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Thesis of
Samantha L. Shore

Submitted in Partial Fulfillment of the Requirements for the Degree of

Master of Science
M.S. Marine Biology

Nova Southeastern University
Halmos College of Natural Sciences and Oceanography

April 2020

Approved:
Thesis Committee

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NOVA SOUTHEASTERN UNIVERSITY

HALMOS COLLEGE OF NATURAL SCIENCES AND OCEANOGRAPHY

Spatial and Temporal Distribution of Essential and Non-Essential Elements
Recorded in Western Arctic Bowhead Whales (*Balaena mysticetus*)

By:

SAMANTHA L. SHORE

Submitted to the Faculty of
Halmos College of Natural Sciences and Oceanography
in partial fulfillment of the requirements for
the degree of Master of Science with a specialty in:

Marine Biology

Nova Southeastern University

April 2020

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Abstract

Western Arctic bowhead whales, *Balaena mysticetus*, migrate annually among the Bering, Chukchi, and Beaufort seas. Foraging along their route, they use keratinous baleen to filter microscopic zooplankton from the water column. A single baleen plate from an adult bowhead whale grows continuously and stores 20+ years of dietary and environmental data. This study utilized induced coupled plasma-mass spectrometry (ICP-MS) to evaluate concentrations of 14 essential and non-essential elements in baleen samples from nine subsistence-harvested whales, yielding continuous data from 1958–1999 (n=148). Stable isotope data previously reported on these samples provided information on location (Beaufort Sea; Bering/Chukchi seas), season (winter; summer), and year per sample. All 14 elements were detected in baleen: aluminum (Al), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), nickel (Ni), manganese (Mn), lead (Pb), selenium (Se), vanadium (V), zinc (Zn). The lowest concentrations of elements were found for As, Cd, V; the highest Al, Cu, Fe, and Zn. Fe and Mn varied coincidentally across the plates of whales from the 1990s. Se and Hg were significantly correlated (ρ=–0.398, p<0.001). Se:Hg molar ratios showed potential Hg toxicity in whales from 1966 and 1995-1999. The highest concentrations of most elements were in one sample per whale, representing the Beaufort Sea (1989-1999). Al, As, Cd, Co, Hg, Mn, Ni, Pb, Se, and Zn concentrations increased as time progressed (r≥0.5). Location did not significantly affect concentrations (p>0.05). These data imply biomagnification, bioaccumulation, and/or toxicity with time, though further studies are necessary to confirm.

Key words: Non-essential elements, Essential elements, Bowhead whale, *Balaena mysticetus,* Baleen

1. INTRODUCTION

1.1. Preface

Essential and non-essential elements that have arisen from natural and anthropogenic sources (e.g. volcanic activity, fossil fuel combustion) enter the marine environment through processes like runoff and atmospheric deposition (Nriagu 1989; Fergusson 1990; Maki 1992; Shallari et al. 1998; Macdonald et al. 2000; Bradl 2002; Osuji and Onojake 2004; Rydberg et al. 2010). Environmental elements can accumulate in marine flora and fauna predominantly via ingestion (Heath 1987; Becker et al. 1997; Das et al. 2003; Vos et al. 2003; Tchounwou et al. 2012; Peterson et al. 2018). Although the sources and pathways of environmental elements are well understood, the toxicological impacts of their concentrations remain largely unknown. Marine mammals are valuable indicators of environmental concentrations, considering their long life spans and ability to biologically remove elements from water (Das *et al.,* 2003). The bowhead whale, *Balaena mysticetus*, spends its life migrating between sub-Arctic and Arctic waters, foraging on lipid-rich zooplankton (Braham 1984; Schell 2000). Analyzing bowhead whale baleen, an inert tissue, provides a novel method for establishing long, continuous temporal records of environmental conditions (Schell 1989a, b, 1992, 2000). Previous research by Donald M. Schell determined temporal and spatial information for the samples utilized in this study via stable isotope analysis. This study established, to our knowledge, the first ever dataset of essential and non-essential element concentrations in baleen from the bowhead whale attributed to changes in the western Arctic marine environment.

1.2. Essential and Non-Essential Elements

Essential and non-essential elements exist naturally in Earth's crust, though human activities (e.g. pollution, fossil fuel exploitation) have amplified natural concentrations (Bard 1999; Rieuwerts 2015). The Arctic's marine and terrestrial environments used to be considered relatively pristine (Bard 1999). However, the Arctic's increasing human activity and connectivity to Earth's environments via atmospheric and oceanic circulation have allowed essential and non-essential elements to be exchanged and deposited worldwide, even in this remote region (Nazarenko et al. 1997; Macdonald et al. 2000; Rieuwerts 2015). These elements are transported to the marine Arctic environment through atmospheric deposition, erosion, runoff, rivers, currents, and ice (Barrie et al. 1992; Pfirman et al. 1995a; Nazarenko et al. 1997; Macdonald et

al. 2000). It should be noted that in a warming Alaskan climate, ice, snow, and glacial melt increase runoff, river flow rate, and coastal erosion (Papineau 2001; Overland et al. 2002; Bieniek and Walsh 2013; Congressional Research Service 2020). Melting glaciers additionally increase sea level which increases coastal erosion. Essential and non-essential elements have been the focus of research as their toxicological potential is becoming better understood and consequently a cause for concern (Das et al. 2003). The lack of experimental data on these elements over time for the Arctic presents a gap in the literature that is critical to fill, as this information can be indicative of environmental and biological changes. Additionally, historical element concentration data are lacking prior to 1980 (McConnell and Edwards 2008). These data are critical to establish to monitor the health of the Arctic marine ecosystem and its organisms upon which subsistence communities depend.

Essential elements are required for physiological function and can be toxic at high enough concentrations (O'Hara et al. 1993; Vos et al. 2003; Tchounwou et al. 2012). Essential elements in this study include chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), selenium (Se), and zinc (Zn). In contrast, non-essential elements are not required and can be toxic even at low concentrations. Non-essential studies in this study include aluminum (Al), arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg), vanadium (V). Environmental elements can enter and accumulate in marine organisms predominantly through ingestion (Heath 1987; Becker et al. 1997; Das et al. 2003; Vos et al. 2003; Tchounwou et al. 2012; Peterson et al. 2018). However, absorption through skin, inhalation into lungs, transfer across the placenta, and via milk through lactation present additional pathways (Becker et al. 1997; Das et al. 2003; Habran et al. 2011; Noel et al. 2016). Differences in element transfer across these biological membranes are based on differences in organismal metabolic rate and solution pH and temperature (Heath 1987). Toxicity is further affected by current element load, entry route, metabolic rate, gender, age, and physiological status (e.g. fasting, pregnancy) (Das et al. 2003; Vos et al. 2003; Tchounwou et al. 2012; Peterson et al. 2018). The presence of other elements can alter toxicity through an additive effect, or synergistic and antagonistic interactions (Rai et al. 1981). Selenium, for example, alters the toxic effects of arsenic, cadmium, and mercury (Becker et al. 2000). Copper can interact with selenium and possibly compete with mercury for selenium (Hammond and Beliles 1980). Elements' long half-lives, poor solubility in

water, and non-degradability contribute to their deleterious effects once in the body (Jakismka et al. 2011).

Marine mammals can be used as valuable indicators of environmental essential and non-essential element concentrations since they have long life spans, can biologically remove elements from water, and have long biological half-lives of contaminant elimination (Dietz et al. 1998; Das et al. 2003; Vos et al. 2003). This permits the bioaccumulation of element ions and puts marine mammals at great toxicological risk. Bioaccumulation occurs as elements accrue in an organism over time (Danus et al. 2006). Additionally, biomagnificiation refers to the movement of metals to higher trophic levels, where concentration increases with consumption of affected prey. Research in element toxicity in marine mammals is limited (Reijnders et al. 1986; Swart et al. 1996; Lavery et al. 2009). However, reported toxic effects of essential and non-essential elements in invertebrates include, but are not limited to, exhaustion, loss of coordination and appetite, induced aborption, skeletal deformations, alterations to interspecific communication and predator recognition, impaired immunity, and damage to reproductive, central nervous, endocrine, and skeletal systems (Forbes and Sanderson 1978; Eisler 1988; Zillioux et al. 1993; Weis and Weis 1995; deSwart et al. 1996; Becker et al. 2000; Das et al. 2003; Alvarez et al. 2006; Tchounwou et al. 2012; Sharma et al. 2014).

1.3. Bowhead Whale

The bowhead whale, *Balaena mysticetus,* is a migrating sub-Arctic/Arctic baleen whale belonging to the order Mysticeti and family Balaenidae (Schell et al. 1989a, b; Keane et al. 2015) (Fig. 1). The bowhead whale is the largest mysticete, reaching lengths of 20 meters and weighing up to nearly 100 tons. This species also has the largest mouth to body length ratio in this taxon (Moore and Reeves 1993; Werth 2004; Lambertsen et al. 2005; Dehn 2006; Keane et al. 2015). Bowheads are considered the longest-living mammal, with an estimated life span over 200 years (Keane et al. 2015). Sexual maturity is reached when the body length is 12-14 meters long (Koski et al. 1993; Lubetkin et al. 2008). Female bowheads are typically larger than males once sexually mature, with females reaching maturity around 13 meters and males between 12.5 and 13 meters (O'Hara et al. 2002; Rosa et al. 2004).

The Western Arctic population of whales follows the coastline and cracks in pack ice

Figure 1. Bowhead whale (Film and Schmedes 2015)

along their migration route among the Bering, Chukchi, and Beaufort seas (Fig. 2) (Braham 1984; Schell et al. 1989a, b; Schell 2000). Winter months (December to March) are spent in the northern Bering Sea before making the summer migration through the Chukchi Sea in spring (April through May) and to the Beaufort Sea in summer (June to October). Feeding is typically most concentrated during summer and early autumn in the Beaufort and Chukchi seas, as large amounts of lipid-rich zooplankton, predominantly euphausiids and large calanoid copepods, are transported through the Bering Strait (Schell 2000). However, bowheads are known to feed along their entire migration path, utilizing the leading edge of the pack ice where their food is most concentrated (Schell et al. 1989b; Würsig et al. 2002).

Bowhead whales, like other balaenids, continuously ram filter feed by swimming slowly through dense aggregations of prey with their mouths open (Pivorunas 1979; Sanderson and Wassersug 1993; Lambertsen et al. 2005). This continuously pushes prey-abundant water through the whales' mouths between a central, frontal gap in the maxilla. Water then passes through baleen racks on either side of the mouth before exiting the oral cavity (Werth 2001). This foraging style is mostly seen near the ocean's surface, but bowhead whales feed throughout the euphotic zone (0-200 meters) (Watkins and Schevill 1979; Mayo and Marx 1990; Lowry 1993; Werth 2001). Western Arctic bowhead whales predominantly prey on microscopic crustaceous zooplankton (copepods and euphausiids) and some benthic organisms (mysids and gammarid amphipods) (Tomilin 1967; Lowry and Burns 1980; Hazard and Lowry 1984; Lowry 1993). Occasionally, pteropods, isopods, polychaetes, crabs, snails, echinoderms and fish are consumed.

1.4. Baleen

Baleen is the filter-feeding organ found solely in mysticete whales and is composed of hard α keratins, like hair and nail (Szewciw et al. 2010; Werth 2013) (Fig. 3). Baleen plates begin in the dermis, where the baleen is covered in a horny, keratinous layer and forms long bristles (Slijper 1962). These bristles are cemented together by a layer of compacted keratin. Friction wears away the compacted plate, resulting in frayed, hollow fringes that intertwine to form a sieve (Werth 2001). This sieve-like formation allows the capture and removal of prey from inflowing water (Werth 2013). The continuously growing plates and fringes maintain a constant length through use and wear (Lubetkin et al. 2008; Werth 2013).
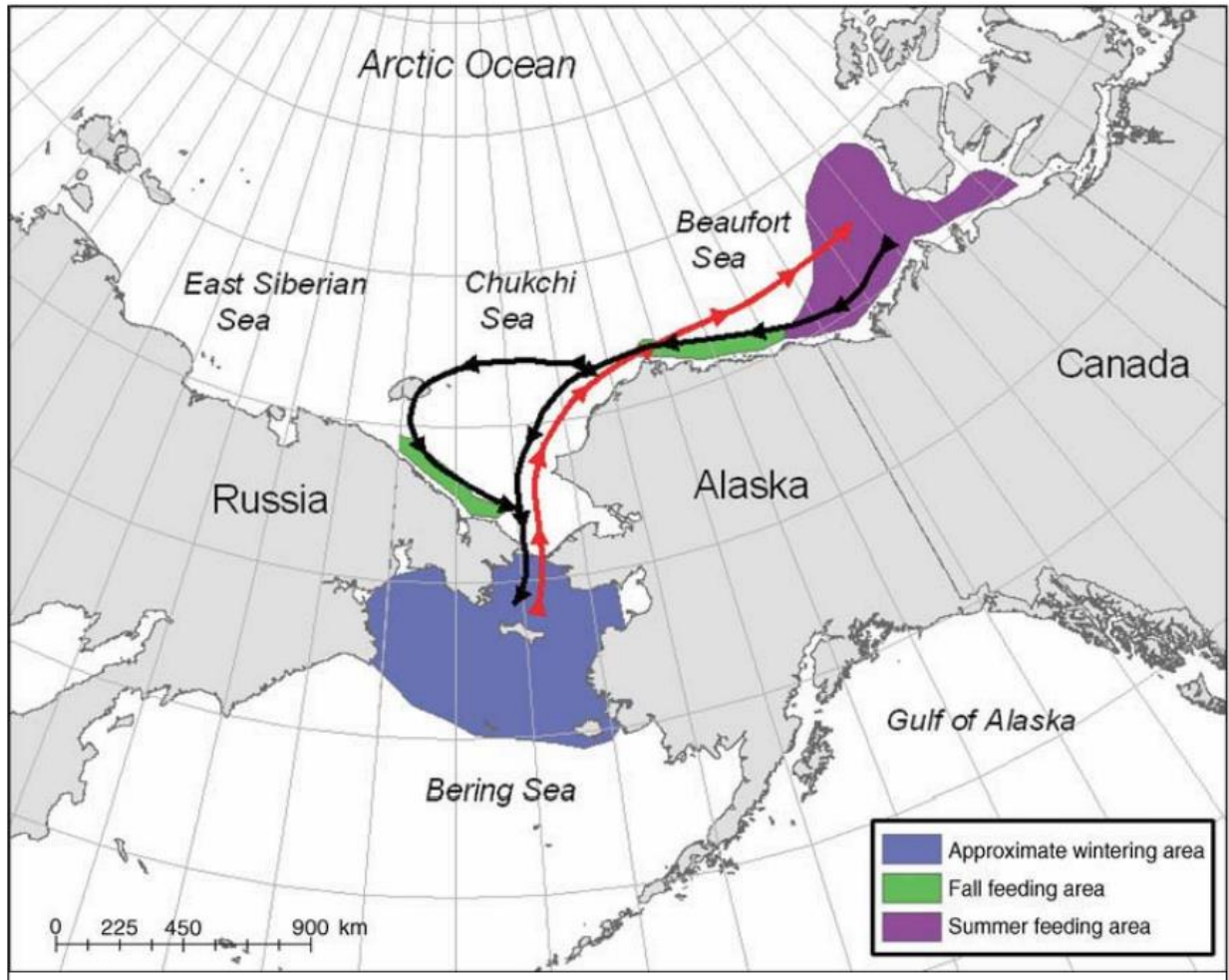
Figure 2. Western Arctic bowhead whale migration with wintering and foraging areas (Mocklin 2009)

Figure 3. A recently harvested bowhead whale with exposed baleen plates and fringes (IWC 2019)

In bowhead whales over 300 fringed, overlapping, triangular, keratinous plates emerge from the gingiva on each side of the maxilla, reaching over four meters in length (Scammon 1969; Nishiwaki and Kasuya 1970; Werth 2001). The plates are flexible, allowing them to fold backwards when the mouth is closed and unfold into a vertical position when the mouth is open (Lowry, 1993). The baleen plate length quickly increases over the first 60 plates on one side, reaching maximum lengths around plate 120 and remaining nearly constant until it decreases near the back of the mouth, around plate 250 (Lambertsen et al. 2005). Adult bowhead whale baleen plates grow approximately 16-25 cm/year as adults (>12 m body length) (Schell et al. 1989a).

