Patterns of total mercury and methylmercury bioaccumulation in Antarctic krill (Euphausia superba) along the West Antarctic Peninsula

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HIGHLIGHTS

• THg and MeHg were measured in coastal populations of Antarctic krill.
• Concentrations of THg and MeHg were higher in juvenile than adult krill.
• MeHg accumulation was similar in krill from sea ice covered and ice-free transects.
• Annual sea ice may indirectly affect krill Hg accumulation through POM formation.

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:
Received 18 February 2019
Received in revised form 19 April 2019
Accepted 11 June 2019
Available online 14 June 2019

Editor: Xinbin Feng

Keywords:
Mercury
Antarctica
Krill development
Sea ice
Primary and export production

ABSTRACT

We examined mercury (Hg) accumulation in juvenile and adult subpopulations of Antarctic krill (Euphausia superba) collected west of the Antarctic Peninsula. Samples were collected along a northern cross-shelf transect beginning near Anvers Island and farther south near the sea ice edge in the austral summers of 2011, 2013, 2014, and 2015. Regardless of geographical position, mean concentrations of total Hg and methylmercury (MeHg), the form of Hg that biomagnifies in marine food webs, were significantly higher in juvenile than adult krill in all years. In 2013, juvenile Antarctic krill collected along the coast near Anvers Island had significantly higher MeHg concentrations than krill collected farther offshore, and in 2013 and 2014, coastal juvenile krill exhibited some of the highest MeHg concentrations of all subpopulations sampled. Across all sampling years, collection in northern (sea ice-free) or southern (sea ice edge) transects did not affect MeHg concentrations of juvenile or adult krill, suggesting similar levels and routes of MeHg exposure across the latitudes sampled. Developmental stage, feeding near the coast, and annual variations in sea ice-driven primary and export production were identified as potentially important factors leading to greater MeHg accumulation in juvenile than adult krill. Krill-dependent predators feeding primarily on juveniles may thus accumulate more MeHg than consumers foraging on older krill. These results report MeHg concentrations in Antarctic krill and will be useful for predicting Hg biomagnification in higher-level consumers in this productive Antarctic ecosystem.

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https://doi.org/10.1016/j.scitotenv.2019.06.176
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1. Introduction

Although remote from anthropogenic sources, Antarctic ecosystems may experience mercury (Hg) contamination at very high levels (Bargagli, 2008), and Hg concentrations in Antarctic seabirds can be as high as in consumers of similar trophic levels from the northern hemisphere (Nygard et al., 2001; Becker et al., 2002). While the accumulation of Hg in zooplankton (Stern and Macdonald, 2005; Gantner et al., 2009) and the biomagnification of Hg in higher level consumers (Campbell et al., 2005) are well documented in Arctic marine ecosystems, fewer studies have examined the bioaccumulation of Hg within prey and predators of Antarctica (Bargagli et al., 1998; Sanchez-Hernandez, 2000; Bargagli, 2001; dos Santos et al., 2006; Polito et al., 2016; Cipro et al., 2017).

In the seasonally productive coastal waters of the West Antarctic Peninsula (WAP), large predators are highly dependent on consumption of macrozooplankton (Steinberg et al., 2015) as other Antarctic prey such as pelagic and demersal fish populations are deficient in this region (Barrera-Oro, 2003) and Antarctic squid are often in low abundance (Van de Putte et al., 2010). Antarctic krill (Euphausia superba) represent an important link for the transfer of carbon, energy, and potentially contaminants between primary producers and upper trophic levels (Szefer et al., 1993; Becker et al., 2002; Chiuchiolo et al., 2004). In the tightly coupled food webs along the continent’s coast, such as that of the WAP (Fraser and Hofmann, 2003), krill may be critical to the biomagnification of Hg in marine consumers. Although concentrations of total mercury (THg) have been measured in Antarctic krill and phytoplankton (Honda et al., 1987; Bargagli et al., 1998), THg in plankton is primarily composed of inorganic Hg. The accumulation of monomethylmercury (MeHg), the form of mercury that biomagnifies in marine food webs (Stern and Macdonald, 2005; Hammerschmidt and Fitzgerald, 2006), is the focus of this study as it has not been examined along the continental shelf of the WAP region.

