

# Reconstructing variability in West Greenland ocean biogeochemistry and bowhead whale (*Balaena mysticetus*) food web structure using amino acid isotope ratios

Corinne Pomerleau<sup>1,2</sup>  · Mads Peter Heide-Jørgensen<sup>2,3</sup> · Steven H. Ferguson<sup>4</sup> · Harry L. Stern<sup>5</sup> · Jacob L. Høyer<sup>6</sup> · Gary A. Stern<sup>1</sup>

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**Abstract** Climate change is causing physical and biological changes in the polar marine environment, which may impact higher trophic level predators such as the bowhead whale (*Balaena mysticetus*) and the structure of their food webs. We used bulk stable isotope analysis and compound-specific isotope analysis (CSIA) of individual amino acids (AA) to examine bowhead whale trophic position and the biogeochemistry of one of their feeding grounds, Disko Bay, West Greenland, over a period of 7 years (2007–2013). We also examined whether environmental conditions such as sea ice concentration and sea surface temperature were causing any interannual variation in isotope data. Bulk  $\delta^{15}\text{N}$  values were consistent across the 7 years of sampling and were similar between sex classes. Bulk  $\delta^{13}\text{C}$  and essential-AA  $\delta^{13}\text{C}$  values displayed an overall temporal decline of 1.0 and 1.4‰, respectively. A significant positive linear relationship was found between  $\delta^{13}\text{C}$  of bulk skin and essential-AAs suggesting that some of the observed isotopic variation in bowhead whales

between years reflect changes in the carbon at the base of the food web. There were no correlations between the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of isotopic tracers with sea ice concentrations or sea surface temperatures. The trophic level of bowhead whales remained stable over time despite large interannual variability in ice and temperature regimes. Our results indicate that the recent environmental changes in West Greenland resulted in no trophic perturbation being transferred to bowhead whales during that time period. Our study shows that the novel approach of CSIA-AA can be used effectively to study the combined temporal variation of bowhead whale food web structure and ecosystem isotopic baseline values and detect changes at the species and ecosystem levels.

**Keywords** Amino acids · Bowhead whale · Carbon · Compound-specific isotope analysis · Nitrogen · Stable isotope analysis

## Introduction

The bowhead whale (*Balaena mysticetus*) with a circumpolar distribution is the largest endemic Arctic cetacean. This baleen whale species is recovering from commercial whaling (1600–1900) that nearly brought their populations to extinction (Woodby and Botkins 1993). The Eastern Canada-West Greenland bowhead whale population (EC-WG) undergoes variable seasonal migrations within their complex range encompassing large land masses such as Baffin Island (Ferguson et al. 2010; Pomerleau et al. 2011a). Satellite tracking and genetic studies have shown that the EC-WG population is highly segregated and that a segment of this population travels across Baffin Bay toward the coast of West Greenland in late winter (Heide-

✉ Corinne Pomerleau  
corinne.pomerleau@umanitoba.ca

<sup>1</sup> Centre for Earth and Observation Science, University of Manitoba, Winnipeg, Canada

<sup>2</sup> Birds and Mammals, Greenland Institute of Natural Resources, Nuuk, Greenland

<sup>3</sup> Natural History Museum of Denmark, University of Copenhagen, Copenhagen, Denmark

<sup>4</sup> Freshwater Institute, Fisheries and Oceans Canada, Winnipeg, Canada

<sup>5</sup> Applied Physics Laboratory, University of Washington, Seattle, USA

<sup>6</sup> Danish Meteorological Institute, Climate and Arctic Research, Copenhagen, Denmark

Jørgensen et al. 2003, 2006; Nielsen et al. 2015a). Since the beginning of 2000, EC-WG bowhead whales have been detected in increasing numbers in Disko Bay, an area along the coast of West Greenland in late winter and spring (Heide-Jørgensen et al. 2007). Over a thousand bowhead whales forage in this highly productive region between the months of February and May (Laidre and Heide-Jørgensen 2012; Heide-Jørgensen et al. 2013; Rekdal et al. 2015), where calanoid copepods thrive on a large algal bloom triggered by sea ice break-up, which normally takes place in April (Laidre et al. 2007).

West Greenland has been warming significantly over the last two decades and has been one of the most affected regions globally over the past 10 years (Rignot et al. 2011; Hanna et al. 2012; Laidre et al. 2015). The ongoing warming in Arctic regions through processes such as the decrease of sea ice cover and thickness and the increase in glacier runoff can impact the timing and magnitude of biological productivity, nutrient inputs, and nitrogen cycling processes (e.g., biological N uptake and regeneration) (Zhang et al. 2010; Wadham et al. 2016) with potential cascading effects (e.g., change in the composition, abundance and reproduction/growth cycles of certain species) throughout the marine food web (Kortsch et al. 2012; Albouy et al. 2014). It remains unknown how the continuous and sustained warming trend at high latitudes have affected the primary and secondary production and the efficiency of the energy transfer to bowhead whales in West Greenland. By studying the foraging ecology of bowhead whales and how they respond to changes in their environment, we can better predict how they might react to future changes.

Stable isotope ratios of carbon ( $\delta^{13}\text{C}$ ) and nitrogen ( $\delta^{15}\text{N}$ ) have been used in a wide range of studies to investigate trophic linkages, foraging ecology, and the relative importance of feeding grounds of marine mammals (e.g., Hobson 1999; Newsome et al. 2010). Consumers incorporate the isotopic composition of their diet during metabolic process with a predictable enrichment of the heavier isotope in their tissues (DeNiro and Epstein 1978; Minagawa and Wada 1984). However, the isotopic signatures of a consumer are influenced by numerous factors making bulk tissue stable isotope analysis a challenging method for disentangling diet and trophic effects from the underlying changes in the environmental conditions (Post 2002). For instance, the isotopic values of marine primary producers are highly variable spatially and temporally and are sensitive to environmental fluctuations such as ocean temperature and nutrient sources (Rau et al. 1989). Additionally, there is also the issue of isotopic routing where isotopes are assimilated differentially into different compounds and tissues (Gannes et al. 1997). As a result, the isotopic composition of an animal tissue does not fully mirror that of its bulk diet.

Compound-specific isotope analysis of amino acids (CSIA-AA) is a developing methodology to study food web structure and is proving to be an efficient tool to address some of the issues with respect to bulk isotopic data (McClelland and Montoya 2002; Larsen et al. 2009; McMahan et al. 2010). For instance, CSIA-AA provide greater clarification in trophic studies by allowing researchers to disentangle trophic and baseline contributions to variation in bulk stable isotope values (Popp et al. 2007). Recently, it has been applied in various ecological studies in marine systems (e.g., Lorrain et al. 2009; Larsen et al. 2012; Choy et al. 2012; Décima et al. 2013; Vokhshoori et al. 2014) including marine mammals (Germain et al. 2013; Ruiz-Cooley et al. 2014; Matthews and Ferguson 2014).

The  $\delta^{15}\text{N}$  of individual-AAs ( $\delta^{15}\text{N-AA}$ ) has been employed for estimating the trophic level of species in food webs based on the fact that the  $\delta^{15}\text{N}$  values of some AAs (trophic-AAs) become heavily enriched from food source to consumer (e.g., Glutamic acid or Glu), while others (source-AAs) exhibit little or no change (e.g., Phenylalanine or Phe) (McClelland and Montoya 2002; Chikaraishi et al. 2009; McMahan et al. 2015). Therefore, the trophic level of a consumer can be estimated while taking into account the  $\delta^{15}\text{N}$  baseline value of food webs (McClelland and Montoya 2002; Popp et al. 2007; Chikaraishi et al. 2009). The CSIA-AA is a relatively new approach for resolving consumer trophic position and recent studies have shown that it has produced low estimates in some marine top predators or higher trophic level consumers (e.g., Lorrain et al. 2009; Dale et al. 2011; Seminoff et al. 2012). This appears to be related to the mode of nitrogen excretion (ammonia vs. uric acid or urea) (McMahan and McCarthy) and/or diet composition (protein quantity and quality; Germain et al. 2013; Hoen et al. 2014; Bradley et al. 2014). Active research in the field of CSIA-AA is ongoing in order to better understand AA dynamics.

