1.2 Effects of Climate Change on Contaminant Cycling in the Coastal and Marine Ecosystems (Contaminants)

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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 & LOMA, respectively) such as zone 1(a)s in the Beaufort Sea.

KEY MESSAGES

Ringed seal organic contaminant trends in relation to sea ice break-up:

- Highly lipophilic organic contaminant concentrations in male ringed seals at Ulukhaktok, NT, increased in years with early sea ice break-up during 1993-2008.

Holocene primary productivity and mercury dynamics trends in Baffin Bay:

- Increases in algal productivity in the Northwater Polynya over the past few centuries have been substantial, as predicted. A significant increase in the proportion of marine versus terrestrial-sourced organic matter occurred in ice-margin sites south of the NOW, but surprisingly not in the NOW itself which continues to be dominated by marine OM.

Standardisation of Rock-Eval Analysis for recent sediments and soils/permafrost:

- We have standardised a rapid, inexpensive method for characterising components of organic matter in sediments and soils/permafrost.

Influence of the Mackenzie River on Beaufort Sea mercury biogeochemical cycling:

- Updated fluxes of mercury (Hg) from the Mackenzie River to the Beaufort Sea of ~4.3 t/yr.
- Largest source of mercury to the Beaudort Sea is from sulfide weathering (~78% of total flux), followed by erosion of coal outcrops (~10%), atmospheric deposition (~6%) and bound to algal matter (~5%).

α-HCH enantiomer fraction (EF) – a novel approach to calculate the ventilation age of water in the Arctic Ocean:

- α-HCH enantiomer fraction (α-HCH EF), and possibly EFs of other chiral substances, can provide a relatively simple way to determine the ventilation age of water in the Arctic Ocean with the assumption of known and relatively constant degradation rates.

Mechanism and biological implication of organic contaminant enrichment in melt pond water on the Arctic sea ice:

- Atmospheric deposition of organic contaminants to the melt pond water over the summer can lead

to contaminant enrichment in the ice that survived at least one melt season (old ice).

- Atmospheric deposition could potentially lead to highly increased levels of some of the current use pesticides (CUPs) in the melt pond water (e.g. endosulfan II, chlorothalonil), posing a great risk for elevated exposures to ice-associated and pelagic algal communities and fauna in the process of melt water drainage.

Dinoflagellate cysts as environmental indicators in the Hudson Bay system:

- The distribution and production of dinoflagellate cyst species in different domains of Hudson Bay are set apart by freshwater inputs, nutrient availability and the length of the open water season. The importance of prey availability is highlighted in Hudson Strait. The distinct environmental niches warrant the use of dinoflagellate cysts to infer past changes in the system.

Modelling the mercury cycle in the Beaufort Sea using a carbon flux model approach:

- A dynamic water column mercury speciation and fate model and a carbon cycling model for the Beaufort Sea were combined, yielding a model to climate sensitive drivers. Initial model results are in good agreement with Hg concentrations in seawater and zooplankton measured previously in the same area. Results from preliminary modeling scenarios suggest that an earlier breakup of sea ice will not significantly alter Hg concentrations in plankton, while a 50% increase in nutrient availability will only marginally decrease Hg concentrations in plankton.

Progress on understanding biogeochemical cycles and organic carbon sources and inputs in Hudson Bay:

- The organic carbon cycle in the Hudson Bay region is greatly influenced by the inputs of terrigenous materials from Arctic rivers. With Arctic warming, there is the potential for increased release of soil organic carbon (SOC) from permafrost soils resulting in both dissolved and particulate OC entering and effecting the Hudson Bay organic carbon cycle. By further understanding the hydrological implications of permafrost degradation on biogeochemical processes, we can better predict changes to the permafrost regimes and organic carbon cycle associated with future climate fluctuations.

Zooplankton as biomonitors of mercury in Hudson Bay:

- A database of mercury concentrations in zooplankton collected on ArcticNet cruises between 2003 and 2010 from across the Hudson's Bay, Hudson's Strait, and Foxe. The database includes: total mercury concentrations (THg), methyl mercury concentrations (MeHg), stable isotopes ($\delta^{15}N$ and $\delta^{13}C$), and the genus/species identification of the zooplankton samples. Marine water concentrations of THg and MeHg were also determined in 2010. This is valuable, unpublished monitoring data and we are analyzing it to assess: the novel application of zooplankton as biomonitors of marine mercury, trophic transfer of mercury in organisms at the base of the food web (an understudied topic), and regional differences in mercury distribution across Hudson's Bay.

Organic Hg species in Arctic air:

- For the first time, we present here data concentrations of organic mercury species, namely monomethylmercury (MMHg) and dimethylmercury (DMHg) in the Arctic lower atmosphere. The Hudson Bay airshed is dominated by MMHg, while concentrations of DMHg are highest in the high Arctic. This supports the possibility that organic mercury species are volatilized from the ocean and contribute to MMHg bioaccumulating in the arctic ecosystem.

Air-surface exchange of persistent organic pollutants in the Canadian Arctic:

- Concentration of the legacy organochlorine pesticides (OCPs) hexachlorocyclohexanes and chlordanes have declined in Canadian Archipelago surface water between 1999-2010, while dieldrin and the current use pesticides (CUPs) dacthal, chlorothalonil, endosulfan, chlorpyrifos and trifluralin have remained stable or increased over the same time period.
- Gas exchange assessments of CUPs indicate net deposition into the Arctic Ocean, where legacy OCPs have generally reached equilibrium or are volatilizing.
- The widespread distribution of perfluorinated compounds (PFCs) in the Canadian Arctic atmosphere shows their potential for long-range atmospheric transport to remote regions. The fluorotelomer alcohols (FTOHs) were the dominant PFCs in the atmosphere in 2007 and 2008.

Arctic contaminants - Determining effective and appropriate communicative means between Inuvialuit communities and researchers:

- The process of communicating contaminants research to Inuvialuit communities requires a collaborative and community-centred focus.
- While locals view northern scientific research to be important, comprehension of contaminants is variable and complex; explanations and interpretations from both science and personal experiences contribute to their understandings of contaminants and causes for concern.
- If important contaminants information is to be viewed as valuable and thus remembered, communicating contaminants research needs to be explored from a community perspective that addresses the message in ways that are applicable and relevant to the daily lives of Inuvialuit.

Mercury and methylmercury in multi-year ice cores :

- Following up on our earlier study on total mercury distribution in sea ice, multi-year ice cores were taken in August 2011 from the Beaufort Sea area and analyzed for total mercury, methylmercury, and oxygen-18 isotope ratios. The total mercury profile agrees well with our earlier study on a multi-year ice core, confirming the presence of periodic signals. Data for methylmercury and isotopes are being analyzed.

Mercury and selenium speciation in beluga whales:

- Toward a better understanding of the metabolic and toxicological implications of high levels of methylmercury in beluga whales, we completed the first analysis on the molecular forms of methylmercury in the muscle, brain, liver, and kidneys of 10 beluga whales from the western Canadian Arctic. In all tissues analyzed, methylmercury was found to be dominated by methylmercuric cysteinate, a specific form of MeHg believed to be able to transport across the blood–brain barrier. Another thiol complex, methylmercuric glutathionate, was also detected in the muscle and, to a much lesser extent, in the liver and brain tissues. Furthermore, a profound inorganic Hg peak was detected in the liver and brain tissues, which showed the same retention time as a selenium (Se) peak, suggesting the presence of an Hg–Se complex, most likely an inorganic Hg complex with a selenoamino acid. These results provide the first analytical support that the binding of MeHg with glutathione and Se may have protected beluga whales from the toxic effect of high concentrations of MeHg in their body.

Mercury chemistry in sea ice:

- With the recent completion of the construction of the Sea-ice Environmental Research Facility (SERF) at the University of Manitoba, experi-

ments are being carried out to study the fundamental transport and transformation process of mercury, among many other chemicals, across the seawater - ice - air interface under semi-controlled conditions. This is Year 1 of the SERF experiment which will continue on until the melting of the sea ice in March 2012.

OBJECTIVES

Ringed seal organic contaminant trends in relation to sea ice break-up:

- To determine the variation in contaminant concentrations in marine mammals both in relation to interannual trends and with indicators of climate change.

Holocene primary productivity and mercury dynamics trends in Baffin Bay:

- To determine the history of organic matter source, production and benthic flux around the Northwater Polynya (NOW), and the effect of OM on sedimentary mercury flux during the late Holocene.

Standardisation of Rock-Eval Analysis for recent sediments and soils/permafrost:

- To standardise a method for determining the type and quantity of organic matter in sediments and soils/permafrost and to relate these data to ecological and chemical parameters (e.g., diatom counts, algal assemblages, chemistry of components) using standardised/pure compounds and biological standards.

Influence of the Mackenzie River on Beaufort Sea mercury biogeochemical cycling:

- To identify and quantify the sources and fluxes of Hg in the Mackenzie River Basin as it empties into the Beaufort Sea and estimate the potential bioavailability of mercury from each source.

α-HCH enantiomer fraction (EF) – a novel approach to calculate the ventilation age of water in the Arctic Ocean:

- Here, we ask the question of whether or not the enantiomeric composition of α-HCH could also provide a clock for ventilation time scales. Using reasonably well determined kinetic rates for α-HCH degradation in the eastern Arctic sea water (Harner et al. 1999), and assuming that deep water masses in the Arctic Ocean are approximately isothermal (~0 ± 2 °C), we estimate apparent ventilation ages as a function of water depth in the southwest Canada Basin based on vertical profiles of α-HCH EF. Further, we determine the PL and AL core depths and calculate their α-HCH EF age. Precision, accuracy and advantages or disadvantages of the α-HCH EF tracer age estimate relative to other tracers are discussed.

Mechanism and biological implication of organic contaminant enrichment in melt pond water on the Arctic sea ice:

- We show how atmospheric deposition of organic contaminants over the summer could potentially lead to increased levels in old ice and melt pond water, resulting in higher exposures to ice-associated and pelagic algal communities and fauna. The mechanism is described using α-HCH as an example, and then translated to other organochlorine pesticides (OCPs) and CUPs.

Dinoflagellate cysts as environmental indicators in the Hudson Bay system:

- To determine the key controls on cyst species distribution and production in order to apply them as environmental tracers of the past.

Modelling the mercury cycle in the Beaufort Sea using a carbon flux model approach:

- The overall objective of this study is to improve our understanding of factors affecting the fate and

bioavailability of mercury species (total mercury (THg) and methylmercury (MeHg)) in Arctic marine ecosystems. This will be accomplished by: Developing and calibrating a comprehensive mercury fate model for the marine ecosystem that links mercury inputs from the atmosphere to uptake in marine foodwebs;

- Using the model to improve our understanding of how changing climate regimes will affect the fate, cycling and bioavailability of mercury in the Arctic marine ecosystem; and
- Using the model to identify data gaps that can then be addressed by further field sampling. One such example involves measuring the partitioning of mercury species between water and suspended particles in the water column of the Beaufort Sea.

Progress on understanding biogeochemical cycles and organic carbon sources and Inputs in Hudson Bay:

- To develop an understanding of the organic carbon cycle (sources, sinks, processes) in Hudson Bay and its sensitivity to recent change occurring in the ocean and adjacent terrestrial watersheds. To understand the implications of permafrost degradation, SOC transport, and hydrological changes to the landscape on the organic carbon cycle of the Hudson Bay. To understand the role of lignin biomarkers in determining the role of terrigenous sources such as permafrost entering the Hudson Bay organic carbon cycle.

Zooplankton as biomonitors of mercury in Hudson Bay:

- Assess the distribution and fate of mercury in Arctic waters from Hudson's Bay.
- Identify which parameters (if any) influence mercury concentrations in marine waters, e.g., temporal, spatial, thermal, oceanic currents, etc.
- Assess the trophic transfer of mercury in zooplankton to predators (including other zooplankton).
- Assess the utility and feasibility of zooplankton as biological monitors of mercury contamination in Arctic marine waters.

Organic Hg species in Arctic air:

- To develop an analytical method to measure MMHg and DMHg in the Arctic lower atmosphere.
- Establish presence of organic Hg species in Arctic air and quantify individual concentrations.

Air-Surface exchange of persistent organic pollutants in the Canadian Arctic:

- Investigate occurrence and air water gas exchange of organochlorine pesticides (OCPs), current-use pesticides (CUPs), perfluorinated compounds (PFCs) and organophosphate compounds (OPCs) in air, water, phytoplankton and zooplankton of the Canadian Arctic.
- Speciate atmospheric PFCs according to their partitioning between the gas and aerosol phases.