Krill life history and associated changes in feeding behavior may play an important role in mercury transfer in the Antarctic food web. An inverse relationship between THg and body length of Antarctic krill collected along the northern and southern WAP (Locarnini and Presley, 1995) and South Shetland Islands (Séco et al., 2019) suggests that Hg concentrations decrease as krill mature. Shifts in the proportions of phytoplankton and zooplankton in the generally omnivorous krill diet (Martin et al., 2006) during development (Polito et al., 2013) could also affect the bioaccumulation of Hg in krill and dietary uptake by their consumers. Antarctic krill spawn and larval populations develop on the continental shelf and farther offshore of the WAP (Wiebe et al., 2011) where eggs sink to deep waters, hatch, and larvae develop as they ascend through mesopelagic depths (Marin et al., 1991). Lying beneath productive surface waters of the Southern Ocean, such deeper waters support high rates of organic matter remineralization (Dumont et al., 2011; Jacquet et al., 2011; Jacquet et al., 2015) and, as a result, elevated concentrations of dissolved metals, including Hg (Cossa et al., 2011; Blum et al., 2004; Heimburger et al., 2015; Munson et al., 2015; Renedo et al., 2018). During the periods of peak summertime (December–January) primary production along the Antarctic Peninsula, the growth of large phytoplankton size classes (Hart, 1942; Holm Hansen and Mitchell, 1991; Schofield et al., 2017) leads to high particle export rates and efficiencies (Buesseler et al., 2010), which transfer organic matter and associated trace elements hundreds of meters below the surface. Foraging in mesopelagic waters was shown to be an important driver of Hg accumulation in marine pelagic consumers (Choy et al., 2009; Brasso et al., 2014) and may also result in the exposure of developing krill to Hg early in life.

Larval krill developing offshore of the shelf break undergo an ontogenetic vertical migration to the epipelagic zone and toward the Antarctic coast (Trahan et al., 1993; Lascara et al., 1999; Daly and Zimmerman, 2004) where THg and MeHg concentrations are higher than in the Southern Ocean (Cossa et al., 2011). Proximity to the shore, with adults generally found farther offshore along the WAP continental shelf than juveniles (Lascara et al., 1999), may therefore result in differences in Hg accumulation since Antarctic coastal areas experience enhanced levels of Hg deposition (Bargagli et al., 2005), glacier retreat (Cook et al., 2005), and higher levels of dissolved THg in surface waters in proximity to coastal sea ice (Cossa et al., 2011; Gionfriddo et al., 2016). Spatial separation may also lead to differences in diet between juvenile and adult krill. During their first winter when water column productivity is low, seasonal sea ice plays an important role in krill recruitment (Saba et al., 2014). Larval and juvenile krill may feed undersea ice (Daly, 1990, 2004), where concentrations of dissolved MeHg are higher than in adjacent ice-free surface seawater (St Louis et al., 2007; Gionfriddo et al., 2016). However, a recent study showed that the winter pack-ice zone is used primarily as shelter and that developing krill feed primarily in the marginal sea ice zone (Meyer et al., 2017), which may limit the transfer of MeHg from sea ice to krill and other consumers.

To examine the biological and environmental factors controlling the accumulation of Hg in the coastal marine food web west of the Antarctic Peninsula, we measured THg and MeHg in whole and dissected adult and juvenile Antarctic krill along a cross-shelf transect beginning near Anvers Island, Antarctica. Krill were also collected at southern stations near the sea ice edge to examine the effects of a persistent sea ice environment on MeHg accumulation. Variation in Hg accumulation among krill populations in the WAP was evaluated with respect to spatial distribution (distance from shore, latitudinally) and developmental stage (juvenile, adult).

2. Materials and methods

2.1. Collection and mercury analysis of Antarctic krill

Adult and juvenile Antarctic krill (Euphausia superba) were collected between the 1st and 14th of January during the austral summers of 2011, 2013, 2014, and 2015 at coastal, shelf, and slope stations west of Anvers Island and at shelf and slope stations along the sea ice edge (Fig. 1) within the Palmer Antarctica Long-Term Ecological Research (PAL LTER) program sampling grid (Steinberg et al., 2015). Krill were sampled using a 2 m-square frame Metro net (700 μm mesh), towed obliquely to 120 m depth using established PAL LTER protocols (Ross et al., 2008; Steinberg et al., 2015). Coastal, shelf, and slope sub regions along the WAP were assigned using bathymetry (Steinberg et al., 2012; Steinberg et al., 2015). Coastal and shelf waters were designated by the shelf break (at a depth of approximately 431 m), while slope waters were identified as those offshore of the 750 m isobath.

Fresh (wet) krill were handled in the field with trace metal clean Teflon forceps and separated into approximate age classes (juvenile and adult) by length (Siegel and Loeb, 1994) to limit cross-contamination. Bulk samples (15–20 individuals) were placed in trace metal clean 50 mL polystyrene tubes and frozen at −20 °C for shipping back to Rutgers University. Prior to analysis for Hg, whole krill were partially thawed to separate individual animals and each animal was lyophilized for 24 h. After lyophilization, official classification of juvenile krill was designated by dry weights <75 mg (Mayzaud et al., 1998; Meyer et al., 2010). Subsamples of fresh adult and juvenile krill were dissected with acid-cleaned, stainless steel scalpsels and forceps to determine the distributions of Hg in muscle, soft tissues (hepatopancreas, hindgut), and exoskeleton.

