Mercury uptake and dynamics in sea ice algae, phytoplankton and grazing copepods from a Beaufort Sea Arctic marine food web

By

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Abstract

Mercury (Hg) is one of the primary contaminants of concern in the Arctic marine ecosystem. Methyl Hg (MeHg) is known to biomagnify in food webs. During the International Polar Year - Circumpolar Flaw Lead study, sea ice, seawater, bottom ice algae, phytoplankton and the herbivorous copepods were collected from the Amundsen Gulf to test whether ice algae and phytoplankton assimilate Hg from their habitat, and whether Hg bioaccumulates from the seawater to the primary consumers. Sea ice algae were found to accumulate Hg primarily from the bulk bottom ice, and the sea ice algae bloom depleted Hg stored within the bottom section of the ice. Furthermore, biodilution of Hg was observed to occur in sea ice algae. Higher concentrations of Hg were also found in phytoplankton and in grazing copepods. A positive correlation between MeHg and trophic level suggests the occurrence of MeHg biomagnification even at these low trophic positions.

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Manuscript Claims

Chapter 2

Burt A, Wang F, Mundy CJ, Philippe B, Gosselin M, Tremblay J-É, and Stern G. Biodilution of mercury within ice algal populations in first-year sea ice during the 2008 spring bloom in Amundsen Gulf of the Arctic Ocean. In preparation for submission to *Environmental Science and Technology*.

A. Burt collected and analyzed all the samples for mercury, and wrote the manuscript with input from co-supervisors Stern and Wang. B. Philippe, M. Gosselin, J-É Tremblay contributed the data for chlorophyll *a*, $\delta^{15}N$, and cell abundance. CJ Mundy provided guidance and edits for the use of biological data.

Chapter 3

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A. Burt collected and analyzed all samples for mercury, and wrote the manuscript with input from co-supervisors Stern and Wang.

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List of Acronyms

AMDE - atmospheric mercury depletion event
BCF - bioconcentration factor
CCGS - Canadian Coast Guard Ship
CFL - Circumpolar Flaw Lead
chl *a* - chlorophyll *a*
CRM - Certified Reference Material
CTD - conductivity-temperature-depth sensor
CV-AAS - Cold Vapour Atomic Absorption Spectroscopy
CV-AFS - Cold Vapour Atomic Fluorescence Spectroscopy
DOC - dissolved organic carbon
dw - dry weight
FSW - filtered seawater
GC-AFS - Gas Chromatography Atomic Fluorescence Spectroscopy
GEM - gaseous elemental mercury
HCH - hexachlorocyclohexane
Hg - mercury
Hg_P - particulate mercury (atmospheric)
INT - ice-water interface
IPY - International Polar Year
MDL - method detection limit
MeHg - methylmercury
MIZ - marginal ice zone
OC - organic contaminant
PFOS - perfluorooctanesulfonate
PHg - total particulate Hg (in water or ice)
PILMS - Portable In-situ Laboratory for Mercury Speciation
PML - polar mixed layer
POM - particulate organic matter
RGM - reactive gaseous mercury
SCM - subsurface chlorophyll maxima
THg - total Hg
TL - trophic level
UCTEL - Ultra-Clean Trace Elements Laboratory (at the University of Manitoba)
WC - water column
ww - wet weight

Chapter 1

Introduction

In the Arctic, it is estimated that up to 100 metric tons of mercury (Hg) could be deposited annually from the atmosphere during atmospheric mercury depletion events (AMDEs; Outridge *et al.* 2008). AMDEs involve the oxidation of gaseous elemental Hg (GEM, Hg (0)) to particulate Hg (Hg_P) and reactive gaseous Hg (RGM) by sunlight-induced reactions in the presence of bromine and bromine oxide (BrO; Schroeder *et al.* 1998, Lindberg *et al.* 2002, Aspmo *et al.* 2005, Steffen *et al.* 2005, Kirk *et al.* 2006, Outridge *et al.* 2008) released from open leads. It has been postulated that the Hg (II) that is deposited to the snow and ice surface during AMDEs, which has survived photo-reduction (Ferrari *et al.* 2005, St. Louis *et al.* 2005, Kirk *et al.* 2006), ends up in the water column where it can then be methylated and consequently accumulate up through the marine food web (Poulain *et al*. 2007b, Chaulk *et al.* 2011). It is currently still unresolved as to the net amount of deposition of AMDE-Hg and its relative importance in contributing to biotic Hg in the Arctic.

In this thesis research project I investigate the potential for sea ice and water column algae to bioconcentrate and/or bioaccumulate Hg and the subsequent transfer of Hg to grazing zooplankton in the Amundsen Gulf of the Arctic Ocean. This study has important implications for northern health in the face of a warming climate, as dramatic reductions in permanent ice moves the Arctic Ocean toward a seasonally ice-free state (Lindsay and Zhang 2005; Maslanik *et al.* 2007), which will have important consequences for the light environment, mixing, upwelling, primary production, habitat and range for large animals like seals and whales. In addition, the timing of feeding and

spawning of primary consumers is based on temperature and light penetration through the ice, and these herbivorous zooplankton face a situation where they must adapt quickly or will miss early access to high energy food sources that sustain their population growth (Søreide *et al.* 2010).

The thesis study was carried out between February and July of 2008, as part of the International Polar Year – Circumpolar Flaw Lead (IPY-CFL) System Study. The primary objective and question of this thesis was to quantify whether 1) AMDEs were the principal avenue for Hg concentration increases in the lower trophic levels (algae and zooplankton) of the Amundsen Gulf food web. To accomplish this, I sampled and measured the Hg levels in the atmosphere, snow, ice, brine, seawater, sympagic algae, under-ice and pelagic phytoplankton and zooplankton. The measurements were done in conjunction with the collection of peripheral data on ice characteristics, light, temperature, salinity, nutrients, stable isotopes, chlorophyll, and algal species counts. Subsequent objectives were to test whether: 2) Sea ice algae take up Hg from their ice habitat, 3) Open water phytoplankton bioconcentrate Hg from the seawater, and 4) Ice and open water algae pass Hg to the next trophic level, where it biomagnifies. This work was conducted while the Canadian Research Icebreaker *CCGS Amundsen* remained mobile in the pack ice, moving into and out of multi-year and seasonal ice-floes, landfast ice and through the open water. Hg, methylmercury (MeHg) and other variables were measured within the ice, brine and seawater over the same period and at the same stations and locations as algae were sampled, thus analogous conditions were experienced between studies. More information about the CFL project and maps of the complete ship track and sampling locations are available in Barber *et al.* (2010).

1.1 Sea Ice and Sea Ice Algae

First-year sea ice forms in the fall of the year and grows vertically throughout the winter. It contains a matrix of ice, brine and air (Perovich and Gow 1996); ions and particulates become trapped between ice crystals, forming brine pockets, during ice formation. Brine channels are important habitat for microorganisms within the ice. Brine pockets vary in size and distribution throughout the ice, and their degree of connectivity depends on ice temperature, texture, and growth rate (Weeks and Ackley 1986, Perovich and Gow 1996). Brine volume fraction, a function of temperature and salinity (Frankenstein and Garner 1967), has a critical value of 5%, above which vertical movement of brine within the ice column may occur (Cox and Weeks 1975). When individual brine pockets converge, due to the porosity of the ice, nutrients are replenished into the ice from the ice-water interface or desalination of the ice occurs due to gravity drainage (Cota *et al.* 1987, Cota *et al.* 1991, Pućko *et al.* 2010b).

The sea ice algal community (sympagic algae) thrives in brine channels at elevated salinity (compared with the bulk ice and underlying sea water) and near-freezing temperatures (Krembs *et al.* 2002). Many organisms live in the sea ice: bacteria, fungi, algae, and protozoa (Horner 1985) and can inhabit a much higher proportion of the ice surface (6 to 64 %) relative to, for example, soils (1%; Krembs *et al.* 2000). The highest abundance of organisms resides within the bottom few centimetres of the sea ice (Horner 1985, Horner *et al.* 1992, Arrigo and Thomas 2004). Differences in local bottom ice abundance can be due to light availability (Michel *et al.* 2006), salinity, temperature, ice texture, ice formation (Cota and Horne 1989), nutrient advection (Cota *et al.* 1987), bottom ice topography (Krembs *et al.* 2002), and trophic interactions (Krembs *et al.*

2002). The ice-water interface is also an important habitat for under-ice algae (Smith *et al.* 1990). Arrigo *et al.* (2012) recently reported the presence of a massive under-ice phytoplankton bloom in the Chukchi Sea and attributed it to climate-enhanced photo-processes. Both sympagic and under-ice algae are a readily available food source to herbivorous zooplankton species in the late spring before the ice melts and the phytoplankton bloom begins in the open ocean (Sime-Ngando *et al.* 1997).

In the Arctic Ocean, sea ice algae may contribute up to 57% of the primary production (water column and sea ice; Gosselin *et al.* 1997), emphasizing the potential importance of the brine concentration process in amplifying lower food web exposures to Hg, translating to high biological exposure (Pućko *et al.* 2010b). Changes in sea ice dynamics in the Arctic may have future impacts on marine productivity and ecosystem structure (Juul-Pedersen *et al.* 2010), as well as contaminant biogeochemistry.

1.2 Open Ocean Phytoplankton

In winter, phytoplankton growth in the Arctic Ocean water column is limited by low light availability. Arctic sunrise in the Beaufort Sea begins in March, a time when the pack ice is still covered by snow thus inhibiting light penetration into the water column (Bergmann *et al*. 1991, Andrea Bjarnarson pers. com.). In spring, the high density of the sympagic and under-ice phytoplankon shades the water column (Horner and Schrader 1982) thus delaying the onset of the water column phytoplankton bloom until after the sloughing-off of ice algae (Michel *et al.* 2006, Horner and Schrader 1982). The spring bloom is often associated with the retreating sea ice edge, and is held in the euphotic zone by the halocline that is created as melt water is released (Juul-Pedersen *et al*. 2010).

Pelagic phytoplankton are important to grazing zooplankton species in the water column in the summer (Falk-Petersen *et al*. 1990, Forest *et al*. 2011), as well as feeding the benthic community when it falls to the ocean floor. It is the largest carbon transport system to the benthos (Michel *et al.* 1996, 2006).

1.3 Contaminants in the Arctic Marine Food Web

While many studies have measured contaminant levels in snow and in bulk ice (Ferrari *et al.* 2005, St. Louis *et al.* 2005, Kirk *et al.* 2006, Poulain *et al*. 2007a, Chaulk *et al.* 2011), little is known about how these contaminants are transferred from the abiotic environment to the food web.

Pućko *et al.* (2010a) found that hexachlorocyclohexane (HCH), an organochlorine pesticide no longer in use in North America (Health Canada 2009), was concentrated in the brine during ice formation and was rejected along with the brine during the seasonal melt period, as it is fairly hydrophilic. In a second study, Pućko *et al.* (2010b) found that as the brine volume fraction moved closer to ca. 10 %, in the late spring, both α- and γ-HCH concentrations decreased as a function of increasing brine volume and decreasing brine salinity (i.e., HCH drained from the ice along with the salt during the spring and summer melt period). The marked change in the α/γ-HCH ratio was attributed to the biological processes (algae and bacterial growth and metabolism) at work within the ice (Pućko *et al.* 2010a).

Hg processes in the cryosphere have also been studied. Chaulk *et al.* (2011) found that AMDEs during the CFL study did not determine Hg concentrations in the ice; however, they did influence the Hg in overlaying snow, which is thought to melt and add

Hg to the seawater later in the season. Chaulk *et al.* (2011) determined, as well, that sea ice brine contained elevated levels of Hg (as high as 70 ng L^{-1}), which sea ice algae are exposed to as they live in the brine channels.

As diet is the main route of exposure of animals to most contaminants including MeHg (Borgå *et al.* 2004), it follows that algae are the major initial entry point for these contaminants into the aquatic food web (Pickhardt and Fisher 2007). There are various ways whereby Hg may act in a food chain. Two of them are: 1) Bloom dilution (biodilution): as a bloom grows, particulate Hg decreases in the particulate organic matter (POM; Chen and Folt 2005). Grazed algae may be impeding Hg accumulation by the next trophic level, and 2) Bioaccumulation or bioconcentration (Kirkwood *et al*. 1999). Bioaccumulation is an inherent property of a chemical that expresses the chemical's capacity to accumulate in organisms (Gobas *et al.* 2010), whereas bioconcentration is a special case of bioaccumulation of a chemical from the water column usually via epithelial tissues or drinking water (Hall 2003). Bioconcentration could be due to increased surface area (cell walls) for Hg to bind (Pickhardt and Fisher 2007). Bioconcentration could be due as well as to an infinite pool of available Hg to supply a growing algal population caused by remineralization of Hg by water column bacteria (Kirkwood *et al*. 1999). This microbial “loop” may be an important process in maintaining suspended Hg levels in the water column (Cole *et al*. 1988, Poulain *et al*. 2007b). The next step is biomagnification, which results when there are relatively low concentrations in water (ppt in arctic waters), high bioconcentration at the first trophic level (ppm in primary producers), and low rates of elimination of the chemical by higher trophic level organisms (Braune *et al.* 2005). Food requirements are controlled by

metabolic rate and production (growth, reproduction and lipid store) for each species, thus metabolic rate is closely linked to uptake of contaminants (Braune *et al.* 2005). For example, homeotherms (mammals) have greater energy requirements than poikilotherms (fish) because of the need to maintain a constant body temperature, so their metabolic rate and caloric requirement is higher. Consequently, the largest biomagnification factors are classically found between fish and mammals and fish and sea birds (Muir *et al.* 1992, Fisk *et al.* 2001).

1.4 Trophic Transfer of Mercury

For Hg to become elevated in high trophic level species, it must be taken up efficiently at the base of the food chain, retained, and passed on to predators (Morel *et al.* 1998). Stable isotopes of carbon and nitrogen are used to determine food web carbon sources, trophic level, and trophic transfer of contaminants (Hobson and Welch 1992; Atwell *et al.* 1998; Tomy *et al.* 2004; Dehn *et al*. 2006; Loseto *et al.* 2008a, b). Tamelander *et al.* (2008) explain, using $\delta^{15}N$ isotope analysis, that zooplankton in the Barents Sea assimilate energy primarily from pelagic primary production; however, ice algae, at times, contribute to zooplankton diets. They reported that trophic levels (TL; calculated using $\delta^{15}N$) for the Calanoid copepods *Calanus hyperboreus* and *C. glacialis* varied from 1.3 – 2.7, the expected TL being 2.0. The TL of *C. glacialis* was significantly and inversely related to the depth of phytoplankton chlorophyll *a* concentration. This relationship indicated that copepods were grazing primarily on the abundant biomass of the subsurface chlorophyll maxima (SCM). Tamelander *et al.* (2008) stated that copepods having a TL of 2.0 or less fed herbivorously, while values above 2.0 suggest that they fed

omnivorously. In this environment an omnivorous diet could include small stages of zooplankton that are close in size to algal cells and are located in the path of the larger grazing zooplankton.

The transfer of energy from algae to grazing zooplankton has been extensively studied. Many studies have outlined the importance of *C. hyperboreus* in the trophic transfer of carbon and nitrogen from algae to predators, and also to the benthos (Dawson 1978, Michel *et al.* 1996, Hirche 1997, Fortier *et al*. 2001, Michel *et al.* 2006). The interactions between herbivorous zooplankton species and both sea ice algae and phytoplankton are important when studying the transfer of Hg from the primary production into the food web. These are the first species to be exposed to bioavailable forms of Hg, and then, in turn, transfer their Hg body burden up the foodweb when predated. Søreide *et al.* (2010) reminds us that, though the primary energy source to herbivorous zooplankton is phytoplankton at the SCM, ice algae play a very important role in trophic transfer of energy. *C. glacialis* account for up to 80 % of the biomass in the Arctic shelf seas (Tremblay *et al.* 2006) and play a key role in the pelagic lipid-based arctic food web (Falk-Petersen *et al*. 1990). Female *C. glacialis* are known to time their maturation and reproduction to coincide with the ice algal bloom, so their offspring may take advantage of the high-quality phytoplankton bloom as they descend through the water column for the winter. *C. hyperboreus* are known to primarily feed on the open water bloom. Due to the specific timing of their life cycle, *C. glacialis* are sensitive to changes in the ice regime (Søreide *et al.* 2010).

