



Limited effects of changing prey fish communities on food quality for aquatic predators in the eastern Canadian Arctic in terms of essential fatty acids, methylmercury and selenium

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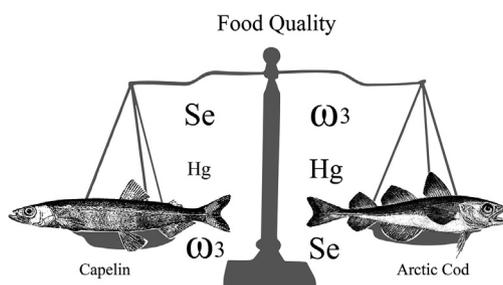
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HIGHLIGHTS

- Essential fatty acids, Se levels and Se:Hg ratios in Arctic vs boreal prey fish.
- Boreal capelin and sand lance had similar EPA + DHA, ω 3, and PUFA levels to Arctic cod.
- Higher Se levels in sand lance compared to other fish and invertebrates.
- Higher Se:Hg molar ratios in sand lance and capelin compared to Arctic cod.
- Overall similar nutritional quality in capelin and sand lance compared to cod.

GRAPHICAL ABSTRACT



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ABSTRACT

We determined concentrations of eicosapentaenoic and docosahexaenoic acids (EPA + DHA), Σ omega-3, polyunsaturated fatty acids (Σ PUFA), selenium, methylmercury, and selenium:methylmercury (Se:Hg) ratios in native and northward-redistributing sub-Arctic marine fish and invertebrates from low, mid-, and high Canadian Arctic latitudes. There was no clear latitudinal trend in nutrient or contaminant concentrations. Among species, EPA + DHA concentrations in native Arctic cod (*Boreogadus saida*) were similar to concentrations in sub-Arctic capelin (*Mallotus villosus*) and sand lance (*Ammodytes* spp.) (444–658 mg.100 g⁻¹), and higher than in most other species. Concentrations of EPA + DHA were related to lipid content, but to a greater extent for higher trophic position species ($R^2 = 0.83$) than for species at lower trophic positions ($R^2 = 0.61$). Selenium concentrations were higher in sand lance ($1.15 \pm 0.16 \mu\text{g g}^{-1}$) than in all other species (0.30–0.69 $\mu\text{g g}^{-1}$), which was significantly, but weakly,

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Species differences

explained by more pelagic feeding in sand lance. Methylmercury concentrations were similar (and Se:Hg ratios were higher) in capelin, sand lance, and Arctic cod ($0.01\text{--}0.03\ \mu\text{g g}^{-1}$ wet weight (ww)) and lower than in other prey ($0.12\text{--}0.26\ \mu\text{g g}^{-1}$ ww), which was significantly explained by the smaller size of these species and more pelagic feeding habits than other fish. These results suggested that a shift in prey fish composition from Arctic cod to capelin and/or sand lance is unlikely to reduce the food quality of the prey available to marine predators at least with respect to concentrations of essential fatty acids, selenium, and Se:Hg ratios.

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1. Introduction

Climate change is driving changes in the distribution and abundance of marine species across the globe (Pecl et al., 2017). In northern marine systems, where sea temperature rise and sea ice loss are double the global average, the rate of shifts in habitat range may average up to four times faster than in other oceans (Fossheim et al., 2015; Laidre et al., 2015). As the summer sea ice extent continues to decrease, sub-Arctic prey species are moving into Arctic regions (Higdon et al., 2014; Fossheim et al., 2015). Yet, little is known about the effects of these movements on food quality for Arctic marine predators eating this new prey.

The occurrence of capelin (*Mallotus villosus*) in Canadian Arctic waters is a primary example of the northward range expansion of sub-Arctic species. The abundance of this migratory sub-Arctic fish appears to have increased in the Canadian Arctic since the 1980s, concurrent with an apparent decrease in the availability of the keystone Arctic prey fish, Arctic cod (*Boreogadus saida*) (Provencher et al., 2012; Chambellant et al., 2013). This change in species occurrence and abundance has led to a shift in major prey consumed by Arctic predators, from Arctic cod to capelin and/or other available fish, including sand lance (*Ammodytes* spp.). This shift in prey consumption has occurred in low to mid-latitude regions of the eastern Canadian Arctic, including Hudson Bay and Cumberland Sound (Gaston et al., 2003; Marcoux et al., 2012; Provencher et al., 2012; Chambellant et al., 2013; Gaston and Elliott, 2014; Yurkowski et al., 2016b). In high Arctic regions, such as Lancaster Sound, where summer sea ice reductions are 10–30% lower compared to lower regions (Comiso et al., 2008), Arctic cod is still the predominant prey in seabird and marine mammal diets (Matley et al., 2012, 2013; Provencher et al., 2012; Yurkowski et al., 2016b; a).

Changes in the composition of Arctic prey fish communities may lead to bottom-up effects on Arctic predators, through changes in food quality (e.g. nutrient and contaminant levels) of the modified prey base. For instance, organic contaminants, including polychlorinated biphenyls, were reported to be up to two times higher in capelin compared to Arctic cod, particularly proportions of less volatile contaminants (Pedro et al., 2017). Thus, capelin could be carrying contaminants into Arctic marine food webs during seasonal migrations, especially the less volatile contaminants, which tend to be found at higher levels at lower latitudes (McKinney et al., 2012; Morris et al., 2016; Pedro et al., 2017, although see Braune et al., 2014). In terms of nutrient content of Arctic cod relative to its 'replacement' species, much less is known. Arctic organisms tend to store large amounts of energy-rich lipids, such as long-chain polyunsaturated fatty acids, to survive periods of reduced food availability in the winter. Conversely, sub-Arctic organisms, which can feed more continuously, do not typically have such a requirement (Kattner et al., 2007). Arctic cod is thought to be one of the most energy-rich prey species in the Arctic (Harter et al., 2013). Moreover, it has been estimated that capelin and sand lance have a

lower energy content than Arctic cod on a per fish basis ($21.2\ \text{kJ g}^{-1}$ dry weight (dw) and $20.1\ \text{kJ g}^{-1}$ dw, respectively relative to $24.2\ \text{kJ g}^{-1}$ dw in Arctic cod; Weslawski et al., 1994; Hop and Gjøsæter 2013).

Marine fish are important dietary sources of nutrients such as essential fatty acids and selenium (Laird et al., 2013; Tocher, 2017). Long-chain polyunsaturated *omega*-3 fatty acids, including eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) play an important role in development and structure of cell membranes (Swanson et al., 2012; Tocher, 2017). Because most aquatic animals are not capable of synthesizing EPA and DHA to any significant extent, these are often considered to be essential fatty acids (Tocher, 2017). Selenium plays a key role in various enzymes, and selenoproteins (e.g. glutathione peroxidase and selenoprotein P) can bind to methylmercury, possibly acting to reduce its bioavailability in organisms (Khan and Wang, 2009; Ralston and Raymond, 2010). Mercury is a non-essential metal and its most toxic form, methylmercury, can bioaccumulate and biomagnify in food webs, exposing top predators to higher risks of neurodevelopmental and other toxicological effects (Dietz et al., 2013; Desforges et al., 2016). Although the exact mechanisms by which selenium interacts with methylmercury are not fully understood, measuring both selenium and methylmercury levels is important to evaluate potential toxicity of both, as selenium can also be toxic above certain levels (Lemly, 2002; Ralston and Raymond, 2010; Burger et al., 2013). Currently, there are only a few studies reporting levels of essential fatty acids in prey fish and invertebrates, and none on Arctic marine fish to our knowledge. More information on essential fatty acids and selenium levels in the Arctic prey base, as well as the intrinsic and extrinsic factors that shape variation among species, is needed to evaluate the possible mechanisms by which prey fish redistribution may influence the fitness and health of marine mammals, predatory fish and seabirds within Arctic marine food webs.

To address this knowledge gap on the effects of a shift in prey composition on Arctic predators, we previously evaluated the levels of various organic contaminants and total mercury in eight important native prey species, and two sub-Arctic fish, in the eastern Canadian Arctic (Pedro et al., 2017). In the current study, we quantify important aspects of the food quality of these previously analyzed species by comparing their 1) concentrations of EPA + DHA, total polyunsaturated fatty acids (ΣPUFA), and Σomega -3s; 2) concentrations of selenium; 3) selenium to methylmercury ratios; and 4) evaluate the intrinsic (fish weight and length) and extrinsic factors (fish trophic position and carbon source, as indicated by nitrogen and carbon stable isotope ratios, respectively) shaping the nutritional composition among and within species. We further examined the relationships among nutrients and methylmercury, as the health benefits of eating fish have been suggested to outweigh the potential risks posed by methylmercury exposure (Laird et al., 2013). Comparisons of food quality are primarily focused on Arctic cod and its 'replacement' species, capelin and sand lance. Coupled with previously reported results on

contaminant levels, the overall aim is to provide a more holistic understanding of the potential implications of climate-induced redistributions of prey species on the health of Arctic marine predators.

2. Material and methods

2.1. Sampling

A total of 125 prey fish and invertebrate samples were collected at three locations in the Canadian Arctic ranging from low to high latitudes, near Arviat (low Arctic, 61° N, 94° W), Clyde River (mid-Arctic, 70° N, 69° W), and Resolute Bay (high Arctic, 75° N, 95° W), Nunavut, Canada (Fig. 1; Table S1; adapted from Pedro et al., 2017). All sampling occurred during the summer between 2012 and 2014. As described in Pedro et al. (2017), fish species important as food sources for Arctic predators were collected near Arviat, including capelin ($n = 11$), sand lance ($n = 13$), sculpin (*Myoxocephalus* spp., $n = 10$) and amphipods (*Gammarus oceanicus*, 1 pool); near Clyde River prey collected included Arctic cod ($n = 20$), sculpin (*Cottuncullus microps*, $n = 10$), northern shrimp (*Pandalus borealis*; $n = 10$) and amphipods (*Themisto libellula*, 1 pool); and near Resolute Bay prey collected included Arctic cod ($n = 20$), amphipods (*Gammarus setosus*, 2 pools) and sculpin (*Myoxocephalus* spp., $n = 10$). Additionally, anadromous cisco (*Coregonus artedii*, $n = 5$) (Morin et al., 1981) and Greenland cod (*Gadus ogac*, $n = 10$) were collected near Arviat and were included in this study to have a better representation of the food web. We were unable to collect samples of all target species at each location despite repeated attempts across multiple field seasons. Following sampling and shipment to the

laboratory, all samples were kept at -80°C until the time of analyses. Fish and shrimp muscle tissues, and whole amphipods, were homogenized prior to chemical analysis.

