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Title: Mercury concentrations in marine species from the Aleutian Islands: spatial and biological determinants

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Abstract: Several species found in the Bering Sea show significant spatial variation in total mercury concentrations ([THg]) longitudinally along the Aleutian Island chain. We assessed [THg] in other members of the Bering Sea food web to better understand the factors shaping regional differences. [THg] and stable carbon and nitrogen isotope ratios (δ^{15}N and δ^{13}C values) were measured in muscle tissue from 1052 fishes and cephalopods from parts of the Bering Sea and North Pacific Ocean adjacent to the Aleutian Islands. The spatial distribution of the samples enabled regional comparisons for 8 species of fish and one species of cephalopod. Four species showed higher mean length-standardized [THg] in the western Aleutian Islands management area. [THg] in yellow Irish lord were very different relative to those observed in other species and when included in multi-species analyses drove the overall regional trends in mean [THg]. Multi-species analyses excluding measurements for yellow Irish lord showed mean length-standardized [THg] was greater in the western Aleutian Islands than in the central Aleutian Islands management area. Linear regression of [THg] and δ^{15}N values showed a significant and positive relationship across all species, varying between regions and across species. Isotopic space of all species was significantly different between the western Aleutian Islands and central Aleutian Islands, driven largely by δ^{13}C values. Stable isotope values observed follow the same regional trend of lower trophic taxa reported in the literature, with significantly lower δ^{13}C values in the western Aleutian Islands. We conclude that there are regional differences in carbon and nitrogen stable isotope ecology, as well as species-specific feeding ecology that influence [THg] dynamics in part of the marine food web along the Aleutian Island chain. These regional differences are likely contributors to the observed regional variations of [THg] in some high-level predators found in these regions.

Keywords: Muscle, North Pacific; mercury; stable isotopes of C and N; fish

Highlights

- [THg], δ^{15}N and δ^{13}C values measured in 1052 fish and cephalopods from Alaska
- Unadjusted muscle [THg] vary by species, length, and region along Aleutian Islands
- Mean muscle [THg] of four species higher in the western Aleutian Islands
- Mean δ^{15}N and δ^{13}C values for each species vary by region
- All species had lower mean δ^{13}C values in the western Aleutian Islands

1.0 Introduction

Mercury (Hg), a global contaminant that originates from natural and anthropogenic sources, is transported via long-range atmospheric transport and deposited in a wide range of ecosystems regardless of proximity to some point sources. Hg becomes more bioavailable after it is methylated and forms monomethylmercury that increases via biota uptake and biomagnification through the aquatic food web reaching concentrations of toxicological concern in some higher trophic organisms, such as Steller sea lions (*Eumetopias jubatus*), Pacific halibut (*Hippoglossus stenolepis*), and humans (Atwell et al., 1998; Bentzen et al., 2016; Fox et al., 2014; Rea et al., 2013). Monomethylmercury in fish can be a human and wildlife health issue (Hamade, 2014) as it is a neurotoxin that can cross the blood brain barrier and act as an endocrine disrupter (Walker et al., 2012) and cause oxidative stress (Lushchak, 2011).

Various ecological and physiological processes drive differences in total Hg concentrations ([THg]) within and between species in the same ecosystem (Jarman et al., 1996; Ward et al., 2010; Willacker et al., 2013). The specific location (e.g., niche) where organisms feed and inhabit can have a significant influence on Hg exposure and accumulation. Proximity to Hg sources, or access to different food webs with different prey assemblages, can provide potential for varying degrees of bioaccumulation and biomagnification that affect observed tissue concentrations of Hg (Cyr et al., 2017). In marine ecosystems, Hg sources (Laurier et al., 2004), ocean currents, upwellings (Gill and Fitzgerald, 1987), and water mass distributions with different geochemical properties (Lehnherr, 2014; Selin, 2009) can varyingly influence how Hg is transported in open oceans and reflected in upper trophic organisms. Additionally, biological and chemical oceanographic differences across marine ecosystems can provide varying conditions for the methylation of Hg, based on factors such as pH (Kelly et al., 2003), the presence of dissolved cations and organic matter (Boening, 2000; Douglas et al., 2012), and temperature (Johnson et al., 2016). Together, these factors can provide regionally specific conditions that can influence how Hg enters and moves through the food chain in a complicated fashion.

A notable example of a regional influence on [THg] is in biota of the Bering Sea and the North Pacific along the Aleutian Islands, from east to west. A pattern of higher [THg] has been documented in Steller sea lions and Pacific halibut from the western Aleutian Islands, Alaska, when compared to populations of those species found in other regions of the Aleutian Islands and Alaska (Bentzen et al., 2016; Rea et al., 2013). A similar geographic pattern was observed in tissues of bald eagles (*Haliaeetus leucocephalus*) and glaucous-winged gulls (*Larus glaucescens*), where [THg] increases from east to west across the Aleutians Islands (Anthony et al., 2007; Ricca et al., 2008). Significantly, Aleutian Island aggregations of Steller sea lions belonging to the western distinct population segment and some rookeries west of Samalga Pass in the western distinct population segment continue to decline in abundance (Atkinson et al., 2008; National Research Council, 2003; Fritz et al., 2014; NMFS, 2013). This pinniped management dilemma combined with the observations of [THg] in biota of the region led to this study to determine if higher [THg] is related to fish consumption.

Measurements of stable isotope ratios of carbon and nitrogen (δ^{13}C and δ^{15}N values, respectively; and together represent isotopic space) provide valuable ecological research tools that add a layer of dietary information for comparisons of [THg] within and among food webs (Cyr et al., 2017; McGrew et al., 2014; Power et al., 2002). δ^{15}N values can be used as a proxy to infer trophic position (Peterson and Fry, 1987), while δ^{13}C values can be used to differentiate the source of the primary production for a food web (Fry, 2006; Peterson and Fry, 1987). δ^{13}C values can therefore be used to infer regional differences by differentiating the influence from different carbon sources (Budge et al., 2008; Wang et al., 2014), such as the degree of influence from marine versus terrestrial inputs (Fry, 2006; McGrew et al., 2014) or pelagic versus benthic sources (Boyle et al., 2012; Doi et al., 2010). Fish [THg] are often, but not always, correlated with increasing δ^{15}N values, and can vary with spatial influences, as elucidated by using δ^{13}C values (Cyr et al., 2017). Together, stable isotopes of carbon and nitrogen can provide information on some of the ecological influences on [THg] within and among species and locations of fish.

Fish and invertebrates sampled from across the Aleutian Islands provide an ideal opportunity to examine regional influences on [THg] in a food web relative to wildlife management zones and oceanographic demarcations. Here we report [THg], $\delta^{15}N$ and $\delta^{13}C$ values, and associated biological data for 1052 specimens of marine fishes and cephalopods, representing 19 species, from an area of the Bering Sea and North Pacific Ocean adjacent to the Aleutian Islands. The primary goal of this research was to analyze patterns and comparisons of muscle [THg] in a diverse group of fish and cephalopod species from the waters along the central and western portion of the Aleutian Islands to assist with understanding observations of [THg] in upper trophic level vertebrates (fish, avian, mammalian). In particular, we examined how geographic location (Steller sea lion management zones and Amchitka Pass, a distinct oceanographic demarcation) shapes the patterns of length (proxy for age), ecology (including $\delta^{13}C$ and $\delta^{15}N$ values), and muscle [THg] of species examined.