Dry whole individual krill and dissected tissues were homogenized and then digested in 5 mL of 4 N Trace Metal grade (Fisher) nitric acid (HNO3) at 55 °C for 16 h (Hintelmann and Nguyen, 2005) and stored at 8 °C prior to analysis. Krill digests were analyzed in duplicate for MeHg by cold vapor atomic fluorescence spectroscopy (CVAFS) after gas chromatographic separation of the ethylated derivative (Liang et al., 1994).
For total Hg (THg), aliquots (<1 mL) of 4 N HNO₃ krill digests were transferred to acid clean 10 mL glass tubes and oxidized with 1:1 (v/v) 0.2 N bromine monochloride (Hammerschmidt and Fitzgerald, 2005) and 5% hydrogen peroxide (H₂O₂). Duplicate aliquots of these digests were analyzed for THg by dual gold amalgamation CVAFS using a Brooks Rand MERX-T analyzer. All MeHg and THg concentrations for krill are expressed in units of ng g⁻¹ (dry wt), and precision as the average relative percent difference (RPD) of duplicate aliquots of sample digests was within 25.9% and 20.9% for MeHg (n = 139) and THg (n = 117), respectively.

The certified reference material, TORT-2 (Lobster Hepatopancreas), was also analyzed for THg and MeHg. Similar masses of TORT-2 to those of Antarctic krill (50–200 mg) were digested so that the amounts of animal tissue matrix were similar for both. Our measured MeHg and THg values for TORT-2 were 0.147 ± 0.034 μg g⁻¹ (n = 22) and 0.27 ± 0.04 μg g⁻¹ (n = 24), respectively, which are within 97% and 99% of certified values. Method detection limits based on 3× the standard deviation of blanks were 0.002 ng g⁻¹ for MeHg and 0.022 ng g⁻¹ for THg.

2.2. Statistical analysis

All statistical analyses were performed using R 3.3.0 (Core Team 2016). One-way ANOVAs were performed to evaluate the significance of differences between calculated means of juvenile and adult krill within all four sampling years. Planned comparisons (Ruxton and Beauchamp, 2008) of one-way ANOVA analyses for juvenile and adult krill within each sampling year, were also used to determine sources of variation in mercury concentrations in krill. The Games-Howell post hoc test was used to identify which sub-populations of krill (juvenile, adult, coastal, shelf, slope) contributed to variation in mercury concentrations at multiple sites near Anvers Island within each sampling year. Games-Howell pairwise comparisons were chosen as this method does not assume equal variances or sample sizes, which is characteristic of our data along the northern transect. A two-tailed Student’s t-test was used to evaluate within year differences between sea ice edge co-located juvenile and adult krill populations where there is only one site within each sampling year, and latitudinal differences between juvenile and adult krill populations across all sampling years at northern and southern sampling sites. All tests were conducted using a significance level of α < 0.05, and means are presented as ±1SD.

2.3. Particulate organic matter and sea ice

Primary production and chlorophyll a (Chl a) in surface waters, and sea ice extents were quantified as part of the PAL LTER monitoring efforts. Particulate organic matter (POM) and sea ice extents for the austral summers of 2013 to 2015, and associated methods are outlined in the supplementary information of the manuscript.

3. Results

3.1. Mercury concentrations in juvenile vs. adult Antarctic krill (E. superba) subpopulations in the northern transect

Mean concentrations of total Hg (THg) in subpopulations of adult Antarctic krill collected across the continental shelf west of Anvers Island varied from 4.04 to 12.6 ng g⁻¹. THg concentrations in juvenile krill from these transects (7.85 to 19.4 ng g⁻¹) were generally higher than those in adult krill (Table 1). Mean concentrations of MeHg varied from 0.74 to 2.94 ng g⁻¹ in juvenile Antarctic krill and from 0.26 to 1.61 ng g⁻¹ in adult krill. Across all four sampling years combined, juvenile Antarctic krill had significantly higher mean concentrations of THg (P < 0.005, F = 8.77) and MeHg (P < 0.001, F = 27.06) than adult krill (Fig. 2A and B). Mean concentration of MeHg was also higher in juvenile than adult krill within each sampling year but was not significantly higher in 2015 (Fig. 2C; Supp 1). Overall, mean concentrations of MeHg in juvenile and adult krill in 2014 were higher than in juveniles and adults in 2011, 2013, and 2015 (Table 1).
Table 1
Northern Transect Antarctic Krill (Euphausia superba). Mean ± standard deviation of total Hg (THg) and methylmercury (MeHg) in krill (n) collected from coastal, shelf, and slope waters west of Anvers Island, Antarctic Peninsula at 65°S to 64°S during the austral summers of 2011, 2013, 2014, and 2015.

