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1 ***TITLE***

2 Arctic Ocean's wintertime Mercury concentrations limited by seasonal loss on the shelf

3

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21

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22 ***ABSTRACT***

23 High biota mercury levels are persisting in the Arctic, threatening ecosystem and human health.  
24 The Arctic Ocean receives large pulsed mercury inputs from rivers and the atmosphere. Yet, the  
25 fate of those inputs and possible seasonal variability of mercury in the Arctic Ocean remain  
26 uncertain. Until now, seawater observations were only possible during summer and fall. Here we  
27 report polar night mercury seawater observations on a gradient from the shelf into the Arctic  
28 Ocean. We observed lower and less variable total mercury concentrations during the polar night  
29 ( $0.46 \pm 0.07 \text{ pmol L}^{-1}$ ) compared to summer ( $0.63 \pm 0.19 \text{ pmol L}^{-1}$ ) and no significant changes in  
30 methylmercury concentrations (summer,  $0.11 \pm 0.03 \text{ pmol L}^{-1}$  and winter,  $0.12 \pm 0.04 \text{ pmol L}^{-1}$ ).  
31 Seasonal changes were estimated by calculating the difference in the integrated mercury pools.  
32 We estimate losses of inorganic mercury of  $208 \pm 41 \text{ pmol m}^{-2} \text{ d}^{-1}$  on the shelf driven by seasonal  
33 particle scavenging. Persistent methylmercury concentrations ( $-1 \pm 16 \text{ pmol m}^{-2} \text{ d}^{-1}$ ) are likely  
34 driven by gaseous species and a lower affinity for particles. Our results update the current  
35 understanding of Arctic mercury cycling and require budgets and models to be reevaluated with a  
36 seasonal aspect.

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37

### 38 *MAIN TEXT*

39 The Arctic Ocean and its biota exhibit elevated levels of toxic mercury (Hg)<sup>1</sup> despite an absence  
40 of important local anthropogenic sources. Mercury is delivered to surface waters of the Arctic  
41 Ocean through atmospheric deposition, inputs from other oceans, riverine discharge, snow and sea  
42 ice melt<sup>2</sup>. High inputs of mainly inorganic mercury (iHg) coincide with the Arctic's biologically  
43 active summer season<sup>3</sup>. However, data on inter- and intra-seasonal Hg concentrations in the Arctic  
44 Ocean, especially during the winter, is lacking so far. The discovery of springtime atmospheric Hg  
45 depletion events<sup>4</sup> over 20 years ago highlighted a distinct seasonal aspect to Hg biogeochemical

46 cycling in the Arctic. Recently, increased attention on pan-Arctic rivers have also confirmed  
47 riverine Hg inputs to the Arctic shelf seas during spring flood events<sup>5</sup>. With increasing evidence  
48 of a highly seasonal Arctic Hg cycle, a lack of seawater observations in winter indicates that the  
49 current paradigm of the Arctic Ocean Hg budget and fluxes are only a “summer snapshot”.

50

51 The seasonal transition from summer to winter in the Arctic Ocean is marked by decreased  
52 biological activity, weakened stratification, and sea ice growth. However, our understanding of Hg  
53 cycling during the Arctic winter is still largely based on assumptions with considerable  
54 uncertainty. Biogeochemical models suggest that water mixing during autumn resupplies Hg to  
55 upper waters<sup>6</sup>. The presence of sea ice restricts Hg exchange with the atmosphere<sup>7</sup> throughout  
56 autumn and winter, allowing potential buildup of gaseous mercury and dimethylmercury (DMHg)  
57 under sea ice<sup>8</sup>. As temperatures rise and light returns, sea ice melt and atmospheric inputs may  
58 explain increased springtime Hg concentrations in polar waters compared to winter Hg  
59 concentrations<sup>9</sup>. The spring freshet delivers additional Hg to surface waters from the major pan-  
60 Arctic rivers<sup>10</sup>. As a result, summer Hg observations in Arctic surface waters are elevated  
61 compared to deeper waters<sup>11</sup>.

62

63 Arctic surface waters lose significant amounts of Hg via atmospheric evasion or scavenging with  
64 sinking particles. During the summer, photochemical reduction of riverine Hg and subsequent  
65 evasion emits a significant fraction of gaseous Hg back to the atmosphere<sup>12</sup>. However, recent  
66 observations indicate low Hg evasion to the atmosphere in late summer and autumn<sup>8</sup>, suggesting  
67 particle scavenging dominates Hg losses from surface waters in autumn and winter. In addition,  
68 Arctic summer and autumn exhibit the highest total particulate matter fluxes due to peak primary

69 productivity<sup>13,14</sup>. Although particle fluxes decline in winter, dissolved Hg has a high affinity to  
70 particles due to high partitioning coefficients ( $K_D$ )<sup>15</sup>. Previous observations, models, and  
71 budgets<sup>2,12,16-19</sup> have hinted at the importance of scavenging of Hg on the shelf yet lack  
72 confirmation, especially during winter.

### 73 **Seasonal loss of Hg on the Arctic shelves**

74 We investigated a shelf to deep basin meridional transect in the northern Barents Sea in August –  
75 summer, and December – winter (Fig. 1). We sampled seawater for unfiltered total Hg (THg), the  
76 sum of all inorganic and organic Hg species, including both particulate and dissolved. We also  
77 collected seawater for unfiltered methylated mercury (MeHg), the sum of organic Hg species,  
78 monomethylmercury (MMHg) and DMHg.

79  
80 Average THg concentrations (Fig. 2) in summer are  $0.63 \pm 0.19$  pmol L<sup>-1</sup> (range: 0.38 – 1.36 pmol  
81 L<sup>-1</sup>, n = 60) and show a scavenged-type profile, similar to THg observations on previous  
82 summertime Arctic expeditions<sup>16,17,20-23</sup>. Our total Hg concentrations on the shelf (< 400 m depth,  
83 P1 – P5) are slightly higher and more variable compared to the shelf break (P6) and Nansen Basin  
84 (P7) stations (Fig. 2). We measured the highest THg concentrations in the polar mixed layer (< 20  
85 m) under the sea ice. The higher Hg concentrations are most likely from Hg contained in pico- and  
86 nanophytoplankton in addition to Hg input from melting sea ice. Elevated surface THg  
87 concentrations in the southerly open water stations (P1 – P3) might also suggest atmospheric  
88 deposition<sup>24</sup>. Average THg concentrations on our transect trend lower than the Canadian  
89 Archipelago and the Siberian shelf seas<sup>25</sup>, although this difference may be explained by the  
90 region's lack of major riverine sources and mixing of Hg-depleted Atlantic Water<sup>17</sup> and Hg-  
91 enriched Polar Water<sup>11,26,27</sup>.