1.5 Thesis Organization

This thesis was designed as a "sandwich thesis"; two manuscripts sandwiched between an introduction and a conclusion. Chapter 1 (this chapter) provides a general introduction to sea ice algae and phytoplankton in the Arctic Ocean. Current literature on contaminant studies in the Arctic cryosphere was reviewed, and the objective of this thesis research identified.

In Chapter 2, I investigated whether AMDEs and Hg levels in the physical environment seasonally influence sea ice algae Hg levels. I explored the relationships between Hg levels in the sea ice, ice-water interface water, sea ice algae and the stable isotopes of nitrogen.

In Chapter 3 I focused on the pelagic producers and zooplankton. Relationships between Hg levels in the environment and the water column algae were studied. Here, I looked at the trophic interactions between primary producers in both ice and open water, and herbivorous calanoid copepods, *C. hyperboreus* and *C. glacialis*.

In Chapter 4, I provide an overview of our findings and conclusions. I present some lessons I have learned, as well as new directions for future research.

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Chapter 2

Biodilution of mercury within ice algal populations in first-year sea ice during the 2008 spring bloom in Amundsen Gulf of the Arctic Ocean

Abstract

Despite a considerable number of studies on algal uptake of mercury (Hg) in the laboratory and in warm regions, little is known about how sea ice algae take up Hg in the Arctic Ocean. Sea ice algae grow within the bottom centimetres of sea ice in the Arctic Ocean. These early spring primary producers live within brine channels, where ions and contaminants such as Hg become concentrated as they are rejected from the developing ice crystal matrix during ice formation. During the International Polar Year - Circumpolar Flaw Lead (IPY - CFL) study, sea ice, seawater, and bottom ice algae were collected from February to May 2008 in the Amundsen Gulf to test whether sea ice algae obtain Hg from their ice habitat. We found that the sea ice brine is highly enriched in Hg (up to 20.1 ng L^{-1}, comparing with seawater concentration of 0.2 ng L^{-1}), and that sea ice algae accumulate Hg from the bulk bottom ice. As total particulate Hg (PHg) in the ice particulate organic matter (POM) increased, total Hg (THg) in the bulk bottom ice decreased ($r^2 = 0.45$, $p < 0.05$, $n = 10$), suggesting the growth of sea ice algae could deplete the Hg stored within the ice. Furthermore, biodilution was observed to occur in the sea ice algae; as cell numbers increased, PHg decreased ($r^2 = 0.99$, $p < 0.001$, $n = 5$).

2.1 Introduction

Since the discovery of atmospheric mercury depletion events (AMDEs; Schroeder *et al.* 1998), it is thought that a fraction of the deposited Hg is able to make its way to the pelagic system and become bioavailable to the low trophic levels of the Arctic Ocean food web. Hg and especially methyl Hg (MeHg) are important contaminants to monitor in marine food webs, as they are known to bioaccumulate and biomagnify up the food chain. In Canada's North, there are many communities who rely on subsistence foods such as fish, seals, and whales, in which MeHg body burdens in the muscle tissue can be elevated, and much of the time, higher (Campbell *et al.* 2005) than the Health Canada consumption guideline (0.5 – 1.0 μg g^{-1} THg in the edible portion of retail fish as of 11 July 2007; Health Canada 2012).

AMDEs, which begin at polar sunrise and end at snow melt, are unique to the polar marine environment and involve the oxidation of gaseous elemental Hg (GEM, Hg^0) to particulate Hg (Hg_P) and reactive gaseous Hg (RGM) by sunlight-induced reactions in the presence of bromine and bromine oxide (BrO; Schroeder *et al.* 1998, Outridge *et al.* 2008). Much of the Hg(II) deposited to snow and ice surfaces during AMDEs is known to undergo rapid photo-reduction and is re-emitted back to the atmosphere (Ferrari *et al*. 2005, St. Louis *et al*. 2005, Kirk *et al*. 2006); the Hg(II) fraction that has survived the photoreduction (e.g., buried by fresh snow) or is directly deposited into the open lead likely ends up in the marine ecosystem where it can be methylated and accumulated up through the food web (Poulain *et al*. 2007, Outridge *et al.* 2008, Larose *et al*. 2011).

Sea ice has an intricate and highly variable internal structure consisting of ice crystals and inclusions of brine and air, often referred to as total porosity. As sea ice forms, salts and particles become trapped between the growing crystalline structure in pockets (Weeks and Ackley 1986). Brine inclusions are sandwiched between the ice crystals, and their size and degree of connectivity are strongly associated with temperature at the time of ice formation (Pućko *et al.* 2010a). In the brine channels solutes are concentrated: salts, contaminants such as hexachlococyclohexane (HCH; Pućko *et al*. 2010a, b) and Hg (Chaulk *et al.* 2011), and particles such as algal and bacterial cells (Różańska *et al.* 2008) are excluded from the developing ice matrix.

Sea ice algae thrive in brine channels within the ice at near freezing temperatures and high salinity (Krembs *et al.* 2002). While the ice-water interface is also an important habitat for Arctic organisms (Horner *et al.* 1992, Thomas and Dieckmann 2010), the highest abundance of algae resides within the bottom few centimeters of first-year sea ice and are a readily available food source to herbivorous zooplankton species prior to spring sea ice melt (Smith *et al*. 1990, Arrigo *et al.* 2010, Sime-Ngando *et al.* 1997). Nutrients are replenished to the under-ice community by the motion of surface waters against the bottom ice (Krembs *et al.* 2000, Brown *et al.* 2010). Sea ice algae contribute nearly 60% of the annual Arctic Ocean primary production (Gosselin *et al*. 1997), emphasizing the potential importance of the brine concentration process in amplifying lower food web contaminant exposures (Pućko *et al*. 2010a, b).

Algae have the ability to accumulate Hg from their surroundings *via* adsorption, absorption and metabolic uptake (Rai *et al*. 1981, Bačkor *et al*. 1998, Kirkwood *et al*. 1999, Schmitt *et al*. 2001). Hg accumulation by algae has been hypothesized to occur in

proportion to its supply in the water column (Watras and Bloom 1992, Hudson *et al*. 1994, Watras *et al*. 1998), by passive uptake of neutrally charged species (e.g., $HgCl_2$, MeHgCl; Mason *et al*. 1996); however, Morel *et al.* (1998) reported that Hg taken up by diatom cells must be in the form of MeHg, as other forms of Hg are permeable to the cell membrane and diffuse out as easily as they diffuse in. Bioaccumulation factors reported by Watras *et al*. (1998) indicate that the uptake of Hg by freshwater phytoplankton is a major step in the bioaccumulation process. Kirkwood *et al*. (1999) discovered that Hg accumulation and concentration, rather than biodilution, occurred experimentally in freshwater phytoplankton. In agreement with Kirkwood *et al*. (1999), Pickhardt and Fisher (2007) reported that cellular uptake of inorganic and organic Hg increased with cell abundance, reflecting the increased number of cell surfaces with which to bind. Pickhardt and Fisher (2007) and Mason *et al*. (1996) agree that about 10% of inorganic and 60% of MeHg is found in the cytoplasm of algal cells, which is retained by the next trophic level, herbivorous zooplankton, rather than eliminated in fecal pellets (Morel *et al*. 1998). In aquatic organisms, accumulation of contaminants results primarily from dietary consumption (Hall 1997). Recent studies suggest that the warming climate in the western Canadian Arctic and the decrease in perennial ice cover (Maslanik *et al*. 2007) may result in an increase in biological Hg exposure due to perturbations to top-down and/or bottom-up processes (Outridge *et al.* 2008, Stern *et al.* 2012).

In this study we examine the biophysical processes associated with primary production in the sea ice and Hg bioavailability under natural conditions in the western Canadian Arctic Ocean during the 2008 spring melt season. As part of the Canadian International Polar Year (IPY) project, the Circumpolar Flaw Lead (CFL) system study

and ArcticNet, the Canadian Research Icebreaker *CCGS Amundsen* was mobile throughout the Beaufort Sea and Amundsen Gulf regions in the western Canadian Arctic. We sampled ice algae along with biological variables in concert with physical monitoring of atmospheric, ice, and water levels of Hg to assess whether AMDEs were adding bioavailable Hg to the sea ice algae.

2.2 Methods

2.2.1 Sampling sites. As part of the IPY-CFL System Study, sea ice cores were collected between February and May of 2008 from 15 stations in the Amundsen Gulf (Figure 2.1, Table 2.1). The *CCGS Amundsen* remained at each of the ice floe stations from 1 up to 10 days. Overview of the CFL project and physical description of the study site can be found in Barber *et al.* (2010). For our purposes sea ice POM samples were collected during sea ice warming and until melt pond formation. Ice algae accumulation (chlorophyll *a* biomass) began to increase in mid-March (day 79), and reached a maximum in early May (Brown *et al.* 2010). There were times (stations F1 and F2; locations available in Table S2.3 in the appendix) when we were able to sample near the receding ice edge; however, most often samples were collected from > 2 km^2 ice floes under full snow cover until melt, then under full ice cover with absence of snow.

Figure 2.1. Stations sampled for ice algae in the Amundsen Gulf region. Stations: D = drifting ice, F = landfast ice.

Table 2.1. Ice core collection dates, locations and results for ice POM, bulk bottom ice, surface water and brine analyses by station and date.

			Ice cores (bottom 10 cm)						Bulk ice[3]	Surface water	Brine	
Date	Day of year	Station	PHg (µg g^{-1})	PHg (pgL^{-1}$_{sc}$)	Total cells (Cells L^{-1})	Chl-*a* (µg L^{-1})	DOC (µmol L^{-1})	PM δ^{15}N	THg$_{BI}$ (ng L^{-1})	THg$_{SW}$ (ng L^{-1})	THg$_{Br}$ (ng L^{-1})	ν_b (%)
9-Feb-08	40	D19	0.017	0.473	-	-	-	-	-	-	-	-
25-Feb-08	56	D26	0.021	0.390	-	-	-	-	-	-	-	-
1-Mar-08	61	D27	0.007	0.480	-	-	-	-	0.37	0.28	-	-
8-Mar-08	68	D29	0.022	0.506	4.13E+07	1.38	-	-	0.18	0.21	-	9.1
18-Mar-08	78	D29	-	-	-	-	-	4.26	-	-	-	-
19-Mar-08	79	D31	0.014	0.252	-	0.12	67.0[1]	-	0.03	-	-	8.8
24-Mar-08	84	D34	0.008	0.146	-	-	-	-	0.65	0.16	-	7.6
25-Mar-08	85	D33	0.008	0.143	8.68E+07	0.34	40.1	4.46	0.52	0.22	15.10	13.5
1-Apr-08	91	D33	-	-	-	-	-	-	-	-	-	-
4-Apr-08	94	D33	-	-	-	-	-	3.84	-	-	-	-
8-Apr-08	99	D36	0.016	0.384	1.58E+08	58.7	61.1	2.42	0.25	0.11	-	10.7
12-Apr-08	103	D38	0.004	0.102	-	127.3	43.6	6.39	0.88	0.22	1.58	9.2
17-Apr-08	108	D41	0.015	0.458	4.48E+08	139.1	531.0	9.43	0.48	0.10	20.13	22.3
20-Apr-08	111	D41	0.018	0.562	-	262.3	-	6.84	0.48	0.10	20.13	22.3
28-Apr-08	119	D43	0.014	0.334	1.55E+09	160.8	369.8	6.21	-	0.25	-	12.7
5-May-08	126	D43	0.020	0.704	-	149.6	1169.9[2]	-	-	0.25	-	12.7
9-May-08	130	F1	0.013	0.505	4.11E+09	1186.0	893.2	6.91	-	-	-	17.4
14-May-08	135	F2	0.013	0.403	3.95E+09	637.9	1005.6	5.20	0.32	0.38	2.74	5.9

NB: - denotes no sample; $\nu_b = 0.1$ SICE $(49.185/|$ TICE$|$ $+ 0.532)$ for $-0.5°C \geq$ TICE $\geq -22.9°C$ (Frankenstein and Garner 1967); [1]March 22, Stn 32; [2]May 08, Stn F1; [3]Bulk ice (BI) sub-samples were taken from just above the algal horizon ~ 4 cm above the bottom of the ice core.

2.2.2 Particulate collection and analysis. Ice particulate samples were collected from the bottom 10 cm section of each ice core using a 9 cm core diameter, Mark II coring system (Kovacs Enterprises, Lebanon, USA) and following the "clean-hands/dirty-hands" protocol (Fitzgerald 1999). All surfaces that contacted the corer were scraped with Hg-clean porcelain blades. All samples were kept frozen and shipped back to Winnipeg for analysis. To prevent cell lysis (Garrison and Buck 1986), core bottoms were first freeze-dried and the remaining particulate re-suspended in a controlled manner using a clean artificial seawater solution (formulated from Milli-q water; salinity of 32 ‰; pers comm CJ Mundy and Debbie Armstrong). The resulting solutions were then filtered onto pre-combusted and weighed 0.7 μm Whatman GF/F filters, oven dried at 60 °C, and weighed prior to analysis. All solutions, filters, and lab equipment were batch tested for total Hg (THg < 0.1 ng L^{-1}) at the University of Manitoba's Ultra-Clean Trace Elements Laboratory (UCTEL).

THg in the filtered particulate (PHg) was extracted using a modified hot acid aqua regia digest (Hendzel and Jameson 1979) and analyzed using Cold Vapour Atomic Absorption Spectroscopy (CV-AAS) following U.S. EPA Method 245.2 (U.S.EPA 1974) at the Freshwater Institute in Winnipeg, Manitoba. Reagent blanks, filter blanks, duplicates, and Certified Reference Materials (CRMs; LUTS-1, SRM 1573a, TORT-2, DORM-3; the National Institute of Standards and Technology and the National Research Council of Canada) were used for quality assurance and control. The method detection limit (MDL) was 0.01 μg g^{-1} dry weight (dw), filter blanks included in each run were subtracted from the samples. Samples were analyzed for MeHg by Flett Research Ltd.

using Cold Vapour Atomic Fluorescence Spectroscopy (CV-AFS) with a detection limit of 0.15 ng g^{-1} dw following U.S. EPA Method 1630 (U.S. EPA 1998).

Chlorophyll *a* (chl *a*) biomass was analyzed as described by Mundy et al. (2011). While on board the *CCGS Amundsen*, core bottoms were melted in filtered (0.2 µm polycarbonate membrane) seawater (FSW) to obtain a 3:1 dilution ratio to minimize osmotic shock (Garrison and Buck 1986). Duplicate sub-samples were filtered through 0.7 µm Whatman GF/F filters. Samples were extracted under dark conditions, for a minimum of 18 hours, in 10 mL of 90% acetone at 5 °C. Biomass was determined (before and after acidification with 5% HCl) using a Turner Designs 10-AU fluorometer (Parsons *et al.* 1984). Volumes filtered ranged from between 2 and 100 mL for the bottom ice sections (0-3 cm), and between 10 and 1000 mL for upper sections (3-7 cm) depending on biomass present.