2.2. Fatty acids analysis

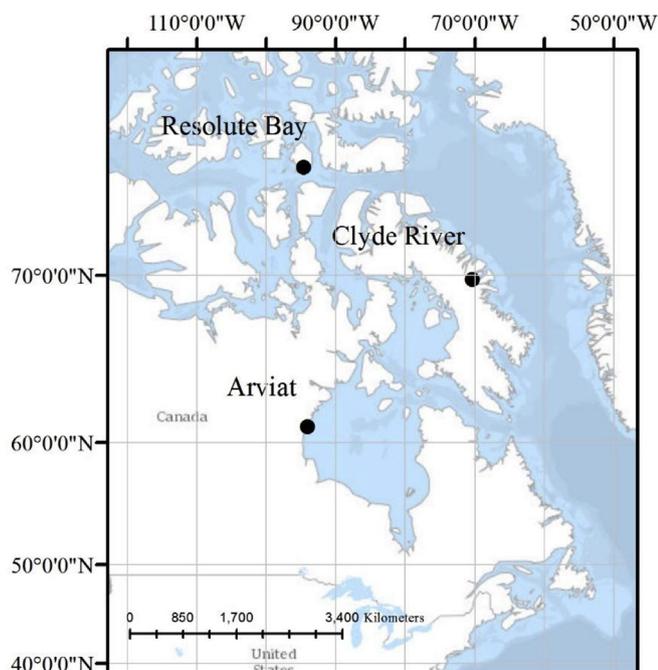
Fatty acid analysis was performed in the McKinney Lab at the Center for Environmental Sciences and Engineering (CESE) in the University of Connecticut (Storrs, CT, USA). The fatty acid extraction method used was modified from Folch et al. (1957). Lipid was extracted from 1.5 g subsamples of homogenized tissue using a solution of 2:1 chloroform:methanol containing 0.01% butylated hydroxytoluene (BHT; v/v/w) to inhibit oxidation, with 0.88% sodium chloride in deionized water, and then filtered through with anhydrous sodium sulfate. After evaporation under nitrogen, lipid content was determined gravimetrically. Fatty acids were *trans*-esterified to their fatty acid methyl ester (FAME) analogues using 0.5 N sulfuric acid in methanol on a heat block at 100°C for 1 h. Subsequently, the fatty acid methyl esters were isolated, brought to a final volume of 50 mg mL^{-1} and analyzed on a Perkin Elmer Clarus[®] 580 gas chromatograph with a flame ionization detector (GC-FID) on a DB-23 column (30 m, 0.25 mm internal diameter, 0.25 μm film thickness; Agilent Technologies, Palo Alto, CA, USA). A total of 69 individual saturated fatty acids (SFA), monounsaturated fatty acids (MUFA), and PUFA, were quantified. Fatty acids were quantified as mass percent (%) of total fatty acid methyl esters (FAME). The nomenclature used was A:BnX, for which A indicates carbon chain length, B indicates the number of double bonds, and X indicates the position of the first double bond counting from the methyl end (n) of the carbon chain.

Quality control included the analysis of instrumental blanks, as well as analysis of a FAME standard mixture (GLC-68B, Nu-Chek Prep, Inc., Elysian, MN, USA) run with each batch of samples. Duplicate fish and invertebrate samples were also extracted and analyzed for all samples for which sufficient mass was available (41%). Accuracy was reported as relative error of our repeated measurement of GLC-68B ($n = 6$) from the documented values, and the averages were within $4.6 \pm 0.4\%$. The limit of quantification, calculated as 10 times the signal to noise ratio, was 0.1%. The relative percent difference of duplicates for EPA + DHA, $\Sigma\text{omega-3}$ and ΣPUFA ranged between 0 and 18%, 1 and 29%, and 2 and 25%, respectively.

2.3. Methylmercury analysis

Methylmercury analysis was performed in the Metals Laboratory at CESE. Aliquots of homogenized wet tissue (0.07–0.10 g) were digested with a 25% potassium hydroxide in methanol solution at 70°C for 3 h. The digested samples were subject to distillation, aqueous ethylation, purge and trap in 1:2:1 sample:sodium acetate:sodium tetraethyl borate, and then methylmercury was quantified using cold-vapor atomic fluorescence spectroscopy (adapted from EPA 1630; Environmental Protection Agency, 1998a).

A calibration curve was run with each batch using a methylmercury stock solution at 5, 10, 25, 100 and 500 ng mL^{-1} . Calibration blanks were analyzed every ten samples. The standard reference material NIST 1946 (NIST, Lake Superior fish tissue), laboratory control samples, duplicates, and preparation blanks were run with every batch of 20 samples. Moisture content of these samples was determined and described previously (Pedro et al., 2017). Recoveries of the standard reference material NIST 1946 ($n = 15$) averaged $94 \pm 11\%$. All blanks were below the limit of detection of $0.006\text{ }\mu\text{g g}^{-1}$. The relative percent difference of duplicate samples was between 7 and 12%, and the recoveries of matrix spikes averaged 84% (range: 53–110%).



Service Layer Credits: USGS The National Map: National Boundaries Dataset, National Elevation Dataset, Geographic Names Information System, National Hydrography Dataset, National Land Cover Database, National Structures Dataset, and National Transportation Dataset; U.S. Census Bureau - TIGER/Line; HERE Road Data. Data Refreshed July, 2017.

Fig. 1. Map showing the three latitudinal sampling locations of prey fish and invertebrate species collected from 2012 to 2014 in the eastern Canadian Arctic Territory of Nunavut. The community of Arviat represents the low Arctic, Clyde River the mid-Arctic, and Resolute Bay the high Arctic.

2.4. Selenium analysis

Selenium analysis was performed in the Metals Laboratory at CESE. Subsamples of 0.5 g of homogenized tissues were digested in capped polypropylene tubes with 5 mL of concentrated trace metal-grade nitric acid in a hot block for 4 h at 95 °C. After cooling down, 2 mL of deionized water and 3 mL of trace metal-grade hydrogen peroxide were added to the samples, which were then re-heated until effervescence settled down. At a final volume of 50 mL deionized water, the samples were analyzed on a Perkin Elmer DRC-e inductive coupled plasma mass spectrometer, adapted from the method EPA 6020A (Environmental Protection Agency, 1998b).

Calibration blanks were run every ten samples, and duplicates, method blanks, post-digestion spiked samples, laboratory control samples, and standard reference materials DORM-3 (NRCC, fish protein) and DOLT-4 (NRCC, dog-fish liver) were analyzed with every batch of 20 samples. The recoveries for the standard reference materials were $117 \pm 8\%$ for DORM-3 ($n = 5$) and $102 \pm 5\%$ for DOLT-4 ($n = 5$). All blanks analyzed were below the detection limit of $0.028 \mu\text{g g}^{-1}$. The recoveries of matrix spikes ranged from 98 to 104%, and the relative percent difference of duplicate samples was between 4 and 37%.

2.5. Selenium:methylmercury molar ratios

The selenium:methylmercury (Se:Hg) ratios were calculated based on selenium and methylmercury concentrations and their molecular weights, following the equation below (Looi et al., 2016):

$$\frac{[\text{Se}] \text{g kg}^{-1}}{78.90 \text{ g mol}^{-1}} \cdot \frac{[\text{MeHg}] \text{g kg}^{-1}}{215.59 \text{ g mol}^{-1}}$$

Ratios above 1 are considered to indicate no effect of methylmercury toxicity (Ralston and Raymond, 2010).

2.6. Stable isotopes analysis

Analyses of nitrogen and carbon stable isotopes for the fish and invertebrates in this study were previously described and reported in Pedro et al. (2017). Briefly, after lipid extraction an aliquot of 400–600 μg was combusted in an elemental analyzer and isotope ratios were quantified using a coupled Delta V Advantage isotope ratio mass spectrometer (Thermo Scientific, Waltham, MA, USA) at the Chemical Tracers Laboratory, University of Windsor (Windsor, ON, Canada). Reference materials NIST-1577c, internal laboratory standard (tilapia muscle), USGS 40, and urea were run with every batch. Instrumental accuracy was tested based on repeated runs of NIST 8573, 8547, and 8574 for $\delta^{15}\text{N}$ and 8542, 8573, and 8574 for $\delta^{13}\text{C}$. The results for USGS 40 ($n = 7$) averaged 0.04‰ for $\delta^{15}\text{N}$ and 0.07‰ for $\delta^{13}\text{C}$ within the reference values (calculated as relative error). Instrumental accuracies of NIST-8573, 8547 and 8574 were within 0.07, 0.14, and 0.19‰ for $\delta^{15}\text{N}$, respectively and NIST-8542, 8573, and 8574 were within 0.04, 0.06, and 0.07‰ for $\delta^{13}\text{C}$, respectively.

