due to phytoplankton blooms influencing the diet of carnivorous zooplankton. Furthermore, ice alge, pelagic algae, and particulate organic matter algae may have enough variation alone to account for our differences in $\delta^{13}C$ among zooplankton (R. Macdonald, pers. comm.)

HgT and MeHg in zooplankton.

This study showed no significant seasonal differences in mean HgT values for *Calanus* sp., *Thysanoessa sp.*, *Themisto* sp., and *Cliona* sp. as shown in Table 4 ($t_{calc} < 2.306$, $p<0.05$, n-1 d.o.f ≥ 8). The notion that different seasons have different body burden strategies i.e. regulation in winter and net accumulation in summer (Ritterhoff and Zauke 1997) was not seen in our Hudson Bay zooplankton samples. This may have been due to the collection times being too close together, namely late summer and early fall, therefore seasonal trends were masked by overall time of year similarities. All zooplankton except *Cliona* sp., *Limacina* sp., *Euchaeta sp.* and *Hyperiid* sp. had HgT values less than 30.0 ng/g dw. These findings agree with previous studies on the marine pelagic food web in California and estuaries in the Western Atlantic that report relatively low levels of HgT in different Copepod families and small fish compared to top predators (Knauer and Martin 1972, Cocoros and Cahn 1973). Our results from the Euphausiid and Chaetognath families also showed low HgT concentrations (< 50.0 ng/g dw) in agreement with current literature (Ritterhoff and Zauke 1997). These findings led to speculation that zooplankton may have adapted excretion methods that aid in regulating HgT in zooplankton, phytoplankton, and other lower trophic level organisms. High levels of HgT in *Cliona* sp., *Limacina* sp., *Hyperiid* sp., and *Euchaeta sp.* was however suggestive that these zooplankton may not have excretion mechanisms that regulate HgT levels. Mason (1995) reports higher than expected levels of HgT in phytoplankton compared to zooplankton, which indicates that there is more naturally occurring Hg for phytoplankton to uptake from their environment than researchers originally anticipated. According to our biomass from Churchill (which consisted of phytoplankton, ice algae, detritus and gelatinous

zooplankton), we did not see elevated HgT compared to zooplankton in Hudson Bay, which was suggestive that there isn't an excess of HgT in the Hudson Bay environment. Due to the wide range of organic material in our biomass, we propose that future projects incorporate individual HgT analyses of phytoplankton, ice algae, and detritus. This will help to determine if there are any differences at the base of the Hudson Bay pelagic food web.

Regional differences in HgT were not observed for *Calanus* sp., *Themisto* sp., *Hyperia* sp., Cnidarian, *Limacina* sp. and *Sagitta* sp. as shown in Figure 7. These findings agree with reports of spatial homogeneity in the Fram Strait and Greenland Sea for similar zooplankton samples (Ritterhoff and Zauke 1997). The regional variation in HgT for *Thysanoessa sp.* may have been due to the smaller total sample size used for the analysis (n = 19), similarily for *Euchaeta sp.* (n = 9) and *Cliona* sp. (n = 19), however *Hyperia* sp., Cnidarian, and *Limacina* sp. also had small total sample sizes analyzed (n < 20) and no regional variation was the result. Multiple year sampling (2003, 2004 MERICA and 2005 ArcticNet collections) may have further contributed to the regional variation for *Thysanoessa sp.*, *Euchaeta sp.*, and *Cliona* sp., compared to only one year of sample collections (ArcticNet 2005) for *Hyperia* sp., Cnidarian, and *Limacina* sp. For future studies, larger sample sizes may factor out regional differences and variations or provide evidence of their existence. Furthermore, this study of Hudson Bay grouped stations into regions, therefore different stations from the same region were treated as replicate samples. This is a problem when dealing with biological oceanography due to the limitations of zooplankton tows allotted to each researcher on a scientific vessel. True

replicate samples are often difficult to obtain. On average, levels of HgT in *Cliona* sp., *Limacina* sp., *Euchaeta sp.*, and *Hyperia* sp. were 2-6 times higher compared to *Calanus* sp. (Table 2c, Figure 7).

Only samples from 2005 were analyzed for MeHg, therefore no annual or seasonal trends with respect to MeHg were discernable for Hudson Bay zooplankton. To our knowledge, this is some of the first MeHg data reported in marine zooplankton at the genus level. Some higher MeHg levels were reported in WHB and CHB stations compared to EHB for some zooplankton. The water chemistry data displayed a trend of relatively low DOC and average MeHg in WHB and CHB (Figure 2). The geology and sediments of WHB may have more bioavailable mercury for uptake into the pelagic food web. We hypothesize that wetlands, estuaries, and other anthropogenic sources from upstream may be contributing to higher MeHg levels in zooplankton analyzed from WHB stations, which consequently influences stations in CHB as well. Old marine deposits may also be a factor, compared to stations in northeast Hudson Bay that have a shield bottom (Kuzyk, pers. comm.). MeHg concentrations in *Calanus* sp., *Thysanoessa* sp. and *Sagitta* sp. was on average less than 10.0 ng/g dw (Figure 4a-d) which was lower than levels reported in *Calanus* sp. (23-28 ng/g dw) from the SHEBA project, with sample stations collected from the Canada Basin to the Mendeleev Basin (Stern and MacDonald 2005). All carnivorous zooplankton analyzed had 3-5 times higher % MeHg compared to their planktivorous relatives, which may be due to the increase in assimilation efficiency of MeHg in amphipods compared to copepods (Lawson and Mason 1998). Lawson and Mason 1998 report that amphipods have developed strategies for extracting nutrients from detritus at more efficient rates compared to copepods, which is due to an adaptive

strategy based on where in the water column that amphipods are feeding in relation to copepods. Amphipods are epi-benthic or benthic, therefore they encounter a lot more detritus and are closer to MeHg sources in sediments compared to pelagic zooplankton such as copepods. This may explain why zooplankton such as *Themisto* sp. and *Sagitta* sp. in our study have higher MeHg assimilation efficiencies, because even though they are not strictly benthic feeders, they are scavengers and will consume more detritus compared to copepods. Studies also show that a 3-5 times increase in assimilation efficiency of MeHg occurs per trophic transfer (Watras and Bloom 1992). This agrees with our findings of the increase in MeHg from 27.3 % (*Limacina* sp.) to 67.1 % in *Cliona* sp. High % MeHg in *Sagitta* sp., *Themisto* sp., and *Euchaeta* sp. may have resulted from an increase in assimilation efficiency as well. The high % MeHg in carnivorous zooplankton may appear alarming, however levels overall for Hudson Bay zooplankton are relatively low compared to those reported in the high arctic (Stern and MacDonald 2005). These results need further investigation, as sample sizes were small and therefore we propose that more research is needed in order to confirm and compare MeHg levels to other studies.

HgT, MeHg and $\delta^{15}N$ relationships.

Figure 9a showed that there was a significant linear relationship in the *Calanus* sp→*Thysanoessa* sp.→*Themisto* sp.→*Euchaeta* sp.→*Hyperia* sp. food chain sampled for HgT and $\delta^{15}N$. Biomagnification transpires when a contaminant is accumulated as an increase in trophic level occurs. The high trophic positioning of predators *Sagitta* sp. and

Cnidarian coupled with low HgT levels and the insignificant linear relationship reflects a lack of biomagnification for some zooplankton. Previous studies report no evidence of inorganic Hg biomagnification with trophic level in zooplankton and small fish species (Knauer and Martin 1972, Cocoros and Cahn 1973). Recent studies also prove that trophic transfer of organic Hg is more efficient than that of inorganic Hg, therefore no biomagnification occurs for inorganic Hg species (Mason et al. 1995) which was reflected in some carnivorous zooplankton. The lack of biomagnification in some of these genera may be explained by the eat-the-grapes-and-spit-the-skins model as previously introduced. This has an effect on the accumulation of Hg species by zooplankton, because they digest cytoplasm and defecate the cell membrane material. There was significant correlation between MeHg and $\delta^{15}N$ in some Hudson Bay zooplankton (Figure 9b) in agreement with studies by Campbell et al. (2005). Similarly, there was insignificant linear correlation and a lack of biomagnification among the *Calanus* sp.→*Thysanoessa* sp. → *Limacina* sp.→*Cliona* sp. and *Calanus* sp.→*Thysanoessa* sp.→*Sagitta* sp. food chains, and some studies support this result (Minganti et al. 1996). We propose that the Hudson Bay pelagic zooplankton community is diverse and therefore feeds on many prey items, which ultimately is reflected in the dynamic ranges of $\delta^{15}N$ (Figure 6a). A diverse diet complicates a simple food chain in which biomagnification may occur, and turns it into a food web, whereupon this relationship may be transparent (Minganti et al. 1996).

The [HgT-MeHg] versus $\delta^{15}N$ plot showed negative slopes (Figure 9c). This verifyed that inorganic Hg biomagnification was not occurring in Hudson Bay. We propose that planktivores *Calanus* sp. and *Thysanoessa* sp. uptake HgT and MeHg by diffusion, which

causes a greater difference between HgT and MeHg levels; whereas diet is more of a factor as we increase in trophic level to carnivorous zooplankton (Watras and Bloom 1992). Unique characteristics of *Cliona* sp. and *Limacina* sp. caused a positive slope to be seen in the *Calanus* sp. → *Thysanoessa* sp. → *Limacina* sp. → *Cliona* sp. food chain (Figure 9c). *Cliona* sp. and *Limacina* sp. had mean levels of HgT six times higher compared to *Calanus* sp., however lower than expected $\delta^{15}N$ signatures. An explanation for the high levels of HgT in *Limacina* sp. may be due to its "trapper" feeding mechanism. *Limacina* sp. secretes a mucus that is able to trap zooplankton such as copepods as well as other pteropods larger than itself, similar to a spider web (Gilmer and Harbison 1991), therefore rendering its feeding behaviour as opportunistically carnivorous, which ultimately drives up its HgT levels. Studies on the lipid and fatty acid signatures of *Limacina* sp. from the Arctic match those seen in copepods, which provides further evidence to carnivorous tendencies (Gannefors et al. 2005). *Limacina* sp. is associated with a calcium carbonate shell (Gilmer and Harbison 1991), which also may be contributing to higher HgT levels. High HgT levels in *Cliona* sp. may have been due to Hg accumulation from *Limacina* sp. previous to a period of starvation that caused $\delta^{15}N$ values to be lower than expected. Furthermore, the extended life cycle of *Cliona* sp. of 2 years allows for accumulation of inorganic Hg, compared to some other zooplankton genera that have life cycles closer to 1 year (Böer et al. 2005).

Stable Isotope relationships.

The graph of $\delta^{15}N$ as a function of $\delta^{13}C$ (Figure 8) was used to show zooplankton expressing enriched or depleted ^{13}C sources, as well as diet. Terrestrial (freshwater)

plants and detritus have $\delta^{13}C$ values ranging from -23 to -28 ‰ (i.e. low) compared to marine diatoms and phytoplankton having $\delta^{13}C$ values ranging from -18 to -25 ‰ (i.e. high), and these values are further reflected in zooplankton $\delta^{13}C$ values (Parsons et al. 1989). There was some M1-F1 overlap of the prey sources, which was indicative of the complexity in the Hudson Bay pelagic food web at the zooplankton level. Most of the depleted ^{13}C values were in the regions of Hudson Bay that supported a river output (Figure 8). Zooplankton expressing low $\delta^{13}C$ are not however eating solely from terrestrial food sources, rather they may exist in regions with more riverine influence (Parsons et al 1989). Of the zooplankton studied, the dominant predators were *Hyperia* sp., *Sagitta* sp. and *Euchaeta sp.* based on their high $\delta^{15}N$ values. This agrees with results based on the carnivorous feeding habits of *Euchaeta sp.* on *Calanus* sp. (Skarra and Kaartvedt 2003) as well as the year-round carnivorous feeding behaviour of *Sagitta* sp. (Falk-Petersen et al. 1987). *Hyperia* sp. exists in symbiotic relationships with cnidarians, therefore its predation is parasitic (Arai 1997). Figure 8 identified prey sources in the low $\delta^{13}C$ range (F-1) more likely to be *Thysanoessa sp.* compared to prey sources in the high $\delta^{13}C$ range (M-1) which were more likely to be *Calanus* sp. This was an indication that *Calanus* sp. displayed a greater marine tolerance compared to *Thysanoessa sp.* in agreement with studies in the Bering and Chukchi Seas (Saupe et al. 1989).

Due to the overlap of M-1 and F-1 as well as M-2 and F-2 and the lack of correlation between $\delta^{15}N$ and $\delta^{13}C$ in Figure 8 ($r^2 = 0.0465$, $P > 0.1$), we propose that there was no trophic enrichment effect in Hudson Bay in contrast to previous results from the NOW dataset (Hobson et al. 2002). Furthermore, for food webs as complex as ones in the arctic

pelagic marine whelm, one must consider many environmental factors as well as intra-species relationships in order to produce an effective isotopic model.

Churchill Polar Ice Camp 2005.

High $\delta^{15}N$ from bulk biomass in this study compared to Kuzyk's POM may be explained by the filtration technique used by Kuzyk to obtain a sample that contains only Particulate Organic Matter (Kuzyk, pers. comm.). The pump used for water filtration has a mesh covering the inflow in order to keep gelatinous organic matter such as cheatognaths and cnidarians out of the POM sample. Our bulk biomass sample was collected by streaming a zooplankton net underneath the ice with a 0.5 m diameter intake. Although our bulk sample consisted of POM, there was also a lot of gelatinous zooplankton that evidently drove the $\delta^{15}N$ signature up compared to Kuzyk's POM sample, which was why we used Kuzyk's $\delta^{15}N$ in POM from Hudson Bay for BMF calculations. Similarly, the high $\delta^{13}C$ signature observed in our bulk biomass compared to Kuzyk's POM was most likely due to the gelatinous zooplankton (for example Cnidarian), which had high $\delta^{13}C$ throughout Hudson Bay as previously discussed. For our HgT analyses in biomass, we used samples collected in Churchill, MB. This provided us with an estimate of HgT in POM. Comparable values for HgT in POM was seen in the NOW and Lancaster Sound (< 20.0 ng/g dw, Table 5). From this HgT value we were able to estimate MeHg in POM from literature values as 15% of HgT (Morel et al. 1998).

Table 5. HgT (ng/g dw) values for POM from literature sources compared to values determined by this study.

Type	Region	HgT (ng/g) dw	Source
POM	Lancaster Sound	< 20.0	Atwell et al. 1998
Phyto	Monterey Bay	207	Knauer et al. 1972
Phyto	Oregon	410	Knauer et al. 1972
Ice Algae	NOW	30.0	Campbell et al. 2005
Biomass	Churchill	7.55	This work

BMFs in zooplankton.

Mean BMFs (± standard error) for MeHg were calculated in order to determine if biomagnification was occurring among pelagic zooplankton in Hudson Bay (Figure 11). BMFs greater than 1 was calculated for *Euchaeta sp.*, *Themisto* sp., *Thysanoessa* sp. (some regions) and *Limacina* sp. BMFs less than 1 (or only slightly higher than 1 in a few regions) were calculated for *Calanus* sp., *Thysanoessa sp.*(some regions), and *Sagitta* sp. The BMF calculated for *Cliona* sp. was difficult to compare with *Themisto* sp., *Sagitta* sp., *Limacina* sp. and *Euchaeta sp.* BMF's due to the monophagous nature of *Cliona* sp. The Hudson Strait regions, including FC and SHS had increased BMF's for zooplankton that preyed on *Calanus* sp. compared to other regions (Figure 11). This may be due to the lower $\delta^{15}N$ in *Calanus* sp. in these regions (Figure 4a), which caused an increase in overall BMF for MeHg. The lower $\delta^{15}N$ in FC and SHS *Calanus* sp. indicated that trophic structure in Hudson Strait was different than in Hudson Bay, which agrees with preliminary results from the MERICA dataset (Harvey et al. 2006). The slope of the lines in the zooplankton food chains were steeper with respect to MeHg compared to HgT (Figure 9a-b). Slope determination allowed for trophic level magnification factors (TLMF) to be considered, where a higher TLMF was indicative that more biomagnification was occurring, i.e. the contaminant was transferring to the next trophic level with a higher efficiency (Dehn et al. 2006). This proved that biomagnification was

accelerated for MeHg species compared to HgT in the pelagic zooplankton of Hudson Bay. TLMF's unfortunately provided an overestimate of BMF's in a food chain, in agreement with previous literature (Fisk, et al. 2001), therefore calculation of BMF's was essential.