Ice core samples were collected and analyzed for dissolved organic carbon (DOC) as described by Song *et al.* (2011). In brief, the center portion of each 10 cm core section was transferred into a 200 mL all-glass syringe (Perfektum®). Meltwater in the 200 mL syringe was passed through 0.2 µm polyethersulfone membrane syringe filters (Whatman) and collected into 60 mL glass bottles (Qorpak®). Prior to use, the filters were cleaned with 10% HCl and Nanopure water and, along with the collections bottles, were tested and verified to be free of DOC contamination. All samples were refrigerated and stored under dark conditions while on board the *CCGS Amundsen* and during transport to the Institut des sciences de la mer de Rimouski where they were analyzed. All samples were acidified to ~ pH 2 using 25% H_3PO_4 to remove the dissolved inorganic carbon and analyzed in triplicate using a Shimadzu TOC-5000A Total Carbon Analyzer calibrated

using potassium biphthalate. The mean coefficient of variation of triplicate measurements was 4% (range: 0.2-13%).

Cells ≥ 4 μm were identified at the Université de Quebec à Rimouski to the lowest possible taxonomic rank and enumerated under an inverted microscope (WILD Heerbrugg) equipped with phase contrast optics (Lund *et al.* 1958). With the exception of low abundance samples, 400 cells or more were counted in each settling chamber. For samples collected during the bloom period, 2 mL was sufficient to obtain the minimum number of protists required. In the lower biomass samples up to 80 mL was required. Samples were allowed to settle in a sedimentation chamber for 18 hours under dark conditions before counting (Philippe 2011).

For analysis of nitrogen stable isotopes, the bottom-ice material was melted slowly in FSW. Replicate samples for sympagic POM were filtered onto pre-combusted Whatman GF/F filters. To obtain enough material for isotopic analysis, a minimum of 20 ml was filtered. Filters were dried at 60°C for 24 hours and stored dry until processing. Isotopic ratios were determined using Europa 20/20 mass spectrometer coupled to an elemental analyzer (Laboratoire Jean-Eric Tremblay, Département de biologie, Québec-Ocean, Université Laval, Québec). Stable isotopic abundance is reported as a deviation (δ in ‰) from known standards:

$$\delta X = [(R_{sample}/R_{standard}) - 1] \times 1000 \quad (1)$$

where X is the stable isotope expressed in δ notation and R is the $^{15}N:^{14}N$ ratio. Atmospheric N_2 was used as standard (Tremblay *et al*. 2006).

2.2.3 Ice, brine and surface water collection and analysis. All samples were collected following clean-hands/dirty-hands protocol (Fitzgerald 1999). Ice was collected as stated above, sectioned into 10 cm pieces and scrapped with Hg-clean porcelain blades to obtain a small sub-sample at the centre of each core section. Bulk ice (BI) sub-samples were taken from above the dense algal horizon ~ 4 cm above the bottom of the ice core. Core sections were melted and run for THg on a Tekran 2600 CV-AFS under clean room conditions in the Portable In-situ Laboratory for Mercury Speciation while on board the *CCGS Amundsen* following EPA Method 1631 (Chaulk *et al.* 2011).

Brine was collected using the sump hole technique as described by Pućko *et al.* (2010b). These samples were diluted with ultrapure water to reduce salinity (Chaulk *et al.* 2011) and analyzed following the same method described above.

Surface water was collected using a hand towed Teflon-coated Niskin bottle, and analyzed for THg as described in Chaulk *et al.* (2011).

2.2.4 Atmospheric mercury. Real time, in-situ atmospheric Hg species were collected continually throughout the field campaign from the lower troposphere on the Tekran 1130/1135 speciation unit mounted on the starboard side of the fore deck of the *CCGS Amundsen*. Detailed methods and result can be found elsewhere (Latonas 2010).

2.3 Results and Discussion

2.3.1 Particulate organic matter (POM) in the sea ice. PHg concentrations in bottom 10 cm core sections ranged from 0.102 – 0.704 pg L_{ice}^{-1} or 0.004 – 0.022 μg g^{-1} dw (n = 15; Table 2.1, Figure 2.2A). MeHg concentrations were below detection limit (n = 2).

Campbell *et al.* (2005) reported a single THg concentration of 0.003 μg g^{-1} wet weight (ww), for an ice algae sample from Northern Baffin Bay.

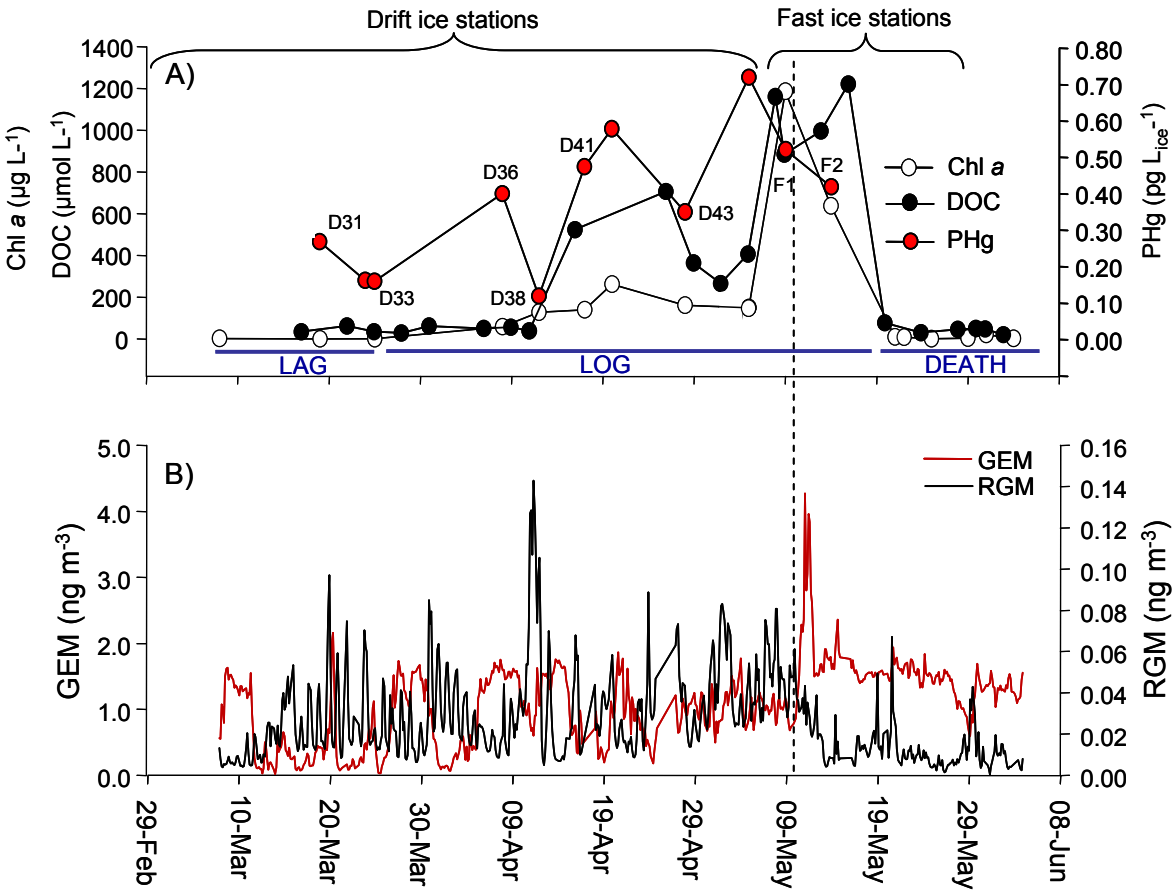

Figure 2.2. A) chl *a*, DOC and PHg concentrations in the bottom 10 cm ice core sections collected between 03 March and 03 June 2008. B) GEM and RGM concentration measured in air over the entire 2008 AMDE season (Latonas 2010). NB: D indicates drift station, F indicates land fast ice station. Lag, log and death denote the cellular growth cycle over the season.

Based on an algal moisture content of between 81- 87.5 % (CRESP 2006), this corresponds to ~ 0.02 μg g^{-1} dw and is, therefore, in good agreement with our values.

Zhong and Wang (2009) studied the effects of natural DOC of varying origins on the uptake of both inorganic Hg(II) and MeHg by marine phytoplankton. They reported that when the DOC is composed primarily of degraded diatoms, inorganic Hg(II) uptake increases as a result of more efficient adsorption to cell wall membranes. DOC and Chl *a* concentrations in the bottom 10 cm core sections in the current study ranged from 40 to 1170 μmol L^{-1} and 0.12 to 1186 μg L^{-1}, respectively (Table 2.1, Figure 2.2A). The significant relationships observed between DOC and Chl *a* concentrations during periods of high Chl *a* concentrations (25 March – 14 May 2008; $r^2 = 0.71$, $p = 0.009$, $n = 8$) strongly implies that primary production is the main contributor to DOC accumulation during this time (Song *et al*. 2011). As predicted by Zhong and Wang (2009), a strong significant positive correlation was observed between DOC and PHg concentrations ($r^2 = 0.71$, $p = 0.005$, $n = 9$).

When looking at the relationship of cells L^{-1} in the bottom ice core samples *vs* collection date as well as *vs* PHg (μg g^{-1} dw) we find the trends outlined in Figure 2.3A and discussed below. Figure 2.3B shows the taxonomic cell composition at each of the 5 drift (D29, D33, D36, D41 and D43) and two fast ice (F1 and F2) stations.

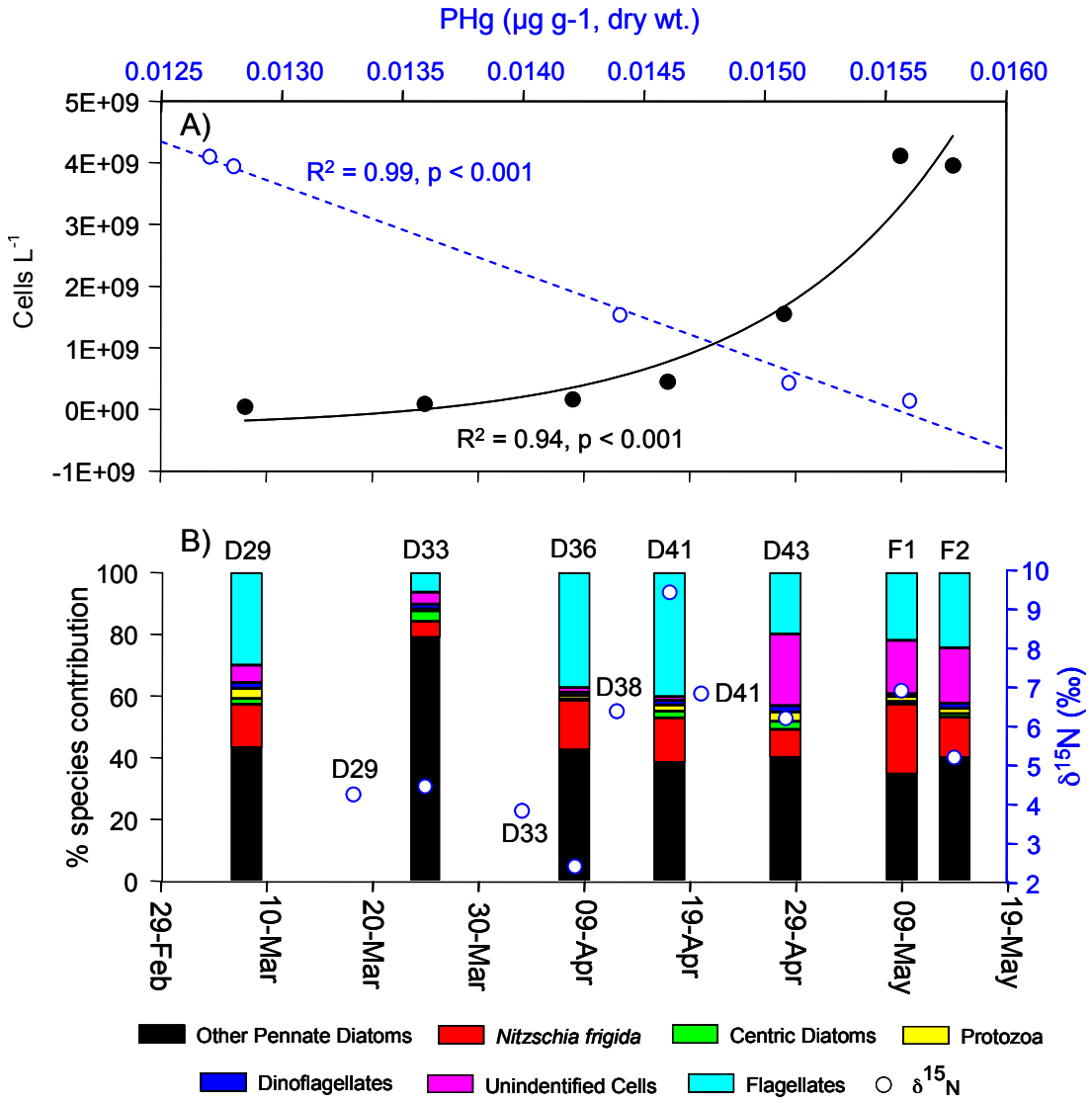

Figure 2.3. A) Total cell concentrations (cells L^{-1}) versus PHg concentrations (µg g^{-1}, dw) and collection date. B) % species contributions to the total algal abundances. Both A and B refer to the bottom 10 cm ice-core sections.

In these ice core sections, as the total cell numbers increased over time, PHg concentrations decreased in the cells ($r^2 = 0.99$, $p < 0.001$). This very strong significant negative relationship can almost certainly be attributed to biomass dilution (Pickhardt *et al*. 2002; Chen and Folt 2005) and suggests that there is a finite amount of Hg available to the algal population within the ice core sections. One noted exception to this was the core sample collected on 25 March 2008 (Station D33; Table 2.1; point not included in Figure 2.3A). In this case, PHg was ~ two-fold lower than what would be expected based on the regression equation ($y = -1 \times 10^{12}x + 2 \times 10^{10}$). Interestingly, this core was composed of a distinct algal community, discussed further below.

With the exception of Station D33, the ice algal communities were dominated by pennate diatoms, in particular *Nitzschia frigida*, and flagellates (11-20 μm; Figure 2.3B). Together they contributed from 69 to 96% of the total algal abundance (Table 2.1) in an approximate 2:1 ratio, respectively. At station D33, however, this ratio was 13:1. Both diatoms and flagellates are autotrophic taxa and, therefore, one would not expect them to differ in trophic level (as compared to, for example, heterotrophic dinoflagellates; Hansen 1991). Interestingly, the mean $\delta^{15}N$ value for POM collected from sea ice cores at earlier stations D29, D33 and D36 (18 March – 8 April 2008; $\delta^{15}N = 3.75 \pm 0.42$ ‰, $n = 4$) was almost a full trophic level lower than the mean value calculated from the cores collected at later stations D38, D41, D43, F1 and F2 (12 April – 14 May 2008; $\delta^{15}N = 6.83 \pm 1.42$ ‰, $n = 6$; Table 2.1, Figure 2.3B; t-test, $p = 0.016$). The greater enrichment in the latter set of samples may reflect seasonal and/or latitudinal productivity changes. Gradinger (2009) noted that ice algal parameters on a regional scale, driven primarily by the physico-chemical settings, can vary by greater than 50%. In addition, $\delta^{15}N$ values

generally increased during the logarithmic growth phase of algal growth (Figure 2.2A LOG) as the surface water became more depleted in dissolved inorganic nitrogen (DIN) and the ice-algae then began to use up the remaining ^{15}N enriched NO_3^- (Kumar *et al.* 2004). Our values compare well with the ranges previously reported by Iken *et al.* (2005) for samples collected in the Canada Basin (19 – 26 July 2008; 2.3 – 6.5 ‰) as well as those collected in the Chukchi and Beaufort Seas (10 May – 18 June 2002; 6.1 – 13.5 ‰; Gradinger 2009).