Stable carbon isotopic composition of essential-AAs ( $\delta^{13}\text{C-AA}$ ) provides proxies for primary producers since animals strictly obtain their essential-AAs from their diet while being unable to synthesize them *de novo* (McMahan et al. 2011; Larsen et al. 2012; Vokhshoori et al. 2014). Essential  $\delta^{13}\text{C-AA}$  provides information on the carbon sources at the base of food webs as their signatures are preserved unchanged throughout the food chain (Larsen et al. 2012, 2013) while non-essential  $\delta^{13}\text{C-AA}$  signatures are thought to mainly reflect the routing of isotope from diet and are related to protein quality and quantity (McMahan et al. 2010; Schiff et al. 2014).

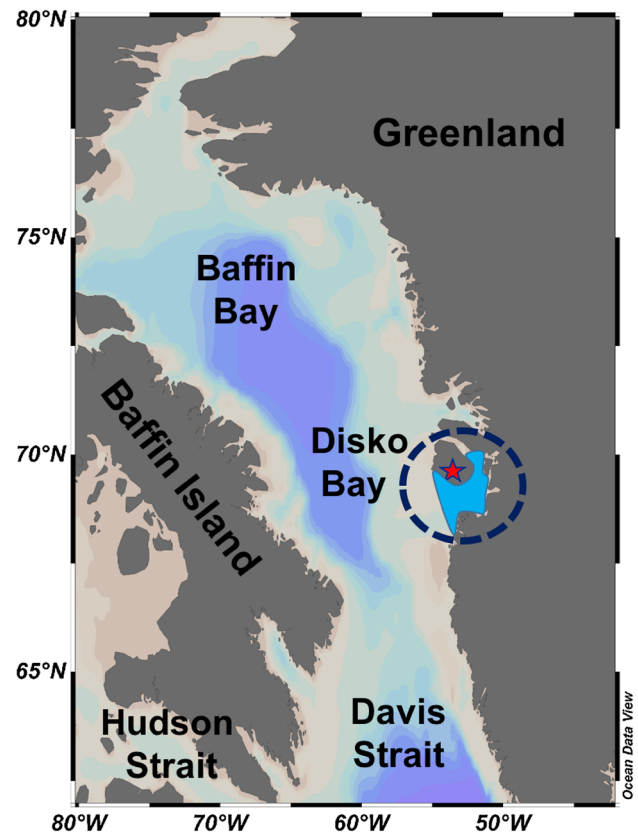
Overall, one of the main applications of nitrogen and carbon stable isotope analysis from individual-AAs quantified from consumers is their application in ecological studies to understand changes in baseline values and

trophic structure in relation to climate. For instance, Ruiz-Cooley et al. (2014) recently published a study on CSIA of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  in individual-AAs in sperm whales (*Physeter microcephalus*) from the California Current. Their results showed a significant decrease of 1.1 and 1.7‰ for bulk  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ , respectively, from 1993 to 2005. Using CSIA of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  in AAs allowed them to determine that these declining trends were attributed to changes in primary producer isotopic values and were related to a major recent change in biochemical cycling and were not attributed to a trophic shift.

The present study examined the trophic ecology of the only baleen whale that is endemic to the Arctic in a region that is undergoing rapid ecosystem change as a function of climate change. We used archived bowhead whale skin samples as a unique biological record of the  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  values of bulk and individual-AAs. Using a time-series of data (2007–2013), we assessed the temporal variability of the trophic position of bowhead whales and the baseline isotope values (ecosystem biogeochemistry) in Disko Bay, West Greenland. Temporal variation of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  in bulk tissue and AAs were related to environmental parameters including sea ice cover, sea surface temperature, the Arctic Oscillation (AO), and the North Atlantic Oscillation (NAO). We included NAO and AO since previous research found that these large scale physical drivers are linked with the timing of the break-up of sea ice in spring (Ferguson et al. 2005). We hypothesize that the continuous and sustained warming in West Greenland may have altered primary production (e.g., timing and duration of bloom, species assemblages) and/or the trophic position of bowhead whale (e.g., changes in diet/prey composition, prey abundance/biomass) which may be apparent in years with exceptionally low winter ice cover (e.g., 2010). For instance, a change in prey assemblages may lead to a shift in diet (e.g., contribution of epibenthic prey vs. pelagic prey; abundance/biomass of the small and lean boreal copepod species *Calanus finmarchicus* and less abundance/biomass of large and lipid-rich endemic to the arctic copepod species *C. glacialis* and *C. hyperboreus*) that would be reflected in the isotopic compositions of bowhead whales.

## Materials and methods

Bowhead whale skin samples ( $n = 68$ , all adult whales) were collected near Disko Bay (Qeqertarsuaq), West Greenland in spring (March–April) of 2007–2013 (Fig. 1). Samples were obtained using a crossbow darting system (Palsbøll et al. 1991) and were stored in saturated sodium chloride and 20% dimethyl sulfoxide (DMSO) and kept at  $-20\text{ }^{\circ}\text{C}$  until isotopic analyses. Sex was determined



**Fig. 1** Map of the study area. Samples were collected in Disko Bay, Greenland (dashed circle). Red star represents the community of Qeqertarsuaq. Blue zone represents the area used for ice analysis. (Color figure online)

genetically following the methodology described by Wiig et al. (2011) and more details about genetic analysis can be found in Rekdal et al. (2015).

## Bulk stable isotope analysis

Bowhead whale skin samples were rinsed three times using deionized water to remove DMSO prior to freeze-drying to remove moisture (Lesage et al. 2010). Samples were then ground and homogenized to a fine powder. Nitrogen isotope ratios were determined from dried homogenized subsamples of skin while carbon isotope ratios were determined from lipid-extracted samples. Lipid extraction was performed using a modified version of Bligh and Dyer (1959) using approximately 0.2 g of dried material and a solvent consisting of 2:1 chloroform:methanol solution (v/v) (See McMeans et al. 2009 for details). Samples were analyzed for bulk stable isotopes of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  at the Chemical Tracers Laboratory, Great Lakes Institute for Environmental Research, University of Windsor, Canada. Values of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  were measured by a Thermo Finnigan DeltaPlus mass spectrometer (Thermo Finnigan,

San Jose, CA, USA) coupled with an elemental analyzer (Costech, Valencia, CA, USA). Stable isotope ratios are expressed as delta ( $\delta$ ) notations, the normalized ratio of an unknown sample to an internationally accepted standard ( $\delta^{15}\text{N}$  or  $\delta^{13}\text{C} = (R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}} \times 1000$ , where  $R$  is  $^{15}\text{N}/^{14}\text{N}$  or  $^{13}\text{C}/^{12}\text{C}$ ). A triplicate was run every ten samples and the standards were atmospheric  $\text{N}_2$  for  $\delta^{15}\text{N}$  and Vienna Pee Dee Belemnite for  $\delta^{13}\text{C}$ . Analytical error based on replicate analyses of samples and laboratory standards were within 0.1‰ for both  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ .

### Amino acid compound-specific isotope analysis

Because of sample size limitations, 40 samples were analyzed for CSIA in individual-AAAs to quantify  $\delta^{15}\text{N}$  values from source- and trophic-AAAs and  $\delta^{13}\text{C}$  values from essential- and non-essential-AAAs. Acid hydrolysis was used to release individual-AAAs from peptide and protein samples (Yarnes and Herszage 2017). Ground and homogenized samples (~2–3 mg) were placed in vials with 0.5 mL of 6 M hydrochloric acid (HCl). The vials were flushed with  $\text{N}_2$ , sealed with PTFE-tape and a heat- and acid-resistant cap, and placed in an oven at 150 °C for 70 min. After hydrolysis, samples were dried in a heating block at 60 °C under a gentle stream of  $\text{N}_2$ . Hydrolysates and amino acid mixtures were first dissolved in 200  $\mu\text{L}$  0.4 M HCl which maintains a  $\text{pH} < 1$  for a variety of matrices. A volume of 100  $\mu\text{L}$  of each solution was combined with 20  $\mu\text{L}$  of internal reference solution, 50  $\mu\text{L}$  of methanol, and 30  $\mu\text{L}$  of pyridine and briefly mixed. A volume of 15  $\mu\text{L}$  of the derivatizing reagent, methyl chloroformate, was then added and vortexed. After 10 min, derivatives were extracted with 100  $\mu\text{L}$  of chloroform and transferred to a GC vial for subsequent analysis.