<table>
<thead>
<tr>
<th>Year</th>
<th>Age class</th>
<th>WAP region</th>
<th>Lat (°S)</th>
<th>Long (°W)</th>
<th>[THg] (ng g⁻¹, dry wt)</th>
<th>[MeHg] (ng g⁻¹, dry wt)</th>
<th>MeHg/THg (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>Juvenile</td>
<td>Coastal</td>
<td>64.9</td>
<td>64.4</td>
<td>NA⁵</td>
<td>1.71 ± 0.07 (3)</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>Adult</td>
<td>Coastal</td>
<td>64.9</td>
<td>64.4</td>
<td>4.04 ± 2.65 (3)</td>
<td>0.26 ± 0.16 (3)</td>
<td>9 ± 9 (3)</td>
</tr>
<tr>
<td>2013</td>
<td>Juvenile</td>
<td>Coastal</td>
<td>64.9</td>
<td>64.3</td>
<td>9.23 ± 3.09 (14)</td>
<td>2.28 ± 0.79 (13)</td>
<td>26 ± 9 (13)</td>
</tr>
<tr>
<td></td>
<td>Adult</td>
<td>Shelf</td>
<td>64.6</td>
<td>65.3</td>
<td>7.85 ± 3.24 (9)</td>
<td>0.74 ± 0.38 (7)</td>
<td>10 ± 7 (7)</td>
</tr>
<tr>
<td>2014</td>
<td>Juvenile</td>
<td>Coastal</td>
<td>64.9</td>
<td>64.3</td>
<td>17.2 ± 9.19 (8)</td>
<td>2.94 ± 0.89 (13)</td>
<td>26 ± 20 (8)</td>
</tr>
<tr>
<td></td>
<td>Adult</td>
<td>Coastal</td>
<td>64.9</td>
<td>64.3</td>
<td>5.52 ± 1.69 (6)</td>
<td>1.61 ± 0.92 (12)</td>
<td>17 ± 13 (6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Slope</td>
<td>64.0</td>
<td>66.9</td>
<td>12.6 ± 3.16 (8)</td>
<td>1.02 ± 0.17 (8)</td>
<td>8 ± 2 (8)</td>
</tr>
<tr>
<td>2015</td>
<td>Juvenile</td>
<td>Coastal</td>
<td>64.9</td>
<td>64.3</td>
<td>19.4 ± 13.6 (8)</td>
<td>1.38 ± 0.89 (8)</td>
<td>11 ± 7 (7)</td>
</tr>
<tr>
<td></td>
<td>Adult</td>
<td>Coastal</td>
<td>64.9</td>
<td>64.3</td>
<td>8.06 ± 1.84 (9)</td>
<td>0.74 ± 0.53 (8)</td>
<td>10 ± 7 (7)</td>
</tr>
</tbody>
</table>

a Number of asterisks indicate significant differences (p < 0.05) within years in pairwise comparisons (Games-Howell post hoc test).
b NA, not analyzed.

Fig. 2. Total Hg (THg) and methylmercury (MeHg) concentrations in Antarctic krill (Euphausia superba) collected from coastal, shelf, and slope waters west of the Antarctic Peninsula at the northern transect (65°S to 64°S) during the austral summers of 2011, 2013, 2014, and 2015. Box plots show mean (black dashed lines), median (grey lines), minimum, 1st and 3rd quartiles, maximum, and outlier (circles) values for adult (red) and juvenile (blue) krill for all years (A and B) and within each year (C). Asterisks indicate significantly different mean values between adults and juveniles at P < 0.005 (I), P < 0.001 (II). Significant differences (p < 0.05) within year pair-wise combinations of juvenile and adult krill were tested using a Games-Howell post-hoc test (Supplementary Table 1).
In krill from the northern transect, the average fraction of THg present as methylmercury (%MeHg) varied from 10 to 26% and 5 to 17% in juvenile and adult Antarctic krill, respectively (Table 1). Although the relationships between %MeHg and MeHg concentration in individual krill were significant in both juveniles and adults (p < 0.001), there was considerably more scatter for juveniles, especially in juvenile krill with MeHg concentrations >2.00 ng g⁻¹ (Fig. 3A and B). The concentration of THg in krill was strongly correlated (p < 0.001, R² = 0.97) to inorganic Hg (THg minus MeHg), but weakly correlated (p < 0.005, R² = 0.12) to MeHg (Fig. 4A and B). In both juvenile and adult krill, THg accumulated primarily in soft tissue (53 ± 1% juveniles; 69 ± 1% adults), while MeHg accumulated primarily in muscle (61 ± 5% juveniles; 54 ± 2% adults) (Table 2). Exoskeleton accounted for 19% and 14% of THg, and 17% and 18% of MeHg in juvenile and adult krill, respectively.

### 3.2. Mercury concentrations in juvenile vs. adult Antarctic krill (E. superba) subpopulations near the southern sea ice edge

In krill from the northern transect, the average fraction of THg present as methylmercury (%MeHg) varied from 10 to 26% and 5 to 17% in juvenile and adult Antarctic krill, respectively (Table 1). Although the relationships between %MeHg and MeHg concentration in individual krill were significant in both juveniles and adults (p < 0.001), there was considerably more scatter for juveniles, especially in juvenile krill with MeHg concentrations >2.00 ng g⁻¹ (Fig. 3A and B). The concentration of THg in krill was strongly correlated (p < 0.001, R² = 0.97) to inorganic Hg (THg minus MeHg), but weakly correlated (p < 0.005, R² = 0.12) to MeHg (Fig. 4A and B). In both juvenile and adult krill, THg accumulated primarily in soft tissue (53 ± 1% juveniles; 69 ± 1% adults), while MeHg accumulated primarily in muscle (61 ± 5% juveniles; 54 ± 2% adults) (Table 2). Exoskeleton accounted for 19% and 14% of THg, and 17% and 18% of MeHg in juvenile and adult krill, respectively.