Arctic contaminants - Determining effective and appropriate communicative means between Inuvialuit communities and researchers:

- Explore Inuvialuit knowledge and perceptions of contaminants, contaminants research, and how research is communicated and made accessible to communities.
- Discuss contaminants issues in the context of their applicability to the daily lives of community members.
- From a community perspective, develop culturally relevant and appropriate means of communicating contaminants research between Inuvialuit communities and researchers.
- Empower community members to engage in contaminants research occurring within and around their communities.

Mercury and methylmercury in multi-year ice cores:

- To determine how mercury and methylmercury transport and transformation would change when the Arctic Ocean is shiftting from the primarily multi-year ice regime to the first-year ice regime.

Mercury and selenium speciation in beluga whales:

- To understand how beluga whales cope with high levels of methylmercury in their bodies.

Mercury chemistry in sea ice:

- To examine fundamental cryospheric chemistry processes of mercury at freezing temperature and high ionic strengths.

INTRODUCTION

Ringed seal organic contaminant trends in relation to sea ice break-up:

Climate change has the potential to impact Inuvialuit food security, including the quality or contaminant load in marine mammals, by means of changes to prey availability and accessibility. We examined concentrations of chlorinated organic contaminants in male ringed seal blubber samples collected at Ulukhaktok (formerly Holman), NT from 1993-2008. Contaminant concentrations were analyzed with age, blubber thickness, and the date of sea ice break-up.

Holocene primary productivity and mercury dynamics trends in Baffin Bay:

Climate change is predicted to influence the primary productivity of polar marine ecosystems and the watercolumn dynamics of contaminants such as mercury (Hg). We are using dated sediment cores collected along transects through the present area of the NOW, to assess how algal productivity has changed with variable sea ice extent during the last few centuries of the Holocene. Mercury trends will be compared with OM and inorganic erosional inputs to infer effects of climate change on Hg dynamics.

Standardisation of Rock-Eval Analysis for recent sediments and soils/permafrost:

Climate change is having drastic effects on the carbon cycle in the Arctic. However, there are few rapid, quantitative methods to determine composite changes to organic carbon in the environment and over time. Such a method could then temporally compare changes to organic carbon with changes in contaminant cycling. We have developed a standardised method to accurately and rapidly quantify organic matter type/source and change.

Influence of the Mackenzie River on Beaufort Sea mercury biogeochemical cycling:

Biota from the Beaufort Sea are often found to contain the highest levels of Hg amongst Canadian and often pan-Arctic populations (e.g., Lockhart et al. 2005). The Mackenzie River is the main source of particulate matter to the Arctic Ocean (55% of total; Gordeev 2006) and a significant contributor to the Hg budget in the Beaufort Sea (Outridge et al. 2008), and the Mackenzie River Plume can reach several hundred km offshore into the Beaufort Sea. It is possible that the Hg from the Mackenzie River is directly impacting biota in the region, and this study examines whether sources of Hg from the Mackenzie are likely to impact the biota or if other factors are responsible for these increases.

α-HCH enantiomer fraction (EF) – a novel approach to calculate the ventilation age of water in the Arctic Ocean:

Approximately 10 Mt of α-HCH was released to the environment between 1948 and 1997 as a constituent of technical HCH, a broad-spectrum pesticide (Li and Macdonald 2005). α-HCH consists of two mirror-image enantiomers, (+) and (-), which have identical physical-chemical properties but different vulnerabilities to metabolic enzymes (Harner et al. 2000, Müller and Kohler 2004). An enantiomer ratio (ER = (+) α-HCH /

(-) α-HCH) differing from 1, or an enantiomer fraction (EF = ER / (ER+1)) differing from 0.5 indicates biological degradation (Hühnerfuss et al., 1992).

The Arctic Ocean is strongly stratified by ~3500 km^3/ year of freshwater runoff (Macdonald et al. 1989). Further stratification in the western Arctic is provided by the density contrast between 'light' Pacific water (~33 salinity) and 'heavier' Atlantic water (~35). In the Beaufort Sea, the stratification is evident as a vertical water distribution that has a fresh Polar Mixed Layer (PML) in the top 30-50 m, more saline waters of predominantly Pacific Origin within the Pacific Mode Layer (PL) from 50-230 m, and waters of predominantly Atlantic origin in the Atlantic Layer (AL) from 230 m downward (Macdonald et al. 1989, Carmack et al. 1989, et al. 2000a).

Given the distances of transport to the Beaufort Sea and the volumes of water involved in the various layers, the transport time periods since ventilation differ widely as indicated by a number of geochemical tracers including reprocessing plant radionuclides (^{129}I, ^{137}Cs; Smith et al. 1998), weapons testing fallout radionuclides (3H/3He; Ekwurzel et al. 2001), and chlorofluorocarbons (CFCs; Wallace and Moore 1985, Smethie et al. 2000b).

Mechanism and biological implication of organic contaminant enrichment in melt pond water on the Arctic sea ice:

Melt ponds are a common feature of the summertime sea ice cover in the Arctic Ocean resulting from the positive net surface energy balance. In late May, the solar radiation in the central Arctic warms up the snow cover sufficiently to initiate the melt onset which is manifested by melt water accumulating in surface ice depressions. The fate of the surface melt water depends strongly on the balance between the melt water production at the surface and the permeability structure of the underlying ice (Eicken et al. 2002). Total surface summer ablation accounts for the removal of the entire snow cover and 0.3 to 0.7 m of ice each summer (Scott and Feltham, 2010). Of the total surface melt water, about 60% is discharged into the ocean, and 40% is retained within the ice cover at the end of the melt season with ~10% in the form of surface melt ponds, ~5% as under-ice melt ponds, and ~25% retained within the ice structure (Eicken et al. 2002).

Hexachlorocyclohexane (HCH) is a legacy OCP which was used as an insecticide between 1950 and 2000 in two main formulations: lindane (pure active γ isomer) and technical HCH (α isomer 60-70%, β isomer 5-12%, and γ isomer 10-15%). α-HCH is the only HCH isomer of chiral nature (forms 2 enantiomers). α-HCH EF is defined as the concentration of the (+) enantiomer to the sum of concentrations of both enantiomers. α-HCH concentrations still remain relatively high in sea water, which together with its enantiomeric properties provide unique opportunities to develop insight into contaminant pathways in the Arctic cryosphere.

Dinoflagellate cysts as environmental indicators in the Hudson Bay system:

Hudson Bay has been highlighted as a rapidly changing system, particularly in terms of changes in the ice-cover season and the seasonality of freshwater inputs. We use dinoflagellate cysts from sediment and particle-intercepting traps together with sediment geochemical tracers and satellite data from Hudson Bay system in order to 1) disentangle the components that govern distribution and production of different cyst taxa under modern conditions and 2) probe changes in cyst communities and their environmental drivers during the past century.

Modelling the mercury cycle in the Beaufort Sea using a carbon flux model approach:

While efforts to reduce mercury emissions in recent decades have generally lead to gradual declines in global atmospheric concentrations, including in the Arctic (Li et al. 2008), concentrations in some Arctic biota and in sediments have either not declined or have increased (Carrie et al. 2010, Outridge et al. 2008). This disconnect between trends in air and those in sediments and biota has led to the hypothesis that climate change is altering the cycling of the existing mercury inventory already in the Arctic, and that these changes outweigh the changes in mercury inputs to the system (Outridge et al.

2008, Macdonald et al. 2008). Potential climate-related mechanisms that could alter mercury cycling in the Arctic marine ecosystem include: changes in sea ice cover affecting air-water exchange of mercury, changes in ice cover and light regime altering food web structure, primary production and the vertical flux of organic carbon and particle-bound mercury. In turn, these may affect the rates of mercury methylation and demethylation that determine the quantity of mono-methylmercury that is available to biomagnify through the foodweb. Recent studies have demonstrated a clear link between Hg methylation rates, primary productivity and organic carbon remineralization in mid-depth seawaters near the oxygen minimum (Sunderland et al. 2009). Algal particulate organic matter scavenges inorganic Hg from the euphotic zone, providing a physical focal point and the carbon substrate for subsequent microbial methylation activity as the particles settle. Thus any changes in primary production and the vertical flux of organic matter may affect the supply and bioavailability of methylmercury entering the foodweb.

The primary objective of this project is to develop a comprehensive mechanistic model of the mercury cycle in the Arctic Ocean with a strong emphasis on linking it to a carbon budget/production model that is sensitive to changes in climate related drivers such as extent of ice cover, light regime and nutrient supply. In addition to providing a cohesive framework for devising a more detailed mercury budget, the model is being developed as a predictive tool to explore the potential implications of different climate change scenarios on mercury cycling.

Progress on understanding biogeochemical cycles and organic carbon sources and inputs in Hudson Bay:

Rivers drive the freshwater budget of the Arctic Ocean by carrying large amounts of particulate and dissolved materials and depositing them on panarctic shelves to be redistributed by ocean circulation and climate. The Hudson Bay region and its latitudinal location is an important area due to its temperature gradients which influence vegetation, freeze/thaw cycles and ultimately the hydrology and inputs of organic carbon into the Hudson Bay organic carbon cycle. We hypothesize that by analyzing both the Δ14C ages of the DOC and POC and lignin biomarkers, we may determine source terrigenous inputs of carbon with a particular focus on permafrost.

Zooplankton as biomonitors of mercury in Hudson Bay:

While much research has been done on mercury in large marine mammals in the Arctic and associated food webs, comparatively less is known about mercury in zooplankton and the transfer of mercury between zooplankton and predators (including other species of zooplankton) in pelagic food webs. However, such data could assist in the interpretation of mercury trends observed in larger organisms, for example, the regional distinctions in mercury concentrations between polar bears from Hudson's Bay and the Beaufort Sea that have recently been reported (St. Louis et al. 2011). Zooplankton occupy the lower trophic levels of pelagic Arctic food webs, thus, accumulated mercury in zooplankton reflects mercury present in marine waters and in prey from short food webs.

Organic Hg species in Arctic Air:

Mercury (Hg) is a global pollutant from both natural and anthropogenic sources that exhibits long range transport due to its persistence in the atmosphere. Mercury bio-accumulates mainly in the aquatic ecosystem in the form of MMHg, the toxic form of mercury. There are uncertainties regarding the sources and fate of MMHg in the ecosystem. In particular, the direct and indirect contribution of the atmosphere as a source of MMHg to the Arctic ecosystem is not clear. Various studies suggest that DMHg can be volatilized from surface water and converted into MMHg or Hg^{2+} in the atmosphere. We hypothesized that atmospheric DMHg quickly degrades to MMHg in the atmosphere and is then deposited from the atmosphere to snow packs on ice fields. In this fashion, DMHg would be a major source of MMHg to snow or the open water itself. This pathway would explain the temporarily high levels of MMHg observed

in snow. However, there is no known reliable method to measure the organic Hg species in the atmosphere.

Air-Surface exchange of persistent organic pollutants in the Canadian Arctic:

Recent studies suggest that the summer sea-ice in the Arctic could disappear by 2040 and some suggest as early as 2015. Decreasing ice cover will open larger areas of the Arctic Ocean and its regional seas to air-water gas exchange. It is expected that loss of ice cover will increase rates of deposition and volatilization of semivolatile chemicals as the system strives to achieve air-water equilibrium. The classes of semivolatile compounds being investigated in this study are:

- OCPs - Hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), dieldrin (DIEL), components of technical chlordane: trans- and cis-chlordane (TC, CC), trans-nonachlor (TN) and metabolite heptachlor exo-epoxide (HEPX). Over the past 20 years concentrations of OCPs in Arctic air have generally declined due to restrictions or bans on usage, but few assessments of spatial/temporal trends and air-water gas exchange have been made for OCPs other than HCHs.
- CUPs - Although less persistent than OCPs, CUPs are amenable to atmospheric transport to non-target regions. CUPs sought here are dacthal (DAC), chlorothalonil (CHT), endosulfan (ENDO), chlorpyrifos (CP), pentachloronitrobenzene (PCNB) and trifluralin (TFN). All of these compounds are currently used in Canada and the USA, although the phase out of ENDO and PCNB has begun. ENDO-I has been found in Arctic Ocean water, snow and air but little is known about other CUPs in the Arctic water, although they have been found in Arctic and Subarctic lakes, ice caps, snow and air.
- Bromoanisoles - Bromoanisoles are formed naturally from reactions between haloperoxidase with humic substances in oceans. They are also formed by biomethylation of bromophenols, which are produced anthropogenically as fumigants, wood preservatives, industrial intermediates and as by-products in chlorination of water containing bromide ions.
- PFCs - In recent years, the fate and transport of PFCs in the atmosphere has been recognized as one of the emerging issues in environmental chemistry. Perfluorooctane sulfonate (PFOS) and longer chain perfluoroalkyl carboxylates (PFCAs), are resistant against typical environmental degradation processes and have been found in human and wildlife in remote regions such as the Arctic. However, the main transport pathway of PFCs to remote regions has not been conclusively characterized.