GC/C/IRMS was performed on a Thermo Trace gas chromatograph coupled to a Delta V Advantage isotope-ratio mass spectrometer via a GC IsoLink combustion interface (Thermo Electron, Bremen, Germany) at the UC Davis Stable Isotope Facility, Davis, California. Derivatized AAAs were injected at 240 °C (splitless, 1 min.) and separated on a DB-23 capillary column (Agilent Technologies; 30 m, 0.25 mm O.D., 0.25 mm film) at constant flow rate of 1.6 ml/min under the following temperature program: 50 °C (hold 2 min.), 120 °C (15 °C/min.), 175 °C (10 °C/min., hold 5 min.), 195 °C (2 °C/min.), 250 °C (8 °C/min., hold 9 min.). The combustion reactor was composed of a NiO tube containing CuO/NiO wires. Furnace temperatures were maintained to 1000 °C. For  $^{15}\text{N}$  analysis, oxidation efficiency was maintained by seed oxidation of the reactor for approximately 20 s. prior to the injection of each sample and  $\text{CO}_2$  was removed from the post-combustion carrier stream through the use of liquid

nitrogen trap to prevent isobaric interference;  $\text{CO}_2$  was subsequently released from the trap following each analysis.

All samples were analyzed in duplicate and ten in triplicate. During measurement, provisional values were calculated by comparison to L-norleucine and/or L-homophenylalanine. Two reference mixtures containing AAAs which calibrated against NIST Standard Reference Materials (IAEA-N1, IAEA-N2, IAEA-N3, USGS-40, and USGS-41) were co-measured with samples and quality assurance materials interspersed. For  $\delta^{13}\text{C}$ , calibration for potential kinetic isotope effects and derivative carbon followed Docherty and Evershed (2001), as described in Walsh et al. (2014). For  $\delta^{15}\text{N}$ , provisional values of each individual-AA were then adjusted to account for the residuals of measured and calibrated values of the first calibrated external mixture, UCD AA 1 (sensu Reinneke et al. 2012). This strategy is prudent because the measured values of AAAs may vary from their known values in direction and magnitude; AAAs differ in the presence of heteroatoms (e.g., Pro, pyroGlu) and functional groups which can lead to different combustion efficiencies (Reinneke et al. 2012). Subsequently, the second AA mixture, spanning  $\delta^{15}\text{N}$  values from -6.6 to +47.6‰, was used to normalize the data to the international reference scale for  $\delta^{15}\text{N}$ , atmospheric nitrogen. These steps allowed for the accounting of instrumental drift as well as scale compression on a compound-by-compound basis. The additional inclusion of quality assurance materials allows for the monitoring of long-term reproducibility.

We measured the  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  values of 12 individual-AAAs: Ala (alanine), Asp (asparagine/aspartic acid), Glu (glutamine/glutamic acid), Gly (glycine), Ile (isoleucine), Leu (leucine), Lys (lysine), Met (methionine), Phe (phenylalanine), Pro (proline), Tyr (tyrosine), and Val (valine). Tyr was excluded from our analyses because of the very low concentrations in our samples (below limit-of-quantification). Average standard deviation of measurements was  $\pm 0.69\%$  across AAAs (within samples) and  $\pm 0.70\%$  across samples (within AAAs) for  $\delta^{15}\text{N}$  and  $\pm 0.65\%$  across AAAs (within samples) and  $\pm 0.65\%$  across samples (within AAAs) for  $\delta^{13}\text{C}$ . Mean analytical precision based on repeated measures of the quality assurance materials, baleen (RWB) and fish muscle (MMS), and two reference mixtures, UCD AA 1 and UCD AA 2, ranged from  $\pm 0.45$  to  $\pm 1.69$  and averaged  $\pm 1.0\%$ .

The advantages of the chloroformate method include rapid, aqueous-phase derivatization, and low exogenous carbon following derivatization (Walsh et al. 2014). There has been some concern expressed that chloroformates may not be suitable for trophic positioning using glutamic acid  $\delta^{15}\text{N}$  due to the formation of pyroGlu as a secondary derivatization product despite evidence from a large controlled feeding study that indicates otherwise (Bowes and

Thorp 2015). Previously, the derivatization conditions necessary for quality  $^{15}\text{N}$ -Glu measurements by chloroformates have been established ( $\text{pH} < 1$ ; Sacks and Brenna 2005) and applied to a wide range of matrices (Walsh et al. 2014). The present contention is that while the measurement of  $\delta^{15}\text{N}$  of Glu has been demonstrated to be suitable below  $\text{pH} 1$ , differences between sample matrix buffering capacities may prevent the maintenance of sufficiently acid conditions. However, a wide range of sample matrices prepared in the acid buffer used for derivatization suggest that this effect is negligible (0.4 M HCl). Recently, a comparison of  $\delta^{15}\text{N}$  measurements from chloroformates and esterification-acetylation across a range of sample materials was conducted (Yarnes and Herszage 2017). Under the same calibration and normalization procedures, amino acid  $\delta^{15}\text{N}$  measurements of all of the commonly measurable amino acids (Ala, Asp, Gly, Gly, Phe, Pro, Val) were within measurement error of the  $\delta^{15}\text{N}$  obtained by either technique ( $\leq \pm 1.0\%$ ). Presently, there are a wide range of amino acid derivatization techniques employed for GC/C/IRMS, all with various potential advantages and shortcomings. For example, Hofmann et al. (2003) found two derivatization products for  $^{15}\text{N}$ -Phe from esterification-pivaloylation, despite its frequent use in trophic positioning by  $\delta^{15}\text{N}$  Glu- $\delta^{15}\text{N}$  Phe. However, international reference materials will need to be developed, common normalization procedures adopted, and proficiency testing conducted before the impact of laboratories, derivatization techniques, and instrumentation on reproducibility of CSIA-AA can be appropriately determined (Jochmann and Schmidt 2012).

### Environmental parameters

Sea ice data were obtained from the National Snow and Ice Data Center in Boulder, CO. We used the Sea Ice Concentrations from Nimbus-7 SMMR and DMSP SSM/I-SSMIS Passive Microwave Data (Cavaliere et al. 1996, updated yearly). These datasets are produced using the NASA Team algorithm and are provided on a polar stereographic grid with nominal cell size  $25 \times 25$  km. We calculated the daily total sea ice area in Disko Bay by summing (over all 20 grid cells in the bay) the product of sea ice concentration and grid cell area. We then averaged the daily values to get monthly values. Sea surface temperature (0–25 m) was provided by Disko Basis/Arctic Station. We used the CTD data that were collected in late March or early April at the monitoring station ( $69^{\circ}11'\text{N}$ ,  $53^{\circ}31'\text{W}$ ) in Disko Bay. The North Atlantic Oscillation (NAO) monthly time-series were obtained from the NOAA Global Climate Observing System Working Group on Surface Pressure and the Arctic Oscillation (AO) monthly time-series were obtained from the National Weather Service Climate Prediction Center (<http://www.cpc.ncep.noaa.gov/>).