#### Table 2

<table>
<thead>
<tr>
<th>Tissue</th>
<th>Developmental stage</th>
<th>Dry weight</th>
<th>THg (%)</th>
<th>MeHg (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muscle</td>
<td>Juveniles</td>
<td>43.5</td>
<td>28 ± 6</td>
<td>61 ± 5</td>
</tr>
<tr>
<td></td>
<td>Adults</td>
<td>33</td>
<td>18 ± 3</td>
<td>54 ± 2</td>
</tr>
<tr>
<td>Soft tissue</td>
<td>Juveniles</td>
<td>27.5</td>
<td>53 ± 1</td>
<td>22 ± 6</td>
</tr>
<tr>
<td></td>
<td>Adults</td>
<td>35</td>
<td>69 ± 1</td>
<td>28 ± 1</td>
</tr>
<tr>
<td>Exoskeleton</td>
<td>Juveniles</td>
<td>29.0</td>
<td>19 ± 1</td>
<td>17 ± 4</td>
</tr>
<tr>
<td></td>
<td>Adults</td>
<td>32</td>
<td>14 ± 0</td>
<td>18 ± 1</td>
</tr>
</tbody>
</table>

* An additional dissection of 6 adults and 6 juveniles was used to determine dry weight percentages of krill tissue.
0.05) higher %MeHg than adults in 2014, however, in 2013 percentages of MeHg were significantly higher (P < 0.05) in adults than juveniles.

### 3.3. Cross-shelf and latitudinal comparisons of mercury concentrations in Antarctic krill (E. superba) along the Antarctic Peninsula

In juvenile and adult Antarctic krill from northern sites, mean THg concentrations varied over a wider range (4.04 to 19.4 ng g\(^{-1}\)) in krill collected near the coast than in krill collected farther offshore on the continental shelf and slope (6.23 to 12.6 ng g\(^{-1}\)) (Table 1). Within 2013, concentrations of THg were slightly higher in juvenile krill near the coast than those on the continental shelf (9.23 and 7.85 ng g\(^{-1}\), respectively). In contrast, THg concentrations of adult krill collected in offshore slope waters in 2014 were significantly higher (P < 0.05) than coastal individuals (Table 1, Supp. 1) and higher than adults in 2011, 2013, and 2015 (Table 1). Methylmercury mean concentrations varied from 0.26 to 2.94 ng g\(^{-1}\) and 0.95 ng g\(^{-1}\), respectively; P = 0.70), nor in juveniles from the shelf in 2013 were lower than coastal krill in 2011, 2014, and 2015 and significantly lower (P < 0.05) than coastal juveniles sampled within the same year (Table 1, Supp. 1). Methylmercury concentrations in adult krill from the coast in 2014 were relatively higher than krill offshore of the shelf break within the same year.

Mean concentrations of THg among juvenile and adult krill collected near the sea ice edge in the south varied over a higher range (4.47 to 9.12 ng g\(^{-1}\)) on the continental shelf than in offshore, slope waters (2.20 to 7.88 ng g\(^{-1}\)) (Table 3). The average concentration of THg was more than two-fold, higher in adult krill collected on the continental shelf than on the slope, while similar THg concentrations were measured in juvenile krill collected in 2013 on the shelf and in 2014 on the continental slope. Mean MeHg concentrations in juvenile and adult krill collected near the sea ice edge varied from 1.03 to 2.11 ng g\(^{-1}\) in krill collected on the continental shelf, and from 0.13 to 1.82 ng g\(^{-1}\) in krill collected offshore of the shelf break. Methylmercury was lower in shelf juveniles collected in 2013 than in slope juveniles from 2014, but MeHg concentrations were similar in juveniles collected in 2014 (slope) and 2015 (continental shelf).

Across all sampling years, average THg concentrations were significantly higher in adults collected in the north near Anvers Island than 700 km to the south near the summer sea ice edge (7.76 and 4.52 ng g\(^{-1}\), respectively; P < 0.001). This pattern was the same for juveniles from northern and southern sites (12.6 ng g\(^{-1}\), and 7.51 ng g\(^{-1}\), respectively; P < 0.001) (Figs. 2B and 5B). However, average MeHg concentrations across all years were not significantly different in adults collected in the north and the south near the sea ice edge (0.89 and 0.95 ng g\(^{-1}\), respectively; P = 0.70), nor in juveniles from the north and the south (2.03 ng g\(^{-1}\), and 1.71 ng g\(^{-1}\), respectively; P = 0.12) (Figs. 2B and 5B).

