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# Influence of the Arctic Sea-Ice Regime Shift on Sea-Ice Methylated Mercury Trends

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1 **Influence of Arctic Sea-Ice Regime Shift on Sea-Ice Methylated Mercury**  
2 **Trends**

3  
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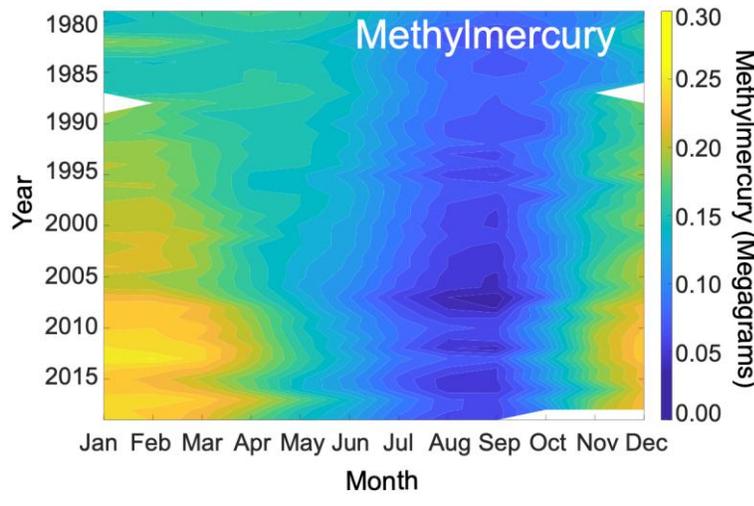
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15  
16 **Abstract**

17 Arctic sea-ice regulates the air-sea exchange of volatile mercury (Hg) species like  
18 dimethylmercury (DMHg) or elemental Hg, and is known to host Hg methylating microbes that  
19 produce neurotoxic and biomagnifying monomethylmercury (MMHg). Arctic sea-ice accounts  
20 for 57% of the total primary production in the Arctic Ocean suggesting that it could be the main  
21 source of MMHg to arctic food-webs. Despite this, little is known about Hg concentrations and  
22 speciation in arctic sea-ice. Here, we report Hg species and show the importance of sea ice  
23 composition on sea-ice methylmercury (MeHg = DMHg+MMHg) budgets. We propose that the  
24 shift from older sea-ice (lower MeHg) to younger sea-ice (higher MeHg) resulted in a 40%  
25 increase in MeHg (per m<sup>2</sup> of sea-ice) since 1979 despite a 45% decline in the total sea-ice

26 volume. About 30% of the MeHg sea-ice budget is DMHg, this means that when the sea-ice  
27 melts in the summer it could contribute  $0.03 - 2.7 \text{ pmol m}^{-2} \text{ day}^{-1}$  of DMHg to the atmosphere  
28 which is comparable to diffusion from water ( $0.48 - 2.8 \text{ pmol m}^{-2} \text{ day}^{-1}$ ). This study shows that  
29 the MeHg content of rapidly shrinking arctic sea-ice and exposure of sea-ice biota may not be  
30 declining as previously thought.



