Contaminants in western Canadian Arctic ringed seals (*Phoca hispida*): Temporal variation and potential effects of a warming climate

by

Ashley Gade

A Thesis submitted to the Faculty of Graduate Studies of

The University of Manitoba

in partial fulfilment of the requirements of the degree of

MASTER OF SCIENCE

Department of Environment and Geography

University of Manitoba

Winnipeg

THE UNIVERSITY OF MANITOBA

FACULTY OF GRADUATE STUDIES
*****
COPYRIGHT PERMISSION

Contaminants in Western Canadian Arctic Ringed Seals (*phoca hispida*): Temporal Variation and Potential Effects of a Warming Climate

BY

Ashley Gade

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

Manitoba in partial fulfillment of the requirement of the degree

Of

Master of Science

ABSTRACT

I reviewed contaminant levels in ringed seals (*Phoca hispida*) from the western Canadian Arctic (Ulukhaktok, NT Canada) along with biological (age, sex, morphometric measurements), ecological ($\delta^{15}N$, $\delta^{13}C$), and sea ice parameters (mercury only). Mercury levels in muscle tissue increased with age and $\delta^{15}N$. Muscle mercury was significantly associated to length of the previous ice-free season (quadratic regression) between 1973-2007. Higher mercury concentrations as a result of short (i.e. two months) and long (i.e. five months) ice-free seasons may reflect particular environmental conditions leading to shifts in the composition and distribution of prey available to ringed seals.

Temporal trends of organochlorine contaminants in blubber illustrated general decreasing levels of chlorobenzenes, hexachlorocyclohexanes, chlordanes, chlorobornanes, dichlorodiphenyl-trichloroethanes and polychlorinated biphenyls in male and female adult ringed seals. Results parallel contaminant trends in Arctic air. Organochlorine contaminants were significantly higher in male adults compared to female adults. Blubber thickness and age were also important variables in determining concentrations.

ACKNOWLEDGEMENTS

The following people have helped me complete my master's project, and for their efforts and time I thank each of them. Dr. Gary Stern, who I first met in Churchill, MB and Dr. Steven Ferguson both served as encouraging co-advisors and mentors. With their help I have upgraded my problem-solving, statistical and writing skills. I will always cherish the opportunities they gave me to travel, learn, and share my research with others. Lois Harwood, whom without her expertise and data on the Ulukhaktok ringed seals the project would certainly not have been a success. She helped me to try to see the bigger picture of my research. Joanne DeLaronde, Gail Boila and Allison MacHutchon's past work yielded a mercury dataset on the Ulukhaktok seals that I was given to analyze. Gail also helped me analyze some additional samples. Bruno Rosenberg and Colin Fuchs assisted me with gas chromatography and helped me to start reading my chromatographs for the organochlorine contaminant (OC) work. Sherri Friesen taught me the lipid extraction and florisilling techniques for OCs. Humfrey Melling provided sea ice data for the study area. Magaly Chambellant provided useful references and taught me about ringed seals. She also taught me the stable isotope preparation techniques. Dan Bailey ran my samples for stables isotopes at the U of W. Tara Bortoluzzi, Brent Young and Beth Ferreira helped me with lab procedures. Dr. Kevin Campbell allowed me to use his freeze drier for some of my samples. Dave, my fiancée, who went through a master's project of his own (mechanical engineering) was very supportive during mine. Both Dave's and my parents were always encouraging.

TABLE OF CONTENTS

LIST OF TABLES

Chapter 1

Chapter 2

LIST OF FIGURES

Thesis Format

The layout of my thesis follows guidelines set by the Faculty of Graduate Studies, University of Manitoba, for a 'sandwich' thesis. Chapter 1 provides introductory information; chapters 2 and 3 are manuscripts containing an abstract, introduction, methods, results and discussion; chapter 4 contains a conclusion of my work.

Listed below is (1) additional information about the co-authors and (2) my responsibilities for each work's completion.

Chapter 2. Mercury in ringed seals *(Phoca hispida)* from the western Canadian Arctic: trends with sea ice

A. Gade, S. H. Ferguson[1, 2], L. Harwood[3], H. Melling[4], G. Stern[1, 2]

With the help of my co-authors, I submitted a manuscript of this paper to Environmental Science & Technology (Nov. 20, 2008). My roles in this paper included preparing tissue samples for stable isotope analysis, organizing trace element, biological and sea ice data and statistically analyzing all variables.

Chapter 3. Organochlorine contaminant trends in western Canadian Arctic ringed seals (*Phoca hispida*)

A. Gade, L. Harwood[3], G. Stern[1, 2], S. H. Ferguson[1, 2]

My co-authors and I may pursue Science of the Total Environment for this manuscript's publication. Before compiling and examining my data, I exercised wet lab procedures for lipid extraction and fractionation of blubber samples. Additionally I analyzed samples with gas chromatography and read the chromatographs.

(1) Department of Environment and Geography, University of Manitoba, Winnipeg, Manitoba, R3T 2N2
(2) Fisheries and Oceans Canada, Freshwater Institute, Winnipeg, Manitoba, R3T 2N6
(3) Fisheries and Oceans Canada, Yellowknife, Northwest Territories, X1A 1E2
(4) Fisheries and Oceans Canada, Institute of Ocean Sciences, Sidney, British Columbia, V8K 4B2

Chapter 1 - Introduction

My research focuses on contaminant levels in ringed seals (*Phoca hispida*). Climate change, as perceived in the Arctic, is also a central theme. The particular population of ringed seals I studied, inhabiting Ulukhaktok (formerly Holman), Northwest Territories is unique in that it has been studied since the early 1970s and therefore has great potential for the study of long-term trends. Temporal trends are required to evaluate historical fluctuations and have a basis off which to make future predictions of variables in question. Biological variation is sometimes better described with environmental parameters as an alternative to time-based study. Such an example is with sea ice. Although the variability of the open-water period is increasing, the seasonal duration of sea ice in the Arctic is generally decreasing (Serreze et al. 2007), and this may have ramifications on ecological processes and contaminant pathways (Macdonald et al. 2005).

Elucidating relationships of contaminant levels with biological and ecological data is also important so that we may better understand what factors pose toxicological risk to this species. My thesis examines these issues, specifically (a) relationships of mercury and organochlorine contaminants (OCs) with age, sex, morphometric measurements and stable isotope ratios, (b) discrepancies in OC levels among 3 classes of seals (male adults, female adults and sub-adults; based off Harwood et al. 2000), (c) trends of mercury with the ice-free season and (d) temporal trends of OCs. Further details are provided at the end of this introduction.

Ringed seals are a suitable candidate for contaminant analyses because they are abundant (Reeves 1998), are well represented in the subarctic and Arctic (Frost and

Lowry 1981), and are an important food source for polar bears (Hammill and Smith 1991, Stirling and Smith 2004). Due to indigenous harvesting samples are available for study. Ringed seals have been studied extensively in subarctic and Arctic regions for contaminant studies (i.e. Muir et al. 1999, Riget et al. 2007).

Not only are ringed seals the mainstream prey for polar bears, but they are also traditional food for indigenous peoples (Riewe and Amsden 1979). Northern communities depend on marine mammals for nutritional, social, spiritual, physical, and economic benefits (Van Oostdam et al. 2005). By investigating the contaminant burdens in country foods, we can try to explain the possible sources of the contaminants and help reduce the risk of chronic health effects observed in northern communities from the consumption of contaminants through the Arctic marine food web (Dewailly et al. 1993; Macdonald and Bewers 1996).

Contaminants are a major consequence of anthropogenic activities since days of the industrial revolution. Coal-burning, agricultural practices and industrial processes are a few examples which release contaminants into the environment. Many contaminants transport from temperate regions to the Earth's poles via convective winds and ocean currents and accumulate over time (Wania 2003).

Once contaminants are introduced into the Arctic, they begin accumulating in the bottom of the food chain and marine mammals are eventually exposed through their diet. Organochlorine contaminants easily bind to lipids in organisms, such as zooplankton, into which OCs filter with particle feeding (Fisk et al. 2001). Methyl mercury binds to organic matter in the state of neutral ion pairs (Rand 1995), and similarly to OCs, is consumed by lower trophic levels. In carnivorous species contaminant levels tend to increase over time because elimination rates are slower than intake rates, a process referred to as bioaccumulation. At each step in the food chain methylmercury and OC concentrations are amplified to a greater extent (a.k.a. biomagnification). Marine mammals occupy high trophic positions in the Arctic and are therefore prone to large contaminant uptake (Addison and Smith 1998, Atwell et al. 1998).

When marine mammals contain large contaminant burdens, they face greater risk of toxicological effects. Both reproductive failure (Reijnders 1986, Reddy et al. 2001) and weakened immune systems (Ross et al. 1996, Mos et al. 2007) are examples of health problems which result from high OC levels. Mercury, on the other hand, is a neurotoxin (Goyer 1986), and high levels have led to reduced activity and feeding in seals (Ronald et al. 1977). These effects have significant implications for both the survival of ringed seal populations and the well-being of their pursuers.

Like many ice-adapted species, ringed seals face much stress already from climate change. Decreasing ice coverage (Maslanik et al. 1996, Rothrock et al. 1999) and changing sea levels, ocean currents, water chemistry, and climate conditions (Learmonth et al. 2006) will potentially affect the critical resources used by marine mammals. Ringed seals depend on snow and ice to excavate subnivean lairs for birthing, rearing young and protection (Smith 1987, Smith et al. 1991). Recent work has already indicated that the timing of break-up and length of the open water season (Harwood et al. 2000) and snow depth (Ferguson et al. 2005) can have significant repercussions on the reproduction and survival of ringed seal populations.

Climate change may alter contaminant pathways. As permafrost thaws and wet precipitation increases as a result of warming temperatures (ACIA 2004), greater quantities of mercury from soil and runoff may release into the marine environment (Leitch et al. 2007). However, currently mercury in the Arctic is understood to be in equilibrium (Outridge et al. 2008, Hare et al. 2008). Global climate change is expected to decrease organic contaminant concentrations in temperate regions in part by increasing their mobility (Dalla Valle et al. 2007), which may lead to greater contamination of northern ecosystems. Prey composition, and thereby dietary exposure to contaminants, also has potential to change as a response of altered environmental processes and ecological interactions (Macdonald et al. 2005, Bluhm and Gradinger 2008).

Climate change and associated environmental and ecological responses bring me back to what was stated in the first paragraphs, with emphasis on the importance of monitoring contaminant levels in the Arctic. Mercury and OCs have been measured and documented in Ulukhaktok ringed seals from 1972 to 2001. Generally OCs in blubber have declined (Addison and Smith 1998, Muir et al. 2001), following suit to Arctic seabirds' eggs (Braune et al. 2007). Mercury concentrations in liver, on the other hand, show no strong trends (Braune et al. 2005) over this time frame. Results contrast to observations of hepatic mercury in Beaufort Sea beluga (*Delphinapterus leucas*) near the area of study (Lockhart et al. 2005). Few contaminant temporal trend studies of marine mammals include data extending into the 2000s or have 10+ years of data. Furthermore, the use of age-sex classes is, to my knowledge, a new categorization of samples for contaminant-based study.

The second chapter links mercury levels in ringed seal muscle with seasonal sea ice cover using 10 years of data over a 34-yr period. Ringed seal and sea ice data were provided by Lois Harwood (Fisheries and Oceans Canada) and Humfrey Melling

(Institute of Ocean Sciences), respectively, and both are co-authors of the paper. While sea ice probably does not have a direct relationship with mercury exposure in seals, it may influence bottom-up processes with respect to the food-chain (i.e. more light exposure, greater primary productivity, more food available for predators). I also reviewed relationships with age, sex, size measurements, $\delta^{15}N$ and $\delta^{13}C$ with mercury in male and female adults and sub-adults.

One of the tools I used in attempting to explain results in both chapters 2 and 3 was stable isotope ratios. Nitrogen that is consumed and excreted from an animal is dominated by the ^{14}N isotope, leaving an enrichment of the ^{15}N isotope in the body (Kelly 2000). The stable isotope ratio of $^{15}N/^{14}N$ ($\delta^{15}N$) tends to increase by 3.8‰ per marine trophic level, but changes in $\delta^{13}C$ appear negligible (Hobson and Welch 1992). Instead, $\delta^{13}C$ acts as a tool to identify the source of carbon in the foodweb. For instance, the enrichment of the ^{13}C isotope (ratio of $^{13}C/^{12}C$) is greater among marine compared to freshwater foodwebs (France and Peters 1997). Benthic organisms also tend to have higher $\delta^{13}C$ than pelagic organisms (France 1995).

In the third chapter, I examined correlations of biological and ecological variables with OCs, analyzed differences in contaminants among age-sex classes, and reviewed OC trends over time. Six years of samples were available for use (1993, 1995, 2002-2005). In a preliminary analysis I tried relating OC levels to sea ice parameters, but after accounting for temporal variability, there was negligible variation in contaminant levels. Low variation in seasonal sea ice duration throughout the years of study likely influenced results, especially between 2002-2005. Nonetheless, OC concentrations in Ulukhaktok ringed seals for years mentioned above remain unknown to the larger scientific community at this time. Information provided in this chapter complements current understanding of long-term trends of OC contamination in this marine mammal species.

References

Arctic Climate Impact Assessment (ACIA). *Impacts of a Warming Arctic*; Cambridge University Press: New York, 2004.

Addison, R.F.; Smith, T.G. Trends in organochlorine residue concentrations in ringed seal (*Phoca hispida*) from Holman, Northwest Territories, 1972-91. *Arctic* **1998**, *51*, 253-261.

Atwell, L.; Hobson, K.A.; Welch, H.E. Biomagnification and bioaccumulation of mercury in an arctic marine food web: insights from stable N isotope analysis. *Can. J. Fish. Aquat. Sci.* **1998**, *55*, 1114-1121.

Bluhm, B.A.; Gradinger, R. Regional variability in food availability for Arctic marine mammals. *Ecol. Appl.* **2008**, *18 (Supplement),* S77-S96.

Braune, B.M.; Outridge, P.M.; Fisk, A.T.; Muir, D.C.G.; Helm, P.A.; Hobbs, K.; Hoekstra, P.F.; Kuzyk, Z.A.; Kwan, M.; Letcher, R.J.; Lockhart, W.L.; Norstrom, R.J.; Stern G.A.; Stirling, I. Persistent organic pollutants and mercury in marine biota of the Canadian Arctic: an overview of spatial and temporal trends. *Sci. Total Environ.* **2005**, *351-352*, 4-56.

Braune, B.M. Temporal trends of organochlorines and mercury in seabird eggs from the Canadian Arctic, 1975-2003. *Environ. Pollut.* **2007**, *148*, 599-613.

Dalla Valle, M.; Codato, E.; Marcomini, A. Climate change influence on POPs distribution and fate: a case study. *Chemosphere* **2007**, *76*, 1287-1295.

Dewailly, É.; Ayotte, P.; Bruneau, S.; Laliberte, C.; Muir, D.C.G.; Norstrom, R.J. Inuit exposure to organochlorines through the aquatic food chain in Arctic Quebec. *Environ. Health Perspect.* **1993**, 101, 618-620.

Ferguson, S.H.; Stirling. I.; McLoughlin, P. Climate change and ringed seal (*Phoca hispida*) recruitment in western Hudson Bay. *Mar. Mam. Sci.* **2005**, *21*, 121-135.

Fisk, A.T.; Hoekstra, P.F.; Gagnon, J-M.; Duffe, J.; Norstrom, R.J.; Hobson, K.; Kwan, M.; Muir, D.C.G. Influence of habitat, trophic ecology and lipids on, and spatial trends of, organochlorine contaminants in Arctic marine invertebrates. *Mar. Ecol. Prog. Ser.* **2003**, *262*, 201-214.

France, R.L. Carbon-13 enrichment in benthic compared to planktonic algae: foodweb implications. *Mar. Ecol. Prog. Ser.* **1995**, *124*, 307-312.

France, R.L.; Peters, R.H. Ecosystem differences in the trophic enrichment of ^{13}C in aquatic food webs. *Can. J. Fish. Aquat. Sci.* **1997**, *54*, 1255-1258.

Frost KJ and Lowry LF. 1981. Ringed, Baikal, and Caspian seals *Phoca hispida* Schreber, 1775; *Phoca sibirica* Gmelin, 1788 and *Phoca caspica* Gmelin, 1788. In Rigdway SH and Harrison RJ (Eds). *Handbook of marine mammals. Vol. 2. Seals*. Academic Press, London, pp.29-53.

Goyer R. Toxic effects of metals. In. *Casarett and Doull's Toxicology, The Basic Science of Poisons*, 3rd ed.; Klaassen, C.D., Amdur, M.O., Doull, J. Eds.; Macmillan Publishing Company: New York, 1986, pp.582-635.

Hammill, M.O.; Smith, T.G. The role of predation in the ecology of the ringed seal in Barrow Strait, Northwest Territories, Canada. *Mar. Mam. Sci.* **1991**, *7*, 123-135.

Hare, A.H.; Stern, G.A.; Macdonald, R.W.; Kuzyk, Z.; Wang, F. Contemporary and preindustrial mass budgets of mercury in the Hudson Bay Marine System: the role of sediment recycling. *Sci. Total Environ.* **2008**, doi:10.1016/j.scitotenv.2008.07.033

Harwood, L.A.; Smith, T.G.; Melling, H. Variation in reproduction and body condition of the ringed seal (*Phoca hispida*) in western Prince Albert Sound, NWT, Canada, as assessed through a harvest-based sampling program. *Arctic* **2000**, *53*, 422-431.

Hobson, K.A.; Welch, H.E. 1992. Determination of trophic relationships within a high Arctic marine food web using $\delta^{13}C$ and $\delta^{15}N$ analysis. *Mar. Ecol. Prog. Ser.* **1992**, *84*, 9-18.

Kelly, J.F. Stable isotopes of carbon and nitrogen in the study of avian and mammalian trophic ecology. *Can. J. Zool.* **2000**, *78*, 1-27.

Learmonth, J.A.; Macleod, C.D.; Santos, M.B.; Pierce, G.J.; Crick, H.Q.P.; Robinson, R.A. Potential effects of climate change on marine mammals. *Oceanogr. Mar. Biol., Annu. Rev.* **2006**, *44*, 431-464.

Leitch, D.R.; Carrie, J.; Lean, D.; Macdonald, R.W.; Stern, G.A.; Wang, F. The delivery of mercury to the Beaufort Sea of the Arctic Ocean by the Mackenzie River. *Sci. Total Environ.* **2007**, *373*, 178-195.

Lockhart, W.L.; Stern, G.A.; Wagemann, R.; Hunt, R.V.; Metner, D.A.; DeLaronde, J.; Dunn, B.; Stewart, R.E.A.; Hyatt, C.K.; Harwood, L.; Mount, K. Concentrations of mercury in tissues of beluga whales (*Delphinapterus leucas*) from several communities in the Canadian Arctic from 1981 to 2002. *Sci. Total Environ.* **2005**, *351-352*, 391-412.

Macdonald, R.W.; Bewers, J.M. Contaminants in the arctic environment: priorities for protection. *ICES J. Mar. Sc.* **1996**. *53*, 537-63.

Macdonald, R.W.; Harner, T.; Fyfe, J. 2005. Recent climate change in the Arctic and its impact on contaminant pathways and interpretation of temporal trend data. *Sci. Total Environ.* **2005**, *342*, 5-86.

Maslanik, J.A.; Serreze, M.C.; Barry, R.G. Recent decreases in Arctic summer ice cover and linkages to atmospheric circulation anomalies. *Geophys. Res. Lett.* **1996**, *23*,1677-1680.

Mos, L.; Tabuchi, M.; Dangerfield, N.; Jeffries, S.J.; Koop, B.F.; Ross, P.S. Contaminant associated disruption of vitamin A and its receptor (retinoic acid receptor α) in free-ranging harbour seals (*Phoca vitulina*). *Aquat. Toxicol.* **2007**, *81*, 319-328.

Muir, D.; Braune, B.; DeMarch B.; Norstrom, R.; Wagemann, R.; Lockhart, L.; Hargrave, B.; Bright, D.; Addison, R.; Payne, J.; Reimer, K. Spatial and temporal trends and effects of contaminants in the Canadian Arctic marine ecosystem: a review. *Sci. Total Environ.* **1999**, *230*. 83-144.

Muir, D.; Fisk, A.; Kwan, M. Temporal trends of persistent organic pollutants and metals in ringed seals from the Canadian Arctic. In: *Synopsis of research Conducted Under the 2000-2001 Northern Contaminants Program*; Kalhok, S., Ed.; Indian and Northern Affairs Canada: Ottawa, 2001; p. 208-214.

Outridge, P.M.; Macdonald, R.W.; Wang, F.; Stern, G.A.; Dastoor, A.P. A mass balance inventory of mercury in the Arctic Ocean. *Environ. Chem.* **2008**, *5*, 89-111.

Rand G. *Fundamentals of Aquatic Toxicology*; Taylor and Francis: Washington, D.C., 1995.

Reddy, M.L.; Reif, J.S.; Bachand, A.; Ridgway, S.H. Opportunites for using Navy marine mammals to explore associations between OCs and unfavorable effects on reproduction. *Sci. Total Environ.* **2001**, *274*, 171-182.

Reeves, R.R. Distribution, abundance and biology of ringed seal (*Phoca hispida*): an overview. NAMMCO Sci. Publ. **1998**, *1*, 9-45.

Reijnders, P.J.H. Reproductive failure in common seals feeding on fish from polluted coastal waters. *Nature* **1986**, *324*, 456-457.

