Effects of Climate Change on Contaminant Cycling in the Coastal and Marine Ecosystems

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Abstract

Contaminants pose a potential hazard to Arctic fish and marine mammal health, and ultimately to northerners that consume the tissues of these animals as part of their traditional diets. It is therefore imperative that we strive to understand how climate variability in physical forcing and the biogeochemical response to this primary forcing will affect among others 1) contaminant transport processes and cycling; 2) biomagnification through Arctic marine food webs; 3) foraging behaviour of marine mammals (e.g. in response to changing sea ice regimes); 4) changes to hunting patterns and diets of northerners to reflect availability of traditional foods (e.g. less ice may lead to reduced reproductive success of ringed seals forcing northerners to consume more beluga tissues which typically have 10-fold higher contaminant concentrations). Overall, results from our research will help assess the vulnerability of coastal Inuit communities to climate change, document and project impacts of climate change on traditional food security and community health and provide the information required by communities, scientists and policy makers to help develop adaptation strategies. Our findings will help to test and shape the policy for the future management of contaminants emissions and long range transport to the Arctic and will support integrated ocean management programs such as Marine Protected and Large Ocean Management Areas (MPA and LOMA, respectively) such as zone 1(a)s in the Beaufort Sea.

Key Messages

Transport and transformation of mercury across the ocean-sea ice-atmosphere (OSA) interface:

- The dynamics of mercury (Hg) in first-year and multi-year sea ice is controlled primarily by the dynamics of particles.
- Up to 30% of the total mercury in multi-year sea ice can be present as methylmercury.
- Seawater total and methylated mercury profiles obtained from the vast regions of the Canadian Arctic Ocean showed similar vertical distribution patterns, though the concentrations varied spatially.

Organic mercury species in the Arctic Ocean/Hg isotope ratios in arctic environments:

- Hg isotope ratios are potentially useful to identify sources of Hg to the Arctic.
- Measuring Hg isotope fractionation will add to our understanding of the cycling of Hg in remote. marine environments.

Mercury uptake within an ice algal community during the spring bloom in first-year Arctic sea ice:

- Bioavailable Hg in brine channels is taken up by the ice algae which colonizes the bottom-ice environment. Once incorporated into algae, Hg can be transported spatially and trophically within the ecosystem by a range of processes including grazing, resuspension, remineralization, and sedimentation.
- Ice algae contribute 10–60% of the annual primary production in the Arctic and may become even more productive and abundant under a mild climate change scenario. Replacement of multi-year ice with first-year ice (FYI) in the Beaufort Sea alone could result in an additional influx of ~48 kg/yr of particle- (algae) bound Hg.

Transformation of mercury at the bottom of the Arctic food web: an overlooked puzzle in the mercury exposure narrative:

- *Calanus hyperboreus* shifts Hg from mainly inorganic forms in pelagic particulate organic matter (POM) (>99.5%) or ambient seawater (>90%) to primarily organic forms (>50%) in their tissue, and Hg transformation within the species, perhaps mediated by gut microbial communities, likely play an overriding role.

Pan-Arctic Hg in zooplankton:

- Pan-Arctic study of Hg in zooplankton shows that zooplankton from the Beaufort and Chukchi seas consistently have the highest concentrations.
- These high concentrations mirror the high concentrations observed in beluga and polar bears.
- A link between carbon source ($\delta^{13}C$) and Hg concentration suggests that influence from rivers plays an important role in Hg accumulation

Climate-driven changes in organic matter-mercury interactions in coastal Arctic lakes:

- During the Medieval Period (pre-1700 A.D.), fluctuations in algal productivity in a northern lake are shown to have caused significant changes in the amount of organic matter-bound Hg and total Hg in sediments, increasing during warmer periods and declining during cooler periods.
- Organic-bound mercury accounts for virtually most of the variation of total sediment Hg during the pre-industrial period.
- Changes in total sediment Hg levels as a result of climate-driven limnological change can confound interpretation of recent sediment Hg increases as being solely due to industrial pollution.

BREA studies of mercury and hydrocarbons in Beaufort Sea sediments and biota:

- First study on Hg in benthic communities in the Arctic.
- Most species biomagnify Hg from the sediments.
- Most species correlate positively with increasing concentrations in sediment farther offshore, although some (certain species of starfish) negatively correlate.
- Hydrocarbon biomarkers, such as polycyclic aromatic hydrocarbons (PAHs), from surface sediments in Beaufort Sea show an overwhelming presence of petrogenic (peat, coal and oil-derived) biomarkers relative to pyrogenic (forest fire, combustion-derived) biomarkers.
- Other biomarkers (n-alkanes) show a predominance of terrestrial plant materials over marine materials.
- Beaufort Sea near the Mackenzie River/Delta thus receives the bulk of its organic matter from the river (terrestrial sources) and has a notable background of petrogenic influence.
- Easily detectable background of petrogenic compounds enables comparisons to any future spills/leaks of these compounds from drilling and/or shipping/maritime traffic.

Petrogenic hydrocarbons in Baffin Bay: Establishing baselines and characterizing sources:

- It is pertinent to establish the baseline levels of hydrocarbons (HCs) and predominant sources in Baffin Bay in advance of proposed petroleum exploration/exploitation and increased shipping activity
- Petrogenic sources of HCs are predominate in the Baffin Bay sediments. Combustion sources typically associated with industrial pollutants, indicative of long-range transport sources, are not nearly as important.
- Organic carbon in the region is derived both from terrigenous higher plants and from marine-based algal sources. The relative proportion of each varies between locations.

Characterization of sedimentary organic matter in recent marine sediments from Hudson Bay, Canada, by Rock Eval Pyrolysis:

- Characterization of sedimentary organic matter (OM) in recent marine sediments by Rock Eval

pyrolysis provides basic information about its sources and state of degradation based on the hydrogen and oxygen content of organic compounds. However, such characterization is obscured in systems with multiple competing or additive processes that simultaneously influence the hydrogen and oxygen content of the sedimentary OM. These situations can be resolved through the use of elemental (e.g. $\delta^{13}C$) and biomarker (e.g. lignin) analyses.

Importance of Arctic zooplankton seasonal migrations for α-Hexachlorocyclohexane (α-HCH) bioaccumulation dynamics:

- Even though a single cycle of *C. hyperboreus* seasonal migration does not result in a significant redistribution of α-HCH in the water column, this process could have a significant cumulative effect over longer time scales with particular local importance where the zooplankton biomass is high and ocean depth great enough to provide substantial vertical concentration gradients.

Organophosphate ester flame retardants and plasticizers (OPEs) in the Arctic environment:

- Organophosphate ester flame retardants and plasticizers (OPEs) have been measured for the first time in the Canadian arctic air, water and zooplankton.

IRIS 1- western and central high Arctic:

- A Kitikmeot sub-committee was established to help guide the development of the Regional Impact Assessment (RIA) with respect to Kitikmeot priorities.
- The 2nd draft of the RIA, including all chapters and Regional Climate Model projections for 2050, was completed in December, 2013.

Objectives

Transport and transformation of mercury across the ocean-sea ice-atmosphere (OSA) interface: To understand the role of sea ice in the occurrence of atmospheric mercury depletion events (AMDEs), quantify the processes by which mercury is transported from the atmosphere to the ocean via snow packs and sea ice and to examine and quantify the sources of methylmercury in Arctic seawater.

Organic mercury species in the Arctic Ocean/Hg isotope ratios in arctic environments: To develop a method for pre-concentration of large volumes of seawater for Hg isotope ratio measurements, to characterize the temporal changes in Hg isotope ratios in arctic sediments and to identify sources of Hg in arctic environments (sediment, water, biota).

Mercury uptake within an ice algal community during the spring bloom in first-year Arctic sea ice: We investigate the seasonal trends of particulate-bound Hg (PHg) levels of the bottom ice, along with environmental levels of total Hg (THg) in sea ice, sea water and air. We look at how Hg is incorporated into the lowest trophic level from the environment, and whether AMDEs have an effect of Hg levels in bottom-ice algae.

Transformation of mercury at the bottom of the Arctic food web: an overlooked puzzle in the mercury exposure narrative: To investigate monomethyl Hg (MMHg) in primary producers, and herbivorous (*C. hyperboreus*) and predator (*Chaetognaths*, *P. glacialis* and *T. abyssorum*) zooplankton species (trophic levels ~1-3) in the Amundsen Gulf and Canadian Beaufort Sea with emphasis on environmental and physiological controls. We pay particular attention to the role of the herbivorous copepods in supporting biomagnification factors (BMFs) and controlling seasonal concentration trends in higher trophic levels.

Pan-Arctic Hg in zooplankton: Examine spatial trends in Hg concentration in zooplankton across the Arctic to look for biogical hotspots which and to provide insight into Hg processes in the Arctic.

Climate-driven changes in organic matter-mercury interactions in coastal Arctic lakes: To examine the chemical speciation of mercury in pre-industrial Arctic lake sediments to test the "algal scavenging" hypothesis which proposes elevated sediment mercury levels during warm climatic periods.

BREA studies of mercury and hydrocarbons in Beaufort Sea sediments and biota: To examine spatial trends of mercury concentrations, biomagnification and bioaccumulation across benthic invertebrates species; Determine background (quantity and quality) of hydrocarbon biomarkers in sediment and biota in the Beaufort Sea prior to large scale drilling (exploration and possibly future exploitation) and expected increases in maritime traffic (shipping or transport).

Petrogenic hydrocarbons in Baffin Bay: Establishing baselines and characterizing sources: To establish HC concentrations and fluxes within the marine sediments of Baffin Bay. To asses, using biomarkers and chemical profiles, the predominant sources of HCs to Baffin Bay sediments. To determine the variability of these measured properties and observations in pre-1900 sediments.

Characterization of sedimentary organic matter in recent marine sediments from Hudson Bay, Canada, by Rock Eval Pyrolysis: The objectives of this project were (Liebezeit and Wiesner, 1990) to use Rock Eval pyrolysis to characterize sedimentary OM in recent marine sediment from Hudson Bay (HB), (Sanei et al., 2000) compare these interpretations with those from elemental and biomarker analyses, and (Marchand et al., 2003) investigate how the process of sediment recycling in HB influences the OM oxidation signal distinguished by Rock Eval pyrolysis.