Fringe diameter, fraying, and shape ultimately reflect prey size and foraging style to maximize foraging efficiency (Werth, 2001). Bowhead whale baleen fibers are longer, finer, and denser compared to other mysticetes, allowing higher particle capture of the microscopic prey that comprise bowhead whale diet (Werth 2013; Werth et al. 2016). The fringes have a diameter of 0.1-0.2 mm and a density of 35-70 fibers per cm^2 (Leatherwood et al. 1983; Schell et al. 1989a; Werth 2013).

Mysticete baleen plates have a similar composition, though the amount of each element differs slightly among species. Bowhead whale baleen fibers are primarily composed of zinc (~216 µg/g) and iron (~20 µg/g), and additionally comprised of copper (8 µg/g), boron (6 µg/g), nitrogen (14.2%), calcium (0.19%), sodium (0.30%), phosphorus (0.10%), magnesium (0.03%), potassium (0.03%) (St. Aubin et al. 1984).

Previous studies have confirmed the biosorbent nature of keratin (Banat et al. 2002; Kar and Misra 2004). Keratin is structurally robust, stable over a wide range of pH values, and has a high surface area, especially when hydrated. This contributes to keratin's success as a biosorbent. The length of contact between adsorbent and adsorbate (element ions) further influence elemental uptake efficiency by keratinous materials (Kar and Misra 2004). It should be noted that bowhead whales continuously filter feed, extending direct contact between water molecules, element ions, and baleen compared to other foraging styles (Werth et al. 2013). This allows more time and contact for the ions to potentially infiltrate and accumulate in the keratinous baleen. Hydrated, soft keratin proteins, like baleen, have a greater surface area than dry keratin proteins (Kar and Misra 2004). This provides more area for water molecules to adhere, making baleen

increasingly hydrophilic with water content and allowing baleen to absorb substantial amounts of water and associated elements.

Baleen plates and fringes can store approximately 20 years of continuous environmental data, including element concentrations and stable isotope (Schell et al. 1989a, b, 1992, 2000; Pomerleau et al. 2018). Stable isotopes such as $\delta^{15}N$ is indicative of prey trophic level while $\delta^{13}C$ provides valuable habitat use information (i.e. migration routes, habitat type). This helped previous researchers confirm bowhead whale prey, baleen growth rate, and migration patterns. Therefore, the analysis of bowhead whale baleen can provide temporal and spatial information on environmental and biotic element concentrations. Since baleen tissue grows continuously, it provides a timeline of whale diet, migration, and environmental data over an average of 20 years (Fig. 4).

Naturally occurring variation in stable isotope ratios are useful when studying organismal habitat use ($\delta^{13}C$) and diet ($\delta^{15}N$) (Crawford et al. 2008). With respect to the western Arctic, the ^{13}C isotopic signature of the Bering and Chukchi seas are not significantly different but are more enriched than the Beaufort Sea (Schell et al. 1989a, 1992, 2000, 2005). Schell found that the Bering and Chukchi seas are not isotopically distinct, so for the purpose of this study, they will be referred to as one water mass. Determining $\delta^{13}C$ stable isotope values in organismal tissues can help biologists determine and better understand habitat use and migration patterns. Zooplankton, the predominant prey for bowhead whales, differ in $\delta^{15}N$ along the bowhead whales' migration route (Bering/Chukchi more enriched; Beaufort Sea depleted) (Schell et al. 1989a, 1992).

Keratinous tissues are metabolically inert after formation and therefore preserve the isotopic record of prey consumed and environments inhabited when the tissue was synthesized (Schell et al. 1989a, b, 1992, 2000, 2005). Schell et al. (1989a, b; 1992) found that bowhead whales have marked annual oscillations in stable carbon and nitrogen isotopes along the length of baleen plates. These oscillations are from the whales' annual migration between the Bering and Beaufort seas, and the isotopic differences between these water masses. These oscillations appear as "peaks" (enriched) or "valleys" (depleted) when plotted. The peaks or troughs represent annual markers, with one enrichment (peak to peak) or depletion (trough to trough) cycle equating one year (Schell et al. 1989b).

(a)

(b)

Tip
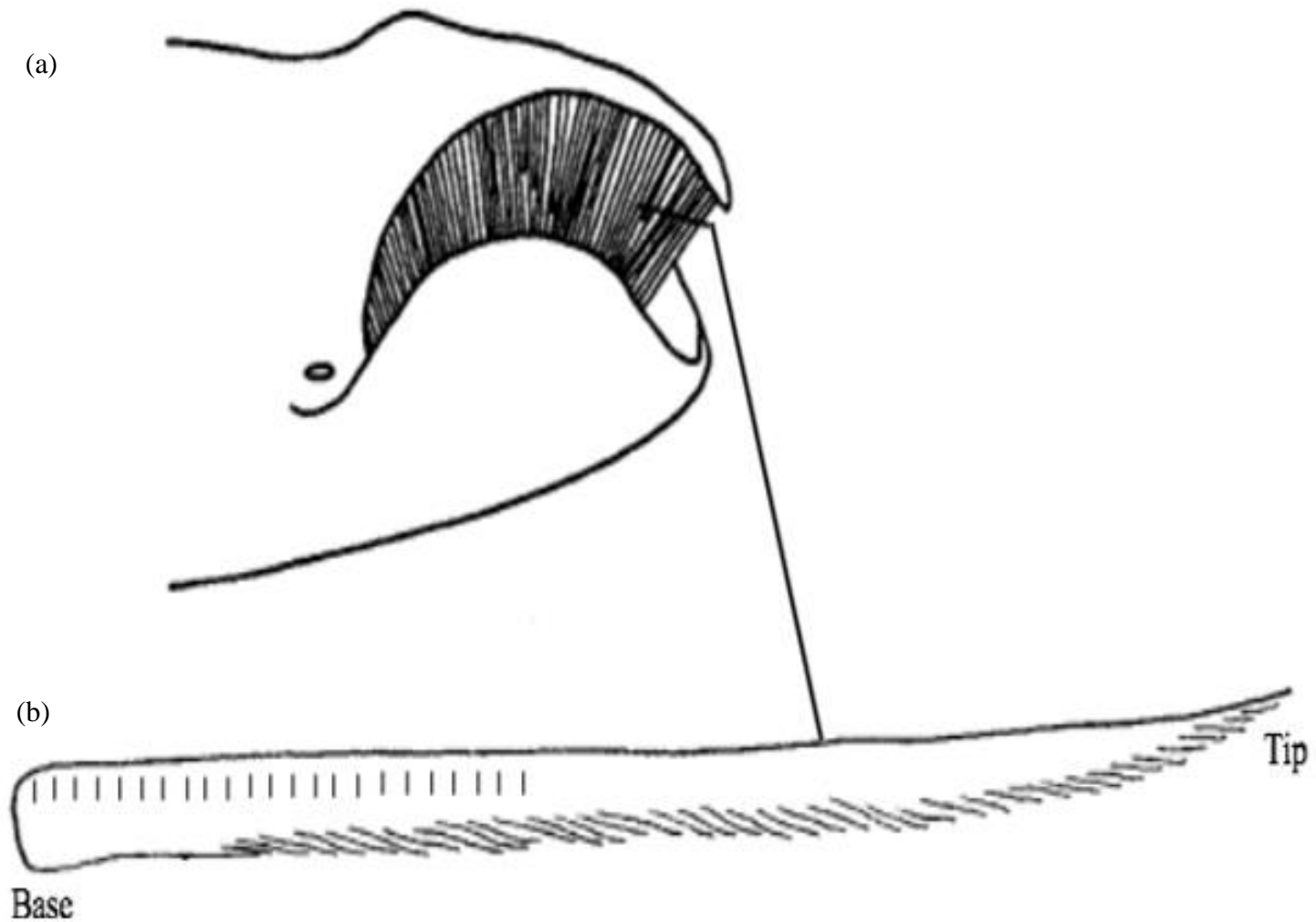
Base

Figure 4. Bowhead whale a) with exposed baleen, b) singular baleen plate indicating how each plate was sampled (modified from Werth, 2001) (Schell 1989a, b, 1992, 2000). Each plate was sampled from base (left) to tip (right) along the entire length

Bowhead whale baleen has previously been analyzed for $\delta^{15}N$ and $\delta^{13}C$ (Schell et al. 1989b, 1992, 2000, 2005). The stable isotope values Schell established for each whale's baleen plates were plotted against the length of the baleen plate (Fig. 5). Each sample from Schell's research represents a point along the baleen plate. Enriched samples represent when the whale was in the Bering/Chukchi seas while depleted samples represent the Beaufort Sea. One $\delta^{13}C$ cycle (i.e. most enriched point to the subsequent most enriched point) represents one year (Schell 1992). This information, in conjunction with bowhead whale age and baleen growth rate, can help back-calculate time and assign season (winter or summer) and year(s) to each sample.

Schell's stable isotope data indicated that zooplankton in the Bering and Chukchi seas are not isotopically distinct, though they do significantly differ from those in the Beaufort Sea. Since these seas are in fact isotopically distinct, it was expected that they might also differ in element concentration considering 1) keratin's success as a biosorbent (Banat et al. 2002; Kar and Misra 2004), 2) bowhead whales' lipid-rich prey containing elemental concentrations (Campbell et al. 2005), 3) baleen's ability to store over 20 years of environmental data (Schell 2000), and 4) baleen's continuous direct contact with water.

1.6. Study Importance

This study provides a first ever comprehensive database of essential and non-essential elements in baleen tissue. The temporal and spatial aspects of these data are valuable first steps to understanding how baleen acquire these elements, if the elements' concentrations are changing over time, and from which water mass these elements are being obtained. This research lays the groundwork for future absorbance research and biological and environmental toxicology studies.

2. OBJECTIVES

1) Establish a comprehensive dataset of essential and non-essential concentrations from 1958 through 1999 in the baleen of western Arctic bowhead whales.

2) Determine if time significantly influenced detected element concentrations.

3) Determine if detected element concentrations significantly vary between the Bering/Chukchi seas and Beaufort Sea.
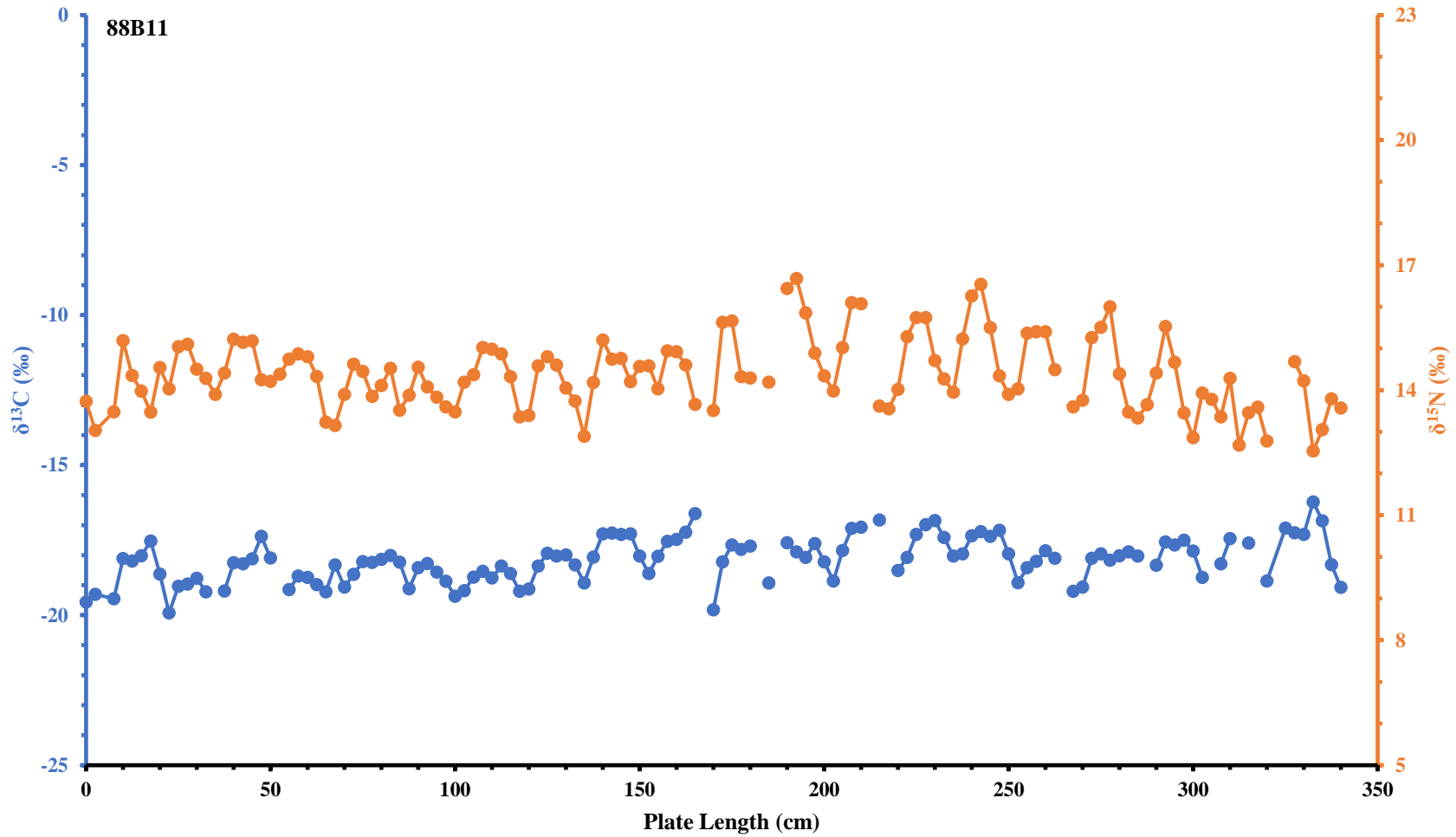
Figure 5. $\delta^{13}C$ and $\delta^{15}N$ values (‰) along the length of the plate (cm) from whale 88B11. The most enriched and depleted samples in an annual oscillation were selected and combined to create a new sample representative of time and location

3. MATERIALS AND METHODS

3.1. Sample Preparation

The samples used for this research were collected during native subsistence hunts in Alaska between 1966 and 1999 and provided to Donald M. Schell, University of Alaska Fairbanks by the North Slope Borough Department of Wildlife Management and Los Angeles County Museum collection (Schell et al. 1989a, b, 1992, 2000). The samples and corresponding stable isotope data were analyzed at the University of Alaska Fairbanks' Stable Isotope Facility.