92  
93 Our average THg concentrations in winter (Fig. 2) are  $0.46 \pm 0.07$  pmol L<sup>-1</sup> (range: 0.34 – 0.66  
94 pmol L<sup>-1</sup>, n = 61) and display less variability than summer concentrations (range: 0.38 – 1.36 pmol  
95 L<sup>-1</sup>). The THg concentrations in the stratified Nansen Basin (P7) continue to exhibit a scavenged-  
96 type profile, while THg concentrations on the shelf stations (P1 – P5) have changed to a more  
97 conservative-type profile. Average winter THg concentrations at shelf stations (P1 – P5) including  
98 all sampled depths were 28 – 41% less than summer. Our overall average winter THg  
99 concentrations are similar to summer THg concentrations in Atlantic Water ( $0.43 \pm 0.14$  pmol L<sup>-1</sup>)  
100 <sup>17</sup> yet less variable. However, all shelf stations except P1 retain Polar Water signatures with  
101 additional sea ice cover. Colder and saltier surface waters in winter display weaker stratification  
102 and suggest mixing throughout the autumn (Extended Data Figs. 1 and 2). Therefore, our lower  
103 winter THg concentrations in surface waters suggest THg is not resupplied from subsurface waters  
104 during autumn as previously thought. Weak stratification and mixing promote downward transport  
105 of particles<sup>28,29</sup>, where surface THg may be scavenged to deeper waters and sediments.

### 106 **Seasonal scavenging of inorganic Hg**

107 We investigated the scavenging dynamics of THg by calculating iHg (pmol L<sup>-1</sup>), the difference  
108 between THg and MeHg concentrations at each discrete sampling depth. Temporal changes in iHg  
109 between summer and winter are represented as  $\Delta$ iHg using the integrated seasonal difference  
110 between iHg concentrations at two depth intervals (Fig. 3). These calculated  $\Delta$ iHg quantities  
111 indicate a gain or loss in the total iHg pool. Six stations (P1 – P6) showed a negative  $\Delta$ iHg, or loss  
112 of iHg, by winter (Fig. 3). On average,  $\Delta$ iHg was  $-208 \pm 41$  pmol m<sup>-2</sup> d<sup>-1</sup> in the upper 100 m on the  
113 shelf (P1 – P5). By taking the absolute value of  $\Delta$ iHg, we can compare to directional fluxes. Our  
114 average  $|\Delta$ iHg| on the shelf is comparable to recent estimates of particulate Hg fluxes ( $173 \pm 78$

115 pmol m<sup>-2</sup> d<sup>-1</sup>) using a radiotracer approach<sup>19</sup>. While particulate Hg is approximately 17% of THg  
116 concentrations in the Barents Sea shelf<sup>19</sup>, our average seasonal iHg decrease of 39 – 50% in the  
117 upper 100 m (P1 – P5) suggests scavenging of both particulate and dissolved iHg species.

118  
119 Previous work has suggested Hg shelf scavenging along the continental margins<sup>30</sup> driven by strong  
120 Hg-particle interactions. Updated estimates of Hg-particle partition coefficients ( $K_D$ ) in the Arctic  
121 Ocean indicate high affinity to manganese and iron oxides<sup>31</sup>. We found high dissolved manganese  
122 (DMn) concentrations on the shelf in both summer and winter (Extended Data Fig. 3). Both DMn  
123 and total manganese (TMn, Extended Data Fig. 4) concentrations are highest near sediments<sup>32</sup>  
124 (Extended Data Figs. 3 – 5). Suboxic reducing conditions in shelf sediments supply Mn<sup>2+</sup> to the  
125 overlying water column through mixing, sediment resuspension and diffusion<sup>33</sup>. Here, we  
126 speculate that seasonal decreases of DMn on the shelf in the upper 100 m (P1 – P5, Extended Data  
127 Figs. 3 and 6) are due to oxidation to insoluble MnO<sub>2</sub>. Colloidal MnO<sub>2</sub> can form precipitates that  
128 can scavenge and shuttle iHg to deeper depths, similar to observations in the Baltic and the Black  
129 Seas<sup>34</sup>. In the absence of late summer POC fluxes, the DMn shuttle on the Arctic shelf may explain  
130 our seasonal losses of DMn (Extended Data Fig. 6), iHg (Fig. 3) and total lead (TPb, Extended  
131 Data Fig. 7). As TPb and THg have comparable  $K_D$  values for manganese particle phases in the  
132 Arctic Ocean<sup>35</sup>, our negative  $\Delta$ TPb values on shelf stations (P1 – P5, Extended Data Fig. 8) reflect  
133 similar trends to  $\Delta$ iHg (Fig. 3). A seasonal loss of TPb on the Barents Sea shelf (P1 – P5) agrees  
134 well with previous hypotheses of strong Pb scavenging on the Arctic shelves<sup>18,36-38</sup>.

135  
136 Losses of gaseous Hg from Arctic surface waters may also influence our seasonal loss of iHg. We  
137 evaluated Hg<sup>0</sup> losses from summer to winter by limiting  $\Delta$ iHg to the wind mixed layer (< 20 m).

138 We assumed our iHg concentrations at the shallowest sampling depth (approx. 10 m) were  
139 representative of the atmosphere-sea surface interface (0 m). Most stations (P1 – P6) exhibit a  
140 negative  $\Delta$ iHg, with an average  $\Delta$ iHg of  $-80 \pm 14$  pmol m<sup>-2</sup> d<sup>-1</sup> on the shelf (P1 – P5). By  
141 comparison, we calculated a net open water Hg<sup>0</sup> evasion rate of only 11 pmol m<sup>-2</sup> d<sup>-1</sup> from a late  
142 summer atmospheric evasion rate<sup>8</sup> combined with their suggested equal Hg inputs from deposition  
143 and meltwater. Accordingly, our low calculated Hg<sup>0</sup> evasion rate compared to high wind-mixed  
144 layer  $|\Delta$ iHg| values suggest minimal losses of gaseous Hg species.

### 145 **Persistent seawater MeHg**

146 While THg concentrations showed significant seasonal differences, average MeHg concentrations  
147 remained constant (Fig. 4). Average summer MeHg concentrations were  $0.11 \pm 0.03$  pmol L<sup>-1</sup>  
148 (range; 0.08 – 0.23 pmol L<sup>-1</sup>, n = 58) and winter concentrations were  $0.12 \pm 0.04$  pmol L<sup>-1</sup> (range;  
149 0.07 – 0.23 pmol L<sup>-1</sup>, n = 55). We found that MeHg concentrations exhibit near uniform  
150 distributions on the shelf (P1 – P5). In addition, a localized shallow MeHg maximum is seen at ~  
151 80 – 120 m depth in the Nansen Basin (P6 – P7), indicative of in situ MeHg production<sup>16,17,21,23</sup>.  
152 Below 200 m, MeHg at P6 and P7 displayed the typical profile of MeHg observed in the Fram  
153 Strait<sup>17</sup> with deeper maxima between 400 – 1000 m depth. Overall, both of our seasonal MeHg  
154 profiles are typical of the summer Arctic Ocean. Surprisingly, our unchanged seasonal MeHg  
155 profiles are in stark contrast to our seasonal THg profiles.