2.3.2 THg_{SW} and PHg. Concentrations of THg in the surface water appeared to have declined from late February until mid-April and then began to increase, reaching a maximum concentration of 0.38 ng L^{-1} in mid-May. Total Hg concentrations measured in the surface water samples (THg_{SW}) at each station are listed in Table 2.1 and plotted in Figure 2.4A. Differences in regional physico-chemical settings may have contributed to the observed variation. No significant correlation between THg_{SW} and PHg in the bottom ice community was observed ($r^2 = 0.038$, $p > 0.05$), suggesting that surface waters were not a significant source of Hg to the ice algal communities during their exponential growth phase to curtail biodilution within the ice (Figure 2.3A).

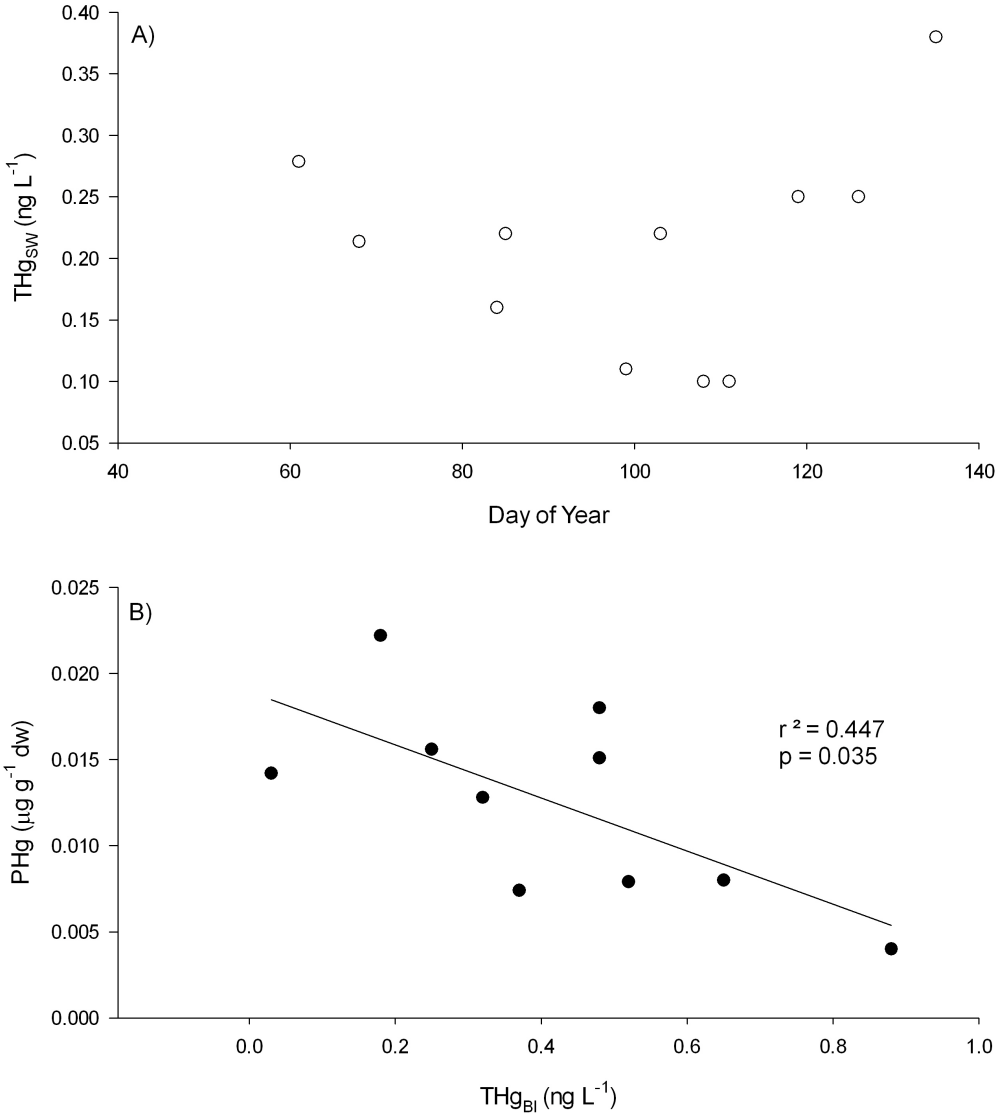

Figure 2.4. A) The relationship between THg in the surface water (THg_{SW}) and collection date has no trend. B) The significant negative relationship between total particulate Hg (PHg) and bulk bottom ice THg (THg_{BI}; $r^2 = 0.447$, $p = 0.035$, $n = 10$). This shows that as PHg increases, the THg within the bulk ice decreases.

2.3.3 THg_{BI}, PHg and THg_{Br}. Once the brine volume fraction increases to over 5%, ice reaches a porosity threshold where brine is able to move vertically within the ice column, individual brine pockets may coalesce, and gravity drainage and replenishment of brine with seawater becomes possible (Cox and Weeks 1975, Weeks and Ackley 1986, Golden *et al*. 1998). In the current study, the brine volume fraction of the bottom 10 cm of sea ice cores ranged from 5.9 up to 22.3 % and so were always above the critical threshold for brine movement within the ice (Table 2.1).

Chaulk *et al.* (2011) used a sump hole technique to study the importance of brine processes for accumulation/rejection of Hg during ice formation and melting. They showed that Hg is generally associated with the brine fraction of sea ice and that a strong logarithmic relationship exists between the Hg concentration and salinity. Brine was collected at four stations that were also sampled for POM (D33, D38, D41, and F2). THg_B values ranged from 1.58 ng L^{-1} at station D38 to 20.13 ng L^{-1} at station D41 and were highly variable (Table 2.1).

THg in the bulk bottom ice (THg_{BI}) ranged from 0.03 – 0.88 ng L^{-1} (Table 2.1). No significant trends with time were observed over the algal growth season ($r^2 = 0.057$, $p > 0.05$, $n = 10$). However, a significant negative correlation was observed to occur between PHg and THg_{BI} ($r^2 = 0.45$, $p < 0.05$, $n = 10$; Figure 2.4B). From these results we infer that the ice algal community was exposed to Hg primarily from their sea ice habitat, where Hg is sequestered in the brine during the formation of ice from the surface seawater (Chaulk *et al.* 2011), and that the growing algal community is able to draw down the THg available in the porous bulk bottom ice. In Table S2.1 (appendix), we calculated the total Hg (ng) present in both the bulk bottom ice (Hg_{BI}) and in PHg. The

total amount of PHg (1.003 ± 0.44 ng) was in the same order of magnitude of Hg_{BI} (1.016 ± 0.65 ng), and their sum remained relatively constant throughout the sampling duration (1.72 ± 0.53 ng, variance = 0.347) which provide further support that the growth of sea ice algae could result in depletion of Hg in the bulk bottom sea ice.

2.3.4 Atmospheric mercury depletion events. AMDEs were defined by periods, after polar sunrise, when atmospheric GEM concentration fell below 1 ng m^{-3} (Latonas 2010). In the current study, 31 AMDEs were observed over the period from Feb 11 – May 10, 2008 (Figure 2.2B). Greater details can be found in Latonas (2010). In brief, early spring AMDEs were multi-day events, lasting from between 31 – 211 hours. The final significant event began on 18 April 2008 and lasted for 52 hours. While AMDEs did occur during the algal logarithmic growth phase (LOG, Figure 2.2A), AMDE deposited RGM does not appear to contribute to PHg enrichment at the bottom of the ice cores ($r^2 = 0.057$, $p > 0.30$, $n = 15$). When samples were taken near open leads, there was no evidence of increased Hg bioavailability to the bottom ice algae (t-test, drift *vs* open leads: $p = 0.07$; Table S2.2 appendix). These two processes are either decoupled and/or AMDE contributions are masked by other, more predominant, processes as discussed previously.

2.4 Conclusion

The results presented suggest that AMDEs and surface waters were not a significant enough source of Hg to the ice algal community during their growth phase to counter act the community's ability to draw down the Hg stored of the bulk bottom ice.

We conclude there was only a finite amount of Hg available to the algae population within the bottom ice. Thus, the decrease in ice algal PHg concentrations while ice algal cell numbers were observed to increase over the spring growth season can be attributed to biodilution within the sea ice algal population. As we witness the transformation of the Arctic Ocean from a multi-year to a first-year ice system, this could give rise to a reduction in Hg exposure in primary consumers (herbivorous amphipods and copepods), which graze the ice algae as part of their natural diets. As grazing species ingest the ice algae, if our future prediction is correct, the Hg that is retained by the primary consumers would be less than in the past.

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Chapter 3

Bioconcentration of mercury in particulate organic matter and herbivorous zooplankton in the Amundsen Gulf of the Arctic Ocean

Abstract

Mercury (Hg), especially its organic form, methylmercury (MeHg), is one of the primary contaminants of concern in the Arctic marine ecosystem. MeHg is known to biomagnify in the food web. Much less is known, however, about how Hg and MeHg are taken up at the base of the Arctic food web. During the International Polar Year (IPY) Circumpolar Flaw Lead (CFL) study, seawater, phytoplankton (sampled as particulate organic matter or POM) and herbivorous copepods *Calanus hyperboreus* and *C. glacialis* were collected from February to July 2008 in the Amundsen Gulf of the Arctic Ocean to test the bioconcentration and biomagnification of Hg from the seawater up to the primary consumers. We found that Hg was bioconcentrating from the seawater to phytoplankton, with bioconcentration factors (BCFs) in the order of $1.42 \pm 1.32 \times 10^5$ L kg^{-1} throughout the sampling season. Though total Hg (THg) concentration did not increase significantly with trophic levels determined from $\delta^{15}N$, there was a strong and significant relationship between MeHg concentrations, based on measured and estimated values, and trophic levels ($r^2 = 0.972$, $p = 0.014$, $n = 4$), suggesting the occurrence of MeHg biomagnification even at these low trophic positions in the Arctic marine ecosystem.

3.1 Introduction

Ice algae and phytoplankton are important carbon sources to both the pelagic and benthic food webs of the Arctic Ocean (Horner and Schrader 1982; Gosselin *et al.* 1997; Martin *et al.* 2010; Michel *et al*. 2006). Dominated by pennate diatoms, ice algae are present primarily during the spring at the bottom surface of sea ice (Chapter 2). The productivity of phytoplankton, the free-floating photosynthetic organisms, increases from the onset of the melting season throughout the summer in both open waters and waters beneath first year sea ice; in nutrient-rich Arctic continental shelves, the under-ice phytoplankton biomass could be much greater than that in open waters (Arrigo *et al.* 2012). Grazing upon phytoplankton are copepods (e.g., genus *Calanus*), which are the most abundant zooplankton taxa in the Arctic Ocean (Falk-Petersen *et al.* 2009). The carbon fixed through sea ice algae and phytoplankton blooms is rapidly converted into large, specialized lipid stores by *Calanus*, being the major source of energy for the large stocks of fish, birds and marine mammals in the Arctic (Falk-Petersen *et al.* 2009). Located at the base of the Arctic marine food web, the composition and productivity of phytoplankton thus have major impacts on the structure, function and dynamics of the Arctic marine ecosystem (Juul-Pedersen *et al.* 2010), as well as on the uptake and accumulation of contaminants.

Mercury (Hg), especially its organic form methylmercury (MeHg), is one of the primary contaminants of concern in the Arctic marine ecosystem due to its ability to biomagnify and its neurotoxicity. Monitoring since the 1970s has indicated that Hg and MeHg concentrations in Arctic top predators such as belugas and seals frequently exceed the safe consumption limit for humans, raising concerns over risks to Northern people

who consume these species, and to the species themselves (AMAP 2011). In freshwaters, phytoplankton are known to be the primary entry point for Hg into the aquatic food web (Pickhardt and Fisher 2007). There are two schools of thought regarding the processes whereby algae take up Hg from the aquatic environment: i) Bloom dilution (biodilution): as the phytoplankton bloom grows, particulate Hg decreases in the particulate organic matter (POM) community (Chen and Folt 2005); and ii) Bioaccumulation and bioconcentration: as the phytoplankton bloom grows, particulate Hg increases (Kirkwood *et al.* 1999). Bioaccumulation is an inherent property of a chemical that expresses the chemical's capacity to accumulate in organisms (Gobas *et al.* 2010), whereas bioconcentration is a special case of bioaccumulation of a chemical from the water column usually via epithelial tissues or drinking water (Hall 2003). Bioconcentration could be due to increased surface area (cell walls) for Hg to bind (Pickhardt and Fisher 2007), but it could also be due to the fact that, in nature, there may be an "infinite" source of Hg caused by remineralization of Hg by water column bacteria (Kirkwood *et al*. 1999). This microbial "loop" may be an important process in maintaining Hg levels in the water column, as it is in carbon and nutrient cycling (Cole *et al*. 1988, Poulain *et al*. 2007). The uptake of contaminants by algae in the water column is the first step in the bioconcentration of contaminants and biomagnification up the food chain (Watras *et al*. 1998). Similar studies have been carried out for Arctic phytoplankton (Atwell *et al*. 1998); however, the findings of these studies are limited by the small sample size and a lack of data for MeHg.

As part of the International Polar Year (IPY) – Circumpolar Flaw Lead (CFL) Study, here we report Hg concentrations in POM, as a measurement of phytoplankton, at

the ice-water interface, in the surface water, and at the sub-surface chlorophyll *a* maximum (SCM), as well as in two herbivorous species of calanoid copepods (*C. hyperboreus* and *C. glacialis*), from the Amundsen Gulf of the Arctic Ocean in spring and summer 2008. We show that phytoplankton takes up Hg from the seawater, which is then biomagnified following the trophic transfer from plankton to the grazing zooplankton.

3.2 Methods

3.2.1 Study Area.

During the IPY-CFL Study, POM and copepod samples were collected onboard the Canadian Research Icebreaker *CCGS Amundsen* between February and July 2008 from 27 stations in the Amundsen Gulf of the Arctic Ocean (Figure 3.1, Table 3.1, Table S3.1 in the appendix). The icebreaker remained in drifting ice floe stations from 1 to 6 days. Thus, samples collected at a same station were not always collected on the same day. The ship also sampled in the marginal ice zone (MIZ), at the receding ice edge, in open water, and re-visited many established stations in the Beaufort Sea and Amundsen Gulf over the sampling season.

Detailed oceanographic and biogeochemical settings of the study area are given in Barber *et al.* (2010). In brief, the Beaufort Sea water masses are characterized by a low salinity (< 31.6), nutrient-poor polar mixed layer (PML) at the surface, underlain by a cold and nutrient-rich layer of Pacific-origin water (Carmack *et al*. 2004, Mundy *et al.* 2009).