Importance of Arctic zooplankton seasonal migrations for α-Hexachlorocyclohexane (α-HCH) bioaccumulation dynamics: We have cultured C. hyperboreus to determine how their α-HCH tissue concentrations, enantiomer fractions (EFs) and bioconcentration factors (BCFs) respond to vertical water concentration gradients are experienced presently in the Canadian high Arctic. Further, we compare experimental results with *C. hyperboreus* samples collected directly from the Arctic waters during periods of dormancy at depth and grazing at surface. Finally, we determine the extent to which zooplankton could actively transfer α-HCH between depth and surface during their seasonal vertical migration.

Organophosphate ester flame retardants and plasticizers (OPEs) in the Arctic environment: To determine occurrence and levels of new and emerging compounds in the Canadian arctic environment.

IRIS 1- western and central high Arctic: The IRIS 1 leader and coordinated strived to compile a complete RIA draft which contained sections previously missing in the first draft (including two chapters), climate projections for 2050, and cross-referencing of the climate projections. Also of importance was to determine if there was support and interest for a Kitikmeot sub-committee, with the purpose of providing Kitikmeot-related expertise and feedback towards the development of the RIA.

Introduction

Transport and transformation of mercury across the ocean-sea ice-atmosphere (OSA) interface: Evidence is now mounting that the highly variable mercury concentrations in Arctic marine mammals in recent decades are no longer a simple function of external, anthropogenic mercury emissions; instead, they are increasingly driven by changes in post-depositional processes that control the transport, transformation, and biological uptake of stored mercury in the Arctic Ocean (AMAP, 2011; Wang et al., 2010). We have

recently shown that the sea ice environment plays a major role in controlling the magnitude and timing of atmospheric Hg flux to the underlying marine ecosystem (Burt et al., 2013; Chaulk et al., 2011; Chaulk, 2011). We have also shown a profound production zone of methylmercury in sub-surface seawater in the Beaufort Sea (Wang et al., 2012). However, major uncertainties exist with respect to the mechanism by which sea ice affects the net transport of mercury, and the process responsible for the sub-surface mercury methylation.

Organic mercury species in the Arctic Ocean/Hg isotope ratios in arctic environments: In some areas of the Arctic, levels of mercury continue to increase in food-webs, while concentrations seem to level off in other regions. However, we are still unable to easily resolve sources to the Arctic and distinguish between natural and anthropogenic sources of mercury, which would be a prerequisite for an effective management of Hg in polar regions. While Hg emissions from Europe and North America declined over the past 20 years (Pacyna et al., 2006), emissions from Asia increased. Biswas et al. (2008) suggested that coal deposits within the United States, China, and Russia-Kazakhstan, which are three of the five greatest coal-producing regions, all have unique Hg isotope signatures that may be used to differentiate the various Hg sources. For example, Carignan et al. (2009) measured Hg isotope ratios in lichens, assuming it would represent the composition of atmospheric Hg. They also concluded that Hg isotope signatures may be used to trace globally relevant sources and pathways of Hg. Therefore, we suggest to use this still relatively new tool of Hg isotope fingerprinting to characterize representative samples from the arctic (water, sediment, biota) to identify similarities and potentially identify pathways of Hg in polar regions. While measurements of Hg isotope ratios in the environment are increasing, information regarding polar environments is still extremely scarce. We believe that Hg isotope ratio measurements in arctic samples will be invaluable to determine the sources of Hg to the Arctic.

Mercury uptake within an ice algal community during the spring bloom in first-year Arctic sea ice: Over 90% of mercury present in the surface seawater is in the form of inorganic mercury (Kirk et al., 2008; Wang et al., 2012); however, the ratio of organic to inorganic mercury increases dramatically as the mercury is transferred up the Arctic marine food web (Rigét et al., 2007). One of the mechanisms by which atmospheric mercury may make its way into the Arctic ecosystem is via AMDEs (Schroeder et al., 1998). Mercury that is already in the water or that is deposited to the open water (leads, polynyas) can then become ice or can be transported under the ice with ocean currents, providing greater biological exposures to the bottom-ice communities. Recent studies suggest that the warming climate in the western Canadian Arctic and the decrease in perennial ice cover may result in increased biological Hg exposure (Maslanik et al., 2007; Outridge et al., 2008; Stern et al., 2012). In this study, we examine mercury sources to, and accumulation by, a thick FYI (>120 cm thick) algal community under natural conditions in the western Canadian Arctic.

Transformation of mercury at the bottom of the Arctic food web: an overlooked puzzle in the mercury exposure narrative: Once incorporated into the food web, the percentage of MMHg in THg increases with trophic level (TL), ranging from <1-12% in aquatic primary producers (TL 1), through 10-80% in zooplankton (TL 2-3), to 80-100% in many fish and marine mammals (TL >3) (Macdonald and Loseto, 2010; Foster et al., 2012; van der Velden et al., 2013). Even though the re-apportionment of MMHg between the first and the third trophic level appears crucial to the ultimate exposure of MeHg in top predators, this component of the food web remains vastly under-researched. Developing an understanding of speciation, biomagnification and transformation at this stage is, arguably, the most important step toward a better understanding of mercury fate in Arctic marine food webs where the vast majority of fish, birds and mammals rely ultimately on herbivorous zooplankton (copepods) as a common early step toward the creation of prey (Stern and Macdonald, 2005; Loseto et al., 2009; Karnovsky et al., 2010; Walkusz et al., 2011).

Pan-Arctic Hg in zooplankton: Examination of patterns across different regions and ecosystems can allow us to better understand global cycles of contaminants. Over a decade of collections of zooplankton across the Arctic, and their analysis for contaminants, allows us to examine where hotspots may occur, and thus what the main drivers are for contamination in foodwebs (Macdonald et al., 2005; Stern and Macdonald, 2005). Focussing on mercury, a toxic metal known to bioaccumulate and biomagnify, we looked at mercury concentrations across common species, as well as their stable isotopes to determine feeding habits.

Climate-driven changes in organic matter-mercury interactions in coastal Arctic lakes: Lake sediments are often used by regulatory agencies to evaluate the amount of pollution from local mining or more distant industrial activities. However in northern Canadian lakes, climate change is believed to be forcing substantial modifications to terrestrial and freshwater carbon and contaminant biogeochemical cycles that may confound interpretation of sediment profiles as pollution. Our research group previously proposed that temporal variation in the amount of algal biomass in lakes as a result of historical and modern climate change could alter sediment Hg levels significantly through elevated rates of Hg scavenging and sedimentation (the algal scavenging hypothesis). This study tests this hypothesis for mercury in sediments of a coastal Arctic lake in the medieval era, which saw significant warming and limnological change but little or no anthropogenic atmospheric Hg.

BREA studies of mercury and hydrocarbons in Beaufort Sea sediments and biota: Increased interest in oil and gas leases in the Beaufort Sea, coupled with stringent environmental regulations, requires a solid understanding of the current status of this important ecosystem. By establishing background (quality and quantity) levels of hydrocarbons, any future spills or leaks can be compared to the background (see also Yunker et al., 2011) to determine (a) responsibility (oil from a drilling platform will be different than that from a cargo ship passing through); (b) degree of responsibility (the quantity of oil spilled will affect the ecosystem more with greater amounts) and (c) the levels at which the ecosystem can operate without significant negative effects. Further, we need to understand Hg biogeochemical cycles in benthic invertebrates, as this group is highly understudied (e.g., Bargagli et al., 1998). Benthic invertebrates may be highly susceptible to negative effects from drilling and/or seafloor leaks from drilling platforms.

Petrogenic hydrocarbons in Baffin Bay: Establishing baselines and characterizing sources: Proposed oil exploration and increased shipping traffic through the Canadian waters of Baffin Bay are associated with the risk of introducing hydrocarbons into the marine environment of this region. Baseline datasets of hydrocarbon concentrations have been established in some regions of the Canadian Arctic such as the Beaufort Sea (AMAP, 2010), but no such dataset exists for Baffin Bay. The establishment of a baseline dataset of hydrocarbon concentrations and fluxes, and the identification and fingerprinting of existing hydrocarbon sources to Baffin Bay is a critical step in hazard preparedness for offshore oil exploration in the region - of particular concern as the largest prospective, untapped reservoir of petroleum in the Arctic occurs in Baffin Bay (Gautier et al, 2009).

Characterization of sedimentary organic matter in recent marine sediments from Hudson Bay, Canada, by Rock Eval Pyrolysis: Rock Eval pyrolysis is a relatively rapid and inexpensive method of obtaining basic information about sedimentary OM that has been increasingly used in recent years to gain information about the recent history of OM dynamics in aquatic systems (Liebezeit and Wiesner, 1990; Marchand et al., 2003; Sanei et al., 2000). However, the presence of multiple OM sources, multiple mechanisms of oxidation, and the specific geochemistry (e.g. Mn parameters) of an aquatic system can render interpretations from its Rock Eval data ambiguous. Selectively using more expensive and time-consuming, but also more diagnostic, analyses such as $\delta^{13}C$ and lignin measurements can unequivocally resolve these scenarios. We used these methods to identify the

sources and state of preservation of sedimentary OM in modern marine sediment from Hudson Bay, Canada.

Importance of Arctic zooplankton seasonal migrations for a-Hexachlorocyclohexane (a-HCH) bioaccumulation dynamics: a-HCH is the most abundant persistent organic pollutant (POP) in Arctic seawater and lower trophic levels of marine biota (Hargrave et al, 2000; Hoekstra et al., 2002). α-HCH concentration and EF in the surface water of the Beaufort Sea and the Amundsen Gulf were reported to be 1.29 ± 0.38 ng/L and 0.442 ± 0.023, respectively (n = 48, October 2007-May 2008) (Pućko et al., 2010), and decrease with depth reaching ~0.30 ng/L and 0.150-0.300, respectively, in the near bottom water (Pućko et al., 2012; Pućko et al., 2013). In general, organic contaminants bioaccumulate in zooplankton passively through exposure to surrounding seawater (bioconcentration) and actively through feeding, although the relative importance of these routes is not yet clearly understood (Sobek et al., 2006; Berrojalbiz et al., 2009).