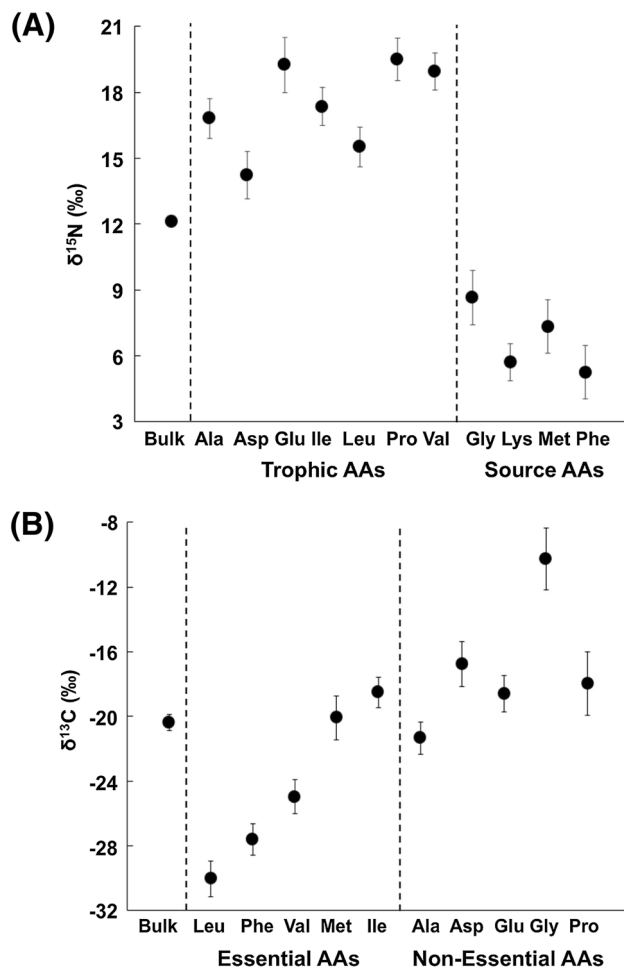
### Data analysis

Statistical tests were performed in R version 3.2.0 using the RStudio interface version 0.99.484 (R Development Core Team 2015). Normality of data was assessed using Shapiro–Wilk normality tests and homogeneity of the variances using the Bartlett's test. The significance level for all tests was set at  $p < 0.05$ . Gender and year effects were tested on bulk skin  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  using a two-way analysis of variance (ANOVA). Data were grouped as either source- or trophic-AAs for  $\delta^{15}\text{N}$  values (McClelland and Montoya 2002; Popp et al. 2007) and essential- or non-essential-AAs for  $\delta^{13}\text{C}$  values (Schiff et al. 2014, Vokhshoori and McCarthy 2014). The literature classification for grouping of  $\delta^{15}\text{N}$ -AAAs of our data was confirmed using a hierarchical cluster analysis (dissimilarity matrix based on Euclidean distances). For nitrogen, we assigned Glu, Asp, Ala, Leu, Ile, Pro, and Val as trophic-AAAs, and Phe, Met, Gly, Lys as source-AAAs (Fig. 2a). For carbon, we assigned Glu, Asp, Ala, Pro, and Gly as non-essential-AAAs, and Leu, Ile, Val, Phe and Met as essential-AAAs (Fig. 2b). We used unweighted averages of AA groupings to analyze our data. The linear relationship (temporal variation) between year and each isotopic tracer for both  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  was assessed using regression analyses. We used separate one-way ANOVAs and Tukey's honestly significant difference (HSD) post hoc tests to examine differences in individual-AA between years. The relationships between each isotopic tracer with sea ice concentration, sea surface temperature, NAO, and AO were investigated using Pearson's correlation. The effects of year and sex on each estimate of TP were tested using a two-way ANOVA.

Bowhead whale trophic position (TP) was estimated using three equations to compare the commonly used bulk skin TP approach to the  $\delta^{15}\text{N}$ -AA derived TP estimates. We estimated  $\text{TP}_{\text{Bulk}}$  based on the equation by Post (2002) using a mean  $\delta^{15}\text{N}$  value of 8.5‰ for the primary consumer *Calanus* spp. (West Greenland, Linneberg et al. 2016). A trophic discrimination factor (TDF) of 2.5‰ between bowhead whale and *Calanus* spp. (primary consumer,  $\text{TP} = 2$ ) was chosen based on recent studies done on captive marine mammals (Caut et al. 2011; Browning et al. 2014):

$$\text{TP}_{\text{Bulk}} = \frac{(\delta^{15}\text{N}_{\text{Bowhead}} - \delta^{15}\text{N}_{\text{Calanus}})}{\text{TDF}_{\text{Bowhead-Calanus}}} + 2 \quad (1)$$

Secondly, we calculated the  $\text{TP}_{\text{CSIA}}$  of bowhead whales from the difference in  $\delta^{15}\text{N}$  values of the most predictable trophic-AA ( $\delta^{15}\text{N}$ -Glu) and the most predictable source-AA ( $\delta^{15}\text{N}$ -Phe) (Chikaraishi et al. 2009). This equation takes into account the isotopic difference between the trophic- and source-AAAs in primary producers ( $\beta = \sim 3.4\%$ , e.g., phytoplankton) (McClelland and



**Fig. 2** **a** Mean  $\delta^{15}\text{N}$  values ( $\pm$ SD) of individual trophic and source-AAs and **b** mean  $\delta^{13}\text{C}$  ( $\pm$ SD) of individual essential- and non-essential-AAs in bowhead whales (*Balaena mysticetus*). Amino acid abbreviations: alanine (Ala), aspartic acid (Asp), glutamic acid (Glu), isoleucine (Ile), leucine (Leu), proline (Pro), valine (Val), glycine (Gly), lysine (Lys), phenylalanine (Phe), and methionine (Met)

Montoya 2002; Chikaraishi et al. 2007) and the TDF between a trophic and source-AA (e.g.,  $\text{TDF}_{\text{Glu-Phe}} = -\Delta_{15}\text{N}_{\text{Glu}} - \Delta_{15}\text{N}_{\text{Phe}} = \sim 7.6\text{‰}$ ) which is the typical literature value used for plankton and lower trophic level species (Chikaraishi et al. 2009):

$$\text{TP}_{\text{CSIA}} = \frac{(\delta^{15}\text{N}_{\text{Glu}} - \delta^{15}\text{N}_{\text{Phe}} - \beta)}{\text{TDF}_{\text{Glu-Phe}}} + 1 \quad (2)$$

Thirdly, we calculated  $\text{TP}_{\text{CSIA}}$  using a dual- $\text{TDF}_{\text{Glu-Phe}}$  equation derived from a controlled feeding study of harbor seals (*Phoca vitulina*) (Germain et al. 2013). The authors of this study found a  $\text{TDF}_{\text{Glu-Phe}}$  of 4.3‰ between the harbor seals and herring. In this dual-TDF equation, the  $\beta$  corresponds to the isotopic difference between the trophic- and source-AAs in primary producers (3.4‰) and the value of  $\text{TDF}_{\text{Glu-Phe(plankton)}}$  is the relative difference between  $\delta^{15}\text{N}_{\text{Glu}} - \delta^{15}\text{N}_{\text{Phe}}$  with each trophic transfer derived from

experimental studies on invertebrates and fish (7.6‰) (Refer to Germain et al. 2013 for more details):

$$\text{TP}_{\text{CSIA}} = \frac{(\delta^{15}\text{N}_{\text{Glu}} - \delta^{15}\text{N}_{\text{Phe}} - \text{TDF}_{(\text{Glu-Phe})\text{seal}} - \beta)}{\text{TDF}_{\text{Glu-Phe(plankton)}}} + 2 \quad (3)$$

## Results

### Bulk isotopic variation of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$

Bowhead whale samples were composed of 55 females and 13 males.  $\delta^{15}\text{N}$  values ranged from 11.7 to 12.7‰ with a mean value of  $12.1 \pm 0.2\text{‰}$  and bulk  $\delta^{13}\text{C}$  values ranged from  $-21.1$  to  $-19.1\text{‰}$  with a mean value of  $-20.3 \pm 0.5\text{‰}$  (Tables 1, 2). Bulk  $\delta^{15}\text{N}$  signatures were consistent across the 7 years of sampling (2007–2013) ( $F = 1.585$ ,  $p = 0.169$ ) (Fig. 2a) and between males and females ( $F = 0.209$ ,  $p = 0.649$ ). Bulk  $\delta^{13}\text{C}$  values were also similar between sexes ( $F = 0.299$ ,  $p = 0.743$ ) but were found to vary significantly among years of sampling ( $F = 11.58$ ,  $p < 0.0001$ ). Linear regression model for bulk  $\delta^{13}\text{C}$  values showed a significant decrease between 2007 and 2013 ( $r^2 = 0.868$ ,  $p = 0.002$ ) (Fig. 3b) with an overall decrease of 1‰ over that period of time. Bulk  $\delta^{15}\text{N}$  values did not show any significant trend with time ( $r^2 = 0.096$ ,  $p = 0.549$ ) (Fig. 3a). All regressions in our study exhibited a random pattern of their residuals. A significant positive correlation was found between bulk  $\delta^{13}\text{C}$  and essential-AAs  $\delta^{13}\text{C}$  values ( $r = 0.554$ ,  $p = 0.0003$ ) and between bulk  $\delta^{13}\text{C}$  and non-essential-AAs  $\delta^{13}\text{C}$  ( $r = 0.361$ ,  $p = 0.03$ ). There was no correlation between bulk  $\delta^{15}\text{N}$  and source-AAs  $\delta^{15}\text{N}$  or trophic-AAs  $\delta^{15}\text{N}$  ( $r = -0.163$ ,  $p = 0.315$  and  $r = -0.002$ ,  $p = 0.993$ , respectively).