Riewe, R.R.; Amsden, C.W. Harvesting and utilization of pinnipeds by Inuit hunters in Canada's Eastern high Arctic. In *Thule Eskimo Culture: an Anthropological Retrospective*; McCartney, A.P. Ed.; National Museum of Man Mercury Series; Archaeological Survey of Canada: Ottawa, 1979. Paper No.88.

Riget, F.; Diets, R.; Born, E.W.; Sonne, C.; Hobson, K.A. Temporal trends of mercury in marine biota of west and northwest Greenland. *Mar. Pollut. Bull.* **2007**, *54*, 72-80.

Ronald, K.; Tessaro, S.V.; Uthe, J.F.; Freeman, H.C.; Frank, R. Methylmercury poisoning in the harp seal (*Phagophilus groenlandicus*). *Sci. Total Environ.***1977**, *8*, 1-11.

Ross, P.S.; De Swart, R.L.; Timmerman, H.H.; Reijnders, P.J.H.; Vos, J.G.; Van Loveren H.; Osterhaus, A.D.M.E. Suppression of natural killer cell activity in harbour seals (*Phoca vitulina*) fed Baltic Sea herring. *Aquat. Toxicol.* **1996**, *34*, 71-84.

Rothrock, D.A.; Yu, Y.; Maykut, G.A. Thinning of the Arctic sea-ice cover. *Geophys. Res. Lett.* **1999**, *26*, 2469-3472.

Serreze, M.C.; Holland, M.M.; Stroeve, J. Perspectives on the arctic's shrinking sea ice cover. *Science* **2007**, *315*, 1533-1536.

Smith, T.G. The Ringed Seal, *Phoca hispida*, of the Canadian western Arctic. *Can. Bull. Fish. Aquat. Sci.* **1987**, *216*, 81p.

Smith, T.G.; Hammill, M.O.; Taugbøl, G. A review of the developmental, behavioural and physiological adaptations of the ringed seal, *Phoca hispida*, to life in the arctic winter. *Arctic* **1991**, *44*, 124-131.

Stirling, I.; Smith, T.G. Implications of warm temperatures, and an unusual rain event for the survival of ringed seals on the coast of southeastern Baffin Island. *Arctic* **2004**, *57*, 59-67.

Van Oostdam, J.; Donaldson, S.G.; Feeley, M.; Arnold, D.; Ayotte, P.; Bondy, G.; Chan, L.; Dewaily, É.; Furgal, C.M.; Kuhnlein, H.; Loring, E.; Muckle, G.; Myles, E.; Receveur, O.; Tracy, B.; Gill, U.; Kalhok, S. Human health implications of environmental contaminants in Arctic Canada: a review. *Sci. Total Environ.* **2005**, *351-352*, 165-246.

Wania, F. Assessing the potential of persistent organic chemicals for long-range transport and accumulation in polar regions. *Environ. Sci. Technol.* **2003**, *37*, 1344-1351.

Chapter 2 - Mercury in ringed seals *(Phoca hispida)* from the western Canadian Arctic: trends with sea ice

Abstract

We examined a unique time series of ringed seal (*Phoca hispida*) samples collected from a single location in the western Canadian Arctic between 1973 and 2007 to test for changes in total mercury (THg) in muscle tissue associated with (1) year and (2) length of ice-free season. Interestingly, while there was no obvious temporal trend with muscle THg, we found that it increased significantly in a non-linear fashion with the number of ice-free days: seals experienced greater THg in short (2 months) *and* long (5 months) ice-free seasons. Although $\delta^{15}N$ and $\delta^{13}C$ in muscle tissue did not illustrate significant trends with ice-free days, $\delta^{15}N$ was significantly correlated to muscle THg, and our discussion explains how summer environmental conditions may influence the composition of prey (mercury exposure) available to ringed seals. Results offer insight into how marine mammals may respond to directional changes in Arctic sea ice resulting from continued warming.

Introduction

During the last several decades contaminant levels have been monitored throughout the Arctic in response to changing climate. In the Canadian Arctic, total mercury (THg) significantly increased from 1975-2003 by ~2% and ~3% in the eggs of northern fulmar (*Fulmarus glacialis*) and thick-billed murre (*Uria Iomvia*), respectively (Braune 2007). THg concentrations in beluga (*Delphinapterus leucas*) liver adjusted for age from the Mackenzie Delta also increased from 1981-2001 (Lockhart et al. 2005). These beluga have some of the greatest THg levels reported in the Canadian Arctic.

Western Canadian Arctic ringed seals (*Phoca hispida*) also have relatively high hepatic THg levels compared to other Arctic regions (Riget et al. 2005). However, ringed seal liver THg in Prince Albert Sound present no clear trend over time from 1972-2001 (Braune et al. 2005).

Outridge et al. (2008) reported mercury inputs and losses from the Arctic were near equilibrium, and therefore variations in mercury concentrations in biota are unlikely due to environmental background levels but possibly ecological processes. Thus, while monitoring mercury in the Arctic provides a history of "what" the concentrations are and have been, an equally important question to examine is "why" the levels fluctuate. Studying fundamental ecosystem dynamics could potentially explain variation observed in mercury levels in biota, particularly ringed seals for which there are no clear temporal trends.

Among the ecosystem changes occurring in the Arctic in response to increasing temperatures [(ACIA), 2004], reduction in sea ice concentration [(IPCC), 2007] is one of the most important for the biota which inhabit the Arctic Ocean. Many ecosystem functions in the Arctic depend, to some extent, on the type (e.g. first year vs. multi-year), concentration and duration of sea ice (i.e. see Carmack and Macdonald 2002). Therefore, we have undertaken to relate mercury, which is linked to the carbon cycle and consumed in the foodweb (Macdonald et al. 2005), to one of the most important parameters influencing biological productivity in the Arctic Ocean (sea ice). Such a linkage may have important implications for long-term future conservation and sustaining healthy subsistence lifestyle among Inuit and northern communities.

Ringed seals are an ideal candidate for the study of climate change and contaminant uptake. As a widely distributed circumpolar species, they occupy a relatively high trophic level in the Arctic marine foodweb and are thus exposed to high levels of mercury through their diet (Atwell et al. 1998, Muir et al. 1999).

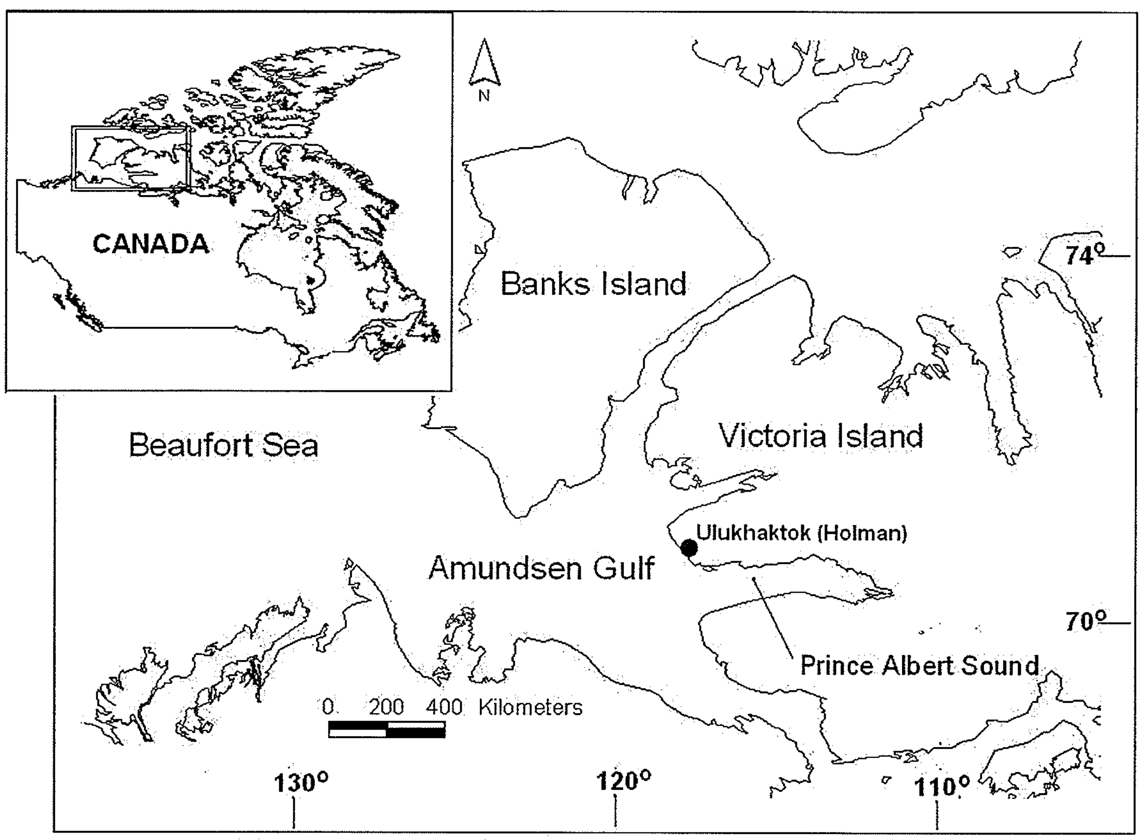
Shifts in prey stocks as a result of climate change (Macdonald et al. 2005, Bluhm and Gradinger, 2008) may alter contaminant exposure to seals. Stable isotope ratios are useful in conveying diet-related information in animals, and as such, the trophic position and foodweb carbon source can be determined by $\delta^{15}N$ and $\delta\ ^{13}C$, respectively (Peterson and Fry 1987, Hobson and Welch 1992).

Here we examine the linkages to trace elements (mercury) in ringed seals in the context of biological (ages and sex), ecological ($\delta^{15}N$ and $\delta^{13}C$) and sea ice variables. Mercury in muscle, rather than liver, was chosen for the analysis because mercury tends to accumulate in liver over time (i.e. Gaskin et al. 1972) and may not be representative of annual changes in contaminant concentrations. Additionally, Loseto et al. (2008b) found mercury, which is in its methylated, toxic form in muscle (Wagemann et al. 1997), to be a better indicator of dietary sources (biomagnification) in muscle compared to liver in beluga. Seals were sampled from the western Canadian Arctic, most commonly in the Prince Albert Sound area of the eastern Amundsen Gulf from 1973-2007. In addition to morphometric measurements, sex and ages, we also compared $\delta^{15}N$ and $\delta^{13}C$ in muscle tissue to THg in muscle.

Methods

Field Sampling. As part of a harvest-based sampling program, ringed seal samples were collected from Ulukhaktok (formerly Holman; 70°43'N, 117°43'W), NT, located along the NW shore of Prince Albert Sound (Figure 1). Approximately 20 seals each year were sampled for mercury in 1993, 1995, 1996, 2002-2005 and 2007, which represented approximately 20% of all the seals sampled in the overall program. Additional samples from 1973 and 1977 were included in our analysis (Smith and Armstrong 1975, 1978). Samples were collected during June-July from all years and were analyzed for trace elements with the same methods, as described below.

Figure 1. Sampling region in the western Canadian Arctic. Ringed seals were sampled near Ulukhaktok (formerly Holman) along the northwest coast of the Prince Albert Sound.



Sex and morphometric measurements were recorded for each sampled seal, and lower jaws were collected for aging purposes (Harwood et al. 2000). Liver and muscle tissue were frozen within 24 hours of collection and shipped to the laboratory at the Freshwater Institute, Fisheries and Oceans Canada, Winnipeg, MB for contaminant analyses.

Aging was performed by counting growth layer groups (GLG) in the dentine layer of lower canines (Smith 1973). Recent studies have indicated that counts of dentinal GLG tend to underestimate ages of seals >10 years compared to the reading of cementum layers (Stewart et al. 1996). However, we used the same aging method (dentinal) that was used for the 1970s samples to ensure the datasets were comparable.

The length of the ice-free season (hereafter called 'summer') in the Eastern Amundsen Gulf was determined for each year using ice charts from the Canadian Ice Service (H. Melling, Institute of Ocean Sciences). For a given year total ice-free days were summed from the first day of ice clearing (the earliest day showing a lead approximately 10km wide near the mouth of Prince Albert Sound) to the first day of ice freeze-up (the first day showing a continuous cover of new ice that did not subsequently dissipate) (Harwood et al. 2000).

Chemical Analysis. Tissue sub-samples were taken from the interior of the frozen sample tissue, eliminating outside contamination. We used approximately 0.2 g muscle for the analyses. After heating and digesting in sulfuric and nitric acids, mercury levels were determined using Cold Vapour Atomic Absorption (CVAAS; Armstrong and Uthe 1971); the limit of detection (LOD) was 0.005μg/g wet weight. Replicates, blanks, and standard reference material (SRM; LUTS-1, TORT-2, CRM 2976) were all used as measures of quality control. 85% of the standard reference material was recovered.

Muscle tissue was analyzed for stable isotope ratios ($\delta^{15}N$ and $\delta^{13}C$). Because the presence of lipids can bias $\delta^{13}C$ values (Kurle and Worthy 2002), lipids were extracted from 0.2g muscle by submerging the tissue in 5ml of a 2:1 mixture of chloroform and methanol for 18 hours. After centrifuging and removing the extract, another 5ml was added and mixed for two hours. The process was repeated twice more with the solution mixed for an hour each time for a total of 4 extractions to sufficiently remove all lipids from the material (based on Folch et al. 1957). After drying the samples were analyzed for $\delta^{15}N$ and $\delta^{13}C$ by Continuous Flow Ion Ratio Mass Spectroscopy (CFIR-MS) at the University of Winnipeg Stable Isotope Laboratory. Isotopic data are presented in units of *per mil* (‰) with δ (delta) notation. Here $\delta^{15}N$ and $\delta^{13}C$ are derived from

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

where R is the ratio of heavy to light isotope ($^{15}N/^{14}N$ or $^{13}C/^{12}C$) in the sample and standard. The nitrogen stable isotope standard was atmospheric nitrogen; Pee Dee belemnite limestone formation was the standard for carbon stable isotopes. Error was ±0.19‰ and ±0.21‰ for $\delta^{15}N$ and $\delta^{13}C$, respectively, from laboratory analysis.

Statistical Analysis. Following the approach used by Harwood et al. (2000) and Smith (1987), we pooled samples by age class categories as pups (0+ y), sub-adults (1-6 y) and adults ($\geq$7 y for males and females separately). We did not separate pups and sub-adults by sex because their sample sizes were not sufficient to do so. Prior to statistical analyses we log-transformed the data, except $\delta^{15}N$ and $\delta^{13}C$ which already had normal distributions, to produce uniform residuals and normally distribute the data.

We assessed muscle THg concentration dependence upon sea ice and other biological variables using a Generalized Linear Model (GLM; SYSTAT v.11, 2004) for male and female adults:

$$\text{Muscle THg} = \mu + \text{age} + \text{length} + \delta^{15}N + \delta^{13}C + \text{ice-free days } (i\text{-}1) + \varepsilon \qquad (2)$$

where μ is a constant, 'ice-free days (i-1)' is the length of the ice-free period in the year before sampling, and ε is the error term. Linear relationships of $\delta^{15}N$ and $\delta^{13}C$ and muscle mercury in adult ringed seals were further assessed with Pearson correlation. A preliminary analysis revealed age and $\delta^{15}N$ were significantly related in sub-adults, so we used simple linear regression to examine the relationships of age, length, $\delta^{15}N$, $\delta^{13}C$ and ice-free days (i-1) on their muscle mercury. We chose $\alpha \leq 0.05$ for statistical results.

Last, we plotted ice-free days (i-1) against muscle THg and $\delta^{15}N$ and $\delta^{13}C$ separately by age-sex class (excluding pups). We used analysis of covariance with significant biological variables as covariates to produce least-square means (LSM) of muscle THg, $\delta^{15}N$ and $\delta^{13}C$ for yearly samples.

Results and Discussion

Mercury and stable isotope ratios by year. In total, 260 samples of muscle tissue were tested for THg. Average muscle THg, $\delta^{15}N$ and $\delta^{13}C$ in ringed seals in this study were compared to ringed seals sampled between 1988-2001 in Ulukhaktok, Barrow, AL, Northwater Polynya and Lancaster Sound (Table 1).

Overall our results are similar to findings from other papers. Average muscle THg from seals in this study fall within the ranges of other mercury values reported in Table 1. Our mean $\delta^{15}N$ and $\delta^{13}C$ values are slightly smaller compared to those in other studies, but average $\delta^{13}C$ in our 2002 ringed seals is nearly identical to 2001 Ulukhaktok ringed seals reported by Dehn et al. (2005).

Lower $\delta^{15}N$ and $\delta^{13}C$ in this study's ringed seals may be explained by several factors. Smaller $\delta^{15}N$ may result from feeding at a lower trophic level compared to elsewhere or because of a smaller number of trophic levels in the food web of Prince Albert Sound ringed seals, effectively reducing the amount of ^{15}N reaching upper level predators. Lower $\delta^{13}C$ may be explained by the nature of the underlying food web: less ^{13}C tends to be transferred through estuarine food webs as compared to those in coastal or open-ocean habitats (France and Peters 1997). Because the Amundsen Gulf and Prince Albert Sound receive some of the Mackenzie River's outflow, the marine carbon in these regions may be more similar to estuarine habitats.

Relationships of mercury with biological and environmental variables. As seen in Table 2, $\delta^{15}N$ and $\delta^{13}C$ were not significantly related to muscle THg in adult ringed seal GLMs, but $\delta^{15}N$ alone was significantly correlated to muscle THg in adults in a separate Pearson correlation (male adults: $r=0.35$, $p=0.004$; female adults: $r=0.46$ $p=0.008$). Sub-adult levels of muscle THg were also significantly related to $\delta^{15}N$ (Table 2).

Table 1. Averages ± standard errors for $\delta^{15}N$, $\delta^{13}C$ and muscle THg concentrations in ringed seals from 1973-2007 across Alaska and the Canadian Arctic including values from the current study.

Location	Year	N	Age average (range)	$\delta^{15}N$ (‰ in muscle)	$\delta^{13}C$ (‰ in muscle)	Muscle THg (µg/g wet weight)	Reference
Holman/ Ulukhaktok, CAN	2007	17	16.2 (8-26)	16.36±1.68	-20.77±1.01	0.58±0.22	This study
	2005	19	14.8 (5-21)	16.06±0.84	-20.74±0.42	0.57±0.26	"
	2004	19	14.4 (3-26)	15.60±0.91	-20.68±0.50	0.45±0.19	"
	2003	20	16.7 (2-26)	15.47±1.00	-20.83±0.53	0.48±0.23	"
	2002	1	< 1	17.12	-20.47	0.11	"
	2002	21	13.2 (2-26)	14.80±0.83	-20.42±0.48	0.47±0.17	"
	1996	2	< 1	14.86±0.03	-20.41±0.21	0.05±0.01	"
	1996	18	12.2 (2-21)	14.97±0.60	-20.68±0.36	0.30±0.12	"
	1995	19	11.5 (4-21)	15.48±0.47	-20.76±0.29	0.58±0.22	"
	1993	13	16 (7-36)			0.32±0.18	"
	1977	2	< 1			0.37±0.19	"
	1977	72	7.9 (1-17)			0.45±0.17	"
	1973	34	13.4 (4-26)			0.89±0.35	"
Holman/Ulukhaktok, CAN	2001	25		17.2±0.7	-20.4±0.4		(1)
Barrow, AL	1996-2001	63-78		16.9±0.6	-18.5±0.8	0.10±0.16	"
Barrow, AL	1995-1997	11-17				0.22±0.33	(2)
Northwater Polynya, CAN	1998	9		17.43±0.28	-18.04±0.38	0.68±0.29	(3)
Lancaster Sound, CAN	1988-1990	9		17.3±1.1	-17.3±0.7		(4)

References: (1) Dehn et al. 2005, (2) Woshner et al. 2001b, (3) Campbell et al. 2005, (4) Hobson and Welch 1992

Table 2. Summary of regression models for Ulukhaktok ringed seal (*Phoca hispida*) age-sex classes. There are two generalized linear models (GLM) of muscle THg for male and female adults and five linear regression models of sub-adult Ulukhaktok ringed seals from 1973-2007. Each GLM and set of linear regressions encompasses biological, ecological and sea-ice variables for each age-sex class. Bold items are statistically significant (α=0.05) in the models.