Nine whales were analyzed; seven were landed in Barrow (1966, 1978, 1988, 1989, 1990, 1995, 1997) and two in Kaktovik (1998, 1999) (Table 1). Baleen sampling interval was either every 1.0cm, 2.0 cm, or 2.5 cm, though sampling interval was constant for each baleen plate (Schell et al. 1989a, b, 1992). Samples were selected and combined for analysis to create a new sample, based on the available stable isotope data, which provided a location and time per sample (Table 2). For example, in whale 66B1, samples 2.5 cm and 5 cm were combined for analysis based on necessary mass; the stable isotope data indicated these were the most enriched samples from winter 1965/1966 (Bering/Chukchi seas). If only one sample was available for a specific location, season, and year, and thus could not be combined with another sample, then the singular sample was selected and used. Winter represents November of one year through March the following year, so two years were attributed to samples representing winter. This provided a total of 148 samples with at least one sample per year from 1958 to 1999 with the exception of 1967.

Samples (0.001 – 0.297 g) were digested with 2 mL of trace metal basis nitric acid in 100 mL PTFE digestion tubes. All samples were placed in a digestion Modblock at 60^0 C for 24 hours or until the samples were completely digested. Some samples required an additional 1-3 mL of nitric acid to fully digest; therefore, the total volume of nitric acid ranged between 2-5 mL. Samples with 2 mL of nitric acid were diluted to 50 mL in a volumetric flask with ultrapure deionized water (18.2 MΩ); samples with 3-5 mL of nitric acid were diluted to 100 mL. This kept nitric acid under 5% per sample. Then, 10 mL of each sample were pipetted into 50 mL PTFE digestion tubes and shipped to the University of Southern Mississippi Center for Trace Analysis. Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the concentrations of 14 trace elements and heavy metals: aluminum [Al], arsenic [As], cadmium

[Cd], cobalt [Co], chromium [Cr], copper [Cu], iron [Fe], mercury [Hg], manganese [Mn], nickel [Ni], lead [Pb], selenium [Se], vanadium [V], zinc [Zn].

3.2. Sample Analysis

Samples were analyzed using a sector-field inductively coupled plasma mass spectrometer (ThermoFisher Element XR) with a Peltier-cooler spray chamber (PC-3; Elemental Scientific, Inc.). Prior to analysis, digested samples were diluted 5-fold in 0.64 M ultrapure nitric acid (Seastar Baseline) containing 2 ppb indium as an internal standard. Diluted samples were held in acid-washed Teflon autosampler vials. Mass spectrometer scans were performed in low (Cd-111, Hg-199,200,201,202, Pb-208), medium (Al-27, V-51, Cr-52, Mn-55, Fe-56, Co-59, Ni-60, Cu-63, Zn-66), and high (As-75, Se-77,82) resolution, depending on the isotope. Mo-98 was monitored to correct for MoO^+ interference on Cd. Standardization was by use of external standards, with a high standard and a blank re-run every eight samples. For the elements (Hg, Se) where multiple isotopes were determined, no significant analytical differences were noted between the isotopes. Two USGS reference water concentrations were also assessed as part of each analytical run in order to verify the standardization. In several cases, sample calibration was also verified by standard additions. Blanks of ultrapure deionized water and trace metal basis nitric acid (3%, 4%, 5%) were used for quality control purposes.

Data were provided in µg/L, or parts per billion, and converted to µg/g, or parts per million, through the following equation:

$$\frac{\left(Solution\ Concentration\left(\frac{\mu g}{L}\right) x\ Total\ Solution\ Volume\ (L)\right)}{Solid\ Sample\ Mass\ (g)}$$

3.3. Data Analyses

Pearson correlations and Wilcoxon rank sum tests assessed concentrations within each individual whale to determine temporal or spatial trends in samples per whale. Statistical analyses did not compare concentrations among whales since a variety of factors (physiology, age, migration route, etc.) remained unknown and, therefore, they could not be accounted for in a statistical model. More specifically, each whale likely differed to varying degrees in migration

path, prey consumption, foraging grounds, physiology, gender, age, and current element load, which influence element uptake and, therefore, the detected concentrations.

Pearson correlations indicated whether time and element concentration were significantly correlated (i.e. if metal concentration increased or decreased with time). All outliers were removed from the data for analyses. Outliers were determined through quantile analyses; any datapoint outside of the 1st and 4th quartile was deemed an outlier. This resulted in some whales, locations, and/or elements not meeting the standard minimum for data points (<5) for a correlation). Positive Pearson correlations indicated an increase in element concentration as time progressed. Correlations were analyzed per location and element in each whale. This yielded more accurate correlation results and revealed at which locations time and element were correlated. Two correlation coefficients were provided per element in each whale: one for the Beaufort Sea and a second value for the Bering/Chukchi seas, respectively (Table 6).

Any insignificant correlations with time meant that time could be ignored in further analyses and were subsequently analyzed with a Wilcoxon rank sum test. Only concentrations that lacked significant correlations in both locations were analyzed. This determined significant differences in concentrations between location. Whale 95B8 was not analyzed with this test since all elements had a significant correlation in at least one location. Whale 78B2 (Cu, Fe, Mn, V), whale 89B10L (Al, As, Cd, Co, Cr, Cu, Fe, Ni, Pb), and whale 97B8 (all elements) were also not analyzed due to lack of data points per location (n<5). Ultimately, location did not significantly affect concentration (p>0.05).

The molar ratio of Se to Hg was calculated for each whale at each location, as well as for each whale at both locations, via:

$$\frac{Se}{Hg} = \left(\frac{Se/78.96}{Hg/200.59}\right)$$

where 78.96 g/mol and 200.59 g/mol are the atomic masses of Se and Hg, respectively (Table 7). Molar ratios more accurately state the proportions of Se and Hg compared to concentration ratios. Spearman rank correlation determined the strength of the statistical relationship between Se and Hg concentrations for each whale.

4. RESULTS AND DISCUSSION

All 14 elements (Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, V, Zn) were detected in the baleen of all whales sampled (n=148) (Tables 3, 4, 5). Covariance and colimitation of Fe, Mn, and Ni was detected in whales hunted in the 1990s as their concentrations varied similarly across the entire baleen plate in each whale. In whales hunted between 1989 and 1999, most elements had their highest concentrations in the same sample, representing a specific time and location. Concentrations of Se and Hg were significantly correlated across all whales, with Hg toxicity suggested in whales hunted in the 1960s and 1970s as well as whales hunted in the 1990s. The highest concentrations of all elements, excluding Cu, were found mostly in whales hunted between 1995 and 1999.

On average Zn had the highest consistent concentrations (110 to 8000 µg/g), with means per whale ranging between 200 and 900 µg/g. Compared to all remaining metal ions tested, Al and Fe had the highest mean concentrations (2000 and 4900 µg/g) and broadest ranges (10.9 – 3000 µg/g, 0 – 40000 µg/g), respectively (Table 3). In contrast, the lowest mean concentrations were detected for As, Cd, Co, Ni, Se, and V. Each whale differed in one, if not all, variables: migration path, prey consumption, foraging grounds, physiology, gender, age, and current element load. This would ultimately influence element uptake and, therefore, the detected concentrations.

4.1. Fe, Mn, Ni Covariance

Whales 90B8, 95B8, 97B8, 98KK1, and 99KK1 each had similar trends (concentration spikes and depressions in the same samples [same season and year]) in Fe and Mn along the baleen plate, though the whales' trends differed among each other (Fig. 6). In whales 90B8 and 95B8, Ni followed the same trend as iron and manganese. Salomon and Keren (2015) suggested that acclimation to environmental Mn concentrations lowers Fe stress responses within cells. They may avoid oxidative damage in Fe-limiting conditions, like environments susceptible to fluctuations in Fe concentrations (i.e. coastal environment). Sharon et al. (2014) reported Fe presence potentially limiting Mn entering the cell. Even more, Ni ions can attach themselves to particles containing Mn or Fe (Cempel & Nikel 2006). It is possible that Fe and Mn were co-limiting each other in these whales. It is also a possibility that Ni attached itself to particles that also had Fe and Mn, and that the elemental ions were dissolved in the water column or
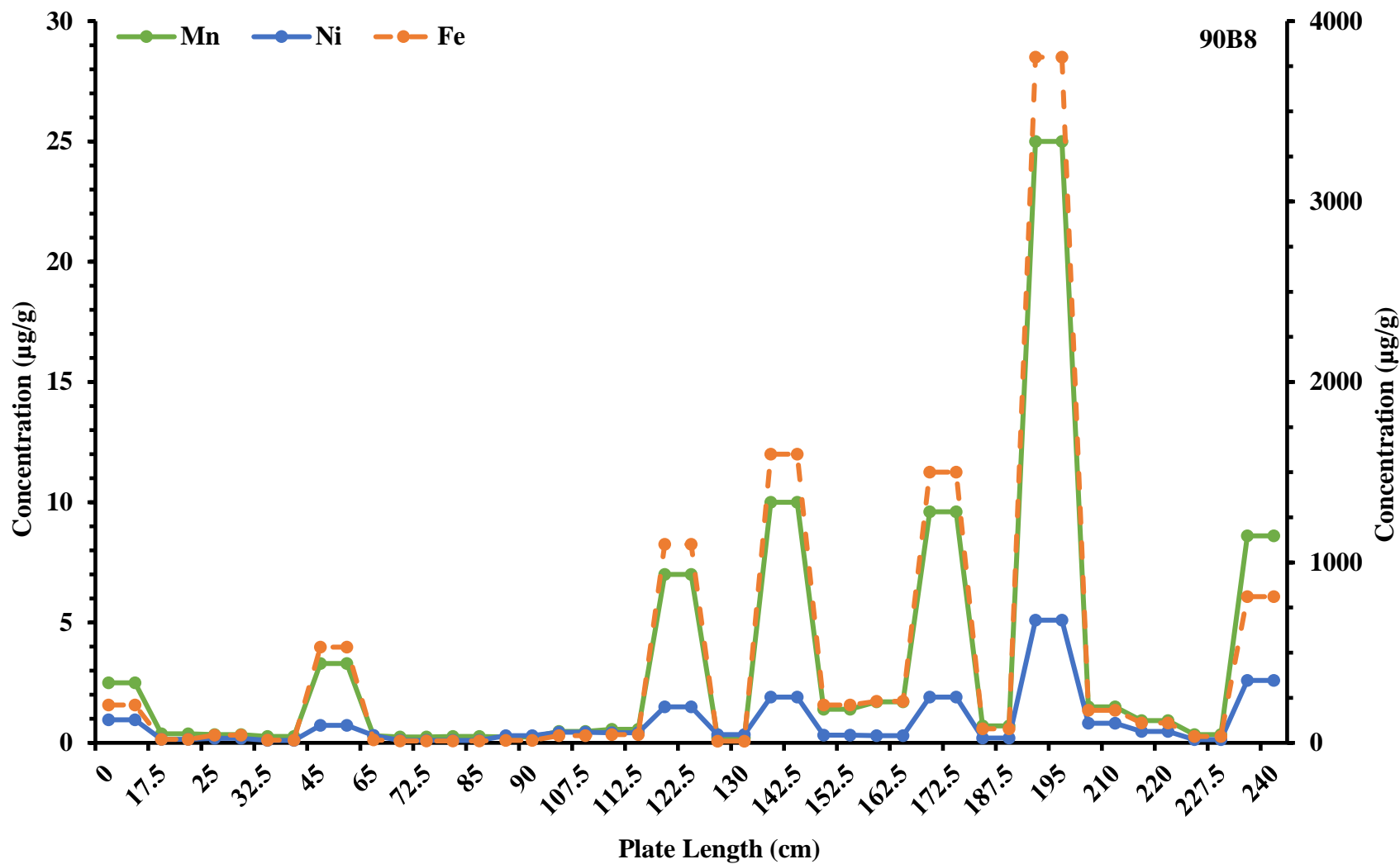
Figure 6. Fe, Mn, and Ni concentrations varied coincidently across the baleen plate in whale 90B8, suggesting intracellular covariance of these elements. Fe, Mn, and Ni interact with each other to control uptake and avoid toxicity. Dashed lines correspond with the secondary axis

incorporated into ice and then melted. The ions could then become incorporated into the baleen of whale 90B8. This potentially explains the similarities in concentration trends over time.

4.2. Relationships Among Concentrations

In some whales, elements had their highest concentrations in the same sample, which represented a specific location and time. Despite being found in different whales, most of these concentrations overlapped in time and location. For example, in whale 78B2, concentrations of Co, Cr, Cu, Fe, Mn, Ni, and V were highest in the sample representing winter 1977-1978 (Bering/Chukchi seas). Whale 89B10L had its highest concentrations of Al, Cd, Co, Cr, Cu, Mn, Ni, and Pb in the oldest sample from the baleen plate (summer 1985, Beaufort Sea). Whale 90B8 had its highest concentrations of As, Cr, Fe, Mn, Ni, and Se in summer 1981 (Beaufort Sea), while Cd, Co, Cu, Hg, Pb, and V were highest in summer 1979 (Beaufort Sea). These elevated concentrations may be explained by the warm phase of the Pacific Inter-Decadal Oscillation (PDO) that reached the Arctic in 1976-1977 (Papineau 2001; Overland et al. 2002; Bieniek and Walsh 2013). PDO acts on a 20-30-year timescale and alternates between warm and cool phases. This may explain why most of these high concentrations for multiple elements were in samples representing the Beaufort Sea. Even more, Barrow (northernmost Alaska) experienced significant warming in 1976 to 1978 compared to other parts of Alaska. Warmer surface and midwater temperatures increase the frequency and intensity of melting events (permafrost, ice, snow), with these events beginning earlier in the year and lasting longer. Permafrost, ice, and snow melts mobilize associated elements and allow them to enter terrestrial and aquatic environments (Pfirman et al. 1995a, b; Sakshaug 2004; Rydberg et al. 2010). This may explain the observed concentration spikes in samples representing the Beaufort Sea around this time. Another possibility to consider is that these whales may have diverted element concentrations from other tissues to baleen tissue to lower their risk of toxicity to more critical organs and tissues, like blubber or kidney.