156

157 While it is difficult to estimate, one could expect seasonal changes of MeHg due to the absence of  
158 photochemistry<sup>39</sup>, sea ice cover limiting evasion to the atmosphere<sup>8</sup>, net demethylation<sup>40</sup> and low  
159 primary productivity during winter<sup>3,41</sup>. Similar to  $\Delta$ iHg, we calculated  $\Delta$ MeHg at each station by  
160 integrating the winter MeHg reservoir and comparing it to the integrated summer MeHg reservoir



161 at two depth intervals (Fig. 3). Our calculated  $\Delta\text{MeHg}$  in the upper 100 m are small and show no  
162 clear trend (range: -25 to 15  $\text{pmol m}^{-2} \text{d}^{-1}$ , SI Table 1). We expect waters to be in a net state of  
163 demethylation<sup>40</sup> as low particulate organic carbon (POC) fluxes on the shelf suggest minimal in  
164 situ production of MeHg<sup>42</sup>. As a result, small variations in our  $\Delta\text{MeHg}$  therefore suggest seasonal  
165 MeHg distributions to be in a locally dynamic equilibrium.

166  
167 On the other hand, our winter MeHg concentrations may remain the same as summer due to the  
168 absence of photodegradation<sup>39,43</sup>. Additionally, reduced losses of DMHg due to the presence of  
169 sea ice may also explain static winter MeHg concentrations, although MMHg is typically the  
170 dominant species on the shelf<sup>17,23</sup>. Particle scavenging can also transport MMHg to deeper waters  
171 and sediments, decreasing MeHg and THg concentrations in the water column. Higher amounts of  
172 gaseous DMHg, with negligible affinity to sinking particles, could also explain the persistence of  
173 MeHg concentrations. In addition, the  $K_D$  of MMHg may be an order of magnitude lower than  
174 THg<sup>44</sup>, reducing its affinity to sinking particles and explaining the difference in our THg and MeHg  
175 trends. Generally, particulate MMHg concentrations in the Arctic Ocean are low, approximately  
176 4% of MeHg<sup>23</sup>. Consequently, our unchanged MeHg concentrations therefore suggest high  
177 proportions of dissolved MeHg in both summer and winter.

### 178 **Implications for the Arctic Hg cycle**

179 The first observations during the polar night demonstrate a seasonal loss of THg. We suggest that  
180 the seasonal loss is primarily driven by particle scavenging of iHg via an Arctic DMn shuttle.  
181 Seasonal scavenging mechanisms on the entire Arctic shelf during the polar night may dominate  
182 water column Hg losses to shelf sediments. We also suggest MeHg concentrations are maintained  
183 in the water column in winter by reduced evasion, low particle affinities, slow demethylation rates

184 and a lack of photodegradation. Although in situ production is the dominant source of the  
185 subsurface MeHg maximum during summer in the Arctic basin, small shelf to basin transport of  
186 MeHg produced in the shelf sediments may contribute partially to the persistent shallow MeHg  
187 maximum and positive  $\Delta\text{MeHg}$  seen in the Arctic basin (P7) in winter (Fig. 3 & 4). Assuming a  
188 shelf seasonal loss of 33 – 46% iHg including all sampled depths (P1 – P5), we estimate a residence  
189 time for iHg of ~ 3 years. However, the persistence of MeHg extends the lifetime of THg in the  
190 Arctic Ocean to ~ 9 years<sup>17</sup>. Our work highlights a potential decoupling of iHg and MeHg species  
191 during the polar night and invites a new seasonally based paradigm of the Arctic Hg budget.

192  
193 In the future, climate change is expected to significantly affect the biogeochemical cycle of Hg<sup>45,46</sup>  
194 and drive MeHg concentrations in the marine food chain<sup>47</sup>. Sea ice loss will increase primary  
195 productivity on the Arctic shelves<sup>48</sup> and lead to greater iHg export to deeper waters and sediments.  
196 In addition, thawing permafrost and increased riverine flux will deliver high iHg inputs to the  
197 Arctic shelves. Recent work has suggested increased Hg uptake in benthic feeding-organisms on  
198 the Arctic shelf<sup>49</sup>. We anticipate that seasonal scavenging during autumn and winter months will  
199 deliver larger amounts of iHg to shelf sediments, driving increased benthic MeHg production and  
200 MeHg accumulation in the future Arctic Ocean.

201 ***CORRESPONDING AUTHOR STATEMENT***

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212 help with preparing the Hg samples for analysis.

213 ***AUTHOR CONTRIBUTIONS STATEMENT***

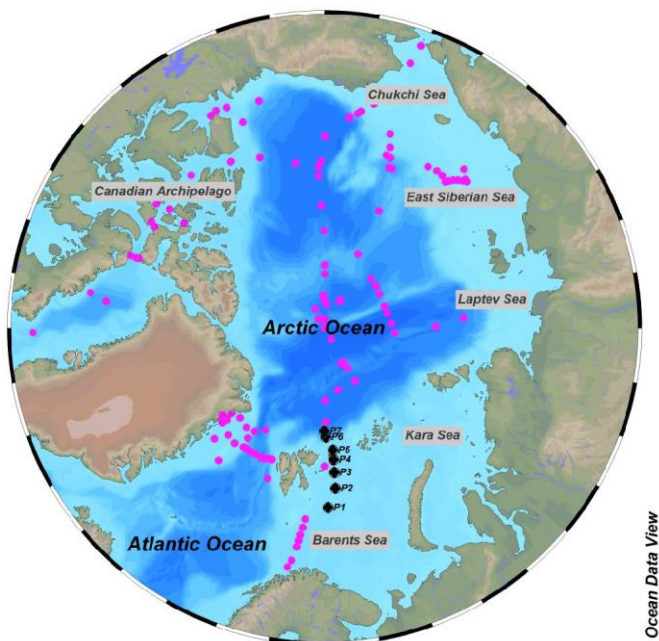
214 **SGK:** Conceptualization, formal analysis, investigation, validation, visualization, writing –  
215 original draft. **LEHB:** Conceptualization, formal analysis, investigation, resources, writing –  
216 review and editing, supervision. **MVP:** Formal analysis, investigation, validation, resources,  
217 writing – review and editing. **MGD:** Investigation, writing – review and editing. **NS:** Formal  
218 analysis, investigation, writing – review and editing. **AD:** Formal analysis, validation, writing –  
219 review and editing. **AS:** Formal analysis, validation, writing – review and editing. **KN:**  
220 Conceptualization, writing – review and editing, supervision. **MVA:** Conceptualization,  
221 investigation, resources, writing – review and editing, supervision, funding acquisition.