Age-sex class and model	Explanatory variable	Coefficient, SE	r	t	P (2 tail)	Overall model (F, p, r^2)
Male adults n=67 (GLM)	Constant	-5.301, 4.588		-1.155	0.252	5.750, <0.001, 0.320
	Age	0.396, 0.141	0.334	2.808	0.007	
	Length	0.903, 0.619	0.176	1.459	0.150	
	$\delta^{15}N$	0.100, 0.063	0.200	1.591	0.117	
	$\delta^{13}C$	-0.104, 0.105	0.122	0.998	0.322	
	Ice-free days (*i*-1)*	-0.063, 0.154	-0.051	-0.405	0.687	
Female adults n=33 (GLM)	Constant	2.155, 6.760		0.319	0.752	6.305, <0.001, 0.539
	Age	0.523, 0.192	0.396	2.722	0.011	
	Length	-2.321, 0.982	-0.336	-2.364	0.026	
	$\delta^{15}N$	0.462, 0.120	0.566	3.862	0.001	
	$\delta^{13}C$	0.136, 0.225	0.086	0.607	0.549	
	Ice-free days (*i*-1)*	0.490, 0.195	0.376	2.508	0.018	
Sub-adults n=36	Age	0.356, 0.205	0.285	1.732	0.092	3.000, 0.092, 0.081
n=26	**Length**	2.218, 0.611	0.596	3.632	0.001	13.193, 0.001, 0.355
n=12	**$\delta^{15}N$**	0.348, 0.089	0.777	3.905	0.003	15.249, 0.003, 0.604
n=12	**$\delta^{13}C$**	1.087, 0.303	0.751	3.405	0.005	12.896, 0.005, 0.563
n=36 (Linear regression)	Ice-free days (i-1)*	-0.251, 0.234	-0.181	-1.075	0.290	1.156, 0.290, 0.033

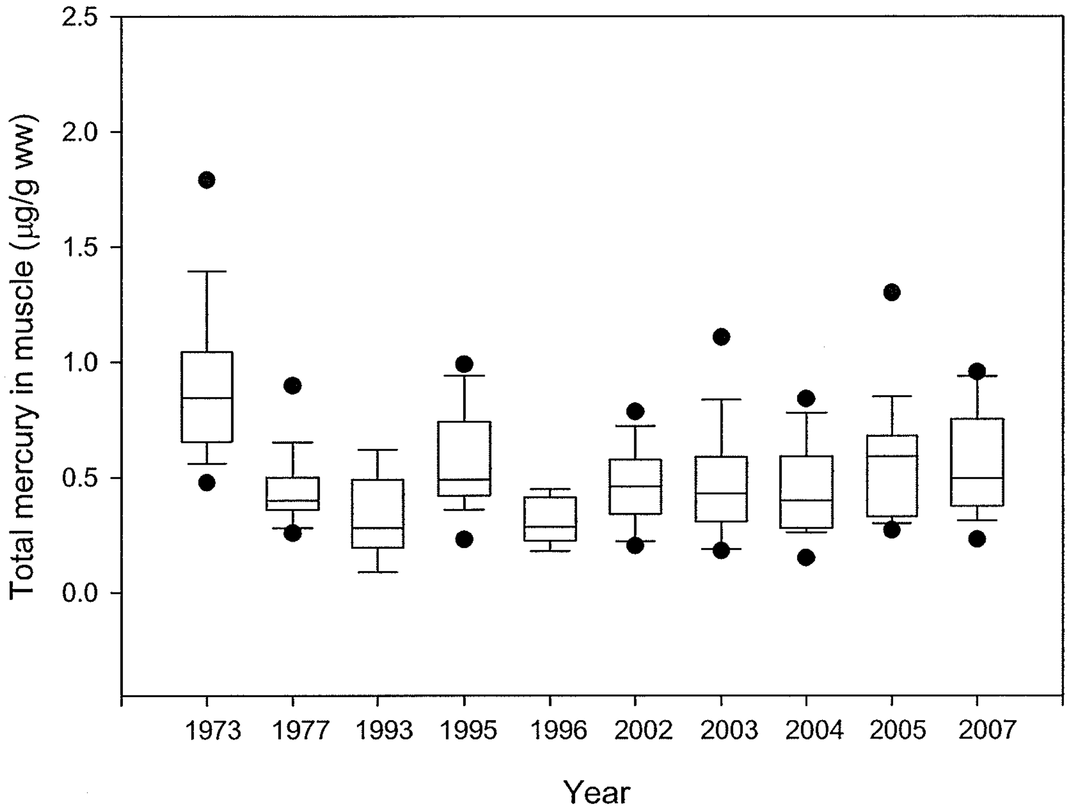
Note. Degrees of freedom: male adults (5,61), female adults (5,27), sub-adults (1,(n-2)).
**i* = year of sampling

Age significantly explained muscle THg in adults $\delta^{15}N$ (Table 2), and the regression models showed standard length significantly correlated with female adult and sub-adult muscle THg levels (Table 2). Muscle THg has correlated positively with $\delta^{15}N$ (Dietz et al. 2004), length (Loseto et al. 2008b), and age (Woshner 2001a) in Arctic marine mammals previously. Although longer summers appear linked to an increase in muscle THg in female adult ringed seals the following year, a curvilinear pattern best describes the relationship for adults and sub-adults as discussed in the next section.

$\delta^{13}C$ significantly explains sub-adult concentrations of muscle THg, indicating that the more prey consumed near inshore/benthic environments (Hobson and Welch 1992) will increase muscle THg in juveniles (Table 2). Sub-adults tend to dwell and forage in the periphery of core adult breeding/feeding areas, presumably to avoid the aggression of adult males maintaining their territories (Smith 1987, Beaufort Sea Seals 2008). The Pearson correlation showed $\delta^{13}C$ was not significant for adult concentrations of muscle THg.

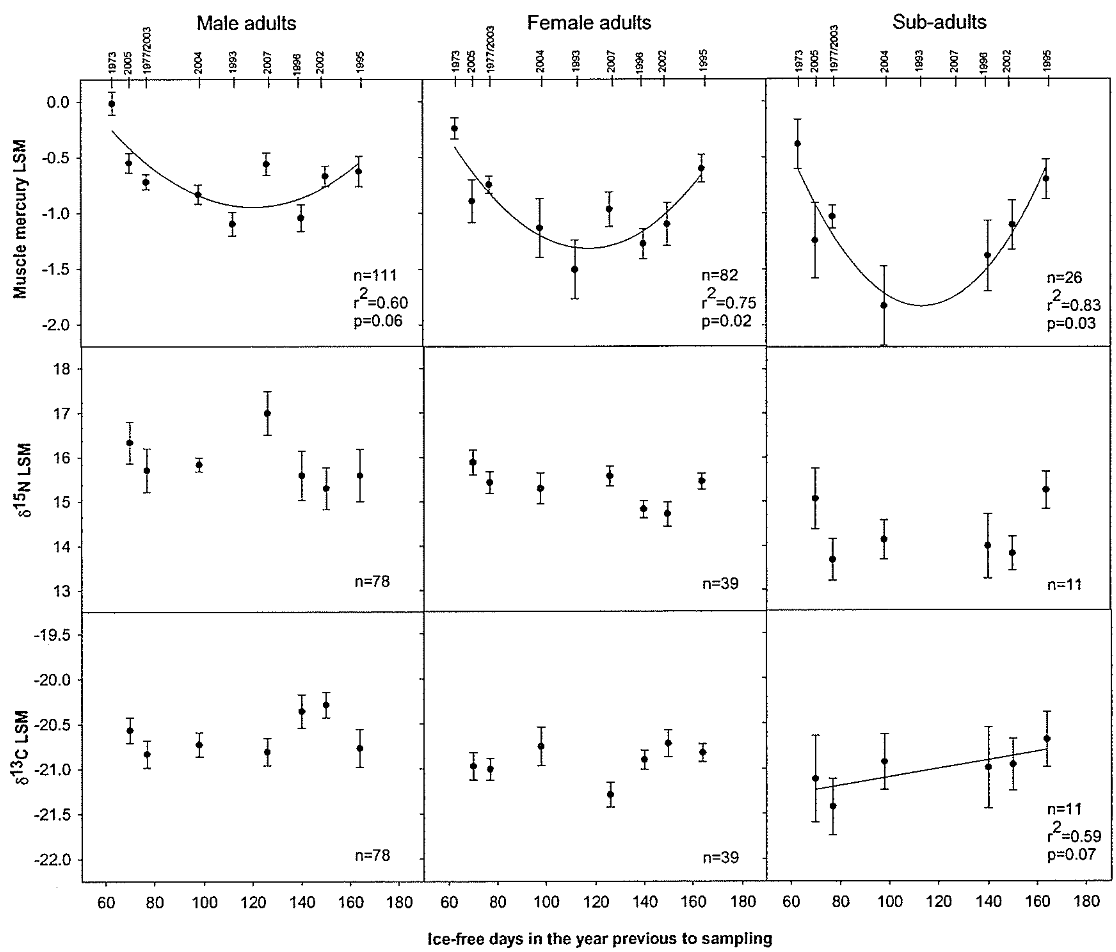
We plotted muscle THg by year to review temporal variation (Figure 2). An analysis of variance showed no significant differences between muscle THg concentrations in male adults, female adults and sub-adults ($F_{2,171}=2.45$, $p=0.09$), so we pooled all of these in Figure 2. No clear trends are evident.

Figure 2. Box and Whisker plot of wet weight (ww) mercury concentrations in muscle of all ringed seals excluding pups at Ulukhaktok, Northwest Territories, Canada.



Trends with sea ice. Muscle THg, $\delta^{15}N$ and $\delta^{13}C$ LSM for male and female adult and sub-adult ringed seals were plotted against the length of summer in the previous year (Figure 3). We included both age and length as covariates in producing ANCOVA least-square means for consistency in all age-sex classes. Muscle THg in all age-sex classes was strongly non-linearly associated with the length of the ice-free season in the previous year, significantly so for female adults and sub-adults. Both long and short summers (outside a narrow range of ~90-120 days) were followed by relatively high THg in the subsequent year.

Figure 3. Scatter plots of least-square means (LSM) and standard error bars of muscle THg, $\delta^{15}N$ and $\delta^{13}C$ in ringed seal male and female adults and sub-adults from Ulukhaktok (1973-2007) against total ice-free days in the year previous to sampling. The years that samples were collected are indicated at the top. Age and length were covariates in determining least-square means in the analysis of covariance. Curves were added for regressions with p<0.10. Curves are plotted for p<0.10 regression. 2nd-order polynomial fits are significant for muscle THg in female adults and sub-adults.



With the exception of $\delta^{13}C$ values in sub-adults, there were no strong trends of $\delta^{15}N$ and $\delta^{13}C$ against ice-free days in the previous year (Figure 3). The strong linear positive trend of sub-adult $\delta^{13}C$ with length of summer in the previous year may be explained by greater seasonal run-off carrying sediment loads in years with longer ice-free seasons (Macdonald et al. 2005). Near-shore foraging habits expose sub-adults closer to shore as land fast ice is removed. Coastal prey is enriched in $\delta^{13}C$ (Hobson and Welch 1992), and thus $\delta^{13}C$ in juveniles would most closely reflect terrestrial carbon inputs into the ocean.

Marine mammals accumulate mercury through the ecosystem directly from their diet (Atwell et al. 1998, Muir et al. 1999). Tissue isotopic turnover, related to protein turnover, and turnover of muscle THg (as methylmercury; Wagemann et al. 1997) in pinnipeds are currently unknown. To compare the timelines of THg, $\delta^{15}N$ and $\delta^{13}C$ incorporation into seal muscle tissue we used turnover rates from pigs as guidelines. Gyrd-Hansen (1981) reported a loss of 0.2ppm and 0.45ppm of muscle MeHg in 2 and 4 weeks, respectively, giving an average half-life of 110 days. Baumann et al. (1994) documented a muscle protein synthesis rate of 1.4%/day in pigs, or a half-life of approximately 50 days. Time taken to lose or replace 75% (2 half-lives) of original quantities is 3 months for protein/isotopes and 7.3 months for THg in muscle. As samples in this study were collected in June-July, this would represent March-April as the initial ^{15}N incorporation period and October-November for original THg exposure. Although in this study muscle THg and $\delta^{15}N$ were significantly positively correlated, this 4 month difference in turnover times between the two chemical biomarkers may explain our observations of a stronger trend of muscle THg with length of summer in the previous year compared to $\delta^{15}N$ (Figure 3) which is probably due to the heavy Arctic cod consumption in the fall (the time period the muscle THg reflects). In contrast, $\delta^{15}N$ reflects the end of winter, when Arctic cod stocks may be lower and their proportion of the ringed seal diet smaller. Over the study period the difference in average $\delta^{15}N$ for each age-sex class per year was not large enough to elucidate a full trophic level shift in prey (3.8‰; Hobson and Welch 1992).

The trends of muscle THg from June-July samples with the ice-free season (*i*-1) duration (Figure 3) suggest summer environmental conditions influence the composition of prey consumed by ringed seals during the following winter. Prior to freeze-up, adult ringed seals return to Prince Albert Sound from summer feeding grounds in Viscount Melville Sound to establish territories in the fall, remaining until break-up (Beaufort Sea Seals, 2008). Sub-adult selection of winter habitat is more variable; some stay in and around Prince Albert Sound while others move to Davis Strait or far east to the Chukchi Sea in the winter months (Beaufort Sea Seals, 2008). Therefore changes in muscle THg levels are most likely a reflection of a changing composition of local prey as opposed to changes in winter foraging locations.

To address the question as to how winter prey selection by ringed seals may have been affected by the previous summer, we first review the types of prey ringed seals feed upon in the winter. Ringed seals are opportunistic feeders, consuming Arctic fishes, crustaceans, squid and benthic invertebrates (Lowry et al. 1980, Smith 1987). Smith (1987) reports fish, particularly Arctic cod (*Boreogadus saida*) are the most frequently consumed item in all ages of Prince Albert Sound ringed seals during the ice-covered period. Other favourable prey items include hyperiid (i.e. *Parathemisto libellula*) and gammariid (i.e. *Anonyx nugax*) amphipods, ice-associated euphasiids (i.e. *Mysis oculata*), and smaller zooplankton like copepods (i.e. *Calanus hyperboreus*), which are also consumed by Arctic cod. Adults appear more skilled at securing cod which is a higher energy food (Smith and Harwood 2001). Lower trophic level organisms (i.e. zooplankton) have relatively low levels of mercury, and higher trophic level animals (i.e. Arctic cod, the preferred prey of seals) contain greater mercury concentrations (Stern and Macdonald 2005).

Variation in ringed seal muscle THg levels may result from prey's population age structure or migration. For example, Michaud et al. (1996) found that young-of-the-year Arctic cod survive better in warmer waters. With shorter summers, a larger percentage of Arctic cod larvae may die and thus leave older, more highly contaminated Arctic cod (Lockhart and Evans 1999) available for predators. Heavy ice years may also reduce the amount of food available for Arctic cod, leading to cannibalism (Hjermann et al. 2004) and associated higher mercury uptake. Loseto et al. (2008a) analyzed mercury content in prey species of beluga from the offshore and shelf environments of the southern Beaufort Sea. They found that within the offshore Amundsen Gulf, the prey species *T. libellula* was significantly higher in mercury compared to those in the continental shelf. In addition, offshore Arctic cod larger than 112mm were older and had relatively greater mercury and $\delta^{15}N$ values compared to Arctic cod on the shelf ecosystem. There was no difference in $\delta^{13}C$ between these two age classes. Findings from these studies suggest that, during winters following shorter summers, seals could be feeding upon Arctic cod that are older or migrate from the offshore waters in the Amundsen Gulf or elsewhere, increasing their exposure to high levels of mercury. In Alaska, Arctic cod have been observed moving into deeper, offshore water during summer (Moulton and Tarbox 1987). Arctic cod from the eastern Amundsen Gulf may also follow a similar movement into an offshore environment where some prey species (i.e. *Calanus hyperboreus* and *Metridia longa*) abound in deep water (Darnis et al. 2007).

Ringed seal mercury concentrations may also vary by the proportions of Arctic cod consumed in relation to lower trophic level prey. Here we consider factors affecting Arctic cod abundance in long summers. During years of earlier sea ice break-up, light penetration into the surface waters, along with sufficient nutrients, would allow for earlier and longer phytoplankton growth and thus greater food availability for herbaceous zooplankton (Bluhm and Gradinger 2008). Assuming phytoplankton and zooplankton cycles are synchronized, productivity could be carried through to zooplankton consumers and higher levels of the food chain (Carroll and Carroll 2003). Because they feed mostly upon pelagic and ice-associated zooplankton (Bradstreet and Cross 1982), Arctic cod populations would likely benefit from the earlier and extended phytoplankton growing seasons made possible by the longer ice-free periods. As discussed above, more Arctic cod larvae survive when hatching in warmer temperatures (Michaud et al. 1996). In addition, these conditions have been predicted to favour larvae prey, *Psuedocalanus* spp. (Darnis et al. 2007).

Harwood et al. (2000) observed greater body condition of Prince Albert Sound ringed seals after light ice years and suggested seals were consuming a greater quality or quantity of prey available when sea ice breaks early. We regressed blubber thickness against muscle THg in ringed seals and observed a positive significant relationship ($r=0.60$, F-ratio=7.36, p-value=0.02) in sub-adults (not significant for adults), thereby reinforcing our argument for greater muscle THg levels as a result of greater Arctic cod consumption after long summers.

Following long summers, we propose that the percentage of fish eaten by seals in the winter would increase as a result of greater Arctic cod survival in the previous summer, thus leading to higher mercury values. Gaston et al. (2003) also suggested increasing periods of open-water may be responsible for influencing the diet of seabirds in Hudson Bay.

Macdonald et al. (2005) suggested longer periods of open water, as a result of climate change, may allow more gaseous mercury to volatize from the ocean into the atmosphere. If mercury evasion exceeded atmospheric depletion, mercury concentrations would decrease from the water and biosphere (Macdonald et al. 2005). However, only the first half of Figure 3 (~40-90 ice-free days) supports this suggestion, after which mercury in seal muscle increases after longer summers. The effect of sea ice duration and extent on mercury cycling remains largely unstudied, although Cole (2008) reported no clear relationship between atmospheric mercury depletion events (AMDE) and coverage of sea ice at Alert from 1995-2000 and 2002-2007.

To summarize, yearly mercury trends in seal muscle may be best explained not by mercury fluctuations in the Arctic Ocean but by ecological dynamics that are influenced, at least in part, by length of the ice-free season. Factors which may lead to higher concentrations in increasingly shorter summers include consumption of higher contaminated prey; specifically this includes older Arctic cod cohorts, and/or fishes spending longer amounts of time in offshore ecosystems prior to winter. In contrast, increasingly longer summers may promote greater pelagic productivity leading to greater

Arctic cod survival for the winter. This may increase the proportion of cod eaten in the seal diet over the winter, effectively raising their mercury values. Here we see a non-linear trend of muscle THg with ice-free days (*i*-1). Ulukhaktok ringed seals have been monitored for 30+ years, comprising one of the oldest and largest datasets for the Arctic, yet we observed no significant temporal trend in muscle THg levels (Figure 2).

Here we have discussed sea ice patterns and contamination sources to ringed seals in a local context. Timing of sea ice break-up in the eastern Amundsen Gulf is determined principally by winds and not necessarily air temperature (Giovando and Herlinveaux 1981, Melling and Riedel 2005). Nevertheless, our work suggests that the net outcome of longer summers/shorter winters in the Arctic, as predicted from global warming, may result in increasing mercury levels in circumpolar seal populations in the future.

Acknowledgements

Thanks to John and Emma Alikamik and the seal harvesters and Hunters and Trappers Committee in Ulukhaktok, NT for providing the seal tissue samples, to Dr. Tom Smith for aging all seal teeth reported here, and to J. DeLaronde, G. Boila and A. MacHutchon for technical support. Funding was provided by the Natural Sciences and Engineering Research Council of Canada, the Fisheries Joint Management Committee, and ArcticNet.

References

Arctic Climate Impact Assessment (ACIA). *Impacts of a Warming Arctic*; Cambridge University Press: New York, 2004.

Armstrong, J.A.J.; Uthe, J.F. Semi-automated determination of mercury in animal tissue. *At. Abs. News.* **1971**, *10*, 101-103.

Atwell, L.; Hobson, K.A.; Welch, H.E. Biomagnification and bioaccumulation of mercury in an arctic marine food web: insights from stable N isotope analysis. *Can. J. Fish. Aquat. Sci.* **1998**, *55*, 1114-1121.

Baumann, P.Q.; Stirewalt, W.S.; O'Rourke, B.D.; Howard, D.; Nair, K.S. Precursor tools of protein synthesis: a stable isotope study in a swine model. *Am. J. Endocrinol. Metab.* **1994**, *267*, 203-209.

Beaufort Sea Seals-Research and Monitoring. www.beaufortseals.com/telemetry.htm (accessed September 29, 2008).

Bluhm, B.A.; Gradinger, R. Regional variability in food availability for Arctic marine mammals. *Ecol. Appl.* **2008**, *18 (Supplement),* S77-S96.

Bradstreet, M.S.W.; Cross, W.E. Trophic relationships at high arctic ice edges. *Arctic* **1982**, *35*, 1-12.

Braune, B.M.; Outridge, P.M.; Fisk, A.T.; Muir, D.C.G.; Helm, P.A.; Hobbs, K.; Hoekstra, P.F.; Kuzyk, Z.A.; Kwan, M.; Letcher, R.J.; Lockhart, W.L.; Norstrom, R.J.; Stern G.A.; Stirling, I. Persistent organic pollutants and mercury in marine biota of the Canadian Arctic: An overview of spatial and temporal trends. *Sci. Total Environ.* **2005**, *351-352*, 4-56.

Braune, B.M. Temporal trends of organochlorines and mercury in seabird eggs from the Canadian Arctic, 1975-2003. *Environ. Pollut.* **2007**, *148*, 599-613.

Campbell, L.M.; Norstrom, R.J.; Hobson, K.A.; Muir, D.C.G.; Backus, S.; Fisk, A.T. Mercury and other trace elements in a pelagic Arctic marine food web (Northwater Polynya, Baffin Bay). *Sci. Total Environ.* **2005**, *351-352*, 247-263.

Carmack, E.C.; Macdonald, R.W. Oceanography of the Canadian Shelf of the Beaufort Sea: A setting for marine life. *Arctic* **2002**, *55(Supplement 1)*, 29-45.

Carroll, M.L.; Carroll, J. The Arctic Seas. In *Biogeochemistry of Marine Systems*; Black, K.D., Shimmield, G.B., Eds.; CRC Press: Boca Raton, 2003; p 127-156.

Cole, A. Effects of climate change on atmospheric mercury depletion in the Canadian Arctic. Arctic Change 2008 Conference, December 9-12, 2008, Quebec City, QC Canada. Session details and abstract available at http://www.arctic-change2008.com/

Darnis, G.; Barber, D.B.; Fortier, L. Sea ice and the onshore-offshore gradient in pre-winter zooplankton assemblages in southeastern Beaufort Sea. *J. Mar. Syst.* **2007**, doi:10.1016/j.jmarsys.2007.09.003.