Additionally, whale 95B8 had its highest concentrations of Al, As, Co, Cr, Cu, Fe, Hg, Mn, Ni, V, and Zn in summer 1995 (Beaufort Sea). Whale 99KK1 had major spikes in concentration for every element except As, Se, and V at this same time and location as well (summer 1995, Beaufort Sea). The overlap in time and location between the two whales may indicate elevated concentrations of As and V in the environment. Additionally, there were two

periods of heavy, prolonged rain in August 1994 that resulted in severe flooding near the Koyukuk River. This area is proximal to the Yukon River which empties into the Bering Strait and Chukchi Sea area. This flooding likely washed usually large amounts of riverine sediments and associated elements into the Bering Strait/Chukchi Sea areas. Since currents transport dissolved elements, it is plausible that these elements were transported in water molecules or in ice into the Beaufort Sea. Generally, these higher concentrations may also be from the environment or prey.

Whale 99KK1 had a second major spike in summer 1999 (Beaufort Sea) for As, Cd, Co, Cr, Fe, Mn, Ni, and Pb. Summer of 1999 (Beaufort Sea) was the most recent sample on the plate from 99KK1, so it is possible that this individual was diverting other tissues' concentrations to the baleen to avoid toxicity (Yamamoto et al. 1987; Cuvin-Aralar and Furness 1991). It is also plausible that environmental concentrations of these elements were relatively higher due to increased industrial activities (Congressional Research Service 2020).

4.3. Se:Hg

Spearman rank correlation confirmed a significant relationship between Se and Hg across all samples from all whales (ρ = -0.398, p < 0.001) (Table 7). The closer the absolute value the rho coefficient (ρ) is to 1, the stronger the relationship. Therefore, a relationship exists, but not as strong as previously noted selenium/mercury relationships noted in other cetaceans (García-Alvarez et al. 2015). When the whales were analyzed independently, there was a significant correlation between Se and Hg in whale 88B11 (ρ= -0.43, p<0.001) and whale 97B8 (ρ=0.71, p<0.05). Molar ratios of each sample exceeding 1:1 indicate that Se may have had a protective effect against Hg toxicity (Berry and Ralston 2008). Alternatively, a molar ratio ≤1 may be indicative of all available Se being bound to Hg, potentially resulting in oxidative stress risk if any un-bound Hg existed (Caceres-Saez et al. 2013). Most samples in whales 66B1, 95B8, 97B8, 98KK1, and 99KK1 had molar ratios smaller than 1:1, indicating that there is less available Se than Hg, which may result in toxicity. More specifically, every sample in whale 66B1 except one (66B1-B2) had a molar ratio under 1. Most samples in whale 95B8 also had a molar ratio less than 1. Every sample from whales 97B8, 98KK1, and 99KK1 (except those with selenium concentrations under the detection limit) also had molar ratios under 1. In contrast, every sample

from whales 78B2 and 89B10L had molar ratios over 1, indicating that Se was bound to all available Hg, leaving an excess of Se. More than half of the samples from whales 88B11 and most samples from 90B8 also had molar ratios exceeding 1.

4.4. Temporal Trends Along the Baleen Plate

Whales hunted from 1995-1999 had the highest concentrations of every element except Cu (Tables 4, 5). Additionally, element concentrations significantly increased as time progressed (Table 6). Concentrations of As, Mn, and Ni increased with time in both locations while Al, Cd, Co, Hg, Pb, Se, and Zn increased with time in at least one location. Cr was the only element to decrease as time progressed, though this only applied to two whales.

Whales 95B8, 97B8, 98KK1, and 99KK1 had the highest concentrations of every element except Cu (Tables 4, 5). The latest hunted whale, 99KK1, had the highest mean concentrations among all whales for Al, As, Cr, Fe, Hg, Mn, Ni, and V. Whales 95B8, 97B8, and 98KK1 had the highest average concentrations among all the whales for Al, Cd, Co, Hg, Mn, Ni, Pb, and Zn. This was likely due to increased anthropogenic activities over time, especially natural resource exploitation and pollution, resulting from a more easily accessible and socio-economically productive Arctic environment (Congressional Research Service 2020). These relatively elevated concentrations may also be due to warming air and sea temperatures in the Arctic. Since 1992 air temperature has been increasing, especially in Barrow, AK (Papineau 2001). This promotes increased length, frequency, and intensity of melting events (permafrost, snow, sea and glacial ice), which in turn would increase erosion. These processes would allow a relatively quicker increase in environmental concentrations compared to previous decades.

Average concentrations of Cu were highest in the earliest landed whales (66B1 and 78B2) (Table 3), although whales 88B11, 90B8, and 99KK1 had a few isolated concentrations that were in the hundreds or thousands of µg/g. This is may be attributed to coal mining, considering Cu is abundant in coal emissions (Demirbas 2005). More coal mines were open between 1941 and 1963 compared to the latter half the century, with these mines proximal to the study area or major rivers. Coal exploration along the coastal Beaufort Sea (1984) may explain the isolated concentrations in the latter hunted whales (Merrit 1986). Additionally, the sporadic elevated concentrations in whales 88B11, 90B8, and 99KK1 may be attributed to Red Dog Mine, which began exploration of 1988 (Teck 2020). The Red Dog Mine, a significant producer of Cu

in the Americas, is situated in northwest Alaska close to the Chukchi Sea. The extraction and production of Cu from Red Dog Mine therefore present a source of Cu from the late 1980s on. Additionally, Cu exists naturally in crustacean blood (hemocyanin) and presents another source of concentrated Cu to bowhead whales via their zooplankton diet. It is possible that whales 66B1 and 78B2 may have consumed prey with higher Cu content than prey available to the latter whales.

Element concentrations significantly fluctuated as time progressed ($r \geq |0.50|$) (Table 6). All reported correlation coefficients for As, Hg, and Zn and more than half of the coefficients for Al, Cd, Mn, Ni, Pb, and Se were positive, indicating that concentration increased as time increased along the baleen plate (from tip (older) to base (younger)). Each trend should be considered entirely independent, even if multiple whales have similar trends for the same element. For example, Al concentrations increased as time progressed in whale 66B1 (Bering/Chukchi seas) ($r = 0.59$), 90B8 (Beaufort Sea) ($r = 0.62$), 95B8 (Beaufort Sea) ($r = 0.93$), and 98KK1 (Beaufort Sea) ($r = 0.64$). Therefore, in 66B1 (Bering/Chukchi seas) Al concentrations increased across the plate from the oldest (1958) to newest (1966) plate growth. In whale 90B8 Al concentrations (Beaufort Sea) increased from 1979 to 1990 while Al concentrations in whale 95B8 (Beaufort Sea) increased from 1991 to 1995. Concentrations increased from 1988 to 1997 in whale 98KK1 (Beaufort Sea). Since each element was analyzed per whale, independent of other whales, it cannot be said that Al increased in concentration from 1958 to 1997, or across all whales as a whole. Several unknown factors (e.g. current element load, physiological status, migration path) likely affected these concentrations and could not be accounted for in statistical models

When looking at both locations, As, Mn, and Ni concentrations significantly increased as time progressed. More specifically, As significantly increased with time for whales 66B1 ($r = 0.90, 0.89$) and 98KK1 ($r = 0.83, 0.74$). The temporal trend of arsenic in bowhead whales 66B1 and 98KK1 is difficult to explain with certainty. The time recorded in the whales' baleen plates do not overlap, and the trend was not detected in any other whales. Therefore, it is uncertain as to the cause of this increase. Concentrations of Mn also increased with time in whales 98KK1 ($r = 0.58, 0.62$) and 99KK1 ($r = 0.61, 0.81$). Since these whales' plates overlapped temporally (1991–1998), it is possible that environmental concentrations increased during this time from anthropogenic activities or environmental processes. Concentrations of Ni increased with time in

whale 66B1 (r = 0.79, 0.67). High fossil fuel combustion and battery production (specifically before the 1980s) potentially explain this trend, though it was only seen in one of the nine whales studied (Broussely et al. 1999; Cempel and Nikel 2006).

In at least one location per whale, Al, Cd, Co, Hg, Pb, Se, and Zn increased in concentration over time for the majority of whales (Table 6). This may be attributed to a variety of factors: a warming Artic environment releasing elements in permafrost, ice, and snow and intensifying erosion, increasing industrial activity, potential bioaccumulation, or a combination of these (Congressional Research Service 2020). Since Al is the most abundant metal and third most common element in Earth's crust, coastal erosion or sediment accumulation allow associated elements to enter the coastal environment (ATSDR 2008; Farquharson et al. 2018). Found in shipping discharges and coal combustion, Cd can enter the environment through anthropogenic activities (Demirbas 2005; Tornero and Hanke 2016). Though a byproduct of lithium batteries and mining, Co is also found in Earth's crust (Miller and Goldfarb 1997; Broussely et al. 1999). Permafrost contains high levels of Hg (Schuster et al. 2018). Warming air temperatures in the Arctic increase the intensity, length, and frequency of melting events, allowing Hg to permeate the aquatic environment through runoff. Melting permafrost and glaciers, as well as runoff, increase coastal erosion. This allows Hg to further penetrate the marine environment. Mining (e.g. Red Dog Mine), shipping discharges, and coal emissions all present sources of Pb in the marine environment from which baleen can absorb (Naidu et al. 1997; Demirbas 2005; O'Hara et al. 2006; Tornero and Hanke 2016). As a natural occurrence in Earth's crust, Se also enters the environment through Cu refinery waste and fossil fuel combustion (GESAMP 1988). The Red Dog Mine has one of the world's largest Zn deposits and is also a significant source of Cu to the Americas (Teck 2020). This mine is near the Chukchi Sea in northwest Alaska and provides a point source for Cu and Zn from which to enter the marine environment from the late 1980s on. Increased industrial activities and erosion likely explain these elements' increasing concentrations with time.

Cr was the only element with mostly negative correlation values (whales 90B8, 95B8), indicating that concentrations decreased as time progressed. Baleen plates from 90B8 and 95B8 did not have overlapping timeframes (1979-1990, 1990-1995), but they did overlap with plates from whales 97B8, 98KK1, and 99KK1, which did not have this temporal trend in Cr concentrations. Therefore, the observed trend was likely due to biological factors (current

element load, physiology, excretion) rather than environmental (i.e. decreased weathering) or anthropogenic (i.e. decreased fossil fuel combustion).

4.4. Spatial Distribution of Elements

Location did not significantly affect concentration ($p > 0.05$) (Fig. 7). However, whale 99KK1 had the highest mean concentrations across all whales for: Al, As, Cr, Fe, Mn, and Ni in both locations; Cd, Fe, Hg, and V in the Beaufort Sea; Zn in the Bering/Chukchi seas (Table 5). Average concentrations in whales 66B1 and 78B2 were higher in the Bering/Chukchi seas than the Beaufort Sea, except for As and Se in both whales and Cu, Hg, and Ni in 66B1. Whales 89B10L, 90B8, 95B8, 98KK1, and 99KK1 had high average concentrations of Cd, Co, Cr, Fe, Mn, and Pb in samples representing the Beaufort Sea compared to those representing the Bering/Chukchi seas.

Mean concentrations of As were higher in samples representative of the Beaufort Sea across all whales (Table 5). Compared to the Bering/Chukchi seas, Cd and Co had higher averages in samples representing the Beaufort Sea across all whales, except 66B1, 78B2, and 97B8. The same was true for Cr except for whales 66B1, 78B2, and 88B11. Whale 89B10L had higher mean concentrations for all metals except V and Zn in samples representative of the Beaufort Sea than in samples representing the Bering/Chukchi seas. This was also true for 90B8 for every element except Fe, and 95B8 for every element except Se and Zn. In contrast, whale 78B2 had higher mean concentrations in samples representing the Bering/Chukchi seas than those representing the Beaufort Sea for all elements except As and Se.

These differences in location-based concentrations are likely due to a variety of factors. Water temperature and pH in the Beaufort Sea may have been more optimal for environmental element absorption (Kar and Misra 2004). Differences in prey, foraging locations, and migration path may have resulted in elevated concentrations obtained from the Beaufort Sea compared to the Bering/Chukchi seas. Current concentration loads in baleen and other tissues, as well as redistribution of concentrations among tissues may have influenced the detected concentrations (Yamamoto et al. 1987; Cuvin-Aralar and Furness 1991; Banat et al. 2002). More industrial activity or pollution in or proximal the Beaufort Sea could have caused these location-specific results (Demirbas 2005; Tornero and Hanke 2016).
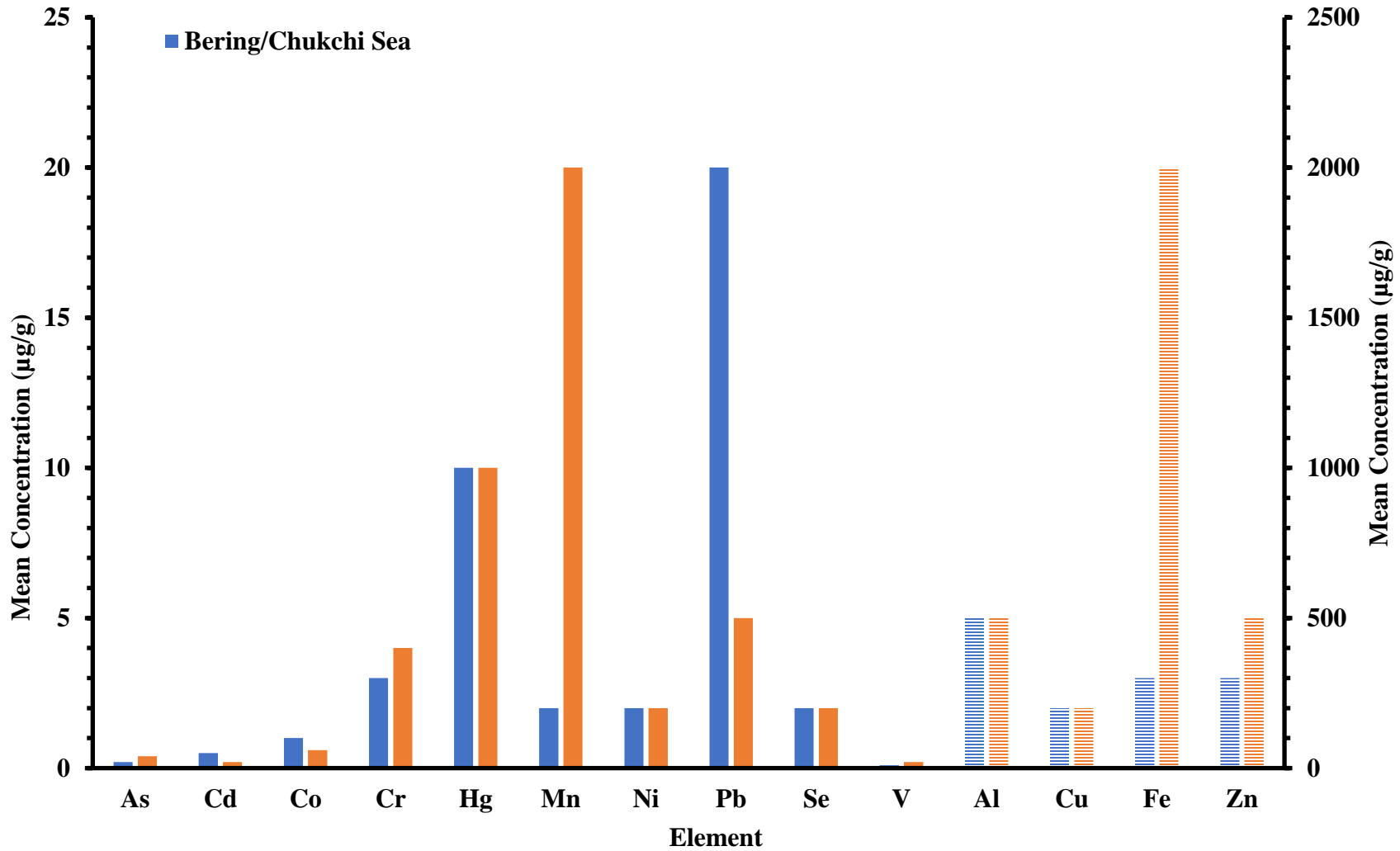
Figure 7. Mean concentrations (µg/g) of each element among all whales in the Bering/Chukchi seas (blue) and Beaufort Sea (orange). Bars with horizontal lines (Al, Cu, Fe, Zn) correspond to the secondary axis