The $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values were used to calculate trophic position (TP) and relative carbon sources, respectively, as detailed in Pedro et al. (2017). Briefly, TPs were calculated relative to amphipods per region, assuming a trophic position of 2.5 for gammarids and *Themisto* spp. (Fisk et al., 2003; Foster et al., 2012; Clayden et al., 2015) and a constant trophic enrichment factor of 3.8‰ (Hobson and Welch, 1992):

$$\text{TP} = 2.5 + \left(\delta^{15}\text{N}_{\text{fish or shrimp}} - \delta^{15}\text{N}_{\text{amphipod}} \right) / 3.8\text{‰}$$

Carbon source was calculated relative to sculpin, given the predominant benthic feeding habits of Cottidae (Giraldo et al., 2016). More pelagic feeding habits are indicated by a carbon source >1 , while more benthic feeding habits are <1 (modified from Fisk et al., 2003):

$$\text{Relative carbon source} = \delta^{13}\text{C}_{\text{fish or shrimp}} / \delta^{13}\text{C}_{\text{sculpin}}$$

2.7. Statistical analysis

Prior to analysis, concentrations of EPA + DHA, $\Sigma\text{omega-3}$ and ΣPUFA (all calculated as mg of fatty acid per 100 g of sample), as well as selenium concentrations ($\mu\text{g g}^{-1}$) and Se:Hg ratios, were tested for normality. In general, fatty acids followed normal distributions, whereas selenium concentrations and Se:Hg ratios were log-transformed to meet normality requirements of linear models. The results were inspected for outliers and one extreme value for lipid content was removed, based on a cut-off for Cook's distances of three times the average lipid content (Kutner et al., 2005). Amphipods were not included in statistical analysis due to the low sample size. Given that it was not possible to collect all species at each location, we considered species/latitude as a single variable. Hereafter, we refer to this variable just as species to avoid confusion. We used linear models (one-way analysis of variance) to compare concentrations of fatty acids, selenium and Se:Hg ratios among species, with species as the independent variable and fatty acid, selenium concentrations or Se:Hg ratios, as the dependent variable, followed by *post-hoc* Tukey's honestly significant difference tests.

We tested the effects of intrinsic (fish length, weight, and lipid content) and extrinsic factors (fish trophic position, and relative carbon source; Table S2) on variation in nutrient concentrations (essential fatty acids and selenium) and Se:Hg ratios, both among and within species. To test for among species variation we used mixed-effects models. We considered fish length and weight due to potential variation of fatty acids concentrations with these variables associated with dietary changes at different life stages (Pekkoeva et al., 2017). Further, length has previously been shown to be associated with bioaccumulation of total mercury (Pedro et al., 2017). Fatty acids have been previously positively associated with lipid content, as these nutrients are a substantial component of lipids (Kainz et al., 2017). We considered trophic position in the analyses to test for biomagnification of methylmercury, as well as potential transfer of nutrients from lower to upper trophic levels. Carbon source was included to evaluate variation of nutrients and methylmercury concentrations in prey species between pelagic and benthic habitats, as well as to test for different availability of selenium in the marine sediment (Burger et al., 2001; Mehdi et al., 2013). Seasonal variation in methylmercury and fatty acids in aquatic species (Muir et al., 1999; Lau et al., 2012) could be confounding variable, however, our samples were collected in a single season. All the biological and ecological variables were considered to test for variation in concentrations of both nutrients and methylmercury for consistency. The variables followed a normal distribution (or log-transformed normal) when considering all samples together. However, we used a Spearman's rank correlation matrix to test for correlations among variables before inclusion in the mixed effects models, to minimize multicollinearity. Of the intrinsic and extrinsic factors, weight and length were significantly correlated ($R_s = 0.91$, $p < 0.001$). Length, and not weight, was included in the models due to the previously reported relationship with total mercury (Pedro et al., 2017). Trophic position and lipid content were also significantly correlated ($R_s = -0.54$, $p < 0.001$); however,

these variables did not show multicollinearity in the models, as indicated by variance inflation factors lower than a cut-off of two. A step-wise model selection was performed for EPA + DHA, $\Sigma\omega$ -3, Σ PUFA, selenium, and Se:Hg with lipid content, trophic position, fish length, relative carbon source, as well as first-order interactions as fixed effects, and species as a random effect, within the package *nlme* (Pinheiro et al., 2015). The best relative fit model was evaluated based on the lowest Akaike information criterion for small sample sizes (AICc) within the package *AICcmodgav* (Mazerolle, 2017). The best fit model was inspected for normality of residuals and homoscedasticity. In addition to amphipods, northern shrimp was also not included in the model due to imprecise length measurements. Within-species effects of intrinsic and extrinsic factors were assessed using Kendall–Theil Sen Siegel nonparametric linear regression within the package *mbim* (Komsta, 2013). Results for within-species variation were included in the Supplementary Material (Section 1. Within-species variation; Fig. S1).

We tested for correlations between nutrient and methylmercury concentrations using Spearman's correlations, among and within species. This nonparametric approach was used because the data did not follow a normal distribution and could not be normalized for individual species using standard transformations (e.g. logarithm, square root transformations). All statistical analyses were performed using R software version 3.4.0 (R Core Team, 2013). Statistical significance was considered at $p < 0.05$.

3. Results

3.1. Essential fatty acids in Arctic prey fish and invertebrate species

We found significant differences among species in concentrations of EPA + DHA ($F_{9,102} = 9.3$, $p < 0.001$), $\Sigma\omega$ -3 ($F_{9,102} = 8.9$, $p < 0.001$), and Σ PUFA ($F_{9,102} = 7.2$, $p < 0.001$). The average EPA + DHA concentrations were similar among Arctic cod, capelin, sand lance, and northern shrimp, but appeared to be lower in Greenland cod, while concentrations in sculpin were variable depending on collection location/latitude (Table S3, Fig. 2a). Although not statistically tested, amphipods in the mid-Arctic showed high concentrations of EPA + DHA (Table S3) relative to amphipods in low and high Arctic, a trend similar to that of Greenland cod and other fish. However, comparisons among species are complicated by the fact that not all species could be sampled at the three latitudinal locations. Variation among species for $\Sigma\omega$ -3 and Σ PUFA followed a similar pattern compared to that of EPA + DHA (Table S3, Fig. 2b and c). Capelin, sand lance, and Arctic cod showed the highest concentrations of EPA + DHA, $\Sigma\omega$ -3 and Σ PUFA, but these concentrations were similar among the three species (Tukey's HSD: $p \sim 1.0$; Fig. 2).

Comparing among locations, there were no significant differences in these nutrients between Arctic cod sampled from the mid- and high Arctic (Tukey's HSD: $p > 0.98$), while sculpin from the high Arctic had higher concentrations of EPA + DHA, $\Sigma\omega$ -3, and Σ PUFA than those from the mid-Arctic (Tukey's HSD: $p < 0.01$; Fig. 2).

Results from the linear mixed-models indicated that concentrations of EPA + DHA, $\Sigma\omega$ -3, and Σ PUFA were strongly positively related with fish lipid content among species (Table 1, Fig. 3a), and there was a significant interaction between this variable and trophic position. That is, levels of EPA + DHA, $\Sigma\omega$ -3 and Σ PUFA in all species with trophic positions >3.5 (Greenland cod and sculpin in the low and mid-Arctic, capelin and sand lance) were more strongly predicted by lipid content ($R^2 = 0.83$) compared to species occupying a lower trophic position (Arctic cod,

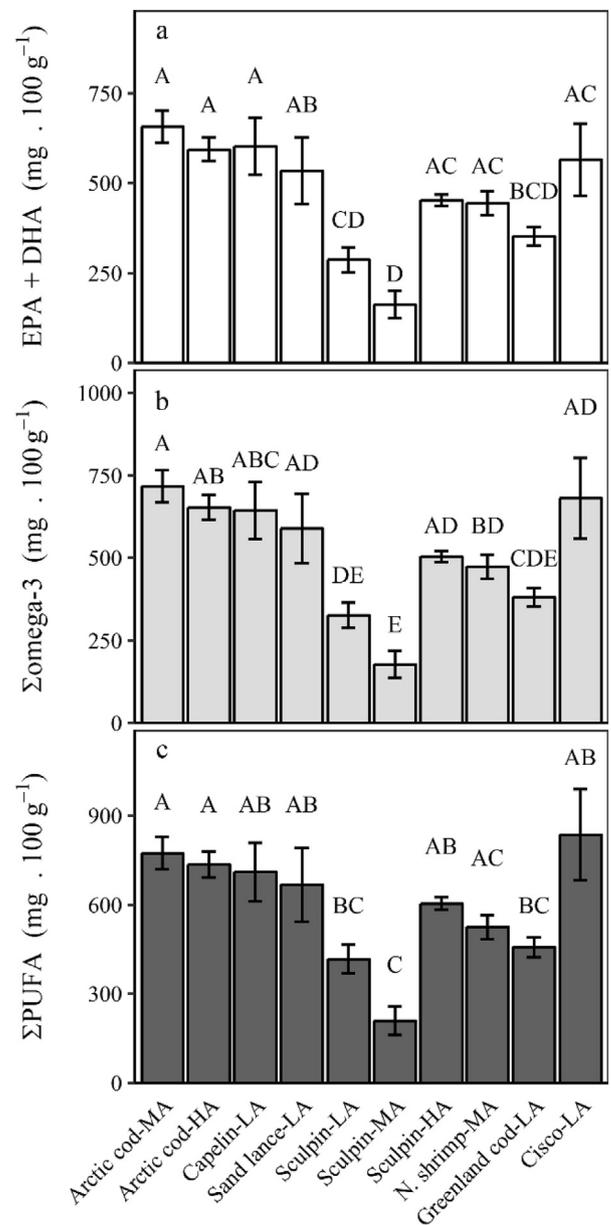


Fig. 2. Average concentrations (\pm SE) of a) EPA + DHA, b) sum (Σ) ω -3 and c) Σ PUFA in muscle of prey fish and whole invertebrate species in the low (LA), mid-(MA) and high (HA) eastern Canadian Arctic from 2012 to 2014. Significant differences among species are indicated by different letters above each bar and were considered at $p < 0.05$.

cisco and sculpin in the high Arctic, $R^2 = 0.61$; Fig. S2). Although not significant, trophic position was also included in the best fitting models as a main effect, with higher trophic level species showing relatively lower concentrations of EPA + DHA, $\Sigma\omega$ -3, or Σ PUFA. Similarly, carbon source, based on $\delta^{13}\text{C}$, its interaction with lipid content, and length did not significantly influence essential fatty acid levels, but these parameters were included in the best fitting models.