Dehn, L.A.; Sheffield, G.G.; Follmann, E.H.; Lawrence, K.D.; Thomas, D.L.; Bratton, G.R.; Taylor, R.J.; O'Hara, T. Trace elements in tissues of phocid seals harvested in the Alaskan and Canadian Arctic: influence of age and feeding ecology. *Can. J. Zool.* **2005**, *83*, 726-746.

Dietz, R.; Riget, F.; Hobson, K.A.; Heide-Jørgensen, M.P.; Møller, P.; Cleemann, M.; De Boer, J.; Glasius, M. Regional and inter annual patterns of heavy metals, organochlorines and stable isotopes in narwhals (*Monodon monoceros*) from West Greenland. *Sci. Total Environ.* **2004**, *331*, 80-105.

France, R.L.; Peters, R.H. Ecosystem differences in the trophic enrichment of ^{13}C in aquatic food webs. *Can. J. Fish. Aquat. Sci.* **1997**, *54*, 1255-1258.

Folch, J.; Lees, M.; Stanley, G.H.S. A simple method for the isolation and purification of total lipids from animal tissues. *J. Biol. Chem.* **1957**, *226*, 497-509.

Gaskin, D.E.; Ishida, K.; Frank, R. Mercury in harbour porpoises (*Phocoena phocoena*) from the Bay of Fundy region. *J. Fish. Res. Board Can.* **1972**, *29*, 1644-1645.

Gaston, A.J.; Woo, K.; Hipfner J.M. Trends in forage fish populations in northern Hudson Bay since 1981, as determined from the diet of nestling thick-billed murres, *Uria lomvia*. *Arctic* **2003**, *56*, 227-233.

Giovando, L.F.; Herlinveaux, R.H. *A Discussion of Factors Influencing Dispersion of Pollutants in the Beaufort Sea. Report 81-4*; Institute of Ocean Sciences: Sidney, British Columbia, 1981.

Gyrd-Hansen, N. Toxicokinetics of methyl mercury in pigs. *Arch. Toxicol.* **1981**, *48*, 173-181.

Harwood, L.A.; Smith, T.G.; Melling, H. Variation in reproduction and body condition of the ringed seal (*Phoca hispida*) in western Prince Albert Sound, NWT, Canada, as assessed through a harvest-based sampling program. *Arctic* **2000**, *53*, 422-431.

Hjermann, D.Ø.; Stenseth, N.C.; Ottersen, G. The population dynamics of Northeast Arctic cod (*Gadus morhua*) through two decades: an analysis based on survey data. *Can. J. Fish. Aquat. Sci.* **2004**, *61*, 1747-1755.

Hobson, K.A.; Welch, H.E. 1992. Determination of trophic relationships within a high

Arctic marine food web using $\delta^{13}C$ and $\delta^{15}N$ analysis. *Mar. Ecol. Prog. Ser.* **1992**, *84*, 9-18.

Intergovernmental Panel on Climate Change (IPCC). *Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Pachauri, R.K., Reisinger, A., Eds.; IPCC: Geneva, Switzerland, 2007.

Kurle, C.M.; Worthy, G.A.J. Stable nitrogen and carbon isotope ratios in multiple tissues of the northern fur seal *Callorhinus ursinus*: implications for dietary and migratory reconstructions. *Mar. Ecol. Prog. Ser.* **2002**, *236*, 289-300.

Lockhart, W.L.; Evans, M. Mercury in Fish from Stock Surveys of Lakes in the Western Northwest Territories: Investigations into the Factors Affecting Mercury Levels. In *Synopsis of research conducted under the 1999/2000 Northern Contaminants Program, R71-19-2000E.* Kalhok, S., Ed.; Indian and Northern Affairs Canada: Ottawa, 2000; p 181-90.

Lockhart, W.L.; Stern, G.A.; Wagemann, R.; Hunt, R.V.; Metner, D.A.; DeLaronde, J.; Dunn, B.; Stewart, R.E.A.; Hyatt, C.K.; Harwood, L.; Mount, K. Concentrations of mercury in tissues of beluga whales (*Delphinapterus leucas*) from several communities in the Canadian Arctic from 1981 to 2002. *Sci. Total Environ.* **2005**, *351-352*, 391-412.

Loseto, L.L.; Stern, G.A.; Deibel, D.; Connelly, T.L.; Prokopowicz, A.; Lean, D.R.S.; Fortier, L.; Ferguson, S.H. Linking mercury exposure to habitat and feeding behaviour in Beaufort Sea beluga whales. *J. Marine Syst.* **2008a**, *74*, 1012-1024.

Loseto, L.L.; Stern, G.A.; Ferguson, S.H. Size and biomagnification: how habitat selection explains beluga mercury levels. *Environ. Sci. Tech.* **2008b**, *42*, 3982-3988.

Lowry, L.F.; Frost, K.J.; Burns, J.J. Variability in the diet of ringed seals, *Phoca hispida*, in Alaska. *Can. J. Fish. Aquat. Sci.* **1980**, *37*, 2254-2261.

Macdonald, R.W.; Harner, T.; Fyfe, J. 2005. Recent climate change in the Arctic and its impact on contaminant pathways and interpretation of temporal trend data. *Sci. Total Environ.* **2005**, *342*, 5-86.

Melling, H.; Riedel, D.A. Trends in the draft and extent of seasonal pack ice, Canadian Beaufort Sea. *Geophys. Res. Lett.* **2005** *32*, L24501, doi:10.1029/2005GL024483.

Michaud, J.; Fortier, L.; Rowe, P.; Ramseier, R. Feeding success and survivorship of Arctic cod larvae, *Boreogadus saida*, in the Northewaster Water polynya (Greenland Sea). *Fish. Oceanogr.* **1996**, *5*, 120-135.

Moulton, L.L.; Tarbox, K.E. Analysis of Arctic cod movements in the Beaufort Sea near-shore region, 1978-1979. *Arctic* **1987**, *40*, 43-49.

Muir, D.; Braune, B.; DeMarch B.; Norstrom, R.; Wagemann, R.; Lockhart, L.; Hargrave, B.; Bright, D.; Addison, R.; Payne, J.; Reimer, K. Spatial and temporal trends and effects of contaminants in the Canadian Arctic marine ecosystem: a review. *Sci. Total Environ.* **1999**, *230*. 83-144.

Outridge, P.M.; Macdonald, R.W.; Wang, F.; Stern, G.A.; Dastoor, A.P. A mass balance inventory of mercury in the Arctic Ocean. *Environ. Chem.* **2008**, *5*, 89-111.

Peterson, B.J.; Fry, B. Stable isotopes in ecosystem studies. *Annu. Rev. Ecol. Syst.* **1987**, *18*, 293-320.

Riget, F.; Muir, D.; Kwan, M.; Savinova, T.; Nyman, M.; Woshner, V.; O'Hara, T. Circumpolar pattern of mercury and cadmium in ringed seals. *Sci. Total Environ.* **2005**, *351-352*, 312-322.

Smith, T.G. Population dynamics of the ringed seal in the Canadian Eastern Arctic. *Bull. Fish. Res. Board Can.* **1973**, *181*, 55p.

Smith, T.G.; Armstrong, F.A.J. Mercury in seals, terrestrial carnivores, and principal food items of the Inuit, from Holman, N.W.T. J. *Fish. Res. Board Can.* **1975**, *32*, 795-801.

Smith, T.G.; Armstrong, F.A.J. Mercury and selenium in ringed and bearded seal tissues from Arctic Canada. *Arctic* **1978**, *31*, 75-84.

Smith, T.G. The Ringed Seal, *Phoca hispida*, of the Canadian western Arctic. *Can. Bull. Fish. Aquat. Sci.* **1987**, *216*, 81p.

Smith, T.G.; Hammill, M.O.; Taugbøl, G. A review of the developmental, behavioural and physiological adaptations of the ringed seal, *Phoca hispida*, to life in the arctic winter. *Arctic* **1991**, *44*, 124-131.

Smith, T.G.; Harwood, H.A. Observations of neonate ringed seals, *Phoca hispida*, after early break-up of the sea ice in Prince Albert Sound, Northwest Territories, Canada, spring 1998. *Polar Biol.* **2001**, *24*, 215-219.

Stern, G.A.; Macdonald, R.W. Biogeographic provinces of total and methyl mercury in zooplankton and fish from the Beaufort and Chukchi Seas: results from the SHEBA drift. *Environ. Sci. Technol.* **2005**, *39*, 4707-4713.

Stewart, R.E.A.; Stewart, B.E.; Stirling, I.; Street, E. Counts of growth layer groups in cementum and dentine in ringed seals (*Phoca hispida*). *Mar. Mammal Sci.* **1996**, *12*, 383-401.

Wagemann, R.; Trebacz, E.; Hunt, R.; Boila, G. Percent methylmercury and organic mercury in tissues of marine mammals and fish using different experimental and calculation methods. *Environ. Toxicol. Chem.* **1997**, *16*, 1859-1866.

Woshner, V.M.; O'Hara, T.M.; Bratton, G.R.; Suydam, R.S.; Beasley, V.R. Concentrations and interactions of selected essential and non-essential elements in bowhead and beluga whales of arctic Alaska. *J. Wildl. Dis.* **2001a**, *37*, 693-710.

Woshner, V.M.; O'Hara, T.M.; Bratton, G.R.; Beasley, V.R. Concentrations and interactions of essential and non-essential elements in ringed seals and polar bears of arctic Alaska. *J. Wildl. Dis.* **2001b**, *37*, 711-721.

Chapter 3 - Organochlorine contaminant trends in western Canadian Arctic ringed seals (*Phoca hispida*)

Abstract

Measuring contaminants in Arctic marine mammals over time is important to establish baseline information, recognize trends, and, to a certain degree, predict future concentrations. In this study, blubber samples of ringed seals (*Phoca hispdia*) collected over the 12 year period from 1993-2005 in the western Canadian Arctic were analyzed for organochlorine contaminants (OCs), both pesticides and polychlorinated biphenyls (PCB). Results showed age and blubber thickness were the most important biological variables influencing OC levels. Male adults ($\geq$7 y) had the highest concentrations compared to female adults and sub-adults (1-6 y). Stable isotope ratios $\delta^{15}N$ and $\delta^{13}C$ in muscle did not appear to relate to OC levels. α–HCH (hexachlorocyclohexane) and ΣPCB decreased significantly throughout the study period for male adults; female adults showed significant declines in ΣCHB (chlorobornane). Additionally, *p,p'*-DDE/ΣDDT increased strongly in both male and female adults over the 12-year study period. Results indicate an overall decrease in chlorinated organic contaminant levels.

Introduction

To evaluate and predict the impacts of climate change on present and future marine mammal stocks, time-based biological and ecological data are required. Arctic marine mammals are particularly exposed to changes in habitat and diet (Tynan and DeMaster 1997, Laidre et al. 2008) as a result of decreasing sea ice coverage and duration (Serreze et al. 2007, Walsh 2008). Such consequences may lead to changes in contaminant exposure (Burek et al. 2008). Organochlorine contaminant (OC) levels in ringed seals (*Phoca hispida*) from Ulukhaktok (formerly Holman), Northwest Territories, Canada were first studied in 1971 (Addison and Smith 1986) and have generally decreased until 2001 (Addison and Smith 1998, Muir et al. 2001), but the extent of increased warming predicted by future scenarios [Intergovernmental Panel on Climate Change (IPCC)] may encourage increased rates of worldwide OC transport to the Arctic (Macdonald et al. 2005, Dalla Valle et al. 2007).

It is because OCs are environmentally stable (resistant to degradation) that they can travel long distances to the Arctic in the atmosphere and oceans, originating from agricultural and industrial sources. Volatile compounds are regulated in the marine ecosystem by air-water partitioning properties. Alpha and beta isomers of HCH (hexachlorocyclohexane) make their way to the Arctic mainly by oceanic transport, more recently for α-HCH (Wania and Mackay 1999, Li et al. 2004). For other organic pesticides such as chlordane, chlorobornanes and DDTs (dichlorodiphenyl-trichloroethane) and industrial waste like chlorobenzenes and polychlorinated biphenyls (PCBs) the main mechanism of transport is through the atmosphere (Bidleman et al. 1989, Barrie et al. 1992, Bidleman et al. 2004). Eventually these deposit on snow and ice surfaces or directly into water bodies (Wania et al. 1998).

OCs are also easily taken up by organisms. These contaminants are lipophilic, possessing large octanol-water partition coefficients (K_{ow}). Such properties allow them to easily bind to lipids in organisms by means of water partitioning (i.e. zooplankton; Fisk et al. 2001) and bioaccumulation in higher trophic levels such as seals (Addison and Smith 1998).

Marine mammals contain large reserves of lipid-rich blubber and are prone to heavy OC burdens (Muir et al. 1992). OCs have demonstrated toxic effects at high concentrations, causing adverse reproductive and immunosuppressive effects. These include abortions, miscarriages, stillbirths, tumours, chronic ulcers, infections, and hormone disruption in marine mammals (Bergman and Olsson 1985, Reijnders 1986, Ross et al. 1996, Reddy et al. 2001, Mos et al. 2007).

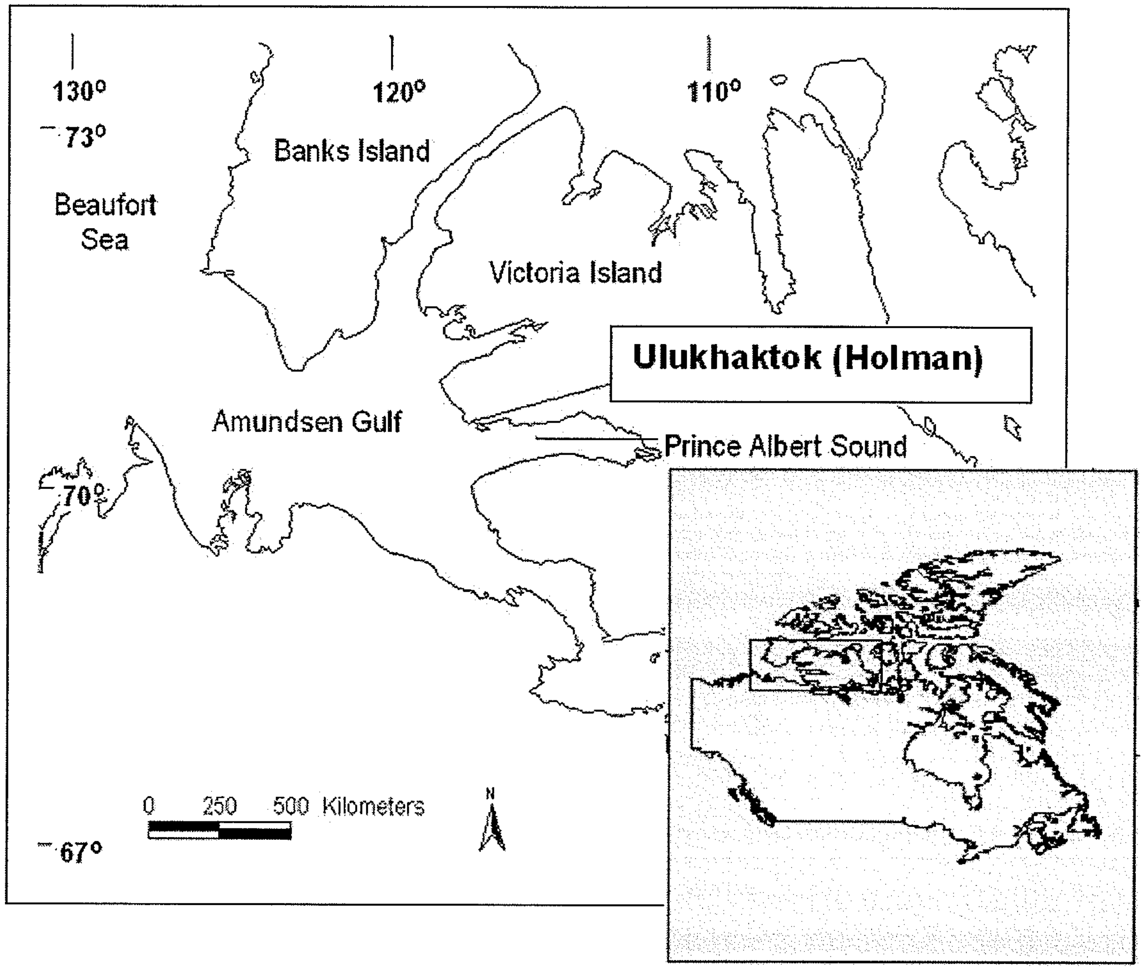
When passed on for human consumption, marine mammal tissues expose consumers to OCs and associated health risk. PCBs and chlorobornanes are known carcinogens (Van Oostdam et al. 2005) and metabolites of DDT influence endocrine disruption (Kelce et al. 1995). The hunting and consumption of country foods is an essential aspect of the Aboriginal culture, and thus monitoring contaminant levels in marine mammals is vital for regulating consumption guidelines for healthy communities.

Focusing on the Ulukhaktok ringed seals, OC concentrations from 1993-2005 blubber samples were analyzed. A select group of contaminants were reviewed with respect to biological variables, such as age and sex of the seals, and on a temporal basis. $\delta^{15}N$ and $\delta^{13}C$ in muscle tissue were included in this analysis to evaluate changes in diet and associated biomagnification of organic contaminants (Hobson and Welch 1992, Borgå et al. 2004).

Methods

Field methods and aging. Members of the Hunters and Trappers Committee in Ulukhaktok (formerly Holman), NT harvested ringed seals from the Mashooyak area near Ulukhaktok located along the NW shore of Prince Albert Sound on Victoria Island (Figure 1). Out of an annual harvest of ~100 seals, 18-22 seal samples in 1995 and 2002-

Figure 1. Ringed seal (*Phoca hispida*) sampling location at Mashooyak, south of Ulukhaktok (formerly Holman; 70°43'N, 117°43'W), Northwest Territories, Canada. Here hunters collected the samples eastward along approximately 70km of the Prince Albert Sound shore.



2005 and 14 samples in 1993 were used for contaminant analyses in this study. All were harvested in June and July. These samples approximated 20% of all the seals inventoried annually in the marine mammal harvest-based sampling program (Harwood et al. 2000).

Sex, standard length (nose to the base of the tail; American Society of Mammalogists, 1967), weight (without correcting for blood loss), and blubber thickness at the hip were measured for each seal (Harwood et al 2000). Lower mandibles were collected for aging purposes. Blubber and muscle tissue were kept at $\leq$-20°C and shipped to Winnipeg for chemical analyses.

Ages for the samples were determined counting growth layer groups (GLG) in the dentine layer of lower canines (Smith 1973). Although Stewart et al. (1996) indicate counts of dentinal GLG tend to underestimate ages of seals >10 years compared to those of cementum layers, the same aging method (dentinal) was used for the 1990s and 2000s ringed seal samples as for those sampled the 1970s for consistency in long-term studies (i.e. see Harwood et al. 2000).

Chemical analysis. Lipids from the blubber samples were extracted for OCs and analysed as previously described by Muir et al. (1990). Briefly, hexane and dried Na_2SO_4 were added to each blubber sample, and then the mixture was ball-milled and centrifuged twice. The extract was weighed for determination of lipid content. Approximately 0.1g of lipid in 1ml of the extract was poured into a glass, Florisil-filled column. Subsequently three solvents (hexane, 85:15 hexane to dichloromethane, and 50:50 hexane to dichloromethane) were separately poured into the column to flush out compounds of increasing polarity from the extract into three separate fractions. A gas chromatograph (GC) unit with a 60x0.25mm i.d. DB-5 column and a ^{63}Ni ECD (electron capture detection) was used to analyze these fractions. External standards from Ultra Scientific (North Kingston, Rhode Island) were used to measure the concentrations of the samples. The unit could detect concentrations of 0.1ng/g lipid weight and higher. Duplicates, blanks, recovery standards (PCB 30/octachloronapthalene) and volume correction (adding Aldrin prior to GC) were measures taken for quality control. Average PCB30/octachloronapthalene recovered was 80%.

Overall, 177 individual chromatographic peaks were quantified representing 4 chlorobenzenes, 47 pesticides, 35 chlorobornanes and 91 polychlorinated biphenyl (PCB) congeners per sample. Pesticide groups included hexachlorocyclohexane (HCH), chlordanes (CHL), dichlorodiphenyltrichloroethane (DDT), endosulfan, dieldrin, endirn, mirex, methoxychlor and mirex. Concentrations were later normalized to 100% lipid.

$\delta^{15}N$ and $\delta^{13}C$ were analyzed from lipid-extracted muscle tissue to prevent bias with interpreting $\delta^{13}C$ (Kelly 2000, Kurle and Worthy 2002). Methods describing the preparation and analysis are based Folch et al. (1957). Briefly, lipids were extracted from 0.2g muscle by exposing the tissue to a 2:1 chloroform/methanol mixture for 18 hours, followed by centrifugation and removal of solution. The procedure was repeated thrice with only 1-2 hours of soaking and mixing each time. Afterwards samples were dried and sent to the University of Winnipeg Stable Isotope Laboratory for Continuous Flow Ion Ratio Mass Spectroscopy (CFIR-MS). Isotopes presented in this paper are in units of *per mil* (‰) with δ (delta) notation. $\delta^{15}N$ and $\delta^{13}C$ are the product of

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

with R representing the ratio of heavy to light isotope ($^{15}N/^{14}N$ or $^{13}C/^{12}C$) in both the sample and the standard.