2.0 Methods

2.1 Sampling. Specimens were obtained from commercial fish trawls (target and bycatch species) in 2013, 2014, and 2015; and donated subsamples from NOAA research cruises SF201401 and MS201401 in 2014 and 2015. Sampling spanned summer and winter seasons. Sampling regions along the Aleutian Islands were based on Steller sea lion management zones (western Aleutian Islands and central Aleutian Islands), located in the North Pacific Ocean and in the southern and western portion of the Bering Sea, between 51.26° N and 53.22° N, and 171.89° W and -173.76° E (Figure 1, York et al., 1996). Samples were also given a second regional assignment based on the longitudinal catch location in relation to Amchitka Pass, -179.98° W (Figure 1) that is considered a significant ecological boundary in the Bering Sea. Fish were collected from commercial trawls, frozen whole at -20°C and shipped to the University of Alaska Fairbanks for analyses. Muscle samples provided from federal research cruises were subsampled from fish measured in the field, frozen at sea and shipped to University of Alaska Fairbanks for analyses.

2.2 Sample processing. For specimens collected from commercial catches, fork length (in mm), and wet mass (in g) were recorded on thawed fish. Mantle length was measured for cephalopods. Approximately five grams of muscle (skin removed) was sampled from the left side of the fish from the area posterior to the pectoral fin, and ventral to the dorsal fin, or from the mantle for cephalopods. Specimens collected from federal research cruises were sampled on board the vessel, and in the lab a 5 gram subsample was taken from the larger subsample. All samples were freeze dried (Labcono, FreeZone 4.5 Liter) for a minimum of 48 h to remove all moisture and homogenized using a stainless-steel ball grinder (Retsch, CryoMill). Percent water content was calculated after drying using the following formula:

$$(\frac{wet\ weight - dry\ weight}{wet\ weight}) * 100$$

2.3 Total Hg analysis. [THg] were measured in freeze dried samples using a Milestone DMA-80 instrument, in accordance with U.S. EPA method #7473-EPA30B, 2007 SW 846, and reported as ng/g wet weight (ww) based on percent water values (Harley et al., 2015). The method detection limit for [THg] determination for muscle was 5 ng/g ww, calculated by the following formula:

$$\left(\frac{0.5\ (g)}{Sample\ mass\ dry\ weight\ (g)}\right) * (1 - sample\ \%\ H2O)$$

Quality assurance and quality control measures included analyses of method blanks, Standard Reference Materials of similar matrices, and check standards. All samples were analyzed in triplicate. Samples for which the coefficient of variation among replicates was >10% were re-analyzed until <10% was reached, with the mean value for all replicates used for statistical comparisons. The standard reference materials used were DORM-4 (National Resource Council Canada; 410.0 ± 55.0 ng/g), and Lake Superior Fish (LSF, National Institute of Standards and Technology, Standard Reference Material® 1946; 433.0 ± 9.0 ng/g ww). Mean percent recoveries (± SD) for each SRM were: 100 ng/g (liquid standard), 96.7 ± 10.9%; DORM-4, 93.5 ± 7.9%; LSF, 100.3 ± 10.1%.

2.4 Stable carbon and nitrogen isotope analysis. Stable carbon and nitrogen isotope ratios of all samples were measured at the Alaska Stable Isotope Facility at the University of Alaska Fairbanks following the methods described in Cyr et al. (2017). Between 0.2 and 0.5 mg of freeze-dried homogenized muscle samples were analyzed using continuous-flow isotope ratio mass spectrometry (CF-IRMS, Thermo DeltaVPlus interfaced with a Costech ESC 4010 elemental analyzer via a ConfloIV system). Stable isotope ratios were expressed in δ notation as parts per thousand (‰) relative to international standards (Vienna PeeDee Belemnite – VPDB for carbon and AIR for nitrogen):

$$\delta X‰ = \left[\left(\frac{R_{Sample}}{R_{Standard}}\right) - 1\right] * 1000$$

where *X* is the element of interest, *R* is the ratio of the heavy to light isotope measured for that element, *Sample* is the sample of interest, and *Standard* is the standard used, VPDB for carbon or AIR for nitrogen. Reference checks using peptone (No. P-7750 meat-based protein, Sigma Chemical Company, Lot #76f-0300) were run every 10th sample, and blanks every 20th sample, with instrument precision typically <0.2 ‰ for both carbon and nitrogen.

2.5 Lipid extraction and correction. Lipids are depleted in ^{13}C relative to ^{12}C compared with protein and carbohydrates, and can affect stable carbon isotope data by lowering the δ^{13}C values with increasing lipid content of a sample (DeNiro and Epstein, 1977; Sweeting et al., 2006). High C:N values present difficulties with mathematical lipid-correction formulas, and can cause significant variability between the relationship of $\Delta\delta^{13}$C in relation to the C:N$_{Bulk}$ (Hoffman and Sutton, 2010; Post et al., 2007). A large proportion (92%) of the samples in this study had atomic C:N ratios above levels considered representative for protein, ~3.7 (Post et al., 2007; Sweeting et al., 2006), and differed between species, individuals and regions (Supplemental Figure 1). To account for this influence, we lipid-extracted a subset of two hundred and forty-five samples from eight of the species following a method modified from Folch et al. (1957). Briefly, 1.0 - 2.0 g of freeze-dried sample muscle was rinsed three times in a mixture of 2:1 chloroform: methanol for 15 minutes, air dried overnight, then freeze-dried for 24 hours. These lipid-extracted samples were analyzed for $\delta^{13}C$ and $\delta^{15}N$ values as described above and recalculated C:N ratios.

We determined that the influence of lipids in samples with $C:N_{Bulk} > 10$ was considerable and introduced more variability and uncertainty than mathematical lipid-correction could reasonably account for (Supplemental Figures 1, 2 and 3), and subsequently removed ten samples with $C:N_{Bulk} > 10$ from $\delta^{13}C$ analyses. The mean C:N ratio for all lipid-extracted samples was 3.7 ± 0.1 ‰ (Supplemental Table 1), and thus enabled the use of the $\delta^{13}C_{Lipid\text{-}extracted}$ values to generate a mathematical correction formula. We followed the methods detailed in Post et al. (2007) by using their formula for % lipid:

$$\%\, lipid = -20.54 + 7.24 * \; C{:}\,N_{Bulk}$$

followed by the equation to determine $\Delta\delta^{13}C$ with our data:

$$\Delta\delta^{13}C = \; 0.45 + (0.094 * \%\, lipid)$$

and then combined the equations to generate the final correction formula (Supplemental Table 1, Supplemental Figure 3, $R^2 = 0.80$, $p << 0.001$) to mathematically correct the $\delta^{13}C_{Bulk}$ values for the remainder of the dataset:

$$\delta^{13}C_{Lipid\text{-}corrected} = \delta^{13}C_{Bulk} -1.48 + 0.65 * C{:}N_{Bulk}$$

2.6 Length standardization of [THg]. To account for regional or allometric effects on [THg] and allow for inter- and intra-species and regional comparisons, a length-standardization of [THg] was performed following the methods detailed in Eagles-Smith et al. (2016). Briefly, we standardized the log-transformed [THg] using the median length for each species by generating a linear mixed effects model with length and species as fixed covariates, and region as a random effect. We added the residuals from each fish back into the model to generate predictive [THg] values for each fish that were then back transformed to obtain the final length-standardized [THg] for each fish.