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34 **TOC abstract**

35

36 **Keywords:** Dimethylmercury, monomethylmercury, climate change, GEOTRACES

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45 **Introduction**

46 The Arctic Ocean's unique physical characteristics and food-web structure influence the  
47 biogeochemical cycle of neurotoxic monomethylmercury (MMHg), allowing it to reach high  
48 levels in arctic biota.<sup>1,2</sup> In the Arctic, MMHg is a health concern for marine wildlife and human  
49 communities dependent on arctic ecosystems for hunting and fishing.<sup>1,3</sup> Among the physical  
50 characteristics, the presence of sea-ice has been identified as a possible explanation for the  
51 higher production and biomagnification of MMHg observed in the Arctic Ocean.<sup>2</sup> Sea-ice  
52 regulates air-sea exchange of volatile Hg species (elemental Hg-Hg<sup>0</sup> and dimethylmercury -  
53 DMHg) by capping the water column and letting Hg build up under the ice.<sup>4,5</sup> The mechanism of  
54 sea-ice production and melting creates a highly stratified surface water column that has been  
55 proposed to enhance MMHg production.<sup>6-8</sup> Sea-ice can also impact MMHg exposure through  
56 biologically mediated MeHg production within the sea-ice itself, as suggested by Beattie *et al.*<sup>9</sup>  
57 based on a study of total methylated Hg species (MeHg = MMHg + DMHg) in two arctic sea-ice  
58 cores. Several studies showed a positive correlation between chlorophyll a (a proxy for primary  
59 production) and MeHg concentration in arctic and antarctic sea-ice, suggesting that MeHg is  
60 biologically produced.<sup>9-11</sup> Recently, Gionfriddo *et al.*<sup>11</sup> further identified putative Hg  
61 methylating bacteria (*Nitrospina*) in antarctic first-year ice (FYI) and arctic frost flowers, but the  
62 mechanism of Hg methylation in sea ice remains unknown. Compared to other arctic MMHg  
63 reservoirs the total amount of MMHg stored in sea-ice is small,<sup>12</sup> but arctic sea-ice algae and  
64 sub-ice phytoplankton account for 57% of the total annual primary production in the Arctic  
65 Ocean.<sup>13,14</sup> This implies that MMHg produced in the sea-ice and bioaccumulated by sea-ice  
66 algae, may contribute disproportionately to arctic biota MMHg exposure. Since 1958, the average

67 sea-ice thickness has declined by over 60% (more than 2 m).<sup>15</sup> Between 2002 and 2017, the  
68 Arctic has lost more than 50% of its oldest multi-year ice (MYI),<sup>15</sup> and is undergoing a regime  
69 shift from a system dominated by MYI (until 2011) to a system dominated by seasonal ice (FYI).  
70 Despite these concerns, relatively few studies have reported concentrations of Hg and MeHg in  
71 sea-ice.<sup>5,9,16</sup> To address this gap, we collected 6 ice cores (2 MYI and 4 FYI), brine, frost  
72 flowers, under-ice water, and melt pond water and ice during the 2015 German GEOTRACES  
73 expedition (GN04). We measured total Hg and MeHg in all the samples and MMHg and DMHg  
74 in 3 of the cores. To extend the spatial coverage of this study we combine our data with sea-ice  
75 total Hg and MeHg samples from 5 additional locations collected in 2015 during the U.S.  
76 GEOTRACES expedition (GN01).<sup>5</sup>

77

## 78 **Methods**

79 Six cores were collected between Aug 25 and Sept 22 during the 2015 GEOTRACES expedition  
80 (Figure 1A, Figure S1). At each site, a Kovacs 9 cm diameter corer (Kovacs Enterprise,  
81 Roseburg, USA) was used. Once retrieved, the cores were sectioned into 10 cm slices, cleaned  
82 with a ceramic knife and transferred into clean plastic bags. The slices were thawed and  
83 transferred into trace metal clean bottles (Nalgene FEP Teflon) while still very cold to minimize  
84 loss of volatile Hg. All samples were acidified to 0.4 % v:v with double-distilled hydrochloric  
85 acid. Temperature and salinity of each slice were measured during and shortly after collection,  
86 respectively (Figure S2). Two of the 6 cores were identified as MYI (Cores 2 and 5) on site.<sup>17</sup>  
87 We also measured total Hg and MeHg in 1 brine, 1 frost flower, 7 under ice seawater, 5 melt  
88 pond water, 2 melt pond ice, and 3 snow samples (Table S2). All samples were shipped and  
89 analyzed for total Hg and MeHg at Harvard University in May 2016 (Figure S3 and S4). We