Statistical analysis. All compounds are listed in Table 1. Ten OC pesticides (including chlorobornanes), 9 PCB congeners and 6 major summed OC groups (ΣCBz (chlorobenzene), ΣHCH (hexachlorocyclohexane), ΣCHL (chlordane), ΣDDT (dichlorodiphenyl-trichloroethane), ΣCHB (chlorobornane) and ΣPCB) were studied in detail for each age-sex class per year. Of these, 8 individual OC pesticides, 5 PCB congeners and the same 6 major groups were chosen for statistical analyses. These compounds are first listed in Table 2 and here after referred to as 'the 19 OCs'. Compounds/congeners were chosen on the basis of (1) their importance (i.e. large proportions) in the OC profile, (2) representation of differing chemical properties (i.e. hydrophobicity) and (3) their reference given in previous Arctic OC studies with which to compare results. Upon statistical analysis all variables were log-transformed for normal distribution of data. Statistical significance was considered $\alpha \leq 0.05$.

The biological and ecological variables which significantly influenced the levels in the 19 OCs in age-sex classes of ringed seals were assessed using Pearson correlation. Biological variables included age, standard length, weight and blubber thickness at hip. $\delta^{15}N$ and $\delta^{13}C$ provided as ecological data. Except for $\delta^{15}N$ and $\delta^{13}C$ (which were already normally distributed), all variables were log-transformed to have normal distributions.

Analysis of covariance (ANCOVA) was conducted on age-sex classes of the seals with the 19 OCs to compare overall concentrations among the classes. Sex, age, blubber thickness and year are important variables affecting OC concentrations in marine mammal blubber (Aguilar 1987, Addison 1989, Hutchinson and Simmonds 1994). Statistical analysis was performed separately on each of 3 age-sex classes: (1) male and (2) female adult ringed seals ($\geq$7 y) and (3) sub-adults (1-6 y) based on the categorization used by Harwood et al. (2000). Sub-adults were pooled together regardless of sex (Harwood et al. 2000). Additionally, Cameron et al. (1997) found the concentrations of PCBs did not differ significantly between male and female seals less than 6 y old. In this study, age, blubber thickness and year were used as covariates in the ANCOVA to account for the remaining variability these introduced into the dataset.

Because age and blubber thickness can significantly affect OC concentrations in marine mammal blubber, the effects of various biological variables needed assessment so as to accurately evaluate contaminant-based temporal trends. The 19 OCs were individually placed into a generalized linear model (GLM) using year, age and blubber thickness as explanatory variables:

$$OC = \mu + \text{Year} + \text{Age} + \text{Blubber thickness} + \varepsilon$$

where μ is a constant ε is the error term. This calculated the least-square means (LSM) of the OC concentrations for each year. Linear regression evaluated the strength of these OC LSM temporal trends. In addition, ratios of CB153/ΣPCB, ppDDE/ΣDDT and oxychlordane/ΣCHL were selected to examine temporal variation with recalcitrant OCs with respect to similar chemical-structured groups. The fraction of *trans*-chlordane relative to the sum of *trans*- and *cis*-chlordane [*trans*-chlordane/(*trans*-chlordane + *cis*-chlordane)] known as F_{TC} was regressed against year to examine how sources of chlordane may have changed over the study period.

Results and Discussion

OC concentrations, $\delta^{15}N$ and $\delta^{13}C$ among age-sex classes. Together samples from all years comprised 67 male adults, 32 female adults, 14 sub-adults and one pup totalling 114 ringed seals. Age, blubber thickness, percent lipid, $\delta^{15}N$, $\delta^{13}C$ and concentrations (±standard error) of the 19 OCs are presented by age-sex class and year in Table 1. Average lipid from blubber in ringed seals from this study was 90% and was similar to the 84% reported in Beaufort/Chukchi Sea ringed seals by Hoekstra et al. (2003). The 10 individual OC pesticide compounds (including chlorobornane congeners) and 9 PCB congeners contributed ~70% and 56% of total OC pesticides and PCBs measured, respectively.

OC concentrations, $\delta^{15}N$ and $\delta^{13}C$ varied by age-sex class. The one pup had the highest $\delta^{15}N$ and $\delta^{13}C$ values, followed by male adults, female adults and then sub-adults. Male adults generally had the greatest levels of chlorobenzene, chlordane, DDT, chlorobornane, dieldrin, and PCBs, whereas the pup or sub-adults contained the lowest concentrations of these compounds. Sub-adult concentrations of HCHs and CB 28 were highest among all other classes. The pup had the highest levels of CB 105 and the 2nd highest levels of *trans*-nonachlor, heptachlor epoxide, ΣCHL, CB 31 and 52. Female adult concentrations of OCs were usually second in magnitude to male adults but were lowest among all classes for heptachlor epoxide, CHB T2 and CB 105. The highest ΣPCB concentration was 3056 ng/g lipid weight from a 1993 male adult seal, and this was much lower than the threshold observed for immunosuppressive effects in captive harbour seals (17,000 ng/g lipid weight; Ross et al. 1995, 1996).

Table 1. Means (standard error) and ranges of select individual and major organochlorine groups per age-sex class of ringed seals (*Phoca hispida)* per year in Ulukhaktok, Canada. Concentrations are expressed in ng/g lipid weight.

Year	1993	1993	1995	1995	1995	2002
Class	Male adults	Female adults	Male adults	Female adults	Sub-adults	Male adults
n	10	4	7	9	4	13
Age	17.2 (2.72)	12.0 (2.9)[a]	12.5 (1.78)[a]	13.4 (1.7)	5.5 (0.5)	15.23 (1.56)
	7-36	7-17	7-17	12-17	4-6	7-26
Blubber thickness	2.97 (0.17)[a]	3.63 (0.19)[a]	3.5 (0.27)	3.14 (0.30)	3.63 (0.24)	2.89 (0.14)
(cm)	2-3.8	3.4-4.0	2.5-4.5	2.0-4.5	3.0-4.0	2-4
% lipid	88.44 (0.77)	91.17 (0.83)	90.59 (1.54)	90.99 (0.69)	92.88 (2.46)	89.86 (0.89)
	84.72-93.35	89.41-93.35	83.35-96.80	88.75-93.43	88.55-98.60	83.19-93.30
$\delta^{15}N$ (‰) (muscle)			15.47 (0.17)	15.41 (0.16)	15.66 (0.26)	15.17 (0.17)
			14.76-16.27	14.77-16.35	15.07-16.12	14.06-16.42
$\delta^{13}C$ (‰) (muscle)			-20.70 (0.11)	-20.80 (0.10)	-20.78 (0.15)	-20.31 (0.12)
			-21.06-(-)20.33	-21.26-(-)20.39	-21.10-(-)20.50	-21.08-(-)19.48
ΣCBz	169.92 (21.95)	86.06 (9.22)	139.30 (31.26)	55.86 (5.53)	73.93 (8.72)	104.95 (13.23)
	72.09-257.29	67.10-110.74	65.61-290.09	31.66-76.67	54.77-95.67	46.24-188.74
α-HCH	343.17 (94.16)	212.85 (38.17)	172.19 (22.96)	150.88 (10.48)	125.43 (17.82)	167.62 (13.73)
	90.06-1115.74	154.30-324.82	66.95-248.21	98.16-187.45	77.22-160.28	97.08-269.71
β-HCH	77.00 (7.50)	48.52 (4.99)	42.07 (6.40)	31.01 (9.00)	32.52 (2.66)	78.34 (8.17)
	47.54-122.37	38.24-61.82	21.93-66.72	19.07-102.58	28.80-40.41	24.55-139.23
ΣHCH	437.88 (104.57)	271.27 (41.51)	226.59 (28.07)	224.55 (48.26)	162.18 (19.29)	282.93 (24.54)
	162.78-1319.21	204.51-392.19	100.01-326.02	125.48-600.53	110.33-195.58	173.06-449.15
trans-nonachlor	267.79 (73.84)	85.57 (17.41)	177.91 (57.71)	116.47 (27.34)	58.10 (15.26)	147.14 (47.13)
	63.65-816.79	44.88-121.29	53.03-482.88	31.82-259.92	37.46-102.32	34.14-681.70
oxychlordane	609.23 (181.75)	128.95 (59.44)	194.67 (52.85)	137.32 (61.38)	74.12 (42.06)	359.97 (82.57)
	50.81-2025.32	49.84-305.98	51.86-456.87	23.03-510.37	24.22-199.95	71.17-1165.71
heptachor epoxide	100.90 (23.02)	42.10 (11.34)	99.41 (35.04)	49.81 (15.00)	33.72 (11.63)[a]	65.42 (13.40)
	27.08-286.14	26.58-75.44	27.59-302.14	17.97-162.77	21.81-56.98	11.07-202.30
ΣCHL	1224.91 (279.69)	436.29 (60.73)	699.41 (136.73)	452.70 (124.97)	242.59 (66.38)	717.43 (150.71)
	265.98-3403.20	261.69-535.88	224.93-1260.18	128.40-1292.44	159.58-440.37	269.67-2340.35

Table 1. (continued)

Year	1993	1993	1995	1995	1995	2002
Class	Male adults	Female adults	Male adults	Female adults	Sub-adults	Male adults
n	10	4	7	9	4	13
p,p'-DDT	420.77 (115.89)	198.58 (81.03)	191.96 (44.43)	127.01 (58.53)	65.90 (39.00)	195.48 (38.02)
	39.17-115.71	48.03-343.80	20.22-393.88	<0.1-567.51	17.77-182.24	23.78-517.90
p,p'-DDE	1088.82 (248.01)	341.19 (71.57)	591.13 (167.31)	274.28 (90.33)	185.11 (17.70)	585.05 (132.01)
	47.72-2103.26	167.81-484.45	198.62-1490.07	57.82-837.69	149.44-220.54	150.10-1521.64
ΣDDT	1894.44 (461.29)	648.29 (181.58)	903.78 (242.16)	457.39 (149.67)	294.61 (41.13)	893.04 (185.44)
	264.03-4325.65	264.42-983.83	265.08-2189.41	142.95-1477.46	209.81-404.46	193.12-2313.21
CHB B6-923	755.70 (266.25)	131.74 (97.17)	132.42 (53.60)	68.48 (46.86)	69.40 (54.38)	457.39 (121.50)
	8.58-2763.82	6.58-420.99	11.65-344.95	7.01-441.41	11.79-232.50	12.02-1596.25
CHB B8-1413 (T2)[b]	74.77 (31.49)	14.88 (10.71)	32.46 (8.45)	10.67 (2.18)	28.97 (20.18)	39.45 (11.63)
	<0.1-327.91	1.67-46.88	3.86-66.96	1.82-20.78	7.63-89.45	7.43-167.90
ΣCHB	1611.46 (431.56)	623.80 (198.37)	699.33 (168.73)	298.69 (80.19)	273.67 (67.50)	962.97 (194.04)
	401.96-4834.83	161.52-1046.37	151.41-1437.06	117.74-925.48	167.40-471.31	211.77-2924.22
Dieldrin	122.28 (21.85)	50.49 (14.53)	278.50 (190.28)	333.78 (279.08)	43.26 (4.66)[a]	481.40 (281.50)
	17.80-218.07	21.88-89.27	29.31-1415.14	21.63-2565.29	35.41-51.54	31.51-3635.47
CB 28	6.95 (2.17)	7.59 (2.38)	9.34 (2.05)	3.21 (0.91)	6.37 (0.37)	3.31 (1.75)
	<0.1-15.68	0.60-10.82	<0.1-15.17	<0.1-7.65	5.55-7.19	<0.1-21.98
CB 31	29.61 (7.73)	3.29 (2.36)	22.02 (14.17)	7.87 (7.52)	3.04 (3.04)	31.94 (7.01)
	<0.1-59.12	<0.1-10.00	<0.1-91.06	<0.1-68.02	<0.1-12.15	<0.1-100.39
CB 52	20.83 (6.05)	20.83 (14.06)	26.61 (5.75)	10.99 (3.71)	8.44 (0.61)	14.46 (2.65)
	4.62-61.21	<0.1-62.14	6.99-48.98	<0.1-37.00	7.06-10.04	2.96-34.75
CB 101	61.17 (13.11)	23.32 (3.64)	51.54 (11.22)	27.35 (5.97)	19.22 (0.85)	24.60 (6.23)
	10.75-134.84	13.57-30.81	17.83-102.74	12.47-72.61	17.52-21.16	4.01-80.93
CB 105	32.80 (9.11)	13.99 (3.18)	23.36 (6.74)	10.62 (3.96)	8.93 (2.14)	20.80 (12.16)
	8.78-106.90	6.17-19.58	1.71-58.30	<0.01-38.39	2.74-12.05	<0.01-164.79
CB 118	90.39 (22.78)	40.40 (7.89)	51.22 (14.03)	19.37 (2.13)	20.86 (4.34)	34.33 (7.73)
	21.46-262.79	20.26-54.96	5.81-120.84	10.61-30.72	8.49-28.79	12.38-95.29

Table 1. (continued)

Year	1993	1993	1995	1995	1995	2002
Class	Male adults	Female adults	Male adults	Female adults	Sub-adults	Male adults
n	10	4	7	9	4	13
CB 138	170.89 (41.75)	63.36 (9.58)	140.12 (37.42)	64.82 (12.72)	36.86 (3.85)	86.98 (27.21)
	49.95-486.68	47.24-89.97	28.80-329.95	27.20-144.12	28.68-46.55	23.55-380.59
CB 153	222.25 (53.29)	90.81 (18.96)	184.91 (41.52)	88.64 (13.72)	61.86 (4.37)	124.74 (42.64)
	59.28-630.02	57.32-144.41	68.67-394.79	40.51-161.51	49.93-69.23	34.34-599.32
CB 180	40.43 (13.66)	14.00 (4.66)	32.15 (10.71)	14.80 (2.15)	8.21 (0.63)	19.88 (9.12)
	6.60-156.82	8.99-27.98	8.45-91.26	7.71-42.01	7.39-10.07	3.07-125.24
ΣPCB	1151.36 (237.63)	604.62 (208.65)	975.21 (207.14)	450.71 (75.92)	313.08 (23.66)	636.60 (166.31)
	390.61-3056.32	266.90-1214.06	294.18-1872.29	221.40-868.38	256.53-355.03	258.24-2399.58

Year	2002	2002	2002	2003	2003	2003
Class	Female adults	Sub-adults	Pups	Male adults	Female adults	Sub-adults
n	4	4	1	10	6	2
Age	19.3 (3.1)	4 (0.8)	0	19.30 (1.18)	16.5 (2.3)	3.2 (1.5)
	11-26	2-6		11-25	11-26	2-5
Blubber thickness	2.75 (0.66)	2.0 (0.41)	3.0	3.5 (0.2)	2.92 (0.27)	2.5 (0)
(cm)	1.0-4.0	1.0-3.0		2.0-4.5	2.0-3.5	2.5
% lipid	88.49 (2.32)	89.79 (1.59)	88.15	88.87 (0.72)	91.51 (1.08)	92.39 (0.79)
	82.27-93.38	88.55-93.25		85.31-91.88	89.00-95.35	91.60-93.18
$\delta^{15}N$ (‰) (muscle)	14.73 (0.35)	13.66 (0.24)	17.12	15.67 (0.26)	15.46 (0.17)	13.41 (0.40)
	14.12-15.36	13.13-14.25		14.17-17.22	14.94-16.16	13.00-13.81
$\delta^{13}C$ (‰) (muscle)	-20.62 (0.19)	-20.58 (0.34)	-20.45	-20.92 (0.10)	-20.92 (0.08)	-21.42 (0.01)
	-21.17-(-)20.29	-21.41-(-)19.73		-21.45-(-)20.52	-21.10-(-)20.59	-21.43-(-)21.41
ΣCBz	93.78 (27.44)	87.82 (18.98)	58.69	206.45 (25.49)	57.20 (20.98)	86.26 (8.94)
	54.52-174.63	54.55-140.79		55.32-339.30	19.62-159.29	77.33-95.21
α-HCH	271.59 (139.48)	224.77 (41.26)	120.39	124.88 (16.96)	89.84 (17.81)	154.68 (18.57)
	108.84-687.50	145.37-340.72		69.01-220.27	58.79-175.59	136.11-173.25

Table 1. (continued)

Year	2002	2002	2002	2003	2003	2003
Class	Female adults	Sub-adults	Pups	Male adults	Female adults	Sub-adults
n	4	4	1	10	6	2
β-HCH	94.34 (47.80)	98.81 (33.79)	41.15	65.58 (7.81)	32.51 (6.80)	69.45 (10.89)
	31.83-236.24	53.90-199.04		24.49-113.34	17.20-59.67	58.55-80.34
ΣHCH	378.76 (187.12)	329.40 (74.34)	175.37	201.70 (22.16)	177.10 (71.63)	229.62 (31.12)
	159.16-938.15	203.42-544.75		97.42-302.74	77.58-530.65	198.50-260.74
trans-nonachlor	158.72 (52.88)	61.88 (21.19)	165.98	131.31 (29.31)	58.60 (11.50)	50.56 (5.81)
	44.20-256.60	37.46-102.32		22.83-338.88	29.44-100.27	44.74-56.37
oxychlordane	323.40 (266.04)	195.66 (74.45)	30.55	317.90 (92.18)	110.93 (40.01)	57.65 (14.97)
	25.75-1118.84	47.56-394.45		77.48-941.89	27.65-290.73	42.68-72.61
heptachor epoxide	79.85 (31.70)	57.55 (15.22)	58.49	64.87 (9.92)	33.10 (5.97)	48.13[a]
	32.24-171.75	38.11-102.69		23.12-113.25	21.50-61.93	
ΣCHL	767.96 (374.39)	441.40 (86.70)	578.38	650.04 (125.41)	299.62 (53.31)	251.34 (67.81)
	194.82-1869.59	205.05-587.30		202.15-1325.04	183.30-548.20	183.53-319.15
p,p'-DDT	91.49 (50.75)	75.04 (26.41)	55.88	194.94 (51.16)	68.00 (17.82)	18.03 (2.55)
	17.36-234.78	21.21-135.67		28.32-482.55	29.32-150.04	15.48-20.58
p,p'-DDE	598.90 (399.33)	332.81 (79.42)	79.17	658.37 (215.12)	224.68 (89.21)	201.93 (26.94)
	73.83-1769.31	123.82-509.33		151.28-2030.92	66.61-647.75	174.99-228.87
ΣDDT	868.65 (473.59)	460.97 (110.95)	193.46	921.64 (262.89)	330.01 (112.66)	251.13 (9.80)
	123.73-2253.54	170.20-709.73		209.32-2429.95	122.39-866.86	241.33-260.93
CHB B6-923	405.52 (379.88)	218.64 (127.31)	23.39	414.03 (135.28)	71.12 (38.13)	13.83 (6.88)
	12.61-1544.96	12.81-544.69		4.72-1294.35	4.09-194.89	6.95-20.71
CHB B8-1413 (T2)[b]	37.32 (18.78)	15.64 (4.20)	24.16	52.06 (17.69)	18.40 (8.40)	8.26 (2.59)
	5.01-88.72	5.35-25.32		9.83-197.57	4.23-56.57	5.67-10.85
ΣCHB	837.37 (534.23)	518.89 (194.88)	268.42	831.78 (179.36)	295.27 (95.15)	210.78 (20.71)
	91.25-2419.22	86.60-991.82		177.27-1945.89	69.55-600.84	190.07-231.45
Dieldrin	111.51 (37.31)	66.47 (9.31)	105.69	315.23 (243.49)	221.42 (164.02)	49.39[a]
	70.54-223.37	50.68-92.00		39.11-2505.59	30.17-1039.94	
CB 28	1.84 (1.84)	3.00 (3.00)	0.87	8.08 (1.69)	4.50 (1.56)	10.60 (2.22)
	<0.1-7.36	<0.1-11.99		1.59-17.81	<0.1-10.50	8.38-12.82

Table 1. (continued)

Year	2002	2002	2002	2003	2003	2003
Class	Female adults	Sub-adults	Pups	Male adults	Female adults	Sub-adults
n	4	4	1	10	6	2
CB 31	18.14 (27.36)	21.17 (7.68)	11.20	22.10 (5.40)	18.64 (9.64)	<0.1 (<0.1)
	<0.1-80.12	<0.1-36.58		4.77-58.95	<0.1-63.08	<0.1
CB 52	19.23 (4.21)	9.54 (3.73)	16.88	17.12 (6.40)	11.16 (4.92)	10.95 (0.58)
	8.91-28.63	<0.1-17.43		<0.1-52.72	<0.1-29.91	10.37-11.53
CB 101	35.54 (14.66)	17.93 (6.74)	13.55	26.84 (6.03)	16.78 (6.29)	18.55 (5.85)
	11.73-76.56	9.05-37.77		5.08-66.15	6.89-47.43	12.71-24.40
CB 105	36.03 (13.54)	21.86 (8.39)	30.11	13.29 (4.49)	6.32 (3.47)	12.39 (3.65)
	7.05-72.27	6.68-45.09		<0.01-40.09	0.16-22.96	8.74-16.04
CB 118	39.97 (15.25)	31.22 (4.23)	16.11	28.12 (7.43)	13.82 (4.67)	26.68 (3.89)
	14.01-81.57	22.33-40.32		6.70-84.40	4.81-36.10	22.79-30.57
CB 138	105.34 (41.08)	50.89 (12.11)	25.80	87.03 (22.07)	46.15 (14.98)	54.35 (3.11)
	32.28-210.47	35.57-86.86		16.14-195.71	21.82-117.82	51.24-57.46
CB 153	143.84 (52.62)	76.49 (16.53)	27.57	121.89 (31.37)	69.23 (24.89)	87.26 (14.98)
	52.53-271.94	42.79-121.10		22.98-276.60	25.45-188.41	72.28-102.24
CB 180	23.03 (6.67)	8.04 (1.23)	3.95	19.32 (5.78)	17.50 (4.80)	8.88 (0.27)
	9.53-41.44	5.13-11.08		2.38-52.02	3.68-36.70	8.61-9.15
ΣPCB	781.16 (182.00)	461.07 (85.38)	444.10	648.90 (122.81)	378.27 (87.88)	419.81 (0.29)
	366.59-1190.16	283.59-694.30		234.18-1276.42	241.45-804.40	419.51-420.10