Approximations such as treating all zooplankton as monophagus, as well as approximating $\delta^{15}N$ values for certain stations where prey species aren't available were necessary in our dataset. Therefore, we propose that BMF's were not the sole factor in determination of biomagnification in zooplankton of Hudson Bay. Furthermore, the definition of biomagnification is somewhat misleading. Biomagnification accounts for contaminant accumulation in relation to an increase in trophic level. Other modes of accumulation may also be considered among zooplankton, including bioconcentration, and bioaccumulation. Bioconcentration is defined as the uptake of a contaminant from the environment irrespective of food intake (Gray 2002). If this was the case, we should have seen correlations between water and zooplankton data, which leads us to the notion of bioaccumulation. Bioaccumulation is defined as the uptake of a contaminant from its food and its environment. We suggest that when assessing mercury levels in zooplankton, bioaccumulation should be addressed, as the influence of environmental variables on bioaccumulation factors of metals in biota has been well studied (Fjeld and Rognerud 1993, Dehn et al. 2006). In summary, we found that BMF's for MeHg were able to provide an estimate as to whether or not different zooplankton genera were capable of biomagnification. We were also able to determine the capability of HgT and MeHg to biomagnify in the food web by calculating TLMFs for the pelagic zooplankton.

Recommendations

For future studies involving zooplankton in Hudson Bay, fatty acid signatures must be considered when interpreting the pelagic food web. This will allow for improved reflection of phytoplankton / POM diet compared to carnivorous diet among different zooplankton genera considering the overlap with respect to stable isotope analyses. Furthermore, collections of phytoplankton, ice algae, and POM where possible alongside zooplankton collections are essential to understanding stable isotope relationships between predator and prey at the base of the pelagic food web. There is speculation that different phytoplankton species have different isotopic signatures. For example, Altabet reports that phytoplankton in the range of < 3μm are 1‰ depleted in $\delta^{15}N$ compared to POM (i.e. all suspended particles) in the euphotic zone (Altabet 1988). This further poses the question as whether or not to fractionate the phytoplankton in order to obtain representative stable isotope values for different sizes of phytoplankton. Furthermore, different types of POM (i.e. suspended in the euphotic zone compared to sinking below the euphotic zone) maintain different nitrogen fixating processes, which should also be investigated (Altabet 1988). This would aid in less error and approximations when calculating BMFs in the pelagic food web, and further our understanding of isotope and contaminant cycling in Hudson Bay.

Zooplankton sampling was conducted using rectangular mid-water trawl (RMT) nets, and oblique tow tucker nets. There is also the complication of collection time. The CCGS Amundsen operated 24 hours per day, so some stations were sampled at night, and some

were sampled during the day. This would have an effect on depth sampling of zooplankton due to the diurnal nature of some genera.

Conclusion

This was the first pelagic food web study in Hudson Bay in which zooplankton were analyzed for mercury at the genus level. The water chemistry in Hudson Bay showed that regions with high freshwater influence had low DOC values, low salinity, and high $\delta^{18}O$, however no specific trends were observed with respect to HgT and MeHg levels in water samples from different regions. Zooplankton analyzed for mercury and stable isotopes included planktivorous, omnivorous, and carnivorous genera. There were no seasonal differences in mercury levels or stable isotope levels, therefore summer data from 2003-2004 was combined with fall data from 2005 for a more robust dataset. Zooplankton collected from stations with more freshwater influence displayed values depleted in ^{13}C, which was indicative of carbon sources from river runoff. Stable isotope $\delta^{15}N$ revealed that *Sagitta* sp., *Euchaeta* sp., and Cnidarian were top predators, and *Calanus* sp. was strictly planktivorous. Highest levels of HgT were found in *Cliona* sp., *Euchaeta* sp., and *Limacina* sp., however top predators *Sagitta* sp. and Cnidarian had some of the lowest levels of HgT. We suspected that year round feeding behaviour due to lack of storage energy wax esters drove $\delta^{15}N$ levels higher in *Sagitta* sp. and Cnidarian, however HgT levels did not increase similarly due to short life cycles in zooplankton. Similar levels of HgT and $\delta^{15}N$ in *Cliona* sp. and its exclusive diet *Limacina* sp. were suspected again to have biological significance. *Cliona* sp. has a particular fatty acid (DAGE) therefore it was capable of long periods of starvation, and subsequently could live off of DAGE

reserves. This in turn allowed for $\delta^{15}N$ levels to be lower than expected. An alternative theory was that *Cliona* sp. lacked an essential amino acid in order to accumulate the source ^{15}N from *Limacina* sp. Highest levels of MeHg were found in *Euchaeta* sp., *Cliona* sp., and *Themisto* sp., with almost 100% of HgT being in the form of MeHg compared to *Calanus* sp. and *Thysanoessa* sp. *Sagitta* sp. again had low levels of MeHg, however %MeHg was almost 100% of HgT. There were some significant linear correlations between $\delta^{15}N$ and MeHg, which was indicative that biomagnification exists in the Hudson Bay zooplankton community. The steeper slope in MeHg compared to HgT as a function of $\delta^{15}N$ in a comparable zooplankton food chain was indicative that MeHg was more readily accumulated in zooplankton. This was also shown by the 100% MeHg assimilation in carnivorous zooplankton. Biomagnification factors (BMFs) for MeHg were used as rough estimates of pelagic food web predator-prey relationships.

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CHAPTER 3

Part II:
Total, methyl mercury and stable isotope levels in pelagic food web members of Hudson Bay.

By Monica Anne Pazerniuk

Abstract

This paper attempts to map out a pelagic food web for Hudson Bay and interpret the relationships between mercury and stable isotopes among food web members in selected Hudson Bay regions. Bioaccumulation is an important assessment of contamination as trophic level increases in a food web. HgT and MeHg levels showed significant increases with age in *Gadus* sp. ($r^2 > 0.90$, $P < 0.05$) as well as with length ($0.19 < r^2 < 0.59$, $P < 0.05$). Stable isotope analyses identified key predator and prey species, as well as a preliminary food web structure. Western Hudson Bay top predators were feeding at a higher trophic level compared to Eastern Hudson Bay top predators, which indicated that similar species potentially have different feeding habits based on habitat regions. Relationships between MeHg and $\delta^{15}N$ was shown for Southeast Hudson Bay. Biomagnification of MeHg exponentially increased with trophic level. We calculated a Trophic Level Magnification Factor for MeHg to be 1.96, and BMFs were calculated to be greater than 1 for all predator/prey relationships. Overall levels of MeHg and HgT in Hudson Bay were lower compared to other high arctic regions. Exponential biomagnification in the pelagic food web was evident.

Dedication

I would like to dedicate this Chapter to all of the Hunters and Fishermen. Sample collections would be almost impossible without their support.

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Introduction

The remote northern waters of Hudson Bay covers over 1 million km^2 of surface area. Many research projects in the area involve rivers that drain into Hudson Bay, which are potential hydroelectric development sites (Ingram and Prinsenberg 1998). Changes to the watershed have impacts on river runoff, which affect freshwater plumes, and the coastal marine environment. Ocean input to Hudson Bay is primarily influenced by channels of Arctic Ocean water running through Foxe Basin, however Atlantic Ocean water running through Hudson Strait is also present (Ingram and Prinsenberg 1998). River runoff and sea ice melt account for the freshwater influences to the bay (Prinsenberg 1986). Variability in sea ice ranges with the season from open water to 100% sea ice cover.

Many pelagic food web members are influenced by the physical changes in the Hudson Bay watershed. There are approximately 30 beluga stocks in the world (Martin et al. 2001) including two in Hudson Bay; the Eastern and Western Hudson Bay stocks. Beluga commit to long periods of migration in order to forage in estuaries across the arctic for a few days up to a few weeks in the short summer months (Smith et al. 1994). Foraging behaviour of belugas is with a vertical dive and a flat-bottomed approach, therefore pelagic and benthic prey is part of their diet (Martin et al. 2001). Arctic cod historically exist in Hudson Bay (Martini 1986). They feed underneath the ice in circumpolar regions on amphipods, copepods, and plankton. Arctic cod is thought of as the link in the arctic marine trophic chain from pelagic copepods to birds, larger fish, and marine mammals (Lowry and Frost 1981, Bradstreet and Cross 1982, Bradstreet et al. 1986, Lønne and Gulliksen 1989, Lønne and Gabrielsen 1992). Capelin is a cold water

pelagic fish that inhabits sub-arctic and arctic waters. They feed on zooplankton such as copepods and euphausiids, amphipods, as well as small fish and marine worms (Eschmeyer et al. 1983). Greenland cod are one of the most common demersal piscivorous fish that exist in Hudson Bay. These arctic survivors are opportunistic predators; however they tend to feed on capelin in the summer, fish and fish eggs, as well as benthic amphipods as their main prey (Mikhail, 1985).

Recently, climate change has been shown to affect members of the Hudson Bay food web. There is less snowfall, lower snow depth, and higher April and May temperatures from 1990 – 2001 in Western Hudson Bay. The frequency of cyclonic atmospheric reversal contributes to surface albedo increases and accelerated sea-ice melt, which in turn affects seal pup survival rates (Ferguson et al. 2005). The feeding behaviour of thick-billed murres has also shifted from a mainly arctic cod diet to capelin in recent years (Gaston et al. 2003), which is linked to decreases in sea-ice. The food web in Hudson Bay is susceptible to nutrient and climate changes that may alter predator-prey relationships permanently, and cause particular species to abandon the Bay or become extinct. The occurrence of harmful algal blooms (HABs) is natural however their presence world wide has increased in most recent decades due to humanity altering nutrient loads to watersheds (Friedl and Wüest 2002). Diatoms are more sensitive to the amount of nutrients in a system compared to phytoplankton. Increases in phosphorous or nitrogen may encourage higher amounts of HABs as well as detriment diatoms and other food web members (Friedl and Wüest 2002). Although this phenomenon is not a danger to the Hudson Bay watershed at this time, eutrophication of the Hudson Bay watershed and

potential HAB growth in the future may be a reality. Contaminant loadings may also change with increases in permafrost melt, hydro-electric damming and changes in the North Atlantic Oscillation, which are all affected by climate change. Scientists predict that Western Hudson Bay may experience the greatest climate warming due to changes in freshwater inputs (Prinsenberg 1986). Gough and Wolfe (2001) devised a General Circulation Model (GCM) that is used to predict changes to Hudson Bay with changes in temperature, CO_2 concentrations, precipitation, and other variables. The GCM predicts a complete loss of sea ice in Hudson Bay with increased CO_2 concentrations. This leads to increased temperatures in land surrounding Hudson Bay, as well as accelerated permafrost melting (Gough and Wolfe 2001). Doubling CO_2 causes a 15% increase in precipitation compared to a 4% increase globally; therefore the model predicts great changes in relation to CO_2 levels in Hudson Bay. A Coastal Ice-Ocean Model was developed in order to predict circulation patterns in Hudson Bay (Saucier et. al. 2004). A dataset from Hudson Bay in the mid 1990's containing tidal force, river runoff, wind conditions, and temperature information was used as key environmental variables for the model (Saucier et al. 2004). Saucier's work concluded that tides affect the localized climate in Hudson Bay. Changes in sea ice cover will affect the tides, which will ultimately influence Hudson Bay.

Contaminant biomagnification in arctic marine food webs has been well studied (Atwell et al. 1998, Fisk et al. 2001, Bayens et al. 2003, Campbell et al. 2005, Dehn et al. 2006). High mercury (Hg) concentrations are a product of geological surroundings as well as atmospheric deposition into a water body (Friedl and Wüest 2002). Atmospheric Hg

deposition in the Arctic is receiving a lot of scientific attention, due mainly to the discovery of atmospheric mercury depletion events (MDEs) in the mid-1990s (Schroeder et al. 1998). After polar sunrise, the concentration of atmospheric elemental mercury (Hg^0) drops significantly with a corresponding increase in Hg concentrations in surface snow, showing a potential mechanism of altering surface flux of Hg in the Arctic. It is apparent that photochemically driven MDEs remove Hg^0 from the lower km of the atmosphere after polar sunrise and deposit it to surfaces in a reactive, biologically available form (Lindberg et al. 2002, Steffen et al. 2005). Lu estimates that about 17 tonnes of Hg is deposited into snowpack of the High Arctic Ocean annually, 90% of which occurs during MDEs (Lu et al. 2001, Kirk et al. 2006). Further studies suggest that much of the Hg deposited in snow during MDEs is photo reduced to Hg^0, re-enters the atmosphere, and does not actually impinge on Arctic aquatic systems (Lalonde et al. 2002, Ferrari et al. 2005, Lahoutifard et al. 2005, St. Louis et al. 2005, Steffen et al. 2005). Therefore, MDEs, global emissions and atmospheric trends do not appear to provide an explanation for observed Hg increases and variation in Arctic aquatic ecosystems. We hypothesize that other processes play a more important role in Hg distribution and trends in Arctic ecosystems. Rivers draining into Hudson Bay have been found to deliver more than 1 tonne of HgT and 70 kg of MeHg annually (Hare, pers. comm.). Hg occurs naturally in sediments in the form of Hg^{2+}, an inorganic form that is able to adsorb to organic matter (OM) and form toxic methylmercury (MeHg) after a chemical transformation involving sulphate reducing bacteria (Barkay and Poulain 2007). High MeHg concentrations in shallow waters right above these sediments may be taken up by plants and small organisms, therefore MeHg enters the base of the food web

(Mason et al. 2000, Friedl and Wüest 2002). The shallow coastal waters of Hudson Bay exhibit some environmental conditions needed to enhance MeHg formation. Biomagnification of MeHg can be 10^6 times greater in predatory fish compared to their environment (Fitzgerald et al. 1998). A plot of Hg or MeHg as a function of stable isotope $\delta^{15}N$ allows for a slope to be determined, which is an indicator of biomagnification in a food web (Campbell et al. 2003). Bioaccumulation is also an indicator of chemical exposure due to the fact that metals are not metabolized by organisms (Luoma and Rainbow 2005), rather they are sequestered and excreted (Macdonald, pers. comm.).

Biomagnification is an important assessment of contamination as trophic level increases in a food web. Our Hudson Bay pelagic food web study incorporates POM, abundant zooplankton genera, juvenile fish families collected on board the CCGS *Amundsen*, adult fish collected from Inuit communities, and archived samples of marine mammals courtesy of Hunter's and Trapper's Organizations (HTOs) and the Department of Fisheries and Oceans Canada.

The objectives of this paper are to report on mercury and methylmercury biomagnification in the pelagic food webs of Western and Southeastern Hudson Bay. Both Western Hudson Bay (WHB) and Southeastern Hudson Bay (SEHB) food webs were chosen based on the diversity of organisms collected from sample stations within these two regions. Biomagnification factors (BMFs) and trophic level magnification

factors (TLMFs) are calculated according to the methods of Dehn et al. (2005). Each food web studied consists of planktivorous invertebrates (*Calanus* sp., *Thysanoessa* sp.), carnivorous invertebrates (*Sagitta* sp., *Themisto* sp.), carnivorous demersal fish larvae, carnivorous pelagic fish larvae, piscivorous demersal fish namely Greenland Cod (Gadidae), and Beluga (*Delphinapterus* sp.). Here we present the first food web study in sub-arctic Hudson Bay that links biological trends to environmental variables.