90 followed well-established analytical procedures for low level total Hg and MeHg  
91 measurements.<sup>18-20</sup> Detailed methods and nutrient profiles are provided in the Supporting  
92 Information (Figure S5). MMHg was measured on samples from which DMHg had been  
93 removed by purging onboard prior to acidification. DMHg was calculated as the difference  
94 between MeHg and MMHg,<sup>21,22</sup> and inorganic Hg ( $\text{Hg}^{\text{II}}$ ) as the difference between total Hg and  
95 MeHg (Figure S3). Table 1 summarizes the Hg speciation and ancillary data in the collected sea-  
96 ice cores. We calculated the brine volume according to Cox & Weeks.<sup>23</sup>  
97  
98 To estimate the impact of the shift from MYI dominated to FYI dominated sea-ice on MeHg, we  
99 obtained monthly sea-ice volumes and total sea area trends from 1979 to 2019 from the U.S.  
100 National Snow and Ice Data Center.<sup>24</sup> We use this information and the empirical relationship  
101 between sea-ice volume and MYI area reported by Kwok<sup>15</sup> to estimate respective contributions  
102 of FYI and MYI to the sea-ice volume and to the sea-ice MeHg budgets from 1979 to 2019.  
103 Total Hg concentrations measured in sea-ice cores in this study,  $2.72 \pm 2.31$  pM ( $n = 78$ ), are not  
104 statistically different (1-way ANOVA,  $p = 0.92$ ,  $n = 126$ ) from concentrations reported by  
105 DiMento *et al.*,<sup>5</sup>  $2.54 \pm 1.46$  pM ( $n = 44$ ; Figure S6). To increase the spatial coverage of this  
106 study, we include the DiMento *et al.*<sup>5</sup> sea-ice data in subsequent calculations. For continuity, we  
107 rename their cores 7-11 (Figure 1A). The cores in DiMento *et al.*<sup>5</sup> were not identified as FYI or  
108 MYI (Table S1), thus we rely on the sea-ice thickness reported for the coring sites in Marsay *et*  
109 *al.*<sup>16</sup> and the relationship between sea-ice thickness and age<sup>25</sup> to differentiate the cores (FYI:  
110 Core 7, 9; MYI: Cores 8, 10 and 11). All statistical analyses are done in MATLAB (Mathworks,  
111 version R2019b).  
112

## 113 Results and Discussion

114

115 Total Hg varies within cores, with concentrations typically higher near the surface that decline  
116 sharply with core depth (Figure 1B; Figure S3). For example, in Core 4, concentrations span  
117 from 0.96 to 16.1 pM. Total Hg concentrations in brine, melt ponds water and ice, under ice  
118 water and snow fall within the ranges measured in the sea-ice cores and range from 2.6 pM in  
119 snow to 17.3 pM in brine (SI Table S2). There is no statistical difference (1-way ANOVA,  $p =$   
120  $0.34$ ,  $n = 110$ ) between total Hg concentrations in FYI ( $3.00 \pm 2.56$  pM,  $n = 57$ ) and MYI cores  
121 ( $2.57 \pm 2.16$  pM,  $n = 53$ ).

122

123 Similar to total Hg, MeHg varies within each core (Figure S4). For example, MeHg  
124 concentrations in Core 3 range from 0.024 to 0.293 pM (Figure 1C). But the location of peaks is  
125 not always at the surface, MeHg peaks are also seen at depth in FYI cores (Core 4, Figure 1C).  
126 MeHg levels in brine, melt ponds water and ice, under ice water and snow also fall within ranges  
127 measured in the sea-ice cores, from 0.05 pM in snow to 0.19 pM in brine (Table S2). MeHg  
128 concentrations in MYI ( $0.026 \pm 0.018$  pM,  $n = 52$ ) cores are lower (1-way ANOVA,  $p < 0.01$ ,  $n$   
129  $= 109$ ) than in FYI cores ( $0.102 \pm 0.071$  pM,  $n = 57$ ). Since the total Hg (and  $\text{Hg}^{\text{II}}$ )  
130 concentrations in FYI and MYI cores are not significantly different, %MeHg is lower in MYI  
131 than FYI cores. Since  $\text{Hg}^{\text{II}}$  concentrations are similar in both types of cores, the difference in  
132 MeHg is probably not due to  $\text{Hg}^{\text{II}}$  limitation, but may instead be due to biological or chemical  
133 differences between the two types of sea-ice cores that affect *in situ* production or degradation of  
134 MeHg from  $\text{Hg}^{\text{II}}$ .<sup>11,26,27</sup>