Arctic contaminants - Determining effective and appropriate communicative means between Inuvialuit communities and researchers:

Northerners continue to receive information about contaminants and their potential impacts on wildlife, their environment, and human health. Despite improved message sensitivity, considerable efforts disseminating this complex information have resulted in only general awareness of contaminants issues (Myers and Furgal 2006), with little evaluation of past communication programs from the perspectives of Northern residents and less consideration of the communication process. To best inform community members about contaminants research, it must not be assumed that the best way to communicate results to communities is known without consulting community members themselves. This project actively involves community members in the research process and aims to develop a genuine collaborative research relationship with the community (Inuit Tapiriit Kanatami & Nunavut Research Institute 2007), as there is a need for community-specific projects that can identify whether the objectives of contaminants communication efforts are being met (Furgal et al. 2005). Contaminants research conducted through the IPY's CFL System Study, Phase II of ArcticNet, and Environmental Monitoring Projects from the NCP, are used to explore the process of communicating technically complex contaminants research results with the Inuvialuit community of Sachs Harbour, NT.

Conducted using a participatory approach, community involvement is fundamental to this relationship-centred study, which emphasizes reciprocal knowledge sharing (Jardine and Furgal, 2010). Participatory video, used during semi-structured interview and focus group discussions, enables participants to determine how their knowledge is represented and to discuss contaminant issues as they relate to Inuvialuit culture and life.

Mercury and methylmercury in multi-year ice cores:

The Arctic Ocean is shifting from a primarily multi-year ice regime to a first-year ice regime. Its implication for the fate and effect of contaminants remains poorly understood. Recently we have shown that the highly saline brine from first-year ice contains very high concentrations of mercury which may have provided an important exposure pathway for mercury uptake by sea ice algae and eventually the marine ecosystem (Chaulk et al. 2011). In that work, we also reported the distribution of mercury in a multi-year ice core which showed very interesting cyclic feature (Chaulk et al., 2011). Since this was done with a single multi-year ice core with very limited anciliary data, further work is needed to see whether the cyclic feature is universal to all multi-year ice cores and whether it records annual thawing and refreezing.

Mercury and selenium speciation in beluga whales:

Mercury (Hg) is a global contaminant and has been found to be present at very high concentrations in marine mammals (e.g., beluga whales, seals, and polar bears) in the western Canadian Arctic. Of particular concern in these animals are the high levels of monomethylmercury (CH_3Hg^+ and its complexes; collectively referred as MeHg hereafter) (AMAP, 2011), which biomagnifies along the food chain and is a known developmental neurotoxicant. For instance, concentrations of total MeHg (MeHgT) in beluga whales typically range from 0.35 to 3.16 µg g-1 (wet wt.) in muscle and 0.11 to 6.13 µg g-1 (wet wt.) in liver (Gaden et al. 2009, Lockhart et al. 2005), frequently well exceeding the Canadian guideline of 0.5 µg g-1 (wet wt.) for MeHg in fish for human consumption (no MeHg consumption guideline currently exists for marine mammal tissues). This raises serious concerns over the health of marine mammals as well as the health of Inuit who consume these animals as part of their traditional diet. One major unknown is, however, the lack of evidence showing direct neurotoxic effects of such high levels of MeHg in Arctic marine mammals. While this may be simply due to the few extensive health survey on these animals, it may also suggest the presence of in vivo detoxification mechanisms. Although most monitoring data distinguish between different chemical and toxicological behaviors of inorganic Hg and MeHg, none have addressed the fact that MeHg is not a single chemical species; instead, it includes CH_3Hg^+ complexes with various ligands that are known to possess markedly different mobility and biochemical reactivity. Once taken up through diet (*e.g.*, fish), MeHg in marine mammals preferentially binds to sulfur- and selenium-containing biomolecules (Wang et al., 2011). While binding with cysteine (CysSH) is thought to be primarily responsible for MeHg transport across the blood-brain barrier and hence neurotoxicity (Ashner and Ashner, 1990), binding with glutathione (GSH) and selenium-containing compounds (e.g., selenocysteine and selenoglutathione) is known to detoxify MeHg via demethylation to produce biochemically inert solids HgSexS1-x ($0 \leq x \leq 1$) (Wang et al. 2011). The protection against MeHg toxicity by thiols and selenium depends on the chemical forms and molar ratios of MeHg, sulfur, and selenium, but may also be tissue-specific. It has been well documented that Hg in marine mammals is predominately in the form of MeHg in the muscle, whereas a significant fraction of inorganic Hg is accumulated in the liver and kidneys (Lockhart et al. 2005). The inorganic Hg in these tissues could result from the direct uptake of inorganic Hg, but it may also suggest that in vivo demethylation of MeHg preferentially occurs in the liver and kidneys. With the recent development in our lab of a highly sensitive, high performance liquid chromatography – inductively coupled

plasma mass spectrometry (HPLC-ICP-MS) technique for MeHg speciation (Lemes and Wang 2009), we set to measure, for the first time, the distribution of various MeHg species, as well as Se, in different tissues of beluga whales from the Beaufort Sea region. Such molecular level information is essential to the understanding of how Arctic marine mammals are coping with Hg contamination and for the development of remediation strategies.

Mercury chemistry in sea ice:

Evidence is merging that the sea ice environment in the Arctic Ocean plays a major role in mercury fate and effects in the Arctic marine ecosystems. The discovery of tropospheric "Br explosion", when reactive Br radicals are activated during polar sunrise and presumably at the surface of sea ice or snow, suggests that the surface of sea ice and "saline" snow is not as chemically inert as once thought. The Br radicals so produced would oxidize rapidly Hg^0, resulting in depletion of atmospheric Hg^0 (known as the mercury depletion events or MDEs) and enhanced deposition of Hg(II) onto snow, sea ice, or in the open lead. A significant fraction of Hg(II) deposited on snow or sea ice can undergo rapid photoreduction and be re-emitted back to the atmosphere, with the remainder entering the ocean via in-ice transport or during the melting season and thus impinging on the marine ecosystems. Furthermore, recent studies suggest that sea ice brine could become anoxic whereby redox and mercury methylation processes may occur. However, fundamental physicochemical processes governing mercury behavior in the sea ice environment are essentially unknown. This is largely attributable to a general lack of understanding of aqueous and aquatic chemistry at subzero temperatures. With the recent completion of the construction of the Sea-ice Environmental Research Facility (SERF) at the University of Manitoba, we propose to study the fundamental transport and transformation process of mercury, among many other chemicals, across the seawater - ice - air interface under semi-controlled conditions.

ACTIVITIES

Ringed seal organic contaminant trends in relation to sea ice break-up:

Marine mammal contaminant activities included wet-lab and analytical chemistry procedures, compiling output from equipment, and statistically analyzing data. These activities were carried out by project staff at the Freshwater Institute, Winnipeg, MB, and the University of Manitoba (May 1, 2010-June 1, 2011).

Holocene primary productivity and mercury dynamics trends in Baffin Bay:

Analytical work (OM characterization, Hg analyses, core dating) was either completed or substantially advanced in 2011. First MS in preparation, concerning how OM sources and productivity have changed spatially and temporally within and on the margins of the NOW over past centuries.

Standardisation of Rock-Eval Analysis for recent sediments and soils/permafrost:

Standards were chosen from environmentally representative chemical compounds (e.g., proteins, lipids, carbohydrates, lignins) and biological entities (e.g., phytoplankton and zooplankton). These were run on a Rock-Eval Analysis instrument by technical staff at the Geological Survey of Canada-Calgary (April 2011-May 2011) and interpretation was done by researchers at the University of Manitoba in Winnipeg (May 2011-Oct 2011). A manuscript was submitted to Organic Geochemistry in October 2011.

α-HCH enantiomer fraction (EF) – a novel approach to calculate the ventilation age of water in the Arctic Ocean:

A manuscript has been submitted to the Journal of Geophysical Research for publication.

Mechanism and biological implication of organic contaminant enrichment in melt pond water on the Arctic sea ice:

Melt pond water, new ice on top of melt ponds, and old ice samples, collected in the southern Beaufort Sea during the CCGS Amundsen ArcticNet/GeoTraces scientific cruise between 31st of August and 9th of September 2009, were analyzed for α-HCH concentration and enantiomeric composition at the Department of Fisheries and Oceans Canada, Winnipeg.

Surface water and air samples, collected during the CCGS Amundsen ArcticNet/IPY-CFL sampling campaign in the Beaufort Sea in the spring and summer of 2008 (April 5 - July 17), were analyzed for OCPs (heptachlor epoxide, trans- and cis-chlordane, trans-nonachlor, dieldrin) and CUPs (dacthal, chlorpyrifos, chlorothalonil, endosulfan I and II) at the Environment Canada, Egbert. A manuscript has been submitted to Environmental Science and Technology.

Dinoflagellate cysts as environmental indicators in the Hudson Bay system:

Dinoflagellate cysts were isolated from sediment and trap material by MH at the Paleoenvironmental/Marine Palynology Laboratory, University of Victoria, BC (Oct 23-Nov 19, 2010; April 25-May 12, 2011). Microscope slides were prepared and cysts were analysed by MH at the Freshwater Institute, Winnipeg, MB (Nov 2010-Apr 2011 for surface sediment, May 2011 box-cores). Biogenic silica (diatom production) was analysed using surface sediment samples by technical staff at the Department of Earth and Ocean Sciences, University of British Columbia (May 2011).

Modelling the mercury cycle in the Beaufort Sea using a carbon flux model approach:

We integrated a mercury speciation model with a carbon flux model (Lavoie et al. 2009, 2010) and are currently performing calibration exercises and adding new model components. Field work included collection of paired water and suspended sediment samples on the Mackenzie shelf slope (71°N, 135°W) on September 25th-October 1st 2011 at the chlorophyll maximum (15-25m). Analysis is pending.

Progress on understanding biogeochemical cycles and organic carbon sources and inputs in Hudson Bay:

Samples have been prepared for analytical procedures at the Freshwater Institute, Winnipeg, MB, where they were then shipped to the Centre for Oceanic and Atmospheric Sciences (COAS) at Oregon State University (OSU) for analysis of carbon/nitrogen (C/N) ratios, $\Delta^{14}C$, $\delta^{13}C$ and $\delta^{15}N$ isotopes in dissolved (DOC) and particulate (POC) organic carbon. Lignin biomarker analysis is also scheduled and partially completed for DOC and POC samples as well as permafrost and soil using isotope-ratio-monitoring gas chromatography/mass spectrometry (irm-GC/MS) at the COAS lab at under the direction of Miguel Goni.

Zooplankton as biomonitors of mercury in Hudson Bay:

Zooplankton were collected in 2003, 2004, 2005, and 2010 from across Hudson's Bay on ArcticNet expedition cruises. The analyses of these samples for: THg, MeHg, stable isotopes ($\delta^{15}N$ and $\delta^{13}C$), and the genus/species identification of the zooplankton samples are complete. Our analyses of THg and MeHg in water samples collected from the 2010 cruise are also complete. We have initiated a partnership with educators at Ataguttaaluk High School in Igloolik to promote the transfer of knowledge between researchers, youth, and educators from local communities near where the zooplankton were collected.

Organic Hg species in Arctic Air:

A method was developed to measure MMHg and DMHg in air. Air samples were collected during CCGS Amundsen expeditions to quantify MMHg and DMHg concentrations in the Arctic lower atmosphere. Concur-

rently, the methylation and demethylation rates of Hg in sea water samples were also investigated to provide a better understanding of Hg methylation and demethylation processes We investigated the importance of particulate matter as the location of MMHg formation by collecting particulate matter from up to 10 L of sea water for the analysis of MMHg.