Methods

Hudson Bay regions.

Both MERICA and ArcticNet expeditions sampled at stations influenced by different water masses, which complemented the grouping of stations into eight regions as shown in Figure 1. These regions were represented in graphs and Figures in accordance with the known surface water cyclonic circulation patterns (Martini, 1986); i) North Hudson Strait (NHS), ii) Foxe Channel (FC), iii) Roes Welcome Sound (RWS), iv) West Hudson Bay (WHB), v) Central Hudson Bay (CHB), vi) South East Hudson Bay (SEHB), (vii) East Hudson Bay (EHB), and (viii) South Hudson Strait (SHS). Communities where marine mammals and pelagic fish collectionsoccured were also shown in Figure 1.

Sample Collection.

Zooplankton

Sample sites along the MERICA (*CCGS Des Groseillers*) cruise transect (August 2003, 2004) and the ArcticNet (*CCGS Amundsen*) leg 2 cruise transect (September – October

2005) were shown in Figure 1. Zooplankton were collected during MERICA using an oblique tow tucker net (d = 1 m^2, 333 μm). During the ArcticNet cruise, oblique (d = 1 m^2, 500 μm), vertical quadrupole (d = 1 m^2, 2 x 200 μm, 2 x 500 μm), and Rectangular Mid-water Trawl (RMT, d = 9 m^2, 1600 μm) nets were used. Bulk zooplankton were sorted in a glass dish and separated into genera as described in Chapter 2.

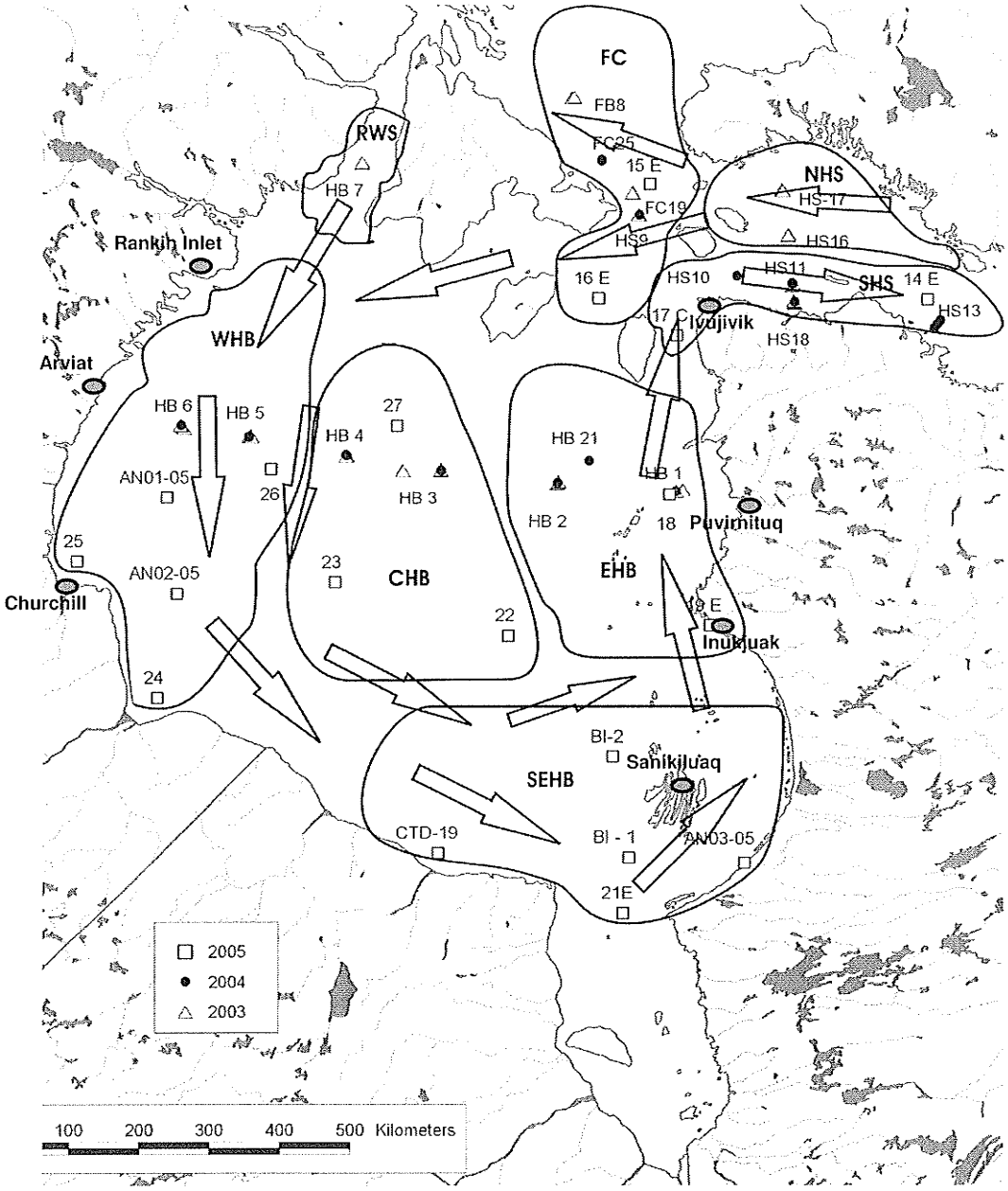
Marine mammals

Collection of marine mammals 2003-2005 was carried out in accordance with the methods of Lockhart et al. (2005) as well as the collaboration of many hunters and trappers in communities surrounding Hudson Bay. Beluga samples (*Delphinapterus* sp.) were obtained from the communities of Arviat and Sanikiluaq during subsistence hunts in 2003.

Pelagic fish

Pelagic fish from 2003 and 2005 were collected from 5 Hudson Bay communities, namely Arviat, Puvirnituq, Inukjuak, Ivujivik, and Rankin Inlet. Local fishermen used the method of jigging through open ice leads in order to catch Greenland cod (Gadidae). The fishermen were hired through the Nunavik Hunters, Fishers, and Trappers Association (HFTA). Fish were caught and killed with one swift blow to the head and they were frozen to maintain the integrity of the sample until shipment to the Department of Fisheries and Oceans Canada for further analysis.

Figure 1. Sample stations and communities in the Hudson Bay watershed. Zooplankton was collected at sample stations. Pelagic fish and marine mammals were collected from coastal communities surrounding Hudson Bay. Point of reference: station 25 latitude: 94°4' W, longitude: 58°45' N.



It was difficult to separate beluga and fish samples into seven distinct regions similarly to the zooplankton. This was due to the locations of marine mammal and fish sample collections; all were caught in the Hudson Bay coastal environment. Zooplankton and larval fish were collected from site specific stations on the CCGS *Pierre Radisson* and *Amundsen*, which allowed for sampling in deeper oceanographic stations in Hudson Bay. Further complications arose when looking at the migration patterns of beluga stocks, given that they only spend a short period of time in coastal marine environments and estuaries before migrating to Hudson Strait for the rest of the year (A. Smith, pers. comm.). It was also difficult to classify the zooplankton collected at each station as existing for its entire life cycle in the region of that particular station. Ocean currents are swift in Hudson Bay, and zooplanktons tend to float around under the influence of the currents and tides. High winds and storms further influence the trajectory of a zooplankton. In order to interpret the food web of Hudson Bay, beluga stocks were characterized as being from the Western Hudson Bay stock i.e. those samples that were collected in Arviat, and the Eastern Hudson Bay stock i.e. those samples that were collected in Sanikiluaq, even though tagging projects have shown that some beluga have been known to migrate from western communities to eastern communities in one summer (Alex Smith, pers. comm.). Greenland cod collected from Rankin Inlet and Arviat were used in conjunction with the Western beluga stock, whereas the samples collected from Ivujivik, Puvirnituq and Inukjuaq were used in conjunction with the Eastern beluga stock. Zooplankton from Hudson Bay as a whole were divided up based on feeding behaviours as planktivorous, carnivorous, and benthic feeders. Mean HgT, methylmercury, stomach contents analysis and stable isotope values were used in order to assess biomagnification

factors and trophic level magnification factors in the pelagic food web of WHB and SEHB.

Sample Analysis.

Beluga muscle tissue samples from the communities of Arviat and Sanikiluaq as well as Gadidae from Arviat were analyzed for HgT, stable isotopes and organic contaminants. This data from sampling year 2003 was archived in a marine mammals database at the Department of Fisheries and Oceans Canada, Winnipeg, Manitoba. We used this data in conjunction with our 2005 sample collections.

Greenland cod (Gadidae) collected for this project were processed for length, weight and age (otoliths) at the Department of Fisheries and Oceans Canada. There were 71 Gadidae (Greenland cod) analyzed for HgT from the 2005 collection year, representing 4 Hudson Bay communities including Inukjuak, Ivujivik, Puvirnituq, and Rankin Inlet. Otoliths from Gadidae were aged from Inukjuak, Ivujivik, Puvirnituq, and Arviat according to the methods of Chilteon and Beamish (1982). Muscle tissue from n = 28 fish were sub-sampled and analyzed for % MeHg. Samples of muscle tissue were analyzed for HgT according to the methods of Armstrong and Uthe (1971). Sub-samples of muscle tissue were sent to the University of Winnipeg Isotope Laboratory (UWIL) for stable isotope analysis similarly to the zooplankton as described in the previous Chapter. Stomach contents analysis of the Gadidae was performed at the Institut Maurice Lamontagne in Mont-Joli Québec under the supervision of Jacques Gagne.

Stable Isotopes $\delta^{13}C$ and $\delta^{15}N$.

There is a lot of variability in stable isotope results due to sample preparation being inconsistent among researchers. Lipid rich tissues such as liver express depleted ^{13}C compared to tissues void in lipids such as hair (Sotiropoulos, 2004, McConnaughey, McRoy, 1979). Evidence suggests that acid washing to remove lipids from sample tissues high in lipid content before isotope analysis will allow a more precise $\delta^{13}C$ value to be expressed in the tissue of interest (Hobson, 1992). This is not ideal when samples are small. Freeze dried whole body composites of invertebrates are used in order to get enough material for stable isotope and mercury analysis. Trophic level information, HgT, MeHg, and basic food web structure can still be interpreted from muscle tissues of higher trophic level species and whole body composites of invertebrates, without precise $\delta^{13}C$ signatures (Sotiropoulos, 2004). Furthermore, the removal of lipids from pelagic fish and marine mammals does not reflect the nature of predators in the pelagic food web, who may seek out the most lipid enriched invertebrate to feed on, especially in the winter when food is scarce. An alternate method to account for lipid effects on $\delta^{13}C$ is to normalize the $^{13}C/^{12}C$ ratio so all tissues analyzed are regarded as having the same lipid content with any alternative fluctuations occurring due to respiration (McConnaughey, McRoy, 1979). According to Kelly (2000), lipid extraction of muscle tissue has no adverse effect on $\delta^{13}C$ in the marine food web as shown in Table 3 of his report. There was no acid washing prior to stable isotope analysis in our methods for the reasons mentioned above.

Biomagnification factors were calculated based on the following formula:

$BMF_{\delta^{15}N\ Corr.} = [[HgT]_{pred}/[HgT]_{prey}]/[\delta^{15}N_{pred}/\delta^{15}N_{prey}]$ (Dehn et al. 2006) (1)

Biomagnification factors greater than 1 are indicative that an organism is bioaccumulating mercury from its prey. Given the fact that MeHg is the species of interest due to its greater ability to biomagnify, we are most interested in the BMFs for the Hudson Bay food web in relation to MeHg and stable isotope information. Further trophic level magnification factors (TLMFs) were calculated based on the slopes of the linear regression lines for the Hudson Bay pelagic food web. Exponential growth equations fit our dataset similar to food web studies in the Northwater Polynya as shown by the following equation:

$\ln[MeHg] = a + b(\delta^{15}N)$ (2) (Fisk et al. 2001)

The extent to which MeHg was biomagnified in the pelagic food web was related to the slope in equation 2 by an exponential relationship:

$TLMF = e^{b}$ (3) (Fisk et al. 2001)

We compared our TLMFs with those from other arctic regions.

Larval fish collections in Hudson Bay.

While Arctic Cod larvae were collected from three select stations, analytical and statistical analyses was difficult due to limited sample sizes. Even though a pelagic trawler was used for zooplankton and fish collections, mostly demersal fish larvae were collected along with zooplankton from Hudson Bay, therefore pelagic fish collection proved more difficult than originally anticipated.

HgT and MeHg as a function of length and age in Gadidae.

% MeHg of 89.6 ± 3.6 % in Gadidae muscle tissue was calculated from our sub-samples. This result indicated that HgT and MeHg may be used interchangeably when correlating length, age and mercury levels due to the % MeHg being close to 100 %. Morphometric data of Gadidae was recorded and archived from the 2005 samples in a similar fashion to the 2003 samples. Stomach contents were observed to have a wide range of pelagic and benthic prey, including Euphausiids, amphipods, copepods, whole fish and rocks.

Statistics

Analysis of Covariance (ANCOVA) was used to test for homogeneity of group means in Gadidae from different sample locations. A General Linear Model (GLM estimate model) using HgT as the dependent variable coupled with location and length as the independent variables was used in Systat Version 10 statistical software. We log transformed our dependent variables in order to obtain a normal distribution. ANCOVA was used to assess the effects of location, length, and length*location interactions (homogeneity of the slope between length and [HgT]). ANCOVA also allowed an extrapolation of mercury concentrations even though different lengths of Gadidae were recorded from different locations.

Linear regression was performed on food webs from different regions in Hudson Bay. Regions with significant correlation and P values <0.05 were considered statistically

significant for further interpretation. Archived samples of marine mammals and fish were used from 2003 along with our sample collections of zooplankton from 2003, 2004 and 2005, as well as our fish collections from 2005. This study aims to show the trophic relationships in the Hudson Bay food web members as well as any mercury accumulation in the food web. Previous food web studies have pooled data from different sampling years, depths, and stations in order to encompass the most variation possible in the food web (Hobson et al. 2002). We chose to pool our data over multiple sampling years, stations and depths as well in order to obtain a representative food web for Hudson Bay that includes as many members as possible.

Results

HgT and MeHg as a function of length and age in Gadidae.

HgT (MeHg) in muscle tissue was compared as a function of length (Figure 2). ANCOVA results are shown in Table 1a and b for Gadidae from the 5 sample locations. Adjusted mean length for N = 97 Gadidae was 36.6 cm. Significant correlation of HgT with length as well as homogeneous slopes (Figure 2, $P < 0.05$, Table 1a) was observed in all locations. Our results also displayed a trend of highest adjusted HgT levels in Gadidae from WHB compared to Gadidae collected from EHB communities; RI = ARV > PUV > IJ > IV, $P < 0.001$ (Table 1). High HgT was also correlated with age. For example, 6 year old Gadidae showed higher mean HgT levels in Arviat (278 ng/g dw, n = 11) compared to Puvirnituq (221 ng/g dw, n = 3), Ivujivik (<100 ng/g dw, n = 2) and Inukjuak (126 ng/g dw, n = 6) as seen in Figure 3. A 7 year old Gadidae caught in

Churchill had a HgT level of 369 ng/g dw, which again was higher than levels of 7 year old Gadidae from the EHB communities (Figure 3). Samples collected in 2005 from Rankin Inlet also had higher levels of HgT compared to the samples from EHB communities. Age was not determined in the Rankin Inlet fish however mean HgT was determined to be 448 ± 57.0 ng/g dw (n = 7).