Year	2004	2004	2004	2005	2005	2005
Class	Male adults	Female adults	Sub-adults	Male adults	Female adults	Sub-adults
n	15	2	3	13	6	1
Age	16.48 (1.55)	9.5 (2.5)	4.7 (0.9)	16 (1.33)	16.6 (3.3)[a]	5
	7-26	7-12	3-6	8-21	7-26	
Blubber thickness	2.97 (0.11)	3.0 (0.50)	1.0 (0)	2.46 (0.19)	2.08 (0.35)	1.5
(cm)	2.0-3.5	2.5-3.5	1.0	1.5-3.5	1.0-3.5	

Table 1. (continued)

Year	2004	2004	2004	2005	2005	2005
Class	Male adults	Female adults	Sub-adults	Male adults	Female adults	Sub-adults
n	15	2	3	13	6	1
% lipid	90.78 (0.48)	91.74 (2.44)	87.35 (1.72)	89.22 (1.02)	82.94 (5.03)	82.3
	88.65-94.88	89.29-94.18	85.51-90.80	82.33-93.77	59.80-92.60	
$\delta^{15}N$ (‰) (muscle)	15.85 (0.18)	15.20 (0.09)	14.56 (0.74)	16.13 (0.26)	15.63 (0.17)	15.38
	14.80-17.06	15.13-15.31	13.10-15.52	14.47-17.35	15.12-16.29	
$\delta^{13}C$ (‰) (muscle)	-20.63 (0.13)	-20.81 (0.32)	-20.93 (0.24)	-20.62 (0.13)	-20.8 (0.12)	-21.23
	-21.21-(-)19.26	-21.12-(-)20.49	-21.36-(-)20.55	-21.61-(-)19.75	-21.03-(-)20.26	
ΣCBz	73.94 (16.99)	45.63 (6.46)	91.13 (25.15)	73.14 (13.62)	52.13 (10.26)	107.52
	15.43-228.73	39.17-52.09	61.40-141.12	21.13-176.89	22.15-83.71	
α-HCH	85.06 (5.78)	111.95 (33.21)	310.48 (75.82)	104.50 (19.36)	124.42 (8.03)	162.17
	47.07-118.39	78.73-145.16	219.93-471.10	31.42-274.64	103.78-156.03	
β-HCH	56.50 (8.79)	41.49 (15.51)	135.31 (13.39)	76.47 (13.74)	61.08 (10.24)	90.6
	18.81-168.21	25.98-56.99	109.94-155.40	30.49-192.96	36.44-95.45	
ΣHCH	148.18 (12.95)	157.92 (49.12)	451.37 (76.55)	188.68 (32.44)	190.01 (18.09)	257.13
	85.78-289.57	108.80-207.04	364.50-603.99	66.28-492.79	144.27-257.63	
trans-nonachlor	188.10 (54.96)	65.88 (22.20)	102.93 (67.46)	313.71 (67.45)	110.37 (32.93)	142.42
	36.98-896.23	43.68-88.08	28.76-237.61	73.69-797.51	40.92-236.86	
oxychlordane	281.02 (42.77)	36.51 (1.70)	125.18 (69.41)	435.63 (79.45)	199.76 (74.32)	157.97
	49.72-562.75	34.81-38.21	54.58-263.99	66.44-1081.66	19.31-513.74	
heptachor epoxide	100.02 (16.02)	27.82 (5.29)	80.40 (16.21)	151.43 (27.13)[a]	88.52 (22.19)	109.84
	25.75-222.91	22.53-33.11	63.00-112.78	49.09-353.23	27.01-178.85	
ΣCHL	835.62 (146.00)	251.17 (14.05)	432.43 (162.26)	1204.13 (193.33)	617.49 (169.92)	741.97
	203.62-2381.63	237.12-265.22	238.97-754.80	364.40-2390.13	159.62-1310.21	
p,p'-DDT	232.51 (44.83)	22.20 (11.10)	120.57 (112.13)	338.96 (76.87)	114.98 (43.14)	63.21
	33.10-547.26	<0.1-22.20	<0.1-344.61	34.62-1078.40	12.50-292.60	
p,p'-DDE	665.72 (123.96)	135.46 (13.03)	195.08 (36.85)	846.20 (150.37)	514.45 (158.45)	676.47
	109.90-1713.76	122.44-148.49	153.57-268.57	181.01-1934.44	55.60-1126.76	
ΣDDT	978.49 (166.15)	174.93 (25.50)	351.30 (146.76)	1249.97 (210.97)	675.85 (205.70)	904.24
	165.75-2401.13	149.44-200.43	186.76-644.06	360.55-2618.95	83.58-1474.30	

Table 1. (continued)

Year	2004	2004	2004	2005	2005	2005
Class	Male adults	Female adults	Sub-adults	Male adults	Female adults	Sub-adults
n	15	2	3	13	6	1
CHB B6-923	138.61 (40.81)	11.96 (3.16)	113.68 (96.63)	279.15 (108.72)	29.22 (10.59)	42.81
	<0.1-482.58	8.81-15.12	9.67-306.76	7.25-1254.60	7.00-73.47	
CHB B8-1413 (T2)[b]	56.65 (20.46)	9.76 (4.11)	60.75 (57.92)	113.41 (47.06)	8.13 (3.21)	14.86
	3.76-228.08	5.65-13.87	<0.01-176.54	<0.1-596.60	3.57-24.04	
ΣCHB	498.66 (104.82)[a]	186.10 (52.85)	374.05 (263.95)	849.43 (212.46)	244.53 (60.80)	617.47
	72.69-1197.46	133.24-238.95	77.77-900.57	128.07-2975.39	104.32-516.03	
Dieldrin	115.67 (20.54)	33.96 (1.45)	74.33 (28.87)	133.15 (18.47)[a]	129.90 (55.11)	118.01
	24.49-292.87	32.51-35.41	39.63-131.64	43.38-233.35	33.28-378.43	
CB 28	5.65 (1.70)	4.74 (1.20)	10.311 (1.11)	4.76 (1.68)	4.67 (2.96)	28.16
	<0.1-20.27	3.54-5.93	8.35-12.18	<0.1-15.36	<0.1-18.71	
CB 31	1.33 (0.98)	<0.1 (<0.1)	1.77 (1.10)	3.96 (1.66)	0.18 (0.18)	<0.1
	<0.1-13.83	<0.1	<0.1-3.78	<0.1-18.62	<0.1-1.09	
CB 52	12.85 (3.37)	8.19 (0.71)	10.94 (2.47)	25.06 (5.27)	16.72 (5.05)	24.69
	<0.1-47.43	7.48-8.90	7.20-15.61	<0.1-74.72	3.29-37.48	
CB 101	42.32 (9.43)	13.95 (0.75)	19.43 (1.10)	67.96 (12.74)	41.48 (11.04)	68.81
	7.21-146.10	13.19-14.70	17.83-21.53	12.67-171.51	9.57-80.08	
CB 105	10.16 (3.82)	6.76 (1.28)	4.97 (2.49)	18.66 (5.56)	18.03 (5.59)	38.11
	<0.01-47.18	5.48-8.03	<0.1-7.77	<0.01-58.35	2.75-41.89	
CB 118	24.22 (6.35)	15.46 (4.83)	14.97 (3.76)	38.86 (10.47)	29.78 (9.70)	100.40
	3.93-107.02	10.62-20.29	7.49-19.32	4.27-141.07	5.77-71.47	
CB 138	101.81 (21.10)	44.77 (1.15)	40.15 (5.67)	124.98 (24.17)	88.28 (23.94)	160.31
	14.25-272.57	43.26-46.28	34.04-51.48	22.37-309.31	17.91-174.76	
CB 153	164.88 (26.80)	68.28 (1.41)	87.00 (31.26)	201.11 (29.12)	143.11 (39.06)	231.99
	24.69-395.07	66.87-69.69	53.83-149.48	61.22-371.75	29.83-300.46	
CB 180	24.38 (4.75)	12.77 (3.26)	15.99 (12.09)	30.23 (4.90)	24.41 (5.98)	26.58
	2.53-61.88	9.51-16.02	3.56-40.15	7.45-64.06	6.50-47.80	
ΣPCB	614.28 (90.36)	289.57 (19.74)	383.12 (101.33)	866.74 (113.40)	543.52 (138.43)	1131.88
	249.30-1350.95	269.83-309.32	265.36-584.84	242.53-1592.37	156.77-1000.41	

Table 1. (continued)

[a] n = one sample less than indicated in table
[b] CHB B8-1413 is also known as T2

ΣCBz – sum of chlorinated benezene isomers: 1,2,4,5-triCBz, 1,2,3,4-triCBz, hexachlorobenzene, pentachlorobenzene
ΣHCH – sum of hexachlorocyclohexane isomers: α-HCH, β-HCH, γ-HCH, δ-HCH; ΣCHLOR – sum of technical chlordane components and other metabolites: *cis*-chlordane, *trans*-chlordane, oxychlordane, *cis*-nonachlor, *trans*-nonachlor, heptachlor, heptachlor epoxide
ΣDDT – dichlorodiphenyltrichloroethane compounds: *o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDE, *p,p'*-DDE
ΣCHB – sum of chlorobornane congeners
ΣPCB – sum of polychlorinated biphenyl congeners: 1, 3, 4, 6, 7, 8/5, 10/4, 16/32, 17, 18, 19, 22, 24/27, 25, 26, 28, 31, 33, 40, 41/71, 42, 44, 45, 46, 47, 48, 49, 52, 56/60, 64, 66, 70/76, 74, 82, 83, 84/89, 85, 87, 91, 95, 97, 99, 101, 105, 110, 114, 118, 128, 130/176, 131, 132, 134, 136, 137, 138, 141, 144/135, 146, 149, 151, 153, 158, 170, 171/156, 172/197, 174, 175, 177, 178/129, 179, 180, 183, 185, 187, 189, 190, 191, 193, 194, 195, 196/203, 198, 199, 200, 201/157, 205, 206, 207, 208, 209

In descending order of magnitude, summed OC groups in male and female adults and sub-adults were ΣDDT>ΣCHL>ΣCHB>ΣPCB>ΣHCH>ΣCBz, ΣDDT>ΣPCB>ΣCHL>ΣCHB>ΣHCH>ΣCBz and ΣPCB>ΣDDT> ΣCHB>ΣCHL>ΣHCH >ΣCBz, respectively. These results are similar to those reported by Addison and Smith (1998) in Ulukhaktok ringed seals between 1972-1991 and Hoekstra et al. (2003) in 1999-2000 for Beaufort-Chukchi Seas ringed seals with the exception that ΣDDT in adults were most prominent in the current study. ΣCHB was not addressed by either Addison and Smith (1998) or Hoekstra et al. (2003). Addison et al. (1986) noticed a 2-fold decline in ΣPCBs from this population of ringed seals from 1972-1981, but they did not observe any decreases in DDTs from the same time period, speculating the cause was associated with a later phase-out of DDT relative to PCBs. Global use of DDT was first reduced in 1972, but it was still used heavily in China and India until 1983 and 1989, respectively (Li and Bidleman 2003), with the potential to relocate atmospherically to the Arctic. This may explain the higher ΣDDT concentrations in seals during the 1990s and 2000s with respect to ΣPCBs in this study.

Biological and ecological relationships with OCs. In general, older male adult seals contained larger OC levels. Similarly, larger male adults and the thinner and lighter seals in all age-sex classes had higher OC concentrations (Table 2).

Age was significantly related to male adult levels of ΣCHL, *p,p'*-DDT, *p,p'*-DDE, ΣDDT, CB 153 and 180. Addison and Smith (1998) also reported that DDTs increased with age in male Ulukhaktok ringed seals sampled during 1972-1991, and with the

Table 2. Correlation coefficients of organochlorine contaminants and biological/ecological variables in ringed seals in Ulukhaktok, Canada. Sample sizes are as follows: male adults (MA; n=67), female adults (FA; n=32), sub-adults (SA; n=14). Bold items are significant (* <0.5, **<0.01, ***<0.001).

	Age			Standard length			Weight		
Compound/group	MA	FA	SA	MA	FA	SA	MA	FA	SA
ΣCBz	0.18	0.239	0.146	0.105	-0.016	-0.253	-0.058	-0.061	-0.364
α-HCH	-0.215	0.022	-0.016	-0.254	-0.19	-0.21	-0.378	-0.259	-0.477
β-HCH	0.278	-0.048	-0.276	0.101	-0.253	-0.337	-0.193	-0.559	-0.62
ΣHCH	-0.112	0.004	-0.262	-0.207	-0.206	-0.313	-0.393	-0.321	-0.618
Oxychlordane	0.436	-0.091	-0.354	0.218	-0.183	-0.576	-0.062	-0.583	-0.67
ΣCHL	**0.502** **	0.047	-0.164	0.266	-0.03	-0.29	-0.013	-0.5	-0.433
p,p'-DDT	**0.508** **	0.016	-0.018	0.233	0.049	-0.26	0.014	-0.256	-0.318
p,p'-DDE	**0.595** ***	-0.217	-0.181	0.246	-0.39	-0.371	0.102	-0.625	-0.481
ΣDDT	**0.609** ***	-0.108	-0.019	0.251	-0.241	-0.176	0.051	-0.541	-0.25
CHB B6-923	0.098	0.073	-0.153	0.037	0.054	-0.279	-0.19	-0.251	-0.319
CHB B8-1413 (T2)	0.207	0.228	0.135	0.188	0.456	0.091	-0.031	0.127	0.028
ΣCHB	0.284	0.175	-0.01	0.042	0.148	-0.212	-0.224	-0.07	-0.265
Dieldrin	0.342	0.094	-0.022	0.123	-0.104	-0.097	-0.002	-0.331	-0.369
CB28	-0.064	-0.037	0.125	0.035	0.182	0.658	0.071	0.365	0.462
CB52	0.09	0.282	0.082	-0.119	0.16	0.327	-0.174	-0.074	0.179
CB101	0.3	-0.111	0.313	0.031	-0.228	0.325	-0.05	-0.538	0.278
CB153	**0.475** *	-0.183	0.1	0.2	-0.312	0.169	0.07	-0.572	-0.051
CB180	**0.496** **	0.153	0.32	0.21	-0.182	0.341	0.097	-0.526	0.127
ΣPCB	0.422	0.046	0.109	0.129	-0.115	-0.011	-0.007	-0.382	-0.143

exception of older females, ΣCHL, ΣDDT and ΣPCB increased with age in ringed seals from the North Water Polynya (Fisk et al. 2002). Findings exemplify the bioaccumulative properties of highly chlorinated contaminants, more so in males because females tend to lose contaminant burdens to offspring primarily through lactation each spring (Addison and Brodie 1987, Aguilar 1987, Wagemann and Muir 1987, Hutchinson and Simmonds 1994).

Female adult ΣCHL and sub-adult concentrations of α-HCH, β-HCH and ΣHCH were significantly inversely affected by blubber thickness. Wang et al. (2007) also

Table 2. (continued)

	Blubber thickness			$\delta^{15}N$			$\delta^{13}C$		
Compound/group	MA	FA	SA	MA	FA	SA	MA	FA	SA
ΣCBz	0.085	-0.1	-0.277	-0.138	-0.294	-0.038	-0.24	-0.001	-0.529
α-HCH	-0.147	-0.346	**-0.848****	-0.377	-0.494	0.007	0.039	0.05	0.073
β-HCH	-0.388	-0.536	**-0.977*****	-0.03	-0.386	-0.171	0.034	-0.059	0.147
ΣHCH	-0.23	-0.417	**-0.923*****	-0.316	-0.52	-0.287	0.145	-0.124	-0.075
Oxychlordane	-0.407	-0.605	-0.657	0.007	-0.281	-0.268	0.103	-0.24	-0.077
ΣCHL	-0.391	**-0.653****	-0.637	0.164	-0.166	-0.04	0.019	-0.164	-0.021
p,p'-DDT	-0.332	-0.269	-0.443	0.06	-0.052	0.113	0.03	-0.294	-0.047
p,p'-DDE	-0.295	-0.409	-0.534	0.203	-0.316	-0.12	0.11	-0.08	-0.419
ΣDDT	-0.315	-0.43	-0.406	0.2	-0.233	0.16	-0.011	-0.124	-0.121
CHB B6-923	-0.262	-0.437	-0.401	-0.279	-0.42	0.033	-0.149	-0.179	0.054
CHB B8-1413 (T2)	-0.296	-0.148	-0.047	-0.197	-0.299	0.352	-0.148	-0.087	0.138
ΣCHB	-0.232	-0.263	-0.285	-0.145	-0.37	0.195	-0.222	-0.074	-0.145
Dieldrin	-0.104	-0.498	-0.77	0.23	-0.062	0.069	0.106	-0.105	-0.039
CB28	0.039	0.389	0.091	0.033	0.247	0.253	-0.14	0.247	-0.081
CB52	-0.104	-0.267	-0.172	-0.007	0.183	0.351	-0.031	0.081	0.209
CB101	-0.308	-0.575	-0.04	0.311	-0.064	0.361	-0.019	-0.044	-0.084
CB153	-0.266	-0.478	-0.303	0.288	-0.174	0.177	-0.055	-0.062	-0.095
CB180	-0.205	-0.546	-0.129	0.29	0.043	0.42	-0.087	0.083	-0.009
ΣPCB	-0.188	-0.389	-0.266	0.278	-0.214	0.101	-0.017	-0.01	0.058

observed negative correlations of ΣHCH with blubber thickness in harbour seals (*Phoca vitulina*) from the Gulf of Alaska. These results can be attributed to the concentration of these contaminants as lipid reserves diminish (Debier et al. 2006).

Relationships of $\delta^{15}N$ and $\delta^{13}C$ varied greatly among all OCs regardless of age-sex class, and no significant correlations were observed among $\delta^{15}N$ and $\delta^{13}C$, length or weight by OCs. Similar findings were documented by Fisk et al. (2002) with Northwater Polynya ringed seals. The comparison of $\delta^{15}N$ in muscle and OCs in blubber may have been mismatched in terms of residence times, and this would lead to the inability of addressing a link between diet and OC contaminants in seals (Fisk et al. 2003). The turnover time of $\delta^{15}N$ and $\delta^{13}C$ in muscle is estimated as several months (Tieszen et al. 1983, Kurle and Worthy 2002) while the half-life of OCs in polar bear (*Ursus maritimus*) fat is estimated as little as 4.5 years for chlorobenzenes in female adults and as long as 20.6 years for *p,p'*-DDE in male adults (Dietz et al. 2004). However, Bentzen et al. (2008) reported strong correlations of $\delta^{15}N$ in blood cells (turnover time 2-3 months, similar to muscle (Hilderbrand et al. 1996)) and PCB congeners 153, 180 and 194 in male polar bear fat and a significant relationship between $\delta^{15}N$ and oxychlordane in female polar bear adipose tissue. $\delta^{13}C$ was also important in explaining ΣPCB, ΣCHL, ΣDDT and *p,p'*-DDE in female bears and CB 180 in male bears. Examining $\delta^{15}N$ and $\delta^{13}C$ in multiple tissues to reflect different dietary periods may have been useful in this study.

$\delta^{13}C$ reflects food web carbon source, so differences in foraging by latitude (Saupe et al. 1989) or distance to shore (France and Peters 1997) may affect the measured $\delta^{13}C$ values. In summer adult ringed seals travel as far north as Viscount Melville Sound to feed, but they return before freeze-up to Prince Albert Sound to maintain winter territories up until and including parturition and lactation (Smith 1987, Harwood and Smith 2003, Beaufort Sea Seals 2008). Changes in summer foraging locations due to greater attractiveness or accessibility may be associated with the changing sea ice regime in the Beaufort Sea (Walsh 2008). However, $\delta^{15}N$ and $\delta^{13}C$ in muscle reflect the diet several months prior to sampling, so differences in spatial foraging activity earlier than winter (the time period in which ringed seals do not pursue travel) cannot be determined.

Several studies have found that regional environmental levels of OCs may be more important in explaining trends in higher trophic-level species than differences in diet. Hoekstra et al. (2003) suggested contaminant exposure via the marine environment was more relevant in explaining different OC profiles amongst different populations of marine mammals rather than diet. Similarly, after finding $\delta^{15}N$ did not change linearly in OC levels in Arctic seabirds (1976 to 2004), Braune et al. (2007) suggested that the observed trends in OCs were associated with the food chain, reflected from the environment. For instance, α-HCH is the predominant HCH isomer in the Beaufort Sea (Li et al. 2002) and is also the largest HCH isomer in ringed seals in this study.

Differences in OCs between age-sex classes. With age, blubber thickness and year as covariates, the ANCOVA reported eight out of 13 individual OCs and five of the six summed OC groups varied significantly among the three age-sex classes (Table 3). Significant differences between age-sex classes existed for many of the bioaccumulative OCs, those with log-transformed octanol-water partition coefficients ≥ 5.0 (United Nations Environmental Program, 2001): oxychlordane, ΣCHL, *p,p'*-DDT, *p,p'*-DDE, ΣDDT, CHB B6-923, CHB B8-1413 (T2), ΣCHB, CB 101, CB 153 and ΣPCB. ΣCBz and β-HCH were also significantly different among age-sex classes.