Given the strong relationship with lipid content observed, we additionally tested for the relationship of lipid content with the proportions of EPA + DHA, $\Sigma\omega$ -3 and Σ PUFA. The proportions of these fatty acids were negatively related to lipid content ($R^2 = 0.32$; $p < 0.001$), i.e. fish with lower lipid content had higher proportions of the essential fatty acids.

Table 1

Best fit linear mixed effects models of the relationship between EPA + DHA, Σ omega-3 and Σ PUFA ($\text{mg} \cdot 100 \text{g}^{-1}$), log-transformed selenium concentrations (μg^{-1}) and Se:Hg molar ratios, and co-variables lipid content, fish length, trophic position (TP), relative carbon source (C) and interactions of these variables in fish species sampled in Nunavut, Canada from 2012 to 2014. Species were included as random effects ($n = 9$) in all models, with a total of 102 observations. Beta estimates of fixed effects included in the best top model (based on the lowest Akaike information criterion for small sample size (AICc)) are shown and significance was set to $p < 0.05$.

	Fixed effects	Estimates	Random effects	Marginal R^2
EPA + DHA	Lipid	−507***	Species	0.75
	Length	−12.4		
	TP	−68.8		
	C	−76.9		
	Lipid:TP	146***		
Omega-3	Lipid:C	222	Species	0.79
	Lipid	−551***		
	Length	−6.64		
	TP	−84.5		
	C	−83.8		
PUFA	Lipid:TP	159***	Species	0.84
	Lipid:C	251		
	Lipid	−618***		
	Length	0.91		
	TP	−92.4		
Selenium	C	−63.3	Species	0.17
	Lipid:TP	180***		
	Lipid:C	286*		
	Length	0.80***		
	C	−0.55		
Methylmercury ^a	Length	0.80***	Species	0.24
	C	−0.55		
	Length	−0.80***		
Se:Hg ^a	Lipid	0.15**	Species	0.58
	Length	−0.80***		
	C	2.94***		

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

^a Methylmercury and Se:Hg had two top best fit models (within Δ AICc of 2). For MeHg, the second model included only Length (0.82***), with a marginal R^2 of 0.27. For Se:Hg, the second best fit model included C (2.88***), and Length (−0.80***), with a marginal R^2 of 0.51.

3.2. Selenium and Se:Hg ratios in Arctic prey fish and invertebrate species

We found significant variation in concentrations of selenium ($F_{9,105} = 17.7$, $p < 0.001$) and methylmercury ($F_{9,105} = 73.5$, $p < 0.001$), as well as Se:Hg ratios ($F_{9,105} = 61.6$, $p < 0.001$) among species (Fig. 4). Sand lance showed selenium concentrations averaging two or more times higher than most other species (Table S3; Fig. 4a; Tukey's HSD: all $p < 0.001$). Cisco showed the lowest concentrations (Tukey's HSD: all $p < 0.01$, except for $p = 0.39$ compared to Greenland cod and $p = 0.13$ compared to Arctic cod from the mid-Arctic). Additionally, sculpin in the low and mid-Arctic had higher selenium concentrations than Arctic cod in the mid-Arctic and Greenland cod (Tukey's HSD: both $p < 0.01$), and the latter also had lower concentrations compared to Arctic cod in the high Arctic (Tukey's HSD: $p = 0.02$). Selenium concentrations in amphipods were more elevated compared to most species, except for sand lance, although low sample size prevented statistical evaluation (Table S3). It is important to note, however, that ~50% of the sand lance sampled showed these high concentrations, while the remaining individuals showed selenium concentrations within the range of the other species analyzed. Although sand lance was analyzed for selenium in two separate batches, both higher and lower concentrations were found in individuals from both batches, indicating that these differences are biological rather than analytical. As for the fatty acid concentrations, selenium and Se:Hg ratios were higher in capelin, sand lance and Arctic cod compared to all other species analyzed. Selenium concentrations were higher in sand lance compared to Arctic cod (Tukey's HSD: $p < 0.001$), although comparable between capelin and Arctic cod ($p = 0.97$).

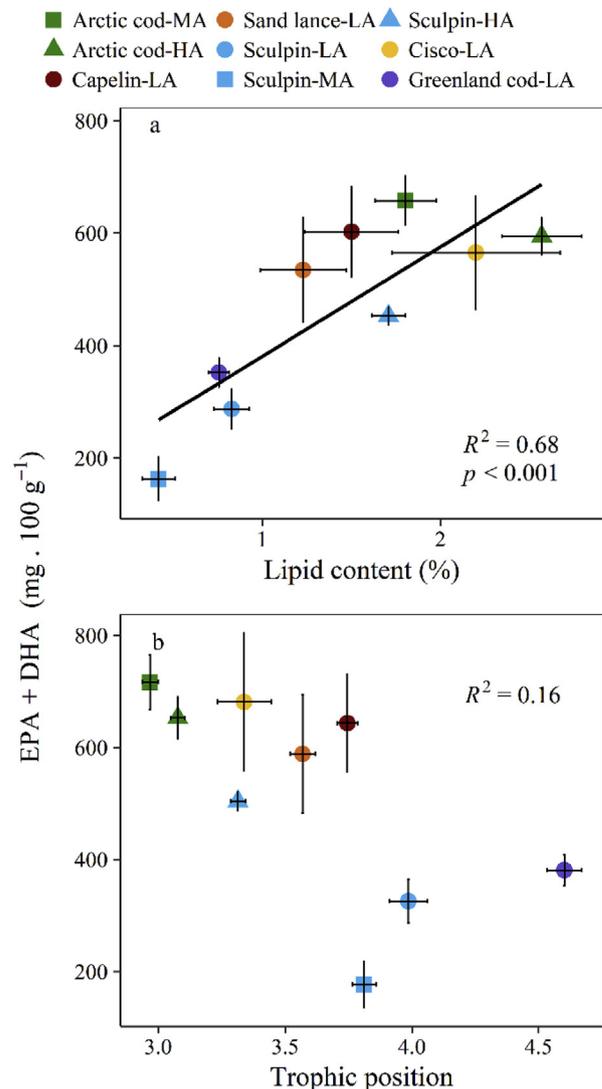


Fig. 3. Relationships of prey fish species' mean (\pm SE) muscle EPA + DHA concentrations to (a) lipid content (%) and (b) trophic position from collections in the low (LA), mid-(MA) and high (HA) eastern Canadian Arctic from 2012 to 2014. Species are represented in different colors while latitudinal locations are represented in different shapes. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Ratios of Se:Hg were two to four times higher in sand lance and capelin compared to Arctic cod ($p < 0.01$), driven in part by lower methylmercury concentrations, at least in capelin ($p < 0.001$). Among regions, selenium concentrations did not vary for sculpin, while Arctic cod from the high Arctic showed higher concentrations compared to cod from the mid-Arctic (Tukey's HSD: $p = 0.01$).

Concentrations of selenium varied significantly with carbon source (Table 1; Fig. 5a), but not with lipid content, fish length, or trophic position. Yet, when sand lance was removed from the analysis, carbon source was no longer significant. This lack of significance indicates that the high concentrations of selenium in some individuals were driving the difference, rather than more general variation between pelagic and benthic species (Fig. S1c).

The Se:Hg ratios were above 1 for all species, averaging 39 in fish and northern shrimp (Table S3; Fig. 4c). Capelin and sand lance showed the highest Se:Hg ratios, with averages two to three times higher than in Arctic cod in the mid- and high Arctic (Tukey's HSD:

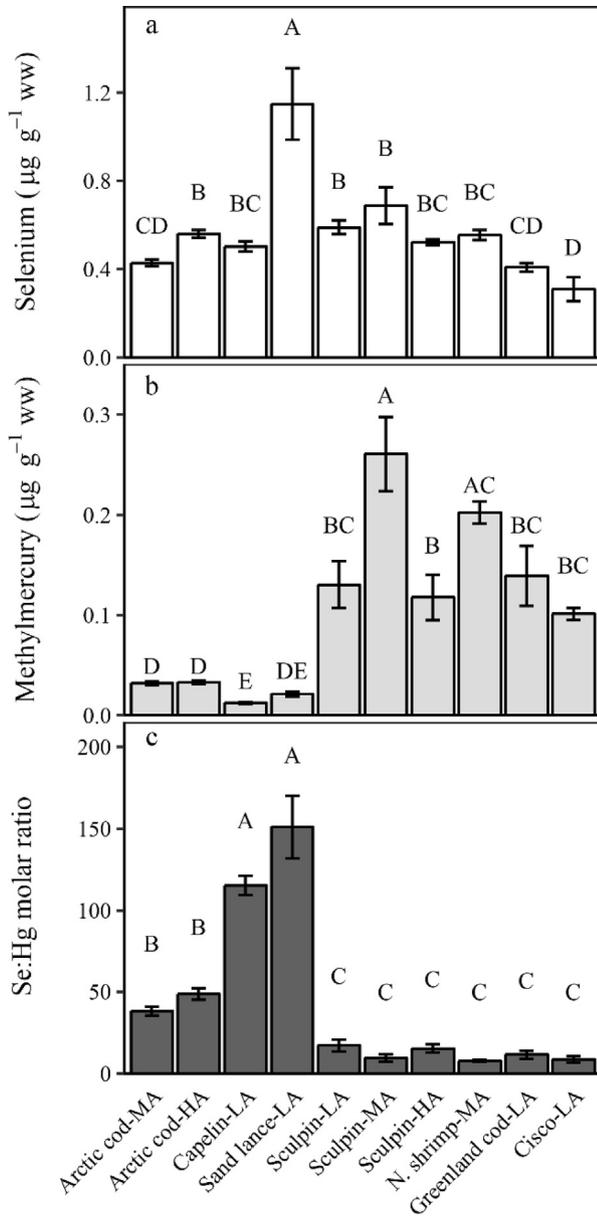


Fig. 4. Average concentrations (\pm SE) of a) selenium; b) methylmercury and ratios of c) Se:Hg in muscle of prey fish and whole invertebrate species in the low (LA), mid-(MA) and high (HA) eastern Canadian Arctic from 2012 to 2014. Significant differences among species are indicated by different letters above each bar and were considered at $p < 0.05$.