Organophosphate ester flame retardants and pasticizers (OPEs) in the Arctic environment: Industrial OPEs have been used for a wide variety of applications including: flame retardants (FRs), plasticizers, in hydraulic fluids and levels in floor waxes. As other FRs are banned/restricted i.e., penta- and octa-PBDEs and HBCDD, the usage of OPEs has increased. They are potentially toxic, high production volume chemicals and the Canadian Chemical Management Plan risk assessors have included several OPEs on their high priority list.

IRIS 1- western and central high Arctic: An Integrated Regional Impact Study (IRIS) is a framework that combines and summarizes all available knowledge of a region affected by change, and facilitates better knowledge accessibility. This knowledge is used to produce a climate change RIA, which includes a prognosis of the extent of socio-economic impacts and benefits of future change. Ashley returned to work from mat leave in March 2013, when Breanne Reinfort updated her on the last eight months of IRIS activity.

Activities

Transport and transformation of mercury across the ocean-sea ice-atmosphere (OSA) interface: From December 2012 to March 2013 and from December 2013 to March 2014, mesocosm-scale experiments were conducted at the Sea-ice Environmental Research Facility (SERF) in Winnipeg. In April, 2013, field studies were conducted at Nuuk, Greenland on the pH environment of sea ice. We also participated in Legs 1 and 2 of the 2013 CCGS *Amundsen* expedition.

Data analysis and interpretation from all three field programs are ongoing.

Organic mercury species in the Arctic Ocean/Hg isotope ratios in arctic environments: Sea water samples and sediment cores were collected during previous ArcticNet expeditions (2012 and 2013) on board the CCGS *Amundsen* in the Canadian Arctic Archipelago (CAA) for Hg isotope ratio measurements. Seawater was either pre-concentrated on board (2013) or shipped back to the lab and processed there (2012). Sediment cores were sectioned on board (2013), frozen and transported back to the laboratory. In addition to Hg isotope ratio measurements, concentrations of total Hg (THg, sediment, seawater) and monomethyl mercury (MMHg, sediments) were determined. While the concentration measurements have been completed, the Hg isotope ratios measurements for sediment cores are still in progress.

Mercury uptake within an ice algal community during the spring bloom in first-year Arctic sea ice: Samples for this study were collected during the CCGS *Amundsen* cruise to the Beaufort Sea and the Amundsen Gulf as a part of the International Polar Year (IPY) - Circumpolar Flaw Lead (CFL) system study in spring 2008 (8 March – 14 May). A manuscript was published in the Journal of Geophysical Research: Oceans: Burt A., Wang F., Pućko M., Mundy CJ., Gosselin M., Philippe B., Poulin M., Tremblay J-É., and Stern G.A. (2013, 118:4746-4754).

Transformation of mercury at the bottom of the Arctic food web: an overlooked puzzle in the mercury exposure narrative: Samples were collected onboard the CCGS *Amundsen* between February (33rd Julian day) and July (187th Julian day) of 2008 as part of the International Polar Year (IPY) - Circumpolar Flaw Lead (CFL) system study in the Amundsen Gulf and the Canadian Beaufort Sea. A manuscript was prepared and submitted to the Environmental Science and Technology (30 October 2013): Pućko M., Burt A., Walkusz W., Wang F., Macdonald R.W., Rysgaard S., Barber D.G., Tremblay J.-E., Stern G.A.

Pan-Arctic Hg in zooplankton: There were two main directions of this project: 1) processing (listing, drying, homogenising, partitioning), analysis (mercury, methyl mercury) and interpretation of 2012 BREA collections, analysis of 2008 Laptev Sea zooplankton collections and, 2) comparing of data from 1998 (SHEBA project) to 2012 (BREA project) across the same zooplankton species as collected in the Laptev, Chukchi, and Beaufort seas, as well as the Canadian Archipelago and Baffin Bay.

Climate-driven changes in organic matter-mercury interactions in coastal Arctic lakes: Sequential extraction using different chemical solutions were used to operationally-define five Hg species using the method of Bloom et al. (2003) as employed by Brooks Rand Laboratories, Seattle (www.brooksrand.com/AnalyticalServicesHome/Capabilities). Freeze-dried sediments were analysed from dated cores from a previously-studied Arctic lake, Lake DV-09, Nunavut (Outridge et al., 2007).

BREA studies of mercury and hydrocarbons in Beaufort Sea sediments and biota: DFO chartered the F/V *Frosti* for the 2013 program. The F/V *Frosti* is a commercial stern trawler that operates out of Richmond, B.C. Two legs were completed (see Figure 1). 22,764 fish were captured during the 2012 and 2013 surveys; across 29 genera (identifications have not been confirmed by independent verification - ongoing). Of these 17,909 (79%) were *Boreogadus saida* (Arctic Cod). Though species level identification

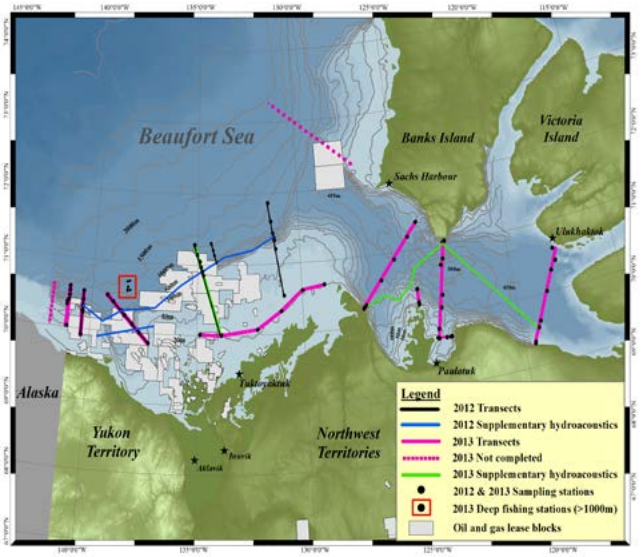

Figure 1. Study area and transects associated with the BREA Marine Fishes Program (2012-2013) and joint Canada-US sampling in the Tukon-Alaska transboundary region.

(including independent verification) is ongoing the number of species caught is estimated at 44. A total of ten transects encompassing 75 stations were sampled for oceanography, zooplankton, sediment, and fish. In order to gain insight into temporal variability two of these transects were sampled in both 2012 and 2013. Hg and hydrocarbon analysis of 2012 are well underway, while the 2013 samples are being processed.

Petrogenic hydrocarbons in Baffin Bay: Establishing baselines and characterizing sources: Sediment cores were collected from eleven sites across northern Baffin Bay (including the North Water Polynya (NOW), Lancaster Sound, Scott Inlet, and Gibbs Fjord) during the ArcticNet 2008 and 2009 cruises. The cores were dated, and slices representing present (surficial sediments) and pre-1900s sediments deeper in the core were analysed by AXYS Analytical Services Ltd. (Sidney, BC) for HCs (PAHs and alkanes). We received the HC data in the spring of 2012, data were interpreted/analyzed, a report was prepared and sent to the Nunavut General Monitoring Program (NGMP) (spring 2013), and community visits were made to Pond Inlet and Iqaluit to present results in spring 2013.

A manuscript has been prepared detailing these results and is in the final stages of review.

Characterization of sedimentary organic matter in recent marine sediments from Hudson Bay, Canada, by Rock Eval Pyrolysis: Datasets produced from sediment sampling of HB during previous years' ArcticNet expeditions were analyzed by Rock Eval pyrolysis through a collaboration with the Geological Survey of Canada. The same box core sample set was also previously analyzed for elemental and biomarker data. The dataset was thoroughly investigated for biochemical signatures and relationships between these signatures and known sources of, and processes influencing, sedimentary organic matter. A scientific manuscript was accepted by the journal Organic Geochemistry in January 2014.

Importance of Arctic zooplankton seasonal migrations for α-Hexachlorocyclohexane (α-HCH) bioaccumulation dynamics: Samples for this study were collected during the CCGS *Amundsen* cruise to the Beaufort Sea and the Amundsen Gulf as a part of the IPY-CFL system study in the winter 2007/2008 (26 December-28 January) and the summer 2008 (11 June-8 July). A manuscript was published in the Environmental Science and Technology: Pućko M., Walkusz W., Macdonald R.W., Barber D.G., Fuchs C., Stern G.A. (2013, 47:4155-4163).

Organophosphate ester flame retardants and plasticizers (OPEs) in the Arctic environment: Air samples collected as part of IPY, CFL and ArcticNet from 2007 to 2011, and were analyzed for new and emerging compounds, including OPEs. Additionally, water and zooplankton collected in 2011 were also analyzed for OPEs. During 2013, a few air and water samples were collected between Resolute Bay and Banks Island, the analysis is ongoing.