2.7 Statistical analysis. All analyses were performed using R statistical computing software (R Core Team 2015). All data were checked for normality by visual inspection of normal quantile-quantile plots, and residual plots (Ciancio et al., 2008), and using either the Shapiro-Wilk's test or the Kruskal-Wallis test. [THg] were log transformed for regression analysis to comply with normality assumptions. To ensure statistical power for comparisons, we restricted our regional and inter-species comparisons to the 9 species that had >10 individuals per region. Species in these comparisons were divided into two major groups: 1) darkfin sculpin (*Malacoccottus zonurus*), Pacific cod (*Gadus macrocephalus*), yellow Irish lord (*Hemilepidotus jordani*), and arrowtooth flounder (*Atheresthes stomias*) were considered piscivorous based on the percentage of diet composed of fish (Yang and Nelson, 1999; Yang, 2003); and 2) walleye pollock (*Gadus chalcogrammus*), Atka mackerel (*Pleurogrammus monopterygius*), northern rockfish (*Sebastes polyspinis*), Pacific Ocean perch (*Sebastes alutus*), and one invertebrate, the magistrate armhook squid (*Berryteuthis magister*) were considered primarily zooplanktivorous based on the percentage of diet composed of invertebrates (Yang and Nelson, 1999; Yang, 2003)

Summary statistics for [THg] are represented as geometric mean ± standard deviation (SD), all other summary statistics are represented as arithmetic mean ± SD. We conducted analysis of variance to determine the overall influence of species, region, and the interaction of species and region. Following this, regional differences for individual species' mass, length, unadjusted [THg], and length-standardized [THg] were using t-tests with a Holm correction to control for familywise errors. Results were considered significant at $\alpha \leq 0.05$. Rank order position for each species and region was determined using analysis of variance followed by the Tukey's Honestly Significant Difference *post hoc* test. Determining the influence of $\delta^{15}N$ values, $\delta^{13}C$ values, the interaction of $\delta^{15}N$ or $\delta^{13}C$ values and region on [THg] was determined using generalized linear models (GLM) for each species. Differences in the isotopic space between seasons and regions for each species were tested using the Hotelling's T^2 test, comparing the mean $\delta^{15}N$ and $\delta^{13}C$ values in multivariate space (Ciancio et al., 2008; Colombini et al., 2011).

3.0 Results

3.1 Data summary. A total of 1052 samples from the western Aleutian Islands and the central Aleutian Islands, representing 19 species of marine fishes and cephalopods were analyzed for [THg], and δ^{15}N and δ^{13}C values. Across all species, mass and length varied considerably, ranging from 15 to 16800 g (1,303.1 g ± 1,963.4). and from 8 to 111 cm (41.3 cm ± 16.9), respectively. Unadjusted [THg] for all fish and cephalopods ranged from 7.5 to 1,578.3 ng/g ww (149.47 ± 173.74). δ^{15}N (‰) values ranged from 5.9 to 15.0 ‰ (11.1 ± 1.5 ‰), bulk δ^{13}C values ranged from -26.5 to -17.6 ‰ (-20.9 ± 1.5 ‰), and lipid-corrected δ^{13}C values ranged from -22.7 to -16.5 ‰ (-19.5 ± 1.2 ‰). Statistical comparisons between central Aleutian Islands and western Aleutian Islands for the nine species with >10 individuals per region are shown in Table 1. Summary statistics for all other species sampled and analyzed are provided in Supplemental Table 2.

3.2 Stable isotopes. The seasonal isotopic space for each species and region was significantly different within the western Aleutian Islands in armhook squid, Atka mackerel, northern rockfish, Pacific cod, and walleye pollock, and within the central Aleutian Islands in all species except armhook squid and darkfin sculpin (Supplemental Table 3). These differences were small (<~1 ‰) and within analytical error and aquatic trophic level variation (Vander Zanden and Rasmussen, 2001), so we considered them not biologically significant. As a result, we pooled the stable isotope measurements within each species and region for our study.

All species occupied significantly different isotopic spaces between the central Aleutian Islands and western Aleutian Islands (Table 2, Figure 2). This is likely driven by the differences in mean lipid-corrected δ^{13}C values between regions (Δcentral Aleutian Islands-western Aleutian Islands) that was different for all species (Table 1), whereas only 4 species had statistically different (Table 1, $\alpha \leq 0.05$) mean δ^{15}N values between the western Aleutian Islands and central Aleutian Islands.

3.3 Regional comparisons. An analysis of variance model indicated that species and the interaction of species and region significantly contributed to the variability in length standardized [THg], while region alone was not significant ($\alpha \leq 0.05$). Unadjusted [THg] were statistically higher in the western Aleutian Islands for arrowtooth flounder, Pacific cod, Pacific Ocean perch, and walleye pollock (4 of 9 species), whereas unadjusted [THg] were statistically higher in the central Aleutian Islands for yellow Irish lord and Atka mackerel ($\alpha \leq 0.05$; Table 1). There was no difference in length-standardized [THg] between western Aleutian Islands and central Aleutian Islands across all fish combined ($\alpha \leq 0.05$). Since this statistic is likely driven by the magnitude of [THg] in yellow Irish lord from the central Aleutian Islands (Figure 3), a further comparison for all species combined except yellow Irish showed the mean length-standardized [THg] was significantly higher in the western Aleutian Islands ($\alpha \leq 0.001$). Intraspecies comparisons of mean length-standardized [THg] were higher in the western Aleutian Islands for arrowtooth flounder, Pacific cod, Pacific Ocean perch, and walleye pollock (four of nine species, Table 1, Figure 3). Only Atka mackerel and yellow Irish lord had higher mean length-standardized [THg] in the central Aleutian Islands (Table 1, Figure 3).

Regional comparisons based on secondary regional assignments using Amchitka Pass as the divide between western Aleutian Islands and central Aleutian Islands revealed that both mean unadjusted [THg] and length-standardized [THg] of all species combined were significantly greater in the western Aleutian Islands ($\alpha \leq 0.001$). Intraspecies comparisons demonstrated that all species except Atka mackerel had greater mean length-standardized [THg] in the western Aleutian Islands, and statistically, the mean length-standardized [THg] of arrowtooth flounder, northern rockfish, Pacific cod, Pacific Ocean perch, walleye pollock, and yellow Irish lord were significantly greater in the western Aleutian Islands ($\alpha \leq 0.05$). Isotopic space was different between the western Aleutian Islands and central Aleutian Islands for all species ($\alpha \leq 0.01$), with consistently lower $\delta^{13}C$ values in the western Aleutian Islands.

The overall descending rank order among species for mean length-standardized [THg] was yellow Irish lord > darkfin sculpin ≥ Pacific cod > arrowtooth flounder ≥ northern rockfish ≥ Pacific

Ocean perch ≥ walleye pollock ≥ Atka mackerel ≥ armhook squid (> indicates statistical difference, $\alpha < 0.05$, and ≥ indicates a greater mean value but no statistical difference). Regionally, in the western Aleutian Islands, the descending rank order for length-standardized [THg] was darkfin sculpin ≥ Pacific cod ≥ arrowtooth flounder ≥ yellow Irish lord ≥ Pacific Ocean perch ≥ walleye pollock ≥ northern rockfish ≥ Atka mackerel ≥ armhook squid (Figure 3). In the central Aleutian Islands, the descending rank order for length-standardized [THg] was yellow Irish lord > darkfin sculpin ≥ Pacific cod > northern rockfish ≥ arrowtooth flounder ≥ Pacific Ocean perch ≥ Atka mackerel ≥ walleye pollock ≥ armhook squid (Figure 3).

3.4 [THg] in relation to trophic position. Unadjusted [THg] increased with increasing δ^{15}N values ($R^2 = 0.31$, $p < 0.001$) across all species examined. Assessing this relationship within each species and region indicated 6 of the species had a significant, positive slope in the western Aleutian Islands; while 4 of the species had a significant, positive slope in the central Aleutian Islands (Table 3). Using GLM the unadjusted [THg] in Pacific cod, Pacific Ocean perch, darkfin sculpin, northern rockfish, and yellow Irish lord were significantly influenced by δ^{15}N values; and by δ^{13}C values in arrowtooth flounder, Pacific cod, Pacific Ocean perch, walleye pollock, darkfin sculpin, and yellow Irish lord (Table 4). Unadjusted [THg] was significantly influenced by the interaction of δ^{15}N values and region in walleye pollock, while the interaction of δ^{13}C values and region significantly influenced [THg] in arrowtooth flounder, Pacific cod, walleye pollock, northern rockfish, and yellow Irish lord (Table 4).