$p < 0.001$) and were an order of magnitude higher than sculpin, northern shrimp, Greenland cod, and cisco (Tukey's HSD: all $p < 0.001$). Amphipods showed high Se:Hg ratios, especially in the high Arctic. Ratios of Se:Hg did not differ significantly among locations, at least based on the results for Arctic cod and sculpin (Tukey's HSD: all $p > 0.08$).

The Se:Hg ratios increased with lipid content, fish length and carbon source, i.e., larger, more pelagic fish tended to have greater selenium relative to methylmercury levels than smaller, more benthic fish (Table 1; Fig. 5b and c). Variation in Se:Hg ratios among species may be mostly driven by methylmercury. Similarly to the case for Se:Hg ratios, fish length had a strong effect on methylmercury concentrations among species, while the carbon source effect on selenium concentrations was mostly driven by sand lance.

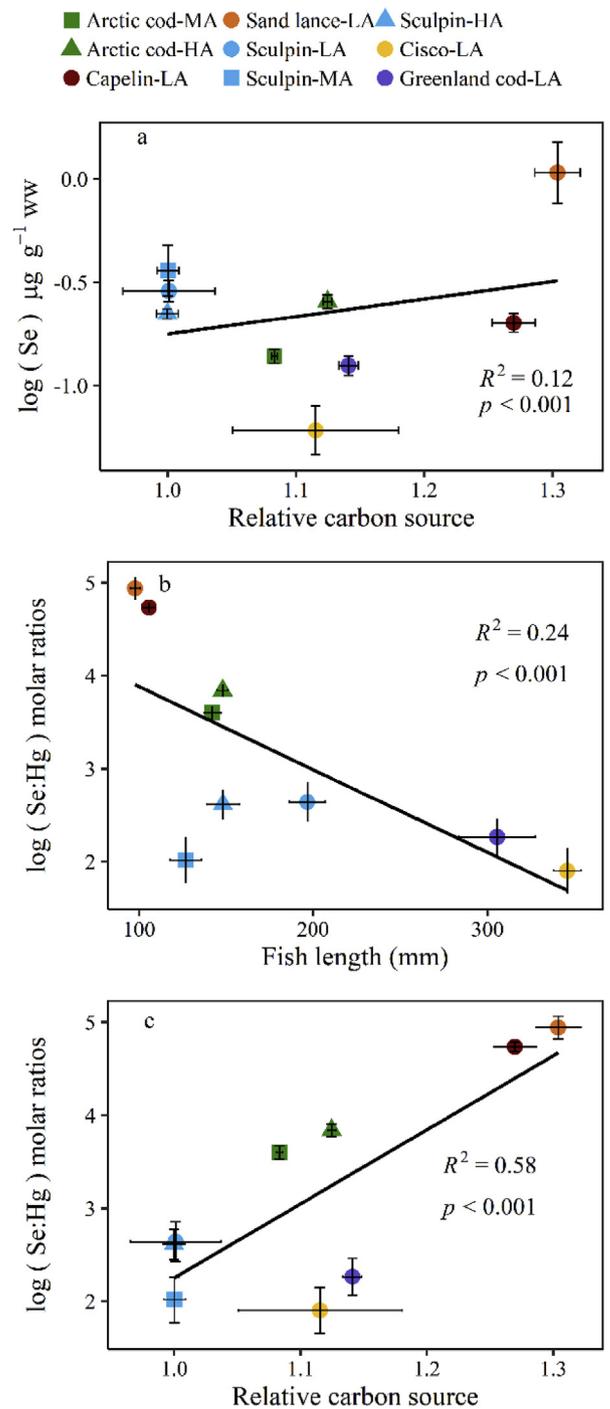


Fig. 5. Relationships of prey fish species' mean (\pm SE) (a) selenium (Se) concentrations to relative carbon source, (b) Se:Hg ratios to fish length (mm) and to (c) relative carbon source, in the low (LA), mid-(MA) and high (HA) eastern Canadian Arctic, from 2012 to 2014. Species are represented in different colors while latitudinal locations are represented in different shapes. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3.3. Correlations between methylmercury and nutrients

Methylmercury concentrations were negatively correlated with concentrations of EPA + DHA ($R_s = -0.51$, $p < 0.001$), $\Sigma\omega$ -3 ($R_s = -0.50$, $p = 0.001$), and Σ PUFA ($R_s = -0.46$, $p = 0.001$) in fish muscle tissues when considering all species together. Conversely, concentrations of selenium and methylmercury (and total mercury)

were not significantly correlated in fish muscle tissues (methylmercury: $R_s = -0.07$, $p = 0.45$; total mercury: $R_s = -0.07$, $p = 0.45$).

4. Discussion

4.1. Essential fatty acids in Arctic prey fish and invertebrate species

Only one previous study measured levels of essential fatty acids in Arctic fish species, which included freshwater fish from three lakes in the Dehcho region, Canadian Arctic (Reyes et al., 2016). Compared to this previous study, marine prey fish here generally had higher concentrations of EPA + DHA, Σ omega-3 and Σ PUFA, except compared to lake trout (*Salvelinus namaycush*; Reyes et al., 2016). Similarly, concentrations of EPA + DHA in freshwater cisco (*Coreoganus clupeaformis*; Reyes et al., 2016) were less than half the levels measured in anadromous cisco collected near Arviat in the current study. In addition to interspecific variation, it is possible that these results relate to variation in fatty acid requirements between marine and freshwater environments (Tocher, 2010). Previous studies have suggested that proper development in marine fish requires dietary intake of long-chain EPA and DHA, while freshwater/diadromous fish can satisfy their nutritional requirements with C_{18} PUFA (Tocher, 2010).

Concentrations of essential fatty acid did not appear to show a clear latitudinal gradient, despite the higher concentrations of EPA + DHA, Σ omega-3, and Σ PUFA measured in sculpin in the high Arctic compared to the mid-Arctic. This variation in fatty acid content between sculpins was likely partially related to variation in lipid content and feeding behavior among the different species of sculpin that were collected (Giraldo et al., 2016), also supported by the inclusion of carbon source in the models (see below). Sculpins are benthic generalist feeders, showing high within and among species variation in diet, which could have influenced concentrations of essential fatty acids (Brewster et al., 2016; Giraldo et al., 2016). Similarly, apparently higher concentrations of essential fatty acids in *Themisto libellula* in the mid-Arctic compared to gammarids in low and high Arctic regions were likely related to variation in diet among species. The predatory amphipod *T. libellula* feeds on lipid-rich calanoid copepods (PUFA of $42.08 \pm 1.74\%$ dw in harpacticoid copepods; Scott et al., 2002; Budge et al., 2008), while gammarids feed on ice algae (PUFA in *Navicula* spp. of $18.48 \pm 5.20\%$ dw; Goecker and Käll, 2003; Budge et al., 2008).

Results from the linear mixed-models supported the importance of lipid content and trophic position in explaining fatty acid concentrations. Similar results were found for a fish community from a subalpine lake in Austria (Kainz et al., 2017), i.e., total lipids predicted Σ PUFA mass fractions for all species studied, but the relationship was stronger for higher trophic level organisms. The strong relationship of lipid content with fatty acid proportions further supports the importance of lipids. Higher proportions of essential fatty acids in fish with lower lipid content could indicate these fish need a larger fraction of their limited lipids as essential fatty acids compared to fatter fish, to meet physiological requirements. In general, higher lipid content and higher proportions of essential fatty acids were found in zooplankton compared to plankton and higher trophic levels, including seabirds and seals (Budge et al., 2008). Previous studies have suggested an increase in PUFAs with trophic position from seston to herbivorous cladocerans and omnivorous copepods (Persson and Vrede, 2006; Budge et al., 2008). This increase in PUFAs may be related to a greater capacity of zooplankton to modify and biosynthesize fatty acids relative to seston, as well as selective retention for storage among taxa (Persson and Vrede, 2006; Budge et al., 2008). Similarly, lower trophic position fish feeding directly on lipid-rich copepods may to some extent be able to adjust and/or modify their PUFA

concentrations, independent of lipid content (Kainz et al., 2017). At upper trophic positions, fatty acid concentrations seemed to be more regulated by dietary sources, as evidenced by the stronger association of these with total lipids for higher trophic level species in this study. A more thorough sampling of the Arctic food-web including a larger number of species spanning all trophic levels is required to further test this hypothesis.

The inclusion of carbon source in the models suggests some level of enrichment in essential fatty acids in more pelagic relative to more benthic organisms. Benthic algae have a lower percentage of long-chain PUFA compared to pelagic algae (Taipale et al., 2013), likely contributing to the higher reserves of essential fatty acids found in pelagic zooplankton relative to benthic organisms (Graeve et al., 1997). Variation among sculpin species may be related to the plasticity in diet characteristic of these genera, i.e., some individuals may include larger proportions of pelagic-derived sources, either through direct or indirect consumption of copepods, in their diet (e.g. amphipods, bivalves; Giraldo et al., 2016).

4.2. Selenium and Se:Hg ratios in Arctic prey fish and invertebrate species

Overall, differences among species were likely related to taxonomic regulation of selenium. For example, the high selenium levels in some sand lance compared to other fish could be due to temporary up-regulation of selenoproteins to meet physiological needs (Ralston and Raymond, 2010). Regardless, selenium concentrations in these species were below those observed to cause teratogenic deformities in other fish and, although there are no advised thresholds for marine predators, selenium concentrations here were below the $8.5 \mu\text{g g}^{-1}$ dw threshold advised for human consumption by the US Environmental Protection Agency (Lemly, 2002; U.S. Environmental Protection Agency, 2016). Selenium is an important structural element in selenoproteins and, once the activity of these proteins is optimized, organisms regulate selenium levels by excreting the excess (Burk and Hill, 2015).