135

136 Methylmercury peaks in FYI Cores 3 and 4 seem to be dictated by peaks in DMHg rather than  
137 MMHg (Figure 1C). On average DMHg is 34% of MeHg in the 3 cores where DMHg and  
138 MMHg were determined, but peaks at >90% at 120 cm in Core 4 (Figure 1C). The distribution of  
139 DMHg within cores is consistent with physically driven processes of bubble nucleation and  
140 migration observed for inert gases such as argon in FYI.<sup>11,28</sup> Since very little field data exists on  
141 trace gas bubble formation and diffusion through the sea-ice, modeling approaches have been  
142 used to test different hypotheses. Moreau *et al.*<sup>29</sup> showed that upward moving argon gas bubbles  
143 explain the change in argon profiles from a bottom peak found in “Early Spring” to a surface  
144 peak found in “Late Spring”. They explain the migration by the melting of the sea-ice allowing  
145 brine channels to form (increasing the brine volume) and bubbles to rise. This is consistent with  
146 our data where Core 3 has a lower brine volume (4.3%) than Core 4 (5.1%, Figure S7). Core 3’s  
147 DMHg profile aligns well with the “Early Spring” scenario while DMHg in Core 4 follows the  
148 “Late Spring” scenario in Moreau *et al.*,<sup>29</sup> indicating that DMHg is at different stages of evasion.  
149

150 We compare potential DMHg release from sea-ice to air with its diffusion from water column to  
151 air. Assuming that DMHg behaves similarly to argon, as described by Moreau *et al.*,<sup>29</sup> it builds  
152 up in the sea-ice during the winter months (January through May/June) and is released to the  
153 atmosphere in the spring when sea-ice starts melting.<sup>30</sup> We calculate that approximately 75 km<sup>3</sup>  
154 day<sup>-1</sup> of FYI are lost due to sea-ice melt between peak and low volume in 2015 (120 days). If  
155 DMHg concentrations are uniform across all the cores (0.030 pM on average, ranging from  
156 0.003 – 0.32 pM), 2.3 mol day<sup>-1</sup> of DMHg (0.23- 24 mol day<sup>-1</sup>) are released from the sea-ice  
157 during the melt season. Thus, melting sea-ice could release 0.25 pmol m<sup>-2</sup> day<sup>-1</sup> of DMHg over  
158 the sea-ice area in 2015 to the marine boundary layer (ranging from 0.03 - 2.7 pmol m<sup>-2</sup> day<sup>-1</sup>).

159 This is a conservative estimate since sea-ice only needs to reach a threshold porosity level (5-  
160 7%), not completely melt, to start releasing DMHg, and some DMHg may have already been lost  
161 prior to our sampling.<sup>29</sup> To compare the sea-ice DMHg release to diffusion from the water  
162 column, we calculate diffusion using a surface water DMHg (1 m; 2015 U.S. GEOTRACES)  
163 concentrations from Agather *et al.*<sup>31</sup> most of which were below their detection limit of 0.012 pM,  
164 atmospheric DMHg concentrations measured by Baya *et al.*<sup>4</sup> for 30% ice cover (0.037 pmol m<sup>-3</sup>),  
165 and wind speed from Lesins *et al.*<sup>32</sup> (3 m s<sup>-1</sup> at 10.4 m). We obtain a diffusion rate from the water  
166 column ranging from 0.48 to 2.8 pmol m<sup>-2</sup> day<sup>-1</sup> depending on the relationship between gas  
167 exchange and wind speed used.<sup>33-35</sup> This flux is in the same range as our conservative estimate  
168 on DMHg degassing from melting sea-ice, which suggests two major impacts on the Arctic  
169 Ocean Hg cycle. 1) It shows that sea-ice is an important source of DMHg to the arctic  
170 atmosphere, and 2) that the early spring release of DMHg to the atmosphere from melting sea-ice  
171 could reduce the concentration gradient between water and air thereby dampening the DMHg  
172 diffusion from the water column.