Air-surface exchange of persistent organic pollutants in the Canadian Arctic:

Air and water sampling was conducted by Environment Canada research groups as part of ArcticNet in 2007, 2008, 2010 and 2011. In 2007-2008, air and water samples were collected for OCPs and CUPs and air samples were collected for PFCs. In 2010, sampling was expanded to include PFCs in the water column. In 2011, OPCs were added as a target compound and phytoplankton and zooplankton were collected.

Air-water gas exchange of target compounds has been calculated for ArcticNet expeditions in 2007, 2008 and 2010. The exchange fluxes of α-HCH in the Canadian Arctic were estimated using a micrometeorological approach and compared to fluxes estimated with the commonly used Whitman two-film model. (Wong et al. 2011b).

Arctic contaminants - Determining effective and appropriate communicative means between Inuvialuit communities and researchers:

Participant interviews were completed in June 2011.

The collaboratively developed survey was discontinued in favour of the interviews, which offered richer cultural and contextual information; surveys were deemed more appropriate for use as a pilot study.

Interview transcription is complete, verification (by participants) and coding is in progress; 3 main nodes, 4 free nodes and 9 sub-nodes are classified thus far.

Mercury and methylmercury in multi-year ice cores:

Multi-year sea ice cores were taken in August 2011 onboard the Amundsen from the Beaufort Sea area and analyzed for total mercury, methylmercury, oxygen-18 isotope ratios, and dissolved organic carbon.

Mercury and selenium speciation in beluga whales:

Belugas whale (*Delphinapterus leucas*) tissues were sampled from whales harvested in 2008 by local Inuit hunters at Hendrickson Island, which is located in the shallow Mackenzie Delta near the community of Tuktoyaktuk, Northwest Territories, Canada. Soft tissue samples were frozen on site in a portable freezer at -20°C. The frozen brain samples were sent to the University of Northern British Columbia (UNBC), and freeze-dried subsamples were shipped to the Department of Fisheries and Oceans (DFO) laboratories in Winnipeg; all the other tissues samples were directly shipped to DFO for storage and archival. Samples of muscle, kidneys, liver, and brain (temporal lobe section) from 10 beluga whales (8 males and 2 females). These tissues were analyzed for total mercury, total methylmercury, and the speciation of methylmercury and selenium.

Mercury chemistry in sea ice:

With the recent completion of the construction of the Sea-ice Environmental Research Facility (SERF) at the University of Manitoba, experiments are being carried out to study the fundamental transport and transformation process of mercury, among many other chemicals, across the seawater - ice - air interface under semi-controlled conditions. The outdoor sea ice pond was formulated with artificial seawater with chemical composition similar to that of the Arctic Ocean water and the ice started to grow on December 23, 2011. This is Year 1 of the SERF experiment which will continue on until the melting of the sea ice in March 2012.

RESULTS

Ringed seal organic contaminant trends in relation to sea ice break-up:

Concentrations of three contaminants declined significantly over the study CHB: r= -0.74,Speriod (HCB: r= -0.32, p=0.002; p,p'- DDT: r= -0.78, p=0.02; p=0.04). Accounting for blubber thickness and age (ANCOVA, least-square means (LSM)), ringed seals showed significant rises in PCB and p,p' DDE concentrations during years of early sea ice break-up (Figure 1).

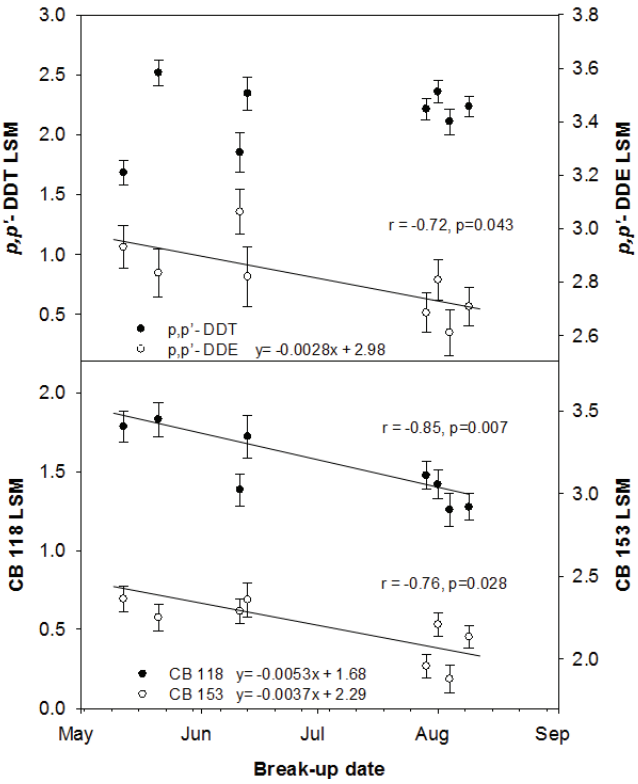

Figure 1: Annual least-square means (LSM) and standard error bars of organic contaminant concentrations in adult male ringed seal blubber (1993-2008), plotted upon break-up date. Regression lines illustrate significant trends.

Holocene primary productivity and mercury dynamics trends in Baffin Bay:

Although dating remodeling is continuing, necessitated by substantial bioturbation in some cores, it is clear that

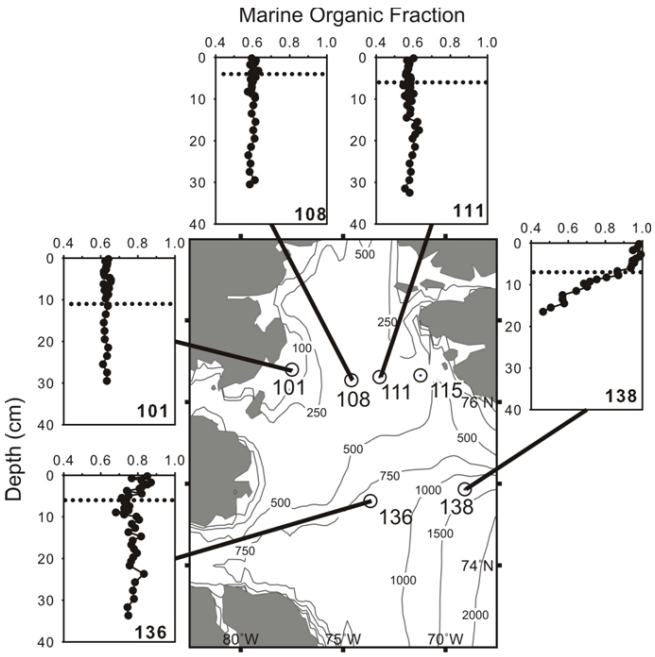

Figure 2: Historical changes in the fraction of marine organic matter of total sediment organic matter across the NOW polynya (sites 101, 111, 115) and polynya margin (sites 136, 138). The dotted horizontal line represents ca. 1900 in each core.

the putative fraction of marine OM in total OM has increased substantially in ice margin sites 136 and 138 in northern Baffin Bay since about 1900 (dotted line in Figure 2). In contrast, the marine OM fraction within the NOW (sites 101, 108, 111) has remained stable. Productivity across the region has increased in recent decades, as indicated by higher TOC concentrations in recent sediments.

Standardisation of Rock-Eval Analysis for recent sediments and soils/permafrost:

We found that lipids and phyto- and zooplankton contribute predominantly to the S2 fraction of the total organic carbon (TOC), and in particular, to the fraction of S2 that evolves prior to 400°C (termed S2a). Carbohydrates and lignins contribute predominantly to the S3 fraction. The ratio of evolved CO and CO_2 can be used to distinguish the predominant source of organic matter (lipids, proteins, carbohydrates, lignins), helping to

identify the relative proportion of autochthonous (i.e., derived from algae) and allochthonous (i.e., derived from terrestrial plants) organic matter. In general, the higher the amount of S3 carbon, the greater the proportion of residual carbon (RC) remained after pyrolysis.

Influence of the Mackenzie River on Beaufort Sea mercury biogeochemical cycling:

Mercury fluxes in water and sediment show that ~3.4 t/yr is released from sulfide mineral weathering, ~0.4 t/yr is from eroded coal outcrops along the shores of the Mackenzie River, ~0.3 t/yr of atmospherically-deposited Hg in runoff reaches the delta and ~0.2 t/yr is found bound to labile organic matter, predominantly as algal matter.

α-HCH enantiomer fraction (EF) – a novel approach to calculate the ventilation age of water in the Arctic Ocean:

The degradation rate constants for (+) and (-) α-HCH are (Harner et al., 1999):

(+) α-HCH1 = (+) α-HCH0 • exp-(kd1)t (Eq. 1)

(-) α-HCH1 = (-) α-HCH0 • exp-(kd2)t (Eq. 2)

where (+) α-HCH1 and (-) α-HCH1 is the (+) and (-) α-HCH concentration after t years of degradation, (+) α-HCH0 and (-) α-HCH0 are the initial (+) and (-) α-HCH concentrations, kd1 and kd2 are degradation rate constants for (+) and (-) α-HCH, respectively (0.128 ± 0.006 and 0.041 ± 0.041; (Harner et al. 1999)), and t is time of degradation [years]. Transforming Equations 1 and 2 into

(+) α-HCH1 / (-) α-HCH1 = (+) α-HCH0 • exp-(kd1)t / (-) α-HCH0 • exp-(kd2)t (Eq. 3)

and using the following equation (Hühnerfuss et al., 1992)

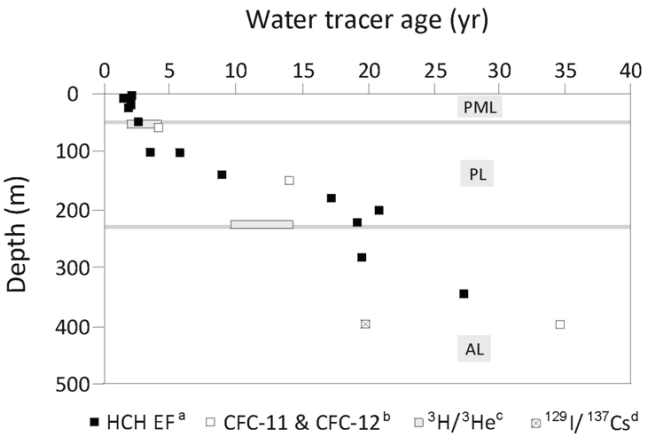

Figure 3: Tracer age of water in the Beaufort Sea and the western Arctic Ocean estimated in this study based on α-HCH EF profiles and in previous studies using CFC-11, CFC-12, $^{3}H/^{3}He$, and $^{129}I/^{137}Cs$. From Pucko et al. 2012.

(+) α-HCH / (-) α-HCH = ER (Eq. 4)

we obtain : ER1 = ER0 • exp-(kd1 – kd2)t (Eq. 5)

thus : t = ln (ER1 / ER0) / -(kd1 - kd2) (Eq. 6)

where ER1 is the α-HCH enantiomer ratio after t years of degradation, ER0 is the initial α-HCH enantiomer ratio, and ER = EF / (1-EF), with EF being the enantiomer fraction.

Using Equation 6, we calculated the age of water as a function of depth in the southern Beaufort Sea based on α-HCH EF vertical profiles (Figure 3).