222 **COMPETING INTERESTS STATEMENT**

223 The authors declare no competing interests.

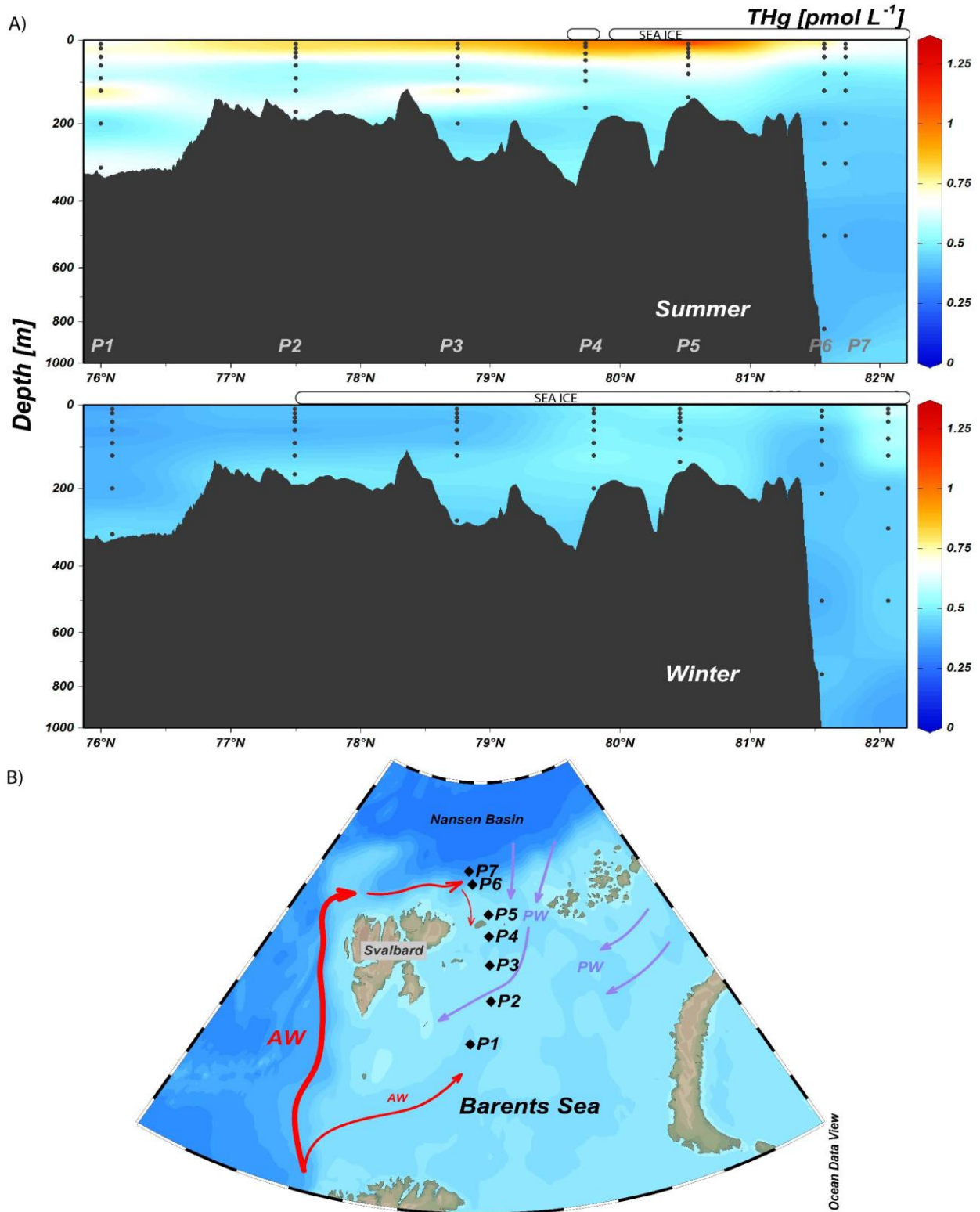
224

225 **FIGURE LEGENDS/CAPTIONS**



226

227 **Figure 1: Map of water column Hg profiles in the Arctic Ocean.** Literature data marked with  
228 pink circles<sup>1,16,17,20,21,23,25,50</sup>. Stations (P1 – P7), sampled during the 2019 summer and winter  
229 cruises, marked with black diamonds.



230

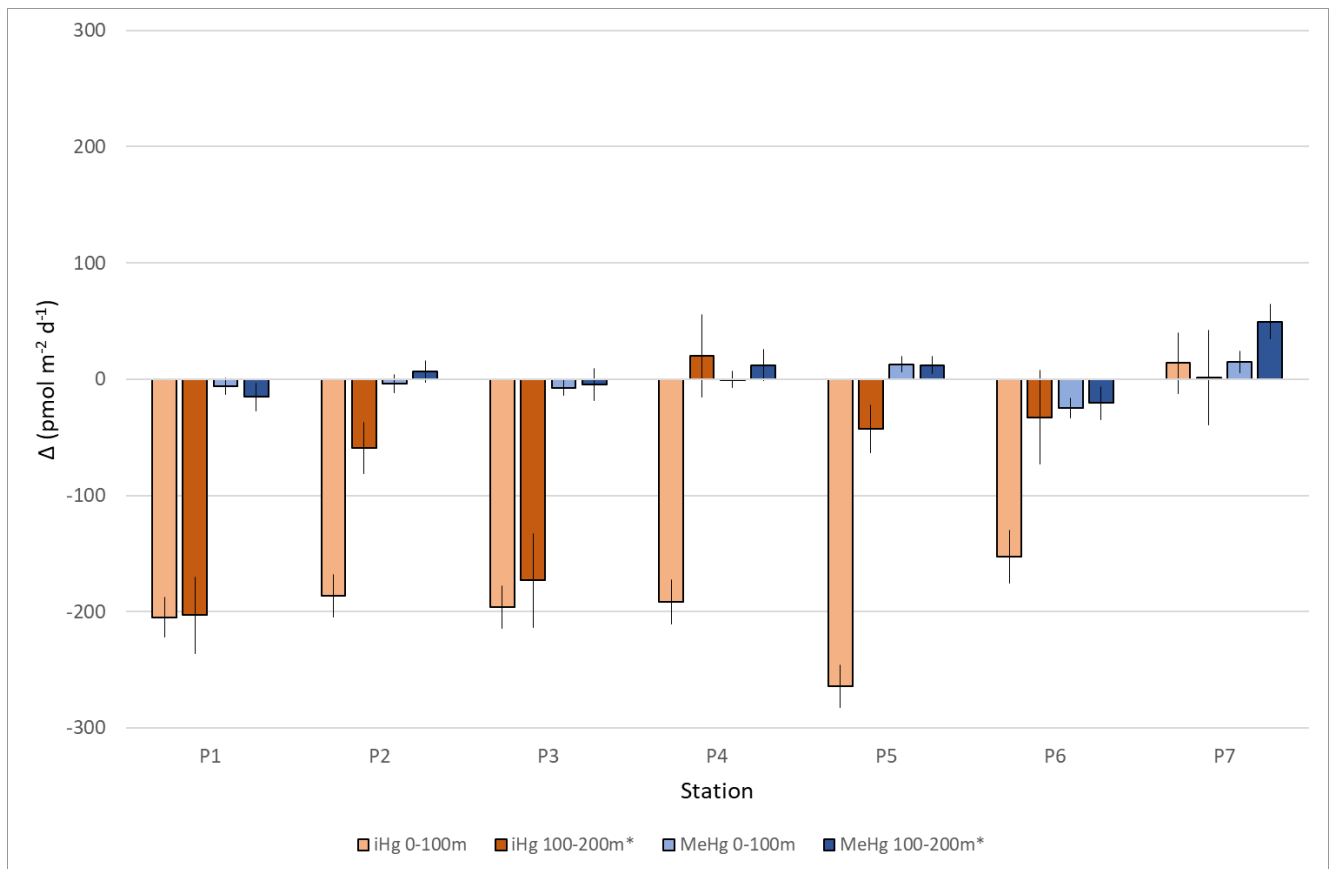
231 **Figure 2: Total mercury (THg) concentrations (pmol L<sup>-1</sup>) along the shelf-deep basin gradient.**