173

174 MeHg levels in FYI cores ( $0.102 \pm 0.071$  pM,  $n = 57$ ) are about 4 times greater than in MYI  
175 cores ( $0.026 \pm 0.018$  pM,  $n = 52$ ). Therefore, we hypothesize that all things kept equal a shift  
176 from MYI to FYI could significantly impact the sea-ice MeHg budget and average  
177 concentrations which could lead to higher sea-ice biota exposure.<sup>1,36</sup> To test this, we calculate the  
178 temporal variability of the MeHg budget considering the impact of the shifts in FYI and MYI.  
179 The purpose of this calculation is to evaluate whether the magnitude of the shift alone, while all  
180 other parameters are kept constant, could result in a different overall trend in the sea-ice MeHg  
181 budget. We do not consider other potential changes that may dampen or exacerbate MeHg

182 concentrations in sea-ice, nor do we attempt to simulate past MeHg concentrations. Figure 2 A  
183 and B illustrate the importance of considering MeHg concentrations in different sea-ice types. In  
184 Figure 2A, we applied the average MeHg concentration to the total volume of sea-ice. We find  
185 that the average sea-ice budget over the 41-year period is 0.33 Mg (ranging from 0.04 Mg for  
186 minimum MeHg and sea-ice volume year, to 1.0 Mg for maximum MeHg and sea-ice volume  
187 year). This is consistent with previously reported reservoir sizes of 0.3-2.6 Mg that were based  
188 on two sea-ice cores collected in the Beaufort Sea and M'Clure Strait.<sup>9,12</sup> This approach results in  
189 a MeHg decline of 5.2 kg year<sup>-1</sup> mirroring the overall decline in sea-ice volume. However, if we  
190 instead account for the regime shift from MYI to FYI and the different MeHg concentrations in  
191 two ice types over the same time period, we arrive at a sea-ice reservoir of 0.16 Mg (ranging  
192 from 0.07 to 0.31 Mg). But more importantly, we do not see a declining MeHg trend despite the  
193 45% sea-ice volume decline, instead we see a slight increase in MeHg of 1.3 kg year<sup>-1</sup>. The  
194 September trend (minimum sea-ice cover; bottom of the shaded blue area in Figure 2B) is  
195 declining 0.5 kg year<sup>-1</sup> because of the large decline in total sea-ice volume. The high bound in  
196 February (maximum sea-ice cover) is increasing 3.3 kg year<sup>-1</sup> driven by the FYI increase over  
197 time. The change in the MeHg mass budget corresponds to an increase in mass of MeHg per area  
198 of sea-ice from 15 ng m<sup>-2</sup> in the 1980s to 21 ng m<sup>-2</sup> in the 2010s (orange line on Figure 2B). This  
199 suggests a 40% increase in the exposure of sea-ice biota and underlines the importance of  
200 understanding MeHg biogeochemistry in different types of sea-ice.

201

202 This study shows that sea-ice plays a role in Hg biogeochemistry that extends beyond “just a  
203 cap” on water column processes. We find that FYI contains more MeHg (and DMHg) than MYI  
204 and calculate that the ongoing shift from a MYI to FYI dominated Arctic Ocean may cancel out

205 the previously expected decline in MeHg contributions from sea-ice. This finding as well as the  
206 shortened window between sea-ice melt and peak plankton activity,<sup>37,38</sup> may have consequences  
207 for the exposure of biota that relies on sea-ice for food and habitat. We also measured relatively  
208 large amounts of DMHg in FYI cores, sometimes reaching >90% of MeHg. A DMHg peak was  
209 for example found near the bottom of a core where sea-ice algae such as *Melosira arctica* was  
210 present. DMHg could passively diffuse through gills of animals feeding on sea-ice algae<sup>39</sup> and  
211 the implications of DMHg in sea-ice highlighted in this study needs further investigation.