### $\delta^{15}\text{N}$ amino acids

Individual-AA  $\delta^{15}\text{N}$  values covered a range of 19.3‰ (Table 1). Trophic-AAs had a higher  $\delta^{15}\text{N}$  values (mean  $17.4 \pm 2.0\text{‰}$ , range 11.9–21.9‰) than source-AAs (mean  $6.6 \pm 1.7\text{‰}$ , range 2.6–12.7‰) (Table 1; Fig. 2a). Linear regression models for average  $\delta^{15}\text{N}$  values from source-AAs and trophic-AAs did not reveal any significant temporal trend ( $r^2 = 0.215$ ,  $p = 0.355$  and  $r^2 = 0.413$ ,  $p = 0.168$ , respectively) (Fig. 3a). The same results were obtained using Phe ( $r^2 = 0.133$ ,  $p = 0.655$ ) and Glu ( $r^2 = 0.267$ ,  $p = 0.244$ ) as source- and trophic-AAs, respectively. Trophic-AAs  $\delta^{15}\text{N}$  values did not vary significantly among years with the exception of Ala.  $\delta^{15}\text{N}$  values of Ala were significantly lower in 2009 compared to 2012 and 2013 (Tukey's HSD tests, both  $p < 0.01$ ). The

**Table 1**  $\delta^{15}\text{N}$  values of bulk skin, trophic-, and source-AA

	2007 ( <i>n</i> = 9)	2008 ( <i>n</i> = 9)	2009 ( <i>n</i> = 10)	2010 ( <i>n</i> = 10)	2011 ( <i>n</i> = 9)	2012 ( <i>n</i> = 11)	2013 ( <i>n</i> = 10)
Bulk $\delta^{15}\text{N}$	12.2 (0.3)	12.1 (0.3)	12.2 (0.2)	12.2 (0.3)	12.1 (0.2)	12.1 (0.3)	12.0 (0.2)
Trophic-AA							
Ala	Na	16.9 (0.9)	16.0 (0.7)	16.8 (0.4)	16.9 (1.1)	17.4 (0.6)	17.5 (0.9)
Asp		15.0 (0.9)	13.2 (0.8)	13.3 (1.7)	14.6 (0.9)	15.0 (1.4)	14.8 (1.0)
<b>Glu</b>		<b>17.1 (0.9)</b>	<b>19.1 (1.4)</b>	<b>19.6 (1.5)</b>	<b>19.6 (1.1)</b>	<b>18.8 (1.1)</b>	<b>19.1 (0.9)</b>
Ile		17.7 (0.5)	17.1 (0.6)	17.4 (0.6)	17.7 (1.4)	17.6 (0.8)	17.0 (0.7)
Leu		17.1 (0.9)	15.0 (0.8)	15.7 (0.6)	15.5 (0.9)	15.7 (0.9)	15.6 (1.3)
Pro		20.2 (0.8)	19.5 (0.5)	19.2 (1.3)	19.7 (1.2)	19.7 (1.0)	19.3 (0.9)
Val		18.9 (0.5)	18.6 (0.7)	19.1 (0.5)	18.9 (1.2)	19.1 (1.1)	19.3 (0.7)
Mean		17.5 (0.7)	16.9 (0.5)	17.4 (0.7)	17.5 (0.8)	17.6 (0.5)	17.5 (0.5)
Source-AA							
<b>Phe</b>	Na	<b>4.1 (1.3)</b>	<b>5.3 (0.9)</b>	<b>5.0 (0.8)</b>	<b>6.0 (1.5)</b>	<b>5.1 (2.0)</b>	<b>4.9 (1.1)</b>
Lys		6.3 (1.3)	4.8 (0.9)	4.6 (1.4)	5.4 (0.9)	6.1 (0.9)	6.1 (0.5)
Gly		7.6 (0.8)	8.2 (1.4)	8.5 (1.4)	9.7 (1.9)	10.0 (1.6)	8.5 (1.0)
Met		6.9 (1.2)	5.6 (0.9)	7.2 (2.3)	8.0 (1.1)	6.7 (0.5)	6.9 (1.5)
Mean		6.2 (1.1)	6.0 (0.5)	6.4 (1.3)	7.2 (0.9)	7.0 (1.0)	6.6 (0.7)

Numbers represent mean value  $\pm$  SD (‰). Glu and Phe (in bold) represent the most commonly used trophic- and source-AA, respectively

**Table 2**  $\delta^{13}\text{C}$  values of bulk skin, essential-, and non-essential-AA. Numbers represent mean value  $\pm$  SD (‰)

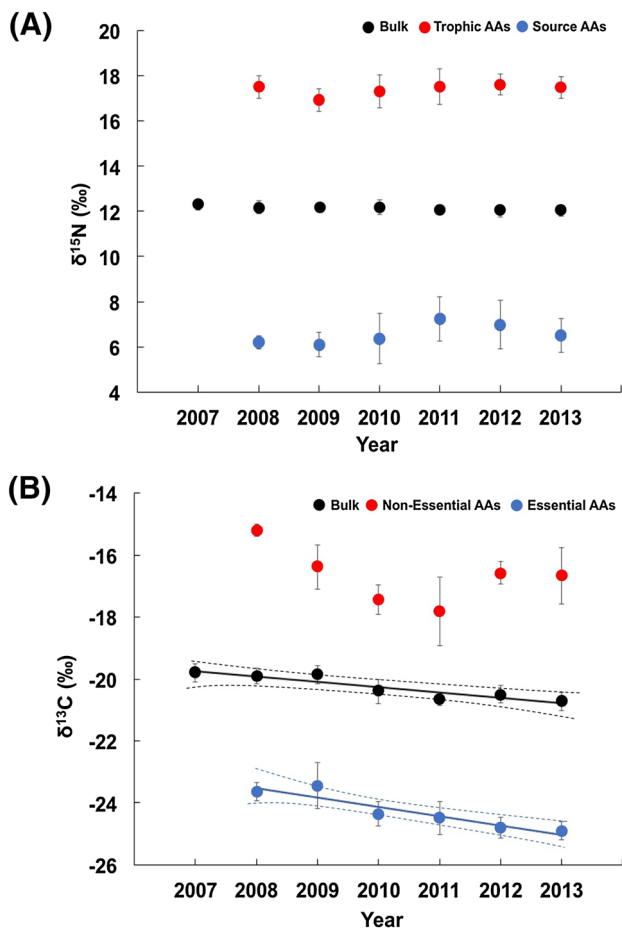
	2007 ( <i>n</i> = 9)	2008 ( <i>n</i> = 9)	2009 ( <i>n</i> = 10)	2010 ( <i>n</i> = 10)	2011 ( <i>n</i> = 9)	2012 ( <i>n</i> = 11)	2013 ( <i>n</i> = 10)
Bulk $\delta^{13}\text{C}$	-19.7 (0.3)	-19.9 (0.4)	-19.9 (0.4)	-20.4 (0.5)	-20.6 (0.1)	-20.5 (0.3)	-20.7 (0.3)
Essential-AA							
Phe	Na	-27.2 (0.5)	-26.5 (1.0)	-27.7 (0.9)	-28.3 (0.8)	-27.9 (0.5)	-28.1 (1.5)
Val		-23.1 (0.6)	-24.3 (0.9)	-25.1 (1.0)	-25.0 (0.8)	-26.0 (0.8)	-25.4 (1.1)
Ile		-17.5 (0.3)	-17.8 (0.6)	-18.9 (0.6)	-18.8 (1.0)	-19.7 (0.2)	-18.5 (0.7)
Leu		-30.1 (0.5)	-29.2 (0.5)	-30.0 (0.9)	-30.1 (1.0)	-29.5 (0.4)	-31.6 (0.9)
Met		-20.1 (0.3)	-18.6 (1.1)	-20.3 (1.5)	-20.2 (1.0)	-21.6 (0.4)	-20.0 (1.1)
Mean		-23.6 (0.4)	-23.4 (0.5)	-24.3 (0.4)	-24.5 (0.5)	-24.9 (0.5)	-24.9 (0.5)
Non-essential-AA							
Ala	Na	-20.3 (0.4)	-20.8 (1.2)	-21.3 (0.6)	-22.1 (0.9)	-21.5 (0.5)	-22.2 (1.0)
Asp		-14.0 (0.2)	-15.9 (0.9)	-17.1 (0.6)	-17.9 (1.0)	-16.0 (0.5)	-17.1 (1.5)
Glu		-16.8 (0.3)	-18.0 (0.8)	-19.2 (1.0)	-19.5 (1.0)	-17.9 (0.4)	-17.9 (0.4)
Gly		-10.7 (1.0)	-10.9 (2.4)	-10.3 (1.0)	-10.8 (1.9)	-9.6 (1.5)	-9.3 (1.0)
Pro		-17.2 (0.4)	-16.4 (0.7)	-19.2 (1.5)	-19.1 (2.0)	-17.9 (0.8)	-16.5 (1.1)
Mean		-15.2 (0.5)	-16.4 (0.7)	-17.4 (0.5)	-18.1 (1.1)	-16.9 (0.4)	-16.7 (0.9)