Table 1.

a. ANCOVA results for Gadidae collected from Hudson Bay communities.
Equation of the line is of the form logHgT = m(length) + b, m = slope, b = y-intercept.
Adjusted least squares mean and y-intercept values in the Table are log transformed and represent true measured values of HgT (ng/g) dw.
Adjusted LS mean length = 36.6 cm (based on N = 97 Gadidae).

Location	m (slope)	y-intercept	r^2	P	Adjusted LS mean	N
Arviat	0.0228	138.87	0.5600	< 0.05	957.69	26
Rankin Inlet	0.0203	190.46	0.5889	< 0.05	1076.00	7
Ivujivik	0.0158	47.25	0.3593	< 0.05	181.25	22
Inukjuak	0.0241	42.85	0.1884	< 0.05	334.45	25
Puvirnituq	0.0273	52.25	0.5786	< 0.05	535.40	17

b. ANCOVA P-values for interaction terms: based on dependent variable logHgT and independent variables length, location, and location*length.

source	P-value
length	0.000
location	0.395
location*length	0.780

Figure 2.
ANCOVA results for logHgT as a function of length in Gadidae from Inukjuak (IJ, n = 25), Ivujivik (IV, n = 22), Puvirnituq (PUV, n = 17), Rankin Inlet (RI, n=7) and Arviat (ARV, n = 26). Mean length (dotted line) = 36.6 cm.

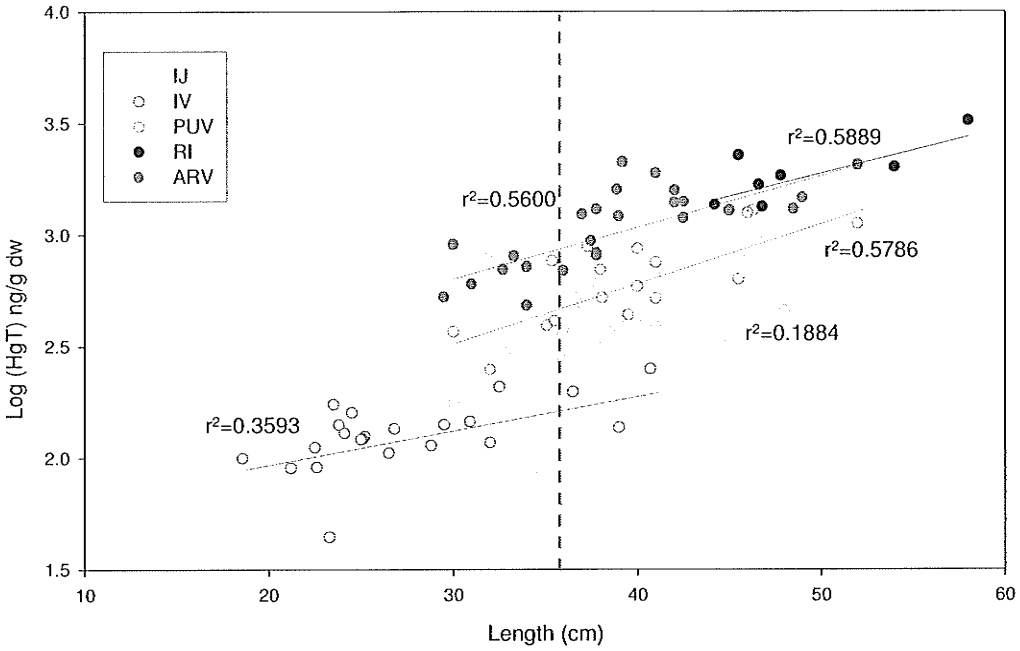
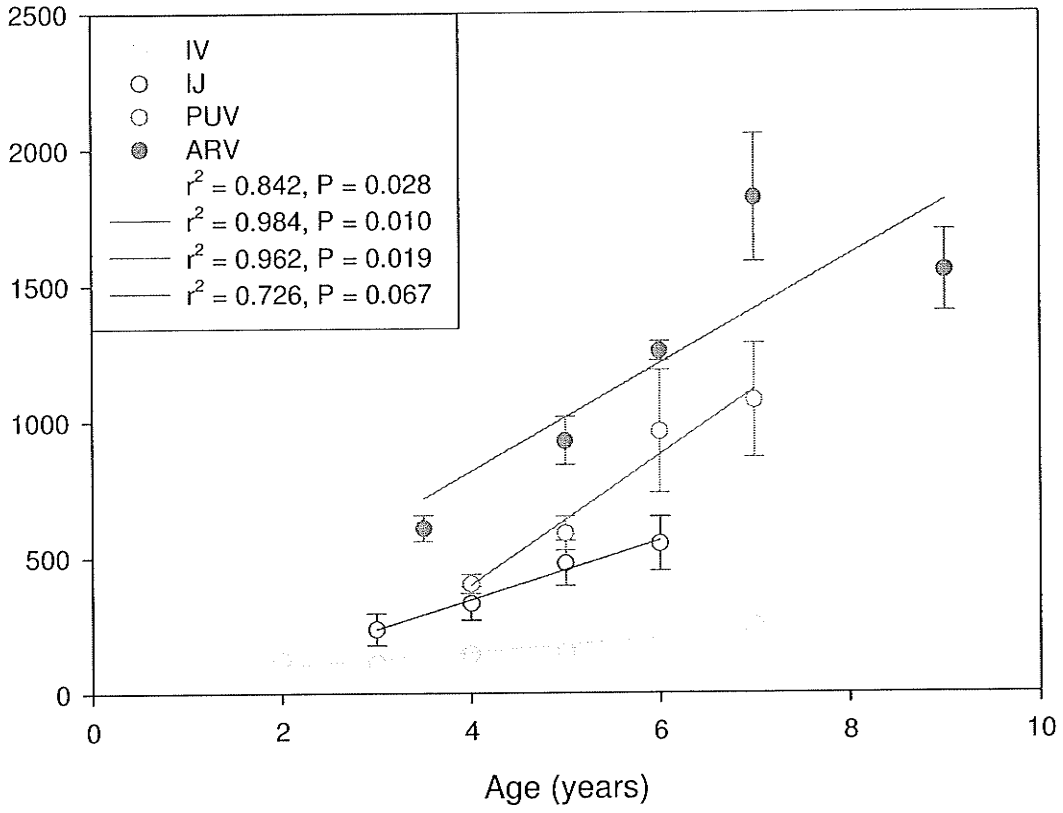


Figure 3. Age as a function of HgT (ng/g dw) in Gadidae from Inukjuak (IJ, n = 25), Ivujivik (IV, n = 22), Puvirnituq (PUV, n = 17), and Arviat (ARV, n = 53).



Arctic food web stable isotope relationships.

Stable isotope signatures $\delta^{15}N$ and $\delta^{13}C$ were compiled for sub-arctic organisms from the Hudson Bay food web as well as from other Arctic food webs (Table 2). POM from Churchill and Hudson Bay were depleted in ^{13}C compared to values reported in Barrow Strait, Lancaster Sound, and the Northwater Polynya. This trend was also observed for *Calanus* sp. and *Themisto* sp. Values depleted in ^{13}C were reported in the Canadian Basin compared to Hudson Bay regions. $\delta^{13}C$ values in zooplankton throughout the Arctic displayed the following isotopic enrichment trend:

Barrow Strait = Lancaster Sound (range -17 to -21 ‰) > Northwater Polynya (range -19 to -22 ‰) > Hudson Bay (range -16 to -25 ‰) > Canadian Basin (range -22 to -27 ‰) which was also observed in *Bore*ogadus (larvae) and Cyclopteridae. Adult *Boreogadus*, Gadidae, and *Delphinapterus* sp. had enriched ^{13}C reported in the literature as well as from this study, regardless of Arctic region. It appeared as though zooplankton and fish larvae were more susceptible to $\delta^{13}C$ fluctuations compared to larger fish and marine mammals (Table 2). Isotope $\delta^{15}N$ values for *Calanus* sp. and *Themisto* sp. in Hudson Bay were low compared to other Arctic regions, with the exception of *Calanus* sp. in SEHB. Overall, zooplankton from Hudson Bay had $\delta^{15}N$ values similar to those in other Arctic regions as shown in Table 2.

Table 2. Stable isotopes for Hudson Bay food web members. Literature values from other high arctic regions were compiled for comparison purposes.

Genera	Region	n	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)	classification	Ref.
POM	Hudson Bay	19	4.61 ± 0.84	-24.73 ± 1.33	Organic	Kuzyk et al.
POM	Lancaster Sd.	1	5.4	-	Organic	Atwell. et al.
POM	Barrow St. / Lancaster Sd.	5	5.4 ± 0.8	-21.6 ± 0.3	Organic	Hobson et al.
POM	Northwater Polynya	38	6.8 ± 0.3	-22.3 ± 0.2	Organic	Hobson et al.
POM	Churchill, MB	12	6.67	-24.49	Organic	Kuzyk et al.
Biomass	Churchill, MB	6	9.79 ± 0.50	-22.85 ± 0.23	Organic	Chapter 2
Calanus sp.	FC	4	6.70 ± 0.48	-21.46 ± 0.49	Planktivorous	Chapter 2
Calanus sp.	CHB	5	7.23 ± 0.50	-23.67 ± 1.18	Planktivorous	Chapter 2
Calanus sp.	SEHB	3	9.55 ± 0.19	-23.79 ± 0.46	Planktivorous	Chapter 2
Calanus sp.	EHB	5	6.24 ± 0.36	-23.58 ± 0.42	Planktivorous	Chapter 2
Calanus sp.	SHS	6	7.10 ± 0.30	-22.10 ± 0.78	Planktivorous	Chapter 2
Calanus sp.	Lancaster Sd.	3	10.2 ± 0.6		Planktivorous	Atwell et al.
Calanus sp.	Barrow St. / Lancaster Sd.	6	9.2 ± 0.5	-20.4 ± 0.4	Planktivorous	Hobson et al.
Calanus sp.	Northwater Polynya	3	7.83 ± 0.01	-21.04 ± 0.05	Planktivorous	Campbell et
Calanus sp.	Canadian Basin	27	9.77± 0.084	-25.94 ±	Planktivorous	Iken et al.
Calanus sp. 1	Northwater Polynya	2	9.1 ± 0.4	-20.6 ± 0.8	Planktivorous	Hobson et al.
Calanus sp. 2	Northwater Polynya	80	7.9 ± 0.1	-21.1 ± 0.1	Planktivorous	Hobson et al.
Thysanoessa sp.	FC	4	9.58 ± 0.97	-21.10 ± 0.19	Planktivorous	Chapter 2
Thysanoessa sp.	CHB	8	8.54 ± 0.50	-24.34 ± 1.00	Planktivorous	Chapter 2
Thysanoessa sp.	SEHB	3	7.58 ± 0.068	-22.64 ± 1.05	Planktivorous	Chapter 2
Thysanoessa sp.	EHB	3	8.42 ± 0.42	-24.44 ±	Planktivorous	Chapter 2
Thysanoessa sp.	SHS	5	7.65 ± 0.44	-20.756 ±	Planktivorous	Chapter 2
Themisto sp.	CHB	9	9.30 ± 0.31	-23.84 ± 0.50	Omnivorous	Chapter 2
Themisto sp.	SEHB	4	9.25 ± 0.98	-22.92 ± 0.37	Omnivorous	Chapter 2
Themisto sp.	EHB	7	8.40 ± 0.27	-22.95 ± 0.30	Omnivorous	Chapter 2
Themisto sp.	SHS	6	8.48 ± 0.54	-21.24 ± 0.70	Omnivorous	Chapter 2
Themisto sp.	Lancaster Sd.	2	11.6	-	Omnivorous	Atwell et al.
Themisto sp.	Barrow St. / Lancaster Sd.	6	9.2 ± 0.5	-20.4 ± 0.4	Omnivorous	Hobson et al.
Themisto sp.	Northwater Polynya	3	9.69 ± 0.05	-20.41 ± 0.07	Omnivorous	Hobson et al.
Themisto sp.	Canadian Basin	6	10.69 ± 0.22	-27.04 ± 0.71	Omnivorous	Iken et al.
Sagitta sp.	FC	4	11.59 ± 0.79	-22.15 ± 1.14	Carnivorous	Chapter 2
Sagitta sp.	CHB	7	11.04 ± 0.38	-24.28 ± 0.29	Carnivorous	Chapter 2
Sagitta sp.	SEHB	4	11.58 ± 0.78	-23.44 ± 0.12	Carnivorous	Chapter 2
Sagitta sp.	SHS	6	11.52 ± 0.39	-21.78 ± 0.31	Carnivorous	Chapter 2
Sagitta sp.	Northwater Polynya	76	10.4 ± 0.1	-21.4 ± 0.1	Carnivorous	Hobson et al.
Euchaeta sp.	FC	2	9.46 ± 0.60	-22.38 ± 0.48	Carnivorous	Chapter 2
Euchaeta sp.	CHB	1	10.74	-25.73	Carnivorous	Chapter 2
Euchaeta sp.	SEHB	1	10.58	-24.34	Carnivorous	Chapter 2
Euchaeta sp.	SHS	4	10.90 ± 0.34	-22.00 ± 0.26	Carnivorous	Chapter 2
Euchaeta sp.	Canadian Basin	8	12.54 ± 0.36	-26.64 ± 0.45	Carnivorous	Iken et al.
Cliona sp.	FC	1	8.77	-23.1	Carnivorous	Chapter 2
Cliona sp.	CHB	6	9.11 ± 0.68	-24.55 ± 0.18	Carnivorous	Chapter 2
Cliona sp.	SEHB	3	9.32 ± 0.41	-25.68 ± 0.79	Carnivorous	Chapter 2
Cliona sp.	EHB	2	7.74 ± 1.76	-25.20 ± 0.76	Carnivorous	Chapter 2
Cliona sp.	SHS	3	8.86 ± 0.85	-23.84 ± 1.01	Carnivorous	Chapter 2
Cliona sp.	Northwater Polynya	37	9.6 ± 0.2	-22.4 ± 0.2	Carnivorous	Hobson et al.
Limacina sp.	FC	2	8.26 ± 0.73	-21.30 ± 0.77	Planktivorous	Chapter 2
Limacina sp.	CHB	3	9.59 ± 0.44	-22.58 ± 0.64	Planktivorous	Chapter 2
Limacina sp.	EHB	1	8.21	-24.09	Planktivorous	Chapter 2
Limacina sp.	SHS	2	8.29 ± 0.27	-22.12 ± 0.88	Planktivorous	Chapter 2
Limacina sp.	Canadian Basin	1	5.91	-22.39	Planktivorous	Iken et al.