212

213

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226

227 **Figure 1:** Mercury concentrations and speciation in arctic sea-ice. Panel (A) is a map showing

228 the location of sea-ice cores in dark blue (1-6) collected for this study during the 2015 German  
229 GEOTRACES cruise, GN04 carried out on board of the research icebreaker Polarstern (PS94,  
230 ARK XXIX/3, TransArc-II), and in light blue (7-11) published in DiMento *et al.*<sup>5</sup> and collected  
231 during the 2015 U.S. GEOTRACES expedition (GN01). The sea-ice extent is an August 16<sup>th</sup>,  
232 2015 Multisensor Analyzed Sea Ice Extent data product, US National Snow and Ice Data Center.  
233 Panel (B) shows total mercury (total Hg) profiles of Cores 3 and 4. Panel (C) shows  
234 monomethylmercury (MMHg), dimethylmercury (DMHg) and total methylated mercury (MeHg)  
235 distribution in Cores 3 and 4.

236

237 **Figure 2:** Sea-ice methylmercury (MeHg) budgets calculated from 1979 to 2019. **A.** Trend  
238 when differences in MeHg levels in multi-year and first-year ice are not considered. The shaded  
239 area captures the lowest (September) and highest (February) bounds of the sea ice MeHg  
240 budgets. **B.** The MeHg total mass budget, considering different contributions from multi-year  
241 and first-year sea-ice, is illustrated by the blue line. The blue shaded area captures the lowest  
242 (September) and highest (February) bounds of the sea-ice MeHg budgets. The MeHg mass per  
243 unit of sea-ice area is the orange line.

244

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**Table 1:** Summary of sea-ice core characteristics and mean speciated mercury (Hg) concentrations (the standard deviation represents downcore variability).

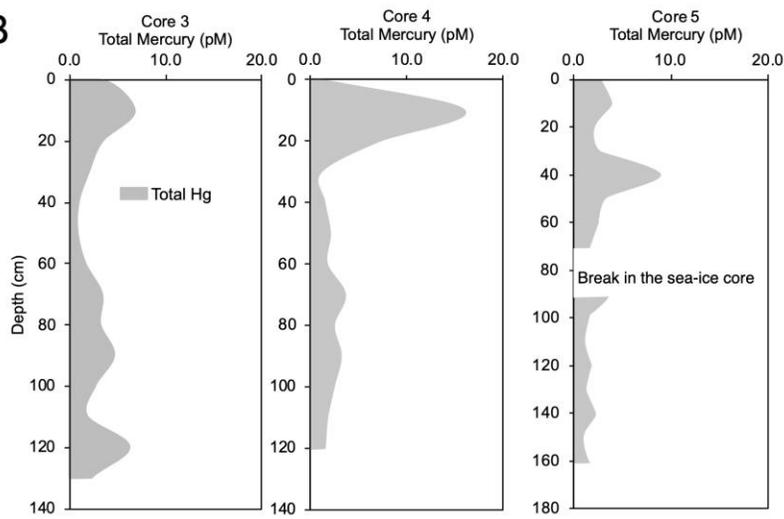
Sea-ice Core	Station	Core thickness cm	Sea-ice Temperature °C	Salinity	Total Hg <sup>†</sup> pM	MeHg <sup>‡</sup> pM	DMHg <sup>‡</sup> pM	MeHg: Total Hg %	DMHg: MeHg %
1	46	85	-1.07	1.31	2.7±3.2	0.120±0.028	--	8.2	--
2	54*	167	-1.57	2.38	2.6±3.1	0.016±0.015	--	1.1	--
3	69	133	-1.73	1.37	3.0±1.9	0.086±0.101	0.048±0.094	3.0	34
4	81	135	-3.40	2.79	3.6±4.6	0.085±0.076	0.027±0.032	2.3	26
5	96*	151	-1.90	3.02	2.6±1.9	0.032±0.017	0.015±0.015	1.0	41
6	101	135	-4.08	3.45	2.5±0.8	0.115±0.043	--	5.0	--