IRIS 1- western and central high Arctic:

- ***Teleconferences with IRIS 1 Steering Committee:*** Meetings on April 22 and November 25 provided members a summary of progress with respect to the RIA, and provided a means for members to ask questions or voice concerns.
- ***Revisions to the RIA's 1st draft:*** Comments and edits to the 1st draft by IRIS 1 Steering Committee members and external reviewers, along with the 2050 climate projections, were sent to chapter lead authors from May 3-10. Authors were instructed to send revised chapters to Ashley by August 9, 2013.
- ***Formation of a Kitikmeot sub-committee:*** Following the recommendations from the consultations in Cambridge Bay (September 2012) and receiving support for this notion from the IRIS 1 Steering Committee (via teleconference on April 22), Kiah Hachey (Nunavut Inuit Research Advisor), Gayle Kabloona (Nunavut Tunngavik Incorporated) and Ashley invited participants from the 2012 Kitikmeot consultations to a newly established Kitikmeot sub-committee. Jaswir Dhillon (Nunavut Impact Review Board, Cambridge Bay), Sonia Aredes (Nunavut Water Board, Gjoa Haven), Miguel Chenier (NTI, Cambridge Bay), Corey Dimitruk (Community and Government Services, Government of Nunavut, Cambridge Bay) and Kevin Taylor (Municipality of Cambridge Bay) answered the call. The first teleconference with this group commenced on July 23, 2013, when a refresher on the IRIS 1 regional impact assessment was given, a timeline of the assessment's development was outlined, and Kitikmeot sub-committee member tasks were proposed.
- ***Completion of the RIA's 2nd draft:*** Revised chapters were received by Ashley between July 11 and November 14. The complete, formatted draft was finalized on Monday, December 2, and this was distributed via email to all lead authors, IRIS 1 steering committee and Kitikmeot sub-committee members, the ArcticNet executive and scientific directors, and the IRIS coordinators.
- ***IRIS 1 topical session at the ArcticNet ASM:*** On Wednesday December 11 during the ArcticNet

Annual Scientific Meeting in Halifax, NS, David Barber and Ashley co-chaired the IRIS 1 topical session (morning and afternoon). Eight of ten lead authors (or designated alternatives) arrived to present the highlights of their chapters.

Results

Transport and transformation of mercury across the ocean-sea ice-atmosphere (OSA) interface: Our SERF experiment confirmed that most Hg in newly formed sea ice is in the particulate form and is always enriched in the surface layer. The first measurement of pH of natural sea ice in Greenland suggested the vertical pH profile in general followed a similar pattern we reported earlier at SERF sea ice (Hare et al., 2013), though the range was much smaller. Methylmercury levels in a new multi-year ice core taken from the McClure Strait showed higher concentrations of both total and methylated mercury ([THg] and [MeTHg], respectively), though the ratios of [MeTHg]/[THg] were comparable to those measured in the multi-year ice core taken from the Beaufort Sea in 2011 (Figure 2). Seawater [THg] profiles obtained from the vast regions of Labrador Sea, Baffin Bay, North Water, and CAA showed similar vertical distribution patterns as we reported earlier in the Beaufort Sea (Wang et al., 2012), though the surface concentrations varied spatially. [MeTHg] samples are being analyzed.

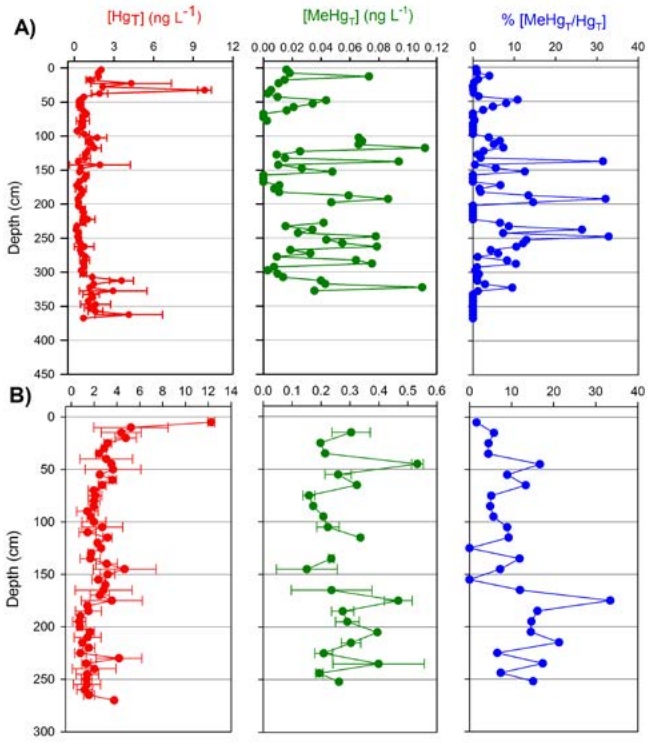

Figure 2. Profiles of total mercury (THg), methylmercury (TMeHg) and the ratio of TMeHg/ THg in Arctic multiyear sea ice from two multiyear sea ice cores (Beattie et al., in review).

Organic mercury species in the Arctic Ocean/Hg isotope ratios in arctic environments: Results for Hg isotope ratios in seawater obtained during the 2012 and 2013 cruises showed differences, based on the sample manipulation protocol used. Pre-concentration on board resulted in higher Hg values than pre-concentration in the laboratory. In sediment cores, THg profiles show elevated levels at the top (40-60 ng/g), which drop to 20-30 ng/g at the bottom of cores. Most profiles show a peak in THg concentrations a few cm below the sediment/water interface. The only exception is the core from Station 250, which is characterized by much lower THg concentrations, ranging only from 10-20 ng/g. MMHg levels are surprisingly high (Figure 3), starting at around 0.1 ng/g at Station 250 to values as high has 1.1 ng/g at the surface of Station 101. Generally, concentrations decrease with depths.

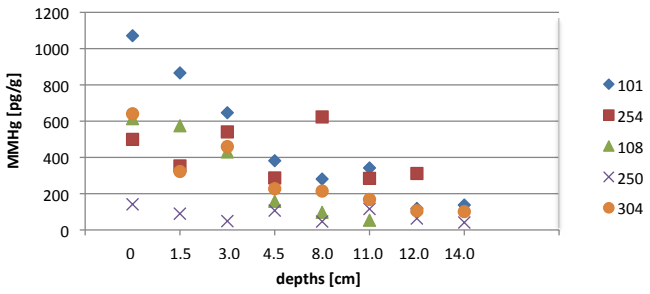

Figure 3. MMHg depths profiles in Arctic sediments at various stations (2013)

Anabelle Baya (PhD student in charge of the organic mercury species measurement in the atmosphere) has completed her experimental work and will be defending her dissertation in April 2014. The results of this research have either been published or manuscripts have been submitted.

Mercury uptake within an ice algal community during the spring bloom in first-year Arctic sea ice: THg concentrations in particulate, PTHg (µg/g), in the bottom 10 cm sections of the ice cores ranged from 0.004 to 0.022 ug/g dw and showed no covarying patterns with dissolved organic carbon (DOC) or chl a concentrations. MeHg concentrations were below detection limit (n=2). Once the protist counts started to increase and contribute significantly to the particulate matter biomass in the bottom 10 cm of ice cores, PHgT became less variable with a decreasing trend as a function of bloom progression. We calculated the concentration of particulate Hg per algal cell, THgcell, as a function of bloom progression (Figure 4a). From 4 April (day 94), THgcell decreased significantly over time, while taxonomic cell composition (Figure 4b) and cell size of major taxonomic groups remained relatively consistent.

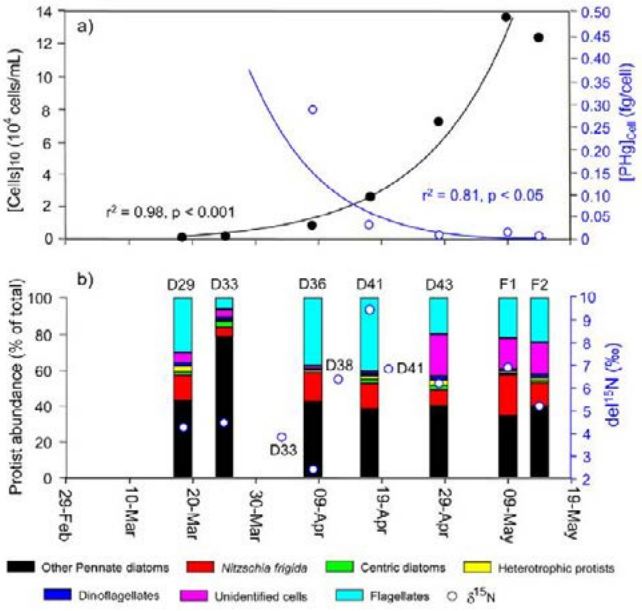

Figure 4. Total cell abundance ($[Cells]_{10}$) and the total amount of mercury per cell ($[PHg]_{cell}$) as a function of bloom progression (a) and percent contribution of different protist groups to the total cell abundance along with δ15N composition (b). Both refer to the bottom 10 cm ice-core sections; markers above columns in Figure 2b refer to stations.

We found the majority of mercury present in the bottom 10 cm of sea ice is bound to particulate, PTHg (mean of 1.04±0.49, ng/0.57 dm^2), and the amounts available for uptake from the bottom ice, THgBI (0.22±0.13, ng/0.57 dm^2) and 10 cm of underlying seawater, THgSW, (0.11±0.0.05, ng/0.57 dm^2) are relatively small. THgBI ranged from 0.02 to 0.45 ng, and no significant trends were observed over the algal growth season (Pearson correlation: r^2=0.057, p>0.05). However, significant negative correlations were observed to occur between PTHg(PBT/sample) and THgBI (Pearson correlation: r^2=0.36, p<0.05) and between PTHg(PB/sample) and THgBI+THgSW (Pearson correlation : r^2=0.70, p<0.05). Conversely, no significant correlation was observed between PTHg(PB/sample) and THgSW (Pearson correlation: r^2=0.01, p>0.05).