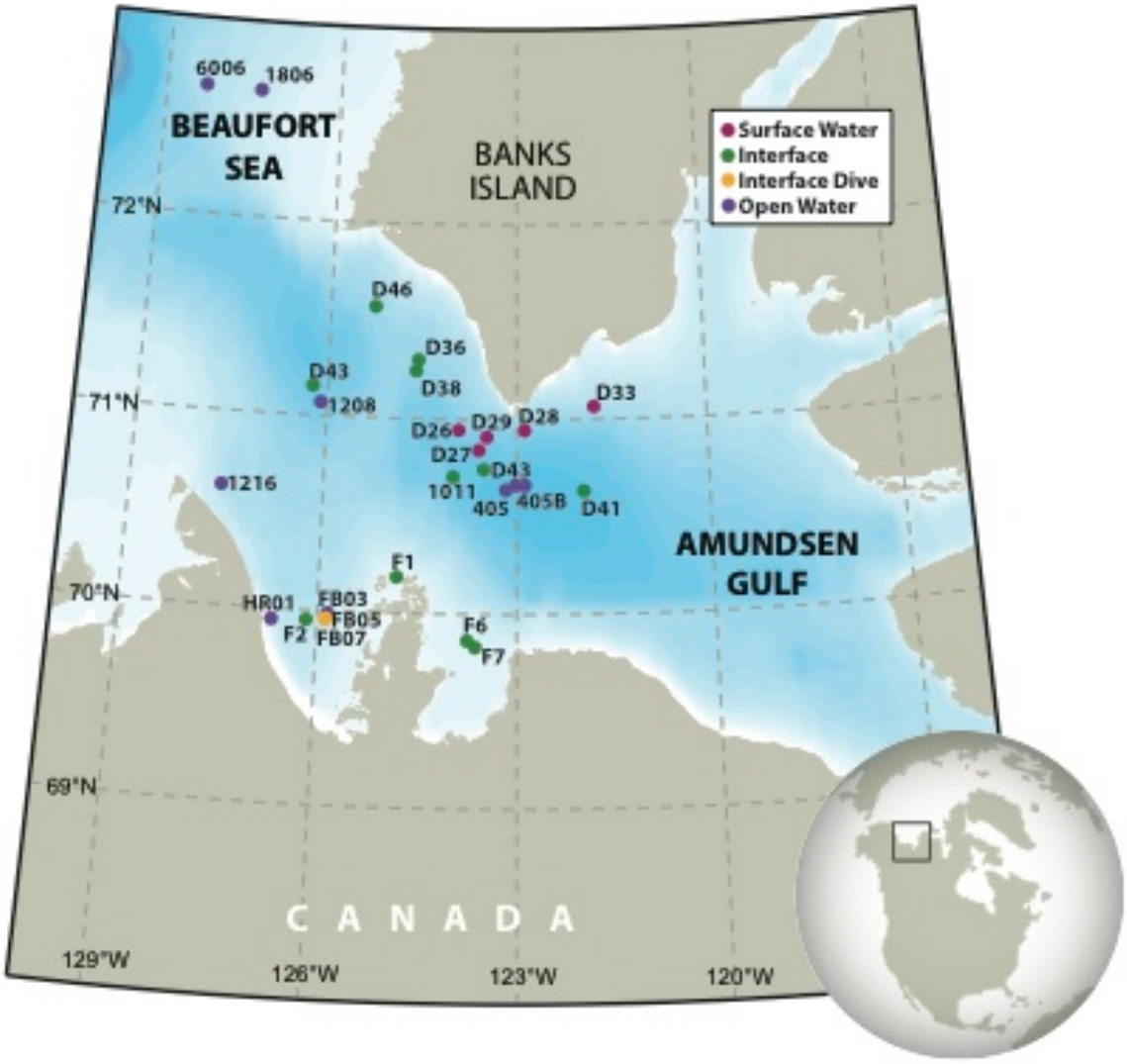

Figure 3.1. Map of all sampling stations for mercury in phytoplankton in the Beaufort Sea and Amundsen Gulf during the CFL project. D - drift station, F/FB - landfast station, HR - Hudson River plume, all others - open water stations.

Table 3.1. Results of surface water (SW), ice-water interface (INT), ice-water interface during the dive program (INTd), and subsurface chlorophyll maxima (SCM) sample analysis by station and day of year.

Sample	Leg	Station	Date	Day of Year	PHg (µg g^{-1} dw)	MeHg (ng g^{-1} dw)	THg_{water} (ng L^{-1})	Sample depth (m)	Chl *a* (µg L^{-1})	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	TL
SW	6	D26	25-Feb-08	56	0.017	na	ns	3	ns	ns	ns	
	6	D27	01-Mar-08	61	0.031	na	ns	3	ns	ns	ns	
	6	D28	03-Mar-08	63	0.010	na	ns	0	ns	ns	ns	
	7	D29	17-Mar-08	77	0.051	na	ns	1	0.10	ns	ns	
	7	D33	27-Mar-08	87	0.007	na	0.240	1	0.05	ns	ns	
	7	D33	01-Apr-08	92	0.019	na	0.195	1	ns	ns	ns	
INT	7	D36	09-Apr-08	100	0.020	0.15	0.111	0	1.26	ns	2.42	0.3
	7	D38	12-Apr-08	103	0.031	na	0.220	0	0.91	-26.58	5.45	1.1
	7	D41	18-Apr-08	109	0.007	na	0.101	0	5.25	-27.10	4.18	0.8
	8	D43	29-Apr-08	120	0.004	na	0.245	0	0.77	-27.95	4.41	0.9
	8	D43	05-May-08	126	0.010	na	0.245	0	0.47	-27.62	5.85	1.2
	8	F1	08-May-08	129	ns	0.16	0.236	0	1.88	-22.02	6.27	1.3
	8	F2	17-May-08	138	0.014	na	0.384	0	0.38	-28.03	7.37	1.6
	8	1011	21-May-08	142	0.020	na	ns	0	ns	-28.25	5.62	1.2
	8	D46	30-May-08	151	0.009	na	ns	0	ns	-22.69	6.01	1.3
	8	F6	02-Jun-08	154	0.508	na	ns	0	ns	-26.43	7.16	1.6
	9	F7	08-Jun-08	160	0.036	na	0.640	0	ns	-25.63	13.19	3.2
	9	F7	09-Jun-08	161	0.037	na	0.530	0	ns	-26.05	4.31	0.8
INTd	9	FB05	17-Jun-08	169	0.071	na	0.870	0	ns	ns	ns	
	9	FB07	21-Jun-08	173	0.088	na	2.195	0	ns	ns	ns	

Table 3.1. Continued.

Sample	Leg	Station	Date	Day of Year	PHg (µg g^{-1} dw)	MeHg (ng g^{-1} dw)	THg_{water} (ng L^{-1})	Sample depth (m)	Chl *a* (µg L^{-1})	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	TL
	8	405B	19-May-08	140	0.018	na	ns	13	5.81	-25.94	4.66	0.9
	8	1806	23-May-08	144	0.025	na	0.216	55	0.72	-23.64	5.01	1.0
	8	9008	27-May-08	148	0.016	na	ns	45	2.21	-23.02	7.49	1.7
	8	405	01-Jun-08	153	0.010	na	ns	42	0.40	-27.73	9.75	2.3
	9	405B	10-Jun-08	162	0.042	na	0.250	36	1.06	-28.13	8.14	1.8
SCM	9	FB03	14-Jun-08	166	0.076	na	0.170	20	0.99	-26.92	5.21	1.1
	9	HR01	17-Jun-08	169	0.028	na	0.235	24	3.29	-24.90	6.07	1.3
	9	1216	23-Jun-08	175	0.085	na	ns	24	0.14	-25.76	12.85	3.1
	9	1208	28-Jun-08	180	0.054	na	0.143	38	0.51	-28.81	12.15	2.9
	9	6006	04-Jul-08	186	0.075	BDL	0.180	51	6.33	-22.73	2.76	0.4
	9	2010	06-Jul-08	188	0.055	na	0.290	34	1.12	-28.70	4.67	0.9

NOTE: BDL - Below detection Limit; na - not analyzed; ns - no sample; ni - no information

This Pacific-origin water mass (max depth of 250 m) is thought to enhance primary production where it mixes with the PML (Carmack *et al*. 2004, Mundy *et al.* 2009). Below the Pacific halocline is the Atlantic water, a deeper component of the cold halocline formed in the Barents Sea, and beneath this the Atlantic Layer with temperatures above 0°C.

3.2.2 Sampling

Seawater. Surface seawater samples were collected from 0 – 3 m below the ice using a hand-towed, Teflon-coated Niskin bottle. Deeper water samples (> 10 m) were obtained onboard the icebreaker using 20 L Niskin bottles mounted on a General Oceanics 24-bottle rosette equipped with a SeaBird conductivity-temperature-depth (CTD) sensor. Details of the sampling techniques can be found elsewhere (Chaulk *et al.* 2011). In brief, sea water samples were collected using "clean-hands/dirty-hands" (Fitzgerald 1999) team sampling into 50 ml falcon tubes, with technique blanks included in each sampling instance.

Particulate organic matter. Water column POM was collected by a hand-towed Niskin bottle (surface water), an under-ice pump (ice-water interface), rosette cast (SCM) and on two occasions (17 and 21 June 2008) using a modified 3.5 L Trident® suction (slurp) gun from ~5 cm below the ice bottom by SCUBA divers as described in Mundy *et al*. (2011). All samples were collected and handled following "clean-hands/dirty-hands" protocol (Fitzgerald 1999). Samples were filtered (Morrison and Watras, 1999) onto pre-combusted and pre-weighed 0.7 μm Whatman GF/F filters and frozen at -30 ˚C for

shipping. As POM was collected onto a filter, all particulates are included and are not limited to phytoplankton. All filtered samples were oven-dried at 60 °C, and weighed prior to analysis. All solutions, filters, and lab equipment were batch tested for acceptable background Hg concentrations (< 0.1 ng L^{-1}) at the University of Manitoba's Ultra-Clean Trace Elements Laboratory, or in the Portable In-situ Laboratory for Mercury Speciation on board the ship, prior to use in the field and laboratory.

Zooplankton. Zooplankton were collected via whole water column net hauls using 200 and 500 μm mesh nets from 10 m above the ocean floor to the surface. Zooplankton were live-sorted to species and growth stage and frozen at -30˚C until analysis. Only the samples of *C. hyperboreus* and *C. glacialis,* the two most common calanoid grazers in the study region (Falk-Petersen *et al*. 1990, Scott *et al.* 2002, Tremblay *et al*. 2006, Søreide *et al*. 2010) were processed for further analysis in this study.

Atmospheric mercury. Real time, in-situ atmospheric Hg speciation were determined throughout the field campaign from the lower troposphere by the Tekran 1130/1135/2537 speciation unit mounted on the starboard side of the fore deck of the *CCGS Amundsen*. Detailed methods are described in Latonas (2010).

3.2.3 Analyses

Total mercury concentration in seawater was analyzed by CV-AFS on a Tekran 2600 mercury analyzer under clean room conditions while on board the *CCGS Amundsen*

following EPA Method 1631. Samples were analyzed within 36 hours of collection. Complete details are given in Chaulk *et al.* (2011).

Total Hg in the filtered POM (PHg) was extracted using a modified hot acid aqua regia digest (Hendzel and Jameson 1979) and analyzed using cold vapour atomic absorption spectroscopy (CV-AAS) following U.S. EPA Method 245.2 (U.S. EPA 1974). Reagent blanks, filter blanks, duplicates, and certified reference materials (CRMs; including LUTS-1 (non-defatted lobster hepatopancreas, TORT-2 (lobster hepatopancreas), and DORM-3 (fish protein) from the National Research Council of Canada, and SRM 1573a (tomato leaves) from the National Institute of Standards and Technology, USA) were included in every analytical run for quality assurance and control and the run only proceeded when recovery was within 5% of reported THg of the CRMs. The method detection limit (MDL) for the instrument, defined as 3 standard deviations of blank values, was 0.001 $\mu g\ g^{-1}$ dry weight (dw), and filter blanks ($0.0012 \pm 0.0005\ \mu g\ g^{-1}$ dw, n = 6) were subtracted from each sample.

Samples for MeHg (n = 3; from stations D36, F1, and 6006) were analyzed by Flett Research Ltd., Winnipeg, using CV-AFS following U.S. EPA Method 1630 (U.S. EPA 1998). The MDL was 0.15 $ng\ g^{-1}$ dw.

Herbivorous zooplankton species (*Calanus glacialis* (from n = 23 stations) and *C. hyperboreus* (from n = 65 stations, CIV - adult females)) were analyzed for THg following the method outlined above for POM. *C. hyperboreus* (n = 47) were analyzed for MeHg by a 3-step extraction after Wagemann *et al.* (1997) and Gas Chromatography Atomic Fluorescence Spectrophotometry (GC-AFS) analysis with EPA Method 1631 (Telliard 2002) at the Freshwater Institute, Winnipeg, Manitoba.

Biomass of algae, represented by chlorophyll *a* (chl *a*), was analyzed as described in Martin *et al*. (2010) and Philippe (2011). Samples were filtered through 0.7 μm Whatman GF/F filters and were extracted with 90 % acetone for 18 h at 4 °C under dark conditions. Chl *a* was determined before and after acidification with 5 % HCl using a Turner Designs 10-AU fluorometer (Parsons *et al.* 1984).

For analysis of carbon and nitrogen stable isotopes, seawater samples (≥ 20 L) were filtered onto pre-combusted Whatman GF/F filters and stored frozen. Prior to analysis, filters were soaked in 0.1 mol L^{-1} HCl to remove inorganic C and dried. Isotopic ratios were determined, following combustion at 1,800 °C, using a Europa 20/20 mass spectrometer coupled to an elemental analyzer at Université Laval (Dr. Jean-Eric Tremblay). Stable isotopic abundance is reported as a deviation (δ in ‰) from known standards:

$$\delta X = [(R_{sample}/R_{standard}) - 1] \times 1000 \quad (1)$$

where X is the stable isotope expressed in δ notation and R is the ^{13}C:^{12}C or ^{15}N:^{14}N ratio. Standards used were Pee Dee Belemnite for ^{13}C and atmospheric N_2 for ^{15}N (Tremblay *et al*. 2006).

Stable isotopes of carbon and nitrogen in zooplankton were analyzed at the University of Winnipeg Stable Isotope Laboratory using Continuous Flow Ion Ratio Mass Spectrometry (CF-IRMS). Using a GV-instruments IsoPrime attached to a peripheral, temperature-controlled EuroVector elemental analyzer (EA), samples were loaded into tin sleeves and placed in the EA autosampler and analyzed with internally calibrated carbon and nitrogen standards.

The bioconcentration factor (BCF, L kg^{-1}) from water to water column POM was calculated after Arnot and Gobas (2006):

$$BCF = C_B / C_W \quad (2)$$

where C_B (g kg^{-1} dw) and C_w (g L^{-1}) are the concentration of the contaminant in the biota and in the water, respectively. Bioconcentration occurs when BCF > 1 L kg^{-1}. Equation 2 is a simplification of the more complex relationship of biota with their habitat:

$$dC_B/dt = (k_1 C_W) - (k_2+k_E+k_M+k_G)\, C_B \quad (3)$$

where t is time (d), k_1 is the chemical uptake rate constant from water (L kg^{-1} d^{-1}), k_2, k_E, k_M, and k_G are rate constants (d^{-1}) representing chemical elimination from the organism via respiration, fecal matter, metabolism, and growth dilution, respectively (Arnot and Gobas 2006). Assuming the system is in steady state, Equation 3 simplifies to Equation 2.

Trophic levels (TL) were calculated for POM and zooplankton as in Fisk *et al*. (2001):

$$TL = 2.0 + (\delta^{15}N_{Sample} - \delta^{15}N_{Calanus\ average})/3.8 \quad (4)$$

where 2.0 is the expected TL for *Calanus* based on the literature, $\delta^{15}N_{Sample}$ is the $\delta^{15}N$ value for each POM sample, and $\delta^{15}N_{Calanus\ average}$ is the mean $\delta^{15}N$ value for *Calanus* from this study (*C. hyperboreus*: 8.76 ± 2.19 ‰, and *C. glacialis*: 6.36 ± 3.00 ‰), and 3.8 is the isotopic enrichment factor between trophic levels (Hobson and Welch 1992, Fisk *et al*. 2001).

3.2.4 Statistical Analysis

To assess the statistical significance of relationships, linear and multiple linear regressions were used. SigmaPlot 12.0 (Systat Software Inc.) was used to apply Students

t-test to compare groups when the data met normality requirements. When the Normality test (Shapiro - Wilk) and/or the Equal Variance test failed, the Mann Whitney Rank Sum test was employed.

3.3 Results

Throughout the study duration, snow depth ranged from 0 (no snow) to 25 cm on ice that ranged in thickness from 20 to 195 cm, while ice cover changed from 100 % coverage to no ice as the season progressed. The water depth ranged from 47 to 554 m for ice-covered stations and 103-562 m for open water stations. The SCM developed around 19 May at the open water station 405B at a depth of 13 m below the water surface. Thereafter, the depth of the sampled SCM ranged from 13 – 55 m.