Previous studies reported higher selenium concentrations in Arctic cod in Greenland and Alaska ($\sim 0.8 \mu\text{g g}^{-1}$ ww in liver and 2.99 ± 0.23 ww whole fish, respectively), and shorthorn sculpin (*Myoxocephalus scorpius*) in Greenland ($\sim 1 \mu\text{g g}^{-1}$ ww; Dietz et al., 2000c) compared to our study. This variation, however, is likely due to differences in the tissue analyzed rather than spatial variation. Selenium is generally found at higher concentrations in liver and kidney compared to other tissues in fish and marine mammals (Dietz et al., 2000c; Burger, 2013).

We found limited research investigating the influence of intrinsic and extrinsic factors on organismal selenium concentrations. An Arctic food web study in Greenland that included seabirds and seals, found moderate trophic accumulation of selenium (Dietz et al., 2000b). A lack of significant association of selenium concentrations with trophic position in our study may be partly related to the dataset only including a limited portion of the food web, i.e., invertebrates and prey fish. Alternatively, the non-significant relationship with fish length may indicate that selenium does not bioaccumulate. Together, the results from the models support a taxa-dependent homeostatic regulation of selenium in these Arctic prey fish (Burk and Hill, 2015).

Molar excess of selenium relative to methylmercury, as well as high variation in Se:Hg ratios among species is commonly found in Arctic marine species (Dietz et al., 2000a) and in fish species elsewhere (Burger et al., 2001). Although there is still debate to which Se:Hg ratios are safe, these results suggest that Arctic prey species have enough selenium to prevent methylmercury toxicity and still maintain selenium-dependent metabolic functions (Ralston and Raymond, 2010). The lower Se:Hg ratios in the larger sculpin

from the low Arctic, and in Greenland cod and cisco, may be due to higher uptake of methylmercury and/or bioaccumulation compared to the smaller Arctic cod, capelin, and sand lance, supported by the importance of length in the models. Methylmercury is difficult to excrete and tends to occur at higher levels in older/larger fish due to increased feeding rates and bioaccumulation (Schneider et al., 2000; Sackett et al., 2013; Clayden et al., 2015). In cisco, lower Se:Hg ratios could additionally be related to its anadromous migration. Arctic rivers are major contributors of mercury into Arctic oceans (Emmerton et al., 2013; Zhang et al., 2015). Thus, cisco could pick up higher methylmercury concentrations when migrating upstream for spawning (Morin et al., 1981).

4.3. Correlations between methylmercury and nutrients

Negative correlations among Σ omega-3 and methylmercury were previously found for predatory fish in the Dehcho Region of the Canadian Arctic (Reyes et al., 2016). While it is possible that a biological mechanism drives this association, it is likely that the strong negative correlation between fatty acids and methylmercury is related to the increase in methylmercury concentrations, but a tendency for fatty acid concentrations to decrease (although not significantly), with fish trophic position. Thus, for marine predators, low trophic level fish may represent a food source of better quality, not just in terms of methylmercury contamination, but also considering the potential benefits of fatty acid intake.

We did not observe a correlation between selenium and mercury probably because strong correlations between these molecules are more commonly found in fish and marine mammal liver and kidneys than in muscle (Dietz et al., 2000a; Burger et al., 2013). The most likely mechanism proposed for the binding of mercury and selenium includes the formation of insoluble complexes of methylmercury or inorganic mercury (Hg^{2+}) with selenoproteins ($\text{HgSe}(s)$), which have been found in the liver of several marine mammals and seabirds (Khan and Wang, 2009; Ralston and Raymond, 2010). The formation of $\text{HgSe}(s)$ in liver explains the stronger correlations between the two elements in this tissue compared to muscle (Dietz et al., 2000a). Additionally, correlations have been shown to be stronger in predators, such as predatory fish and marine mammals, given their higher levels of mercury. Woshner et al. (2001) suggested that a 1:1 M ratio may only occur after surpassing a certain mercury threshold needed to activate detoxification processes (suggested at $8\text{--}10\ \mu\text{g g}^{-1}$ dw for different species; Scheuhammer et al., 2015).

4.4. Influence of a changing Arctic food web on the health of marine predators

In sum, capelin, sand lance, and Arctic cod showed similar concentrations of EPA + DHA, Σ omega-3, and Σ PUFA, while selenium concentrations were higher in sand lance compared to Arctic cod and capelin, likely due to physiological needs. Ratios of Se:Hg were higher in sand lance and capelin compared to Arctic cod partly due to lower methylmercury concentrations at least in capelin compared to Arctic cod. Previously, variation in total mercury concentrations (methylmercury \approx total mercury, see Table S3) among these species was found to be influenced by the smaller size and more pelagic feeding habits of capelin compared to Arctic cod (Pedro et al., 2017). In the same study, slightly elevated concentrations of PCBs and some organochlorine contaminants in capelin relative to Arctic cod were also reported (Pedro et al., 2017). Still, based on total mercury results reported by Pedro et al. (2017), and methylmercury and Se:Hg ratios reported in the current study, consumption of these sub-Arctic species relative to Arctic cod, could act to reduce risks posed by mercury exposure to predators.

Such prey consumption shifts also do not appear to be likely to alter the uptake of essential fatty acids. Consequently, our results suggest that the replacement of Arctic cod with capelin and sand lance is unlikely to have substantial effects on the food quality of the prey base for Arctic predators, at least based on tissue concentrations of mercury, legacy organic contaminants, selenium, and essential fatty acids. Regarding human health, shifts in the prey base would only indirectly affect humans since capelin, sand lance and Arctic cod are consumed by ringed seals and belugas, which are important foods for Indigenous populations (Binnington et al., 2016).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2018.09.167>.

References

- Binnington, M.J., Curren, M.S., Chan, H.M., Wania, F., 2016. Balancing the benefits and costs of traditional food substitution by indigenous Arctic women of childbearing age: impacts on persistent organic pollutant, mercury, and nutrient intakes. *Environ. Int.* 94, 554–566. <https://doi.org/10.1016/j.envint.2016.06.016>.
- Braune, B.M., Gaston, A.J., Elliott, K.H., Provencher, J.F., Woo, K.J., Chambellant, M., Ferguson, S.H., Letcher, R.J., 2014. Organohalogen contaminants and total mercury in forage fish preyed upon by thick-billed murres in northern Hudson Bay. *Mar. Pollut. Bull.* 78, 258–266. <https://doi.org/10.1016/j.marpolbul.2013.11.003>.
- Brewster, J.D., Giraldo, C., Swanson, H., Walkusz, W., Loewen, T.N., Reist, J.D., Stern, G.A., Loseto, L.L., 2016. Ecological niche of coastal Beaufort Sea fishes defined by stable isotopes and fatty acids. *Mar. Ecol. Prog. Ser.* 559, 159–173. <https://doi.org/10.3354/meps11887>.
- Budge, S.M., Wooller, A.M.J., Springer, A.A.M., Iverson, A.S.J., McRoy, A.C.P., Divoky, G.J., 2008. Tracing carbon flow in an arctic marine food web using fatty acid-stable isotope analysis. *Oecologia* 157, 117–129. <https://doi.org/10.1007/s00442-008-1053-7>.
- Burger, J., 2013. Temporal trends (1989–2011) in levels of mercury and other heavy metals in feathers of fledgling great egrets nesting in Barnegat Bay, NJ. *Environ. Res.* 122, 11–17. <https://doi.org/10.1016/j.envres.2013.01.003>.
- Burger, J., Gaines, K.F., Boring, C.S., Stephens, W.L., Snodgrass, J., Gochfeld, M., 2001. Mercury and selenium in fish from the Savannah River: species, trophic level, and locational differences. *Environ. Res. Sect. A* 87, 108–118. doi: 10.1006.
- Burger, J., Jeitner, C., Donio, M., Pittfield, T., Gochfeld, M., 2013. Mercury and selenium levels, and selenium:mercury molar ratios of brain, muscle and other tissues in bluefish (*Pomatomus saltatrix*) from New Jersey, USA. *Sci. Total*