Transformation of mercury at the bottom of the Arctic food web: an overlooked puzzle in the mercury exposure narrative: The mean THg concentration in *C. hyperboreus* was 0.014 ± 0.004 µg/g dw (n = 65), which is comparable to data from the wider Beaufort and Chukchi seas (Stern and Macdonald, 2005). The THg trends in *C. hyperboreus* from our study region can be divided into four distinct time periods based on concentration: I (<75 Julian day or <March 15), II (75-144 Julian day or March 15 – May 23), III (145-160 Julian day or May 24 – June 8), and IV (>160 Julian day or >June 8. In period I, THg concentrations were relatively low (0.012 ± 0.004 µg/g dw), but then increased slightly to 0.016 ± 0.003 ug/g dw in period II (t-test, α = 0.95, p < 0.001). In period III, THg peaked sharply with concentrations as high as 0.030 ug/g dw, and then decreased in period IV to below the pre-peak levels (0.012 ± 0.003 ug/g dw). Higher THg concentrations in Darnley and Franklin bays did not translate into higher concentrations of

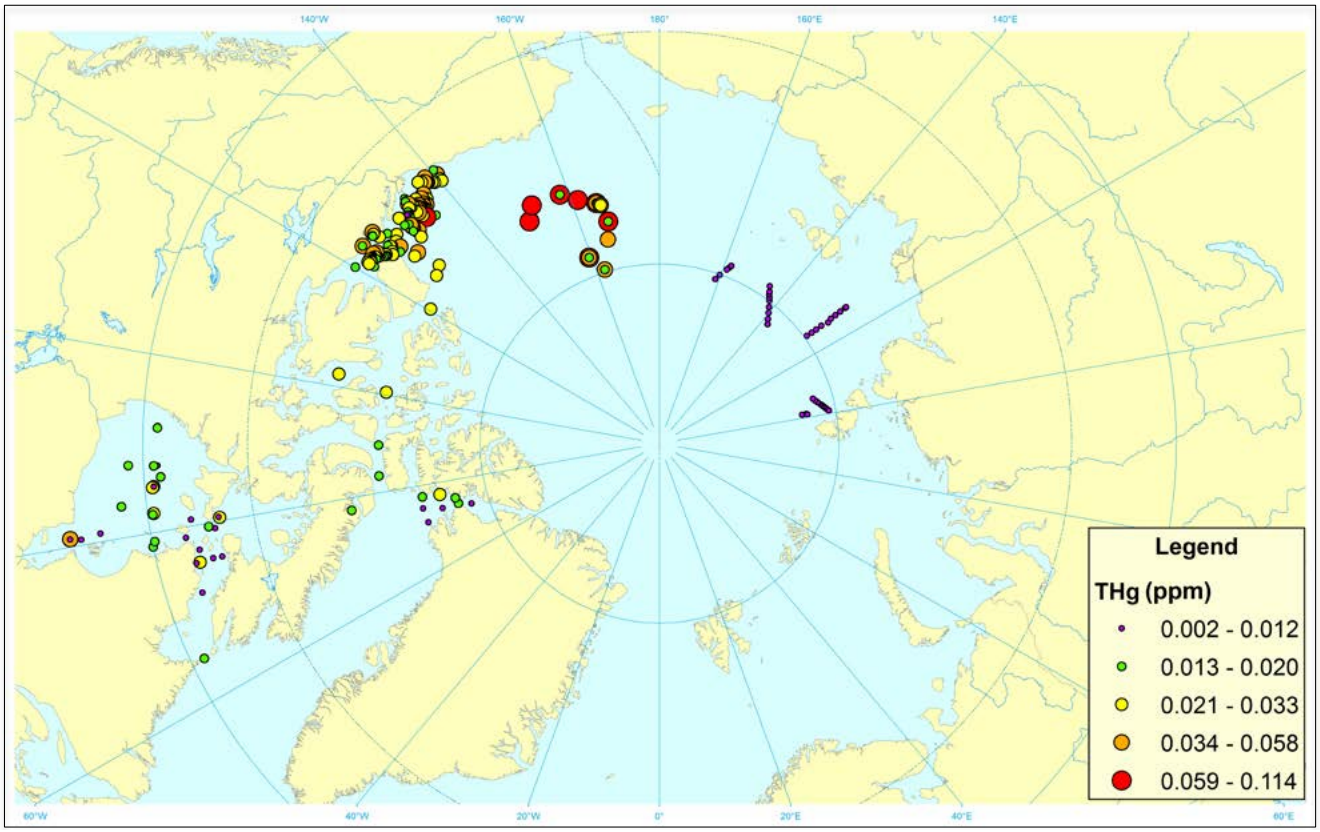

Figure 5. Total mercury concentration (in ppm) in Calanus hyperboreus from across tue Arctic. The highest observed concentrations were from the Beafort Sea and Chukchi Sea.

THg in *C. hyperboreus*. Furthermore, THg trends in *C. hyperboreus* did not reflect THg variability in its diet (pelagic POM). Therefore, it seems likely that the seasonal THg concentration trends in *C. hyperboreus* are controlled by physiological, not environmental, factors especially given that the observed THg concentration patterns defined as periods I – IV can be linked to physiological milestones.

Mean concentrations of THg were 0.024 ± 0.005, 0.056 ± 0.022, and 0.159 ± 0.103 ug/g dw for Chaetognaths, *P. glacialis* and *T. abyssorum*, respectively. In general, the trends in THg in all studied predator zooplankton species closely follow trends described in their prey (*C. hyperboreus)*, suggesting that THg tissue concentration in these TL 3 animals is primarily controlled by that of their prey.

Pan-Arctic Hg in zooplankton: Mercury concentrations ranged from 0.02 µg/g to 0.4 µg/g across all species. Methyl mercury ranged from ~20% to ~100% of the total mercury, dependent upon species. *Calanus hyperboreus*, Themisto spp. and Paraeuchaeta were the most common species. Mercury concentrations were consistently highest across all species in the Chukchi and Beaufort seas (Figure 5), and these generally coincided with the most heavily depleted $\delta^{13}C$, or terrestrial-derived organic carbon.

Climate-driven changes in organic matter-mercury interactions in coastal Arctic lakes: There was a temporary increase of diatoms and algal "S2" carbon during the early-mid 15th century (late Medieval Period associated with a significant ($p<0.01$) increase in "organic-bound" Hg concentrations in sediments (Figure 6). The subsequent decline in

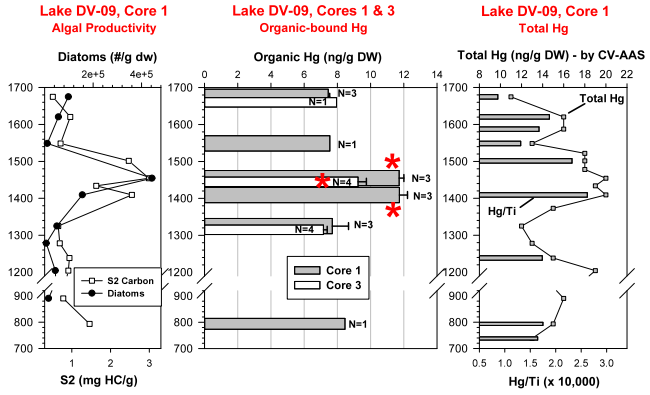

Figure 6. Changes in algal productivity indicators (diatom abundance and "S2" carbon), and the concentrations of organic-bond and total THg in lake DV-09, Devon Island, before, during and after Medieval Warm Period (MWP) in the 15th century. The red stars indicate significant differences (p<0.01) in organic-bond Hg in cores 1 and 3, between the MWP sediments and those deposited during colder periods before and afterwards.

algal productivity after 1500 A.D. coincided with a significant decline in organic-bound Hg. No other Hg fraction showed significant changes. Algal S2 carbon explained 84% of the variance in organic-bound Hg (p<0.001). The changes in organic-bound Hg caused parallel changes in total Hg and Hg normalized against titanium (Hg/Ti), a conservative geogenic element.

BREA studies of mercury and hydrocarbons in Beaufort sediments and biota: Sediment PAH concentrations ranged from below detection limits to ~500 ng/g for various PAH compounds, with alkylated PAHs much more abundant than parent compounds. n-alkanes ranged from below detection limits to 1000 ng/g, with most falling within the C20-C30 range (where C stands for carbon number). Most species analysed had significantly higher Hg concentrations than those found in the sediments. Sediment concentrations ranged from 0.05 to 0.09 ug/g, while those of the benthic invertebrates ranged from 0.1 to 2.2ug/g. Starfish species generally had lower concentrations, while *Sabina septemcarinata* and *Sclerocrangon* ferox had much higher concentrations.

Petrogenic hydrocarbons in Baffin Bay: Establishing baselines and characterizing sources: Concentrations of total PAHs ranged from 2693 ng g^{-1} dw at site 111 at the northern boundary of the NOW, to 341 ng g^{-1} dw at Gibbs Fjord (see Figure 7). Concentrations were below the interim sediment quality guideline (ISQG) values for all samples except one. The concentration of pyrene, a US EPA priority pollutant, exceeded the ISQG in post-1900s, 3-3.5 cm deep sediments at site 111 with a concentration of 188 ng g^{-1} dw compared to the ISQG value of 153 ng g^{-1} dw. Computed odd-to-even preference (OEP), terrigenous/aquatic ratios, and alkane profiles indicated that terrigenous higher plants and marine plankton sources of organic carbon were important at all sites, though terrigenous sources seemed more important at coastal sites and marine sources more important at sites within Baffin Basin. The percentage of total PAH concentrations comprised of the parent compounds, characteristic of combustion sources, ranged from 7 to 21% indicating a similar, low overall influence of combustion sources and a predominance of petrogenic sources of PAHs to the area. This was supported by low values of the standard biomarker ratios of fluoranthene to pyrene and benz[*a*]anthracene to chrysene in almost all samples. Similarly, branched PAH homologues (with one or more carbon substitutions), as opposed to parent (un-substituted) PAHs, consistently were measured at the

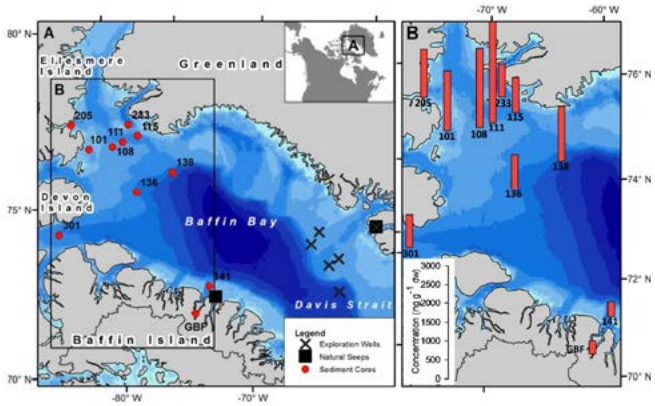

Figure 7. Locations of sediment cores collected from Baffin Bay. Basin watershed map sources: http://geogratis.cgdi.gc.ca/, bathymetrical data (SRTM30 PLUS) sources: http://topex.ecsd.edu/. Greenland ecploration wells locations: http://www.bmp.gl (A). Concentrations of total polycyclic aromatic hudrocarbons (ΣPATHs) in post-1900s sediment (B).

highest concentration at all sites and for all three PAH groups (naphthalenes, phenanthrene/anthracenes and fluoranthenes/pyrenes) investigated, supporting that the main source of PAHs to Baffin Bay sediments are petrogenic.