$\delta^{13}C$ for water column (WC) POM ranged from -22.02 to -28.81 ‰, while $\delta^{15}N$ ranged from 2.42 – 13.19 ‰ (average -26.16 ± 2.00 ‰, and 6.84 ± 2.93 ‰, respectively; Table 3.1). We compared these to the $\delta^{13}C$ and $\delta^{15}N$ in ice POM (see Chapter 2; average $\delta^{13}C$: -21.31 ± 5.43 ‰, and $\delta^{15}N$: 6.13 ± 2.11 ‰), *C. glacialis* ($\delta^{13}C$: -25.83 ± 0.95 ‰, and $\delta^{15}N$: 6.36 ± 3.00 ‰; Table 3.2) and *C. hyperboreus* ($\delta^{13}C$: -25.57 ± 1.01 ‰, and $\delta^{15}N$: 8.76 ± 2.19 ‰; Table 3.2). Significant differences in the means were found between the $\delta^{13}C$ of ice algae and all other variables, and also between *C. hyperboreus* and WC POM ($p = 0.037$). Significant differences in the means were only found between the $\delta^{15}N$ of *C. hyperboreus* and all other variables. The p-values are reported in Table 3.3.

Trophic levels (TL) of POM averaged 1.42 ± 0.78 (range: 0.33 – 3.17; Table 3.1). TL of *C. hyperboreus* and *C. glacialis* averaged 2.03 ± 0.56 and 2.13 ± 0.73 respectively (Table 3.2).

3.3.1 Hg in POM

Over the sampling period PHg in the water column POM ranged from 0.004 - 0.088 μg g^{-1} dw (n = 29; Table 3.1), agreeing well with a few reported values for PHg in Arctic POM (Atwell *et al*. 1998), ice POM (Campbell *et al*. 2005), and periphyton (Poulin *et al*. 2007). Only three POM samples were analyzed for MeHg, and the concentrations ranged from below the MDL (< 0.15 ng g^{-1} dw) at station 6006, to 0.015 ng g^{-1} dw at station D36, and 0.16 ng g^{-1} dw at station F1, accounting for up to 4 % of total Hg measured (Table 3.1).

The PHg concentrations in POM were generally low from late February to early May, but increased sharply from May to early July (Figure 3.2). Overall, PHg was observed to have a positive and significant relationship with time ($r^2 = 0.305$, $p = 0.002$) and with THg in the surface water ($r^2 = 0.274$, $p = 0.031$).

Table 3.2. Means (± standard deviation) of analyzed zooplankton species (*Calanus hyperboreus* and *C. glacialis*) including THg (μg g^{-1}), MeHg (μg g^{-1}), $\delta^{13}C$ (‰), $\delta^{15}N$ (‰), and trophic level (TL).

Species	n	THg (μg g^{-1})	MeHg (μg g^{-1})	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	TL
Calanus hyperboreus	65	0.014 ± 0.004	0.007 ± 0.001	-25.57 ± 1.01	8.76 ± 2.19	2.03 ± 0.56
Calanus glacialis	23	0.023 ± 0.007	na	-25.83 ± 0.95	6.36 ± 3.00	2.13 ± 0.73

NB: na = not analyzed

Table 3.3. Results of t-tests on stable isotopes of ice particulate organic matter (POM), water column (WC) POM, and two herbivorous zooplankton species, *Calanus glacialis* and *C. hyperboreus*.

$\delta^{13}C$ p values	Ice POM	WC POM	*Calanus glacialis*	*Calanus hyperboreus*
Ice POM	-	0.048*	0.032*	0.013*
WC POM		-	0.138	0.037*
Calanus glacialis			-	0.833
Calanus hyperboreus				-

$\delta^{15}N$ p values	Ice POM	WC POM	*Calanus glacialis*	*Calanus hyperboreus*
Ice POM	-	0.831	0.896	0.012*
WC POM		-	0.548	0.003*
Calanus glacialis			-	0.002*
Calanus hyperboreus				-

* significant difference in means ($p < \alpha = 0.05$)

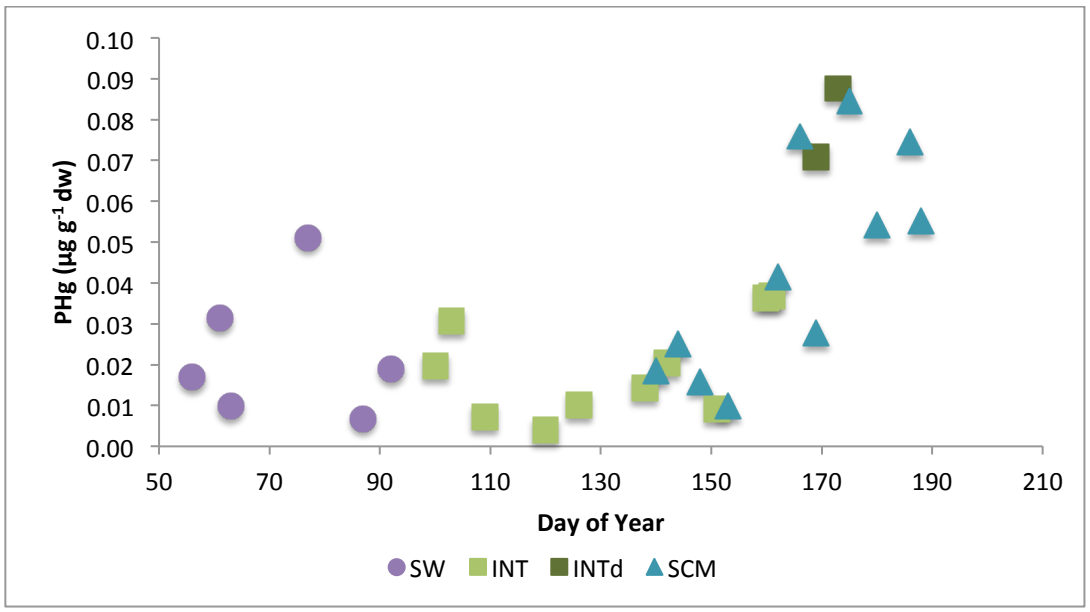

Figure 3.2. The types of POM present over time changed as samples were taken from completely ice covered seas to marginal ice zone to open water. SW - Surface water; INT – Ice-water interface; INTd – Ice-water interface during dive program; SCM – Subsurface chlorophyll *a* maximum.

POM in surface water

PHg in surface water POM (PHg_{SW}) was only analyzed from late February to early April. It averaged 0.023 ± 0.016 µg g^{-1} dw (n = 6), and displayed no significant trend with time (Figure 3.2 circle) during the short sampling period. Surface water POM had BCFs of 2.82 and 9.71 × 10^4 L kg^{-1} (n = 2). In contrast to the SW, Hg in POM at the INT and SCM together (Figure 3.2 square and triangle) follow a significantly increasing trend over the sampling season ($r^2 = 0.5$, $p < 0.001$).

POM at the ice-water interface

PHg at the ice-water interface (PHg_{INT}; Figure 3.2 square) varied greatly from 0.004 to 0.088 μg g^{-1} dw (n = 13), with much higher concentrations (0.071 - 0.088 μg g^{-1} dw, n = 2) later in June (Days 169 and 173; sampled during the dive program) than earlier sampling events (0.063 ± 0.15 μg g^{-1} dw, n = 11).

The much higher THg_{INT} observed during the dive program in late June seems to be related to THg in the water at the ice-water interface, which was significantly higher (Mann-Whitney $p < 0.05$) at the dive sites than at the other ice-water interface sites sampled earlier in the season. Indeed, THg in the water at the ice-water interface increased over time ($r^2 = 0.566$, $p = 0.008$) over the entire study duration. As shown in Figure 3, the variability of THg in the water at ice-water interface sites predicted 78.6 % of the variability in the PHg_{INT} ($r^2 = 0.786$; $p < 0.001$).

Throughout the season the POM_{INT} had an average BCF of $7.6 \times 10^4 \pm 5.5 \times 10^4$ L kg^{-1}, and its trend with time was not significant ($r^2 = 0.24$, $p = 0.15$; Figure S3.1A).

POM at the Subsurface Chlorophyll Maximum

SCM PHg (PHg_{SCM}; Figure 3.2 triangle) was determined from mid-May to early July and averaged 0.044 ± 0.03 μg g^{-1} dw (n = 11). Depth of the SCM in the water column (13-55 m) did not change significantly over the sampling period ($r^2 < 0.001$, $p = 0.936$), nor did the depth of the SCM help explain the levels of PHg in the POM sampled at the same depths ($r^2 = 0.026$, $p = 0.634$). However, the concentrations of PHg_{SCM} increased significantly over time ($r^2 = 0.566$, $p = 0.008$).

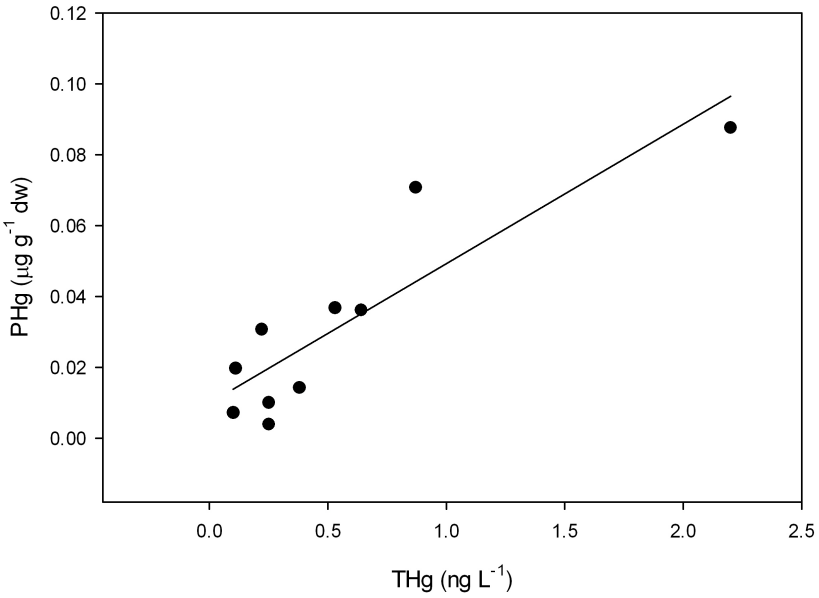

Figure 3.3. THg in the water at ice-water interface sites predicts more than 78 % of the variability in the PHg of the ice-water interface POM ($r^2 = 0.786$, $p < 0.001$). Dive sites included in analysis.

BCFs for POM_{SCM} were $2.62 \times 10^5 \pm 1.46 \times 10^5$ L kg^{-1}, which were significantly higher than those in the SW and INT (Mann-Whitney, n (SCM) = 7, n (SW & INT) = 12, $p = 0.002$). No significant trend was found between BCFs for POM_{SCM} and time ($r^2 = 0.215$, $p = 0.294$; Figure S3.1B).

3.3.2 Hg in Zooplankton

THg levels in *C. hyperboreus* ranged from 0.007 – 0.32 µg g^{-1} dw (n = 65), and MeHg ranged from 0.005 – 0.01 µg g^{-1} dw (n = 47; Table 3.2), accounting from as little as 25.0 % to as high as 78.5 % MeHg of THg. THg levels in *Calanus glacialis* were much higher, ranging from 0.014 – 0.043 µg g^{-1} dw (n = 23; Table 3.2), and MeHg could not be analyzed due to high sample weight required for the method.

3.4 Discussion

3.4.1 $\delta^{13}C$, $\delta^{15}N$ and trophic levels of phytoplankton and Calanus

Our observation that water column POM is significantly ($p = 0.048$; Table 3) more depleted in $\delta^{13}C$ (-26.2 ± 2.0 ‰; Figure 3.4) than sea ice POM (-21.3 ± 5.43 ‰; previous chapter) is in agreement with earlier study in the European Arctic (Søreide *et al*. 2006). This is probably because sea ice algae are exposed to a more CO_2-limited growth environment as they are contained within the ice, compared with being in the open water (Søreide *et al*. 2006).

Because the $\delta^{15}N$ value in marine POM depends on the source of nitrogen (isotopically heavy nitrate (NO_3^-) or lighter ammonium (NH_4^+); Waser *et al*. 1999), there is a large variability in the reported $\delta^{15}N$ of POM in the literature, which is mirrored in our data set (Table 3.1). The range of $\delta^{15}N$ of pelagic POM has been found to be 4 ‰ in the European Arctic (Søreide *et al*. 2006) to 8.3 ‰ in the Barents Sea (Tamelander *et al*. 2006). A much larger degree of variation is found in our $\delta^{15}N$ values for pelagic POM of 2.42 – 13.19 ‰ from the Amundsen Gulf, potentially due to the seasonal differences.

Ice POM was found to be significantly different in $\delta^{15}N$ (Table 3.3) from *C. hyperboreus* ($p = 0.012$), in agreement with the findings of Søreide *et al*. (2006). However, Søreide *et al*. (2006) reported that *Calanus* spp. are part of the pelagic POM-based food web, while the herbivorous ice amphipod *Apherusa glacialis* mainly uses the ice POM-based pathway. We found that *Calanus* spp. cannot be lumped together as they have significantly different $\delta^{15}N$ values ($p = 0.002$). While *C. glacialis* were not significantly different from water column (WC) POM in $\delta^{13}C$ ($p = 0.138$),

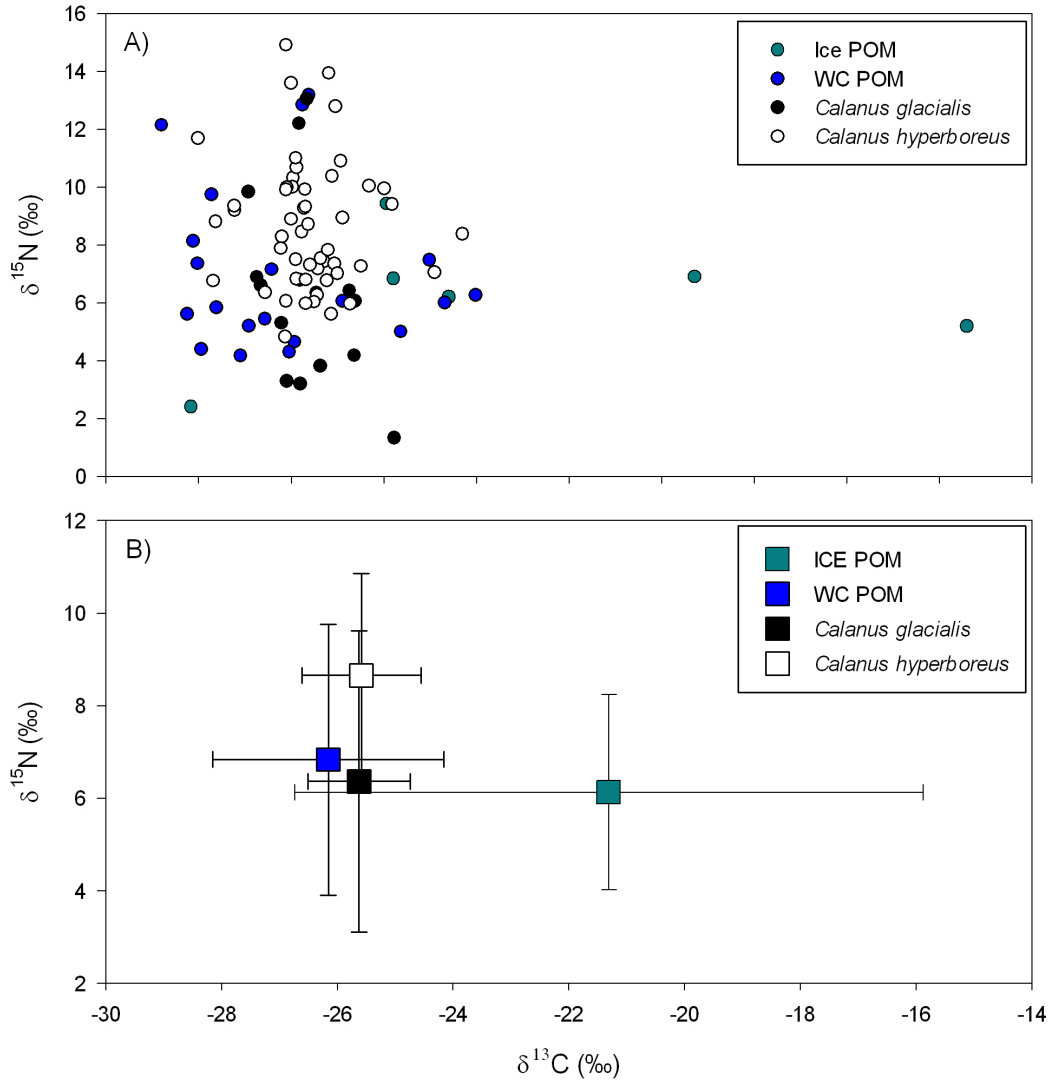

Figure 3.4. A) This figure shows the individual spread of stable isotopes of the two algae types and two herbivorous zooplankton species. B) Shows the means ± SD of the SI composition of both algae types and both Calanoid copepods. Significant differences between groups are shown in Table 3.