Mechanism and biological implication of organic contaminant enrichment in melt pond water on the Arctic sea ice:

Average α-HCH concentration in the melt pond water at the end of the summer was relatively high (0.34 ± 0.08 ng/L) compared to the concentration in the top 1 m of old ice melt water from which melt ponds originally formed (0.07 ± 0.02 ng/L). Melt pond water was found to be at equilibrium with the atmosphere with the α-HCH equilibrium concentration calculated at 0.34

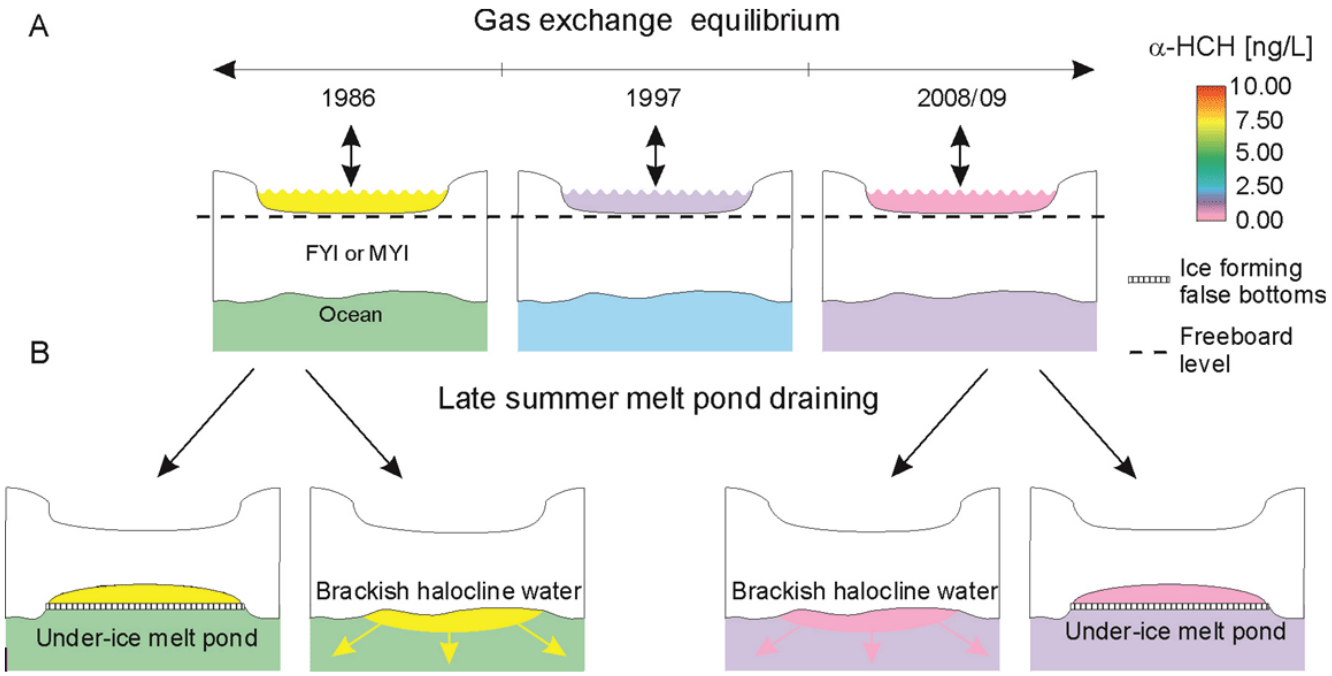

Figure 4: Conceptual schematic illustrating α-HCH concentration in melt pond water at the gas exchange equilibrium with the atmosphere in relation to the surface sea water concentration in 1986, 1997, and 2008/09; water colours denote α-HCH concentration (A); and two scenarios of melt pond water fate during late summer draining for 1986 and 2008/09 (B).

ng/L for the air concentration of 16 pg/m^3. Atmospheric origin of the increase was further supported by significantly higher α-HCH EF in the melt pond water (0.510 ± 0.008) than in the old ice samples (0.490 ± 0.017, p=0.005), with the assumption of racemic α-HCH EF (enantiomer ratio of 1:1) in the atmosphere in the sampling region under ice-covered conditions (Wong et al. 2011, Jantunen et al. 2008). A ratio of α-HCH melt pond water concentration to surface sea water concentration (MEF, Melt pond Enrichment Factor) equalled 0.4 in 2009, however, it was higher in the past when α-HCH was still in use with MEF of 2.0 in 1986 modelled based on historical air, sea ice and surface sea water data (Figure 4A).

Current MEFs for other pesticides were predicted based on air and surface water levels measured in the spring and summer of 2008 in the Beaufort Sea assuming the melt pond reached the equilibrium partitioning with air. MEFs for OCPs other than α-HCH equalled 0.5 – 1.4, but were significantly higher for CUPs, ranging from 2.3 for dacthal to as high as ~20 for chlorothalonil or ~800 for endosulfan II.

Dinoflagellate Cysts as Environmental Indicators in the Hudson Bay system:

The multivariate analyses (Figure 5) highlight three geographically and compositionally separate cyst groups. Group I (southeastern Hudson Bay) is related to high terrestrial organic matter inputs from river inflow and long open water seasons. Group II (western Hudson Bay) is related to low terrestrial inputs and nutrient limitation. Group III is confined to northern Hudson Bay and Hudson Strait and consists of heterotrophic taxa, e.g. typically arctic *Islandinium minutum* and *Echinidinium karaense*. This group is linked to higher accumulation rates of biogenic silica. Preliminary results of historical changes in Hudson Bay cyst assemblages manifest a recent reduction in the proportion of these heterotrophic species.

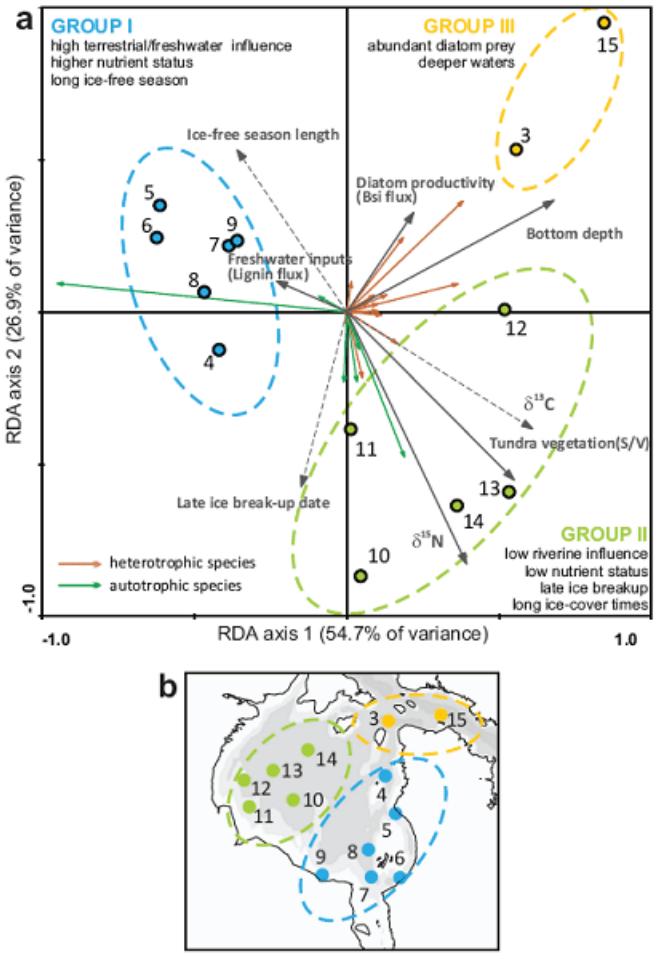

Figure 5: a) Ordination triplot (RDA) illustrating the separation of three study site (coloured dots) groups based on compositional dinoflagellate cyst data, as well as autotrophic (green arrows) and heterotrophic (brown arrows) species in environmental space. Solid grey arrows represent statistically significant ($p < 0.05$) environmental variables. b) A map of the study sites and their geographical grouping based on the RDA presented above. Heikkilä et al., submitted.

Modelling the mercury cycle in the Beaufort Sea using a carbon flux model approach:

The model was seeded with a total Hg water column profile derived from data collected in the Beaufort Sea during the Circumpolar Flaw Lead Study (Stern 2008. unpublished data) and run for 1 year (Figure 6). The model was closed to the atmosphere to emphasize the influence of the carbon cycle on mercury transport.

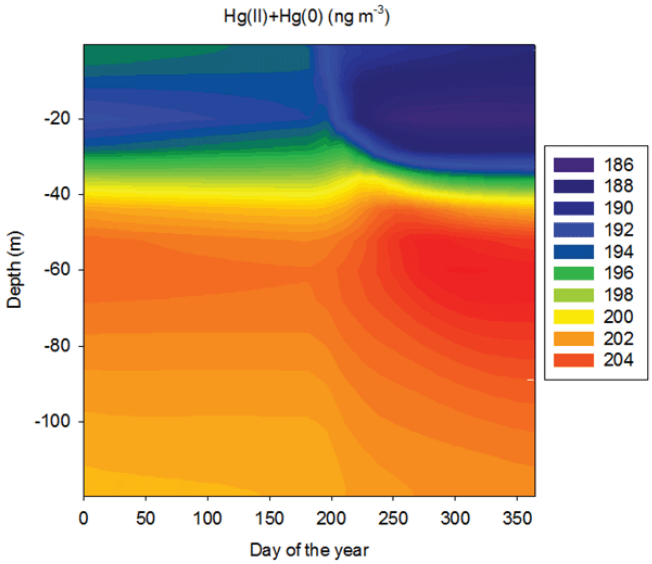

Figure 6: Modelled inorganic mercury (Hg(II) + Hg(0)) concentration in seawater over one year where ice break-up occurs on July 6th (Julian day 187).

For the duration of the 1-year simulation, total Hg concentrations in the upper 40m of the water column are noticeably lower than Hg concentrations below 40m, and this gap between Hg concentrations becomes more pronounced after the break-up of sea ice in spring. The model indicates that the depletion of surface total mercury is tightly associated with primary productivity and the subsequent fate of the organic carbon pool. For most of the year phytoplankton is light limited. Consequently the break-up of sea ice in spring (July 6th in the default model scenario) results in increased sunlight enabling a large phytoplankton bloom which then rapidly consumes surface nutrients and shades lower depths. Once the nutrients at the surface are depleted, phytoplankton sinks as detritus, subsequently reducing shading and allowing the bloom to continue at lower depths in relatively nutrient rich waters. Sorbed Hg(II) will be transported down the water column with the sinking algal detritus and will be released back to the water column as the detritus is remineralized (nearly all slow sinking detritus is remineralized above 60m). This cycle thus explains the sharp difference between Hg concentrations at the surface and 40-60m. Algorithms addressing mercury methylation were excluded in the results of this report as they require further refinement.

Progress on understanding biogeochemical cycles and organic carbon sources and inputs in Hudson Bay:

Although results are in the preliminary stages, it is apparent that there is potential for the use of lignin biomarkers and isotopes when understanding the terrigenous inputs of OC into the Hudson Bay from Arctic rivers (Figure 7). The composition of OC from source to sink may be determined by quantifying permafrost soils, river dissolved and particulate constituents and ocean sediments using bulk measurements on OC, carbon/nitrogen (C/N) ratios, $\delta^{13}C$ and $\Delta^{14}C$. The method of isotope-ratio-monitoring gas chromatography/ mass spectrometry (irm-GC/MS) has enhanced the source specificity of biomarkers when coupled with stable carbon isotope analysis (Hedges and Oades 1997).

Zooplankton as biomonitors of mercury in Hudson Bay:

This dataset represents short zooplankton food webs and includes planktivorous, omnivorous, and carnivorous genera of zooplankton (e.g., *Themisto libellula*, *Limacina helicina*, *Sagitta sp.*, *Calanus sp.*). Preliminary results indicate regional differences in THg and MeHg concentrations for some zooplankton genera across Hudson's Bay. $\delta^{15}N$ and $\delta^{13}C$ signatures in zoo-