Characterization of sedimentary organic matter in recent marine sediments from Hudson Bay, Canada, by Rock Eval Pyrolysis: Rock Eval data indicated that a mixture of terrigenous and marine OM exists in modern marine sediment in HB, with the former primarily accumulated along the southern and western coasts, and the latter composing the majority of sediment from the far west, central offshore and north eastern regions. The total amount of OM is low, and may be composed of large amounts of humic substances, with fresher OM only in the northeast near Hudson Strait, and near the Winisk River. High levels of OM oxygen content in the central offshore region are strongly associated with high Mn levels (Figure 8).

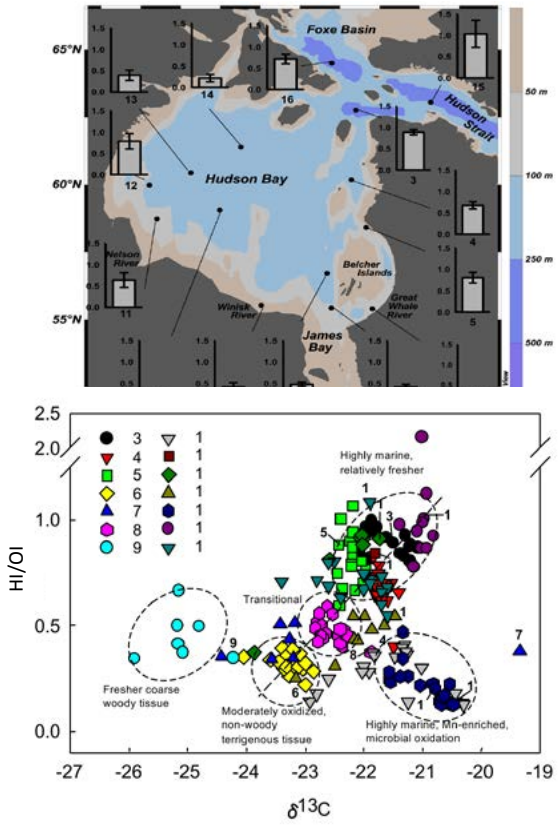

Figure 8. (Top) Location and HI/OI ratios of sediment cores collected in the Hudson Bay system. Numbers refer to the cores described in the text and following figure, bar charts indicate the mean ± stadard deviation of the HI/OI ratios for each cores; (Bottom) HI/OI vs $\delta^{13}C$ in HB sediment. The long-dashed line represents the modeled mixing line between marine and terrigenous OM in HB sediment, while the text in the figure indicates general characteristics of the sediment within groupings enclosed by short-dashed lines. Numbers identify the surface layer of each core.

Importance of Arctic zooplankton seasonal migrations for α-Hexachlorocyclohexane (α-HCH) bioaccumulation dynamics: Concentration of α-HCH in *C. hyperboreus* was significantly higher in summer than in winter (2-3 times, Figure 9); that is 27.1 ± 8.0 (SD) ng/g lipid versus 14.3 ± 6.8 (SD) ng/g lipid (two-sample t-test, CI = 95%, $p<0.001$), or 3.3 ± 1.2 (SD) ng/g ww versus 1.2 ± 0.5 (SD) ng/g ww (two-sample t-test, CI = 95%, $p<0.001$) on lipid basis and ww basis, respectively. LogBAF in environmental samples from the summer (4.4; intense feeding) did not exceed the logBCF estimated at the end of culture (4.5-4.6), confirming that *C. hyperboreus* accumulates α-HCH primarily through diffusion via body membranes, and BCF and BAF can be used interchangeably.

α-HCH concentration in *C. hyperboreus* increased linearly throughout the culturing experiment when expressed in lipid normalized units; however, it

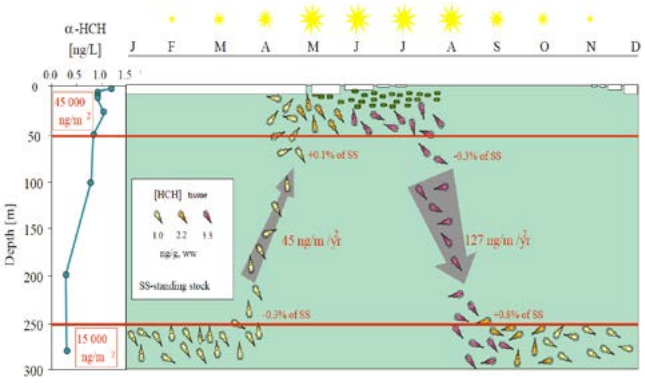

Figure 9. Conceptual shamatic of the influence of C. hyperboreus seasonal migration on α-HCH tissue concentration and cycling in the water column along with α-HCH concentration vertical profile in the water.

reached a plateau after about 4 weeks suggesting a steady state when presented on the wet weight basis. Measured logBAF in *C. hyperboreus* was slightly above the theoretical equilibrium partitioning value (logBAFT) of 4.5 in environmental samples from winter (4.6) and slightly below equilibrium in samples from summer (4.4). Ascent of *C. hyperboreus* from depths to the surface layer of the ocean would significantly decrease apparent logBCF (~3.9) due to migration to the relatively HCH-rich surface waters.

C. hyperboreus samples from the summer had significantly higher α-HCH EF than those from the winter (0.458 ± 0.024 (SD) compared to 0.310 ± 0.029 (SD); two-sample t-test, CI = 95%, $p<0.001$). The α-HCH chiral signature in zooplankton reflects surface-water versus deep-water dwelling as seawater α-HCH EFs were measured at ~0.45 in the top 50 m of the water column and at ~0.15-0.30 below 150 m in the study region in 2007/2008.

Organophosphate ester flame retardants and plasticizers (OPEs) in the Arctic environment: In the previous study funded by the Northern Contaminants Program (NCP) and ArcticNet, we identified and determined for the first time in the Canadian arctic, concentrations of OPEs in air during the summer of 2010 and fall of 2011. Additionally, air samples from the Alert monitoring station from 2008/2009/2012, archived air samples form ArcticNet 2007-2008 and air samples from Resolute Bay 2012 were all analyzed for OPEs. This provides baseline concentrators for OPEs in which future trends can be gauged. Such temporal information is vital in determining whether a new chemical is a candidate for national and international regulations. OPEs identified in arctic air were: tris-chloroethyl phosphate (TCEP), tris-chloropropyl phosphate (TCPP), triphenyl phosphate (TPhP) and tris-dichloropropyl phosphate (TDCPP). TCEP had the highest concentration found, followed by TCPP, TPhP and the lowest is TDCPP. The levels of OPEs are much higher than the sum of PBDEs (Figure 10).

OPEs were also sought in water and zooplankton samples taken in 2011 as a part of an earlier NCP

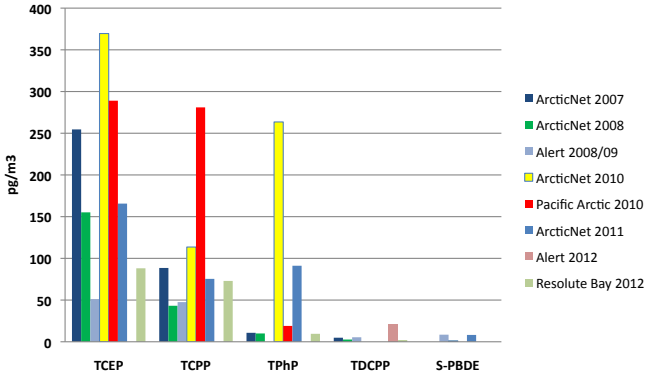

Figure 10. Average concentration of OPEs in the Canadian Arctic air, 2007-2012. ArcticNet 2007: shipboard August in the Labrador Sea and Hudson Bay areas; ArcticNet 2008: shipboard Beaufort Sea in May-June; Alert 2008-2009: land based December 2008 to August 2009 (blank problem for TPhP); Pacific Arctic 2010: ship based Bering-Chukchi-Beaufort seas summer of 2010 is from Moller et al., 2012; ArcticNet 2011: shipboard central and east archipelago; Alert 2012: land based February to August 2012 (only TDCPP has been quantified) and Resolute Bay: land based July 2012. Compared to the sum-PBDEs in Greenland, Ny Alesund and the Alert monitoring station (see Xiao et al., 2012 for references).

project and ArcticNet. Concentration of OPEs in arctic ocean water is up to 1 ng/L, where TCEP>TCPP>TPhP>TDCPP. OPE compounds found in zooplankton samples were on average TCEP~TPhP>TCPP~ethyl-hexyl diphenyl phosphate (EHDPP)>TDCPP. EHDPP was only recently added to the OPE analysis; archived arctic water and air will be screened and quantified for in the future. The presence of EHDPP in the arctic is not surprising since it is abundant in household dust and indoor air (Shoeib et al., 2013 and Jantunen unpublished data).

IRIS 1- western and central high Arctic: A Kitikmeot sub-committee was established. The sub-committee members' tasks include participating in scheduled meetings (mostly teleconferences), reviewing chapters and providing feedback on Kitikmeot-related content or gaps, assisting to fill in said gaps where possible, and provide feedback for suggestions regarding key recommendations to come out of the assessment for the Science to Policy Synthesis.

The 2nd draft of the RIA, including all chapters and Regional Climate Model projections for 2050, was completed. Furthermore, the preliminary findings of the chapters were presented at the ArcticNet ASM in Halifax. This exercise was coordinated as an effort to help lead authors (the presenters) learn of the material presented in the other chapters (assisting with later cross-referencing) and to deliver preliminary findings to the audience, which included representatives from the ISR and Kitikmeot region.