$\delta^{15}\text{N}$  values of the source-AA, Phe, and Gly, did not change over time but the  $\delta^{15}\text{N}$  values of Lys were lower in 2010 compared to 2013 (Tukey's HSD tests,  $p = 0.037$ ).

### $\delta^{13}\text{C}$ amino acids

Individual-AA  $\delta^{13}\text{C}$  values covered a range of 26.5‰ (Table 2). Essential-AAs were on average lower (mean  $-24.3 \pm 4.9\%$ , range  $-32.5$  to  $-15.8\%$ ) than non-

essential-AAs (mean  $-17.1 \pm 4.2\%$ , range  $-29.9$  to  $-6.0\%$ ) (Table 2; Fig. 2b). Average essential-AAs  $\delta^{13}\text{C}$  values displayed a significant temporal decrease between 2008 and 2013 ( $r^2 = 0.855$ ,  $p = 0.008$ ) (Fig. 3b) with an overall decline of 1.4‰ between 2008 and 2013. No significant temporal trend was observed in non-essential-AAs  $\delta^{13}\text{C}$  values ( $r^2 = 0.317$ ,  $p = 0.245$ ) (Fig. 3b). All essential-AAs  $\delta^{13}\text{C}$  values varied significantly between years (Tukey's HSD tests, all  $p < 0.01$ ).  $\delta^{13}\text{C}$  values of Ile, Met,



**Fig. 3** Time-series of isotopic data from bowhead whale (*Balaena mysticetus*) skin samples. **a**  $\delta^{15}\text{N}$  values in bulk skin, average source-AAAs, and average trophic-AAAs ( $\pm\text{SD}$ ) and **b**  $\delta^{13}\text{C}$  values in bulk skin, average non-essential-AAAs, and average essential-AAAs ( $\pm\text{SD}$ ). (Color figure online)

Val, and Phe were significantly higher in 2009 compared to all other years (Tukey's HSD tests, all  $p < 0.001$ ) and  $\delta^{13}\text{C}$  values of Ile and Leu were lower in 2013 (Tukey's HSD tests, all  $p < 0.01$ ). Non-essential-AAAs  $\delta^{13}\text{C}$  values of Asp and Pro varied significantly between years (Tukey's HSD tests, all  $p < 0.03$ ).  $\delta^{13}\text{C}$  values of Pro were higher in 2009 and 2013 compared to other years, while  $\delta^{13}\text{C}$  values of Asp were lower in 2011 compared to 2009 and 2012. No significant trends were observed for Ala, Glu, and Gly (Tukey's HSD tests, all  $p > 0.05$ ).

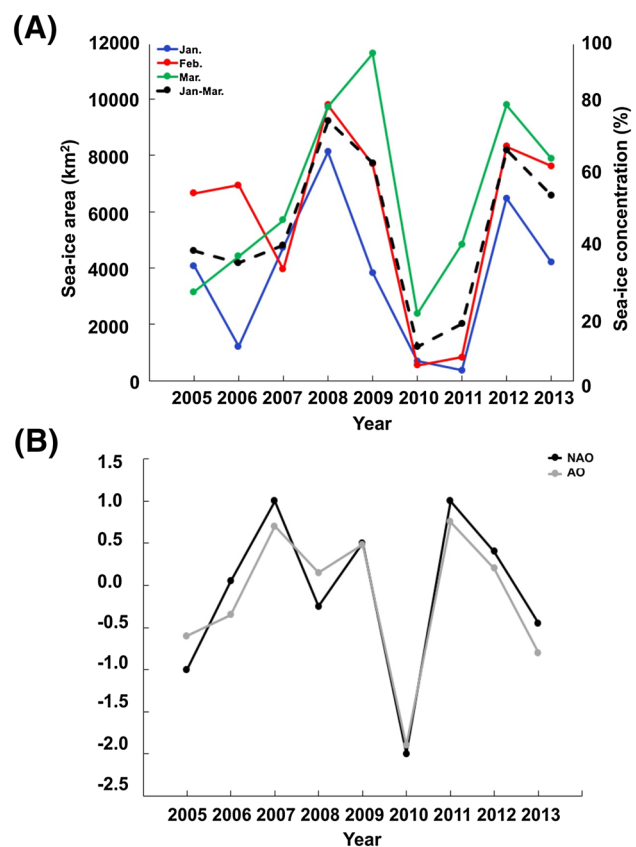
#### Correlation between isotopic markers and environmental parameters

A consistent trend was not observed for maximum sea ice coverage in Disko Bay between 2005 and 2013. However, there was large variation in sea ice area during this time period. For example, 2009 corresponded to the year with the greatest average maximum sea ice cover in the month

of March (11,500 km<sup>2</sup>, 95% ice cover), while 2010 exhibited a minimum (1028 km<sup>2</sup>, 10% ice cover) for the time period covered in this study (Fig. 4a). Similarly, there was no consistent trend between 2005 and 2013 for the AO and the NAO (Fig. 4b). No significant correlations were found between sea ice cover and average AAAs (trophic/source) or bulk  $\delta^{15}\text{N}$  (all  $p > 0.05$ ) or between AAAs (essential/non-essential) or bulk  $\delta^{13}\text{C}$  (all  $p > 0.05$ ) despite the prevalence of a tendency toward higher  $\delta^{13}\text{C}$  values with larger ice areas. Similarly, no significant correlations were found between  $\delta^{13}\text{C}$  or  $\delta^{15}\text{N}$  with sea surface temperature, AO and NAO (all  $p > 0.05$ ).

#### Trophic position of bowhead whales

Trophic level estimates are presented in Table 3 and ranged from 2.4 to 3.5. None of the TP estimates were found to vary significantly between years or sexes (two-way ANOVA, all  $p > 0.05$ ). Trophic index ( $\Delta\delta^{15}\text{N}$ ) ranged from 11.3 to 16.9‰ for  $\Delta\delta^{15}\text{N}_{\text{Glu-Phe}}$  and from 9.4 to 12.6 for  $\Delta\delta^{15}\text{N}_{\Sigma\text{trophicAA} - \Sigma\text{sourceAA}}$  (Table 3).