4.0 Discussion

4.1 Overview. We sought to gain a better understanding of the influence of region and feeding ecology on observed [THg] in fish and cephalopod species by investigating a portion of the food web of the Bering Sea and North Pacific Ocean along the Aleutian Islands. We found a pattern of higher muscle [THg] in many of the fish from the western Aleutian Islands compared to the central Aleutian Islands. We also found a consistent pattern of differences in the isotopic space (δ^{15}N and δ^{13}C values) between the western Aleutian Island and central Aleutian Island regions for all species (Table 4.2, Figure 4.2). Finally, we demonstrated that fish muscle [THg] is highly variable and influenced by known drivers of Hg tissue concentrations.

4.2 Isotopes and feeding ecology. The seasonal ranges of stable isotope values measured in our fish suggest negligible biological differences and allowed us to pool the isotope data by year. The decision to do this was further supported by related feeding ecology work from the Aleutian Islands that demonstrated that the seasonal variation in stable isotopes in Steller sea lion vibrissa was 2 - 5 ‰, and 3 - 7 ‰ respectively for $\delta^{13}C$ values and $\delta^{15}N$ (Rea et al., 2015), far greater than the isotope variations measured in our fish. Doll et al. (2018) also noted the magnitude of the seasonal variation of Steller sea lion vibrissa, together with the minimal seasonal variation of their prey isotope values, and subsequently pooled their prey isotope values together seasonally.

The regional patterns of isotopic space were mostly driven by the differences in $\delta^{13}C$ values rather than $\delta^{15}N$ values. In both bulk $\delta^{13}C$ data and lipid-corrected $\delta^{13}C$ data, mean $\delta^{13}C$ values in the western Aleutian Islands were lower than those from the central Aleutian Islands for each species (Table 4.1, Figure 4.2). These measured differences in $\delta^{13}C$ values are consistent with the literature, where Schell et al. (1998) determined that the $\delta^{13}C$ values of both euphausiids and chaetognaths were lower in the western portion of the Aleutians. We suspect this is indicative of a difference in baseline stable isotope values, notably $\delta^{13}C$ values, between the western Aleutian Islands and the central Aleutian Islands. If baseline differences occur at the level of primary production, assuming other isotope factors were roughly equal in the food web, that difference would be transferred up through the food web, resulting in differences in upper trophic level prey.

Across all fishes combined, muscle [THg] increased positively and significantly with increasing $\delta^{15}N$ values, indicating biomagnification through the food web, an expected finding well supported in the literature (Atwell et al., 1998; Coelho et al., 2013; Power et al., 2002). The parameters of this correlation however, varied strongly by species and regions. Most notably, $\delta^{15}N$ values were generally lower in the western Aleutian Islands than in the central Aleutian Islands, but muscle [THg] were generally higher in the western Aleutian Islands than in the central Aleutian Islands, a pattern opposite of expected assumptions based on known biomagnification dynamics of Hg. This pattern is also consistent with previous findings, in which Pacific halibut from the western Aleutian Islands had the lowest δ^{15}N values, yet the highest muscle [THg] (Bentzen et al., 2016). The δ^{15}N values of Pacific cod, walleye pollock, arrowtooth flounder, and yellow Irish lord were all lower than those reported by Gorbatenko et al. (2008) from Cape Olutorski and Cape Navarin in the western Bering Sea. These patterns suggest regional differences in [THg] along the Aleutian Islands likely originate at the base of the food chain and are amplified through feeding ecology, but not driven strictly by feeding ecology.

Consistent trends in differences of the biology and chemistry of the biota from central or eastern and western areas of the Aleutian Islands reinforce the idea that oceanographic and ecological conditions are likely driving differences in [THg] in biota between the western Aleutian Islands and central Aleutian Islands, with these differences amplified through the food web. Feeding ecology is likely a major driver of the observed differences in [THg] of higher trophic level prey, because modeling research has demonstrated that regional deposition of [THg] across the Bering Sea and Aleutian Islands does not differ regionally (Strode et al., 2008), and Hg contributions from various sources to the Bering Sea are similar (Sunderland et al., 2009). We highlight feeding ecology, because fish have limited capacity for redistributing, demethylating or eliminating THg or $MeHg^+$ that allows for efficient accumulation and retention of THg or $MeHg^+$ in muscle tissue (Amlund et al., 2007; Trudel and Rasmussen, 1997). These factors, in conjunction with the efficient assimilation of Hg in the fish gut allow biomagnification of Hg through the aquatic food web (Atwell et al., 1998; Coelho et al., 2013). Thus, higher trophic level fish tend to have higher [THg] than lower trophic fish and prey items. Our study supports this generalization as three of the species with the largest differences between western Aleutian Islands and central Aleutian Islands, arrowtooth flounder, Pacific cod, and yellow Irish lord are known to be higher trophic predators that feed primarily on fish or crustaceans (Yang, 2003). Darkfin sculpin had some of the highest mean muscle [THg], and their diet includes at least some shrimp. These four species also had the highest δ^{15}N values (Table 4.1, Figure 4.2), and occupy trophic levels ranging from 3.8 to 4.5 (Aydin et al., 2007; Gorbatenko et al., 2008; Marsh et al., 2012). All other species in this study feed almost exclusively on some type of zooplankton (Yang, 2003), and occupy trophic levels ranging from 3.0 to 3.8, a full trophic level lower on the food web, providing less potential for biomagnification.

4.3 Geographic trends. Our data demonstrate a general trend of higher muscle [THg] in western Aleutian Island fish compared to central Aleutian Island fish. Four of the nine species had statistically greater mean length-standardized [THg] in the western Aleutian Islands than in the central Aleutian Islands. This geographical trend in [THg] is consistent with the literature regarding other marine-based taxa, such as Steller sea lion (Rea et al., 2013), Pacific halibut (Bentzen et al., 2016), glaucous-winged gulls (Ricca et al., 2008), and bald eagles (Anthony et al., 2007). The strong influence of yellow Irish lord on the overall regional patterns of [THg] are unique and discussed in subsequent paragraphs.

Amchitka Pass on the western end of the central Aleutian Islands (Figure 4.1) is considered a discrete ecological divide in the Bering Sea, with chemical and biological oceanographic processes differing from the west to the east of the pass (Logerwell et al., 2005). The consistent differences in [THg] we found by using Amchitka Pass as the boundary for western Aleutian Islands and central Aleutian Islands are likely related to the consistent differences in isotopic spaces, where specific chemical oceanographic differences east and west of Amchitka Pass have caused differences in isotope baseline values, and then feeding ecology influences the accumulation of THg in each food web.