On average, Fe and Mn had higher concentrations in the Beaufort Sea for all whales except 66B1, 78B2, 88B11, and 90B8 (Fe only). Mean Fe concentrations from samples representing the Beaufort Sea were at least double the concentrations found in the Bering/Chukchi seas in all whales (Table 4). Major rivers like the Mackenzie and Colville deposit Fe-laden sediment into the coastal marine environment. During formation of sea ice, glaciers, and icebergs, sediment and associated elements, like Fe, are incorporated into the ice while passing over land and continental shelves (de Baar and de Jong 2001). As this ice melts, sediment and associated elements are released into the ocean environment where they are weathered and transported further (Pfirman et al. 1995a, b).

Whale 89B10L had higher mean concentrations for all elements in samples representative of the Beaufort Sea, except V which had the same average concentrations in both locations, and Zn which was higher in the Bering/Chukchi seas. This trend in 89B10L could have been due to this individual staying in the Beaufort Sea longer than what is considered typical for this population. The western Arctic experienced a warm period from the 1970s through mid-1980s (Overland et al. 2002). If there was later and less ice growth in the Beaufort Sea to encourage the population to migrate to their overwintering grounds, then it is possible that some individuals, like 89B10L, stayed in their foraging habitat of the Beaufort Sea longer than what is typical. Although this follows the assumption that the Beaufort Sea has higher concentrations than the Bering/Chukchi seas, this is simply a hypothesis and cannot be confidently stated since water samples were not collected to compare to the baleen samples. Alternatively, this warmer phase likely increased permafrost, ice, and snow melt frequency and intensity. This likely released higher concentrations of elements into the environment compared to cooler temperature years.

Marine mammals have been known to redistribute elements among tissues, which was thought to protect against toxicity (Yamamoto et al. 1987; Cuvin-Aralar and Furness 1991). This should be kept in mind when looking at location- and time-specific concentrations, as the detected concentrations in this study may not be entirely representative of concentrations in that location or the time the sample signifies. Element concentrations from the environment and prey need to be determined and compared with baleen concentrations in order to confidently say the source of such concentrations. Even more, nutrient limitation and co-limitation may be influencing the determined concentrations, and therefore should be considered when using organisms as indicators of environmental concentrations. Ultimately, the sources of the detected

concentrations cannot be pinpointed beyond the general water mass in this study. These concentrations also may not accurately represent the environment if physiology is limiting or encouraging uptake.

4.5. Element Concentrations in Baleen

The highest concentrations in baleen were Al, Cu, Fe, and Zn, likely due to Alaska's geology and bowhead whale composition (St. Aubin et al. 1984). It should be noted that Cu, Fe, and Zn are essential elements, while Al is non-essential. Among the lowest concentrations were As, Cd, and V.

Concentrations of Al were between 10.9 and 3000 µg/g. As the most abundant metallic cation found in Earth's crust, Al is the most widely distributed metal in the environment (McLean 1976; Nayak 2002). Weathering and waste rock from mining activity release Al into the environment (McLean 1976; Nayak 2002). Dissolved oceanic Al is relatively low compared to riverine dissolved Al, possibly due to Al removal by biogenic particles in highly productive surface waters (Orions and Bruland 1986; Gehlen et al. 2002). However, river deltas (e.g. Mackenzie River Delta in Beaufort Sea) present an environment where dissolved and sediment-associated Al may be concentrated. In this environment Al would likely not dissolve into the water column enough to compensate for continual input of high concentrations.

Detected concentrations of Cu (3.1 – 4,220 µg/g) exceeded concentrations that naturally exist in bowhead whale baleen (8 µg/g) (St. Aubin et al. 1984). Concentrations exceeding baleen's natural composition are likely from the environment or prey. Lithium batteries and associated wastes contain Cu (Broussely et al. 1999). Significant amounts of Cu have been mined during the study timeframe (1958 – 1999) (Miller and Goldfarb 1997). Waste or large concentrations in sediments carry Cu to the coast by rivers. Crustaceans, bowhead whales' predominant prey, have Cu-based blood (hemocyanin) (Terwiliger 2015). Since bowhead whales consume approximately 100 metric tons of zooplankton, prey present a large source of Cu for bowhead whales (Bohn and McElroy 1976; Thomson 1987).

Fe in baleen had a broad range (0–40,000 µg/g). Approximately 20 µg/g exist naturally in bowhead whale baleen. Fe is also a vital micronutrient upon which most life is dependent (Raven et al. 1999). Phytoplankton are especially dependent upon Fe for photosynthesis compared to other trophic levels that are heterotrophic. Zooplankton then consume phytoplankton where

element concentrations can biomagnify through the food chain. Since bowhead whales mainly consume zooplankton, and a large volume of them, the ingested crustaceans present a large source of Fe for bowhead whales that are further biomagnified (Bohn and McElroy 1976; Thomson 1987). Even more, large Fe deposits can be found throughout Alaska, particularly in the western and northwestern regions (Athey et al. 2013). This may explain the incredibly high concentrations of Fe compared to bowhead whale baleen composition.

It should be noted that the physiological and biological concentrations of Cu and Fe are interdependent, as they interact to control physiological needs based on environmental availability. The Bering Sea is Fe-limited (Coale 1991; Peers et al. 2005). Some phytoplankton have adapted to this by decreasing Fe dependency but increasing the demand for Cu. This could account for the colimitations of Cu and Fe previously observed in the Bering Sea and may explain why detected Cu concentrations were higher than what is naturally found in baleen. Alternatively, Schoffman et al. (2016) found that the presence of Cu encouraged increased Fe uptake. It has been suggested that some cells are able to alleviate Cu toxicity by binding Cu to molecules that bind to metal ions and alleviate toxicity by decreasing ion load (Clarke et al. 1978; Nicolaisen et al. 2010).

Despite a broad range (110 – 8000 µg/g) and a few sporadic outliers, Zn had the most consistent concentrations across all samples. This was probably because bowhead whale baleen naturally has 216 µg/g of Zn (St. Aubin et al. 1984). Any deviations from the amount that's naturally in baleen is most likely derived from the environment or prey. Significant amounts of Zn have been produced from mining throughout the time frame of this study (1958-1999), especially at Red Dog Mine proximal the Chukchi Sea and Ruby Creek at Bornite along the Yukon River (Naidu et al. 1997; O'Hara et al. 2006). Additionally, Zn can be found in shipping discharges (Tornero and Hanke 206). These industrial activities permit Zn to enter Alaska's marine environment during this time.

Levels of As for all samples ranged between 0.08 and 3 µg/g. Shipping discharges and coal emissions allow As to enter aquatic ecosystems (Demirbas 2005; Tornero and Hanke 2016). Although direction element ion absorption from water into baleen has not been proven, it is still possible that direct absorption of As from water into baleen tissue may have contributed to these elevated concentrations. Even more, ingested prey presents another source of elements which can biomagnify and concentrate in baleen over time.

Concentrations of Cd ranged from not detected (N/D) to 10 µg/g, and may have resulted from industrial activity (coal combustion, shipping discharges), consuming prey, or transferring Cd from another tissue to baleen to avoid toxicity (Yamamoto et al. 1987; Cuvin-Aralar and Furness 1991; Demirbas 2005; Tornero and Hanke 2016).

Levels of V had a small range (0.00–2 µg/g). Invertebrates comprise the majority of bowhead whale prey and present a source of V in baleen tissue (Becker et al. 1997; Das et al. 2003). A constituent of crude oil, V can also infiltrate the marine environment through operational discharges and seepage relating to petroleum activities (Maki 1992; Osuji and Onojake 2004).

Concentrations of Mn ranged from 0.19 – 200 µg/g, although most samples had concentrations ranging between 0.19 and 12 µg/g. Large amounts of Mn are found in minerals and Earth's crust (Howe et al. 2005; Khamkhash et al. 2017). Erosion and volcanic activity, as well as mining and pollution, release Mn into the environment. The relatively higher concentrations of Mn were in whales from the late 1990's, which may have resulted from increased industrial activity and pollution during that time.

Levels of Ni in baleen ranged between 0.085 and 20 µg/g. This element has not been determined in any bowhead whale tissue to our knowledge, so it was critical to include this element in our analyses. Nickel is widespread in the environment, as there are nearly 100 minerals of which Ni is a significant constituent (Cempel and Nikel 2006). It is the 5th most abundant element by weight and comprises approximately 3% of Earth. Combustion of fossil fuels (coal, oil), domestic wastewater effluents, and battery production (especially before the 1980s) are human activities that increase environmental concentrations of Ni (Broussely et al. 1999; Cempel and Nikel 2006).

Concentrations of Co ranged from 0.0 to 20 µg/g. The evolution of lithium batteries led to the inclusion of Co in the late 1980s (Broussely et al. 1999). Waste from battery production and use likely contributed to environmental Co concentrations from the 1980s onward. Naturally in Earth's crust, Co is typically found in concentrations less than one percent with Cu, Fe, Pb, Ni, and Ag ores (Elinder and Friberg 1986). Most environmental Co is a by-product of Cu and Ni production (Miller and Goldfarb 1997). These elements are largely mined in Alaska and probably mobilize Co during excavations.

Concentrations of Se in baleen ranged from not detected to 20 µg/g. Naturally in Earth's crust, Se can enter the environment through erosion, with its average environmental concentration estimated around 0.09 µg/g (Lakin and Davidson 1967; GESAMP 1988). Despite Se being a major component of 40 minerals, these minerals are finely dispersed without forming a concentrated Se ore (Painter 1941). This may explain the relatively low concentrations found in bowhead whale baleen. Refinery waste and burning of fossil fuels (coal, crude oil) additionally increase environmental Se concentrations (GESAMP 1988).

Concentrations of Cr ranged between 0.1 and 30 µg/g. Associated with drilling fluids, formation waters, crude oil, and coal emissions, Cr can enter the environment through various anthropogenic activities (Naidu et al. 1997; Boesch and Rabalais 2003; Demirbas 2005). As Cr enters the environment and bowhead whales continuously skim feed, direct contact between ions and baleen's proteins likely encourage ion absorption (Kar and Misra 2004; Werth et al. 2013). This may explain why concentrations in baleen were generally higher than concentrations found in other tissues.

Concentrations of Hg were between 0.85 and 60 µg/g. Pomerleau et al. (2018) looked at Hg cycling in baleen and found a much narrower range of 0.0325 – 0.5937 µg/g. Though some values from this study correlate with Pomerleau et al.'s findings, most concentrations were relatively higher. The higher concentrations may be due to permafrost melting or the individual whales diverting toxic concentrations away from other tissues (Yamamoto et al. 1987; Cuvin-Aralar and Furness 1991). Permafrost contains high levels of Hg and an increasingly warming Arctic promotes melting (Schuster et al. 2018). This releases Hg into rivers and runoff, and subsequently the coastal marine environment. Even more, melting permafrost and glaciers increase erosion which further amplify environmental concentrations. It is also possible that the whales are diverting toxic concentrations from other tissues to the baleen since Hg can be toxic even at low concentrations (Das et al. 2003). Consumption of prey from different areas at varying times may also contribute to the difference between Pomerleau et al. (2018) and our findings. Copepods and euphausiids are main constituents of bowhead whale diet and generally have low levels of Hg (Honda et al. 1983). However, bowhead whales consume large quantities of these prey which would allow biomagnification and result in relatively elevated concentrations.

Baleen concentrations of Pb had a broad range (0.171 – 500 µg/g), though most concentrations were between 0.17 and 9.4 µg/g. Mining, shipping discharges, and coal emissions present sources of Pb to the marine environment (Naidu et al. 1997; Demirbas 2005; O'Hara et al. 2006; Tornero and Hanke 2016). The Red Dog Mine in western Alaska contains Pb ores.

4.6. Baleen Concentrations Compared to Other Bowhead Tissues

Compared to other bowhead whale tissues (blubber, liver, kidney, muscle, spleen), only Cd, Cr, Hg, Pb, Se, and Zn had higher concentrations in baleen (Byrne et al. 1985; Bratton et al. 1993; Becker et al. 1997; Krone et al. 1999; Woshner et al. 2001; Rosa et al. 2008). It should be noted that, to my knowledge, Ni has never previously been reported in any bowhead whale tissues and is therefore excluded from this section.

Concentrations of Cd in baleen were similar to concentrations in bowhead whale blubber, kidney, muscle, and spleen (Byrne et al. 1985; Becker et al. 1997; Woshner et al. 2001; Rosa et al. 2008). However, Krone et al. (1999) and Rosa et al. (2008) found much higher liver concentrations with means ranging from 2.41 to 88.0 µg/g. Cd is commonly reported in high levels in marine mammal livers due to Cd's affinity for lipids (Becker 2000).