**Fig. 4** Time-series of **a** sea ice covered area (sq km) in January, February, March and these three months averaged in Disko Bay and **b** mean winter month values of North Atlantic Oscillation (NAO) and Arctic Oscillation (AO) index. (Color figure online)



**Table 3** Trophic position and trophic index calculated for bowhead whales (*Balaena mysticetus*)

	2007	2008	2009	2010	2011	2012	2013	Mean
Trophic position (TP)								
$\frac{(\delta^{15}\text{N}_{\text{Bowhead}} - \delta^{15}\text{N}_{\text{Calanus}})}{\text{TDF}_{\text{Bowhead-Calanus}}} + 2$ (eq. 1)	3.5 (0.1)	3.5 (0.1)	3.4 (0.1)	3.4 (0.1)	3.5 (0.1)	3.4 (0.0)	3.5 (0.1)	3.5 (0.1)
$\frac{(\delta^{15}\text{N}_{\text{Glu}} - \delta^{15}\text{N}_{\text{Phe}} - \beta)}{\text{TDF}_{\text{Glu-Phe}}} + 1$ (eq. 2)	Na	2.3 (0.1)	2.4 (0.2)	2.5 (0.2)	2.3 (0.2)	2.4 (0.2)	2.4 (0.1)	2.4 (0.2)
$\frac{(\delta^{15}\text{N}_{\text{Glu}} - \delta^{15}\text{N}_{\text{Phe}} - \text{TDF}_{(\text{Glu-Phe})\text{seal}} - \beta)}{\text{TDF}_{\text{Glu-Phe(plankton)}}} + 2$ (eq. 3)	Na	2.8 (0.1)	2.8 (0.1)	2.9 (0.1)	2.8 (0.1)	2.8 (0.1)	2.9 (0.1)	2.9 (0.1)
Trophic index								
$\Delta\delta^{15}\text{N}_{\text{Glu-Phe}}$	Na	13.0	13.9 (1.8)	14.7 (1.6)	13.6 (1.3)	13.8 (1.5)	14.2 (1.0)	14.0 (1.4)
$\Delta\delta^{15}\text{N}_{\sum\text{trophicAA}} - \sum\text{sourceAA}$	Na	11.3	11.0 (0.6)	11.0 (0.9)	10.3 (0.6)	10.6 (0.6)	10.9 (0.6)	11.0 (0.7)

Numbers represent mean value  $\pm$  SD (‰)

## Discussion

### Bulk and AA isotopic variation of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$

Bowhead whales were mainly sampled in April reflecting the isotopic values of their diet and feeding areas integrated over late winter and early spring. The isotopic incorporation rate in the skin of whales has been estimated to reflect the diet over a period of two to three months prior to skin collection in seals and beluga whales (*Delphinapterus leucas*) (St-Aubin et al. 1990; Hobson et al. 1996) and more recently bottlenose dolphins (*Tursiops truncatus*) (Browning et al. 2014). Bowhead whales feed on zooplankton (Pomerleau et al. 2011b, 2012, 2014) and the food web upon which they rely is short and strongly influenced by sea ice processes (e.g., ice algae production, timing of ice break-up, and freeze-up). The productivity in late winter and early spring in high latitude systems mainly comprises particulate organic matter (POM) and ice algae, the latter contributing large amount to pelagic biomass especially during ice melt (Pineault et al. 2013). In our study, the bulk  $\delta^{13}\text{C}$  values in skin ( $-20.3 \pm 0.5\text{‰}$ ) were close to the previously reported  $\delta^{13}\text{C}$  values for pelagic POM ( $-22.3\text{‰}$ ) and ice POM ( $-17.7\text{‰}$ ) in eastern Baffin Bay (Hobson et al. 2002) where marine carbon tends to dominate (Dunton et al. 2006; Iken et al. 2010). The vast majority of the bowhead whales in our study arrived from Hudson Strait, the main wintering area for this population (Heide-Jørgensen et al. 2003; Koski et al. 2006), where the winter POM- $\delta^{13}\text{C}$  values tend to be more depleted ( $-24.1 \pm 1.5\text{‰}$ ) (Kuzyk et al. 2010). Additionally, the bulk  $\delta^{13}\text{C}$  values in bowhead skin closely resembled the  $\delta^{13}\text{C}$  values of their main prey items, *C. finmarchicus* ( $-20.4\text{‰}$ ), *C. glacialis* ( $-19.2\text{‰}$ ) and *C. hyperboreus* ( $-18.9\text{‰}$ ) along the coast of West Greenland and Disko Bay in late winter/early spring (Linneberg et al. 2016) suggesting recent feeding activity within the Disko Bay/eastern Baffin Bay system.

In our study, we only found a significant decrease in  $\delta^{13}\text{C}$  between 2007 and 2013 with no indication of a decrease in  $\delta^{15}\text{N}$  as both the bulk skin  $\delta^{15}\text{N}$  values and the  $\delta^{15}\text{N}$  values of specific-AAs in bowhead whale skin showed no temporal trend over those years. Although we did not expect  $\delta^{15}\text{N}$ -Phe values to match bulk nitrogen values from POM or ice algae (e.g., Chikaraishi et al. 2009), the  $\delta^{15}\text{N}$ -Phe values in our samples ( $5.3 \pm 1.2\text{‰}$ ) were close to bulk  $\delta^{15}\text{N}$  values measured in ice algae and POM in Baffin Bay ( $5.1 \pm 0.3$  and  $6.9 \pm 0.3\text{‰}$ , respectively) (Hobson et al. 2002). Because of the very small amount of trophic fractionation in Phe, this amino acid has been commonly used as a proxy for  $\delta^{15}\text{N}$  values of primary producers and as an isotopic baseline indicator for the ecosystem (Chikaraishi et al. 2009). Source-AAs did not undergo any significant changes in their  $\delta^{15}\text{N}$  values over the study period, which suggests that there was no baseline variation in the community of primary producers or in the biogeochemical cycling of nitrogen within our study area. The absence of changes in  $\delta^{15}\text{N}$  in our time-series is an interesting result considering that the two highest Greenland Ice Sheet melt years on record (2010, 2012) occurred during that time period (Hawkings et al. 2015). In Polar regions, the biogeochemical impacts of Arctic warming remain unclear but nutrient supply especially of allochthonous N subsidies to the euphotic zone and light availability are both strongly affected by the stratification of the water column. Nutrient can be supply via deep waters as nitrate, from the atmosphere as  $\text{N}_2$  or from precipitation and rivers as inorganic or organic N (Tremblay et al. 2002). Our bulk  $\delta^{15}\text{N}$  and  $\delta^{15}\text{N}$ -AA results suggest that larger scale environmental changes have not affected the food webs of bowhead whales in Disko Bay between 2007 and 2013. A much longer time-series of  $\delta^{15}\text{N}$ -AA data in deep-sea gorgonian corals in the western North Atlantic highlighted no significant change in the trophic structure of the coral's food source over the last century (Sherwood et al. 2011). They attributed the lack of temporal trend in trophic

level to a stable and/or resilient plankton community despite the persistence of a warm and nutrient rich regime. In our study, the lack of interannual variability in  $\delta^{15}\text{N}$  values of source-AAAs, in particular Phe, and the small differences in bulk  $\delta^{15}\text{N}$  values among individuals in a given year ( $\pm 0.2\text{‰}$ ) or between years ( $\pm 0.2\text{‰}$ ) suggest that bowhead whales were foraging on similar prey assemblages within the same location each year, presumably Disko Bay.

Bowhead whales and all other eukaryotes are unable to synthesize essential-AAAs *de novo* and can only acquire them via their food sources. Previous studies have shown that  $\delta^{13}\text{C}$  values for essential-AAAs are unchanged with trophic transfer and resemble the  $\delta^{13}\text{C}$  values at the base of food web while the  $\delta^{13}\text{C}$  values of non-essential-AAAs originate from various diet-to-tissue isotopic discrimination and *de novo* synthesis (McMahon et al. 2010; Vokhshoori et al. 2014). A significant temporal decrease was observed in bulk  $\delta^{13}\text{C}$  and the average of essential-AAAs  $\delta^{13}\text{C}$ . Similar but longer term decrease in bulk and  $\delta^{13}\text{C}$ -AA has also been observed in other systems such as the California current (e.g.,  $-1.1\text{‰}$  over 1993–2005, Ruiz-Cooley et al. 2014). Longer time-series of bulk  $\delta^{13}\text{C}$  in bowhead whales from the Western Arctic and in Steller sea lions (*Eumetopias jubatus*) have also shown a significant decrease over several decades ( $-2.7\text{‰}$  over 30 years and  $-2\text{‰}$  over 47 years, respectively) (Schell 2000, Hirons et al. 2001) that have been attributed to a decline in primary productivity. Newsome et al. (2007) found a relatively small but significant long-term decrease in  $\delta^{13}\text{C}$  ( $-1.1\text{‰}$  from 1948 to 2000) in northern fur seal (*Callorhinus ursinus*) that was attributed to an increase in  $\delta^{13}\text{C}$ -depleted atmospheric  $\text{CO}_2$ . Since our time-series is relatively short (7 years), it is difficult to assess the overall ecological significance of the temporal decrease in bowhead whales  $\delta^{13}\text{C}$  values. However, the positive linear relationship between bulk  $\delta^{13}\text{C}$  and essential-AA  $\delta^{13}\text{C}$  values suggest that some of the observed isotopic variation in bowhead whales between years reflects changes in the carbon baseline isotope values (primary producers). While no overall significant linear trend was observed in non-essential-AAAs  $\delta^{13}\text{C}$  values,  $\delta^{13}\text{C}$  decreased by almost 3‰ between 2008 and 2011, which may be related to a temporal change in protein quality/quantity (McMahon et al. 2010; Newsome et al. 2011) or in the energy density of their prey items (Newsome et al. 2014). To the best of our knowledge, there are currently no  $\delta^{13}\text{C}$  essential-AAAs data available in primary producers from Disko Bay or from neighboring areas (e.g., Baffin Bay, Davis Strait). The  $\delta^{13}\text{C}$  decrease that we observed in bulk samples ( $\sim 1\text{‰}$ ) and in essential-AAAs ( $\sim 1.4\text{‰}$ ) over this time-series is too large to be attributed to the surface ocean Suess effect which is around  $-0.1$  to  $-0.2\text{‰}$  per decade in the subpolar oceans (Sonnerup et al. 1999; Tanaka et al.