4.4 Yellow Irish lord. Although yellow Irish lord were similar in size between the western Aleutian Islands and central Aleutian Islands regions, the mean length-standardized [THg] in the central Aleutian Islands was over two times higher than the western Aleutian Islands, a regional trend that is opposite to the one detected for the other species (Table 4.1, Figure 4.3). This may be related to trophic level, as yellow Irish lord in the central Aleutian Islands had higher $\delta^{15}N$ values than those from the western Aleutian Islands. Yellow Irish lord feed on fish and benthic crustaceans (Yang, 2003) that are higher trophic level prey than the zooplankton prey that many of the other fish species in this study consume. Yellow Irish lord could also simply be older fish. Long-lived fishes will eventually reach the asymptote of their length-at-age relationship, when they will continue to age and continue to accumulate Hg, but not exhibit a related increase in length (Eagles-Smith et al., 2014). The mean length-standardized [THg] of yellow Irish lord in the western Aleutian Islands was comparable to the mean length-standardized [THg] of several other species in this study, while the length-standardized [THg] of those from the central Aleutian Islands were much greater than any other species measured in this study. Based on the longer mean fork length for yellow Irish lord in the central Aleutian Islands, we suspect that these fish may be at or approaching the asymptote of their growth curve, approximately 46 cm for males and females combined (TenBrink and Buckley, 2013), indicating they are older individuals, but this age is not reflected in their length, and has allowed a greater amount of time for the accumulation of Hg in their muscle tissue (Eagles-Smith et al., 2014; Lange et al., 1994). Additionally, the maximum age of yellow Irish lord in the western Aleutian Islands has been reported to be less than more easterly portions of the Bering Sea (TenBrink and Aydin, 2009), further indicating the yellow Irish lord caught in the central Aleutian Islands may have been older individuals. Using only the length of a fish to understand Hg feeding ecology and accumulation dynamics would miss this level of important detail, consequently causing inappropriate comparisons of fish that are years apart in age. Age data greatly improves the ability to understand situations like this, and we recommend age estimations be conducted for fish that exhibit extreme relationships of [THg] and other metrics such as species, fish length, δ^{15}N values, or location.

4.5 Food web dietary exposure. The muscle [THg] of many of the fish from the central Aleutian Islands are in general agreement with other published studies of Pacific cod (Burger et al., 2014, 2007; Burger and Gochfeld, 2007), yellow Irish lord (Burger et al., 2014, 2007), and Atka mackerel (Alaska, 2017; Burger et al., 2007). The muscle [THg] for several species of fish from the western Aleutian Islands however, were higher than those reported in the literature, where the mean [THg] measured in Pacific cod were nearly 150 ng/g ww greater than those measured by Burger et al. (2014), or the State of Alaska Hg biomonitoring study from 2001 to 2016 (Alaska, 2017). The [THg] of arrowtooth flounder from the central Aleutian Islands were comparable to those identified in Oregon by Childs and Gaffke (1973), while those from the central Aleutian Islands were higher than those measured in arrowtooth flounder from the Bering Sea by Gerber et al. (2012), and those from western Aleutian Islands were higher than values reported in any literature we identified. Our [THg] for walleye pollock and yellow Irish lord were also higher than those reported by the State of Alaska (Alaska, 2015), and were similar to reports of halibut across Alaska (Bentzen et al., 2016). Although these comparisons demonstrate the high degree of variability of fish [THg], given the consistency of the patterns, they also reinforce the overarching regional pattern of increased [THg] in the western Aleutian Islands.

These results point to influential regional food web differences resulting in mean muscle [THg] differences along the Aleutian chain for most species we examined. Where mean [THg] are different between the western Aleutian Islands and the central Aleutian Islands, the differences are substantial, such as 92 ng/g ww difference for Pacific cod (57 % increase), or 140 ng/g ww difference for arrowtooth flounder (180 % increase). It is also important to note that regardless of region, yellow Irish lord contained elevated [THg] compared to the other species measured. These differences may translate to different Hg exposure potential between the western Aleutian Islands and central Aleutian Islands regions for Steller sea lion and other top predators occupying those areas. These differences prove to be more directly associated with Amchitka Pass, as a biogeographical divide, when compared to Steller sea lion resource management zones.

5.0 Conclusions

We compiled an extensive set of [THg] and stable isotope data for 19 species found in the Bering Sea and North Pacific along the Aleutian Islands. These data enabled us to generate and validate a mathematical lipid-correction formula for Bering Sea and North Pacific fishes with $C{:}N_{Bulk} < 10$. We showed a general trend of elevated [THg] in fish from the western Aleutian Islands, compared to the central Aleutian Islands, when using the management regions defined for Steller sea lion. When considering a regional delineation based on ecosystem characteristics, we note that Amchitka Pass offers a clearer and more consistent explanation for the observed trends in $\delta^{13}C$ and $\delta^{15}N$ values and [THg] than those based on marine mammal species management zones. We document a consistent trend of lower $\delta^{13}C$ values in the western Aleutian Islands, providing a starting point to assess differences in primary production and feeding ecology, and subsequently the increase of [THg] through multiple trophic levels. These findings, in conjunction with previous research indicates potential regional differences in feeding ecology, resulting in both inter- and intraspecies biomagnification differences that drive higher [THg] in the western Aleutian Islands. Further research on this topic should include more comprehensive food web analysis of [THg] and stable isotopes (C and N), from primary production to top predators of the same location. Additionally, these measurements and analyses will be useful to others interested in Hg and other contaminants in this region and for determining consumption advice for humans. As such, these data have been shared with the State of Alaska Department of Environmental Conservation for this purpose.

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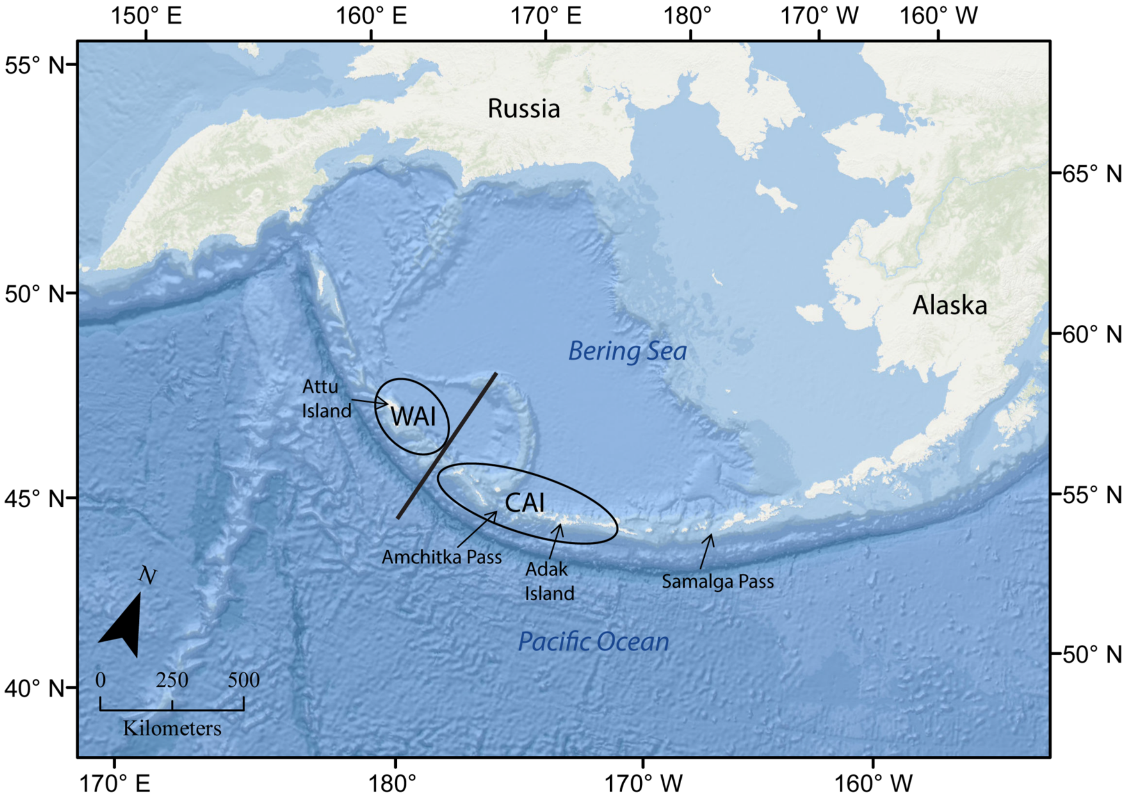
Figure 1. Map depicting the approximate extent of sample collection, within the context of Steller sea lion management regions. WAI is Western Aleutian Islands, and CAI is Central Aleutian Islands.