Discussion

Organic mercury species in the Arctic Ocean/Hg isotope ratios in arctic environments: The observed differences in Hg levels in pre-concentrated water samples could be caused by contamination on board during sample processing or Hg was lost to container walls during storage in large glass containers. This discrepancy must be resolved, before Hg isotope ratio measurements can commence in future campaigns. The core from station 108 is characterized by very fluffy, silty material, which is likely glacial silt, and naturally low in Hg. Generally, THg is as expected, elevated at the top, reflecting recent anthropogenic increases of global Hg in the atmosphere. Sub-surface peaks suggest that levels decreased somewhat over the last decade (dating of cores is planned, but still pending). MMHg is generally elevated that the top of cores, which has presumably the layer of highest bacterial activity generating highest MMHg.

Mercury uptake within an ice algal community during the spring bloom in first-year Arctic sea ice: As protist counts started to increase and contribute significantly to the particulate matter biomass in the bottom 10 cm of ice cores, PTHg became less variable with a decreasing trend as a function of bloom progression. The strong and significant decreasing trend of THgcell (Figure 2a) with time is most likely attributed to biomass dilution (Chen and Folt, 2005). This suggests that there is a finite amount of Hg available within the ice-core sections curtailing the uptake by the protist community.

Brine and seawater are both sources of Hg to the ice algal community. Even though levels of Hg in seawater were relatively low compared to PTHg and PTHg(PB), it probably acted as a more continuous source where turbulence would allow for the supply to remain relatively constant over time as opposed to brine. The brine volume fraction of the bottom 10 cm of sea-ice cores ranged from 5.9 to 22.3% and so was always above the critical threshold of 5% when brine can migrate vertically within the ice allowing convective mixing with seawater below (Golden et al., 1998). This suggests that there is a finite amount of Hg available within the ice-core sections curtailing the uptake by the protist community.

Once incorporated into the algal biomass, mercury can be transported spatially and trophically within the Arctic ecosystem via release of algae from melting ice, its subsequent resuspension in the water column where they constitute a readily available food source for zooplankton species (~65%), or their sedimentation to the bottom of the ocean (~35%) (Michel et al., 1996). Mercury bound in the algae-derived sinking sediments can then be grazed upon, remineralized to supply Hg(II) for uptake and methylation deeper in the water column (Wang et al., 2012), or sequestered into the ocean sediments where it can undergo bacterial methylation (King et al., 2000). In each case this could lead to increased exposure of pelagic and benthic marine species to inorganic mercury and methylmercury.

Transformation of mercury at the bottom of the Arctic food web: an overlooked puzzle in the mercury exposure narrative: Recently, it has been proposed that the vulnerability of the Arctic to Hg toxicity may derive more from internal processes, particularly those associated with methylation, than from processes associated with transport and deposition. Here, we hypothesize that the lowest trophic levels (1-3) of Arctic marine food webs, almost completely neglected in research on mercury biomagnification, could present a crucial point of mercury transformation, by shifting the balance of THg toward MMHg. Mechanisms of

Hg transformation by *C. hyperboreus* have yet to be determined. Here, we simply address plausible explanations for the observed phenomenon. MMHg in *C. hyperboreus* could derive from two potential sources of exposure: exchange with ambient seawater and uptake through ingestion of pelagic POM. Annual dietary uptake of MMHg per single individual of *C. hyperboreus* was estimated at $<6.6 \times 10^{-6}$ ug, which would supply only about 30% of the body burden of MMHg in a single individual estimated at 21.0×10^{-6} ug. Thus, another source (or sources) of MMHg in addition to the direct dietary uptake is required to sustain the amount of organic Hg found in this species. The most obvious mechanism to produce higher concentrations of MMHg would be for the methylation process to occur within *C. hyperboreus* itself. Very recently, the guts of *C. hyperboreus* and *C. glacialis* have been proposed as biogeochemical "hotspots" where acidic and suboxic/anoxic conditions might support iron dissolution and anaerobic microbial activities (Tang et al., 2011).

These conditions promote mercury methylation by iron-reducing anaerobic bacteria. If correct, the hypothesis that herbivorous copepods provide a seasonally-active, widely distributed source of MMHg implies that this trophic level is crucial to understanding seasonal and spatial variation in higher levels of the food web, and potentially why there are sustained differences between regions as observed in the Arctic.

Pan-Arctic Hg in zooplankton: In species present across the Arctic in numbers sufficient for trend analysis, mercury concentrations were consistently highest in the Beaufort and Chukchi seas. The stable isotope signatures of these samples were also different from the other regions, showing a higher terrestrial influence (i.e., from rivers). The mercury levels seen in zooplankton mirror trends observed in polar bears across Canada, indicating that the processes governing bioaccumulation and biomagnification are present throughout the foodweb. Future work establishing how a stronger terrestrial influence affects mercury bioaccumulation and biomagnification in marine foodwebs across the Arctic is thus warranted.

Climate-driven changes in organic matter-mercury interactions in coastal Arctic lakes: The increase in algal productivity indicators in the 15th century may be associated with the Medieval Warm Period, although this is thought to have occurred one to two centuries earlier elsewhere in the Arctic. However, for our purposes the key finding is evidence of significant changes in Hg speciation associated with fluctuations of algal productivity throughout the Medieval Period. Importantly, when algal productivity declined after 1500 A.D., organic-bound Hg also declined. These changes drove changes in total sediment Hg, in fact organic Hg explained 94% of the variance in total Hg in this lake prior to 1700 AD. Thus, significant changes in total Hg occurred in the pre-industrial period (when anthropogenic Hg was absent) as a result solely of natural limnological responses to climate warming and cooling. We are evaluating the impact that warming during the 20th century may have had on organic and total Hg levels in this and other Arctic lakes.

BREA studies of mercury and hydrocarbons in Beaufort sediments and biota: Sediments showed a highly petrogenic PAH signature, indicating a predominance of peat, coal and oil-derived hydrocarbons relative to combustion-derived hydrocarbons (Figure 11). A slight influence of forest fire hydrocarbons was observed in sediments closer to shore. n-alkane data showed a predominance of terrestrial plant material, indicating a strong influence from the Mackenzie River. Both sediment and benthic invertebrate Hg oncentrations increased with distance offshore (Figure 12). Forthcoming stable isotope ($\delta^{13}C$, $\delta^{15}N$) data will allow us to better understand the dynamics governing the observed trends in Hg concentrations across the Hg species.

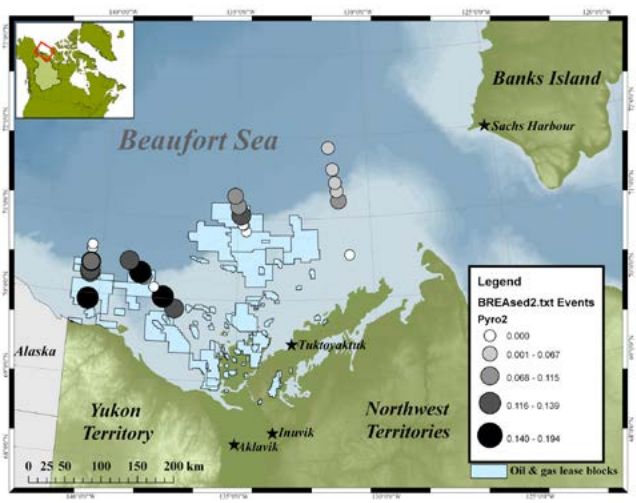

Figure 11. Map of PAH pyrogenic index from surface sediments showing strong petrogenic influence at all sites. However, there is some influence from pyrogenic compounds due to forest fires in the three westernmost transects (darker shades of gray) and closer to shore. N.B. The pyrogenic index is from Wang et al. (1999), wich is derived from ration of 12 parent PAH to 5 different PAH and their repective methilated analogues. For reference, diesel soot has a pyrogenic index of 1.6, and values bellow 0.5 are considered petrogenic.

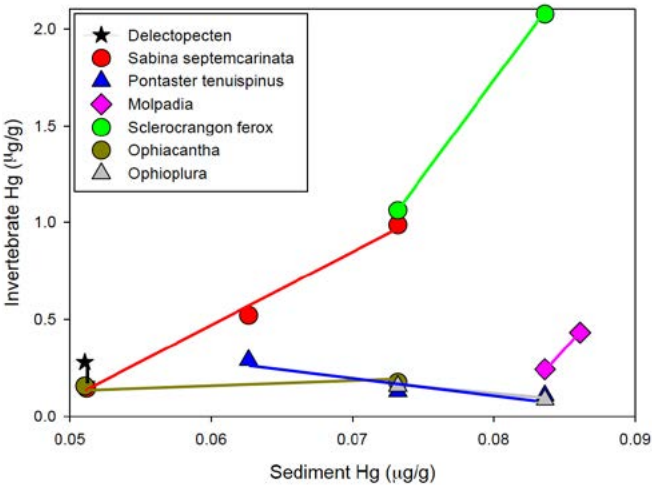

Figure 12. Plot of concentration of mercury in sediment vs. concentration of mercury in benthic invertebrates from the TBS transect, 2012 BREA collection. Various rates of biomagnification from the sediment are observed for different species, with Sclerocrangon ferox showing the highest rate (green circles).

Petrogenic hydrocarbons in Baffin Bay: Establishing baselines and characterizing sources: This dataset of HC concentrations in Baffin Bay sediments serves to initiate a baseline record in Baffin Bay sediments at these 11 sites. The present and historic concentrations of PAHs were not found to be at concentrations of concern for marine aquatic life, with one exception noted at site 111 (of seven samples). Hydrocarbon biomarkers, including alkane profiles, OEP, and TAR (terrigenous/aquatic ratio) values, indicated that organic carbon in these sites is derived from both terrigenous higher plants and marine algae, the former being of greater significance at coastal sites, and the latter to the deepest sites at the lower boundary of the NOW. Petrogenic sources, as opposed to combustion, were found to be the dominant source of PAHs to Baffin Bay sediments. Site 111 is an area that requires additional study, with high concentrations of petrogenic PAHs, among the lowest OEP C29 and TAR values, and a clear UCM (unresolved complex mixture), suggesting the presence of thermally mature hydrocarbons and possibly a nearby source of petrogenic hydrocarbons such as a seep. The upper boundary of the NOW is a region of ecological importance and further research is required to establish baseline concentrations and sources of hydrocarbons in this region.