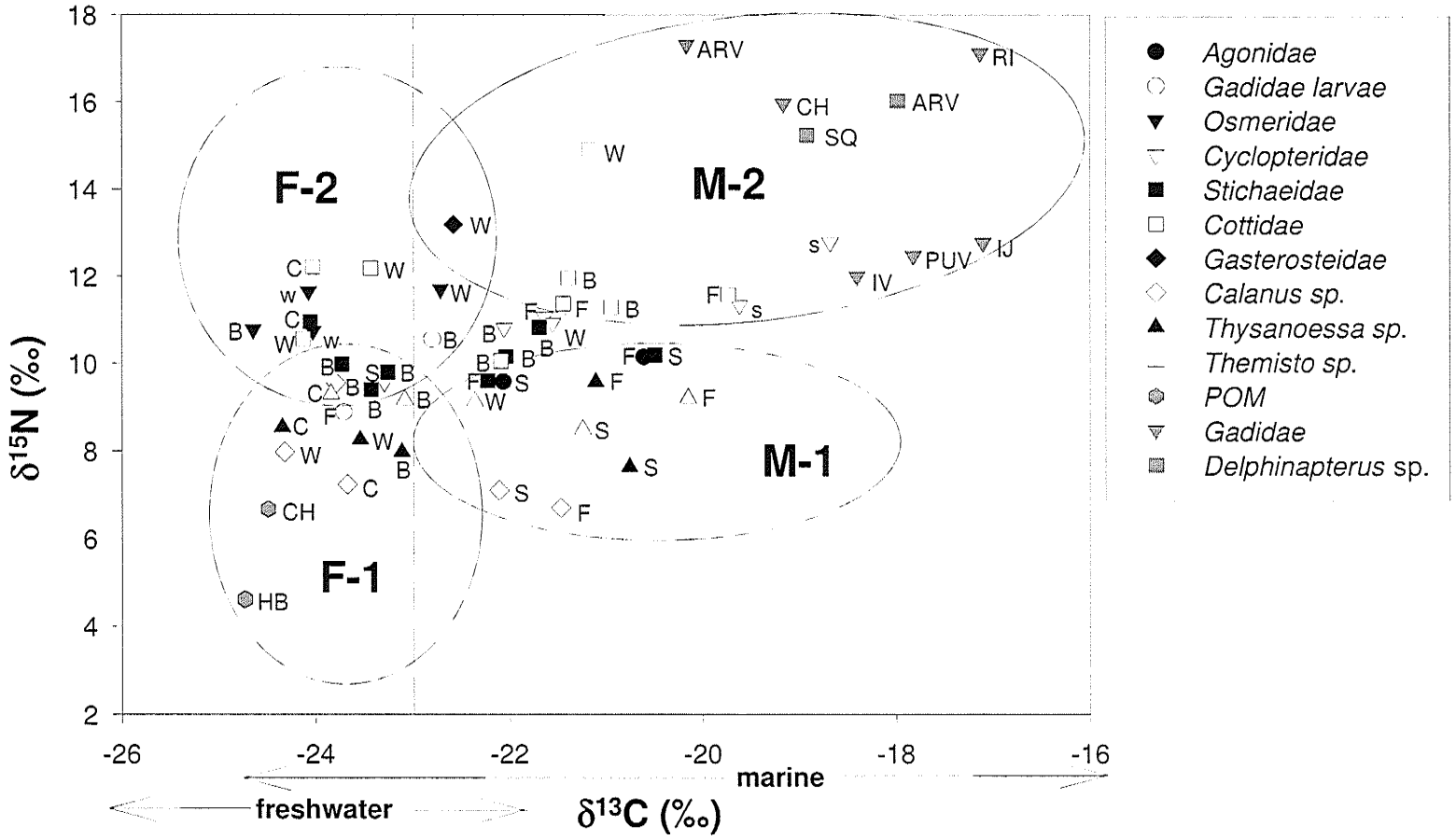
Table 2 continued

Genera	Region	n	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)	classification	Ref.
Hyperiid sp.	SEHB	2	10.57 ± 0.12	-22.50 ± 0.56	Planktivorous	Chapter 2
Hyperiid sp.	Canadian Basin	3	10.32 ± 0.88	-26.22 ± 0.19	Planktivorous	Iken et al.
Cnidarian	FC	1	12.58	-23.09	Carnivorous	Chapter 2
Cnidarian	CHB	3	10.88 ± 0.55	-18.75 ± 0.86	Carnivorous	Chapter 2
Cnidarian	SEHB	3	10.71 ±	-18.50 ± 1.32	Carnivorous	Chapter 2
Cnidarian	EHB	2	9.61 ± 0.050	-17.32 ± 1.02	Carnivorous	Chapter 2
Cnidarian	SHS	2	10.07 ± 0.72	-14.52 ± 1.15	Carnivorous	Chapter 2
Anonyx sp.	Churchill, MB	12	11.62 ± 0.25	-19.64 ± 0.14	Benthic	Chapter 2
Agonidae	SHS	1	9.59	-22.07	Epibenthic	this study
Agonidae	FC	1	10.15	-20.61	Epibenthic	this study
*Boreo*Gadidae (larvae)	SEHB	1	10.56	-22.8	Pelagic	this study
*Boreo*Gadidae (larvae)	FC	1	8.89	-23.71	Pelagic	this study
*Boreo*Gadidae (adult)	Northwater Polynya	1	13.88	-19.39	Pelagic	Campbell et al.
*Boreo*Gadidae (adult)	Barrow St. / Lancaster Sd.	26	15.2 ± 0.7	-18.9 ± 1.0	Pelagic	Hobson et al.
*Boreo*Gadidae (larvae)	Barrow St. / Lancaster Sd.	1	11.1	-19.8	Pelagic	Hobson et al.
*Boreo*Gadidae (adult)	Lancaster Sd.	9	14.7 ± 0.1		Pelagic	Atwell et al.
*Boreo*Gadidae (adult)	Northwater Polynya	8	14.0 ± 0.2	-19.3 ± 0.1	Pelagic	Hobson et. al
*Boreo*Gadidae (larvae)	Northwater Polynya	3	10.7 ± 0.8	-20.0 ± 0.5	Pelagic	Hobson et al.
Osmeridae	SEHB	1	10.77	-24.64	Pelagic	this study
Cottidae	SEHB	3	11.09 ± 0.55	21.48 ± 0.33	Benthic	this study
Cottidae	CHB	1	12.21	-24.03	Benthic	this study
Cottidae	FC	1	11.57	-19.74	Benthic	this study
Cottidae	SHS	1	11.36	-21.44	Benthic	this study
Stichaeidae	SEHB	5	10.03 ± 0.23	22.82 ± 0.40	Pelagic	this study
Stichaeidae	CHB	1	10.95	-24.06	Pelagic	this study
Stichaeidae	SHS	1	10.19	-20.5	Pelagic	this study
Stichaeidae	FB	1	9.59	-22.23	Pelagic	this study
Cyclopteridae	SHS	3	11.22 ± 0.93	20.53 ± 1.41	Pelagic	this study
Cyclopteridae	FC	1	11.05	-21.64	Pelagic	this study
Cyclopteridae	SEHB	1	10.8	-22.05	Pelagic	this study
Cyclopteridae	Barrow St. / Lancaster Sd.	4	15.0 ± 0.4	-17.4 ± 0.5	Pelagic	this study
Clams	Arviat, NU	9	7.87 ± 0.40	-19.87 ± 0.22	Filter feeders	this study
Gadidae	Arviat, NU	25	17.32 ± 0.12	-20.09 ± 0.27	Piscivorous	this study
Gadidae	Rankin Inlet, NU	7	17.12 ± 0.27	-17.13 ± 0.73	Piscivorous	this study
Gadidae	Churchill, MB	1	15.96	-19.16	Piscivorous	this study
Gadidae	Ivujivik, QC	23	11.95 ± 0.15	-18.66 ± 0.22	Piscivorous	this study
Gadidae	Inukjuak, QC	25	12.74 ± 0.24	-16.94 ± 0.32	Piscivorous	this study
Gadidae	Puvirnituq, QC	17	12.65 ± 0.321	-17.70 ± 0.337	Piscivorous	this study
Delphinapterus sp.	Arviat, NU	30	16.02 ± 0.20	-17.98 ± 0.11	Carnivorous	DFO archives
Delphinapterus sp.	Sanikiluaq, NU	13	15.23 ± 0.09	-18.92 ± 0.18	Carnivorous	DFO archives
Delphinapterus sp.	Barrow St. / Lancaster Sd.	6	16.6 ± 0.6	-18.1 ± 0.5	Carnivorous	Hobson et al.
Delphinapterus sp.	Lancaster Sd.	4	16.4 ± 0.3		Carnivorous	Atwell et al.
Delphinapterus sp.	Alaska	49	16.5 ± 0.6	-18.4 ± 0.6	Carnivorous	Dehn et al.
Delphinapterus sp. (f)	St. Lawrence estuary	16	15.1 ± 0.4	-17.3 ± 0.2	Carnivorous	Lesage et al.
Delphinapterus sp. (m)	St. Lawrence estuary	11	15.8 ± 0.6	-16.7 ± 0.2	Carnivorous	Lesage et al.
Delphinapterus sp.	Greenland	40	16.9 ± 0.2	-17.6 ± 0.1	Carnivorous	Hobson et al.
Delphinapterus sp.	Baffin	30	16.0 ± 0.2	-17.7 ± 0.2	Carnivorous	Hobson et al.

Hudson Bay food web stable isotope relationships.

A food web consisting of the most predominant zooplankton, larval and adult fish collected in Hudson Bay was compiled. It is widely known and accepted that organisms with high $\delta^{15}N$ are predators. We used stable isotope analysis to assess organism behaviour as predator or prey and whether they exhibited marine (M) or freshwater (T) characteristics (Figure 4). Adult Gadidae (*Gadus* sp.) exhibited marine character (enriched in ^{13}C), even though they were all caught in close proximity to freshwater (depleted in ^{13}C) regions. Gadidae and *Delphinapterus* sp. had the highest $\delta^{15}N$ values (Figure 4, Table 2). Gadidae from WHB displayed higher $\delta^{15}N$ by one trophic level compared to EHB Gadidae and *Delphinapterus* sp. ANCOVA was used to test $\delta^{15}N$ as a function of length, location, as well as their interaction term. P-values were insignificant ($P_{location} = 0.126$, $P_{length} = 0.653$, $P_{location*length} = 0.701$), therefore we conclude that $\delta^{15}N$ was independent of length, location, and their interaction term. Families Cottidae and Cyclopteridae had $\delta^{15}N$ similar to EHB Gadidae, and higher than prey zooplankton by approximately one trophic level. Stichaeidae and Agonidae from SHS and FC regions had lower levels of $\delta^{15}N$. Values enriched in ^{13}C dominated in FC and SHS;coastal Gadidae and Cottidae from region SEHB also displayed this trend.

Figure 4. Food web stable isotope relationships in marine and coastal Hudson Bay regions.
M = marine, F = freshwater, 1 = prey, 2 = predator; HB = average POM signal over all regions in Hudson Bay, CH = Churchill, ARV = Arviat, RI = Rankin Inlet, PUV = Puvirnituq, IV = Ivujivik, IJ = Inukjuak, SQ = Sanikiluaq, W = West HB, C = Central HB, B = Southeast HB, F = Foxe Channel, S = South Hudson Strait. Gadidae larvae = *Boreo*Gadidae, Gadidae = Gadidae

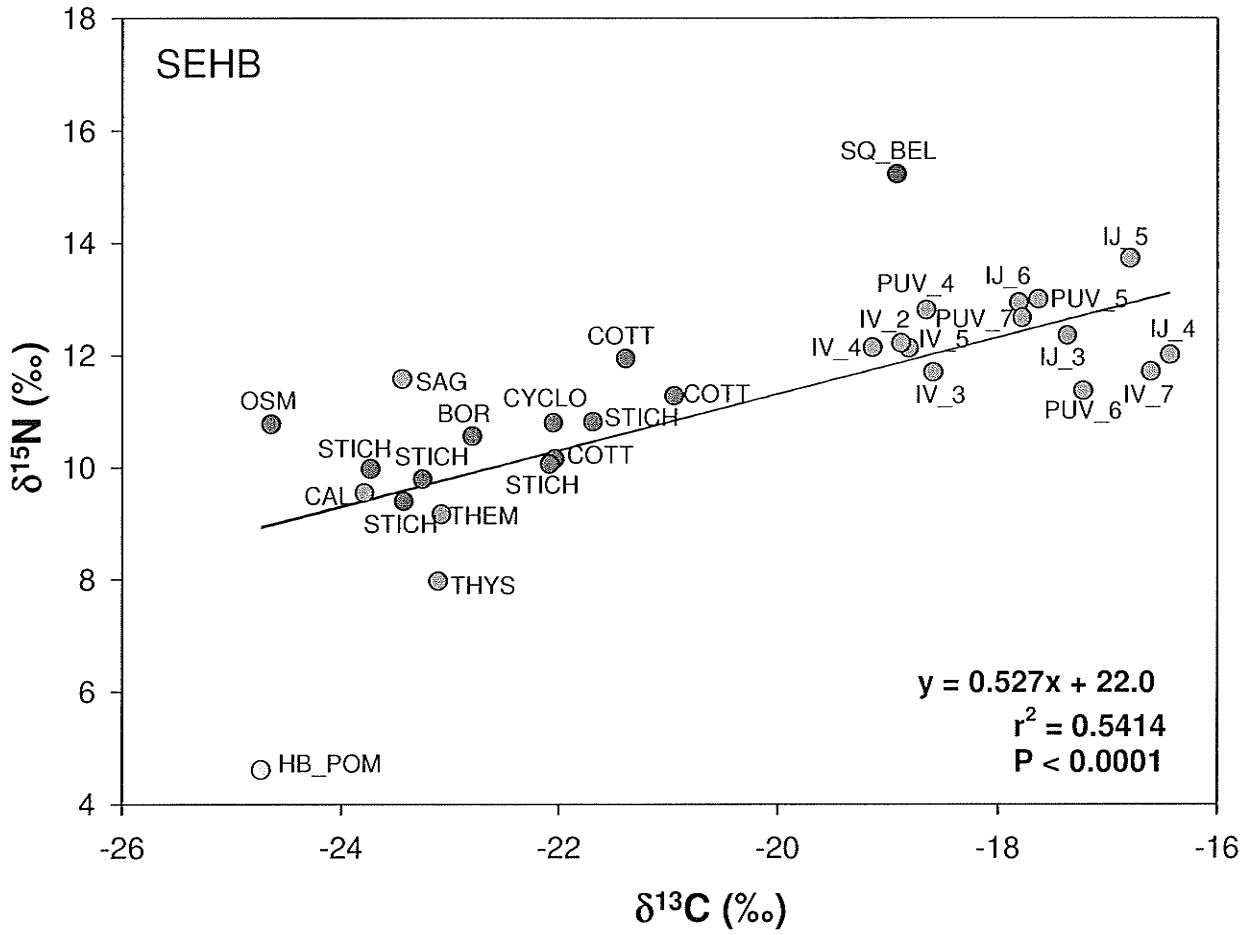


Stable Isotope Relationships in SEHB compared to WHB.