- Environ. 443, 278–286. <https://doi.org/10.1016/j.scitotenv.2012.10.040>.
- Burk, R.F., Hill, K.E., 2015. Regulation of selenium metabolism and transport. *Annu. Rev. Nutr.* 35, 109–134. <https://doi.org/10.1146/annurev-nutr-071714-034250>.
- Chambellant, M., Stirling, I., Ferguson, S.H., 2013. Temporal variation in western Hudson Bay ringed seal (*Phoca hispida*) diet in relation to environment. *Mar. Ecol. Prog. Ser.* 481, 269.
- Clayden, M.G., Arsenault, L.M., Kidd, K.A., O'Driscoll, N.J., Mallory, M.L., 2015. Mercury bioaccumulation and biomagnification in a small Arctic polynya ecosystem. *Sci. Total Environ.* 509 (510), 206–215. <https://doi.org/10.1016/j.scitotenv.2014.07.087>.
- Comiso, J.C., Parkinson, C.L., Gersten, R., Stock, L., 2008. Accelerated decline in the Arctic sea ice cover. *Geophys. Res. Lett.* 35, 1–6. <https://doi.org/10.1029/2007GL031972>.
- Desforges, J.-P.W., Sonne, C., Levin, M., Siebert, U., De Guise, S., Dietz, R., 2016. Immunotoxic effects of environmental pollutants in marine mammals. *Environ. Int.* 86, 126–139. <https://doi.org/10.1016/j.envint.2015.10.007>.
- Dietz, R., Riget, F., Born, E.W., 2000a. An assessment of selenium to mercury in Greenland marine animals. *Sci. Total Environ.* 245, 15–24.
- Dietz, R., Riget, F., Cleemann, M., Aarkrog, A., Johansen, P., Hansen, J.C., 2000b. Comparison of contaminants from different trophic levels and ecosystems. *Sci. Total Environ.* 245, 221–231. [https://doi.org/10.1016/S0048-9697\(99\)00447-7](https://doi.org/10.1016/S0048-9697(99)00447-7).
- Dietz, R., Riget, F., Born, E.W., 2000c. Geographical differences of zinc, cadmium, mercury and selenium in polar bears (*Ursus maritimus*) from Greenland. *Sci. Total Environ.* 245, 25–47.
- Dietz, R., Sonne, C., Basu, N., Braune, B., O'Hara, T., Letcher, R.J., Scheuhammer, T., Andersen, M., Andreasen, C., Andriashchik, D., Asmund, G., Aubail, A., Baagaard, H., Born, E.W., Chan, H.M., Derocler, A.E., Grandjean, P., Knott, K., Kirkegaard, M., Krey, A., Lunn, N., Messier, F., Obbard, M., Olsen, M.T., Ostertag, S., Peacock, E., Renzoni, A., Riget, F.F., Skaare, J.U., Stern, G., Stirling, I., Taylor, M., Wiig, Ø., Wilson, S., Aars, J., 2013. What are the toxicological effects of mercury in Arctic biota? *Sci. Total Environ.* 443, 775–790. <https://doi.org/10.1016/j.scitotenv.2012.11.046>.
- Emmerton, C.A., Graydon, J.A., Gareis, J.A.L., St Louis, V.L., Lesack, L.F.W., Banack, J.K.A., Hicks, F., Nafziger, J., 2013. Mercury export to the Arctic ocean from the Mackenzie river, Canada. *Environ. Sci. Technol.* 47, 7644–7654. <https://doi.org/10.1021/es400715r>.
- Environmental Protection Agency, 1998a. Method 1630 Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, vol. 46.
- Environmental Protection Agency, 1998b. Method 6020A Inductively Coupled Plasma-mass Spectrometry, vol. 23.
- Fisk, A.T., Hoekstra, P.F., Gagnon, J.M., Duffe, J., Norstrom, R.J., Hobson, K.A., Kwan, M., Muir, D.C.G., 2003. Influence of habitat, trophic ecology and lipids on, and spatial trends of, organochlorine contaminants in Arctic marine invertebrates. *Mar. Ecol. Prog. Ser.* 262, 201–214. <https://doi.org/10.3354/meps262201>.
- Folch, J., Lees, M., Stanley, G.H.S., 1957. A simple method for the isolation and purification of total lipids from animal tissues. *J. Biol. Chem.* 226, 497–509. <https://doi.org/10.1007/s10858-011-9570-9>.
- Fossheim, M., Primicerio, R., Johannesen, E., Ingvaldsen, R.B., Aschan, M.M., Dolgov, A.V., 2015. Recent warming leads to a rapid borealization of fish communities in the Arctic. *Nature* 5, 673–678. <https://doi.org/10.1038/NCLIMATE2647>.
- Foster, K.L., Stern, G.A., Pazerniuk, M.A., Hickie, B., Walkusz, W., Wang, F., Macdonald, R.W., 2012. Mercury biomagnification in marine zooplankton food webs in Hudson Bay. *Environ. Sci. Technol.* 46, 12952–12959.
- Gaston, A., Elliott, K., 2014. Seabird diet changes in northern Hudson Bay, 1981–2013, reflect the availability of schooling prey. *Mar. Ecol. Prog. Ser.* 513, 211–223. <https://doi.org/10.3354/meps10945>.
- Gaston, A.J., Woo, K., Hipfner, J.M., 2003. Trends in forage fish populations in Northern Hudson Bay since 1981, as determined from the diet of nestling thick-billed murres *Uria lomvia*. *Arctic* 56, 227–233.
- Giraldo, C., Stasko, A., Choy, E.S., Rosenberg, B., Majewski, A., Power, M., Swanson, H., Loseto, L., Reist, J.D., 2016. Trophic variability of Arctic fishes in the Canadian Beaufort Sea: a fatty acids and stable isotopes approach. *Polar Biol.* 39, 1267–1282. <https://doi.org/10.1007/s00300-015-1851-4>.
- Goecker, M.E., Käll, S.E., 2003. Grazing preferences of marine isopods and amphipods on three prominent algal species of the Baltic Sea. *J. Sea Res.* 50, 309–314. <https://doi.org/10.1016/j.seares.2003.04.003>.
- Graeve, M., Kattner, G., Piepenburg, D., 1997. Lipids in arctic benthos: does the fatty acid and alcohol composition reflect feeding and trophic interactions? *Polar Biol.* 18, 53–61. <https://doi.org/10.1007/s0030000051058>.
- Harter, B.B., Elliott, K.H., Divoky, G.J., Davoren, G.K., 2013. Arctic cod (*Boreogadus saida*) as prey: fish length-energetics relationships in the Beaufort Sea and Hudson Bay. *Arctic* 66, 191–196.
- Higdon, J.W., Westdal, K.H., Ferguson, S.H., 2014. Distribution and abundance of killer whales (*Orcinus orca*) in Nunavut, Canada—an Inuit knowledge survey. *J. Mar. Biol. Assoc. U. K.* 94, 1293–1304. <https://doi.org/10.1017/S0025315413000921>.
- Hobson, K.A., Welch, H.E., 1992. Determination of trophic relationships within a high Arctic marine food web using delta-13C and delta-15N analysis. *Mar. Ecol. Prog. Ser.* 84, 9–18. <https://doi.org/10.3354/meps084009>.
- Hop, H., Gjøsaeter, H., 2013. Polar cod (*Boreogadus saida*) and capelin (*Mallotus villosus*) as key species in marine food webs of the Arctic and the Barents Sea. *Mar. Biol. Res.* 9, 878–894. <https://doi.org/10.1080/17451000.2013.775458>.
- Kainz, M.J., Hager, H.H., Rasconi, S., Kahilainen, K.K., Amundsen, P.-A., Hayden, B., 2017. Polyunsaturated fatty acids in fishes increase with total lipids irrespective of feeding sources and trophic position. *Ecosphere* 8, e01753. <https://doi.org/10.1002/ecs2.1753>.
- Kattner, G., Hagen, W., Lee, R.F., Campbell, R., Deibel, D., Falk-Petersen, S., Graeve, M., Hansen, B.W., Hirche, H.J., Jónasdóttir, S.H., Madsen, M.L., Mayzaud, P., Müller-Navarra, D., Nichols, P.D., Paffenhöfer, G.-A., Pond, D., Saito, H., Stübing, D., Virtue, P., 2007. Perspectives on marine zooplankton lipids. *Can. J. Fish. Aquat. Sci.* 64, 1628–1639. <https://doi.org/10.1139/f07-122>.
- Khan, M.A.K., Wang, F., 2009. Mercury-selenium compounds and their toxicological significance: toward a molecular understanding of the mercury-selenium antagonism. *Environ. Toxicol. Chem.* 28, 1567–1577. <https://doi.org/10.1897/08-375.1>.
- Komsta, L., 2013. Mblm: Median-based Linear Models. R Package Version 0.12, p. 6. <https://CRAN.R-project.org/package=mblm>.
- Kutner, M.H., Nachtsheim, C.J., Neter, J., Li, W., 2005. *Applied Linear Statistical Models*, fifth ed. McGraw-Hill Irwin, Boston.
- Laidre, K.L., Stern, H., Kovacs, K.M., Lowry, L., Moore, S.E., Regehr, E.V., Ferguson, S.H., Wiig, Ø., Boveng, P., Angliss, R.P., Born, E.W., Litovka, D., Quakenbush, L., Lydersen, C., Vongraven, D., Ugarte, F., 2015. Arctic marine mammal population status, sea ice habitat loss, and conservation recommendations for the 21st century. *Conserv. Biol.* 29, 724–737. <https://doi.org/10.1111/cobi.12474>.
- Laird, B.D., Goncharov, A.B., Egeland, G.M., Chan, H.M., 2013. Dietary advice on Inuit traditional food use needs to balance benefits and risks of mercury, selenium, and n3 fatty acids. *J. Nutr.* 143, 923–930. <https://doi.org/10.3945/jn.112.173351>.
- Lau, D.C.P., Vrede, T., Pickova, J., Goedkoop, W., 2012. Fatty acid composition of consumers in boreal lakes - variation across species, space and time. *Freshw. Biol.* 57, 24–38. <https://doi.org/10.1111/j.1365-2427.2011.02690.x>.
- Lemly, A.D., 2002. Symptoms and implications of selenium toxicity in fish: the Belews Lake case example. *Aquat. Toxicol.* 57, 39–49.
- Looi, L.J., Aris, A.Z., Haris, H., Yusoff, F.M., Hashim, Z., 2016. The levels of mercury, methylmercury and selenium and the selenium health benefit value in grey-eel catfish (*Plotosus canius*) and giant mudskipper (*Periophthalmodon schlosseri*) from the Strait of Malacca. *Chemosphere* 152, 265–273. <https://doi.org/10.1016/j.chemosphere.2016.02.126>.
- Marcoux, M., McMeans, B.C., Fisk, A.T., Ferguson, S.H., 2012. Composition and temporal variation in the diet of beluga whales, derived from stable isotopes. *Mar. Ecol. Prog. Ser.* 471, 283–291.
- Matley, J.K., Fisk, A.T., Dick, T.A., 2012. Seabird predation on arctic cod during summer in the Canadian arctic. *Mar. Ecol. Prog. Ser.* 450, 219–228. <https://doi.org/10.3354/meps09561>.
- Matley, J.K., Fisk, A.T., Dick, T.A., 2013. The foraging ecology of arctic cod (*Boreogadus saida*) during open water (July–August) in allen Bay, arctic Canada. *Mar. Biol.* 160, 2993–3004. <https://doi.org/10.1007/s00227-013-2289-2>.
- Mazerolle, M.J., 2017. AICcmmodavg: Model Selection and Multimodel Inference Based on (Q)AIC(c). R Package Version 2.1-1. <https://cran.r-project.org/package=AICcmmodavg>.
- McKinney, M.A., McMeans, B.C., Tomy, G.T., Rosenberg, B., Ferguson, S.H., Morris, A., Muir, D.C.G., Fisk, A.T., 2012. Trophic transfer of contaminants in a changing arctic marine food web: Cumberland sound, Nunavut, Canada. *Environ. Sci. Technol.* 46, 9914–9922. <https://doi.org/10.1021/es302761p>.
- Mehdi, Y., Hornick, J.L., Istasse, L., Dufrasne, I., 2013. Selenium in the environment, metabolism and involvement in body functions. *Molecules* 18, 3292–3311. <https://doi.org/10.3390/molecules18033292>.
- Morin, R., Dodson, J.J., Power, G., 1981. The migrations of anadromous cisco (*Coregonus artedii*) and lake whitefish (*Coregonus clupeaformis*) in estuaries of eastern James Bay. *Can. J. Zool.* 59, 1600–1607. <https://doi.org/10.1139/z81-219>.
- Morris, A.D., Muir, D.C.G., Solomon, K.R., Letcher, R.J., McKinney, M.A., Fisk, A.T., McMeans, B.C., Tomy, G.T., Teixeira, C., Wang, X., Duric, M., 2016. Current-use pesticides in seawater and their bioaccumulation in polar bear–ringed seal food chains of the Canadian Arctic. *Environ. Toxicol. Chem.* 35, 1695–1707. <https://doi.org/10.1002/etc.3427>.
- Muir, D., Braune, B., DeMarch, B., Norstrom, R., Wagemann, R., Lockhart, L., Hargrave, B., Bright, D., Addison, R., Payne, J., Reimer, K., 1999. Spatial and temporal trends and effects of contaminants in the Canadian Arctic marine ecosystem: a review. *Sci. Total Environ.* 230, 83–144. [https://doi.org/10.1016/S0048-9697\(99\)00037-6](https://doi.org/10.1016/S0048-9697(99)00037-6).
- Pecl, G.T., Araújo, M.B., Bell, J.D., Blanchard, J., Bonebrake, T.C., Chen, I.-C., Clark, T.D., Colwell, R.K., Danielsen, F., Evengård, B., Falconi, L., Ferrier, S., Frusher, S., Garcia, R.A., Griffis, R.B., Hobday, A.J., Janion-Scheepers, C., Jarzyna, M.A., Jennings, S., Lenoir, J., Linnetved, H.I., Martin, V.Y., McCormack, P.C., McDonald, J., Mitchell, N.J., Mustonen, T., Pandolfi, J.M., Pettolelli, N., Popova, E., Robinson, S.A., Scheffers, B.R., Shaw, J.D., Sorte, C.J.B., Strugnelli, J.M., Sunday, J.M., Tuanmu, M.-N., Vergés, A., Villanueva, C., Wernberg, T., Wapstra, E., Williams, S.E., 2017. Biodiversity redistribution under climate change: impacts on ecosystems and human well-being. *Science* 80. <https://doi.org/10.1126/science.aai9214>.
- Pedro, S., Fisk, A.T., Tomy, G.T., Ferguson, S.H., Hussey, N.E., Kessel, S.T., McKinney, M.A., 2017. Mercury and persistent organic pollutants in native and invading forage species of the Canadian Arctic: consequences for food web dynamics. *Environ. Pollut.* 229, 229–240. <https://doi.org/10.1016/j.envpol.2017.05.085>.
- Pekkoeva, S.N., Murzina, S.A., Nefedova, Z.A., Ripatti, P.O., Falk-Petersen, S., Berge, J., Lonne, O., Nemova, N.N., 2017. Ecological role of lipids and fatty acids in the early postembryonic development of the daubed shanny, *Leptoclinius maculatus* (Fries, 1838) from Kongsfjorden, West Spitsbergen in Winter. *ISSN Russ. J. Ecol.*