Characterization of sedimentary organic matter in recent marine sediments from Hudson Bay, Canada, by Rock Eval Pyrolysis: The distribution of marine and terrigenous OM according to the Rock Eval analysis is consistent with known sources of marine and terrestrial OM to HB, and with a highly degraded nature of OM, attributable to substantial sediment recycling along the southern coast. However, OM in sediment far offshore cannot be conclusively identified based on Rock Eval pyrolysis alone. High Mn concentrations in offshore sediment appear to contribute to a high OM oxidation signal, which is indicative of either highly oxidized marine OM or terrigenous OM. Based on elemental and biomarker data, highly oxidized OM of marine origin exists in sediment from this region.

Importance of Arctic zooplankton seasonal migrations for α-Hexachlorocyclohexane (α-HCH) bioaccumulation dynamics: Seasonal migration of copepods causes a major biomass translocation between depth and surface, resulting in a significant active downward transport of carbon. We hypothesize that zooplankton actively transfer α-HCH through bioaccumulation at the surface and release at depth via exchange with the water. This annual process has the potential to affect the α-HCH vertical distribution in the water column (Figure 9). Zooplankton biomass in the Beaufort Sea and the Amundsen Gulf region ranges from 7.5 g/m^2, ww, on the Mackenzie shelf to 55 ± 29 g/m^2, ww, in the polynya region adjacent to our sampling locations. Based on the biomass in our study region, we calculated that migrating zooplankters could actively transfer a net amount (total flux associated with descent minus total flux associated with ascent) of ~82 ng of α-HCH under an area of 1 m^2. Compared to the standing stock of α-HCH in the surface and bottom 50 m present under an area of 1 m^2 in the region (45000 and 15000 ng, respectively), the α-HCH net amount zooplankton could transfer annually would account for 0.2 and 0.5% of the stock, respectively. Active transfer of a-HCH by zooplankton seasonal migration can be perceived as an output route of this contaminant from the surface layers of the Arctic Ocean, and its magnitude is comparable to the one estimated for the ice export (~1% of the standing stock in the top 200 m), but significantly smaller than output estimates by water outflow (~49%), degradation (~43%) or volatilization (~7%) (Li et al., 2002).

Organophosphate Ester Flame Retardants and Plasticizers (OPEs) in the Arctic Environment: Levels of OPEs at Alert are lower than levels found during ArcticNet 2010/11 because the data from Alert is an annual average where POPs levels generally have a seasonal cycle. Additionally, there were some blank issues with Alert samples so these are very conservative numbers. OPEs in the same range have been seen in the North Sea (Möller et al., 2012) and the Bering and Chukchi Seas (Möller et al., 2011). Levels found in arctic air are lower than those over lakes Superior and Erie (Jantunen et al., 2012) and much lower than in urban air in Toronto and at a sewage treatment plant in southern Ontario (Shoeib et al., 2013). Sum-PBDEs in these southern locations show the same trend as in the arctic with levels of individual OPEs 10-100 times higher than the sum-PBDE.

IRIS 1- western and central high Arctic: With the completion of the 2nd, full draft of the IRIS 1 RIA, the lead authors, IRIS 1 steering committee members and Kitikmeot sub-committee members have been tasked with reviewing the document until March-April 2014, with specific tasks assigned to each of the three groups. Once the review is complete and most gaps are filled (where possible), an in-person meeting will be coordinated with the steering committees to develop a Science to Policy document. The outlook for publication is September 2014.

Conclusion

Transport and transformation of mercury across the ocean-sea ice-atmosphere (OSA) interface:

- The alkaline nature of surface sea ice calls for a revisit of how sea ice participates in mercury depletion events. Efforts are being directed to cryospheric behavior of halogens.
- The reason for considerable amount of methylmercury in multi-year sea ice remains unknown. We do not have evidence to support the occurrence of mercury methylation in multi-year ice. The methylmercury is likely transported from the underlying seawater or from overlying snow.
- The process responsible for subsurface seawater methylmercury peak remains unknown. Process-oriented studies are being planned for 2014.

Mercury uptake within an ice algal community during the spring bloom in first-year Arctic sea ice:

- As cell counts increased Hg in cells decreased: this is attributed to biodilution.
- Both brine and seawater are sources of Hg to bottom ice algae. Seawater is a constant low concentration source, while brine is a finite but highly concentrated source.
- Algae is the first step at which dietary contaminants are introduced into the marine food web via grazing, remineralization, or resuspension.

Transformation of mercury at the bottom of the Arctic food web: an overlooked puzzle in the mercury exposure narrative:

- We show that *C. hyperboreus* plays a hitherto unrecognized central role in mercury transformation while, itself, not manifesting inordinately high levels of THg compared to its prey (pelagic POM).
- *C. hyperboreus* shifts Hg from mainly inorganic forms in pelagic POM (>99.5%) or ambient seawater (>90%) to primarily organic forms (>50%) in their tissue.
- We calculate that annual dietary intake of MMeHg could supply only ~30% of the MMHg body burden in *C. hyperboreus* and, thus, transformation within the species, perhaps mediated by gut microbial communities, or bioconcentration from ambient seawater likely play overriding roles.
- Seasonal THg trends in *C. hyperboreus* are variable and controlled by species-specific physiology, e.g. egg laying and grazing.
- Zooplankton that predate on species such as *C. hyperboreus* provide a further biomagnification of MMHg and reflect seasonal trends observed in their prey.

Pan-Arctic Hg in zooplankton:

- Mercury concentrations in zooplankton were consistently highest in the Beaufort and Chukchi Seas, indicating a regional hotspot.
- These regions also showed the most pronounced terrestrial signal of $\delta^{13}C$, indicating some influence from rivers on mercury bioaccumulation and biomagnification.

Climate-driven changes in organic matter-mercury interactions in coastal Arctic lakes:

- These findings strongly support the algal scavenging hypothesis, because they show that changes in Hg speciation in sediments, specifically in the amount of organic-associated Hg, occurred as a result of changes in algal productivity. These changes in turn controlled variations in total Hg concentrations.

BREA studies of mercury and hydrocarbons in Beaufort sediments and biota:

- There is a distinct petrogenic signal to the sediments, while also showing a predominantly terrestrial signal. This shows that peat and coal (mainly near the confluence of the Great Bear and Mackenzie rivers) are the main sources of hydrocarbons, with the influence felt far offshore. This also indicates that any future spills or leaks (drilling platforms, maritime traffic) should be easily distinguishable from background hydrocarbon sources, making legal and financial penalties more readily applicable.
- For most species, there is a distinct trend of increasing mercury concentration with increasing distance offshore coincident with trends in sediment. It is also clear that virtually every species analysed exhibited some degree of biomagnification relative to the concentration observed in the sediments, with the largest being observed in *Sclerocrangon ferox*. Interestingly, two species of starfish exhibited negative trends in mercury concentration with distance offshore.

Forthcoming stable isotope analyses will allow for a better understanding of the drivers affecting these concentrations.

Petrogenic hydrocarbons in Baffin Bay: Establishing baselines and characterizing sources:

- Concentrations of PAHs in the sediments of Baffin Bay do not exceed thresholds for sediment quality.
- Petrogenic sources of PAHs are predominant in present day surficial sediments.
- Baffin Bay sediments are dependent on both terrigenous and marine-based organic matter.

Characterization of sedimentary organic matter in recent marine sediments from Hudson Bay, Canada, by Rock Eval Pyrolysis:

- Interpretations of the nature of sedimentary OM based on Rock Eval pyrolysis were consistent with the widely accepted oligotrophic nature of HB, with known sources of marine and terrestrial OM, and with the strong occurrence of sediment recycling along the southern coast.
- High Mn concentrations in the offshore region influenced the oxidation signal and rendered the Rock Eval interpretations ambiguous. This scenario was resolved by examining $\delta^{13}C$ and biomarker data, which identified highly oxidized marine OM as the predominant organic material in these sediments.

Importance of Arctic zooplankton seasonal migrations for α-Hexachlorocyclohexane (α-HCH) bioaccumulation dynamics:

- Concentration of α-HCH was 2-3 times higher in individuals from the summer than from the winter.
- An example of 'differentiated' processes is atmospheric loading of contaminants to melt ponds over the summer, and their subsequent leakage to the ocean.
- LogBAF from the summer (feeding period) does not exceed logBCF (bioconcentration factor) from the culturing experiment (no feeding), suggesting that α-HCH concentration in *C. hyperboreus* is maintained through equilibration rather than feeding.
- After the spring ascent from deep waters, *C. hyperboreus* approach equilibrium partitioning with the higher surface-water concentrations of α-HCH within 3-4 weeks with about 60% of bioconcentration taking place in the first week.
- The *C. hyperboreus* α-HCH chiral signature reflects ambient seawater, and can therefore be used as a determinant of residence depth.

Organophosphate Ester Flame Retardants and Plasticizers (OPEs) in the Arctic Environment:

- Although transport and fate models predict the OPEs will not be long range atmospherically transported to the arctic, our study and another study by Moller et al. (2012) found OPEs in the arctic atmosphere.
- Models used to predict the atmospheric half-life of OPEs only uses gas phase OPEs where we found OPEs are only found in the particle phase.
- When sorbed to particles, OPEs have much longer life-time in air.

IRIS 1- western and central high Arctic:

- The development of the IRIS 1 RIA is well on track and should be published before the 2014 ArcticNet ASM.

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Transport and transformation of mercury across the ocean-sea ice-atmosphere (OSA) interface:

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Publications

(All ArcticNet refereed publications are available on the ASTIS website (http://www.aina.ucalgary.ca/arcticnet/).

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