232 A) Stations P1 – P7, (Latitude) are on the x-axis for summer 2019 and winter 2019 cruises. B)

233 Map of sampling stations with warmer Atlantic Water (AW) advected into the Barents Sea from  
234 the south and west, and Polar Water (PW) advected from the north and east<sup>27</sup>.

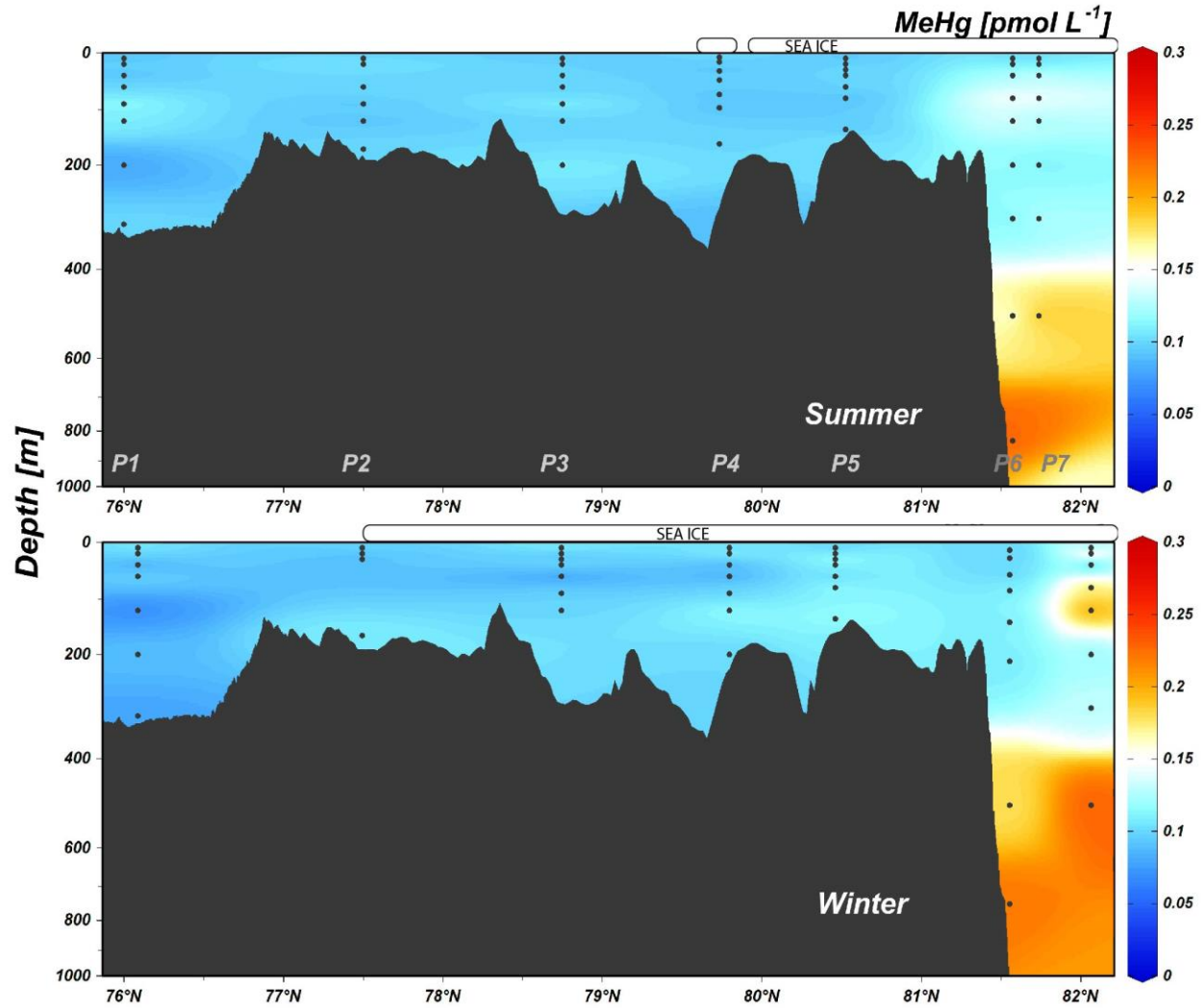
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237

238 **Figure 3:  $\Delta$ iHg ( $\text{pmol m}^{-2} \text{d}^{-1}$ ) and  $\Delta$ MeHg ( $\text{pmol m}^{-2} \text{d}^{-1}$ ) at specified depth intervals for each**  
239 **station.** iHg 0-100 m is in light orange, iHg 100-200 m in dark orange, MeHg 0-100 m in light  
240 blue, and MeHg 100-200 m in dark blue. A positive  $\Delta$  value indicates a temporal gain in the iHg  
241 or MeHg pool while a negative  $\Delta$  value indicates a temporal loss in the iHg or MeHg pool. Error  
242 bars represent combined standard uncertainty ( $\pm 1\sigma$ ). Values associated with Figure 3 are compiled  
243 in SI Table 1. \*Stations P2 and P5 were integrated from 100 m to sample depth less than 200 m.



244

245 **Figure 4: Total methylated mercury (MeHg) concentrations ( $\text{pmol L}^{-1}$ ) along the shelf-deep**  
 246 **basin gradient.** Stations P1 – P7, (Latitude) are on the x-axis for summer 2019 (top) and winter  
 247 2019 cruises (bottom).