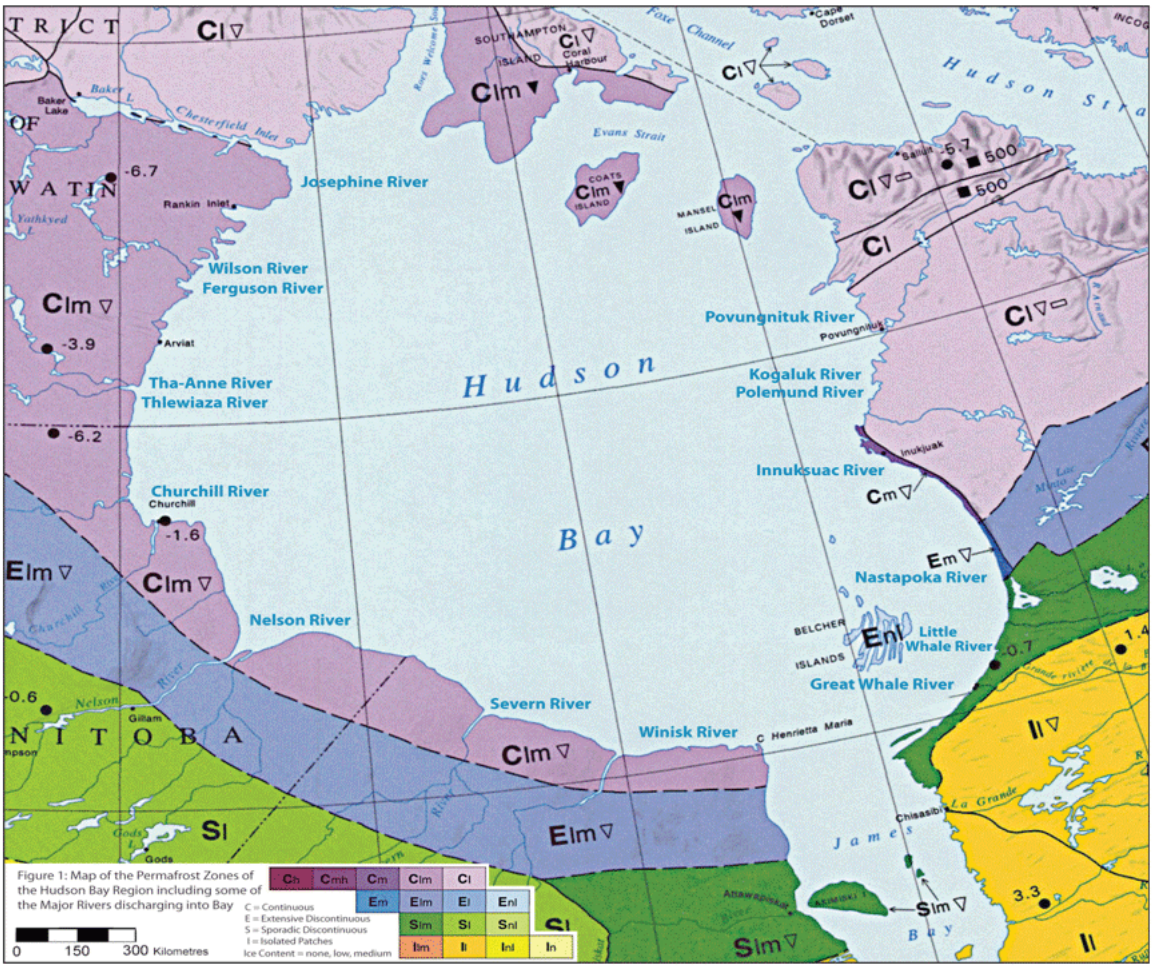

Figure 7: Map of the permafrost zones of the Hudson Bay including names of the 16 major rivers discharging into the Bay that were sampled during this study. Figure © 2012 HM The Queen in right of Canada, Natural Resources Canada, 1995.

plankton were used to establish trophic levels for each genera as well as predator-prey linkages within regional zooplankton food webs. Strong correlations between trophic levels and THg and MeHg concentrations in zooplankton food web members were observed. The results of our research indicate that mercury is not evenly distributed across Hudson Bay and Foxe Basin, which is in agreement with the mercury trends in bottom sediments (Hare et al. 2010).

Organic Hg species in Arctic Air:

The method for measurement of atmospheric organic Hg species is based on species specific Hg isotopic dilution and online ethylation of MMHg from air samples and trapping of ethylated MMHg and DMHg on Tenax traps. The method consists of collecting DMHg and MMHg (after inline ethylation to MeEtHg) on Tenax traps. Up to 50 L of air are sampled and collected Hg species from up to 4 field traps are then desorbed onto an analytical Tenax traps to form a composite sample, which is stored and later analyzed in the lab at Trent University. In the field, isotope enriched MMHg and DMHg standards from a permeation tube are mixed in-line with the air sample as a yield tracer to assess the overall method performance. Since the GC-ICP/MS method can detect as little as 0.1 pg of Hg absolute, a 200 L sample volume translates to an overall method detection limit of 0.5 pg/ m^3.

During the most recent 2010 Amundsen cruise, we were for the first time able to routinely capture and quantify DMHg and MMHg concentrations in the lower Arctic atmosphere. In the Hudson Bay, MMHg levels ranged from 3.9 – 8.1 (mean = 5.5 ± 2.0, n=5) pg/m^3 and were on average higher (at 4 our of 5 stations) than DMHg concentrations, which ranged from < LOD to 1.6 pg/ m3 with one outlier showing 8.1 pg/m^3 (mean = 0.8 ± 0.6, n = 4; or 2.3 ± 3.3, n= 5). The picture changed, when sampling the atmosphere in the Canadian high Arctic, where DMHg concentrations were consistently higher than those of MMHg and significantly higher than DMHg levels observed in Hudson Bay. DMHg ranged from 1.8 to 9.6 (mean = 4.3 ± 2.1, n = 12) pg/m^3. MMHg levels were now significantly lower than those measured in Hudson Bay ranging from < LOD (at 5 out of 12 stations) to 5.2 (mean = 1.7 ± 1.7, n = 12) pg/m^3.

Air-surface exchange of persistent organic pollutants in the Canadian Arctic:

Compounds found in air and water were hexachlorocyclohexanes, chlordanes, heptachlor epoxide, dieldrin, endosulfans, hexachlorobenzene, bromoanisoles, dacthal, chlorothalonil, chlorpyrifos and trifluralin. Concentration of hexachlorocyclohexanes and chlordanes have declined in Canadian Archipelago surface water between 1999-2010, while dieldrin and the CUPs dacthal, chlorothalonil, endosulfan, chlorpyrifos and trifluralin have remained stable or increased over the same period.

Legacy OCPs were close to air-water equilibrium or undergoing net volatilization during all ArcticNet cruises. The ice break-up near Banks Island in 2008 was accompanied by an increase in air -HCH in the air boundary-HCH and appearance of non-racemic concentrations of layer due to its volatilization from seawater (Wong et al. 2011a). Comparison of α-HCH fluxes estimated by micrometeorology and the two-film model showed that the overall net flux was from water to air. Flux estimates for individual events agreed in direction and within a factor of two in magnitude for six of eight events (Wong et al. 2011b). A temporal assessment of air-water exchange suggests that chlordanes have been near equilibrium or volatilizing throughout the 1990s and this trend continues to the present day. Similar TC/CC ratios in air sampled from ships and in surface water suggests that chlordane volatilization influences the composition in the air boundary layer. This effect is not seen in air at the monitoring stations which are farther away from open water (Alert) or at higher altitude (Zeppelin) (Hung et al. 2010).

The CUPs were depositing in 2007-2008, and gas exchange estimates in 2010 suggest that they are tending towards equilibrium. An exception is endosulfan, which continues to undergo net deposition.

In 2007-2008, the ∑PFC concentrations in air were ~3 times lower than in urban areas (Shoeib et al. 2006, Jahnke et al. 2007). FTOHs were the dominant PFCs in the gas phase. There were significant positive correlation between some PFCs concentrations in the gas phase and ambient air temperature. Analysis of 2011 air and water samples and 2010 water samples for PFCs is ongoing.

Arctic contaminants - Determining effective and appropriate communicative means between Inuvialuit communities and researchers :

The target range for participant interviews (25-30% of the population of Sachs Harbour) was attained (n=19), representing 27% of the population, with an age range of 18-76 years of age (mean = 45, median =43).

Key themes identified: research relationships (positive/neutral/negative impressions of any/all interactions; frequency and duration of time in community); conceptions/perceptions of contaminants (yes/no concerns/risk, local knowledge of what contaminants are/look like, etc.); methods of communication (positive/negative impressions, recommendations).

Mercury and methylmercury in multi-year ice cores:

The total mercury profiles from the multi-year ice cores collected in 2011 agree well with our earlier study on a multi-year ice core taken in 2008, confirming the presence of periodic signals. Data for methylmercury and isotopes are being analyzed.

Mercury and selenium speciation in beluga whales:

The concentration of total Hg in beluga ranged from 0.66 – 2.66 μg g^{-1} in the muscle, 2.32 – 6.35 μg g^{-1} in the brain (temporal lobe), 2.45 – 11.9 μg g^{-1} in the kidneys, and 12.2 – 31.6 μg g^{-1} in the liver. The values in the liver, kidneys and muscle and their relative abundance (i.e., liver > kidneys > muscle) are comparable to those previously reported for beluga whales from the region. To our knowledge this is the first time Hg has been measured in brain tissues of beluga whales from this region. Although the HgT concentration varied over more than one order of magnitude in different beluga tissues, the tissue MeHgT concentration was remarkably similar: 0.79 – 1.72 μg g^{-1} in the muscle, 0.39 – 1.11 μg g^{-1} in the brain, 1.03 – 2.92 μg g^{-1} in the liver, and 0.34 – 0.90 μg g^{-1} in the kidneys. The ratio of MeHgT to HgT is the highest in the muscle (84.0 ± 28.8%), followed by the brain (22.0 ± 6.8 %), liver (9.5 ± 3.4%), and kidneys (9.0 ± 3.8%). While the MeHgT concentration and MeHgT/HgT ratio in the muscle and liver are in good agreement with those from beluga collected in the early to mid-1990s, the MeHgT/HgT ratio in the brain of the beluga is much lower than that reported to occur in pilot whales and polar bears.

Essentially all of the MeHg (>97%) was present as $CH_3HgSCys$ in all the tissues except for the muscle where a considerable fraction of MeHg (up to 44%) was present as CH_3HgSG. While neither CH_3HgX nor HgX were detectable in the beluga tissues analyzed, two new unknown peaks were observed: U1 in all the tissues, and U2 in all the kidneys samples. Both peaks were eluted before CH3HgSCys. A comparison of retention times with known Hg and MeHg standards suggests that U1 and U2 could correspond to inorganic Hg-thiol complexes $Hg(SCys)_2$ and $Hg(SG)_2$, respectively. However, as discussed below, U1 could also be due to a Hg-Se complex. Further efforts to establish the molecular structures of U1 and U2 with electrospray ionization – triple quadrupole mass spectrometry (ESI-QQQ-MS; Agilent 6410) were unfortunately unsuccessful due to the poor detection limit and interferences when using ESI-QQQ-MS.

Several Se species were also identified in the beluga tissues: SeMet, CH_3SeCys, and inorganic Se(IV). Se(VI) and CysSeSeCys did not appear to be present. The highest concentration of Se was found in the liver and was present predominantly as Se(IV). Se(IV) was also the most prevalent Se species measured in the brain and

kidneys, while in the muscle SeMet and CH_3SeCys predominated. Two unknown Se species, U3 and U4, were also present in all the tissue samples analyzed. Since the retention time of inorganic Se (VI) is much longer, both peaks must be due to organoseleno species.

The fact that no Hg peak was detected along the Se peaks in the anion-exchange HPLC-ICP-MS chromatograms suggests that Hg or MeHg was not present as a complex of the identified Se species, i.e., SeMet, CH_3SeCys or Se(IV). However, two sets of Hg and Se peaks overlapped in the reversed-phase HPLC-ICP-MS chromatograms. One set of these peaks overlaps at a retention time of 2.5 min. While one of these peaks has been previously established to correspond to CH_3Hg-SCys, the overlapping Se peak cannot be assigned to its selenium analog, methylmercuric selenocysteinate ($CH_3HgSeCys$), as its retention time (3.1 min) is significantly different from that of $CH_3HgSCys$.

Furthermore, a Se peak also appeared at the same retention time (1.6 min) of the unknown Hg peak U1 in the beluga liver sample. Based on retention time matching and the chemical similarities, this peak might correspond to both inorganic $Hg(SCys)_2$ and its selenium analogue Hg selenocysteinate $Hg(SeCys)_2$. Alternatively, the presence of HgSexS1-x granules has been reported in the livers of marine mammals known to be present in marine mammal livers, and it has been established that HgSexS1-x could be rendered water soluble in the presence of selenoprotein] or glutathione.

Despite extensive efforts of analysis by X-ray diffraction, scanning electron microscope, and ESI-QQQ-MS, the identities of the co-occurring Se peaks at 1.6 min and 2.5 min on the reversed phase HPLC-ICP-MS chromatograms remain elusive due to the analytical challenge.

Mercury chemistry in sea ice:

The Year-1 experiment started on December 23, 2011 and data are being collected.

DISCUSSION

Ringed seal organic contaminant trends in relation to sea ice break-up:

The decline of p,p'- DDT and ΣCHB in ringed seals can likely be attributed to decreasing concentrations in the environment (Li and Mcdonald 2005, Hung et al. 2010), whereas decreasing HCB concentrations may be a result of in situ metabolic processes (Wiberg et al. 2000). Given the high food web magnification ability of highly lipophilic (fat-soluble) PCBs and p,p' DDE (Fisk et al. 2001, Hoekstra et al. 2003), the concentrations of these contaminants may be increasing in years of early ice clearing due to earlier foraging opportunities and/or an increase in highly contaminated prey (Gaden et al. submitted).