### 4. Discussion

#### 4.1. Total mercury and methylmercury concentrations in Antarctic krill (E. superba) west of the Antarctic Peninsula

Concentrations of total Hg (THg) measured in Antarctic krill collected near Anvers Island in the present study are similar to those for Antarctic krill collected near the northern tip of the WAP during the austral summer (8 ng g\(^{-1}\)) (Brasso et al., 2012) and in feed meal (8 ng g\(^{-1}\)) (Moren et al., 2006) and dietary supplements (13 ng g\(^{-1}\)) (Leblond et al., 2008) prepared from Southern Ocean Antarctic krill. However, they are lower than THg concentrations in Antarctic krill collected along the WAP during the fall of 1993 (13 to 49 ng g\(^{-1}\)) (Locarnini

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### Table 3

Sea Ice Edge Antarctic Krill (Euphausia superba). Concentrations (mean ± standard deviation) of total Hg (THg) and methylmercury (MeHg) in krill (n) collected from coastal and shelf waters at the sea ice edge west of the Antarctic Peninsula in the austral summers of 2011, 2013, 2014, and 2015.

<table>
<thead>
<tr>
<th>Year</th>
<th>Organism</th>
<th>WAP Region</th>
<th>Lat (°S)</th>
<th>Long (°W)</th>
<th>[THg] (ng g(^{-1}), dry wt)</th>
<th>[MeHg] (ng g(^{-1}), dry wt)</th>
<th>MeHg/THg (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>Adult</td>
<td>Shelf</td>
<td>69.1</td>
<td>76.4</td>
<td>1.22 ± 0.37 (5)</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>2013</td>
<td>Juvenile</td>
<td>Shelf</td>
<td>69.1</td>
<td>76.5</td>
<td>7.25 ± 1.20 (8)</td>
<td>1.07 ± 0.25 (8)</td>
<td>0.13 ± 0.06 (7)</td>
</tr>
<tr>
<td>2014</td>
<td>Juvenile</td>
<td>Shelf</td>
<td>69.1</td>
<td>76.5</td>
<td>4.47 ± 1.12 (9)</td>
<td>1.03 ± 0.24 (8)</td>
<td>24 ± 4 (7)</td>
</tr>
<tr>
<td>2015</td>
<td>Adult</td>
<td>Shelf</td>
<td>69.3</td>
<td>76.0</td>
<td>2.20 ± 0.52 (8)</td>
<td>0.13 ± 0.06 (7)</td>
<td>6 ± 3 (5)</td>
</tr>
</tbody>
</table>

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* Asterisks (*) indicate significant differences (p < 0.05) between co-located juveniles and adults within years based on two-tailed Student’s t-test.

b NA, not analyzed or samples failed quality criterion.
and Presley, 1995), near the South Orkney Islands and the Antarctic Polar Front (Séco et al., 2019), and nearly ten times lower than THg in Antarctic krill collected from the Ross Sea (77 ng g\(^{-1}\)) (Bargagli et al., 1998).

Distributions of MeHg in populations of Antarctic krill we measured encompass the value for the MURST-ISS-A2 krill standard reference material (1.1 ng g\(^{-1}\)) (Pacheco et al., 2010) and are slightly lower than krill from the Scotia Sea (2 to 8 ng g\(^{-1}\)) (Séco et al., 2019), the other reported analyses of MeHg in Southern Ocean krill.

Our observations of higher THg and MeHg concentrations in juvenile than adult krill, and previous findings that THg was higher in smaller and, presumably, younger krill (Locarnini and Presley, 1995; Séco et al., 2019), are unexpected since in other aquatic animals, Hg tends to accumulate to higher levels in larger, slower growing adults than in smaller, faster growing juveniles (McArthur et al., 2003; Hammerschmidt and Fitzgerald, 2006; Cossa et al., 2012; Lescord et al., 2015). Molting cannot account for these differences since exoskeleton renewal is faster in juvenile than adult krill (Daly, 1990) and would favor higher turnover and lower concentrations of Hg in juveniles. Moreover, most of the THg and MeHg in juvenile and adult krill was in muscle and other soft tissues, rather than exoskeleton (Table 2).

If MeHg is accumulated by krill nearly entirely from food, as is the case for other crustacean zooplankton (Wright et al., 2010), higher concentrations of MeHg in juvenile than adult krill indicate that juvenile krill have higher MeHg assimilation efficiencies from prey than adults, are less efficient at excreting MeHg, or consume prey with higher concentrations of bioavailable MeHg. Alternatively, MeHg concentrations may be lower in prey where adult krill predominantly feed such as in near surface waters (Wiebe et al., 2011; Siegel et al., 2013) or near the benthos (Clarke and Tyler, 2008). In this case, we would expect a slow biodilution of MeHg in Antarctic krill as they develop from juveniles into adults.

While physiological differences that may affect the assimilation and retention of Hg in juvenile and adult krill are beyond the scope of this study, we can address the potential influence of environmental factors on the accumulation of Hg among various krill populations.