Tukey post-hoc analysis revealed male adult concentrations of these OCs were significantly higher than those of female adults. For most OCs the order of increasing concentrations among age-sex classes was female adults<sub-adults<male adults, although exceptions appeared for CB 28, 52 and 180 where female adults and sub-adults had the lowest and highest levels, respectively. Within the same population of ringed seals sampled during 1972, 1981, 1989 and 1991, males also had larger ΣDDT, oxychlordane and ΣPCB concentrations than females (Addison et al. 1986, Addison and Smith 1998). However, the previous studies did not observe significant differences

Table 3. Analysis of covariance results of organochlorine contaminants between male adult, female adult and sub-adult ringed seals (*Phoca hispida*) in Ulukhaktok, Canada.

Compounds	F	p
ΣCBz	9.75	<0.001
α-HCH	0.40	0.67
β-HCH	11.24	<0.001
ΣHCH	2.02	0.14
Oxychlordane	25.55	<0.001
ΣCHL	17.76	<0.001
p,p'-DDT	14.64	<0.001
p,p'-DDE	13.16	<0.001
ΣDDT	16.61	<0.001
CHB B6-923	12.35	<0.001
CHB B8-1413 (T2)	6.94	0.001
ΣCHB	10.68	<0.001
Dieldrin	1.95	0.15
CB 28	1.07	0.35
CB 52	1.08	0.34
CB101	3.65	0.03
CB 153	4.95	0.01
CB 180	0.80	0.45
ΣPCB	6.70	0.002

between sexes for hexachlorobenzene (HCB, a component of ΣCBz), whereas in this study female adults had significantly lower levels of ΣCBz compared to male adults and sub-adults. Male ringed seals from the North Water Polynya were significantly enriched in ΣCHL, ΣDDT and ΣPCB (Fisk et al. 2002). Weis and Muir (1997) also reported that these groups, in addition to ΣCHB, were significantly higher in males in comparison to female ringed seals across the Canadian Arctic. Similar to the results reported here, there were no significant differences in α-HCH between eastern Greenland adult and juvenile ringed seals, but adult seals contained significantly higher levels of β-HCH than juveniles (Riget et al. 2008).

Once again the bioaccumulative properties of OCs result in male adult ringed seals containing the highest OC concentrations. Male adult seals are older than sub-adults and thus accumulate greater OC burdens as a result of longer exposure time to contaminants through the diet. In the case of female adults, the issue of OC burden is not associated with exposure time but with the subsequent lactation and transfer of contaminant load to pups. Sub-adults may have had the highest levels of CB 28, 52 and 180 as a result of the OCs' persistence from past exposure to mothers' milk.

Temporal trends of OCs among age-sex classes. Linear regression results of the 19 OC concentrations and contaminant ratios in male and female adult ringed seals against year (1993-2005) are shown in Table 4. Sub-adults were not included in the temporal trend analysis. OC levels decreased or remained relatively constant over the 6 years of study. Male adult ringed seals showed significant declines in α-HCH and ΣPCB by 3-fold and 1.3-fold, respectively, in the 12 year period from 1993-2005. Female adult concentrations of ΣCHB decreased significantly by 2.5-fold in the same period. Chlorobornane is the most water soluble compound assessed in this study ($0.5 g/m^3$; Mackay et al. 1992, Mackay et al. 1997). Less soluble (more hydrophobic) compounds are more likely to transfer to offspring via lactation (Subramanian et al. 1988, Cameron et al. 1997) because seal milk is ~50% fat (Cook and Baker 1969), thus biasing the detection of a temporal trend. For example, the pup in this study contained relatively high levels of *trans*-nonachlor, heptachlor epoxide, CB 31 and 52, all of which are more hydrophobic than chlorobornane.

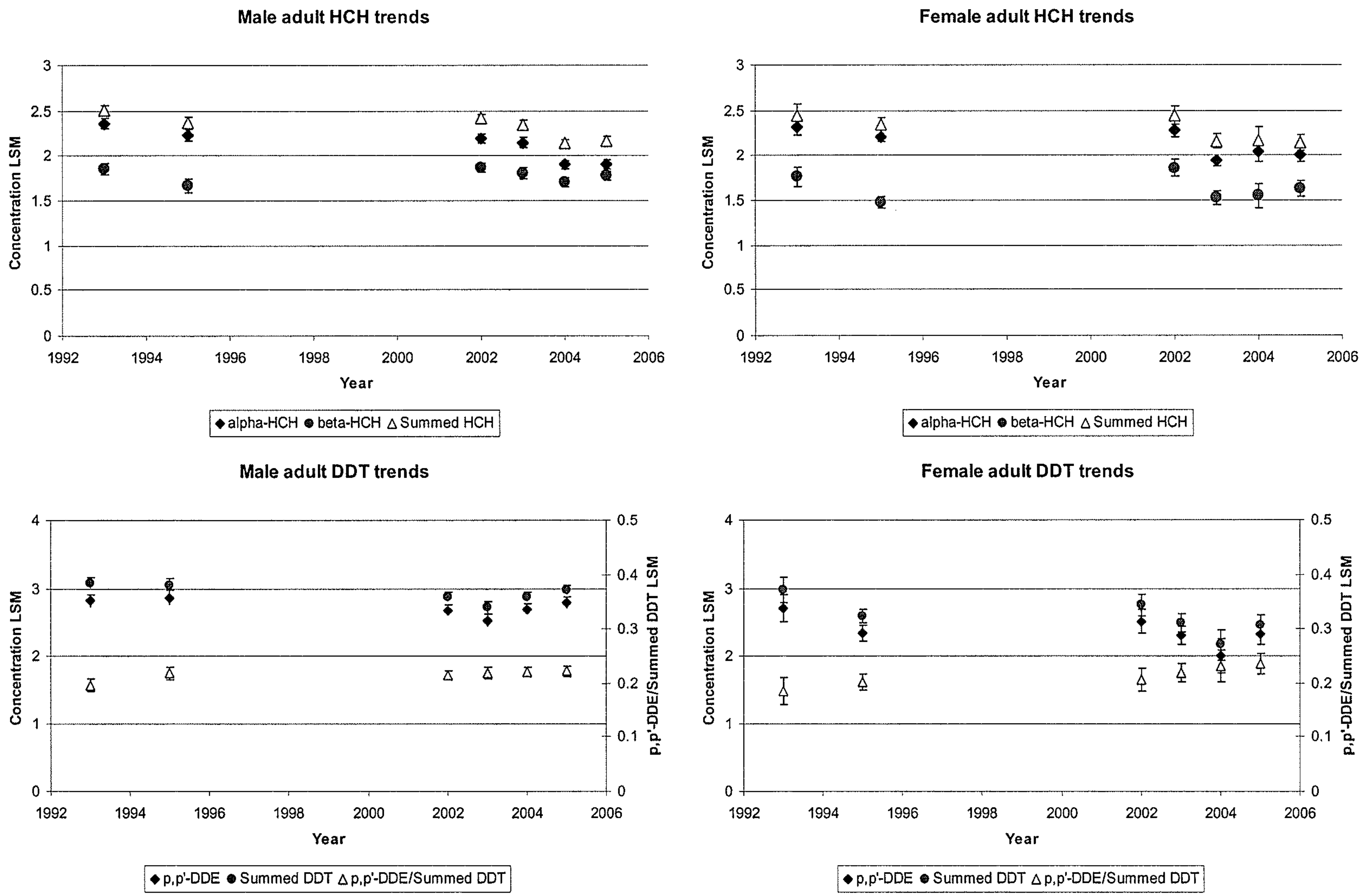
Table 4. Linear regression of organochlorine contaminants (least-square means of concentrations and ratios) with sampling years (1993-2005) among male and female adult ringed seals from Ulukhaktok, Canada.

	Male adults (n=66)			Female adults (n=30)		
Compounds	r	F	p	r	F	p
ΣCBz	-0.60	2.20	0.21	-0.74	4.48	0.09
α-HCH	-0.86	10.90	0.03	-0.75	4.99	0.09
β-HCH	-0.02	0.002	0.97	-0.09	0.03	0.87
ΣHCH	-0.76	5.60	0.08	-0.74	4.88	0.09
Oxychlordane	-0.31	0.44	0.54	-0.68	3.42	0.14
F_{TC}^{*}	-0.37	0.62	0.47	0.54	1.62	0.27
oxychlordane/ΣCHL	0.11	0.05	0.84	-0.56	1.81	0.25
ΣCHL	-0.44	0.98	0.38	-0.64	2.77	0.17
p,p'-DDT	-0.71	4.07	0.11	-0.63	2.66	0.18
p,p'-DDE	-0.59	2.12	0.22	-0.65	2.89	0.16
p,p'-DDE/ΣDDT	0.76	5.57	0.08	0.91	19.71	0.01
ΣDDT	-0.71	4.13	0.11	-0.72	4.26	0.11
CHB B6-923	-0.20	0.16	0.71	-0.78	6.23	0.07
CHB B8-1413 (T2)	0.05	0.01	0.92	-0.36	0.60	0.48
ΣCHB	-0.72	4.24	0.11	-0.82	8.44	0.04
Dieldrin	-0.12	0.06	0.82	-0.36	0.60	0.48
CB 28	-0.46	1.09	0.36	0.02	0.00	0.98
CB 52	-0.71	4.03	0.12	0.07	0.02	0.90
CB101	-0.48	1.21	0.33	-0.60	2.23	0.21
CB 153	-0.60	2.22	0.21	-0.49	1.26	0.33
CB 153/ΣPCB	0.30	0.40	0.56	0.52	1.50	0.29
CB 180	-0.65	2.98	0.16	-0.38	0.66	0.46
ΣPCB	-0.82	8.40	0.04	-0.57	1.94	0.24

* – *trans*-chlordane/(*trans*-chlordane + *cis*-chlordane)

Although α-HCH significantly declined but β-HCH did not in male adult seals in this study, Addison et al. (2008) found contrasting results in Ulukhaktok female ringed seals between 1991-2006. Blubber samples taken from four sampling intervals throughout the study period showed β-HCH increased 5-fold in female ringed seals. In this study, trends of β-HCH in female adults were unclear (Figure 2). The only apparent increase in β-HCH occurred between 2003 and 2005 from ~30ng/g to ~60ng/g lipid weight, respectively. More data is required to verify trends.

Figure 2. HCH and DDT least-square means and standard error bars of male and female adult Ulukhaktok ringed seals plotted against year (male adult n= 66, female adult n=30).



In adult seals α-HCH and ΣHCH appear to decrease and β-HCH remained relatively unchanged (Figure 3), and therefore the ratio of β-HCH/ΣHCH is increasing. Riget et al. (2008) also noted an increasing ratio of β-HCH/α-HCH in Greenland ringed seals from the late 1980s/early 1990s to 2006 due to significantly decreasing α-HCH levels. α-HCH is one of the most water soluble (least hydrophobic) OCs. α-HCH does not bioaccumulate to the same extent in organisms as β-HCH, which is less soluble in water (Mackay et al. 1997). ΣHCH concentrations from ringed seal and polar bear populations across the Arctic were strongly correlated to the ΣHCH concentrations in the waters they inhabited (Muir and Norstrom 2000). Therefore the lower ΣHCH levels observed in ringed seals near the end of this study period would likely reflect reduced ΣHCH concentrations in Arctic waters. Jantunen and Bidleman (1996) proposed that HCH-supersaturated oceans have become a source of α-HCH to the atmosphere, resulting in lower concentrations in the Arctic Ocean over time.

p,p'-DDE/ΣDDT increased over the study period in both male and female adult seals (significantly for the latter; Table 4, Figure 3). From the 1970s/80s to 1989 and 1991, Addison and Smith (1998) observed a similar increasing trend with *p,p'*-DDE/ΣDDT in Ulukhaktok ringed seals. DDT breaks down into DDD (dichlorodiphenyldichlorethane) and then DDE (dichlorodiphenyl-dichloroethylene), in which the latter is highly persistent in the environment. Aguilar (1984) suspected the break-down time of DDT to produce the DDE metabolite took many years when he observed the DDE/ΣDDT ratio increased during 1964-1981 in North Atlantic marine mammals. This would explain why DDE/ΣDDT is increasing in this study's ringed seals even though usage of DDT ended several decades ago. Aguilar (1984) further predicted the ratio of DDE/ΣDDT would reach a steady state of 0.6 for both cetaceans and pinnipeds. In both male and female adult ringed seals the average ratio was 0.64.

The remaining OC ratios in seal blubber did not change significantly from 1993-2005 (Table 4). Work by Bidleman et al. (2002) and Stern et al. (2005) regarding a significant decrease F_{tc} in Arctic air and lake sediments, respectively, contrast with this study's findings, likely explained by the biotransformation process of *trans*- and *cis*-chlordane in the foodweb.

Declining trends of OCs is likely a result of usage patterns. Many OC pesticides and PCBs were banned in North America and Europe in the 1970s and 1980s, and as a result, some OCs have been declining in the atmosphere since. For example, Hung et al. (2002) sampled air at Alert, NU, weekly from 1992 until the end of 1997. Over the years they observed significantly decreasing levels of α- and γ-HCH and chlordanes. Bidleman et al. (2002) also noted significant declines in these OCs and PCBs in Arctic air from 1984-1998. Lower chlorinated PCBs and CB 180 significantly fell in the 1990s (Hung et al. 2001). ΣDDT air concentrations have declined at Alert since the late1980s (reviewed by Li and Macdonald 2005), and furthermore, DDT levels decreased in sediment cores from an Arctic Lake commencing in the 1960s until late 1990s (Stern et al. 2005). Chlorobornane levels have declined in Arctic air [Arctic Monitoring and Assessment Program (AMAP) 2004, Li and Macdonald et al. 2005]. There were no clear temporal trends in HCB at Alert from 1993-1998 (AMAP 2004).

An additional mechanism by which OC levels in ringed seal blubber in this study are decreasing over time may be related to sea ice dynamics and subsequent contaminant uptake through the food chain. Once the Beaufort Sea begins to break up, wind is the principal mechanism for clearing ice from out of the Amundsen Gulf and Prince Albert Sound (Giovando and Herlinveaux 1981, Melling and Riedel 2005). Nonetheless, some melting of the pack ice and landfast ice occurs. As snow and ice melt, ice-inhabiting invertebrates such as gammarid amphipods, harpacticoid and cyclopoid copepods and mysids, which are food for Arctic cod and ringed seals (Cross 1982), may become exposed to PCBs and DDTs via contaminant-bound particles deposited from Arctic haze (Pfirman et al. 1995, Norstrom et al. 1998, Meyer et al. 2006). During winter, Arctic haze is created from aerosols produced and blown northward from southern regions. This is one medium on which higher chlorinated PCBs and other OCs hitch a ride to the Arctic (Barrie 1986). Hung et al. (2002) reported 20-80% of *p,p'*-DDE alone was carried to the Arctic in winter from southern dust particles. Sea ice in the Eastern Amundsen Gulf broke up earlier in 1993 and 1995 (late May-early June) compared to the early 2000s (late July-early August) in the Eastern Amundsen Gulf (data from Dr. H. Melling, Institute of Ocean Sciences; cited in Harwood and Alikamik 2006). The relatively longer exposure of prey to PCBs and DDTs via snow and ice melt before the seal harvest (June-July) may help to explain the larger concentrations of higher chlorinated PCB congeners in 1993 and 1995 compared to levels in the early 2000s (Table 1).

In addition to later sea ice break-up, the Beaufort Sea is generally experiencing longer ice-free seasons as impacts from climate change (Barber and Hanesiak 2004, Walsh 2008). 'Scavenging' effects by algae and phytoplankton would dilute OC concentrations entering the food web. Here 'scavenging' refers to the process by which organic contaminants enter water bodies and subsequently bind to organic matter

(Sonzogni and Swain 1980), effectively lowering OC concentrations in the water column. Longer open water seasons may promote greater primary productivity, create more biomass in the water column, and effectively dilute OC concentrations in the ocean. For example, OC levels in zooplankton in the Lancaster Sound were lower in the ice-free season as opposed to the ice-covered season due to lower water and algae contaminant concentrations (Hargrave et al. 2000). Stern et al. (2005) also suggested longer open water seasons in the Arctic as a result of climate change may have influenced greater OC scavenging by phytoplankton, playing a role in increased HCH concentrations in top sediment layers in an Arctic lake. Although the Amundsen Gulf experienced shorter ice-free seasons during the early 2000s compared to 1993 and 1995 (data from Dr. H. Melling, Institute of Ocean Sciences; cited in Harwood and Alikamik 2006), the impacts of scavenging and outgassing (Hargrave et al. 1997) in the year before seal sampling may have been important processes for lowering OC concentrations from the water column for the subsequent sampling years.

Throughout the 1970s to early 1990s, OC levels declined in Ulukhaktok ringed seals. DDTs, PCBs and HCB all decreased in ringed seal blubber although the greatest drops in PCBs occurred during the 1970s and HCB in the 1980s (Addison et al. 1986, Addison and Smith 1998). HCHs showed no signs of decline until 1991, and Addison and Smith (1998) predicted HCHs would continue to decline in ringed seals throughout the 1990s due to the release of α-HCH from the Arctic Ocean (Jantunen and Bidleman 1996). Indeed, as mentioned earlier, results from this study illustrate strong declines in α-HCH from this ringed seal population in the 1990s and early 2000s. Reviewing OC data from the Ulukhaktok population, Muir and Kwan (2003) reported ΣPCB, ΣDDT and

ΣHCH dropped less than 2% while ΣCHL increased almost 2% from the 1980s until 2001.

In addition to ringed seals, other Arctic species have shown decreasing trends in OCs over the years. Braune (2007) reported significant declines in ΣCBz, HCB, ΣDDT and ΣPCB for thick-billed murres, northern fulmars and black-legged kittiwake eggs in the high Canadian Arctic between 1975-2003. The kittiwake and murre eggs also showed significant decreases in chlordane compounds and dieldrin. ΣDDT, ΣPCB, ΣCBz and dieldrin decreased from 1976-2004 in ivory gull eggs (Braune et al. 2007). Beluga and polar bears experienced decreasing OC levels from the 1980s to the early 2000s (reviewed by Braune et al. 2005).

Work here shows OC concentrations in Ulukhaktok ringed seals have decreased or changed little from the 1990s up until the mid-2000s, although trends in OC levels from the 1970s to the 1980s showed significant decreases (Addison and Smith 1986, 1998). Our research suggests the need for continual contaminant monitoring in the Arctic using a 10-year interval.

Acknowledgements

Seal tissue samples were provided by John and Emma Alikamik and fellow seal harvesters in the Hunters and Trappers Committee in Ulukhaktok, NT. Dr. Tom Smith aged samples. Funding was provided by the Natural Sciences and Engineering Research Council of Canada, the Fisheries Joint Management Committee, and ArcticNet.

References

Addison, R.F.; Zinck, M.E.; Smith, T.H. PCBs have declined more than DDT-group residues in Arctic ringed seal (*Phoca hispida*) between 1972 and 1981. *Environ. Sci. Technol.* **1986**, *20*, 253-256.

Addison, R.F.; Brodie, P.F. Transfer of organochlorine residues from blubber through the circulatory system to milk in the lactating grey seal *Halichoerus grypus*. *Can. J. Fish. Aquat. Sci.* **1987**, *44*, 782-286.

Addison, R.F. Organochlorines and marine mammal reproduction. *Can. J. Fish Aquat. Sci.* **1989**, *46*, 360-368.

Addison, R.F.; Smith, T.G. Trends in organochlorine residue concentrations in ringed seal (*Phoca hispida*) from Holman, Northwest Territories, 1972-91. *Arctic* **1998**, *51*, 253-261.

Addison, R.F.; Ikonomou, M.G.; Muir, D.C.G. Long-term trends in HCH and PCCD/F in Holman ringed seals: testing past predictions of current and future trends. In: *Synopsis of research conducted under the 2007-2008 Northern Contaminants Program*; Northern Science and Contaminants and Research Directorate M., Ed.; Indian and Northern Affairs Canada: Ottawa, 2008; p. 73-75.

Aguilar, A.. Relationship of DDE/tDDT in marine mammals to the chronology of DDT input into the ecosystem. *Can. J. Fish. Aquat. Sci.* **1984**, *41*, 840-844.

Aguilar, A. Using organlochlorine pollutants to discriminate marine mammal populations: a review and critique of methods. *Mar. Mam. Sci.* **1987**, *3*, 242-262.

Arctic Monitoring and Assessment Programme (AMAP). *AMAP Assessment 2002: Persistent Organic Pollutants in the Arctic*; AMAP: Oslo, 2004.

American Society of Mammalogists. Standard measurements of seals. *J. Mammal.* **1967**, *48*, 459-462.

Barber, D.G.; Hanesiak, J.M. Meteorological forcing of sea ice concentrations in the southern Beaufort Sea over the period 1978 to 2001. *J Geophysl Res.* **2004**, *109*, C06014.

Barrie, L.A. Arctic air pollution: an overview of current knowledge. *Atmos. Environ.* **1986**, *20*, 643-663.

Beaufort Sea Seals-Research and Monitoring. www.beaufortseals.com/telemetry.htm (accessed September 29, 2008).

Bergman, A.; Olsson, M. Pathology of Baltic grey seal and ringed seal females with special reference to adrenocortical hyperplasia: is environmental pollution the cause of a widely distributed disease syndrome? *Finn. Game Res.* **1985**, *44*, 47-62.

Bentzen, T.W.; Follmann, E.H.; Amstrup, S.C.; York, G.S.; Wooller, M.J.; Muir, D.C.G.; O'Hara, T.M. Dietary biomagnification of organochlorine contaminants in Alaskan polar bears. *Can. J. Zool.* **2008**, *86*, 177-191.