Holocene primary productivity and mercury dynamics trends in Baffin Bay:

This part of the study has found a coincidence between average seasonal ice extent and marine OM flux to sediments across northern Baffin Bay. Although all sites inside and outside the NOW showed OM increases during the 20th Century, unexpectedly, the ice margin sites show clearest evidence of a putative climate effect on the relative abundance of marine algal productivity. This runs counter to predictions.

Standardisation of Rock-Eval Analysis for recent sediments and soils/permafrost:

Our results are generally consistent with established interpretations of data from fossil fuel samples (coal, petroleum) showing that lipids and algae contribute to the S2 fraction and terrestrial plant matter to the S3 fraction (Peters et al. 2005). However, our results show the importance of separating the S2 fraction into two portions, as unlike in fossil carbon samples (one peak in the S2 fraction), there are two distinct peaks, which can be used to interpret organic matter (OM) source. Examining only the total S2 may confound interpretations of changes to the OM cycle, as terrestrial and algal sources of OM show distinct differences in S2 signatures. We also show that the relative contribution of S2/S2a to the total organic carbon (TOC) is also important

to determine OM source, as phyto- and zooplankton are the dominant sources amongst studied standards. S3 to TOC ratios (OICO and $OICO_2$) which have been neglected in previous studies, are shown here to be of utmost importance in determining OM source. In particular, high OICO (>60) tends to be associated with carbohydrates, lignins and terrestrial plant material, while below that we find lipids, proteins and aquatic biota (e.g., phytoplankton). The ratio of OICO to the total TOC-normalised S3 (OIRE6) also separates out groups. Above OICO:OIRE6 ~0.15, we find lipids, carbohydrates and plant standards, while all other standards fall below that. Biplots can thus be used to distinguish sources quite well (Figure 8).

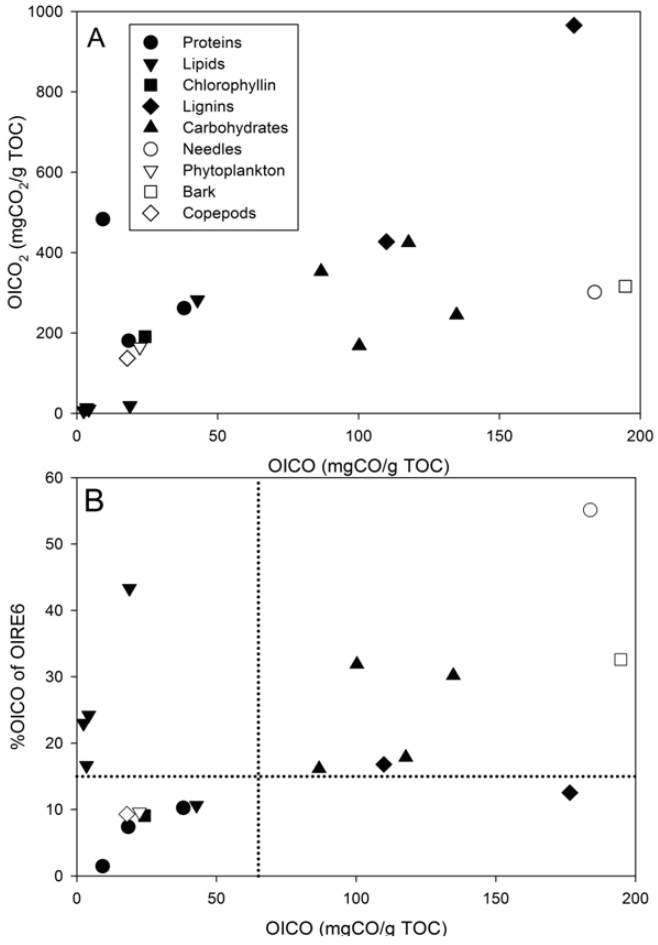

Figure 8: Biplots of oxygen indices (OI) from CO (OICO) and CO_2 ($OICO_2$). OIRE6 is derived from the sum of both OICO and $OICO_2$.

Influence of the Mackenzie River on Beaufort Sea mercury biogeochemical cycling:

Unlike more temperate regions closer to anthropogenic sources of Hg, the Hg budget in the Mackenzie River Basin (MRB) is not as strongly affected by atmospheric/anthropogenic sources of Hg. In fact, naturally occurring geological sources account for ~90% of the total Hg flux, suggesting little anthropogenic influence on the amount of Hg entering the Beaufort Sea from the Mackenzie River. In addition, these geological sources are likely of low bioavailability, which suggests that other factors from the Mackenzie River (e.g., organic carbon, nutrients, relatively warm water) are influencing high Hg levels in biota. However, smaller sub-regions of the MRB, in particular lake-fed sites, show a larger proportion of algal-bound Hg. Algal-bound Hg is assumed to have a greater bioavailability, which may have important local effects on biota.

α-HCH enantiomer fraction (EF) – a novel approach to calculate the ventilation age of water in the Arctic Ocean:

Starting with the Polar Mixed Layer (PML), we get a reasonable assignment of 1.7 years compared to the 3H/3He estimates of < 4 years for western Arctic Ocean (Ekwurzel et al., 2001).

Within the Canada Basin, water in the Pacific Mode Layer (PL) has entered from the Pacific Ocean by passing over a 50 m sill at Bering Strait. The water within the PL has a residence time of approximately 10 years (Macdonald et al. 2005), although that time period likely varies on the decadal scale depending on storage within the upper Canada Basin (Proshutinsky et al. 2002). For the PL water, estimated in this study to be 2 to about 20 years old, Ekwurzel et al. (2001) provide 3H/3He tracer ages increasing from 2 to about 10-14 years at 230 m in the western Arctic Ocean, which agrees with the CFC ages of 4 to 14 years over the Lomonosov Ridge (Wallace et al. 1985).

The estimated transit time of the AL (below 230 m), from where it last was in contact with the atmosphere in the Barents and Greenland Seas, is 15 years or longer

(Macdonald et al., 2005). In this study, the AL core was estimated to have an α-HCH EF ventilation age of about 22 years. Water at this depth over the Lomonsov Ridge had an apparent age of > 30 years based on CFC measurements (Wallace and Moore, 1985). However, an independent measure of transit time in boundary currents from Fram Strait to the Beaufort Sea, based on ^{129}I-^{137}Cs distributions, was only 20 years (Smith et al. 2011).

Mechanism and biological implication of organic contaminant enrichment in melt pond water on the Arctic sea ice:

During the latter half of the melt season, most of the surface melt water will percolate into the ice, with major fraction being discharged under the ice to form brackish halocline layer (60%) or under-ice melt ponds (5%) (Eicken et al., 2002), thus posing a risk of elevated biological exposures as depicted in Figure 4b using α-HCH current and historical concentrations as an example. All of the ice-associated algal habitats (surface melt pond flora, bottom (interstitial) and sub-ice algal community, under-ice pond flora, and brackish halocline flora (Mundy et al., 2011)) as well as pelagic flora and fauna in the upper layer of the ocean could currently be at risk of seasonally elevated exposures to CUPs.

Dinoflagellate cysts as environmental indicators in the Hudson Bay system:

Our results show clear taxon-specific responses to main environmental controls manifested by sediment geochemical indicators and satellite data. This lends support to the use of dinoflagellate cysts to track past changes in freshwater inputs, nutrient availability, and potentially ice-cover. Indeed, preliminary results of downcore analyses show temporal changes in the abundance of key taxa. The clearest manifestation of our data is the distinct response of autotrophic vs. heterotrophic species. The latter are controlled by prey availability and/or ice-cover seasons in somewhat different manner than elsewhere in the Arctic. This stresses the importance of understanding regional controls on cyst species distributions before attempting their use in past reconstructions. Ongoing analyses on seasonal behaviour of cyst species (particle-intercepting traps) in the Hudson Bay system will give more detailed insight into the production of cysts during open-water vs. ice-covered seasons.

Modelling the mercury cycle in the Beaufort Sea using a carbon flux model approach:

It is likely that decreased sea-ice cover and earlier break-up over the shelf break area of the Beaufort Sea will increase the probability of upwelling events, consequently transporting nutrients from lower depths to the near surface (AMAP 2005). We prescribed an arbitrary 50% increase in initial nutrient (NO_3, PO_4, and Si) concentration and tracked the changes in the mercury cycle relative to the default scenario. In this scenario, annual primary productivity increased by ~17% with most of the increase occurring in the upper 25m of the water column. Consequently, total mercury concentrations in the upper 20m decreased by ~3% due to increased Hg scavenging by POC and subsequent particle settling. Annual average Hg concentrations in phyto- and zooplankton decreased by less than 1% relative to the default nutrient scenario. The model thus indicates that increased POC scavenging will not significantly decrease the stock of total mercury in the upper ocean and will not significantly affect inorganic Hg concentrations in the base of the food web. The effects of changes in primary production on atmospheric Hg exchange and methylation have yet to be addressed.

Macdonald et al. (2005) suggest that an earlier break-up of sea ice has the potential to move up the start of spring phytoplankton bloom due to increased sunlight availability. Sea-ice break-up was forced two weeks early in the model (June 22nd) and the mercury cycle was compared to the default scenario. Primary productivity increased rapidly after breakup and was virtually of the same scale and duration as the bloom in the default scenario. As a result, all modelled Hg patterns described previously in this document remained nearly identical to the default scenario and were shifted two weeks earlier.

Progress on understanding biogeochemical cycles and organic carbon sources and inputs in Hudson Bay:

In order to gain further knowledge on the impacts of permafrost degradation on the Hudson Bay carbon cycle, it is imperative that bulk measurements and isotopic and radiocarbon measurements on DOC, POC and lignin biomarkers be applied to understand permafrost DOC and POC transport into the Hudson Bay region, ocean sediments and beyond. The CuO oxidation method when combined with the irm-GC-MS will further increase our understanding of the terrigenous sources of OC and their transport from Arctic Rivers to the Hudson Bay. By monitoring changes to permafrost and river hydrology and ^{14}C ages of SOC biomarkers in rivers and ocean sediments we may ascertain a better understanding of permafrost thaw dynamics and the alterations occurring to OC pools of the terrestrial environment and Hudson Bay (Gustafsson et al. 2011).

Zooplankton as biomonitors of mercury in Hudson Bay:

Frequently, spatial differences in Hg concentration in large marine mammals, such as polar bears, are assumed to be the result of regional differences in marine water concentrations (*e.g.*, St. Louis et al. 2011). While this could be the case, we hypothesize that zooplankton are an improved indicator of marine aqueous mercury concentrations. Hg uptake and transfer in the lower trophic level food web, comprised of a diverse number of zooplankton species (including planktivorous, omnivorous, and carnivorous species), is an under-studied research theme. Yet, it is these processes that control the introduction and distribution of Hg into marine Arctic food webs. The use of zooplankton as biomonitors of mercury in Arctic marine waters could be an important tool for communities in Nunavut for the long-term, community-directed monitoring of water quality.

Organic Hg species in Arctic Air:

We hypothesize that observed atmospheric concentrations are a direct result of corresponding concentrations of organic Hg species in surface ocean water. Hudson Bay has previously shown higher MMHg than DMHg levels in water, while the situation was the opposite for water samples collected in the Arctic polynya. Alternatively, there is a possibility that DMHg is more photosensitive than DMHg and degrades easily to MMHg, which is the more persistent organic species in the atmosphere. Considering the longer exposure to sunlight in southern Hudson Bay compared to high Arctic latitudes, this may affect the composition of Arctic air with respect to DMHg and MMHg.

Air-surface exchange of persistent organic pollutants in the Canadian Arctic:

The net deposition of CUPs, some of which have been used for almost as long as the OCPs, might be explained by two factors. CUPs continue to be applied whereas use of most OCPs declined over several decades and has now stopped. CUPs are generally less persistent than OCPs and are more likely to break down even under arctic conditions, so the water remains undersaturated.