4.2. Influence of proximity to shore and coastal sea ice on higher mercury accumulation in juvenile Antarctic krill

Greater accumulation of THg and MeHg in juvenile than adult krill along the WAP may reflect the longer periods of time juveniles spend in the nearshore (coastal) environment (Lascara et al., 1999; Daly, 2004; Daly and Zimmerman, 2004; Siegel et al., 2013). Nearshore marine surface waters and coastal bays along the WAP receive Hg from atmospheric depletion events (Ebinghaus et al., 2002; Bargagli et al., 2005; Mascromonaco et al., 2016). In addition, runoff of glacial meltwater during summer months, which is a pulsed source of inorganic Hg and other heavy metals to coastal Arctic environments (Douglas et al., 2017), may provide a seasonal source of Hg to the coastal Antarctic. Over decades, glacial retreat along the Antarctic Peninsula (Cook et al., 2005; Cook et al., 2016) may result in the perennial release of Hg accumulated in glaciers over millennia. Higher Hg accumulation in proximity to the coast was more evident in krill west of Anvers Island (Table 1) than near the sea ice edge (Table 3). This is likely attributed to higher inputs of Hg from atmospheric deposition to ice-free, northern surface waters, and glacial retreat, which began earlier at northern latitudes than farther south (Cook et al., 2005). Sea ice may also provide a source of Hg to coastal waters along the WAP. In the East Antarctic, dissolved THg and MeHg concentrations are higher near the shore and in seawater in proximity to coastal sea ice than in the open Southern Ocean (Cossa et al., 2011; Gionfriddo et al., 2016). Furthermore, high proportions of THg in seawater as MeHg are found under sea ice in the Arctic (St Louis et al., 2007). Sea ice has been identified as a potential site of methylmercury production based on the identification of a microorganism containing a gene related to those required for Hg methylation (Gionfriddo et al., 2016; Sunderland and Schartup, 2016), although the methylation of Hg in sea ice has not been directly measured. Despite higher MeHg concentrations in the dissolved phase under sea ice in the Arctic and Antarctica, there is little evidence that this MeHg is accumulated by marine zooplankton. The observation that regions of high sea ice coverage may provide little food for developing krill in winter (Meyer et al., 2017) suggests that exposure to MeHg through feeding under sea ice is not an important route of Hg accumulation. However, the importance of melting sea ice as a direct source of Hg to juvenile krill requires further investigation.

4.3. Influence of primary and export production on mercury accumulation in juvenile Antarctic krill

Phytoplankton production and the associated export of (POM) may indirectly support higher Hg accumulation in juvenile than adult krill along the WAP by means of shifts in foraging ecology during krill development and differences in the bioavailability of Hg bound to biogenic particles at various depths. Primary productivity along the WAP is driven in part by variations in annual sea ice conditions (Saba et al., 2014) such that high rates of summertime production are typically associated with high extents of annual sea ice the preceding winter (dataset) (Stammerjohann, 2017). For example, increased total surface area of sea ice and a later sea ice retreat during the 2013/2014 austral spring/summer compared with previous and subsequent years resulted in a very productive austral summer in the areas from which krill were collected for this study (Supplementary Figs. 2, 3, and 4).

High rates of primary production along the WAP are coupled to high vertical fluxes of biogenic particles (Buesseler et al., 2010) and enhanced production of heterotrophic bacteria (Ducklow et al., 2012). Exported particles may undergo transformations at depth converting POM and bound metals, such as Hg, into more bioavailable forms in deeper waters where larval krill spend most of their time and where juvenile krill are often present in greater abundance than adults (Brinton, 1991; Marin et al., 1991; Ashjian et al., 2004). Larval and juvenile krill have limited mobility compared to free-swimming adults known to form swarms where few juvenile krill are present (Watkins et al., 1992). Holoplanktonic larval and juvenile krill may reside longer in deeper waters thus resulting in increased feeding below the epipelagic zone (Ashjian et al., 2008) and therefore have a greater opportunity to accumulate Hg through the ingestion of sinking particulate matter than adults.

The export and transformation of sinking particles releases aqueous inorganic mercury (Hg\(^{2+}\)) into the dissolved phase at depth (Cossa et al., 2011; Blum et al., 2013; Heimburger et al., 2015; Munson et al., 2015; Renedo et al., 2018). Juvenile krill residing in subsurface waters may therefore accumulate Hg\(^{2+}\) the dominant form in water, through direct uptake from the dissolved phase (Wright et al., 2010). The accumulation of variable amounts of inorganic Hg by juvenile krill may explain why the relationship between %MeHg (MeHg/THg) and MeHg concentrations was more variable for juvenile krill than adult krill (Fig. 3). While the krill examined in this study were collected at relatively shallow depths (0–120 m), total Hg and MeHg concentrations were significantly higher in juveniles than adults at both northern and southern latitudes only in the highly productive summer of 2014 (Tables 1, 3, Fig. 2C). This suggests that greater sea extent along the Peninsula in 2014, which leads to a more strongly stratified surface-mixed layer and higher primary production rates (Vernet et al., 2008; Vennables et al., 2013) provided favorable conditions for higher Hg accumulation than in other years in this study.