Concentrations of Cr were higher in baleen tissue (0.1 – 30 µg/g) than blubber, kidney, muscle, spleen, and liver (Byrne et al. 1985; Becker et al. 1997; Krone et al. 1999; Woshner et al. 2001; Rosa et al. 2008). Associated with drilling fluids, formation waters, crude oil, and coal emissions, Cr can enter the environment through various anthropogenic activities (Naidu et al. 1997; Boesch and Rabalais 2003; Demirbas 2005). As Cr enters the environment and bowhead whales continuously skim feed, direct contact between ions and baleen's proteins likely encourage ion absorption (Kar and Misra 2004; Werth et al. 2013). This may explain why concentrations in baleen were generally higher than concentrations found in other tissues.

Concentrations of Hg were drastically higher in baleen (0.85 – 60 µg/g) compared to other tissues, which had a maximum of 0.04 µg/g (Byrne et al. 1985; Bratton et al. 1993; Mackey et al. 1996; Becker et al. 1997; Krone et al. 1999; Woshner et al. 2001; Rosa et al. 2008). The higher concentrations may be due to several possibilities. Permafrost and peat are known to contain high levels of Hg (Schuster et al. 2018), and an increasingly warming Arctic would release higher concentrations of Hg into rivers and, subsequently, the coastal marine environment. It is also possible that the whales are diverting toxic concentrations from other

tissues to the baleen since Hg can be toxic even at low concentrations (Yamamoto et al. 1987; Cuvin-Aralar and Furness 1991; Das et al. 2003). The direct contact between the baleen proteins and metal ions may allow for quicker and greater absorption than other tissues, though this has not yet been experimentally proven in whales (Kar and Misra 2004; Werth et al. 2013). Copepods and euphausiids, bowhead whales' main prey, generally have low levels of Hg (Honda et al. 1983). However, bowhead whales consume large quantities of these prey, which would allow biomagnification and extend direct contact between baleen and Hg in prey.

Baleen concentrations of Pb had a broad range (0.171 – 500 µg/g), though most concentrations were between 0.17 and 9.4 µg/g. Concentrations in baleen were higher than concentrations in blubber, liver, kidney, muscle, and spleen which never exceed 1 µg/g (Byrne et al. 1985; Krone et al. 1999; Woshner et al. 2001). Pb is toxic at low concentrations (Das et al. 2003). The observed elevated concentrations compared to other tissues may have resulted from the whales diverting toxic concentrations from other tissues to the baleen to avoid damage to critical organs and tissues even at low concentrations (Yamamoto et al. 1987; Cuvin-Aralar and Furness 1991).

Concentrations of Se in baleen (not detected to 20 µg/g) were higher than concentrations found in other tissues like liver and kidney (Byrne et al. 1985; Bratton et al. 1993; Mackey et al. 1996; Woshner et al. 2001; Rosa et al. 2008), but lower compared to blubber (Byrne et al. 1985). If the bowhead whales shunted Hg from other tissues to baleen, as previously stated, then it is possible that Se was also shunted from other tissues to baleen (Yamamoto et al. 1987; Cuvin-Aralar and Furness 1991). Se has been known to binds to Hg, potentially reducing toxicity (Berry and Ralston 2009). Previous studies have shown Hg accumulation in marine mammals via ingestion or exposure was accompanied by increased accumulation or retention of Se (Koelman et al. 1973; Kosta et al. 1975).

Concentrations of Zn in baleen (110 – 8000 µg/g) were higher compared to kidney, liver, muscle, blubber (Byrne et al. 1985; Woshner et al. 2001; Rosa et al. 2008). These tissues had concentrations under 40 µg/g. This discrepancy between baleen and other tissues may be best explained by bowhead whale baleen's natural composition. Bowhead baleen naturally has 216 µg/g of Zn so most concentrations in baleen were around 200 µg/g, despite a few outliers (St. Aubin et al. 1984).

5. CONCLUSION

5.1. Conclusions

All 14 elements (Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, V, and Zn) were detected in bowhead whale baleen from whales landed between 1966 and 1999. Fe, Mn, and Ni varied similarly across the plate for whales from the 1990s. In whales from 1989-1999, there was at least one sample where most elements had their highest concentrations; these samples mostly represented the Beaufort Sea and coincided with flooding events or PDO climatic shifts. Se and Hg were significantly correlated across all whales (ρ = -0.398, p < 0.001). Se:Hg in whales 66B1, 95B8, 97B8, 98KK1, and 99KK1 suggested Hg toxicity.

Concentrations of Al, As, Cd, Hg, Mn, Ni, Pb, Se, and Zn increased as time progressed (r $\geq$ |0.50|), though Cr decreased. All elements except Cu had their highest concentrations in whales from the mid to late 1990s. The earliest hunted whales had the highest concentrations of Cu. Al, Fe, and Zn had the highest mean concentrations, while As, Cd, and V had the lowest. Location did not significantly affect concentration (p>0.05), though several location-specific trends were observed. Average concentrations of As, Cd, Co, Cr, Mn, Ni were highest for most whales in samples representing the Beaufort Sea.

Temporal and spatial variations in element concentrations were likely a result of both natural and anthropogenic factors. This may include, but is not limited to, the spatial and temporal differences in Alaska's geology, its weather, anthropogenic activities, prey items, foraging locations, and migration paths, as well as baleen's natural composition. Current element load in each whale's body likely contributed to these trends as well since elements interact with each other, and some animals have been known to shunt concentrations away from vital organs and systems into less critical tissues. Though whales could not be statistically compared due to unknown physiological conditions, shared trends in concentrations are likely due to environmental factors, such as flooding events, or biological factors, like similar migration route or foraging grounds during overlapping seasons and years.

This study provided the first baseline dataset of concentrations in baleen and offered a general understanding of time and space of environmental and biological concentrations. Comparing this study to recent bowhead whale baleen samples, as well as comparing bowhead whale baleen samples to prey and water samples, will better determine whether these concentrations are changing over time and space and with the source of these elements. Analyses

of subsistence-harvested animals and baleen tissue offer a novel way to obtain and analyze organismal tissue for potentially toxic concentrations. It is critical to understand biological and environmental elemental concentrations, as biota play a critical role in the cycling and distribution of trace elements and metals in the world's oceans. Even more, the human population is dependent upon the environment and Earth's animals for survival.

5.2. Future Considerations

Analysis of baleen samples, as well as concomitant prey and water samples, would provide a better idea as to where the whales are obtaining their elemental concentrations. Toxicological studies would yield insight into which of the reported concentrations are detrimental to bowhead whales. Comparing this project's data to more recent baleen samples would extend the temporal aspect from this project and better show whether this population is being exposed to or obtaining higher element concentrations. In today's environment, Earth's climate, especially the Arctic's, is warming and human needs are met through rapid production and material use. This makes it critical to understand how the byproducts of today's world are affecting not only biota, but also the Earth's ecosystems.

Table 1. Harvest date and location, age (years) and age class, body length (meters), and sex for the bowhead whales sampled.
N/A = data not available. * Pregnant. (Schell et al. 1989a, b, 1992, 2000, 2005)

Whale ID	Harvest Date	Harvest Location	Age (years) [Age Class]	Body Length (meters)	Sex
66B1	10 May, 1966	Barrow	9 [Subadult]	9.5	Male
78B2	May, 1978	Barrow	4.5 [Subadult]	N/A	Male
88B11	17 Sept., 1988	Barrow	>22.5 [Adult]	N/A	Female
89B10L	28 Oct., 1989	Barrow	N/A [N/A]	8.1	Female
90B8	2 Oct., 1990	Barrow	>13.5 [N/A]	12.9	Male
95B8	1 June, 1995	Barrow	N/A [Adult]	15.2	Female*
97B8	15 May, 1997	Barrow	N/A [Adult]	N/A	Female
98KK1	4 Sept., 1998	Kaktovik	N/A [Subadult]	N/A	Male
99KK1	11 Sept., 1999	Kaktovik	N/A [Subadult]	N/A	Female

Table 2. Location (B=Beaufort Sea, BC=Bering/Chukchi seas), time (season & year(s)), δ^{13}C (‰), and δ^{15}N (‰) for each sample (n=148). Samples were created by combining two samples per enrichment cycle and separately combining two samples per depletion cycle to accurately represent location and season/year. Some samples were not combined if only one sample was available. Winter is reported as two years and represent November through March. The δ^{13}C and δ^{15}N values are reported for each sample before combination, and then averaged to represent the new combined sample used in this project. Sample weight (g) represents combined sample weights. -- = not available

Sample ID	Location (B, BC)	Season and Year(s)	δ^{13}C	δ^{13}C	Avg δ^{13}C	δ^{15}N	δ^{15}N	Avg δ^{15}N	Sample Weight (g)
66B1-BC1	BC	Winter 66/65	-17.7	-18.0	-17.9	16.9	--	16.9	0.090
66B1-B1	B	Summer 65	-19.9	-19.8	-19.8	12.3	14.3	13.3	0.297
66B1-BC2	BC	Winter 65/64	-18.5	-17.4	-18.0	15.8	14.5	17.9	0.285
66B1-B2	B	Summer 64	-20.6	-20.1	-20.3	11.1	15.0	13.1	0.159
66B1-BC3	BC	Winter 64/63	-18.2	-17.8	-18.0	16.3	14.3	18.9	0.053
66B1-B3	B	Summer 63	-19.6	-20.2	-19.9	14.3	12.0	13.1	0.171
66B1-BC4	BC	Winter 63/62	-18.1	-17.8	-17.9	15.3	14.2	19.9	0.185
66B1-B4	B	Summer 62	-19.6	-19.0	-19.3	--	13.5	13.5	0.151
66B1-BC5	BC	Winter 62/61	-17.9	-17.8	-17.9	--	15.6	15.6	0.293
66B1-B5	B	Summer 61	-18.2	-18.6	-18.4	14.1	14.5	14.3	0.142
66B1-BC6	BC	Winter 61/60	-18.2	-18.8	-18.5	15.7	16.3	16.0	0.165
66B1-B6	B	Summer 60	-21.4	--	-21.4	14.1	--	14.1	0.083
66B1-BC7	BC	Winter 60/59	-17.5	-17.7	-17.6	16.6	16.6	16.6	0.133
66B1-B7	B	Summer 59	--	-18.9	-18.9	15.2	15.7	15.5	0.141
66B1-BC8	BC	Winter 59/58	-17.6	-17.5	-17.5	17.3	18.6	18.0	0.113
78B2-BC1	BC	Winter 78/77	-19.3	-19.1	--	15.9	16.7	16.3	0.036
78B2-B1	B	Summer 77	-23.0	--	-23.0	11.7	--	11.7	0.041
78B2-BC2	BC	Winter 77/76	-17.7	-17.9	-17.8	15.7	15.0	15.4	0.085
78B2-B2	B	Summer 76	-18.9	-18.8	-18.9	--	13.5	13.5	0.096
78B2-BC3	BC	Winter 76/75	-17.9	-17.7	-17.8	15.3	14.8	15.1	0.121
78B2-B3	B	Summer 75	-19.4	-19.5	-19.5	14.0	--	14	0.088
78B2-BC4	BC	Winter 75/74	-17.4	-17.7	-17.6	15.8	16.0	15.9	0.103
78B2-B4	B	Summer 74	-21.2	-20.2	-20.7	12.8	13.3	13.1	0.129
78B2-BC5	BC	Winter 74/73	-17.8	-17.7	-17.8	16.3	--	16.3	0.062

88B11-B1	B	Summer 88	-19.6	--	-19.6	13.7	--	13.7	0.035
88B11-BC1	BC	Winter 88/87	-18.1	-18.2	-18.2	15.2	14.4	14.8	0.031
88B11-B2	B	Summer 87	-17.5	-19.9	-18.7	13.5	14.0	11.2	0.017
88B11-BC2	BC	Winter 87/86	-19.0	-18.8	-18.9	15.1	14.5	14.8	0.024
88B11-B3	B	Summer 86	-19.2	--	-19.2	14.3	13.9	14.1	0.030
88B11-BC3	BC	Winter 86/85	-18.1	-17.4	-17.7	15.2	14.3	14.7	0.021
88B11-B4	B	Summer 85	-18.1	--	-18.1	14.2	14.4	14.3	0.037
88B11-BC4	BC	Winter 85/84	-18.7	-18.7	-18.2	14.9	14.8	14.8	0.011
88B11-B5	B	Summer 84	-19.2	-18.3	-18.8	13.2	13.2	13.2	0.011
88B11-BC5	BC	Winter 84/83	-18.6	-18.0	-18.3	14.6	14.5	14.6	0.009
88B11-B6	B	Summer 83	-18.2	-19.1	-17.2	13.5	13.9	13.7	0.019
88B11-BC6	BC	Winter 83/82	-18.4	-18.3	-18.3	14.6	14.1	14.3	0.011
88B11-B7	B	Summer 82	-18.9	-19.4	-17.2	13.6	13.5	13.5	0.030
88B11-BC7	BC	Winter 82/81	-18.5	-18.4	-18.5	15.0	14.9	14.9	0.028
88B11-B8	B	Summer 81	-19.2	-19.1	-19.2	13.4	13.4	13.4	0.031
88B11-BC8	BC	Winter 81/80	-17.9	-18.0	-16.2	14.8	14.6	14.7	0.012
88B11-B9	B	Summer 80	-18.9	--	-18.9	12.9	--	12.9	0.012
88B11-BC9	BC	Winter 80/79	-17.3	-17.3	-17.3	14.7	14.8	14.8	0.021
88B11-B10	B	Summer 79	-18.6	-18.0	-16.2	14.6	14.0	14.3	0.017
88B11-BC10	BC	Winter 79/78	-17.2	-16.6	-16.9	14.6	13.7	14.1	0.032
88B11-B11	B	Summer 78	-19.8	--	-19.8	13.5	--	13.5	0.018
88B11-BC11	BC	Winter 78/77	-17.7	-17.7	-15.2	15.7	14.3	15.0	0.023
88B11-B12	B	Summer 77	-18.9	--	-18.9	14.2	--	14.2	0.010
88B11-BC12	BC	Winter 77/76	-17.6	-17.9	-17.7	16.4	16.7	16.6	0.022
88B11-B13	B	Summer 76	-18.2	-18.9	-15.2	14.3	14.0	14.2	0.025
88B11-BC13	BC	Winter 76/75	-17.1	-16.8	-16.9	16.1	13.6	14.8	0.020
88B11-B14	B	Summer 75	-18.5	--	-18.5	13.6	14.0	13.8	0.026
88B11-BC14	BC	Winter 75/74	-17.0	-16.8	-14.2	15.7	14.7	15.2	0.037
88B11-B15	B	Summer 74	-18.0	-18.0	-18.0	14.0	15.2	14.6	0.023
88B11-BC15	BC	Winter 74/73	-17.4	-17.2	-17.3	16.3	16.5	16.4	0.014
88B11-B16	B	Summer 73	-18.0	-18.9	-14.2	13.9	14.0	14.0	0.064