Transport processes which bring PFCs to the Arctic are uncertain; e.g., air vs. ocean currents, or transport of precursors that than undergo transformation. Significant correlations between some FTOH compounds in the gaseous phase and air temperature indicated that seawater could be a source of PFCs in the atmosphere. However, for other PFCs no correlation was found which suggests that other PFCs in the Canadian Arctic may originate from long-range transport

Arctic contaminants - Determining effective and appropriate communicative means between Inuvialuit communities and researchers:

Local perceptions, concerns, and levels of understanding about contaminants are variable and complex, consistent with previous findings (Oakes 2008, Myers and Furgal 2006, Tyrell 2006, Furgal et al. 2005), and no consensus exists with respect to contaminant causes or sources: they are viewed broadly to include both local, observable concerns in addition to invisible toxins traveling through air and water that escape local descriptors and whose impacts are uncertain. Information presented by researchers is stated to be helpful, informative and easy to understand, but also confusing and complicat-

ed. Most locals acknowledge their interest in, and the importance of learning about contaminants, especially with regard to future generations and scientific research. Only one participant was aware of communication materials (e.g. posters that had since been taken down) about contaminants and country food. Participants are concerned about contaminants in country foods and are concerned for their personal health, but they are very aware that country foods are both nutritionally and culturally superior to store-bought food and there remains the overall conviction that contaminants have not yet made their way to Banks Island. Yet, there exists a deep concern for environmental, animal and human well-being in the future, including the worry that there will be no more animals left, which leads to the questions of what will happen to Inuvialuit culture, traditions, and identity. Meetings, presentations, and reports given by researchers are seen to be mostly positive because researchers are visible in the community, but spending time one-on-one, in small groups, or using storytelling and pictures are mentioned as being potential ways to communicate the importance of contaminants on a local level (analysis in progress).

Mercury and methylmercury in multi-year ice cores:

The observation of similar total mercury profiles in multi-year ice cores supports our earlier finding in the difference between mercury behavior in first-year and multi-year sea ice. Data are being completed on methylmercury and other anciliary variables.

Mercury and selenium speciation in beluga whales:

CH_3Hg^+ ions are soft Lewis acids, and therefore have strong thermodynamic affinities for thiolic and selenol groups which are soft Lewis bases. Therefore, once taken up by biota, MeHg is expected to be preferentially bound to thiol- and selenol-containing biomolecules. Thiolic groups in a biological system are present mainly in cysteine, tripeptide glutathione, and cysteine residues of proteins and enzymes. Being located within the active sites of many enzymes and directly involved in catalysis, these thiols play fundamentally important structural and functional roles in protein chemistry. Chemically resembling thiols, selenols readily replace thiols in amino acids and proteins and are, among many other functions, important antioxidants in cells. The binding of CH_3Hg^+ to these thiols and selenols constitutes may suppress their biochemical functions and thus give rise to the toxicity of MeHg. On another hand, the bonding of Hg to S or Se is so strong that it will decrease the strength of the C-Hg bond and thus may result in detoxification of MeHg due to MeHg demethylation and subsequent formation of inert HgSxSe1-x. To our knowledge, the present study is the first effort in identifying MeHg-thiol and MeHg-selenol species in different tissues of beluga whales. Our ability of probing the detailed metabolic pathways of MeHg is hindered by the unsuccessful identification of several unknown Hg and/or Se compounds. Nevertheless, a few important observations can be made from this study. The dominance of $CH_3HgSCys$ in all the beluga tissues is consistent with our earlier studies on fish muscle and rice grains, suggesting free cysteine and cysteine moieties of proteins are the primary binding sites of MeHg. The relatively high abundance of CH_3HgSG in the beluga muscle is surprising and may be of potential significance, as the muscle happens to have the highest MeHgT/HgT ratio. Although it is generally thought, though without analytical evidence, binding of CH_3HgSG results in detoxification of MeHg, our results suggest that such detoxification may not necessarily involve demethylation of MeHg. Furthermore, the presence of an unidentified inorganic Hg-Se compound in the brain and liver is a direct support of in vivo Se-aided demethylation of MeHg, and may explain the relative accumulation (when compared with the muscle) of HgT and relatively low MeHgT/HgT. Although we cannot conclude U1 is indeed the inert HgSexS1-x species, it is highly probably that U1 is less reactive and bioavailable than MeHg and offers protection from its toxicity.

Mercury chemistry in sea ice:

Data are being collected.

CONCLUSION

Ringed seal organic contaminant trends in relation to sea ice break-up:

Organic contaminant concentrations in western Canadian Arctic ringed seals appear to be increasing in years with early sea ice break-up, possibly as a result of an extended foraging season and changes within the underlying marine food web structure.

Holocene primary productivity and mercury dynamics trends in Baffin Bay:

Contrary to expectations, the ice-margin sites south of the NOW appear to show more evidence of climate effects on OM sources and types than sites in the NOW proper. However, all areas showed marked increases of marine OM productivity in recent decades compared to historical times.

Standardisation of Rock-Eval Analysis for recent sediments and soils/permafrost:

We have standardised Rock-Eval Analysis for use in recent sediments and soils showing that specific ratios (e.g., OICO, OICO2, S2a) can be used to determine the source of organic matter. These ratios can then be used to determine what changes have occurred and/or are occurring in a given system using dated sediment/soil/permafrost cores.

Influence of the Mackenzie River on Beaufort Sea mercury biogeochemical cycling:

Updated fluxes of mercury (Hg) from the Mackenzie River to the Beaufort Sea of ~4.3 t/yr are estimated. The weathering of sulfide minerals dominates the total Hg flux to the Beaufort Sea (3.4 t/yr; ~78%) followed by erosion of coal outcrops (~10%), atmospheric deposition (~6%) and bound to algal matter (~5%). The predominance of natural geological Hg is assumed to be of low bioavailability, and thus to have a minor impact on biota in the Beaufort Sea. This study also suggests that other factors related to the Mackenzie River (e.g., organic carbon, nutrients) are responsible for the high Hg burdens in aquatic biota.

α-HCH enantiomer fraction (EF) – a novel approach to calculate the ventilation age of water in the Arctic Ocean:

α-HCH enantiomer fraction (α-HCH EF), and possibly EFs of other chiral substances, can provide a relatively simple way to determine the ventilation age of water in the Arctic Ocean with the assumption of known and relatively constant degradation rates.

α-HCH EF tracer ages are in good agreement with ventilation ages for different water masses in the Beaufort Sea and the western Arctic Ocean available in the literature.

Error of the α-HCH EF tracer age calculation was estimated at 48%, however, calculation based on a ratio will introduce additional error associated with downward mixing, and thus, particularly significant at depths of increased water mass mixing (e.g. 80 and 220 m; Macdonald et al., 1989).

Mechanism and biological implication of organic contaminant enrichment in melt pond water on the Arctic sea ice:

Melt ponds will most likely reach equilibrium gas exchange concentration of organic contaminants over the summer due to their relative shallowness and greatly reduced water mixing capacity with the underlying ocean for most of the pond coverage duration (38-58 days; Scott and Feltham, 2010).

Depending on the contaminant global emission and physical-chemical properties (Henry's law constant, photo-degradation rates, long range transport potential), atmospheric deposition could potentially lead to highly increased levels of some of the CUPs in the melt pond water, posing a great risk for elevated exposures to ice-associated and pelagic algal communities and fauna.

Dinoflagellate cysts as environmental indicators in the Hudson Bay system:

Dinoflagellate cysts are evidently related to main environmental controls in the HBS, encouraging their prospective use in environmental reconstructions. In

order to use certain heterotrophic cyst species as tracers of sea-ice cover, however, it is necessary to gain more detailed understanding of their dependence on diatom productivity – and perhaps the dependence of diatom productivity on sea-ice regime as well.

Modelling the mercury cycle in the Beaufort Sea using a carbon flux model approach:

Model simulations reveal Hg in the near surface (<30m) is drawn down during the spring phytoplankton bloom which occurs shortly after the break-up of sea ice. The model indicates little change in the bioavailability of total mercury to the food web with either an earlier break-up of sea ice, or increased nutrient availability. Integration of methylmercury dynamics with the model is in need of refinement and is underway.

Progress on understanding biogeochemical cycles and organic carbon sources and inputs in Hudson Bay:

Permafrost thaw and degradation due to climate change has now been well documented throughout the Arctic. These Cryosolic soils contain as much as 1672 Pg of carbon accounting for around 50 percent of the belowground global organic carbon pool (Tarnocai et al. 2009). There is approximately 0.4 Gt of POC and DOC entering the oceans from rivers annually (Hedges and Oades 1997). Projected increases in river runoff, coastal erosion and permafrost thaw will all influence OC budgets with an increase in terrigenous inputs and alterations to biogeochemical cycling influencing both the Hudson Bay and global carbon cycle and including regional sea-ice formation (Guo and Macdonald 2006). The freshwater system therefore provides a linkage between the Arctic and terrestrial climate and by understanding composition and pathways we may further understand the influence of permafrost degradation on these systems and the feedbacks.

Zooplankton as biomonitors of mercury in Hudson Bay :

Mercury is not evenly distributed in marine water across Hudson's bay.

$\delta^{15}N$ and $\delta^{13}C$ signatures in zooplankton are useful for establishing trophic levels for each genera. The resulting predator-prey linkages are complementary with the known diets of the zooplankton genera. Correlations between trophic levels and THg/MeHg concentrations are evident.

Organic Hg species in Arctic Air:

This project established a working method for the determination of organic mercury species in air, and we are now in a position to address questions regarding the origin and fate of organic Hg species in the Arctic atmosphere. We will be able to compare predicted water-air fluxes with actual atmospheric concentrations and determine if the atmosphere is a significant source of organic Hg to snow, ice and eventually biota.

Air-surface exchange of persistent organic pollutants in the Canadian Arctic:

The OCPs and several PFCs found in this study have been banned at the national and international levels (Stockholm Convention and the United Nations Economic Commission for Europe Convention on Long Range Transboundary Air Pollution (CLRTAP)). Some of the CUPs detected in this study are in the process of being phased out in Canada and the U.S., namely endosulfan and pentachloronitrobenzene/quintozene. Additionally, endosulfan and trifluralin are candidates for the Stockholm Convention and/or the CLRTAP and are no longer used in the European Union. Water sampling during this project is establishing baseline levels so the effectiveness of future controls on usage can be assessed.

Arctic contaminants - Determining effective and appropriate communicative means between Inuvialuit communities and researchers:

Establishing mutual rapport and trust is the result of spending many months within the community, and has enabled participants to speak candidly and honestly about their knowledge and perceptions. The need for culturally appropriate communication of contaminants

messages has been stressed over the past several years; this project emphasizes community collaboration to explore a different way of approaching the concept of communication, distinguishing it from previous contaminant communication efforts.

Mercury and methylmercury in multi-year ice cores:

The similar total methylmercury profiles observed in the multi-year ice cores support our earlier proposal that the seasonal increase in first-year sea ice in the Arctic Ocean will likely provide more Hg-rich environments (i.e., brine) for primary producers, potentially increasing food web exposure to this contaminant. Data for methylmercury and isotopes are being analyzed.

Mercury and selenium speciation in beluga whales:

The speciation data provide the first analytical support that the binding of MeHg with glutathione and Se may have protected beluga whales from the toxic effect of high concentrations of MeHg in their body.

Mercury chemistry in sea ice:

Work in progress.

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Ringed seal organic contaminant trends in relation to sea ice break-up:

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Holocene Primary Productivity and Mercury Dynamics Trends in Baffin Bay:

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Standardisation of Rock-Eval Analysis for recent sediments and soils/permafrost:

Funding from ArcticNet, DFO and NRCan.

Influence of the Mackenzie River on Beaufort Sea mer- cury biogeochemical cycling:

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α-HCH enantiomer fraction (EF) – a novel approach to calculate the ventilation age of water in the Arctic Ocean:

We thank the crew of CCGS Amundsen for the field work assistance. We also thank Joanne DeLaronde, Allison MacHutchon, Paul Helm, and Debbie Armstrong for collecting the samples. Finally, we thank ArcticNet, the Canadian program office of the International Polar Year, the Natural Sciences and Engineering Research Council (NSERC), Canada Foundation for Innovation (CFI), Canada Research Chairs (CRC), the Department of Fisheries and Oceans Canada, and the University of Manitoba for funding.

Mechanism and biological implication of organic con- taminant enrichment in melt pond water on the Arctic sea ice:

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Dinoflagellate Cysts as Environmental Indicators in the Hudson Bay system:

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Organic Hg species in Arctic Air:

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Air-Surface Exchange of Persistent Organic Pollutants in the Canadian Arctic:

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Arctic contaminants - Determining effective and appro- priate communicative means between Inuvialuit com- munities and researchers:

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Mercury and Methylmercury in multi-year ice cores:

We thank Dr. David Barber's sea ice team and the crew of the CCGS Amundsen for field work assistance.

Mercury and selenium speciation in beluga whales:

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