Figure 2. Mean δ^{15}N and lipid-corrected δ^{13}C values (± 1 standard deviation) of muscle samples for each fish and invertebrate species, categorized by western Aleutian Islands (WAI) and central Aleutian Islands (CAI). VPDB is the isotopic standard Vienna Pee-Dee Belemnite, AIR is the isotopic standard atmospheric air.

Figure 3. Box and whisker plot representing the length-standardized muscle [THg] for each fish and invertebrate species, characterized by region. Data presented on a log scale on the y-axis. Bold horizontal lines inside each box represent median values, bottom and top edges of boxes represent 25th and 75th percentiles, respectively, and the ends of the vertical solid lines represent ± 1.5 * interquartile range. Length-standardized [THg] beyond this range are displayed as individual points. * denotes significance level between regions for the species indicated, $\alpha \leq 0.01$; **, denotes significance $\alpha \leq 0.001$. WAI is Western Aleutian Islands, and CAI is Central Aleutian Islands.

Figure 4. [THg] and δ^{15}N values for muscle samples, individual species' regression slopes. [THg] and δ^{15}N values for muscle samples, individual species' regression slopes. WAI is Western Aleutian Islands, and CAI is Central Aleutian Islands. AIR is the isotopic standard atmospheric air.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Russia
Alaska
Bering Sea
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WAI
CAI
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Adak Island
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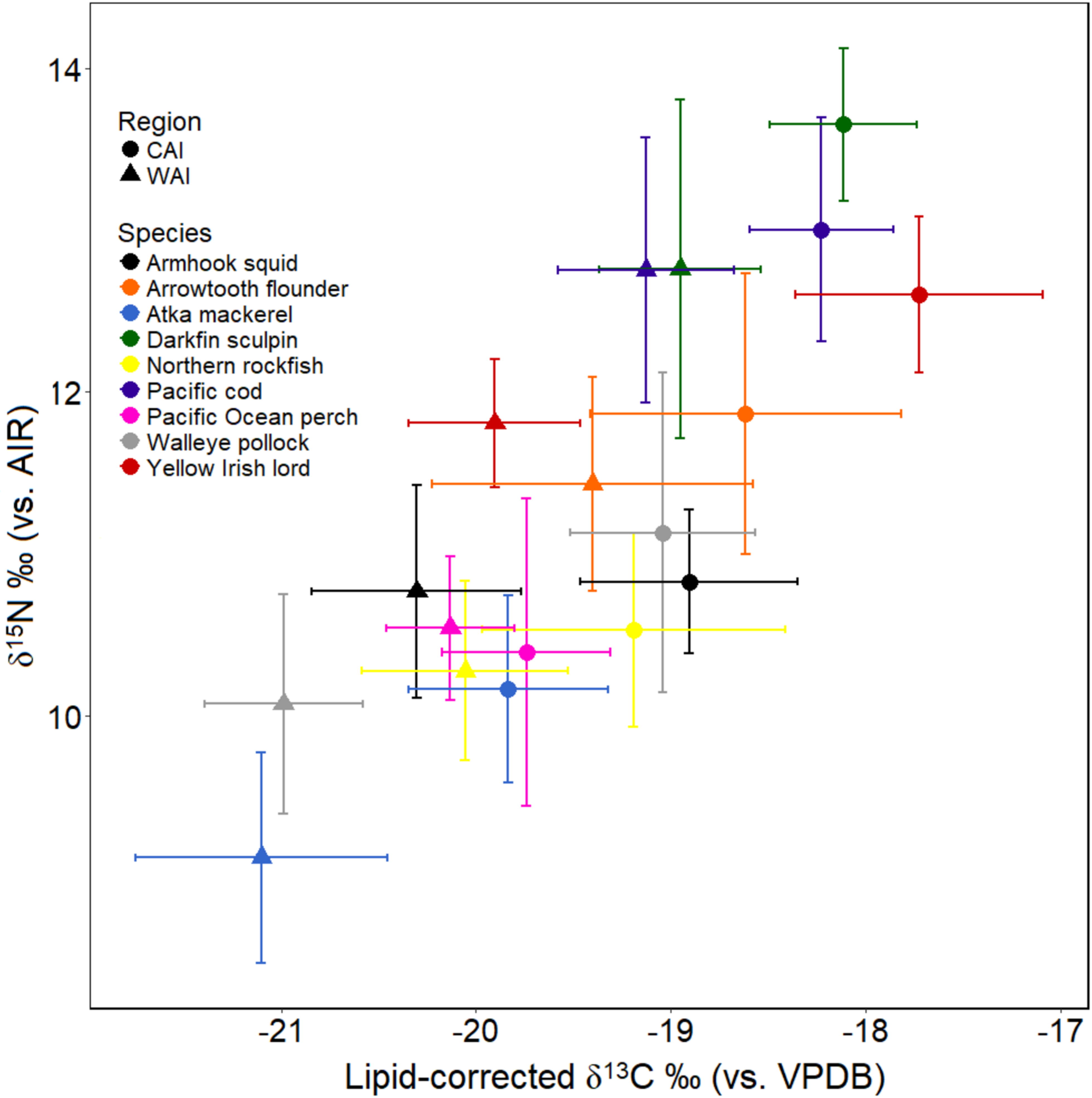
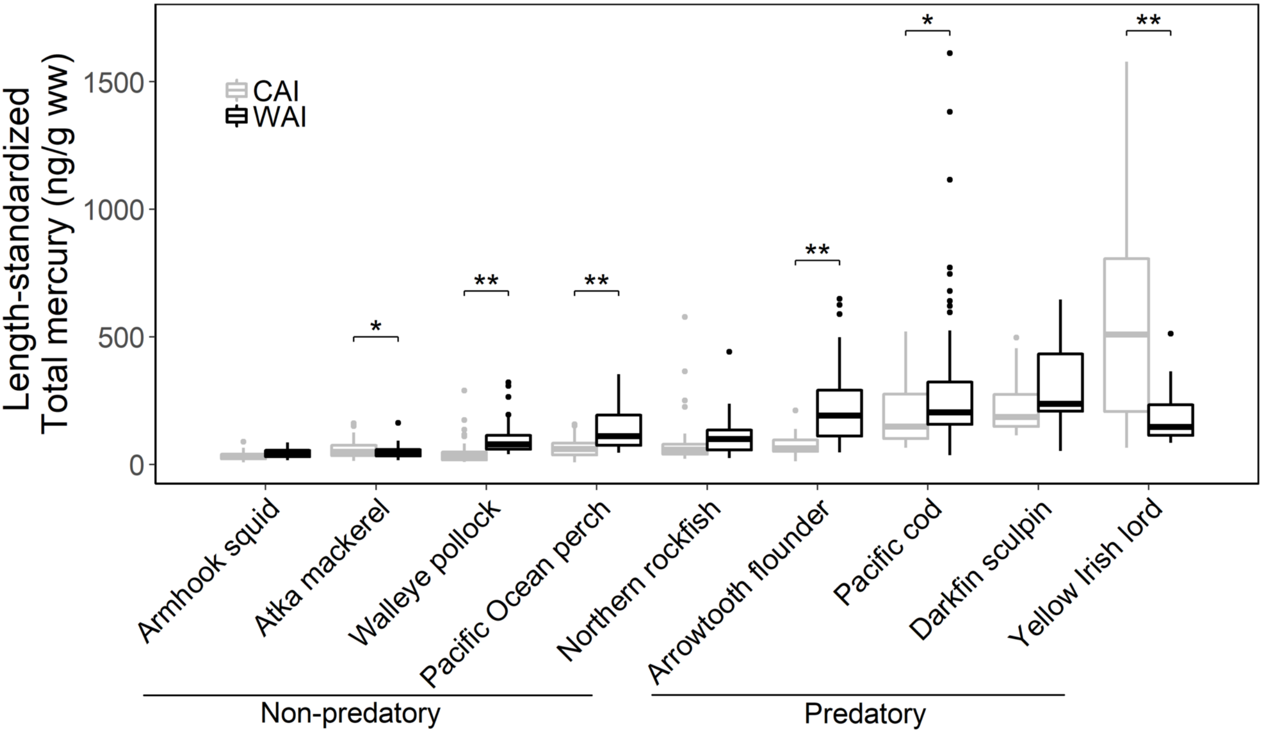
500
Kilometers