2003). Lower  $\delta^{13}\text{C}$  in primary producers can be attributed to colder sea surface temperatures, which enhance the solubility of  $\text{CO}_2$  and change the rate of carbon fixation (Rau et al. 1989). The amount of sea ice cover along the coast of West Greenland limits the availability of satellite-derived data for ocean temperature and the monitoring program in Disko Bay only sampled at the *Fast Station* once a month and/or depending on ice conditions. Despite the limited amount of sea surface temperature data that were available from Disko Bay, we did not observe any significant changes in ocean temperature (no cooling or warming trend) in early spring and no significant correlations were found between  $\delta^{13}\text{C}$  with either sea surface temperature or sea ice area.  $\delta^{13}\text{C}$  values are also influenced by plankton species composition and plankton cell size (Goericke et al. 1994). However, there was no assessment of the types of primary producers contributing to the production in Disko Bay during that time period. Lower  $\delta^{13}\text{C}$  values over time can be linked to a change in phytoplankton cell growth rate that could be interpreted as a decline in the photosynthetic rate and decrease in primary production in recent years (Laws et al. 1995; Burkhardt et al. 1999). Additionally, decreasing  $\delta^{13}\text{C}$  values over time could also, in part, be attributed to the increased contribution of meltwater and associated input of terrestrial OM via glacial/surface runoff from the Jakobshavn Isbræ glacier to Disko Bay in recent years (Holland et al. 2008; Gladish et al. 2015).

The factors that affect bulk  $\delta^{13}\text{C}$  and  $\delta^{13}\text{C}$ -AA patterns are distinct. Patterns of  $\delta^{13}\text{C}$ -AA are largely determined by the main metabolic pathways of AAAs of an animal rather than variation in environmental parameters and other factors affecting bulk  $\delta^{13}\text{C}$  (Larsen et al. 2013). Results from previous AA stable isotope fingerprinting studies indicated that  $\delta^{13}\text{C}$  patterns in essential-AAAs are largely conserved across environmental gradients and are representative of the biosynthetic origin of the dominant primary producers in the system, reflecting the value of the dietary sources when measured in a consumer (Larsen et al. 2009, 2013). However, more research is needed in arctic marine systems in terms of the characterization of the AAAs synthesized by a wide range of primary producers, including ice algae, in order to better understand the underlying cause of the  $\delta^{13}\text{C}$  decline and distinguish between ice and pelagic primary production sources.

### Trophic position

The similarity in bowhead whale's trophic position as indicated by the difference in  $\delta^{15}\text{N}$  values of Glu (trophic-AA) relative to Phe (source-AA) indicates that there have been no changes in the trophic ecology of bowhead whales and that no trophic perturbation within the system of Disko Bay has transferred to bowhead whales during that period

of time despite West Greenland being one of the strongest warming regions globally over the past 10 years (Rignot et al. 2011; Hanna et al. 2012; Laidre et al. 2015). Using the equation by Post (2002) that utilizes bulk  $\delta^{15}\text{N}$  values provided trophic position (TP) estimates of about 3.5 with little to no change between years. This TP value is higher compared to those of other planktivorous cetacean species and should be around 3.15 for bowhead whales according to previous studies using stomach content data from the Bering-Chukchi-Beaufort (BCB) bowhead whale population (Pauly et al. 1998). Bowhead whales from the BCB population consume large amount of pelagic zooplankton and epibenthic preys such as copepods, euphausiids, mysids, and other invertebrates (Lowry et al. 2004). A similar diet composed of a mixed of herbivorous, omnivorous, and carnivorous zooplankton prey species is also observed in summer in the Canadian Arctic for the EC-WG bowhead whale population (Pomerleau et al. 2011a, b, 2012). However, the expected TP of bowhead whales from our study should be closer to 3 given that stomach content data from Disko Bay indicated that they feed almost exclusively (>99%) on the large and lipid-rich herbivorous copepod species *C. hyperboreus* (>3 mm) in late winter and early spring (Heide-Jørgensen et al. 2012). Although this bulk  $\delta^{15}\text{N}$  method of calculation has been applied to produce TP estimates in a wide range of species, it has several limiting factors including the need to use appropriate species-specific TDF and prey  $\delta^{15}\text{N}$  value (Post et al. 2007).

The TP of bowhead whales calculated using the difference in  $\delta^{15}\text{N}$  values of the most reliable trophic-AA ( $\delta^{15}\text{N}$  Glu) and the most reliable source-AA ( $\delta^{15}\text{N}$  Phe) as presented by Chikaraishi et al. (2009) yielded a lower TP value (2.4) than the one using bulk  $\delta^{15}\text{N}$  in the equation by Post (2002). The equation by Chikaraishi et al. (2009) takes into account the isotopic difference between the trophic- and source-AAs in primary producers (McClelland and Montoya 2002) and the inter-trophic enrichment factor between a trophic- and source-AA ( $\sim 7.6\text{‰}$ ) which is the typical literature value used for plankton and other lower trophic level species (Chikaraishi et al. 2009). A TP estimate of 2.4 is too low for bowhead whales and closer to that of their main prey *Calanus* spp. Several studies have concluded that this equation tends to produce lower than expected TP estimates for upper trophic level consumers and that a lower TDF should be used for higher trophic level species (Dale et al. 2011; Choy et al. 2012). In their large meta-analysis of TP estimate from AAs, Nielsen et al. (2015b) found that applying an incorrect TDF produced a wrong TP estimate.

Germain et al. (2013) recently proposed another approach to calculate TP in secondary consumer using a dual-TDF equation. This equation is derived from a

controlled feeding study on harbor seal and takes into account two trophic transfers and assume a significant change in mode of nitrogen excretion, diet quality (protein), or both (Hoen et al. 2014; Nielsen et al. 2015a, b). This method yielded a more realistic TP estimate, closer to 3, compared to the two other equations. Like the harbor seal, bowhead whales are urea producers, which tend to result in lower TDF values compared to ammonium producers (Choy et al. 2012; Nielsen et al. 2015b). These results highlight the potential of CSIA-AA in trophic ecological studies to predict the TP of an organism but also the need to conduct further marine mammal control feeding studies to determine more appropriate marine mammal specific TDF. Nevertheless, our results indicate that the TP of bowhead whales were stable over time regardless of the method of calculation and that using the  $\delta^{15}\text{N}$  of individual source (Phe) and trophic (Glu) AAs in a dual-TDF equation allowed us to reconstruct the variability in TP estimates of bowhead whales and tracked it over time.

Between 1979 and 2013, the length of ice-free season has increased by more than two months in the Disko Bay area, together with increasing mean annual air temperatures in the order of 0.4 °C per year (Laidre et al. 2015). Despite the large interannual changes in sea ice cover during our time-series, the lower trophic structure of Disko Bay as indicated by  $\delta^{15}\text{N}$  in AAs of bowhead whales remained largely unaffected. Continued and sustained warming is expected in Arctic regions and will likely result in further decline of sea ice extent with potential cascading effects on the timing, duration, and spatial extent of the spring algal bloom and the community composition of *Calanus* spp. in Disko Bay (Swailethorp et al. 2011). In the context of climate change, continued monitoring using advanced methodologies such as CSIA-AA in higher trophic level species such as the bowhead whale appears essential in detecting changes at the species and ecosystem levels.

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