248

249

250 **REFERENCES**

251 1 Wang, K. *et al.* Subsurface seawater methylmercury maximum explains biotic mercury  
 252 concentrations in the Canadian Arctic. *Sci Rep* **8**, 14465, (2018).

- 253 2 Soerensen, A. L. *et al.* A mass budget for mercury and methylmercury in the Arctic  
254 Ocean. *Global Biogeochemical Cycles* **30**, 560-575, (2016).
- 255 3 Wassmann, P. Arctic marine ecosystems in an era of rapid climate change. *Progress in*  
256 *Oceanography* **90**, 1-17, (2011).
- 257 4 Schroeder, W. H. *et al.* Arctic springtime depletion of mercury. *Nature* **394**, 331-332,  
258 (1998).
- 259 5 Sonke, J. E. *et al.* Eurasian river spring flood observations support net Arctic Ocean  
260 mercury export to the atmosphere and Atlantic Ocean. *Proc Natl Acad Sci U S A* **115**,  
261 E11586-E11594, (2018).
- 262 6 Fisher, J. A. *et al.* Riverine source of Arctic Ocean mercury inferred from atmospheric  
263 observations. *Nat Geosci* **5**, 499-504, (2012).
- 264 7 Andersson, M. E., Sommar, J., Gårdfeldt, K. & Lindqvist, O. Enhanced concentrations of  
265 dissolved gaseous mercury in the surface waters of the Arctic Ocean. *Marine Chemistry*  
266 **110**, 190-194, (2008).
- 267 8 DiMento, B. P., Mason, R. P., Brooks, S. & Moore, C. The impact of sea ice on the air-  
268 sea exchange of mercury in the Arctic Ocean. *Deep-Sea Res Pt I* **144**, 28-38, (2019).
- 269 9 Nerentorp Mastromonaco, M. G., Gårdfeldt, K., Langer, S. & Dommergue, A. Seasonal  
270 Study of Mercury Species in the Antarctic Sea Ice Environment. *Environ Sci Technol* **50**,  
271 12705-12712, (2016).
- 272 10 Zolkos, S. *et al.* Mercury Export from Arctic Great Rivers. *Environ Sci Technol* **54**,  
273 4140-4148, (2020).
- 274 11 Bowman, K. L., Lamborg, C. H. & Agather, A. M. A global perspective on mercury  
275 cycling in the ocean. *Sci Total Environ* **710**, 136166, (2020).



- 276 12 Zhang, Y. *et al.* Biogeochemical drivers of the fate of riverine mercury discharged to the  
277 global and Arctic oceans. *Global Biogeochemical Cycles* **29**, 854-864, (2015).
- 278 13 Nöthig, E. M. *et al.* Summertime Chlorophyll a and Particulate Organic Carbon Standing  
279 Stocks in Surface Waters of the Fram Strait and the Arctic Ocean (1991–2015). *Frontiers*  
280 *in Marine Science* **7**, 350, (2020).
- 281 14 Nöthig, E. M. *et al.* Annual cycle of downward particle fluxes on each side of the Gakkel  
282 Ridge in the central Arctic Ocean. *Philos Trans A Math Phys Eng Sci* **378**, 20190368,  
283 (2020).
- 284 15 Lamborg, C. H., Hammerschmidt, C. R. & Bowman, K. L. An examination of the role of  
285 particles in oceanic mercury cycling. *Philos Trans A Math Phys Eng Sci* **374**, 20150297,  
286 (2016).
- 287 16 Wang, F., Macdonald, R. W., Armstrong, D. A. & Stern, G. A. Total and methylated  
288 mercury in the Beaufort Sea: the role of local and recent organic remineralization.  
289 *Environ Sci Technol* **46**, 11821-11828, (2012).
- 290 17 Petrova, M. V. *et al.* Mercury species export from the Arctic to the Atlantic Ocean.  
291 *Marine Chemistry* **225**, 103855, (2020).
- 292 18 Charette, M. A. *et al.* The Transpolar Drift as a Source of Riverine and Shelf-Derived  
293 Trace Elements to the Central Arctic Ocean. *J Geophys Res-Oceans* **125**,  
294 e2019JC015920, (2020).
- 295 19 Tesán, J. *et al.* Mercury export flux in the Arctic Ocean estimated from <sup>234</sup>Th: <sup>238</sup>U  
296 disequilibria. *ACS Earth and Space Chemistry* **4**, 795-801 (2020).
- 297 20 Kirk, J. L. *et al.* Methylated mercury species in marine waters of the Canadian high and  
298 sub Arctic. *Environ Sci Technol* **42**, 8367-8373, (2008).

- 299 21 Heimbürger, L. E. *et al.* Shallow methylmercury production in the marginal sea ice zone  
300 of the central Arctic Ocean. *Sci Rep* **5**, 1-6, (2015).
- 301 22 Cossa, D. *et al.* Sources, cycling and transfer of mercury in the Labrador Sea  
302 (GEOTRACES-GEOVIDE cruise). *Marine Chemistry* **198**, 64-69, (2018).
- 303 23 Agather, A. M., Bowman, K. L., Lamborg, C. H. & Hammerschmidt, C. R. Distribution  
304 of mercury species in the Western Arctic Ocean (US GEOTRACES GN01). *Marine*  
305 *Chemistry* **216**, 103686, (2019).
- 306 24 Hirdman, D. *et al.* Transport of mercury in the Arctic atmosphere: Evidence for a spring-  
307 time net sink and summer-time source. *Geophysical Research Letters* **36**, L12814,  
308 (2009).
- 309 25 Kim, J. *et al.* Mass Budget of Methylmercury in the East Siberian Sea: The Importance of  
310 Sediment Sources. *Environ Sci Technol* **54**, 9949-9957, (2020).
- 311 26 Loeng, H. Features of the Physical Oceanographic Conditions of the Barents Sea. *Polar*  
312 *Research* **10**, 5-18, (1991).
- 313 27 Sundfjord, A., Assmann, K.M, Lundesgaard, Ø., Renner, A.H.H, & Ingvaldsen, R.B.  
314 Suggested water mass definitions for the central and northern Barents Sea, and the  
315 adjacent Nansen Basin: Workshop Report. *The Nansen Legacy Report Series* **8**, (2020).
- 316 28 Olli, K. *et al.* Seasonal variation in vertical flux of biogenic matter in the marginal ice  
317 zone and the central Barents Sea. *Journal of Marine Systems* **38**, 189-204, (2002).
- 318 29 Reigstad, M., Riser, C. W., Wassmann, P. & Ratkova, T. Vertical export of particulate  
319 organic carbon: Attenuation, composition and loss rates in the northern Barents Sea.  
320 *Deep-Sea Research Part II-Topical Studies in Oceanography* **55**, 2308-2319, (2008).