In addition to the transfer of particle-bound Hg from surface to deep waters, high primary production along the WAP may also favor subsurface production of MeHg in the marine water column (Lehnherr et al., 2011). Mercury methylation has been measured in settling particles of oxic lakes (Diez et al., 2016), on surfaces of marine aggregates in the laboratory (Ortiz et al., 2015), and in the water column of Lake Melville, a
large estuary (Schartup et al., 2015). However, redox conditions in the well-mixed and oxygenated WAP water column (Mastromonaco et al., 2017) are unfavorable for the growth of known Hg methylating microorganisms, which are all anaerobes (Gilmour et al., 2013), and anaerobic bacteria capable of Hg methylation have yet to be identified in seawater of oxygen deficient zones (Malcolm et al., 2010; Gionfriddo et al., 2016). The production of MeHg in the coastal Southern Ocean water column has yet to be demonstrated and the responsible biological or abiotic pathways for this production remain to be examined.

4.4. Varying patterns of MeHg and THg accumulation between northern and southern Antarctic krill

Despite geographic differences, MeHg concentrations in adult and juvenile Antarctic krill varied over relatively narrow and similar ranges in northern (0.26 to 1.61 ng g⁻¹ and 0.74 to 2.94 ng g⁻¹ respectively) and southern (0.13 to 1.50 ng g⁻¹ and 1.07 to 2.11 ng g⁻¹ respectively) populations. This suggests similar levels and routes of MeHg exposure in krill across WAP waters from Anvers Island to the sea ice edge in the south.

Although no geographical differences were seen in MeHg accumulation of juvenile and adult krill along the WAP, concentrations of THg (primarily inorganic Hg) were significantly higher in adult (P < 0.001) and juvenile (P = 0.001) krill west of Anvers Island than in krill sampled at the sea ice edge across all sampling years. This may reflect a greater accumulation of inorganic Hg in subpopulations of Antarctic krill in the north than near the annual sea ice edge. Although the sources and bioavailability of various forms of inorganic Hg to krill is unknown, this result suggests that sea ice has little direct contribution to THg accumulation in Antarctic krill.

Although MeHg accounts for a minor fraction of THg in WAP krill (Tables 1, 3, Fig. 3A, B), MeHg biomagnifies in marine food webs, while inorganic Hg decreases at successive trophic levels (Mason et al., 1996; Stern and Macdonald, 2005). Thus, the comparatively small amounts of MeHg in juvenile and adult krill are critical to the accumulation of Hg almost entirely as MeHg in top predators of the Antarctic food web.

5. Conclusions

In addition to providing an analysis of MeHg concentrations in coastal Southern Ocean populations of Antarctic krill, the present results clearly show that juvenile krill accumulate more total Hg and MeHg than adults. Proximity to the coast, krill development in deeper waters, and feeding at subsurface depths appear to be the dominant factors leading to greater accumulation of inorganic Hg and MeHg in juvenile krill than adults. The direct influence of sea ice on MeHg accumulation in krill along the WAP may be limited to the WAP coastline, but the role of melting sea ice requires further investigation. Moreover, sea ice may have an indirect effect on Hg accumulation in juvenile krill through the promotion of primary and export production and the transfer of particle-bound Hg from surface waters to depth where larval and juvenile krill feed. Further studies of MeHg in mesopelagic krill populations and their prey are needed to delineate the source of higher MeHg concentrations in juvenile Antarctic krill. MeHg is the form of mercury that biomagnifies in marine food webs and is most toxic in vertebrates, and the present results will be useful in predicting the accumulation of MeHg in higher trophic level consumers in productive coastal Antarctic ecosystems. Regardless of the mechanism(s) controlling the differential accumulation of MeHg in different developmental stages of Antarctic krill, our observations of higher concentrations of MeHg in juveniles than adults indicate that consumers of predominantly juvenile krill may accumulate more MeHg than consumers of adults. Finally, the geographic distribution of Antarctic krill in this region has contracted poleward due to changes in Antarctic climate, with the mean body size of krill increasing over time perhaps as a result of declining proportions of juvenile krill among these populations (Atkinson et al., 2019). Thus changes in krill abundance and differences in MeHg accumulation by developmental stage may result in long-term changes in the accumulation of MeHg in the WAP food web.

CRediT authorship contribution statement

Philip T. Sontag: Conceptualization, Formal analysis, Investigation, Methodology, Software, Visualization, Writing - original draft, Writing - review & editing. Deborah K. Steinberg: Investigation, Methodology, Project administration, Resources, Supervision, Validation, Writing - review & editing. John R. Reinfelder: Funding acquisition, Investigation, Project administration, Resources, Supervision, Validation, Writing - review & editing.

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Declaration of Competing Interest

The authors declare no competing financial interest.

Acknowledgements

We thank the Captain, officers, and crew of the ARSV Laurence M. Gould, and Raytheon Polar Services and Lockheed Martin personnel for their scientific and logistical support. This research was supported by the National Science Foundation Antarctic Organisms and Ecosystems Program (OPP NSF PLR 1440435), the NSF Chemical Oceanography Program (OCE-1634154), and a Hatch/McIntyre-Stennis grant through the New Jersey Agricultural Experiment Station. This is contribution number XXX from the Virginia Institute of Marine Science.

A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.06.176.

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