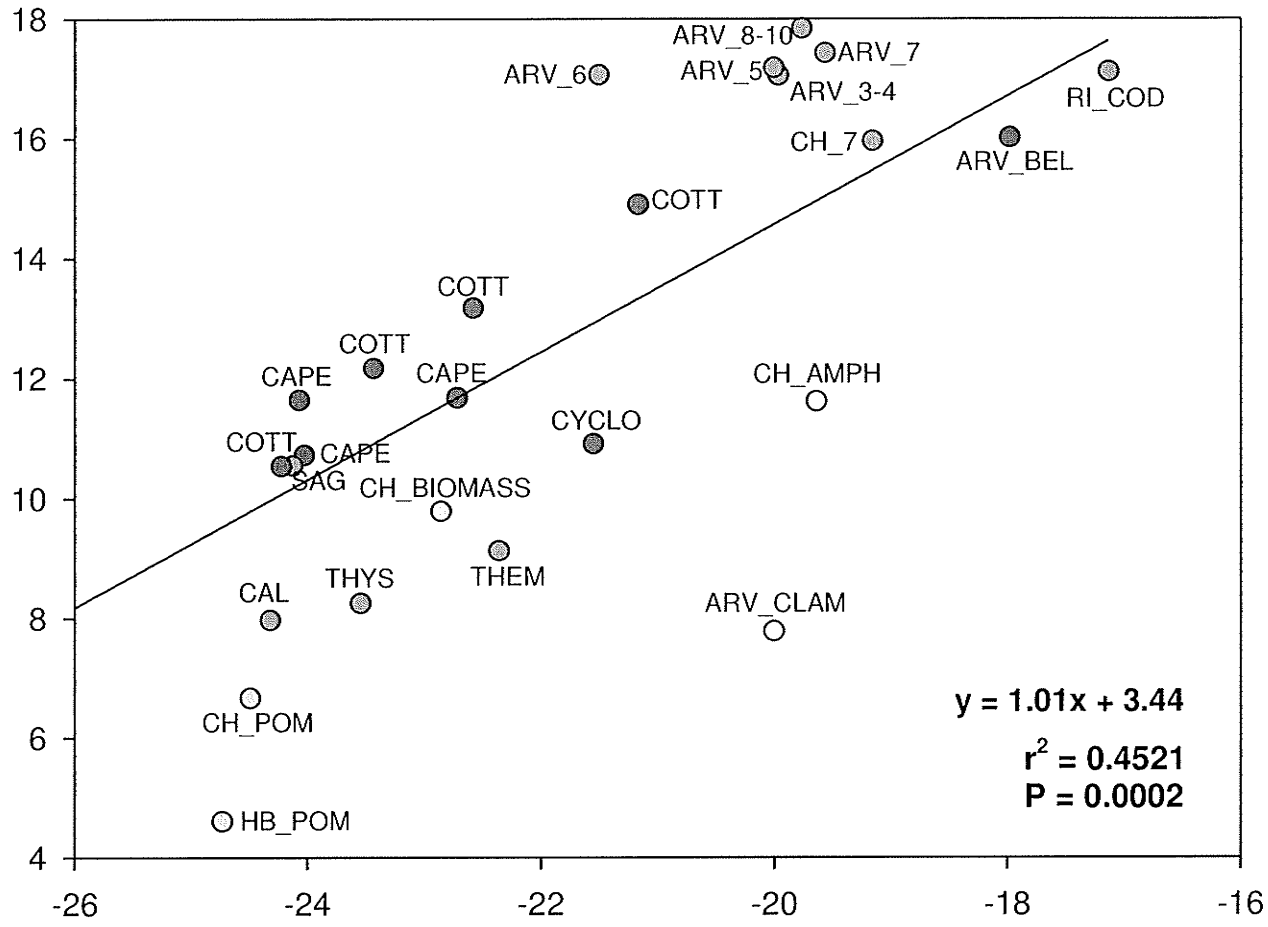
There was no significant correlation between $\delta^{15}N$ and $\delta^{13}C$ ($r^2 < 0.500$, $P > 0.05$ Figure 4) when considering Hudson Bay in its entirety. Food web stable isotope relationships were examined in two distinct regions of Hudson Bay including WHB and SEHB. There was significant correlation between $\delta^{15}N$ and $\delta^{13}C$ in the SEHB pelagic food web (Figure 5a). Zooplankton and larval fish had values depleted in ^{13}C compared to adult fish. Overall, zooplankton had higher than expected $\delta^{15}N$; however values were still one trophic level (1 TL = 3-3.4‰, (Atwell et al. 1998)) below the adult fish, some larval fish, and the carnivorous zooplankton *Sagitta* sp. Figure 5b examined the stable isotope relationships in WHB. In this food web, POM and the planktivorous/herbivorous zooplankton were on average one trophic level below some of the larval fish organisms, and between 2-3 trophic levels below adult fish. Adult Gadidae from WHB collections (Arviat, Rankin Inlet, Churchill) had $\delta^{15}N$ values similar to those of *Delphinapterus* sp. from Arviat (Table 2, Figure 5b). Our ANCOVA results indicated no significance of $\delta^{15}N$ with length, location and the interaction term, indicating that $\delta^{15}N$ was independent of size as well as location of Gadidae. We conclude that $\delta^{15}N$ values in WHB are higher compared to EHB Gadidae, however size of Gadidae is not driving this trend.

Figure 5. Food web stable isotope relationships in (a) Southeast Hudson Bay (b) West Hudson Bay. POM = Particulate Organic Matter, CAL = *Calanus* sp., THYS = *Thysanoessa* sp., THEM = *Themisto* sp., SAG = *Sagitta* sp., BOR = *Boreo*Gadidae, OSM = Osmeridae, STICH = Stichaeidae, COTT = Cottidae, CYCLO = Cyclopteridae, AMPH = *Anonyx* sp. HB = Hudson Bay, CH = Churchill, ARV = Arviat, RI = Rankin Inlet, PUV = Puvirnituq, IV = Ivujivik, IJ = Inukjuak, SQ_BEL = Sanikiluaq *Delphinapterus* sp., ARV_BEL = Arviat *Delphinapterus* sp. Numbers indicate age of adult Gadidae Green points: POM, red points: zooplankton, blue points: larval fish, grey points: adult Gadidae

a.



b.


18
16
14
12
10
8
6
4
-26
-24
-22
-20
-18
-16
ARV_8-10
ARV_7
ARV_6
ARV_5
ARV_3-4
RI_COD
CH_7
ARV_BEL
COTT
COTT
COTT
CAPE
CAPE
CH_AMPH
CYCLO
COTT
CAPE
SAG
CH_BIOMASS
THEM
THYS
CAL
ARV_CLAM
CH_POM
HB_POM
y = 1.01x + 3.44
r2 = 0.4521
P = 0.0002

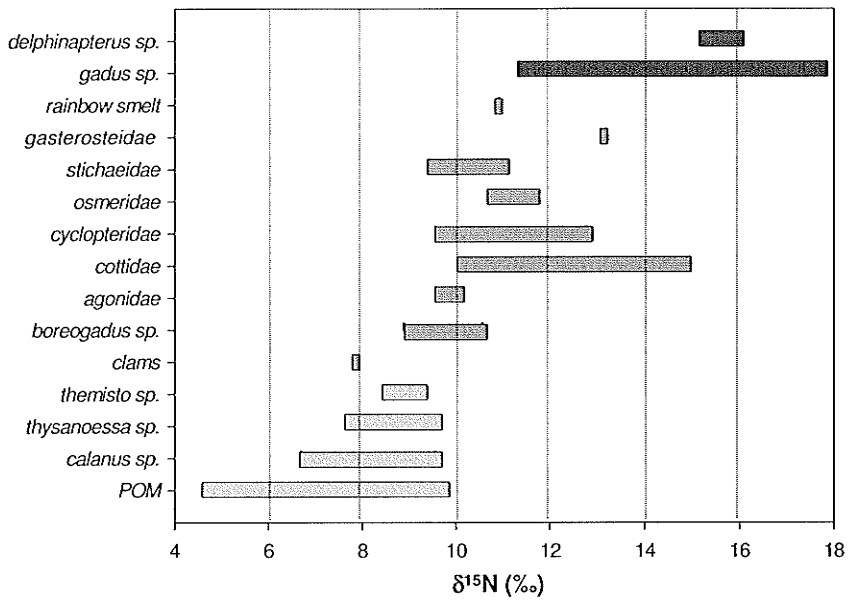
Ranges of stable isotope values for $\delta^{15}N$ and $\delta^{13}C$ are shown in Figure 6 a-b. $\delta^{15}N$ for SEHB and WHB (green bars) varied up to one trophic level, and POM ranged across almost 2 trophic levels. Juvenile and larval fish (red bars) were eating at higher trophic levels compared to zooplankton and POM. Blue bars suggest a wide range of $\delta^{15}N$ for adult fish (Gadidae); WHB and SEHB Gadidae may be feeding at different trophic levels. ANCOVA results of $\delta^{15}N$ indicated that trophic level was independent of size as well as location (P-value insiginificant). The narrow range of $\delta^{15}N$ in *Delphinapterus* sp. indicated that marine mammals had similar diets even though samples were coming from WHB and EHB beluga stocks. Figure 6b verified that most pelagic food web members had values enriched in ^{13}C signatures of marine character. The one obvious exception was a juvenile Rainbow Smelt collected in a WHB estuary (Nelson River) which showed a strong freshwater $\delta^{13}C$ signal. This was expected in a freshwater fish such as a smelt.

Stomach contents analysis of Gadidae.

Preliminary results of stomach contents analysis revealed that Gadidae from Rankin Inlet had a higher percentage of fish in their diet compared to Gadidae analyzed from Puvirnituq, Ivujivik, and Inukjuaq as shown in Figure 7. Due to the larger sample size from the eastern Hudson Bay communities, we cannot conclude that this is indeed a trend. This information does however coincide with higher trophic level results for Gadidae observed from western Hudson Bay communities.

Figure 6. Stable isotope (a) $\delta^{15}N$ (b) $\delta^{13}C$ ranges in the Hudson Bay pelagic food web.
Green bars = POM and zooplankton; Red bars = fish larvae and juvenile fish;
Blue bars = Adult fish and marine mammals (lipids not removed).

a.



b.

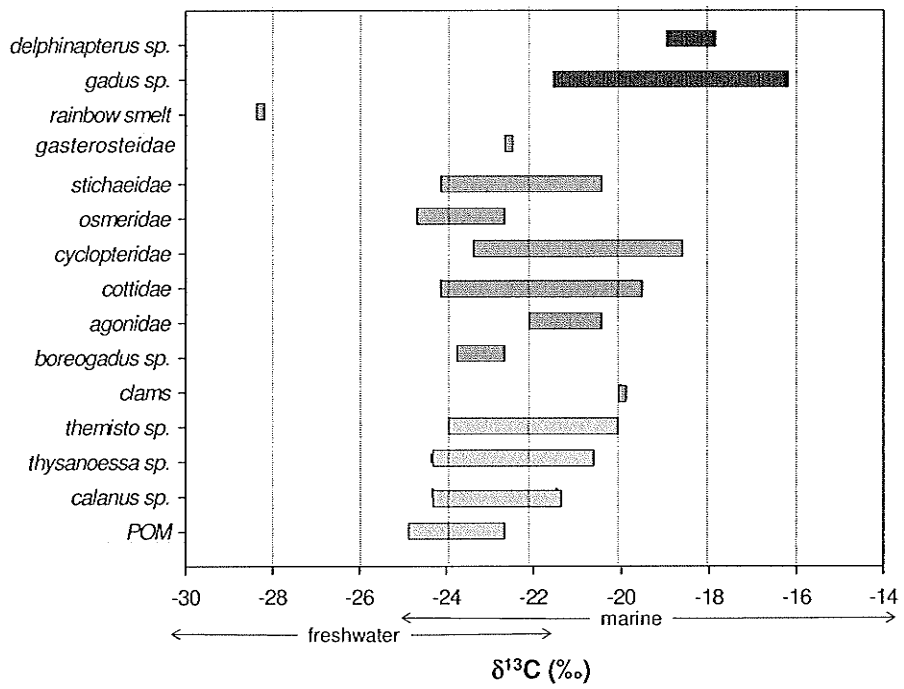
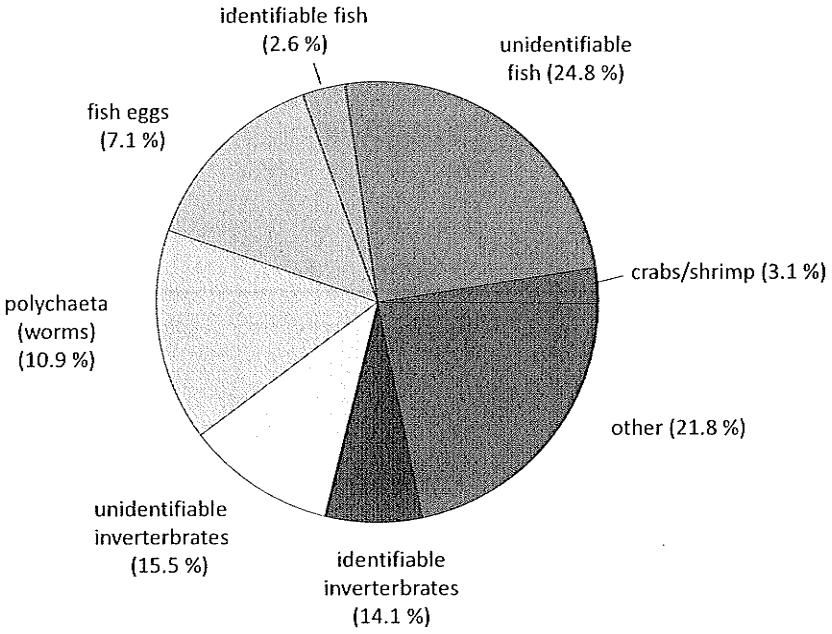
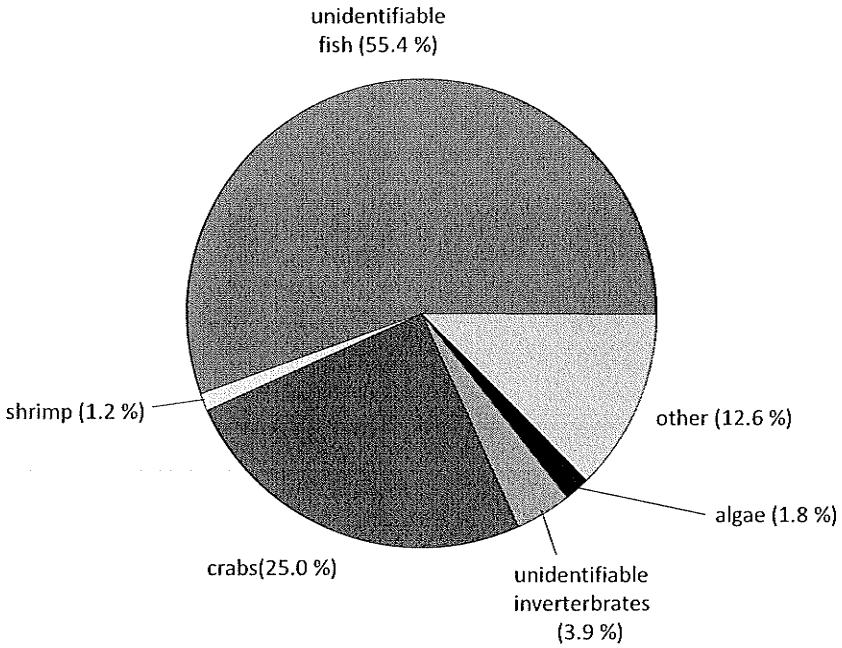


Figure 7. Stomach contents analysis for Gadidae sampled from (a) Puvirnituq, Ivujivik, and Inukjuaq communities (n = 54) (b) Rankin Inlet (n = 4).

a.



b.



BMF's and TLMF's in the Hudson Bay pelagic food web.

Figure 8 shows magnification of MeHg versus $\delta^{15}N$ in the SEHB pelagic food web. In part I of this thesis, we showed that biomagnification was not occurring with respect to HgT for zooplankton (Chapter 2, Figure 9c), therefore we chose to highlight TLMFs and BMFs for MeHg only in Hudson Bay. We chose SEHB due to the diversity of samples collected in this region, as well as the number of sample stations from this region. Our exponential growth equation for MeHg was significant and strong (Figure 8). The TLMF for MeHg calculated in Figure 8 from equation 3 was 1.96. Alternatively, magnification from prey to predator was observed when calculated BMF's were greater than 1 as seen in Table 3 for all food web members. We calculated highest BMF's (above 100) for MeHg from fish larvae to muscle tissue of marine mammals (data not shown).