321 30 Cossa, D., Cotté-Krief, M. H., Mason, R. P. & Bretaudeau-Sanjuan, J. Total mercury in  
322 the water column near the shelf edge of the European continental margin. *Marine*  
323 *Chemistry* **90**, 21-29, (2004).

324 31 Cui, X., Lamborg, C. H., Hammerschmidt, C. R., Xiang, Y. & Lam, P. J. The Effect of  
325 Particle Composition and Concentration on the Partitioning Coefficient for Mercury in  
326 Three Ocean Basins. *Frontiers in Environmental Chemistry* **2**, 6, (2021).

327 32 Middag, R., de Baar, H. J. W., Laan, P. & Klunder, M. B. Fluvial and hydrothermal input  
328 of manganese into the Arctic Ocean. *Geochimica Et Cosmochimica Acta* **75**, 2393-2408,  
329 (2011).

330 33 Vieira, L. H. *et al.* Benthic fluxes of trace metals in the Chukchi Sea and their transport  
331 into the Arctic Ocean. *Marine Chemistry* **208**, 43-55, (2019).

332 34 Rosati, G. *et al.* Mercury in the Black Sea: New Insights From Measurements and  
333 Numerical Modeling. *Global Biogeochem Cycles* **32**, 529-550, (2018).

334 35 Bam, W. *et al.* Variability in <sup>210</sup>Pb and <sup>210</sup>Po partition coefficients (K<sub>d</sub>) along the US  
335 GEOTRACES Arctic transect. *Marine Chemistry* **219**, 103749, (2020).

336 36 Smith, J. N., Moran, S. B. & Macdonald, R. W. Shelf–basin interactions in the Arctic  
337 Ocean based on <sup>210</sup>Pb and Ra isotope tracer distributions. *Deep Sea Research Part I:*  
338 *Oceanographic Research Papers* **50**, 397-416, (2003).

339 37 Lepore, K., Moran, S. B. & Smith, J. N. <sup>210</sup>Pb as a tracer of shelf–basin transport and  
340 sediment focusing in the Chukchi Sea. *Deep Sea Research Part II: Topical Studies in*  
341 *Oceanography* **56**, 1305-1315, (2009).

342 38 Kadko, D. *et al.* The residence times of trace elements determined in the surface Arctic  
343 Ocean during the 2015 US Arctic GEOTRACES expedition. *Marine Chemistry* **208**, 56-  
344 69, (2019).

345 39 Point, D. *et al.* Methylmercury photodegradation influenced by sea-ice cover in Arctic  
346 marine ecosystems. *Nat Geosci* **4**, 188-194, (2011).

347 40 Lehnherr, I., St Louis, V. L., Hintelmann, H. & Kirk, J. L. Methylation of inorganic  
348 mercury in polar marine waters. *Nat Geosci* **4**, 298-302, (2011).

349 41 Heimbürger, L. E. *et al.* Methyl mercury distributions in relation to the presence of nano-  
350 and picophytoplankton in an oceanic water column (Ligurian Sea, North-western  
351 Mediterranean). *Geochimica et Cosmochimica Acta* **74**, 5549-5559, (2010).

352 42 Sunderland, E. M., Krabbenhoft, D. P., Moreau, J. W., Strode, S. A. & Landing, W. M.  
353 Mercury sources, distribution, and bioavailability in the North Pacific Ocean: Insights  
354 from data and models. *Global Biogeochemical Cycles* **23**, GB2010, (2009).

355 43 Seller, P., Kelly, C. A., Rudd, J. W. M. & MacHutchon, A. R. Photodegradation of  
356 methylmercury in lakes. *Nature* **380**, 694-697, (1996).

357 44 Lawson, N. M., Mason, R. P. & Laporte, J. M. The fate and transport of mercury,  
358 methylmercury, and other trace metals in Chesapeake Bay tributaries. *Water Res* **35**, 501-  
359 515, (2001).

360 45 Stern, G. A. *et al.* How does climate change influence Arctic mercury? *Sci Total Environ*  
361 **414**, 22-42, (2012).

362 46 Krabbenhoft, D. P. & Sunderland, E. M. Environmental science. Global change and  
363 mercury. *Science* **341**, 1457-1458, (2013).

364 47 Schartup, A. T. *et al.* Climate change and overfishing increase neurotoxicant in marine  
365 predators. *Nature* **572**, 648-650, (2019).

366 48 Arrigo, K. R. & van Dijken, G. L. Continued increases in Arctic Ocean primary  
367 production. *Progress in Oceanography* **136**, 60-70, (2015).

368 49 Gopakumar, A., Giebichenstein, J., Raskhozheva, E. & Borgå, K. Mercury in Barents Sea  
369 fish in the Arctic polar night: Species and spatial comparison. *Mar Pollut Bull* **169**,  
370 112501, (2021).

371 **METHODS**

372 **Sample collection**

373 The transect in the northern Barents Sea and Nansen Basin (76°N – 83°N) was sampled on two  
374 cruises, Q3 and Q4, in August 2019 and December 2019 on *R/V Kronprins Haakon* as part of The  
375 Nansen Legacy project. Water samples were collected manually using Teflon-coated GOFLO  
376 bottles attached sequentially to a 600 m Aramid rope. Seawater was sampled at seven stations at 8  
377 depths up to 500 m. Depths deeper than 500 m were sampled with 10 L Niskin bottles mounted to  
378 a rosette with a SeaBird SBE 9 CTD unit. Upon GOFLO retrieval, bottles were transported  
379 immediately to an onboard custom-made clean lab. High-efficiency particulate air filter cartridges  
380 were attached to the pressure release valve. THg samples were collected unfiltered with no  
381 headspace into pre-cleaned<sup>51</sup> 40 mL borosilicate glass bottles with PTFE-lined caps and kept  
382 unpreserved. MeHg samples were collected unfiltered into brand new 125 mL PET bottles and  
383 were acidified to 0.4 % v/v double-distilled HCl under a Class 100 clean air laminar flow hood.  
384 Upon acidification, dimethylmercury (DMHg) converts quantitatively to monomethylmercury  
385 (MMHg)<sup>52</sup>; thus, total methylated mercury (MeHg) is measured as the sum of MMHg and DMHg.  
386 All samples were double-bagged and stored in the dark at 4°C until analysis.

387

388 **Hg measurements**

389 The THg concentration in the samples was measured according to USEPA Method 1631 at the  
390 Mediterranean Institute of Oceanography (MIO) using a custom-made single gold trap setup  
391 described elsewhere<sup>21</sup> within six months after sampling. To adapt to the low concentrations  
392 expected in seawater, potassium bromide (Sigma Aldrich, USA) and potassium bromate (Sigma  
393 Aldrich, USA) are heated for 4h at 250°C to remove Hg traces before making up BrCl solution

394 with freshly double-distilled HCl. The BrCl solution was blank checked prior to use using a  
395 standard addition protocol. Field blanks were measured for both summer (0.01 pmol L<sup>-1</sup>, n = 4)  
396 and winter (0.09 pmol L<sup>-1</sup>, n = 3) cruises. Average THg concentrations are reported in the main  
397 text plus the standard deviation of the mean ( $\pm 1SD$ ).