C. hyperboreus were significantly different both from $\delta^{13}C$ of ice POM and WC POM ($p = 0.013$ and 0.037, respectively). *C. hyperboreus* differed significantly in $\delta^{15}N$ from all other species (ice POM $p = 0.012$, WC POM $p = 0.003$, and *C. glacialis* $p = 0.002$) and

shared a positive slope with water column POM. *C. glacialis* did not differ significantly in $\delta^{15}N$ from either ice POM or WC POM.

3.4.2 Phytoplankton uptake of Hg from water

We observed that BCFs for POM were always much greater than one (average: $1.42 \times 10^5 \pm 1.32 \times 10^5$ L kg^{-1}), demonstrating that POM bioconcentrate Hg from water. As mentioned earlier, the variability of the concentration of THg in the water explained about 27% of the variability in the concentration of PHg in the POM sampled from the same water masses.

In agreement with the findings of Kirkwood *et al.* (1999) for Hg in freshwater phytoplankton, we observed no evidence supporting the occurrence of biodilution in the water column. This is most likely due to the "infinite" supply of Hg, when comparing with the Hg accumulated in the phytoplankton biomass, in the water column, which can replenish the euphotic zone through mixing, eddies and upwelling (Cole *et al*. 1988, Mundy *et al.* 2009).

The significant increasing trend between PHg_{INT} and time was likely biased by the samples taken during the dive program at sites FB05 (day 169) and FB07 (day 173). We found that the samples taken late in the season (t-test: $t = -3.803$, $df = 10$, $p = 0.003$) and taken at dive sites (t-test: $t = -6.459$, $df = 10$, $p < 0.001$) were significantly higher in PHg than other ice-water interface sites sampled earlier. The dive program took place during a time of increased biological activity in Franklin Bay, where our samples were collected, and in Darnley Bay. Mundy *et al.* (2011) reported that, in spring to summer of 2008, environmental factors such as timing of ice retreat, light and nutrient availability in

combination with an ice edge upwelling event (Mundy *et al.* 2009), which mixed nutrient-rich Pacific-origin waters to the surface in Darnley Bay also increased the under-ice primary production. The phytoplankton bloom was able to use the influx of nutrients, and Mundy *et al.* (2009) reported that the chl *a* biomass accumulated along the nutricline, which dropped steadily as the water column settled following the upwelling event. This upwelling may have also been Hg rich, which would explain why the THg and PHg in the surface waters were elevated compared with the other sites.

PHg_{SCM} increased significantly over time while BCFs at the SCM showed a positive slope with time, remaining much greater than one over the season, suggesting high extent of bioconcentration at depths > 15 m. BCFs at the SCM were significantly higher (Mann-Whitney, $p = 0.002$) than SW and INT, suggesting that there may have been greater concentrations of bioavailable Hg at depth in the water column.

We found that PHg_{SCM} can be predicted ($r^2 = 0.865$) from a linear combination of the independent variables of THg_{water} (ng L^{-1}; $p = 0.028$), $\delta^{13}C$ of POM (‰; $p = 0.043$), and $\delta^{15}N$ of POM (‰, $p = 0.033$):

$$PHg\ (\mu g\ g^{-1}\ dw) = -0.0447 - 0.423 \times THg_W - 0.0091 \times \delta^{13}C - 0.0087 \times \delta^{15}N.$$

When chl *a* (μg L^{-1}; $p = 0.123$) was added to the multiple linear regression, the correlation coefficient increased to $r^2 = 0.969$:

$$PHg\ (\mu g\ g^{-1}\ dw) = -0.112 - 0.394 \times THg_W + 0.004 \times Chl\ a - 0.011 \times \delta^{13}C - 0.0077 \times \delta^{15}N.$$

From the equation of the line, we see that the slopes of the independent variables (THg_W, $\delta^{13}C$, and $\delta^{15}N$) were all negative, hence, as the independent variables decreased the PHg_{SCM} increased.

3.4.3 Biomagnification of Hg and MeHg from Phytoplankton to Grazing Zooplankton

When plotting the TL vs THg relationship between ice POM, pelagic POM, *C. hyperboreus*, and *C. glacialis*, we found that THg was not biomagnifying (Figure 3.5A) in this food chain. This is not surprising as the lipophilic MeHg - the form of Hg that is known to biomagnify - only accounts for a small fraction in THg at the base of the food chain.

To further test whether MeHg biomagnification occurs from phytoplankton to zooplankton, we explored the relationship between MeHg and TL. Unfortunately only three POM samples were analyzed for MeHg due to funding constraints. Using the highest MeHg to THg ratio of these three samples (0.04), MeHg concentrations in POM were estimated to range from 0.15 – 3.51 ng g^{-1} (1.4 ± 1.1 ng g^{-1}). However, this may represent a conservative estimate, as higher ratios of up to 0.15 have been reported for freshwater POM (Morel *et al.* 1998). Furthermore, the MeHg levels in *C. glacialis* were not analyzed. As a first approximation, we estimated the MeHg levels in *C. glacialis* from THg based on the average ratio of MeHg to THg in *C. hyperboreus* (51.5%).

As shown in Figure 3.5B, a strongly significant and positive relationship was found between MeHg and TL ($r^2 = 0.972$, $p = 0.014$), suggesting biomagnification of MeHg is indeed occurring even at the base of the Arctic marine ecosystem. Biomagnification of perfluorooctanesulfonate (PFOS) has also been reported at the lower food trophic levels in the Arctic marine ecosystem (Tomy *et al.* 2004). However, further studies are needed to reduce or understand the high degrees of variations in the dataset.

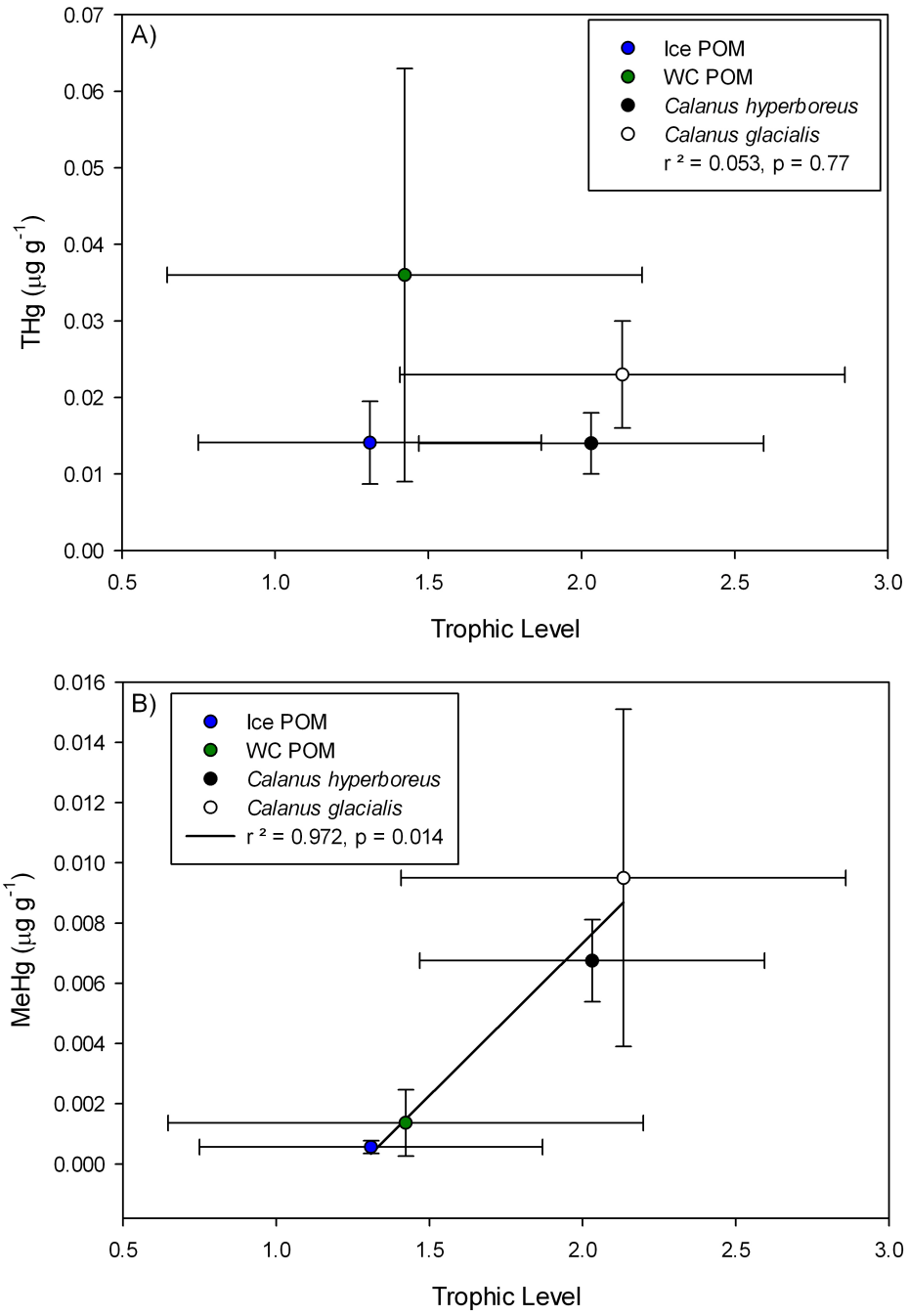

Figure 3.5. Mean (± SD) of A) THg (µg g^{-1} dw) *vs* trophic level relationship of Ice POM, WC POM, *Calanus glacialis*, and *C. hyperboreus*, which displays no trend and B) MeHg (µg g^{-1} dw) *vs* trophic level relationship of the same species, which is a strong, positively correlated and significant relationship ($r^2 = 0.972$, $p = 0.014$), showing biomagnification of MeHg in the base of the food web. Note: MeHg of Ice POM and WC POM were estimated based on 4% MeHg or THg of analyzed POM samples. MeHg in *C. glacialis* was estimated based on the mean %MeHg of *C. hyperboreus* (51.5%).

3.5 Conclusion

After analysis of total particulate Hg concentration in water column POM in each of their habitats (as defined in Gosselin *et al.* 1997), we conclude that there is evidence, supported by bioconcentration factors, for the accumulation of Hg by the POM from the water in which it is growing over the sampling season. The significant relationship between MeHg and TL also supports the occurrence of biomagnification of MeHg from primary producers (sea ice algae and phytoplankton) to grazing calanoid copepods.

Based on the large variations in $\delta^{13}C$ and $\delta^{15}N$, we also conclude that this food web is more complex than previously reported, and further study should be carried out throughout the feeding and spawning season to determine whether *C. hyperboreus* and *C. glacialis* depend differently upon ice vs. pelagic algal blooms seasonally.

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Chapter 4

Conclusion

4.1 Main Findings

The objective of this thesis was to answer the question of whether or not atmospheric mercury depletion events (AMDEs) can give rise to an increase in the Hg burden at the level of the primary producers and primary consumers in the Amundsen Gulf and Beaufort Sea food web. In Chapter 2 we found that, while AMDEs did occur during the ice algal logarithmic growth phase, AMDE deposited reactive gaseous mercury (RGM) did not appear to contribute to the particulate mercury (PHg) enrichment in the bottom 10 cm of the ice. These two processes are likely decoupled, and certainly not instantaneous. Ice-associated particulates collected near open leads did not contain higher PHg concentrations than when collected under full ice cover, which would be expected if AMDE deposited Hg was instantly bioavailable. Chaulk (2011) found that THg in melt ponds was 20 – 40 times higher than levels in the underlying sea water, adding to the hypothesis that sea ice melt processes may be adding high levels of Hg into the euphotic zone upon ice melt. Further study is needed to study the ice melt season and whether Hg is added to the system at this time.

I studied the mercury (Hg) uptake mechanisms in ice-associated particulate organic matter (POM), as suggested in the work of Pazerniuk (2007). It was found that in bottom ice core sections, as the total number of cells increased over time, PHg concentrations declined significantly in the cells ($r^2 = 0.99$, $p < 0.001$; Figure 2.4A dashed), which we attributed to biomass dilution (Pickhardt *et al*. 2002; Chen and Folt 2005). This suggests that there was a finite amount of Hg available to the algal population

within the bottom 10 cm of the ice cores. We observed a significant negative correlation between PHg and total Hg (THg) in the bulk bottom ice ($r^2 = 0.447$, $p = 0.035$; Figure 2.5B). From these results we propose that the ice algal community accumulated Hg primarily from their sea ice habitat, where Hg was sequestered in brine during the formation of sea ice (Chaulk *et al.* 2011). Mass balance calculations (Table 2.2) provide further support to our hypothesis that the growth of sea ice algae could result in depletion of Hg in the bottom sea ice.

After $\delta^{15}N$ analysis, we noted the mean $\delta^{15}N$ value for POM collected from sea ice cores at early drift stations ($\delta^{15}N = 3.58 \pm 1.02$, $n = 5$) was significantly lower than the mean value calculated from the cores collected at later drift and fast ice stations ($\delta^{15}N = 6.83 \pm 1.41$, $n = 6$; Table 2.1, Figure 2.4B; t-test, $p = 0.002$). Such significance suggests early populations of ice algae depleted levels of light ^{14}N isotope leaving only heavy ^{15}N isotope for later populations causing an enrichment in $\delta^{15}N$ of ice particulates as the season progressed.

In Chapter 3 we investigated the transfer of total Hg (THg) from the water column to the pelagic primary producers, and in turn to the primary consumers. The data illustrated significant trends of increasing levels of PHg in the water column POM over time, and we concluded that the variability in the concentration of THg in the water significantly predicted the variability of the concentration of PHg in the POM sampled from the same water masses ($r^2 = 0.274$, $p = 0.031$).

We observed bioconcentration factors (BCFs) for POM >> 1, which confirmed our hypothesis that water column POM bioconcentrate Hg from the water. We found no evidence of biodilution in water column POM, which is in agreement with the findings of

Kirkwood *et al*. (1999). There is always a supply of Hg in the water column, as suggested by Cole *et al*. (1988) which can replenish the euphotic zone through mixing, eddies and up-welling as pointed out by Mundy *et al.* (2009).