Figure 8. Food web MeHg (logarithmic scale) as a function of $\delta^{15}N$ in Southeast Hudson Bay. CAL = *Calanus* sp., THYS = *Thysanoessa* sp., THEM = *Themisto* sp., SAG = *Sagitta* sp., BOR = *Boreogadus* sp., OSM = Osmeridae, STICH = Stichaeidae, COTT = Cottidae, CYCLO = Cyclopteridae, GAST = gasterosteidae, adult Gadidae from: PUV = Puvirnituq, IV = Ivujivik, IJ = Inukjuak; red points: zooplankton, blue points: larval fish, grey points: adult Gadidae, black points: *Delphinapterus* sp. from SQ = Sanikiluaq

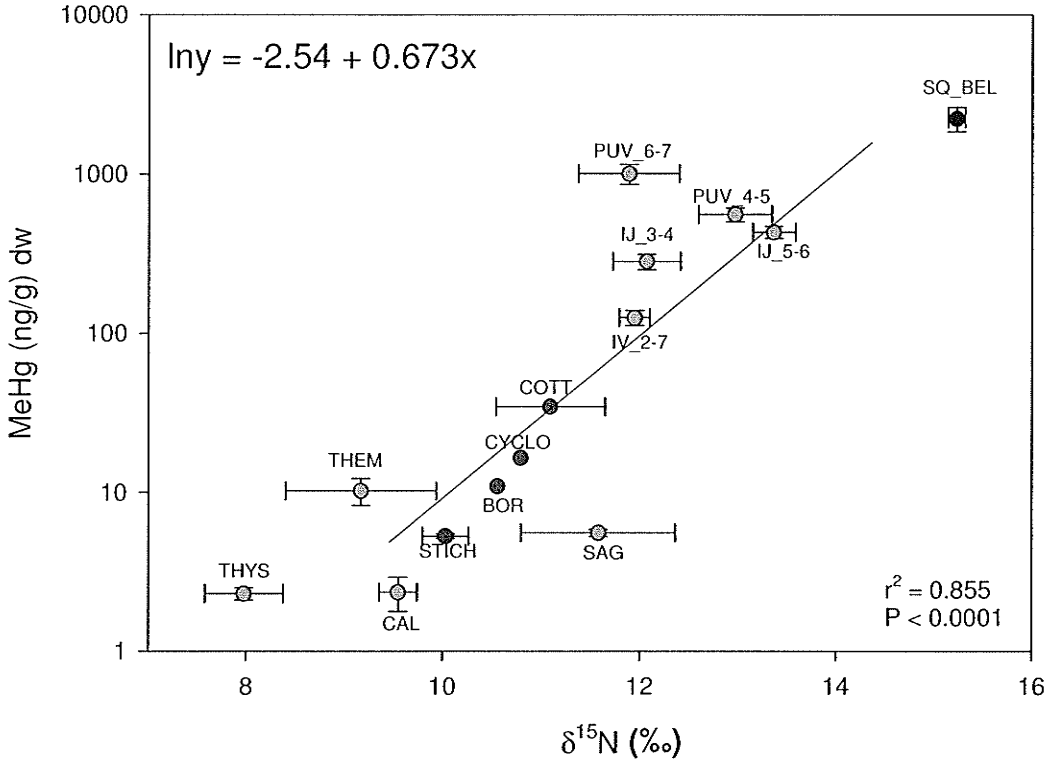


Table 3. Biomagnification factors (BMF's) for MeHg in the SEHB pelagic food web.

Predator / Prey*	MeHg BMF	Standard Error
calanus sp./POM	1.32	0.54
thysanoessa sp. /POM	2.49	0.75
themisto sp. /*calanus* sp.	5.96	2.0
sagitta sp. /*calanus* sp.	2.80	1.2
boreogadus sp. /*calanus* sp.	4.56	
cottidae/*calanus* sp.	11.5	
stichaeidae/*calanus* sp.	3.45	1.4
cyclopteridae/*calanus* sp.	7.74	1.7
Ivujivik G. Cod (2-7 years) /juvenille fish	8.37	1.5
Inukjuaq G. Cod (3-4 years)/juvenille fish	17.1	2.6
Inukjuaq G. Cod (5-6 years)/juvenille fish	24.8	1.1
Puvirnituq G.Cod (4-5 years)/juvenille fish	29.5	5.3
Puvirnituq G. Cod (6-7 years)/juvenille fish	65.2	0.086
Sanikiluaq Beluga/juvenille fish	113	20

MeHg and HgT as a function of $\delta^{15}N$ in the Hudson Bay pelagic food web.

A significant correlation between HgT and $\delta^{15}N$ was also observed in the pelagic food web of SEHB (Figure 9a). The equation that best fit the data was an exponential growth equation. Larval fish species analyzed had little variation in $\delta^{15}N$ and HgT levels. HgT (and corresponding MeHg) levels in muscle tissue of *Delphinapterus* sp. were more than 100 times higher than zooplankton and fish larvae levels, as well as in some adult Gadidae as shown in Table 4. A similar correlation between HgT and $\delta^{15}N$ in WHB was shown in Figure 9b. Levels of HgT in *Delphinapterus* sp. were 2-3 times higher than levels shown in Gadidae from WHB even though $\delta^{15}N$ values were not very different in these two marine organisms (Figure 9b). Some pelagic fish larvae had higher levels of HgT, however this did not coincide with enriched $\delta^{15}N$ values. This indicated that

processes other than biomagnificaion may be occurring in these organisms, or the % MeHg is less than 100 %.

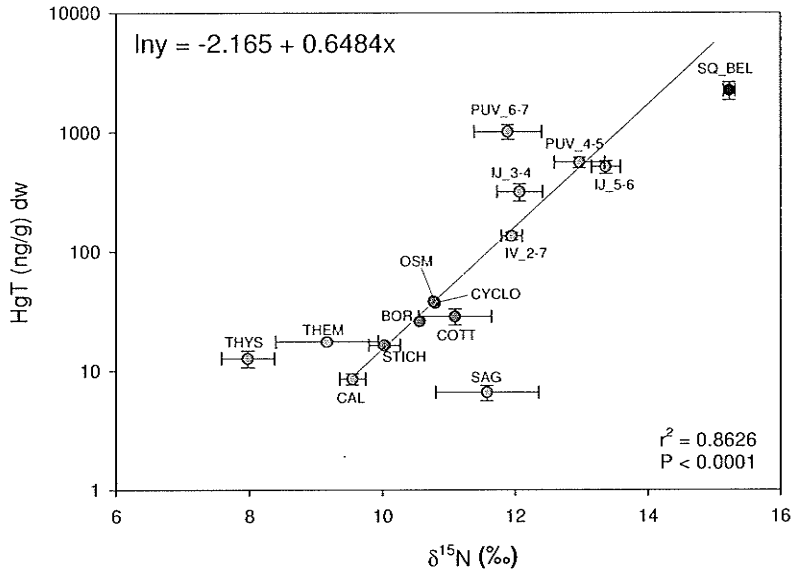
Table 4. Food web HgT, MeHg and % MeHg for SEHB.

SEHB	n	HgT (ng/g) dw	MeHg (ng/g) dw	% MeHg
POM_HB *	6-19	7.53 ± 1.3	1.13	15.0
Calanus sp.	3	8.56 ± 0.915	2.35 ± 0.571	22.8 ± 5.53
Thysanoessa sp.	3	12.7 ± 2.01	2.30 ± 0.204	21.2 ± 4.08
Themisto sp.	4	17.5 ± 0.548	10.2 ± 1.96	58.1 ± 10.1
Sagitta sp.	4	6.59 ± 0.960	5.56 ± 0.288	95.9 ± 12.1
Cottidae	1-3	28.6 ± 4.33	34.7	>100
Stichaeidae	5	16.4 ± 0.548	5.30 ± 0.180	32.2 ± 1.87
Cyclopteridae	1	37.0	16.5	44.6
*Boreo*Gadidae (larvae)	1	26.0	10.9	41.9
PUV_4-5 Gadidae *	12	558.5 ± 55.6	558.5 ± 55.6	100
PUV_6-7 Gadidae *	5	1009.1 ± 143	1009.1 ± 143	100
IJ_3-4 Gadidae	12	316.2 ± 52.6	283.3 ± 31.2	94.0 ± 4.98
IJ_5-6 Gadidae	13	512.5 ± 62.2	432.7 ± 37.5	>100
IV_2-7 Gadidae	22	134.8 ± 9.47	125.8 ± 13.8	77.4 ± 4.49
SQ *Delphinapterus* sp. *	13	2233 ± 385	2233 ± 385	100

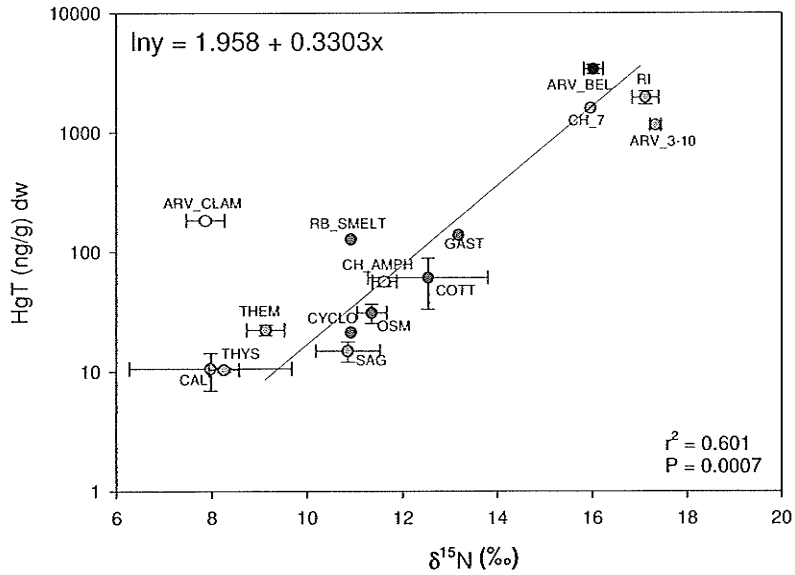
* estimates based on HgT values

Figure 9. Food web HgT (logarithmic) as a function of $\delta^{15}N$ in (a) Southeast Hudson Bay (b) West Hudson Bay.
CAL = *Calanus* sp., THYS = *Thysanoessa* sp., THEM = *Themisto* sp., SAG = *Sagitta* sp., BOR = *Boreo*Gadidae, OSM = Osmeridae, STICH = Stichaeidae, COTT = Cottidae, CYCLO = Cyclopteridae, GAST = gasterosteidae, RB_SMELT = rainbow smelt, ARV_CLAM = unknown Arviat clam species, AMPH = *Anonyx* sp. Adult Gadidae from: CH = Churchill, ARV = Arviat, RI = Rankin Inlet, PUV = Puvirnituq, IV = Ivujivik, IJ = Inukjuak. Green points: POM, red points: zooplankton, blue points: larval fish, grey points: adult Gadidae, black points: *Delphinapterus* sp. from ARV = Arviat, SQ = Sanikiluaq, white points: miscellaneous food web members.

a.



b.



Discussion

Larval fish collections in Hudson Bay.

It was a challenge to collect representative fish and larval fish samples for our Hudson Bay food web. Early studies on Hudson Bay and the ecosystem foreshadows the problems with sample collections from essentially a "desert sea" (Bajkov 1975). Even the most current studies highlight the nutrient limited productivity of Hudson Bay and Hudson Strait at the macrozooplankton and mesozooplankton levels (Harvey et al. 2006). In order to obtain representative pelagic fish and larval fish samples, more effort has to be put into collaborating and networking with communities surrounding Hudson Bay, and the Hunter's and Trapper's Organizations (HTO's) in order to obtain representative fish samples. We collaborated with the Nunavik Hunter's Fisher's and Trapper's Association (NHFTA) which provided us with representative samples of Greenland Cod (Gadidae), as well as with the Department of Fisheries and Oceans Canada (DFO) for archived samples of marine mammals (*Delphinapterus* sp.). We anticipate that these types of collaborations will allow further studies on food web structure in Hudson Bay to continue in the future.

HgT as a function of length and age in Gadidae.

Studies show that 95-100% of mercury in arctic marine mammal and piscivorous pelagic fish muscle tissue is in the form of toxic methylmercury (Wagemann 1994, Wagemann et al. 1997, Wagemann et al. 1998, Baeyens et al. 2003). Levels in whole body zooplankton and other invertebrates is less than 100% for some genera as shown in Part 1 of this thesis as well as in current literature (Stern and MacDonald 2005). Analysis techniques to

detect MeHg are often time consuming and labour intensive. In this study, we analyzed tissues for total mercury wherever possible, which provided us with an estimate of the MeHg levels in marine mammals and pelagic fish of Hudson Bay. Sub-samples of pelagic fish and invertebrates were extracted and analyzed for MeHg, in order to verify our estimates. Our sub-sampling of Gadidae from 2005 sample collections (Ivujivik, Inukjuak, Rankin Inlet) resulted in an average % MeHg content of 89.6 ± 3.6 % in the muscle tissue (n = 27 fish), which indicated that HgT and MeHg could be used interchangeably when correlating length, age and mercury levels.

Levels of MeHg were highest in Gadidae from WHB communities compared to EHB communities as shown by the LS means and y-intercepts in Table 1. ANCOVA results verified the homogeneity of slopes in Figure 2. We extrapolated HgT levels to the y-intercept which may be the background levels of HgT and consequently MeHg in Hudson Bay Gadidae. Overall, MeHg levels in Gadidae from WHB are anywhere from 2.5 - 4.4 times higher in MeHg compared to EHB Gadidae during the first larval year. Age of the fish was also important, because higher HgT levels correspond to longer exposure times in older fish (Qian et al. 2001). Long exposure times led to increases in HgT levels as age of Gadidae increases, which agrees with current literature (Somers and Jackson 1993, Tremblay et al. 1998, Sonesten 2003, Lockhart et al. 2005, Trudel and Rasmussen 2006). We also propose that Gadidae collected from EHB were on average younger compared to those from WHB, however similar aged fish from the different regions had higher levels of MeHg in WHB. The geology and sediments of WHB may have more bioavailable MeHg for uptake into the pelagic food web. We propose that river runoff and

anthropogenic sources from upstream may be contributing to higher MeHg levels in fish analyzed from WHB stations. Old marine deposits may also be a factor, compared to stations in northeast Hudson Bay that have a shield bottom (Kuzyk, pers. comm.). Granskog recently published a study on Chromophoric Dissolved Organic Matter (CDOM) levels in the major rivers contributing to Hudson Bay. Higher CDOM concentrations were found in the Churchill and Nelson estuaries compared to the rivers sampled from EHB (Granskog et. al. 2007), which may be related to our higher mercury levels found in WHB fish. Overall, MeHg levels in Gadidae from WHB were higher in Arviat, and Rankin Inlet compared to levels in Puvirnituq, Ivujivik, and Inukjuak based on length. All samples were collected in 2005 except for those from Arviat in 2003.

Our study focused on marine pelagic food chains in Hudson Bay, however there is an important benthic community which ultimately completes the food web. Benthic invertebrates such as amphipods, crabs, sea stars and clams are contributors to the diet of pelagic fish, marine mammals, and birds. Benthic algae is an important flora in the coastal marine community, providing food and shelter for benthic organisms. It also provides one of the sources of fixed carbon in the coastal marine environment (MacLaren Atlantic Limited, 1977). In Chapter 3 Figure 7, stomach contents analyses for Greenland cod revealed a substantial contribution of stomach contents were from the benthic community, including crabs, shrimps and polychaeta (worms). Sediments and anoxic waters (close to the sediment) are known to be sources of methylmercury (Morel et. al. 1998) Therefore we propose that a higher percentage of benthos in Figure 7b (25% crabs, 1.2% shrimp) compared to Figure 7a (10.9% polychaeta, 3.1% crabs/shrimp) may be a

contributing factor to the higher MeHg levels in cod from WHB. Future food web investigations in Hudson Bay must consider sampling for benthic organisms to better understand the contribution to the food web.