Region
● CAI
▲ WAI
Species
● Armhook squid
● Arrowtooth flounder
● Atka mackerel
● Darkfin sculpin
● Northern rockfish
● Pacific cod
● Pacific Ocean perch
● Walleye pollock
● Yellow Irish lord
14
12
10
δ15N ‰ (vs. AIR)
-21
-20
-19
-18
-17
Lipid-corrected δ13C ‰ (vs. VPDB)



Length-standardized
Total mercury (ng/g ww)
1500
1000
500
0
CAI
WAI
*
**
**
**
*
**
Armhook squid
Atka mackerel
Walleye pollock
Pacific Ocean perch
Northern rockfish
Arrowtooth flounder
Pacific cod
Darkfin sculpin
Yellow Irish lord
Non-predatory
Predatory

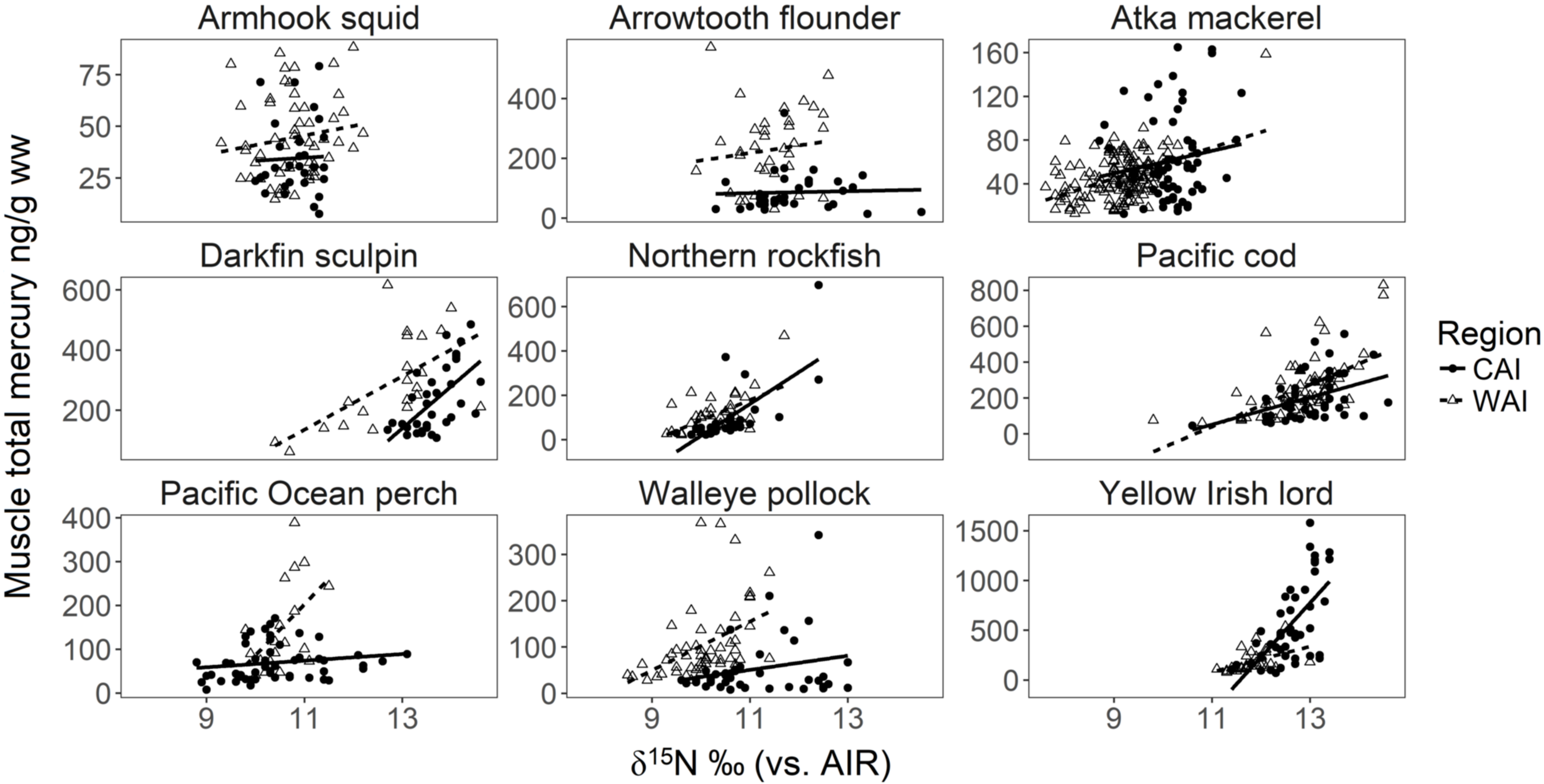

Armhook squid
Arrowtooth flounder
Atka mackerel
Darkfin sculpin
Northern rockfish
Pacific cod
Pacific Ocean perch
Walleye pollock
Yellow Irish lord
Muscle total mercury ng/g ww
δ15N ‰ (vs. AIR)
9
11
13
25
50
75
0
200
400
40
80
120
160
600
800
1000
1500
100
300
500
Region
CAI
WAI

Table 1. Total mercury concentrations ([THg]) and stable nitrogen and carbon isotope values for western Aleutian Islands (WAI) and central Aleutian Islands (CAI) fishes and cephalopods. Sample sizes (N) for each region, fork length (cm), mass (g), [THg] as measured (ng/g ww), length-standardized [THg] in ng/g ww, δ^{15}N values, bulk δ^{13}C values, and lipid-corrected δ^{13}C values for each species in the dataset. Data are means ± SD, geometric mean for [THg].