88B11-BC16	BC	Winter 73/72	-18.2	-17.9	-18.0	15.4	15.4	15.4	0.111
88B11-B17	B	Summer 72	-19.2	-19.1	-19.1	13.6	13.8	13.7	0.052
88B11-BC17	BC	Winter 72/71	-18.0	-18.2	-13.2	15.5	16.0	15.8	0.044
88B11-B18	B	Summer 71	-17.9	-18.0	-18.0	13.5	13.3	13.4	0.065
88B11-BC18	BC	Winter 71/70	-17.6	-17.7	-17.6	15.5	14.7	15.1	0.054
88B11-B19	B	Summer 70	-17.9	-18.7	-13.2	12.9	13.9	13.4	0.032
88B11-BC19	BC	Winter 70/69	-17.4	-17.6	-17.5	14.3	13.5	13.9	0.065
88B11-B20	B	Summer 69	-18.9	--	-18.9	12.8	--	12.8	0.015
88B11-BC20	BC	Winter 69/68	-17.3	-16.2	-12.2	14.7	12.5	13.6	0.032
89B10L-B1	B	Summer 89	-24.4	-23.1	-23.8	11.9	11.9	11.9	0.083
89B10L-BC1	BC	Winter 89/88	-19.2	-19.2	-19.2	14.8	14.5	14.6	0.093
89B10L-B2	B	Summer 88	-21.1	-21.2	-12.2	13.6	12.4	13.0	0.097
89B10L-BC2	BC	Winter 88/87	-18.4	-18.4	-18.4	15.2	14.9	15.0	0.086
89B10L-B3	B	Summer 87	-21.0	-20.9	-21.0	12.3	13.4	12.9	0.076
89B10L-BC3	BC	Winter 87/86	-19.0	-19.4	-19.2	15.9	15.7	15.8	0.074
89B10L-B4	B	Summer 86	-22.2	-22.0	-22.1	12.5	12.3	12.4	0.093
89B10L-BC4	BC	Winter 86/85	-18.4	-18.5	-18.4	15.8	15.8	15.8	0.072
89B10L-B5	B	Summer 85	-18.2	-18.9	-18.6	14.6	15.0	14.8	0.056
90B8-B1	B	Summer 90	-20.0	-19.7	-19.9	--	--	--	0.036
90B8-BC1	BC	Winter 89/90	-18.4	-18.3	-18.4	--	--	--	0.045
90B8-B2	B	Summer 89	-19.8	-20.8	-20.3	--	--	--	0.040
90B8-BC2	BC	Winter 88/89	-19.1	-19.2	-19.2	--	--	--	0.035
90B8-B3	B	Summer 88	-19.1	-19.5	-19.3	--	--	--	0.033
90B8-BC3	BC	Winter 87/88	-18.3	--	-18.3	--	--	--	0.016
90B8-B4	B	Summer 87	-20.6	-19.8	-20.2	--	--	--	0.031
90B8-BC4	BC	Winter 86/87	-18.5	-18.7	-18.6	--	--	--	0.036
90B8-B5	B	Summer 86	-20.0	-20.4	-20.2	--	--	--	0.042
90B8-BC5	BC	Winter 85/86	-18.2	-17.9	-18.1	--	--	--	0.033
90B8-B6	B	Summer 85	-19.8	-19.4	-19.6	--	--	--	0.033
90B8-BC6	BC	Winter 84/85	-18.9	-19.3	-19.1	--	--	--	0.046
90B8-B7	B	Summer 84	-20.0	-20.0	-20.0	--	--	--	0.041

90B8-BC7	BC	Winter 83/84	-18.3	-18.3	-18.3	--	--	--	0.063
90B8-B8	B	Summer 83	-19.6	-19.6	-19.6	--	--	--	0.057
90B8-BC8	BC	Winter 82/83	-18.3	-18.4	-18.4	--	--	--	0.080
90B8-B9	B	Summer 82	-19.1	-19.1	-19.1	--	--	--	0.045
90B8-BC9	BC	Winter 81/82	-18.5	-18.4	-18.5	--	--	--	0.067
90B8-B10	B	Summer 81	-19.5	-19.5	-19.5	--	--	--	0.068
90B8-BC10	BC	Winter 80/81	-18.3	-18.2	-18.3	--	--	--	0.056
90B8-B11	B	Summer 80	-19.9	-19.9	-19.9	--	--	--	0.043
90B8-BC11	BC	Winter 80/79	-17.5	-17.6	-17.6	--	--	--	0.056
90B8-B12	B	Summer 79	-18.9	-18.8	-18.9	--	--	--	0.045
95B8-B1	B	Summer 95	-19.8	--	-19.8	15.2	--	15.2	0.002
95B8-BC1	BC	Winter 94/95	-19.1	-19.4	-19.2	13.5	14.6	14.0	0.010
95B8-B2	B	Summer 94	-21.0	--	-21.0	13.6	--	13.6	0.004
95B8-BC2	BC	Winter 93/94	-19.2	-19.7	-19.4	13.7	15.1	14.4	0.010
95B8-B3	B	Summer 93	-20.1	-20.3	-20.2	13.0	13.8	13.4	0.009
95B8-BC3	BC	Winter 92/93	-18.1	-18.0	-18.0	16.5	16.4	16.5	0.008
95B8-B4	B	Summer 92	-20.4	-20.0	-20.2	13.9	13.4	13.7	0.010
95B8-BC4	BC	Winter 91/92	-17.8	-17.8	-17.8	16.7	16.5	16.6	0.005
95B8-B5	B	Summer 91	-19.5	-19.3	-19.4	13.4	13.1	13.3	0.014
95B8-BC5	BC	Winter 90/91	-18.3	-18.4	-18.3	15.9	15.3	15.6	0.011
97B8-BC1	BC	Winter 96/97	-18.4	-19.6	-19.0	13.7	14.4	14.0	0.004
97B8-B1	B	Summer 96	-19.1	-19.4	-19.3	14.1	13.8	13.9	0.003
97B8-BC2	BC	Winter 95/96	-18.6	-17.4	-16.8	15.5	14.5	15.0	0.004
97B8-B2	B	Summer 95	-18.4	-18.5	-18.4	12.8	13.2	13.0	0.002
97B8-BC3	BC	Winter 94/95	-19.9	-19.2	-19.6	13.4	13.8	13.6	0.002
98KK1-BC1	BC	Winter 97/98	-19.8	-19.5	-19.6	14.4	13.5	13.9	0.002
98KK1-B1	B	Summer 96/97	-20.9	-20.9	-15.8	13.2	13.6	13.4	0.003
98KK1-BC2	BC	Winter 95/96	-19.5	-19.1	-19.3	14.3	13.5	13.9	0.002
98KK1-B2	B	Summer 95	-20.0	-21.4	-20.7	13.2	12.3	12.8	0.003
98KK1-BC3	BC	Winter 95/96	-19.0	-17.4	-18.2	14.5	13.1	13.8	0.004

98KK1-B3	B	Summer 93/94	-20.5	-20.3	-15.8	12.5	13.0	12.8	0.003
98KK1-BC4	BC	Winter 92/93	-19.9	-19.9	-19.9	14.6	13.5	14.0	0.005
98KK1-B4	B	Summer 91/92	-22.3	-22.5	-22.4	13.0	12.7	12.9	0.005
98KK1-BC5	BC	Winter 90/91	-19.4	-19.0	-19.2	14.6	13.7	14.1	0.003
98KK1-B5	B	Summer 90	-20.4	-20.2	-14.8	13.0	12.8	12.9	0.004
98KK1-BC6	BC	Winter 89/90	-18.5	-18.5	-18.5	15.4	15.3	15.4	0.004
98KK1-B6	B	Summer 89	-20.3	-20.7	-20.5	13.5	13.4	13.5	0.004
98KK1-BC7	BC	Winter 88/89	-18.6	-19.0	-18.8	15.3	15.3	15.3	0.005
98KK1-B7	B	Summer 88	-18.8	-22.1	-20.4	12.8	13.7	13.3	0.005
98KK1-BC8	BC	Winter 87/88	-18.0	-18.3	-14.8	15.7	16.0	15.8	0.007
99KK1-B1	B	Summer 99	-20.0	-19.8	-19.9	15.6	15.5	15.6	0.002
99KK1-BC1	BC	Winter 98/99	-19.8	-19.7	-19.8	14.9	15.2	15.1	0.002
99KK1-B2	B	Summer 98	-20.1	-20.3	-20.2	14.7	14.4	14.5	0.005
99KK1-BC2	BC	Winter 97/98	-19.2	-19.1	-19.1	16.4	16.3	16.3	0.002
99KK1-B3	B	Summer 97	-19.1	-19.2	-13.8	15.1	15.2	15.2	0.004
99KK1-BC3	BC	Winter 96/97	-19.4	-19.4	-19.4	15.4	15.5	15.4	0.003
99KK1-B4	B	Summer 96	-20.1	-19.9	-20.0	14.7	14.7	14.7	0.001
99KK1-BC4	BC	Winter 95/96	-18.6	-18.6	-18.6	15.1	14.9	15.0	0.001
99KK1-B5	B	Summer 95	-18.9	-19.0	-18.9	15.1	15.0	15.0	0.004
99KK1-BC5	BC	Winter 94/92	-18.2	-18.2	-18.2	14.4	14.5	14.4	0.002
99KK1-B6	B	Summer 92	-19.5	-19.5	-19.5	14.5	14.7	14.6	0.002
99KK1-BC6	BC	Winter 91/92	-18.1	-18.1	-18.1	14.9	15.1	15.0	0.002

Table 3. The range of concentrations (µg/g) in baleen per whale (n=148). N/D = Not detected (or under detection limit)

	66B1	78B2	88B11	89B10L	90B8	95B8	97B8	98KK1	99KK1
Al	10.9 - 65	16 - 67	33 - 320	25 - 110	32 - 210	200 - 1000	600 - 2000	400 - 2000	500 - 3000
As	0.10 - 0.53	0.15 - 0.55	0.1 - 0.63	0.08 - 0.63	0.12 - 0.89	0.1 - 0.5	0.1 - 0.5	0.1 - 3	0.1 - 3
Cd	0.029 - 1.0	N/D - 0.065	N/D - 1.2	0.0088 - 0.21	0.0082 - 0.84	0.02 - 2	0.1 - 10	0.01 - 0.6	0.04 - 1
Co	0.020 - 0.783	0.01 - 0.08	0.02 - 2.2	0.01 - 0.85	0.00 - 0.51	0 - 7	0.2 - 20	0 - 3.2	0 - 2
Cr	0.67 - 2.0	0.16 - 2.2	0.1 - 4.0	0.13 - 0.46	0.1 - 3.52	0.30 - 5	6 - 20	1 - 30	2 - 30
Cu	42.8 - 4220	5.1 - 1900	4.6 - 390	4.9 - 15.0	3.1 - 170	6 - 30	20 - 30	10 - 60	10 - 400
Fe	16.1 - 58.4	8.8 - 210	8.11 - 380	5.0 - 42	9.5 - 1100	16 - 7000	100 - 2000	0 - 40000	100 - 20000
Hg	7.9 - 28.3	0.85 - 3.9	1.7 - 33	1.7 - 4.6	2.3 - 46.3	3.0 - 28	10 - 30	10 - 40	8 - 60
Mn	0.25 - 0.699	0.26 - 1.7	0.19 - 30	0.25 - 0.78	0.21 - 25	0.44 - 80	1 - 10	0.6 - 100	2 - 200
Ni	0.34 - 4.61	0.085 - 3.5	0.16 - 3.8	0.15 - 0.64	0.1 - 5.1	0.2 - 9	2 - 2	0.6 - 9	0.9 - 20
Pb	0.560 - 3.2	0.58 - 2.13	0.171 - 13	0.38 - 5.09	0.2 - 15	1.1 - 100	5 - 500	0.9 - 9	1 - 20
Se	2.3 - 4.0	1.6 - 3.5	1 - 3.8	2.1 - 3.0	0.9 - 3.8	N/D - 2	N/D - 0	N/D - 5	N/D - 20
V	0.02 - 0.053	0.01 - 0.07	0.00 - 0.63	0.01 - 0.03	0.00 - 0.39	0.00 - 0.8	0.2 - 1	0.1 - 0.6	0.1 - 2
Zn	206 - 290	200 - 240	110 - 1900	180 - 220	148 - 281	200 - 500	200 - 400	200 - 8000	200 - 1000

Table 4. Mean essential element concentrations ± standard deviation (µg/g) in baleen per whale in the Bering and Chukchi (white) and Beaufort seas (shaded) (n=148). N/D = Not detected (or under detection limit)

Whale ID	Co	Cr	Cu	Fe	Mn	Ni	Se	Zn
66B1	0.1 ± 0.3	1.2 ± 0.35	1400 ± 1400	32 ± 14	0.45 ± 0.16	1.6 ± 1.7	3.1 ± 0.40	250 ± 25
	0.06 ± 0.07	0.92 ± 0.25	1400 ± 1400	23 ± 6.8	0.36 ± 0.066	1.6 ± 1.8	3.4 ± 0.44	230 ± 17
78B2	0.04 ± 0.04	3.9 ± 7.9	390 ± 850	55 ± 87	0.61 ± 0.61	0.85 ± 1.5	2.2 ± 0.39	230 ± 13
	0.02 ± 0.02	0.89 ± 0.90	240 ± 440	21 ± 13	0.37 ± 0.12	0.20 ± 0.08	3.2 ± 0.22	220 ± 20
88B11	0.07 ± 0.09	0.8 ± 0.6	50 ± 92	100 ± 100	3.2 ± 7	0.7 ± 0.6	2 ± 0.5	300 ± 40
	0.2 ± 0.5	0.80 ± 0.83	19 ± 40	55 ± 90	1.4 ± 2	0.74 ± 0.9	2 ± 0.5	320 ± 400
89B10L	0.02 ± 0.01	0.22 ± 0.043	6.7 ± 0.98	7.7 ± 2.5	0.29 ± 0.037	0.19 ± 0.048	2.3 ± 0.15	200 ± 0
	0.2 ± 0.4	0.26 ± 0.12	8.7 ± 3.89	19 ± 16.1	0.51 ± 0.3	0.34 ± 0.2	2.7 ± 0.3	198 ± 18
90B8	0.09 ± 0.1	0.54 ± 0.49	10 ± 6.3	1200 ± 500	2 ± 3	0.5 ± 0.6	2 ± 0.54	230 ± 29
	0.1 ± 0.2	1.2 ± 1	25 ± 50	610 ± 1000	4.4 ± 7.2	1 ± 1	1.9 ± 0.72	243 ± 21
95B8	0.07 ± 0.04	1.0 ± 0.5	8 ± 2	40 ± 20	0.9 ± 0.32	0.6 ± 0.3	1 ± 0	300 ± 71
	2 ± 3	2 ± 2	10 ± 11	1000 ± 3000	20 ± 35	2 ± 4	1 ± 0.5	300 ± 100
97B8	8 ± 10	6 ± 0	20 ± 6	100 ± 60	2 ± 0.6	2 ± 0	0 ± 0.3	300 ± 100
	0.2 ± 0.07	11 ± 8	20 ± 0	1000 ± 1000	6.5 ± 5	2 ± 0	N/D	300 ± 100
98KK1	0.2 ± 0.2	5 ± 4	20 ± 20	100 ± 200	2 ± 2	3 ± 3	0.4 ± 0.1	400 ± 200
	1 ± 1	6.9 ± 10	20 ± 7	6000 ± 15000	30 ± 40	3 ± 2	1 ± 0.8	1600 ± 3000
99KK1	0.3 ± 0.2	7 ± 3	100 ± 100	800 ± 700	9 ± 6	7 ± 4	1 ± 2	600 ± 200
	0.7 ± 0.8	20 ± 10	60 ± 40	9000 ± 8000	80 ± 100	8.9 ± 7	0 ± 0	660 ± 570