Arctic food web stable isotope relationships

We provided a summary of current stable isotope values for different zooplankton, larval fish, adult fish, and marine mammals (Table 2). Stable isotopes are useful in validating food web structures as well as providing evidence for particular energy transfer pathways (Campbell et al. 2005). The overall $\delta^{13}C$ isotopic enrichment trend seen across the arctic (Barrow Strait – Lancaster Sound > Northwater Polynya > Hudson Bay > Canadian Basin) was indicative of the freshwater and marine carbon influences across the arctic. We conclude that Hudson Bay had values depleted in ^{13}C compared to the high arctic in most regions. This coincides with the large amount of freshwater inputs and relatively shallow waters combined with its continental shelf nature (Martini 1986, Prinsenberg 1986).

Hudson Bay food web stable isotope relationships

At the top of our food web, beluga in both SEHB and WHB have $\delta^{13}C$ ranging from -17 to -19 ‰ (Figure 6b). Studies show that values enriched in ^{13}C (-12 to -14 ‰) in Beluga from the early and mid 1900's have shifted to relatively depleted trends (-18 to -20 ‰) in the 1990's (Outridge et al. 2005). Our results agree with this trend, which suggests a

change in diet compared to historic data in arctic marine mammals. A change in diet may be due to present day anthropogenic inputs of contaminants, environmental changes in temperature, feeding habit changes, and other ecological parameters. The narrow ranges of $\delta^{15}N$ and $\delta^{13}C$ in our samples of beluga (Figure 6a-b) further reflect the lack of diversity in the diet of these marine mammals compared to early 1900's reported stable isotope signatures (Outridge et al. 2005). This trend was not reflected in Greenland cod (Gadidae) from our study, which showed a wide range of both $\delta^{15}N$ and $\delta^{13}C$ signatures (Figure 6a-b). We propose that Gadidae was not a major component in the diet of Beluga, simply because the range in stable isotope signatures reported in our Gadidae was not seen in Beluga.

Cottidae and Cyclopteridae had similar $\delta^{15}N$ to EHB Gadidae and higher $\delta^{15}N$ compared to prey zooplankton by approximately one trophic level (Figure 4). We suspect that enrichment of ^{13}C in Cottidae from SEHB had to do with sampling technique, as Cottidae from this region were small and difficult to sample "headless", therefore whole body composites were analyzed for stable isotopes. This may have consequently altered the isotope signal in this region. In summary, the SEHB region had a diverse range of $\delta^{13}C$ (Figure 4) which was not exclusively characteristic of a marine or freshwater influence. This was most likely due to sampling techniques in larval fish, freshwater influences and nutrient input into SEHB, which in turn altered the food chain dynamics in this region.

Increases in capelin abundance paralleled with diminishing ice cover since the 1980's in Hudson Bay is evident (Dunbar 1983, Gaston et al. 2003). The decline of sea ice couples

with the decline of arctic cod due to the use of sea ice for foraging and shelter from predators such as birds. It appears as though capelin are filling the new niche in open water Hudson Bay as the climate warms, which was reflected based on our fishing efforts during the 2005 *Amundsen* cruise.

Stable Isotope Relationships in SEHB compared to WHB.

There were significant correlations between stable isotopes in the WHB and SEHB food webs (Figure 5a-b). Due to the wide ranges in stable isotopes for Gadidae and the relatively small range in stable isotopes for beluga, we conclude that beluga were feeding primarily on fish other than Gadidae with very specific isotope signatures, as well as zooplankton and POM, therefore two food chains were proposed to exist in our Hudson Bay food web:

1. POM → zooplankton → larval fish → Gadidae
2. POM → zooplankton → larval fish → piscivorous fish other than Gadidae → Beluga

HgT and MeHg as a function of $\delta^{15}N$ in the Hudson Bay pelagic food web.

Hg levels in beluga livers from many Hudson Bay communities were significantly lower compared to those levels seen in communities in the Western and Eastern Arctic (Lockhart et al. 2005). This was reflected in the relatively short pelagic food webs in SEHB and WHB. There were only 8 ‰ and 10 ‰ differences in $\delta^{15}N$ from top predator to zooplankton in SEHB and WHB, therefore approximately 2 - 3 trophic transfers in the

food web did not leave a lot of bioaccumulation potential (Campbell et al. 2003). This was in agreement with studies on food web structure in the high arctic (Hobson and Welch 1992, Hobson et al. 2002). Secondly, higher trophic level fish such as Gadidae may have self limited their population by cannibalism, which ultimately made the Hudson Bay food web lengths shorter than originally anticipated, therefore less chance for bioaccumulation (Campbell et al. 2003). A third reason may be due to the overall geology in the Hudson Bay region. Wagemann postulated that the mercury contaminating polar marine mammals has a lot to do with the anthropogenic sources coming from the geology of the land surrounding the Arctic (Wagemann et al. 1995). A generalization of the geology surrounding Hudson Bay shows that most of the inland sea is surrounded by Pre-Cambrian Shield consisting of both ignious and metamorphic rocks compared to the Eastern and Western Arctic, which consists of mostly Pre-Cambrian Shield and mostly unmetamorphosed (i.e. volcanic and sedimentary) rock. Levels of Hg in marine mammal tissues from the Eastern and Western Arctic were reported higher than those levels seen in marine mammals from Hudson Bay, which may correspond to the different geology in the region (Wagemann et al. 1995).

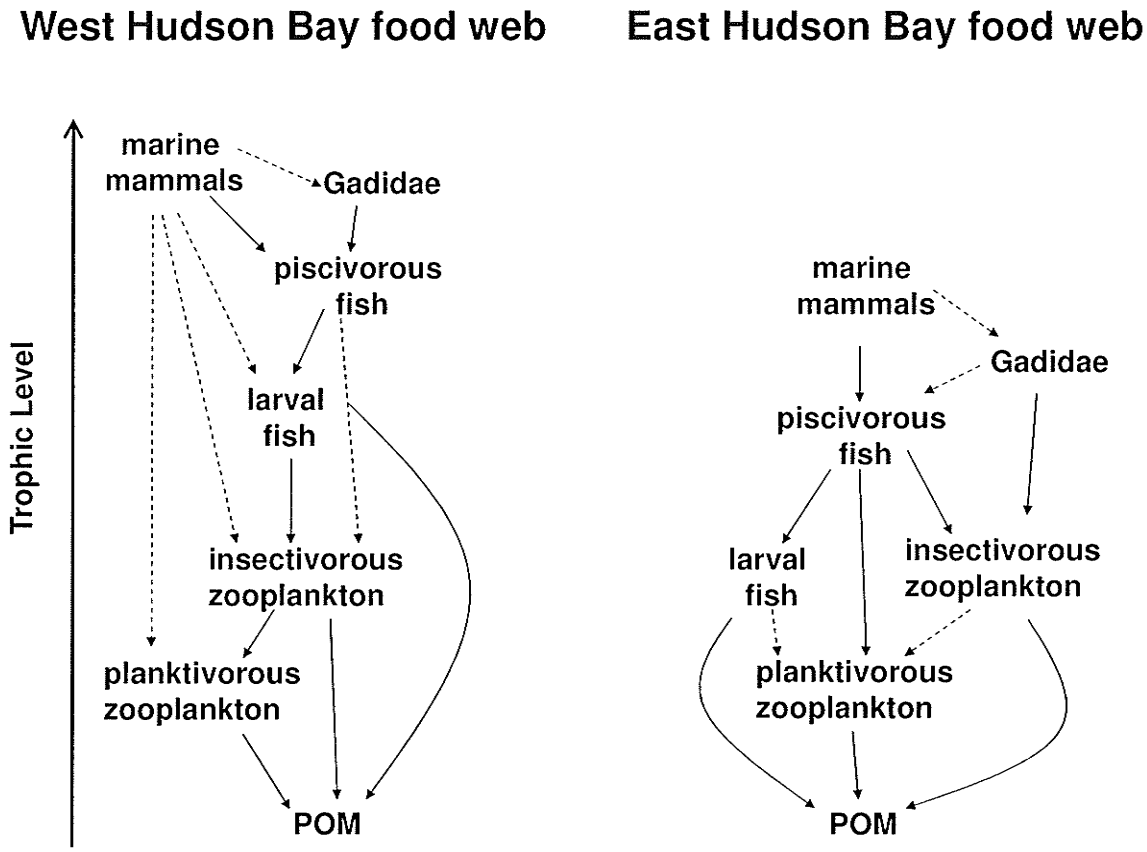
Wide ranges in $\delta^{15}N$ in for Gadidae and other pelagic food web members (Figure 6a) indicated that a broad range of prey species was in the diet of Gadidae. ANCOVA results revealed that $\delta^{15}N$ was independent of length, location, and their interaction term ($P > 0.05$). We conclude that diet of Gadidae influenced $\delta^{15}N$ in different regions, however there was no evidence to suggest that Gadidae from different communities were selecting for any prey species in particular. Future stomach contents analyses with more

samples from WHB may provide insight as to why the Gadidae from WHB had higher MeHg and $\delta^{15}N$ levels in muscle compared to the Gadidae collected from EHB communities. One possibility was due to more MeHg bioavailable at the base of the food web in WHB i.e. in zooplankton and POM at the base of the food web; therefore more MeHg was bioaccumulated in these fish (Campbell et al. 2003). Levels of MeHg in zooplankton from WHB however did not show significantly higher MeHg levels (Chapter 2, Table 2c, Figure 3, 7). We postulate that trophic transfer from zooplankton to top predator of 8 ‰ in SEHB compared to 10 ‰ in WHB may be enough of a difference to influence the top predators in the Hudson Bay pelagic food web.

Gadidae from WHB had enriched $\delta^{15}N$ (and higher MeHg levels) by one trophic level compared to EHB Gadidae and *Delphinapterus* sp. (Figure 4, Figure 5a-b, Figure 9a-b), which was indicative that a shorter food chain exists in the EHB food web. This may be due to the increased freshwater influence in this region from James Bay and the Great Whale River compared to WHB (Martini 1986, Prinsenberg 1986). These water masses may trigger a flux of nutrients to spawn productivity during the short arctic summer, which in turn promotes feeding and foraging in top predators. An increase in productivity due to higher Dissolved Organic Carbon (DOC) (Chapter 2, Figure 2) and nutrients in SEHB may have led to opportunistic predators (piscivorous fish such as Gadidae) to feed on the abundance of POM and zooplankton, which ultimately lowered trophic and MeHg levels due to selective omnivorous behaviour. Therefore, we mapped out food chains unique to WHB and SEHB in Figure 10 (adapted from Figure 5a-b). Our Gadidae stomach contents results further suggest that the WHB food chain may be longer

due to the diet consisting of more fish compared to SEHB Gadidae (Figure 7). It is not possible to conclude these findings as fact due to the small sample size of fish from Western Hudson Bay (Gagne, pers. comm.) Accumulation of Hg in fish is a result of long term feeding habits, and the stomach contents analyses presented here provided a mere snapshot of the diet of Gadidae. We propose that Gadidae feed opportunistically on fish and invertebrate prey in comparable volumes (Gagne, pers. comm.) The link to higher mercury levels in Gadidae from the west may be environmental as well as biological.

Figure 10. Food chains for West Hudson Bay and East Hudson Bay. Solid arrows indicate strong predator/prey relationships, dashed arrows indicate weaker predator/prey relationships.



BMF's and TLMF's in the Hudson Bay pelagic food web.

The TLMF for MeHg in the SEHB food web was lower than levels seen in persistant organic pollutants (POPs) from the NOW (Fisk et al. 2001), and comparable to TLMFs calculated in the Alaskan Arctic (Dehn et al. 2006). TLMFs greater than 1 indicated that food web magnification (i.e. TLMF) was occurring. A significant correlation was shown in Figures 7, 8a-b, which was an indication that magnification of MeHg in the Hudson Bay food web increased exponentially when top predators were included in the food chain. Methylmercury pathways through a food chain are difficult to trace, however its

accumulation in muscle tissue is well known (Wagemann et al. 1998), therefore we chose muscle tissue in higher trophic level organisms in order to assess magnification.

BMF's for MeHg in the SEHB food web were greater than 1 as seen in Table 3. One problem with BMF calculations that we encountered was that we had to assume a monophagus diet or prey species (Dehn et al. 2006), which even though corrected for differences in $\delta^{15}N$, it did not account for the true diverse nature of predator prey relationships which for the most part are not strictly monophagous. Our highest BMF values were approximately 1/3 the levels calculated for HgT in recent studies (Dehn et al. 2006). We conclude that either we have underestimated MeHg BMF values, or Hudson Bay is more pristine compared to the Alaskan Arctic coastal region. Studies show high HgT and MeHg in marine mammals from the western Beaufort and the high Arctic compared to Hudson Bay (Wagemann 1994, Wagemann et al. 1998, Stern and MacDonald 2005), therefore we propose that our BMF calculations were similarly lower to reflect the lower amounts of HgT in this sub-arctic system.

Conclusion

We successfully mapped out a pelagic food web for Hudson Bay and the relationships between mercury and stable isotopes within this food web. HgT and MeHg increased with age in adult *Gadus* sp. sampled from different communities surrounding Hudson Bay. Stable isotopes were used to interpret food web structure. We conclude that western Hudson Bay had a longer pelagic food chain compared to eastern Hudson Bay by approximately one trophic level. HgT versus $\delta^{15}N$ relationships were shown for WHB and SEHB. Exponential growth equations were used to interpret the food web relationships. Overall correlations between MeHg and $\delta^{15}N$ were strong and significant. Furthermore, a TLMF was calculated to be 1.96, and BMFs were calculated to be greater than 1 for all predator/prey relationships. This indicated that MeHg exponentially increased in the pelagic food web of Hudson Bay.

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CHAPTER 4

Conclusion

We investigated the biological interactions of zooplankton in the Hudson Bay pelagic food web and reported biomagnification of MeHg in Part I. We concluded that MeHg indeed was biomagnifying in some zooplankton based on the calculation of biomagnifications factors, and further applied this knowledge in Part II of this dissertation. There were many biological as well as spatial trends observed among the zooplankton in Hudson Bay with respect to mercury, and we provided adequate explanations for these trends supported by current literature. Stable isotope analysis was an invaluable tool used to assess our food web relationships in both Part I and Part II.

The pelagic food web in sub-arctic Hudson Bay was shown to have spatial variability (Part II). We conclude that levels of mercury in western pelagic fish and marine mammals were higher compared to samples collected from eastern Hudson Bay communities. We proposed two possible explanations for this trend; one based on biological differences due to pelagic fish in the west eating more fish compared to those analyzed from the east, and the second due to environmental differences in the river inputs and geology of west Hudson Bay compared to the east. Both of our explanations require more investigation, as sample sizes were small therefore biological trends were not able to be concluded as fact. Furthermore, the extent of this project focused on the biological variations, and so a more thorough investigation of environmental parameters is needed in order to draw some important conclusions.

We also showed that biomagnification of HgT was not occurring, however MeHg was biomagnifying in the pelagic food web. We are the first to report this finding in the Hudson Bay region. Biomagnification factors were also calculated and further estimated for some of the most ubiquitous food web members. Note that these values may have been over or under estimated due to the limited number of samples analyzed, as well as the approximations made in POM values for HgT, and MeHg. We propose that future food web studies incorporate POM into the regular sample collections, in order to provide more accurate values for Hudson Bay. Similar studies conducted in the high arctic have shown that mercury may be related to freshwater inputs (Pomerleau, pers. comm.). There are many food webs that have been studied in the high arctic oceans, and we successfully have contributed a food web contaminants study of Hudson Bay to this knowledge base. This is important to all of the surrounding communities that rely on Hudson Bay for subsistence. We project that our study will be linked to climate change and contaminants researchers who are using the Arctic as their study area.