\* Multi-year sea-ice cores  
<sup>†</sup> The method detection limit is 0.08 pM  
<sup>‡</sup> The method detection limit is 0.011 pM

A



B



C

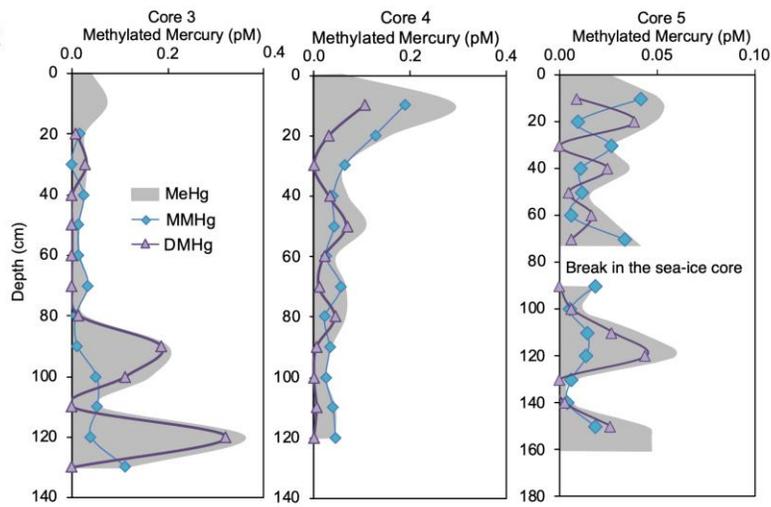
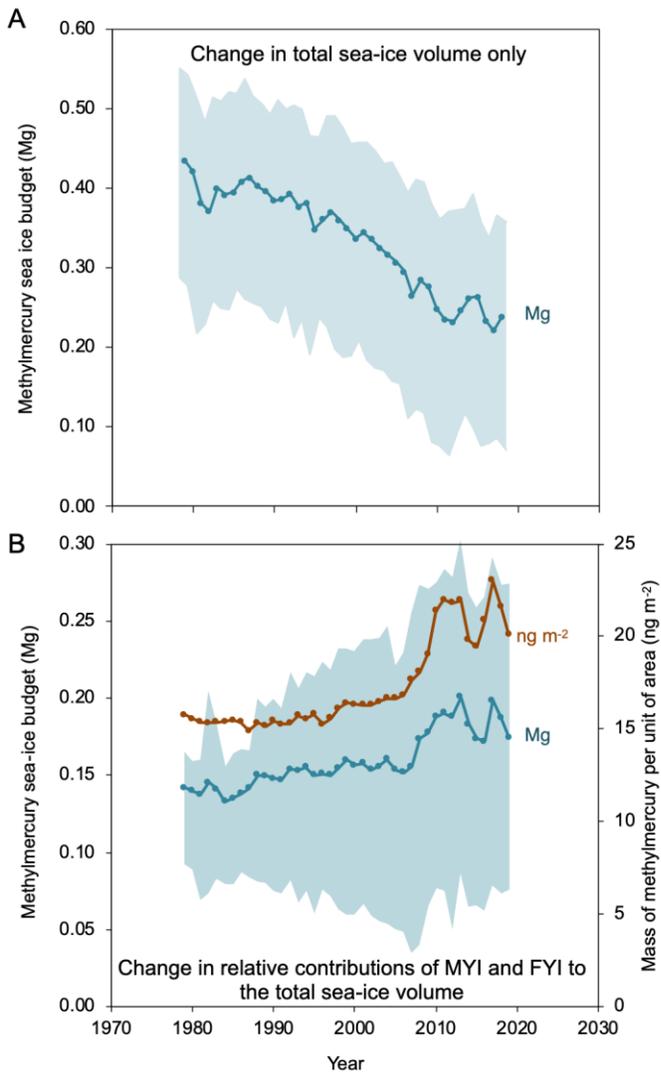


Figure 1

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**Figure 2**