We analyzed the data separately by habitat (eg. Gosselin *et al*. 1997), to examine the trends in ice-water interface and subsurface chlorophyll maxima (SCM) POM. At ice-water interface (INT) sites it was observed that PHg in the POM taken from dive sites was significantly higher than POM sampled from other INT sites ($p < 0.001$). The variability of THg_{INT} significantly predicted 78 % of the variability in the PHg_{INT} (Figure 3.3; $r^2 = 0.786$, $p < 0.001$). We concluded that the POM_{INT} accumulated Hg from the water. BCFs supported the conclusion that the POM_{INT} are bioconcentrating Hg from their habitat in nature.

When we looked at the SCM POM, we discovered that concentrations of PHg increased significantly over time ($r^2 = 0.566$, $p = 0.008$). We found that the variability in a linear combination of the independent variables: THg_{water} (ng L^{-1}) $p = 0.028$, $\delta^{13}C$ (‰) $p = 0.043$, and $\delta^{15}N$ (‰) $p = 0.033$ significantly predicted 86.5 % of the variability of concentrations of PHg at the SCM. BCFs at the SCM exhibited a positive slope with time, and they remained much greater than 1 over the season, which suggested that bioconcentration was occurring from the water, even at depths > 15 m. BCFs at the SCM were significantly higher ($p = 0.002$) than BCFs for INT samples, therefore we may assume that there were greater concentrations of bioavailable Hg at depth in the water column.

Once the Hg trends between the water column and the POM were described, we then linked herbivorous zooplankton Hg uptake to their dependence on both ice and

pelagic algae for growth and reproduction. It is known that herbivorous copepods graze the ice algae followed by the pelagic phytoplankton bloom (Forest *et al*. 2011). Søreide *et al*. (2006) reported that *Calanus* spp. are part of the pelagic POM-based food web, while the herbivorous ice amphipod *Apherusa glacialis* mainly uses the ice POM-based pathway. We found that *Calanus* spp. cannot be lumped together as we observed a significantly different $\delta^{15}N$ ($p = 0.002$; Table 3.3) between the two herbivorous species (*Calanus glacialis* and *Calanus hyperboreus*). We concluded that this food web is more complex than previously reported, and further study should be carried out throughout the feeding and spawning season to determine whether *C. hyperboreus* and *C. glacialis* depend differently upon ice vs. pelagic algal blooms seasonally with respect to Hg and methyl Hg (MeHg) dietary accumulation. Despite food web complexity, and even at these low trophic levels, MeHg biomagnifies up the food chain illustrated in the significant relationship between analyzed and estimated MeHg levels and TL based on $\delta^{15}N$ (Figure 3.5; $r^2 = 0.972$, $p = 0.014$).

4.2 Lessons Learned

There are many things that would be done differently if we were to carry out this study again. First, freeze drying ice cores to gather the ice algae was probably not the best way to have collected the samples. Freeze drying could potentially damage cells, and upon re-suspension and filtration, it is possible to lose cell contents through the filter resulting in lower Hg concentrations. If done again, we would find a way to make Hg-free filtered seawater solution to melt ice core sections, and then filter them in a clean environment. A second limitation that our study had was that we filtered 20L of water at

a time. Due to the fact that it takes upwards of 8 hours to filter one 20L jug of water, there is potential for algal cell settling in the sample as it sits on the counter during filtration. This results in lost sample and lower particulate weight on each filter. In later years my suggestion has been to place each sample on a stir plate during filtration to keep cells suspended in the sample for the duration of the filtration.

4.3 Future Research

Future ice-associated algae studies should concentrate on MeHg accumulation in the ice POM. Sampling should occur more frequently during high bloom time in concert with biological sampling, with replicates at 3 cm and 7 cm as well as bulk ice, perhaps filtered and unfiltered. POM samples would be better treated by melting core sections in Hg-clean prepared seawater solution and filtering in a clean lab in the field rather than transporting whole ice core bottoms from the field. Pelagic POM studies should focus on frequent sampling and analysis of particulate and water column MeHg, as the algal bloom increases quickly during the short growing season.

New questions that have arisen from this work are: working with algal biologists, can we quantify algal species differences in $\delta^{15}N$, THg and MeHg? And, can we work out the two-source food web model based on dietary THg and MeHg uptake from the ice-associated algae adding herbivorous amphipods? In the future we will be continuing the food web analysis to include omnivorous and predatory zooplankton.

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Appendix

Supplementary Tables and Figures

Table S2.1. Mass balance calculations and results between mercury stores in the bottom particulate (P) and bulk ice (BI). Both the mean particulate Hg ($\bar{x}_P$) and the mean bulk ice Hg ($\bar{x}_{BI}$) are in the same order of magnitude therefore we conclude that the Hg store may be significantly depleted in the bulk bottom ice by the bottom ice particulates.

Date	Day of Year	Station	Particulate			Bulk ice		
			PHg ($\mu g\ g^{-1}$)	Weight (g)	PHg (ng)	THg_{BI} ($ng\ L^{-1}$)	Volume (L)	HgB_{BI} (ng)
9-Feb-08	40	D19	0.017	0.047	0.793	-	-	-
25-Feb-08	56	D26	0.021	0.047	1.004	-	-	-
1-Mar-08	61	D27	0.007	0.109	0.808	0.37	2.09	0.775
8-Mar-08	68	D29	0.022	0.051	1.127	0.18	1.27	0.223
19-Mar-08	79	D31	0.014	0.061	0.865	0.03	2.54	0.064
24-Mar-08	84	D34	0.008	0.046	0.371	0.65	2.54	1.654
25-Mar-08	85	D33	0.008	0.058	0.455	0.52	2.54	1.323
8-Apr-08	99	D36	0.016	0.083	1.297	0.25	2.54	0.640
12-Apr-08	103	D38	0.004	0.071	0.285	0.88	2.54	2.243
17-Apr-08	108	D41	0.015	0.074	1.117	0.48	2.54	1.210
20-Apr-08	111	D41	0.018	0.080	1.430	0.48	2.54	1.210
28-Apr-08	119	D43	0.014	0.074	1.068	-	-	-
5-May-08	126	D43	0.020	0.089	1.791	-	-	-
9-May-08	130	F1	0.013	0.131	1.667	-	-	-
14-May-08	135	F2	0.013	0.076	0.974	0.32	2.54	0.821
				$\bar{x}_P$	1.003 ± 0.44		$\bar{x}_{BI}$	1.016 ± 0.65

NB: - indicates no sample was available.

Table S2.2. The differences in the bottom ice PHg (μg g^{-1} dw) means across three groups of stations, drift ice (D), fast ice (F), and near open leads (O). There was no significant difference found between Hg concentrations in algae sampled under full ice cover or near open leads.

Group	$\bar{x}_{PHg}$	±	**n**	**p Values**	**Test**
Drift ice	0.015	0.005	13	$p_{D-F} > 0.07$	T-test
Fast ice	0.013	0.0001	2	$p_{F-O} > 0.07$	Mann-Whitney
Open leads	0.008	0.0007	2	$p_{D-O} = 0.07$	T-test

Table S2.3. Auxiliary information for ice algae samples by station and day of year.

Leg	Station	Date	Day of Year	Ice Thickness (cm)	Snow Thickness (cm)	Surface Water Salinity (‰)	Latitude (N)	Longitude (W)	Station Depth (m)	Ice Cover (0 - 10)
6	D19	09-Feb-08	40	92	-	30.2	71.07	124.77	365	10
6	D26	25-Feb-08	56	-	-	-	70.94	123.92	360	9.5
6	D27	01-Mar-08	61	20	0	-	70.84	123.60	450	9.8
6	D29	08-Mar-08	68	120	5	32.5	71.01	123.64	307	9.5
7	D31	19-Mar-08	79	28	0	-	70.91	123.02	425	9.5
7	D34	24-Mar-08	84	45	0	27.9	71.06	121.79	187	10
7	D33	25-Mar-08	85	140	35	31.8	71.07	121.79	188	10
7	D36	08-Apr-08	99	166	2	31.9	71.29	124.51	260	9
7	D38	12-Apr-08	103	111.5	5	29.6	71.25	124.61	286	9
7	D41	17-Apr-08	108	129	9	-	70.74	122.14	541	9.5
7	D41	20-Apr-08	111	130	8	28.6	70.66	121.91	536	9.5
8a	D43	28-Apr-08	119	130	25	32.0	70.69	123.00	560	9
8a	D43	05-May-08	126	145	4	-	71.15	126.25	411	9
8a	F1	09-May-08	130	120	25	32.8	70.18	124.83	52	9
8a	F2	14-May-08	135	170	10	33.4	69.95	126.17	199	10

NB: - indicated data not available

Table S3.1. Auxiliary information for surface water (SW), ice-water interface (INT), ice-water interface during the dive program (INTd), and subsurface chlorophyll maxima (SCM) samples by station and day of year.

Sample	Station	Date	Day of Year	Ice thickness (cm)	Snow depth (cm)	Station depth (m)	Latitude (N)	Longitude (W)	Ice cover (0 - 10)	Atm Hg GEM (ng m^{-3})	Atm Hg HgP (ng m^{-3})
SW	D26	25-Feb-08	56	ni	ni	360	70.94	123.92	9.5	1.622	0.004
	D27	01-Mar-08	61	20.0	0.0	450	70.84	123.60	9.8	1.251	0.018
	D28	03-Mar-08	63	0.0	0.0	295	70.94	122.88	8.5	1.154	0.045
	D29	17-Mar-08	77	125.0	7.0	401	70.91	123.48	9.5	0.208	0.094
	D33	27-Mar-08	87	140.0	35.0	188	71.07	121.79	10	1.450	0.054
	D33	01-Apr-08	92	ni	ni	188	71.07	121.79	10	0.126	0.469
INT	D36	09-Apr-08	100	160.0	7.0	234	71.30	124.58	9	1.501	0.023
	D38	12-Apr-08	103	111.5	5.0	286	71.25	124.61	9	1.406	0.030
	D41	18-Apr-08	109	128.5	6.5	500	70.63	121.97	9.5	0.494	0.086
	D43	29-Apr-08	120	130.0	25.0	534	70.74	123.52	9	1.061	0.142
	D43	05-May-08	126	145.0	4.0	411	71.15	126.25	9	1.018	0.052
	F1	08-May-08	129	130.0	10.0	47	70.18	124.83	9	1.044	0.009
	F2	17-May-08	138	176.0	6.0	199	69.95	126.17	10	1.459	0.003
	1011	21-May-08	142	85.0	6.0	460	70.70	124.00	4	1.641	0.001
	D46	30-May-08	151	79.3	2.7	288	71.57	125.29	9.5	1.359	0.000
	F6	02-Jun-08	154	160.7	3.0	71	69.86	123.75	10	1.381	0.001
	F7	08-Jun-08	160	138.0	1.0	78.7	69.83	123.63	10	1.718	0.001
	F7	09-Jun-08	161	125.4	4.1	78.3	69.83	123.63	10	1.715	0.001
INTd	FB05	17-Jun-08	169	195.0	0.0	106	69.96	125.88	10	ns	ns
	FB07	21-Jun-08	173	111.0	0.0	110	69.95	125.89	10	1.717	0.011

Table S3.1. Continued.

Sample	Station	Date	Day of Year	Ice thickness (cm)	Snow depth (cm)	Station depth (m)	Latitude (N)	Longitude (W)	Ice cover (0 - 10)	Atm Hg GEM (ng m^{-3})	Atm Hg HgP (ng m^{-3})
	405B	19-May-08	140	no ice	no snow	511	70.66	122.88	0	1.542	0.002
	1806	23-May-08	144	no ice	no snow	134	72.65	127.40	0.5	1.488	0.001
	9008	27-May-08	148	no ice	no snow	346	74.34	127.00	1	1.225	0.001
	405	01-Jun-08	153	no ice	no snow	542	70.64	123.18	6	1.284	0.002
	405B	10-Jun-08	162	no ice	no snow	562	70.66	123.03	0	1.511	0.004
SCM	FB03	14-Jun-08	166	no ice	no snow	103	69.98	125.86	1.5	ns	ns
	HR01	17-Jun-08	169	no ice	no snow	108	69.94	126.70	1	1.659	0.001
	1216	23-Jun-08	175	no ice	no snow	161	70.62	127.59	0	1.499	0.002
	1208	28-Jun-08	180	no ice	no snow	397	71.07	126.11	0	ns	ns
	6006	04-Jul-08	186	no ice	no snow	222	72.66	128.35	0	1.280	0.002
	2010	06-Jul-08	188	no ice	no snow	422	75.13	120.39	0	1.693	0.001

NOTE: ns - no sample

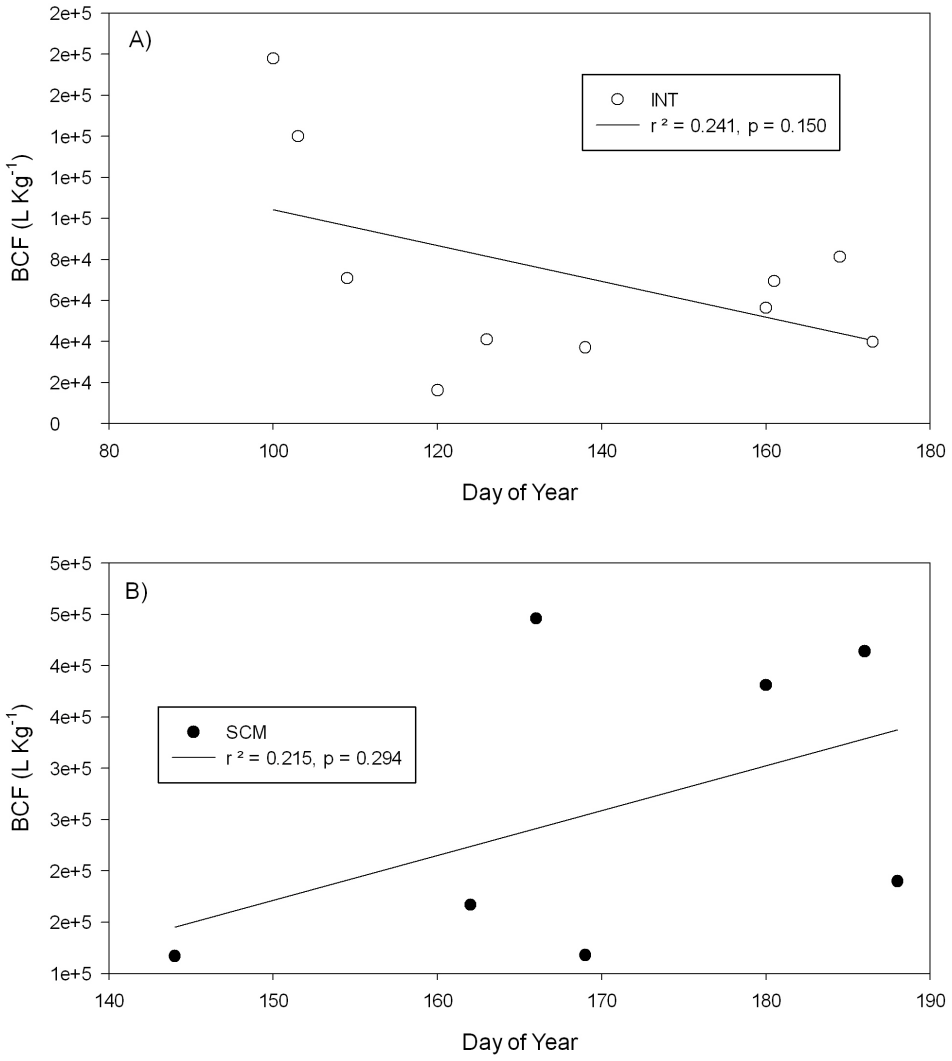

Figure S3.1. Bioconcentration factors at the A) ice-water interface decrease over time and B) subsurface chlorophyll maximum increase over time. BCFs are always >> 1, therefore Hg is bioconcentrating in the POM.