Bidleman, T.F.; Patton, G.W.; Walla, M.D.; Hargrave, B.T.; Vass, W.P.; Erickson, P.; Fowler, B.; Scott, V.; Gregor, D.J. Toxaphene and other organochlorines in Arctic ocean fauna: evidence for atmospheric delivery. *Arctic* **1989**, *4*, 307-313.

Bidleman, T.F.; Jantunen, L.M.; Helm, P.A.; Brorström-Lundén, E.; Juntto, S. Chlordane enantiomers and temporal trends of chlordane isomers in Arctic air. *Environ. Sci. Technol.* **2002,** *36*, 539-544.

Bidleman, T.F.; Wong, F.; Back, C.; Södergren, A.; Brorström-Lundén, E.; Helm, P.A.; Stern, G.A. Chiral signatures of chlordanes indicate changing sources to the atmosphere over the past 30 years. *Atmos. Environ.* **2004**, *38*, 5963-5970.

Borgå, K.; Fisk, A.T.; Hoekstra, P.F.; Muir, D.C.G. Biological and chemical factors of importance in the bioaccumulation and trophic transfer of persistent organochlorine contaminants in arctic marine food webs. *Environ. Toxicol. Chem.* **2004**, *23*, 2367-2385.

Braune, B.M.; Outridge, P.M.; Fisk, A.T.; Muir, D.C.G.; Helm, P.A.; Hobbs, K.; Hoekstra, P.F.; Kuzyk, Z.A.; Kwan, M.; Letcher, R.J.; Lockhart, W.L.; Norstrom, R.J.; Stern G.A.; Stirling, I. Persistent organic pollutants and mercury in marine biota of the Canadian Arctic: an overview of spatial and temporal trends. *Sci. Total Environ.* **2005**, *351-352*, 4-56.

Braune, B.M.; Mallory, M.L.; Gilchrist, H.G.; Letcher, R.J.; Drouillard, K.G. Levels and trends of ivory gull eggs from the Canadian Arctic, 1976-2004. *Sci. Tot. Environ.* **2007**, *378*, 403-417.

Braune, B.M. Temporal trends of organochlorines and mercury in seabird eggs from the Canadian Arctic, 1975-2003. *Environ. Pollut.* **2007**, *148*, 599-613.

Burek, K.A.; Gulland, F.M.D.; O'Hara, T.M. Effects of climate change on Arctic marine mammal health. *Ecol. Appl.* **2008**, *8 (Supplement)*, S126-S134.

Cameron, M.E.; Metcalfe, T.L.; Metcalfe, C.D.; Macdonald, C.R. Persistent organochlorine compounds in the blubber of ringed seals (*Phoca hispida*) from the Belcher Islands, Northwest Territories, Canada. *Mar. Environ. Res.* **1997**, *43*, 99-116.

Cook, H.W.; Baker, B.E. Seal milk. I. Harp Seal (*Phagophilus groenlandicus*) milk: composition and pesticide residue content. *Can. J. Zool.* **1969**, *47*, 1129-1132.

Cross, W.E. Under-ice biota at the Pond Inlet ice edge and in adjacent fast ice areas during spring. *Arctic* **1982**, *35*, 13-27.

Dalla Valle, M.; Codato, E.; Marcomini, A. Climate change influence on POPs distribution and fate: a case study. *Chemosphere* **2007**, *76*, 1287-1295.

Debier, C.; Chalon, C.; Le Bœu,f B.J.; de Tillesse, T.; Larondelle, Y.; Thomé, J-P. Mobilization of PCBs from blubber to blood in northern elephant seals (*Mirounga angustirostris*) during the post-weaning fast. *Aquat. Toxicol.* **2006**, *80*, 149-157.

Dietz, R.; Riget, F.F.; Sonne, C.; Letcher, R.; Born, E.W.; Muir, D.C.G. Seasonal and temporal trends in polychlorinated biphenyls and organochlorine pesticides in East Greenland polar bears (*Ursus maritimus*), 1990-2001. *Sci. Total Environ.* **2004**, *331*, 107-124.

Folch, J.; Lees, M.; Stanley, G.H.S. A simple method for the isolation and purification of total lipids from animal tissues. *J. Biol. Chem.* **1957**, *226*, 497-509.

Fisk, A.T.; Stern, G.A.; Hobson, K.A.; Strachan, W.J.; Loewen, M.D.; Norstrom, R.J. Persistent organic pollutants (POPs) in a small, herbivorous, arctic marine zooplankton (*Calanus hyperboreus)*: trends from April to July and the influence of lipids and trophic transfer. *Mar. Pollut. Bull.* **2001**, *43*, 93-101.

Fisk, A.T.; Holst, M.; Hobson, K.A.; Duffe, J.; Moisey, J.; Norstrom, R.J. Persistent organochlorine contaminants and enantiomeric signatures of chiral pollutants in ringed seals (*Phoca hispida*) collected on the east and west side of the Northwater Polynya, Canadian Arctic. *Arch. Environ. Contam.Toxicol.* **2002**, *42*, 118-126.

France, R.L.; Peters, R.H. Ecosystem differences in the trophic enrichment of ^{13}C in aquatic food webs. *Can. J. Fish. Aquat. Sci.* **1997**, *54*, 255-1258.

Giovando, L.F.; Herlinveaux, R.H. *A Discussion of Factors Influencing Dispersion of Pollutants in the Beaufort Sea. Report 81-4*; Institute of Ocean Sciences: Sidney, British Columbia, 1981.

Hargrave, B.T.; Barrie, L.A.; Bidleman, T.F.; Welch, H.E. Seasonality in exchange of organochlorines between Arctic air and seawater. *Environ. Sci.Technol.* **1997**, 31, 3258-3266.

Hargrave, B.T.; Phillips, G.A.; Vass, W.P.; Bruecker, P.; Welch, H.E.; Siferd, T.D. Seasonality in bioaccumulation of organochlorines in lower trophic level arctic marine biota. *Environ. Sci.Technol.* **2000**, *34*, 980-987.

Harwood, L.A.; Smith, T.G.; Melling, H. Variation in reproduction and body condition of the ringed seal (*Phoca hispida*) in western Prince Albert Sound, NWT, Canada, as assessed through a harvest-based sampling program. *Arctic* **2000**, *53*, 422-431.

Harwood, L.A.; Smith, T.G. Movements and diving of ringed seals in the Beaufort and Chukchi seas, 1999-2003. In: *Abstracts of the 15th Biennial conference on the biology of marine mammals*; Society for Marine Mammalogy: Greensboro, 14-19 December 2003.

Harwood, L.A.; Alikamik, J. Ringed seals as indicators of change: harvest-based sampling near Holman, NT 1992-2005. Coastal Zone Canada Conference, August 14-18, 2006, Tuktoyaktuk, NT Canada Z0E 1C0. Session details and abstracts of papers. Available: Department of Fisheries and Oceans, Freshwater Institute, Winnipeg, MB Canada.

Hilderbrand, G.U.; Garley, S.D.; Robbins, C.T.; Hanley, T.A.; Titus, K.; Servheen, C. Use of stable isotopes to determine diets of living and extinct bears. *Can. J. Zool.* **1996**, *74*, 2080-2088.

Hobson, K.A.; Welch, H.E. 1992. Determination of trophic relationships within a high Arctic marine food web using $\delta^{13}C$ and $\delta^{15}N$ analysis. *Mar. Ecol. Prog. Ser.* **1992**, *84*, 9-18.

Hoekstra, P.F.; O'Hara, T.M.; Teixeira, C.; Backus, S.; Fisk, A.T.; Muir, D.C.G. Spatial trends and bioaccumulation of organochlorine pollutants in marine zooplankton from the Alaskan and Canadian Arctic. *Environ. Toxicol. Chem.* **2002**, *21*, 575-583.

Hoekstra, P.F.; O'Hara, T.M.; Fisk, A.T.; Borgå, K.; Solomon, K.R.; Muir D.C.G. Trophic transfer of persistent organochlorine contaminants (OCs) within an Arctic marine food web from the southern Beaufort-Chukchi Seas. *Environ. Pollut.* **2003**, *124*, 509-522.

Hung, H.; Halsall, C.J.; Blanchard, P.; Li, H.H.; Felling, P.; Stern, G.; Rosenberg, B. Are PCBs in the Canadian Arctic atmosphere declining? Evidence from 5 years of monitoring. *Environ. Sci.Technol.* **2001**, *35*, 1303-1311.

Hung, H.; Halsall, C.J.; Blanchard, P.; Li, H.H.; Fellin, P.; Stern, G.; Rosenberg, B. Temporal trends of organochlorine pesticides in the Canadian Arctic Atmosphere. *Environ. Sci.Technol.* **2002**, 36, 862-868.

Hutchinson, D.J.; Simmonds, M.P. Organochlorine contamination in pinnipeds. *Rev. Environ. Contam. Toxicol.* **1994**, 136, 123-167.

Intergovernmental Panel on Climate Change (IPCC). *Climate Change 2007: Synthesis*

Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change; Pachauri, R.K., Reisinger, A., Eds.; IPCC: Geneva, Switzerland, 2007.

Jantunen, L.M.M.; Bidleman, T.F. Air-water gas exchange of hexachlorocyclohexanes (HCHs) and the enantiomers of a-HCH in Arctic regions. *J.Geophys. Res.* **1996**, *101*, 28837-28846.

Kelce, W.R.; Stone, C.R.; Laws, S.C.; Gray, L.E.; Kemppainen, J.A.; Wilson, E.M. Persistent DDT metabolite *p,p'*-DDE is a potent androgen receptor agonist. *Nature* **1996**, *375*, 581–585.

Kelly, J.F. Stable isotopes of nitrogen and carbon in the study of avian and mammalian trophic ecology. *Can. J. Zool.* **2000**, *78*, 1-27.

Kurle, C.M.; Worthy, G.A.J. Stable nitrogen and carbon isotope ratios in multiple tissues of the northern fur seal *Callorhinus ursinus*: implications for dietary and migratory reconstructions. *Mar. Ecol. Prog. Ser.* **2002,** 236, 289-300.

Laidre, K.L.; Stirling, I.; Lowry, L.F.; Wiig, Ø.; Heide-Jørgensen, M.P.; Ferguson, S.H. Quantifying the sensitivity of Arctic marine mammals to climate-induced habitat change. *Ecol. Appl.* **2008**, *18* (Supplement), S97-S125.

Li, Y.-F.; Macdonald, R.W.; Jantunen, L.M.M.; Harner, H.; Bidleman, T.F.; Strachan, W.M.J. The transport of β-hexachlorocyclohexane to the western Arctic Ocean: a contrast to α-HCH. *Sci. Total Environ.* **2002**, *291*, 229-246.

Li, Y.-F.; Bidleman, T.F. Usage and emissions of organochlorine pesticides. In *Canadian Arctic contaminants assessment report II: sources, occurrence, trends and pathways in the physical environment*; Indian and Northern Affairs Canada: Ottawa, 2003; Chap. A.2., p. 49-70.

Li, Y.-F.; Macdonald, R.W.; Ma, J.; Hung, H.; Venkatesh, S. α-HCH budget in the arctic ocean: the arctic mass balance box model (AMBBM). *Sci. Total Environ.* **2004**, *324*, 115-139.

Li, Y.-F.; Macdonald, R.W. Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: a review. *Sci. Total Environ.* **2005**, *342*, 87-106.

Macdonald, R.W.; Harner, T.; Fyfe, J. 2005. Recent climate change in the Arctic and its impact on contaminant pathways and interpretation of temporal trend data. *Sci. Total Environ.* **2005**, *342*, 5-86.

Mackay, D.; Shiu, W.-Y.; Ma, K.-C. *Illustrated Handbook of Physical-Chemical*

Properties and Environmental Fate for Organic Chemicals: Volume 1; CRC Press LLC: Boca Raton, 1992.

Mackay, D.; Shiu, W.-Y.; Ma, K.-C. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Volume 5*; CRC Press LLC: Boca Raton, 1997.

Melling, H.; Riedel, D.A. Trends in the draft and extent of seasonal pack ice, Canadian Beaufort Sea. *Geophys. Res. Lett.* **2005** *32*, L24501, doi:10.1029/2005GL024483.

Mos, L.; Tabuchi, M.; Dangerfield, N.; Jeffries, S.J.; Koop, B.F.; Ross, P.S. Contaminant associated disruption of vitamin A and its receptor (retinoic acid receptor α) in free-ranging harbour seals (*Phoca vitulina*). *Aquat. Toxicol.* **2007**, *81*, 319-328.

Muir, D.C.G.; Ford, C.A.; Stwart, R.E.A.; Smith, T.G.; Addison, R.F.; Zinck, M.T.; Beland, P. Organochlorine contaminants in beluga (*Delphinapterus leucas*) from Canadian waters. *Can. Bull. Fish. Aquat. Sci.* **1990**, *224*, 165-190.

Muir, D.C.G.; Wagemann, R.; Hargrave, B.T.; Thomas, B.J.; Peakall, D.B.; Norstrom, R.J. Arctic marine ecosystem contamination. *Sci. Total Environ.* **1992**, *122*, 75-134.

Muir, D.C.G.; Norstrom, R.J. Geographical differences and time trends of persistent organic pollutants in the Arctic. *Toxicol. Lett.* **2000**, *112-113*, 93-101.

Muir, D.; Fisk, A.; Kwan, M. Temporal trends of persistent organic pollutants and metals in ringed seals from the Canadian Arctic. In: *Synopsis of research Conducted Under the 2000-2001 Northern Contaminants Program*; Kalhok, S., Ed.; Indian and Northern Affairs Canada: Ottawa, 2001; p. 208-214.

Muir, D.; Kwan, M. Temporal trends of persistent organic pollutants and metals in ringed seals from the Canadian Arctic. In: *Synopsis of research conducted under the 2001-2003 Northern Contaminants Program*; Northern Science and Contaminants and Research Directorate M., Ed.; Indian and Northern Affairs Canada: Ottawa, 2003; p. 318-327.

Meyer, T., Lei,Y.D.; Wania, F. Measuring the release of organic contaminants from melting snow under controlled conditions. *Environ.l Sci. Technol.* **2006**, *40*, 3320-3326.

Norstrom, R.J.; Belikov, S.E.; Born, E.W.; Garner, G.W.; Malone, B.; Olpinski, S.; Ramsay, M.A.; Schliebe, S.; Stirling, I.; Stishov, M.S.; Taylor, M.K.; Wiig, Ø. Chlorinated hydrocarbon contaminants in polar bears from eastern Russia, North America, Greenland, and Svalbard: biomonitoring of Arctic Pollution. *Arch. Environ. Contam. Toxicol.* **1998**, *35*, 354-376.

Pfirman, S.L.; Eicken, H.; Bauch, D.; Weeks, W.F. The potential transport of pollutants by Arctic sea ice. *Sci. Total Environ.* **1995**, *159*,129-146.

Reddy, M.L.; Reif, J.S.; Bachand, A.; Ridgway, S.H. Opportunites for using Navy marine mammals to explore associations between OCs and unfavorable effects on reproduction. *Sci. Total Environ.* **2001**, *274*, 171-182.

Reijnders, P.J.H. Reproductive failure in common seals feeding on fish from polluted coastal waters. *Nature* **1986**, *324*, 456-457.

Riget, F.; Vorkamp, K.; Dietz, R.; Muir, D.C.G. Levels and temporal trends of HCH isomers in ringed seals from West and East Greenland. *J. Environ. Monit.* **2008**, *10*, 935-940.

Ross, P.S.; De Swart, R.L.; Reijnders, P.J.H.; Van Loveren, H.; Vos, J.G.; Osterhaus, A.D.M.E. Contaminant-related suppression of delayed-type hypersensitivity and antibody responses in harbour seals fed herring from the Baltic Sea. *Environ. Health Perspect.* **1995**, *103*, 162-167.

Ross, P.S.; De Swart, R.L.; Timmerman, H.H.; Reijnders, P.J.H.; Vos, J.G.; Van Loveren H.; Osterhaus, A.D.M.E. Suppression of natural killer cell activity in harbour seals (*Phoca vitulina*) fed Baltic Sea herring. *Aquat. Toxicol.* **1996**, *34*, 71-84.

Saupe, S.M.; Schell, D.M.; Griffiths, W.B. Carbon-isotope ratio gradients in western arctic zooplankton. *Mar. Biol.* **1989**, *103*, 427-432.

Serreze, M.C.; Holland, M.M.; Stroeve, J. Perspectives on the arctic's shrinking sea ice cover. *Science* **2007**, *315*, 1533-1536.

Smith, T.G. Population dynamics of the ringed seal in the Canadian Eastern Arctic. *Bull. Fish. Res. Board Can.* **1973**, *181*, 55p.

Sonzogni, W.C.; Swain, W.R. Perspectives on U.S. Great Lakes chemical toxic substances research. *J. Great Lakes Res.* **1980**, *6*, 265-274.

Stern, G.A.; Braekevelt, E.; Helm, P.A.; Bidleman, T.F.; Outridge, P.M.; Lockhart, W.L.; McNeeley, R.; Rosenberg, B.; Ikonomou, M.G.; Hamilton, P.; Tomy, G.T.; Wilkinson, P. Modern and nistorical fluxes of halogenated organic contaminants to a lake in the Canadian arctic, as determined from annually laminated sediment cores. *Sci. Total Environ.* **2005**, *342*, 223-243.

Stewart, R.E.A.; Stewart, B.E.; Stirling, I.; Street, E. Counts of growth layer groups in cementum and dentine in ringed seals (*Phoca hispida*). *Mar. Mammal Sci.* **1996**, *12*, 383-401.

Subramanian, A.; Tanabe, S.; Tatsukawa, R. Use of organochlorines as chemical tracers in determining some reproductive parameters in Dalli-type Dall's porpoises *Phocoenoides dalli*. *Mar. Environ. Res.* **1988**, *25*, 161-174.

Tieszen, L.L.; Boutton, T.W.; Tesdahl, K.G.; Slade, N.A. Fractionation and turnover of stable carbon isotopes in animal tissues: implications for $\delta^{13}C$ analysis of diet. *Oecologia* **1983**, *57*, 32-37.

Tynan, C.; DeMaster, D. Observations and predictions of Arctic climate change: potential effect on marine mammals. *Arctic* **1997**, *50*, 308-322.

United Nations Environment Program (UNEP). *Final Act of the Conference of Plenipotentiaries on the Stockholm Convention on Persistent Organic Pollutants*; UNEP: Geneva Switzerland, 2001.

Van Oostdam, J.; Donaldson, S.G.; Feeley, M.; Arnold, D.; Ayotte, P.; Bondy, G.; Chan, L.; Dewaily, É.; Furgal, C.M.; Kuhnlein, H.; Loring, E.; Muckle, G.; Myles, E.; Receveur, O.; Tracy, B.; Gill, U.; Kalhok, S. Human health implications of environmental contaminants in Arctic Canada: a review. *Sci. Total Environ.* **2005**, *351-352*, 165-246.

Wagemann, R.; Muir, D.C.G. Concentrations of heavy metals and organochlorines in marine mammals from northern waters: overview and evaluation. *Can Tech Rep Fish Aquat Sci* **1984**, *1279*, 1-97.

Walsh, J.E. Climate of the Arctic marine environment. *Ecol. Appl.* **2008**, *18 (Supplement)*, S3-S22.

Wang, D.; Atkinson. S.; Hoover-Miller, A.; Lee, S-E.; Li, Q.X. Organochlorines in the harbor seal (*Phoca vitulina*) tissues from the northern Gulf of Alaska. *Environ. Pollut.* **2007**, *146*, 268-280.

Wania, F.; Hoff, J.T.; Jia, C.Q.; Mackay, D. The effects of snow and ice on the environmental behaviour of hydrophobic organic chemicals. *Environ. Pollut.* **1998**, *102*, 25-41.

Wania, F.; Mackay, D. Global chemical fate of a-hexachlorocyclohexane. 2. Use of a global distrubtion model for mass balancing, source apportionment, and trend prediction. *Environ. Toxicol. Chem.* **1999**, *18*, 1400-1407.

Weis, M.I.; Muir, D.C.G. Geographic variation of persistent organochlorine concentrations in blubber of ringed seal (*Phoca hispida*) from the Canadian Arctic: univariate and multivariate approaches. *Environ. Pollut.* **1997**, *96*, 321-333.

Chapter 4 - Conclusion

My research has produced exciting and insightful knowledge into the realm of marine mammal contaminant studies. The organochlorine aspect of the project illustrated that present contaminant trends in ringed seals were largely influenced by environmental background levels of contaminants in the Arctic. Conversely, there were no distinct temporal trends with mercury concentrations in the seals. Instead sea ice dynamics appear partly responsible for affecting shifts in prey composition and distribution in a nonlinear fashion. Here dietary exposure seemed influenced more strongly by ecological interactions rather than concentrations in the surrounding environment.

I also found $\delta^{15}N$ was an important complementary ecological variable in the mercury study. $\delta^{15}N$ was strongly related to mercury in all age-sex classes, but its trend with sea ice was not similar to the relationship of mercury and sea ice likely due to a mismatch in residence times between $\delta^{15}N$ and mercury. $\delta^{15}N$ and $\delta^{13}C$ were not significant variables in determining organochlorine contaminants.

Biological factors attributed much of the variation in the contaminant levels. Older ringed seals contained higher levels of both mercury (males and females) and organochlorine contaminant levels (males only). Blubber thickness also played an important role in determining organochlorine concentrations: thin seals tended to have higher contaminant burdens. These results confirm the necessity of including age, sex, and morphometric measurements in marine mammals as part of contaminant studies.