Species	**Region**	**N**	**Fork Length (cm)**	**Mass (g)**	**Unadjusted [THg] ng/g ww**	**Length-standardized [THg] ng/g ww**	**δ^{15}N (‰)**	**δ^{13}C (‰)**	**Lipid-corrected δ^{13}C (‰)**
Armhook squid	CAI	30	22.3 ± 3.2	414.7 ± 141.6	29.1 ± 18.4	28.9 ± 18.9	10.8 ± 0.5	***-20.4 ± 0.5***	***-18.9 ± 0.6***
Berryteuthis magister	WAI	67	25.1 ± 6.2	471.6 ± 144.4	42.1 ± 22.1	39.4 ± 18.4	10.8 ± 0.7	-21.7 ± 0.5	-20.3 ± 0.5
Arrowtooth flounder	CAI	41	48.1 ± 10.2	1,226.8 ± 824.6	69.8 ± 64.0	62.4 ± 39.3	11.9 ± 0.9	***-20.4 ± 1.7***	***-18.6 ± 0.8***
Atheresthes stomias	WAI	39	***59.6 ± 17.2***	***2,705.1 ± 1,971.0***	***188.8 ± 127.9***	***184.4 ± 161.8***	11.4 ± 0.7	-22.3 ± 2.0	-19.4 ± 0.8
Atka mackerel	CAI	73	***40.2 ± 7.1***	***913.7 ± 456.8***	***50.5 ± 38.0***	***51.1 ± 37.4***	***10.2 ± 0.6***	***-22.0 ± 1.2***	***-19.8 ± 0.5***
Pleurogrammus monopterygius	WAI	148	36.8 ± 3.1	520.9 ± 239.4	42.8 ± 20.8	42.7 ± 19.4	9.1 ± 0.6	-22.8 ± 1.0	-21.1 ± 0.6
Darkfin sculpin	CAI	34	***20.2 ± 3.3***	***158.8 ± 74.3***	207.6 ± 109.7	208.0 ± 99.5	***13.7 ± 0.5***	***-19.2 ± 0.4***	***-18.1 ± 0.4***
Malacoccottus zonurus	WAI	21	16.9 ± 2.9	71.4 ± 46.3	250.2 ± 153.6	251.1 ± 158.3	12.8 ± 1.0	-20.0 ± 0.4	-19.0 ± 0.4
Northern rockfish	CAI	41	32.4 ± 3.9	485.4 ± 193.1	63.7 ± 121.0	64.3 ± 104.0	10.5 ± 0.6	***-20.3 ± 0.7***	***-19.2 ± 0.8***
Sebastes polyspinis	WAI	36	31.3 ± 3.4	496.4 ± 236.4	87.1 ± 86.8	87.6 ± 80.6	10.3 ± 0.6	-21.2 ± 0.7	-20.1 ± 0.5
Pacific cod	CAI	44	59.2 ± 11.0	2,915.9 ± 2,050.4	170.2 ± 127.6	162.5 ± 114.7	13.0 ± 0.7	***-19.3 ± 0.4***	***-18.2 ± 0.4***
Gadus macrocephalus	WAI	88	***68.9 ± 25.5***	***4,475.0 ± 4,372.7***	***225.3 ± 163.3***	***236.6 ± 279.5***	12.8 ± 0.8	-20.2 ± 0.6	-19.1 ± 0.5
Pacific Ocean perch	CAI	53	36.5 ± 2.8	700.0 ± 174.3	58.1 ± 39.9	57.5 ± 36.6	10.4 ± 1.0	***-21.4 ± 0.9***	***-19.7 ± 0.4***
Sebastes alutus	WAI	20	***39.5 ± 3.2***	***935.0 ± 306.6***	***116.1 ± 100.2***	***118.8 ± 87.3***	10.5 ± 0.4	-21.8 ± 0.8	-20.1 ± 0.3
Walleye pollock	CAI	41	54.5 ± 4.6	***1,412.2 ± 321.9***	33.7 ± 64.3	34.1 ± 87.3	***11.1 ± 1.0***	***-20.0 ± 0.5***	***-19.0 ± 0.5***
Gadus chalcogrammus	WAI	52	52.3 ± 7.5	1,051.9 ± 435.0	***85.7 ± 80.9***	***88.2 ± 62.6***	10.1 ± 0.7	-22.0 ± 0.4	-21.0 ± 0.4
Yellow Irish lord	CAI	45	***39.8 ± 3.6***	780.0 ± 225.2	***410.3 ± 408.7***	***412.2 ± 390.7***	***12.6 ± 0.5***	***-18.9 ± 0.6***	***-17.7 ± 0.6***
Hemilepidotus jordani	WAI	29	36.4 ± 5.2	627.6 ± 332.6	160.6 ± 108.9	162.9 ± 103.3	11.8 ± 0.4	-21.0 ± 0.4	-19.9 ± 0.4

Bold text indicates significant difference between WAI and CAI for the means of the given metric within a species, the larger value in bold, significance level α ≤ 0.05

WAI and CAI are Steller sea lion management sub-regions

Table 2. Differences in the lipid-corrected $\delta^{13}C$ values regionally (ΔCAI-WAI), and the regional difference (P values) for isotopic space comparisons for each species. Significance determined by Hotelling's T^2 test comparing mean $\delta^{15}N$ and $\delta^{13}C$ values in multivariate space.

Species	**ΔCAI-WAI Lipid-corrected $\delta^{13}C$ (‰)**	**Isotopic space $\delta^{15}N$ ‰ and Lipid-corrected $\delta^{13}C$ (‰)**
Armhook squid	1.4*	0.001
Arrowtooth flounder	0.8*	0.001
Atka mackerel	1.3*	0.001
Darkfin sculpin	0.8*	0.001
Northern rockfish	0.9*	0.001
Pacific cod	0.9*	0.001
Pacific Ocean perch	0.4*	0.01
Walleye pollock	1.9*	0.001
Yellow Irish lord	2.2*	0.001

WAI is western Aleutian Islands, CAI is central Aleutian Islands Steller sea lion management sub-regions

* indicates a significant difference between WAI and CAI in mean lipid-corrected $\delta^{13}C$ values, $\alpha<0.05$.

Table 3. Variance explained (R^2) and significance (P value) for linear regression of unadjusted total mercury concentrations ([THg]) and $\delta^{15}N$ values for western (WAI) and central (CAI) Aleutian Islands.

Species	**WAI**	**CAI**
Armhook squid	0.03 (0.2)	0.00 (0.86)
Atka mackerel	***0.17 (0.001)***	0.02 (0.28)
Arrowtooth flounder	0.01 (0.52)	0.00 (0.84)
Pacific cod	***0.51 (0.0001)***	***0.24 (0.001)***
Pacific Ocean perch	***0.27 (0.02)***	0.08 (0.06)
Walleye pollock	0.3 (0.3)	0.00 (0.6)
Darkfin sculpin	***0.55 (0.001)***	***0.36 (0.001)***
Northern rockfish	***0.35 (0.001)***	***0.62 (0.0001)***
Yellow Irish lord	***0.28 (0.01)***	***0.40 (0.0001)***

Data displayed as: R^2 (P value)

Bold text indicates significant relationship for [THg] and $\delta^{15}N$ values for each region, significance level $\alpha \leq 0.05$

WAI and CAI are Steller sea lion management sub-regions

Table 4. Significance (P value) from general linear models for the influence of $\delta^{15}N$ values, lipid-corrected $\delta^{13}C$ values, the interaction of $\delta^{15}N$ values and region, and the interaction of lipid-corrected $\delta^{13}C$ values and region on unadjusted total mercury concentrations ([THg]) for each species.

Species	**$\delta^{15}N$ (‰)**	**Lipid-corrected $\delta^{13}C$ (‰)**	**Region* $\delta^{15}N$ (‰)**	**Region * lipid-corrected $\delta^{13}C$ (‰)**
Armhook squid	n.s.	n.s.	n.s.	n.s.
Atka mackerel	n.s.	n.s.	n.s.	n.s.
Arrowtooth flounder	n.s.	0.01	n.s.	0.01
Pacific cod	0.001	0.001	n.s.	0.001
Pacific Ocean perch	0.05	0.01	n.s.	n.s.
Walleye pollock	n.s.	0.01	0.05	0.001
Darkfin sculpin	0.001	0.001	n.s.	n.s.
Northern rockfish	0.001	n.s.	n.s.	0.01
Yellow Irish lord	0.001	0.001	n.s.	0.01

n.s. indicates not significant.