- 48, 1067–4136. <https://doi.org/10.1134/S1067413617030134>.
- Persson, J., Vrede, T., 2006. Polyunsaturated fatty acids in zooplankton: variation due to taxonomy and trophic position. *Freshw. Biol.* 51, 887–900. <https://doi.org/10.1111/j.1365-2427.2006.01540.x>.
- Pinheiro, J., Bates, D., DebRoy, S., Sarkar, D., Team, R.C., 2015. nlme: linear and nonlinear mixed effects models. In: R Packag. Version 3.1-120. <http://cran.r-project.org/package=nlme>. (Accessed 25 March 2015).
- Provencher, J.F., Gaston, A.J., O'Hara, P.D., Gilchrist, H.G., 2012. Seabird diet indicates changing Arctic marine communities in eastern Canada. *Mar. Ecol. Prog. Ser.* 454, 171–182. <https://doi.org/10.3354/meps09299>.
- R Core Team, 2013. R: a language and environment for statistical computing. In: R Found. Stat. Comput. http://web.mit.edu/r/r_v3.0.1/fullrefman.pdf.
- Ralston, N.V.C., Raymond, L.J., 2010. Dietary selenium's protective effects against methylmercury toxicity. *Toxicology* 278, 112–123. <https://doi.org/10.1016/j.tox.2010.06.004>.
- Reyes, E.S., Aristizabal Henao, J.J., Kornobis, K.M., Hanning, R.M., Majowicz, S.E., Liber, K., Stark, K.D., Low, G., Swanson, H.K., Laird, B.D., 2016. Associations between omega-3 fatty acids, selenium content, and mercury levels in wild-harvested fish from the Dehcho Region, Northwest Territories, Canada. *J. Toxicol. Environ. Health Part A* 80, 1–14. <https://doi.org/10.1080/15287394.2016.1230916>.
- Sackett, D.K., Cope, W.G., Rice, J.A., Aday, D.D., 2013. The influence of fish length on tissue mercury dynamics: implications for natural resource management and human health risk. *Int. J. Environ. Res. Publ. Health* 10, 638–659. <https://doi.org/10.3390/ijerph10020638>.
- Scheuhammer, A., Braune, B., Chan, H.M., Frouin, H., Krey, A., Letcher, R., Loseto, L., Noël, M., Ostertag, S., Ross, P., Wayland, M., 2015. Recent progress on our understanding of the biological effects of mercury in fish and wildlife in the Canadian Arctic. *Sci. Total Environ.* 509 (510), 91–103. <https://doi.org/10.1016/j.scitotenv.2014.05.142>.
- Schneider, J.C., Laarman, P.W., Gowing, H., 2000. Chapter 9: age and growth methods and state averages. In: *Manual of Fisheries Survey Methods II: with Periodic Updates*.
- Scott, C.L., Kwasniewski, S., Falk-Petersen, S., Sargent, J.R., 2002. Species differences, origins and functions of fatty alcohols and fatty acids in the wax esters and phospholipids of *Calanus hyperboreus*, *C. glacialis* and *C. finmarchicus* from Arctic waters. *Mar. Ecol. Prog. Ser.* 235, 127–134. <https://doi.org/10.3354/meps235127>.
- Swanson, D., Block, R., Mousa, S.A., 2012. Omega-3 fatty acids EPA and DHA: health benefits throughout life. *Adv. Nutr.* 3, 1–7. <https://doi.org/10.3945/an.111.000893>.
- Taipale, S., Strandberg, U., Peltomaa, E., Galloway, A.W.E., Ojala, A., Brett, M.T., 2013. Fatty acid composition as biomarkers of freshwater microalgae: analysis of 37 strains of microalgae in 22 genera and in seven classes. *Aquat. Microb. Ecol.* 71, 165–178. <https://doi.org/10.3354/ame01671>.
- Tocher, D.R., 2010. Fatty acid requirements in ontogeny of marine and freshwater fish. *Aquacult. Res.* 41, 717–732. <https://doi.org/10.1111/j.1365-2109.2008.02150.x>.
- Tocher, D.R., 2017. Metabolism and functions of lipids and fatty acids in teleost fish. *Rev. Fish. Sci.* 11, 107–184. <https://doi.org/10.1080/713610925>.
- U.S. Environmental Protection Agency, 2016. *Aquatic life ambient water quality criterion for selenium-freshwater 2016*. Washington D.C.
- Weslawski, J.M., Ryg, M., Smith, T.G., Oritsland, N.A., 1994. Diet of ringed seals (*Phoca hispida*) in a Fjord of West Svalbard. *Arctic* 47, 109–114.
- Woshner, V.M., O'Hara, T.M., Bratton, G.R., Beasley, V.R., 2001. Concentrations and interactions of selected essential and non-essential elements in ringed seals and polar bears of arctic Alaska. *J. Wildl. Dis.* 37, 711–721. <https://doi.org/10.7589/0090-3558-37.4.693>.
- Yurkowski, D.J., Ferguson, S., Choy, E.S., Loseto, L.L., Brown, T.M., Muir, D.C.G., Semeniuk, C.A.D., Fisk, A.T., 2016a. Latitudinal variation in ecological opportunity and intraspecific competition indicates differences in niche variability and diet specialization of Arctic marine predators. *Ecol. Evol.* 6, 1666–1678. <https://doi.org/10.1002/ece3.1980>.
- Yurkowski, D.J., Ferguson, S.H., Semeniuk, C.A.D., Brown, T.M., Muir, D.C.G., Fisk, A.T., 2016b. Spatial and temporal variation of an ice-adapted predator's feeding ecology in a changing Arctic marine ecosystem. *Oecologia* 180, 631–644. <https://doi.org/10.1007/s00442-015-3384-5>.
- Zhang, Y., Jacob, D.J., Dutkiewicz, S., Amos, H.M., Long, M.S., Sunderland, E.M., 2015. Biogeochemical drivers of the fate of riverine mercury discharged to the global and Arctic oceans. *Global Biogeochem. Cycles* 29, 854–864. <https://doi.org/10.1002/2015GB005124>. Received.