Table 5. Mean non-essential element concentrations ± standard deviation (µg/g) in baleen per whale in the Bering and Chukchi (white) and Beaufort seas (shaded) (n=148). N/D = Not detected (or under detection limit)

Whale ID	Al	As	Cd	Hg	Pb	V
66B1	33 ± 18	0.27 ± 0.11	0.1 ± 0.32	13 ± 2.9	1.9 ± 0.88	0.04 ± 0.01
	26 ± 8.1	0.37 ± 0.14	0.049 ± 0.018	14 ± 7.2	1.23 ± 0.44	0.03 ± 0.01
78B2	34 ± 14	0.21 ± 0. 056	0.049 ± 0.012	2.1 ± 1.1	1.4 ± 0.67	0.02 ± 0.03
	33 ± 24	0.37 ± 0.13	0.023 ± 0. 0047	2.0 ± 1.1	1.2 ± 0.39	0.01 ± 0
88B11	200 ± 80	0.2 ± 0.09	0.07 ± 0.1	6 ± 5.8	2 ± 2	0.07 ± 0.2
	144 ± 79	0.3 ± 0.2	0.14 ± 0.3	5.4 ± 6.6	2.3 ± 3.7	0.06 ± 0.1
89B10L	33 ± 6	0.15 ± 0.08	0.016 ± 0.0073	2.7 ± 1.2	0.66 ± 0.43	0.02 ± 0.006
	52 ± 34	0.28 ± 0.20	0.057 ± 0.085	3.1 ± 1	1.56 ± 2	0.02 ± 0.006
90B8	76 ± 50	0.25 ± 0.079	0.03 ± 0.04	3.8 ± 1.2	0.98 ± 0.85	0.03 ± 0.03
	79 ± 30	0.37 ± 0.19	0.1 ± 0.25	7.1 ± 12	2.12 ± 4.21	0.07 ± 0.1
95B8	300 ± 100	0.2 ± 0.04	0.05 ± 0.02	5 ± 2	2 ± 3.5	0.05 ± 0.4
	500 ± 300	0.3 ± 0.1	0.5 ± 0.8	10 ± 10	20 ± 300	0.2 ± 0.1
97B8	1000 ± 700	0.2 ± 0.2	3.5 ± 6	20 ± 10	200 ± 270	0.5 ± 0.5
	900 ± 100	0.3 ± 0	0.1 ± 0.07	20 ± 0	8.4 ± 5.9	0.3 ± 0.1
98KK1	900 ± 500	0.2 ± 0.1	0.09 ± 0.07	20 ± 10	3 ± 3	0.2 ± 0.1
	800 ± 200	0.6 ± 1	0.2 ± 0.2	20 ± 6	3.2 ± 2	0.2 ± 0.2
99KK1	2000 ± 500	0.5 ± 0.1	0.2 ± 0.09	20 ± 10	8 ± 6	0.3 ± 0.06
	2000 ± 2000	1 ± 1	0.6 ± 0.8	30 ± 20	9 ± 12	0.7 ± 0.9

Table 6. Significant correlation coefficients between concentration and time (year) in the Bering/Chukchi seas (white) and Beaufort Sea (shaded). Negative values represent an inverse relationship between concentration and time, while positive coefficients indicate a direct relationship. Blank spaces represent non-significant correlations. ---- = omitted from correlation analysis due to insufficient sample size per location (n<5)

Whale ID	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	V	Zn
66B1	0.59	0.89								0.67			-0.58	0.76
	-0.56	0.90		-0.60				0.60		0.79		0.52		
78B2		0.79	-0.89	0.58	0.71	----	----	0.94	----			0.89	----	0.86
	----	----	----	----	----	----	----	----	----	----	----	----	----	----
88B11													-0.96	
		0.65												
89B10L	----	----	----	----	----	----	----	----	----	----	----	----	----	----
	----	----	----	----	----	----	----	0.92		----	----	0.66		0.78
90B8		0.56					-0.59				0.56			
	0.62			0.54	-0.54								0.55	
95B8	-0.57			0.71	0.73	-0.73			-0.76					
	0.93	0.69	----	----	----	----	----	----	----	----	----	-0.77	----	0.69
97B8	----	----	----	----	----	----	----	----	----	----	----	----	----	----
	----	----	----	----	----	----	----	----	----	----	----	----	----	----
98KK1		0.74					-0.47	0.93	0.62	-0.61	-0.56	0.79	0.50	
	0.64	0.83	0.55				0.79		0.58					0.52
99KK1			0.57	0.67		----	0.76			0.81		0.73	0.53	
			----	----	-0.60		----			0.61	0.45	0.58	-0.50	

Table 7. Selenium and mercury concentrations (µg/g), molar selenium and mercury concentrations (µg/g), and the molar ratio of selenium to mercury for each sample. N/D = not detected. N/A = not available

Sample ID	Hg	Se	Molar Hg	Molar Se	Molar Ratio Se:Hg
66B1-B1	15.7	3.53	0.0780	0.0447	0.573
66B1-B2	8.74	3.9	0.0436	0.050	1.1
66B1-B3	17.1	3.04	0.0851	0.0384	0.452
66B1-B4	28.2	3.56	0.141	0.0451	0.321
66B1-B5	10.2	2.8	0.0510	0.036	0.70
66B1-B6	9.8	3.7	0.049	0.046	0.95
66B1-B7	8.40	2.9	0.0419	0.037	0.89
66B1-BC1	7.9	2.9	0.039	0.037	0.94
66B1-BC2	10.6	3.49	0.0528	0.0442	0.837
66B1-BC3	15	3.1	0.075	0.039	0.52
66B1-BC4	15.5	2.9	0.0773	0.036	0.47
66B1-BC5	11.5	3.57	0.0573	0.0452	0.790
66B1-BC6	17.1	3.17	0.0850	0.0402	0.472
66B1-BC7	12.5	3.2	0.0623	0.041	0.65
66B1-BC8	13.1	2.3	0.0653	0.029	0.45
78B2-B1	2.2	3.5	0.011	0.044	4.0
78B2-B2	3.4	3.2	0.017	0.040	2.4
78B2-B3	1.4	3.0	0.007	0.038	5.4
78B2-B4	0.84	3.0	0.0042	0.039	9.2
78B2-BC1	3.9	2.4	0.020	0.030	1.5
78B2-BC2	2.3	2.6	0.012	0.034	2.9
78B2-BC3	1.7	2.3	0.008	0.029	3.5
78B2-BC4	1.5	2.0	0.008	0.026	3.4
78B2-BC5	0.95	1.6	0.0047	0.020	4.2
88B11-B1	4.8	1.7	0.024	0.021	0.9
88B11-B10	4.6	2	0.020	0.03	1
88B11-B11	5.1	2	0.016	0.030	1.9

88B11-B12	5.2	2	0.011	0.038	3.3
88B11-B13	3.2	2.3	0.027	0.04	1
88B11-B14	3.3	2.4	0.031	0.02	0.7
88B11-B15	3.4	2.2	0.024	0.027	1.2
88B11-B16	3.4	2.9	0.019	0.030	1.6
88B11-B17	2.9	2.9	0.023	0.02	0.9
88B11-B18	1.7	3.8	0.023	0.03	1
88B11-B19	3.5	2.9	0.026	0.03	1
88B11-B2	4.0	2	0.026	0.02	0.9
88B11-B20	33	3	0.016	0.029	1.8
88B11-B3	3.2	2.4	0.017	0.030	1.8
88B11-B4	2.3	3.0	0.017	0.028	1.6
88B11-B5	5.3	3	0.017	0.036	2.1
88B11-B6	6.2	2	0.015	0.036	2.5
88B11-B7	4.7	2.2	0.008	0.049	5.8
88B11-B8	3.8	2.4	0.017	0.037	2.1
88B11-B9	4.6	2	0.16	0.03	0.2
88B11-BC1	3.2	1.7	0.016	0.022	1.4
88B11-BC10	3.5	2.2	0.019	0.02	1
88B11-BC11	3.9	2	0.013	0.03	2
88B11-BC12	12	2	0.024	0.02	0.8
88B11-BC13	3.0	2	0.033	0.01	0.4
88B11-BC14	2.4	2.2	0.031	0.02	0.7
88B11-BC15	5.0	1	0.019	0.025	1.4
88B11-BC16	2.3	2.5	0.029	0.03	0.9
88B11-BC17	3.0	2.3	0.015	0.03	2
88B11-BC18	2.8	2.5	0.017	0.027	1.6
88B11-BC19	14	2.4	0.019	0.02	1
88B11-BC2	3.8	2	0.062	0.02	0.4
88B11-BC20	27	2.3	0.015	0.03	2
88B11-BC3	2.7	2	0.012	0.028	2.4

88B11-BC4	4.9	1	0.025	0.02	0.7
88B11-BC5	6.5	1	0.011	0.031	2.8
88B11-BC6	6.3	2	0.015	0.029	2.0
88B11-BC7	3.7	2.0	0.014	0.032	2.3
88B11-BC8	5.9	2	0.068	0.030	0.45
88B11-BC9	3.1	2	0.13	0.030	0.22
89B10L-B1	4.5	2.7	0.022	0.034	1.5
89B10L-B2	4.6	3.0	0.023	0.038	1.7
89B10L-B3	2.8	2.7	0.014	0.035	2.5
89B10L-B4	1.7	2.8	0.009	0.035	4.1
89B10L-B5	1.9	2.0	0.009	0.026	2.7
89B10L-BC1	4.5	2.4	0.022	0.031	1.4
89B10L-BC2	2.6	2.2	0.013	0.028	2.2
89B10L-BC3	2.0	2.4	0.010	0.031	3.1
89B10L-BC4	1.9	2.1	0.010	0.026	2.7
90B8-B1	3.2	1.3	0.016	0.017	1.0
90B8-B10	4.5	3.8	0.021	0.021	1.0
90B8-B11	3.5	1.6	0.017	0.017	1.0
90B8-B12	46.3	1.3	0.013	0.017	1.3
90B8-B2	4.3	1.7	0.016	0.027	1.7
90B8-B3	3.3	1.3	0.022	0.022	1.0
90B8-B4	2.7	1.3	0.017	0.027	1.5
90B8-B5	3.2	2.1	0.018	0.028	1.6
90B8-B6	4.4	1.7	0.012	0.031	2.6
90B8-B7	3.5	2.1	0.022	0.048	2.2
90B8-B8	3.6	2.2	0.018	0.021	1.2
90B8-B9	2.4	2.4	0.231	0.016	0.071
90B8-BC1	5.3	1.6	0.026	0.020	0.75
90B8-BC10	3.2	2.8	0.015	0.018	1.2
90B8-BC11	2.6	1.4	0.022	0.012	0.55
90B8-BC2	3.0	1.4	0.013	0.028	2.1

90B8-BC3	4.5	0.97	0.020	0.027	1.3
90B8-BC4	2.6	2.2	0.019	0.023	1.2
90B8-BC5	4.1	2.1	0.031	0.029	0.93
90B8-BC6	3.8	1.8	0.019	0.025	1.3
90B8-BC7	6.3	2.3	0.014	0.028	2.0
90B8-BC8	3.8	2.0	0.016	0.036	2.2
90B8-BC9	2.8	2.2	0.013	0.017	1.4
95B8-B1	28	N/D	0.14	NA	NA
95B8-B2	14	1	0.070	0.01	0.2
95B8-B3	4	2	0.02	0.02	1
95B8-B4	2	1	0.01	0.02	2
95B8-B5	4.0	2	0.020	0.02	1
95B8-BC1	3	1	0.0	0.01	0.9
95B8-BC2	4	1	0.0	0.01	0.6
95B8-BC3	8.1	1	0.040	0.01	0.3
95B8-BC4	7	1	0.03	0.01	0.4
95B8-BC5	4	1	0.02	0.02	1
97B8-B1	15	N/D	0.07	NA	NA
97B8-B2	20	N/D	0.10	NA	NA
97B8-BC1	16	0.3	0.082	0.004	0.05
97B8-BC2	16	N/D	0.079	NA	NA
97B8-BC3	28	1	0.14	0.01	0.09
98KK1-B1	27	2	0.13	0.02	0.1
98KK1-B2	10	0.2	0.050	0.003	0.05
98KK1-B3	34	1	0.17	0.02	0.1
98KK1-B4	25	1	0.12	0.01	0.1
98KK1-B5	18	0.4	0.088	0.004	0.05
98KK1-B6	25	0.8	0.12	0.01	0.09
98KK1-B7	15	1	0.075	0.02	0.2
98KK1-BC1	40	0.7	0.20	0.008	0.04
98KK1-BC2	33		0.16	NA	NA

98KK1-BC3	30	0.9	0.15	0.01	0.08
98KK1-BC4	20	0.5	0.10	0.006	0.06
98KK1-BC5	30	0.7	0.15	0.009	0.06
98KK1-BC6	21	0.5	0.11	0.006	0.06
98KK1-BC7	10	0.6	0.051	0.007	0.1
98KK1-BC8	10	0.7	0.052	0.009	0.2
99KK1-B1	30	N/D	0.15	NA	NA
99KK1-B2	9.7	0.5	0.048	0.006	0.1
99KK1-B3	10	0.6	0.050	0.007	0.1
99KK1-B4	60	N/D	0.30	NA	NA
99KK1-B5	10	0.5	0.050	0.006	0.1
99KK1-B6	35	N/D	0.17	NA	NA
99KK1-BC1	8	N/D	0.04	NA	NA
99KK1-BC2	26	N/D	0.13	NA	NA
99KK1-BC3	21	0.7	0.10	0.008	0.08
99KK1-BC4	30	0.7	0.15	0.009	0.06
99KK1-BC5	30	2	0.15	0.03	0.2
99KK1-BC6	10	0.8	0.052	0.01	0.2

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