398  
399 THg measurements were calibrated against NIST 3133 (National Institute of Standards and  
400 Technology), with a 6-point calibration curve in Hg-free seawater ( $R^2$  values of 0.9998 – 1),  
401 accounting for matrix effects. A NIST quality control sample was spiked into previously purged  
402 Hg-free sample seawater matrix and analyzed after every 6 samples (standard-bracketing) to  
403 monitor instrumental drift. Initial recovery and precision of this quality control sample for our  
404 batches is  $94 \pm 7\%$ . Ongoing recovery of this quality control sample was monitored and checked  
405 against the recovery guidelines outlined in EPA Method 1631, Revision E, Table 2 (77 – 123%).  
406 The detection limit of 0.003 pmol L<sup>-1</sup> was evaluated as 3x the standard deviation of the  
407 instrumental CVAFS “bubbler” blank. To test our analytical method, certified reference materials  
408 ORMS-5 and BCR-579 were spiked into previously purged Hg-free seawater matrix to test for  
409 recovery. Both standards were within the certified ranges, with additional analytical details  
410 provided in Supplemental Information.

411  
412 The MeHg concentration in seawater samples was measured using the isotope dilution (ID)  
413 technique via gas chromatography – sector field ICP-MS (GC-SF-ICP-MS)<sup>21</sup> at MIO within six  
414 months after sampling. Briefly, enriched isotopic spikes of  $i^{199}\text{Hg}$  and  $\text{MM}^{201}\text{Hg}$  (ISC Science)  
415 were added to approximately 110 mL of seawater sample in pre-combusted borosilicate glass  
416 bottles and equilibrated for 15 minutes. Samples were adjusted to pH 3.9 using a sodium acetate

417 buffer solution (ULTREX® II Ultrapure Reagent, J.T. Baker, USA) and NH<sub>3</sub> (ULTREX® II  
 418 Ultrapure Reagent, J.T. Baker, USA). A freshly made 1% solution of sodium tetrapropylborate  
 419 (Merseburger Spezialchemikalien) and 200 µL of hexane (Sigma Aldrich) were added to derivatize  
 420 and extract Hg species. Bottles were sealed and shaken for 15 minutes before the organic layer  
 421 was transferred to GC vials for injection on a coupled GC (THERMO GC 1300 with GC220  
 422 transfer module) SF-ICP-MS (Thermo Element XR) system. The coupling to a high resolution  
 423 ICP-MS and application of ultra-trace clean techniques allows reaching a detection limit of 0.001  
 424 pmol L<sup>-1</sup>. We determined that the accuracy of our MM<sup>201</sup>Hg spike concentration compared to its  
 425 theoretical concentration was 96.6 ± 7.9%, calculated with reverse isotope dilution using the  
 426 Brooks Rand MeHgCl standard, traceable to NIST1641E. Additional analytical details are  
 427 provided in Supplemental Information. Average MeHg concentrations are reported in the main  
 428 text plus the standard deviation of the mean (±1SD).

429

### 430 **Δ calculations**

431 We calculate iHg for each depth as the difference between THg and MeHg. iHg and MeHg in the  
 432 upper 200 m water column at each station were depth integrated using the trapezoidal method.  
 433 ΔMeHg (Equation 1) and ΔiHg (Equation 2) were calculated from summer (s) to winter (w) using  
 434 the specific sampling dates. We assumed the same concentrations of THg and MeHg at 0 m until  
 435 observations begin at 10 m. When sampling depths differ or are missing, concentrations were  
 436 extrapolated by linear regression from the closest available sampling depths to calculate Δ values.

437

$$438 \quad \Delta MeHg = \left( \int_0^z [MeHg]_s dz - \int_0^z [MeHg]_w dz \right) / dt \quad (1)$$

$$439 \quad \Delta iHg = \left( \int_0^z ([THg]_s - [MeHg]_s) dz - \int_0^z ([THg]_w - [MeHg]_w) dz \right) / dt \quad (2)$$



440

441 A positive  $\Delta$  value indicates a temporal gain in iHg and MeHg while a negative  $\Delta$  value indicates  
442 a temporal loss in iHg and MeHg. To compare directly to published fluxes, we present absolute  
443 values of  $\Delta$ iHg and  $\Delta$ MeHg as  $|\Delta$ iHg| and  $|\Delta$ MeHg|. Uncertainty in  $\Delta$  values is reported as  
444 combined standard uncertainty ( $\pm 1\sigma$ ) calculated from the uncertainty in measured THg  
445 concentrations and uncertainty in measured MeHg concentrations.

#### 446 **Data availability statement**

447 Figures 1, 2, and 4 and Extended Data Figures 1-5 and 7 were created by the publicly available  
448 Ocean Data View<sup>55</sup> and edited in Adobe Illustrator. Temperature and salinity data from seasonal  
449 cruises are publicly available from the Norwegian Marine Data Centre (<https://nmdc.no>)<sup>53,54</sup>.  
450 Mercury and trace element concentration data for all depths and stations are publicly available  
451 from the Norwegian Marine Data Centre (<https://nmdc.no>)<sup>56,57</sup>. Figure 3 and Extended Data  
452 Figures 6 and 8 were created in Microsoft Excel with data displayed in Supplementary Tables 1  
453 and 3.

#### 454 **References**

- 455 50 GEOTRACES Intermediate Data Product Group (2021). The GEOTRACES Intermediate  
456 Data Product 2021 (IDP2021). NERC EDS British Oceanographic Data Centre NOC.  
457 DOI: 10.5285/cf2d9ba9-d51d-3b7c-e053-8486abc0f5fd .
- 458 51 Hammerschmidt, C. R., Bowman, K. L., Tabatchnick, M. D. & Lamborg, C. H. Storage  
459 bottle material and cleaning for determination of total mercury in seawater. *Limnol*  
460 *Oceanogr-Meth* **9**, 426-431, (2011).

461 52 Black, F. J., Conaway, C. H. & Flegal, A. R. Stability of dimethyl mercury in seawater  
462 and its conversion to monomethyl mercury. *Environ Sci Technol* **43**, 4056-4062, (2009).

463 53 Reigstad, M. CTD data from Nansen Legacy Cruise - Seasonal cruise Q3. Norwegian  
464 Marine Data Centre <https://doi.org/10.21335/NMDC-1107597377> (2022).

465 54 Søreide, J. CTD data from Nansen Legacy Cruise - Seasonal cruise Q4. Norwegian Marine  
466 Data Centre <https://doi.org/10.21335/NMDC-301551919> (2022).

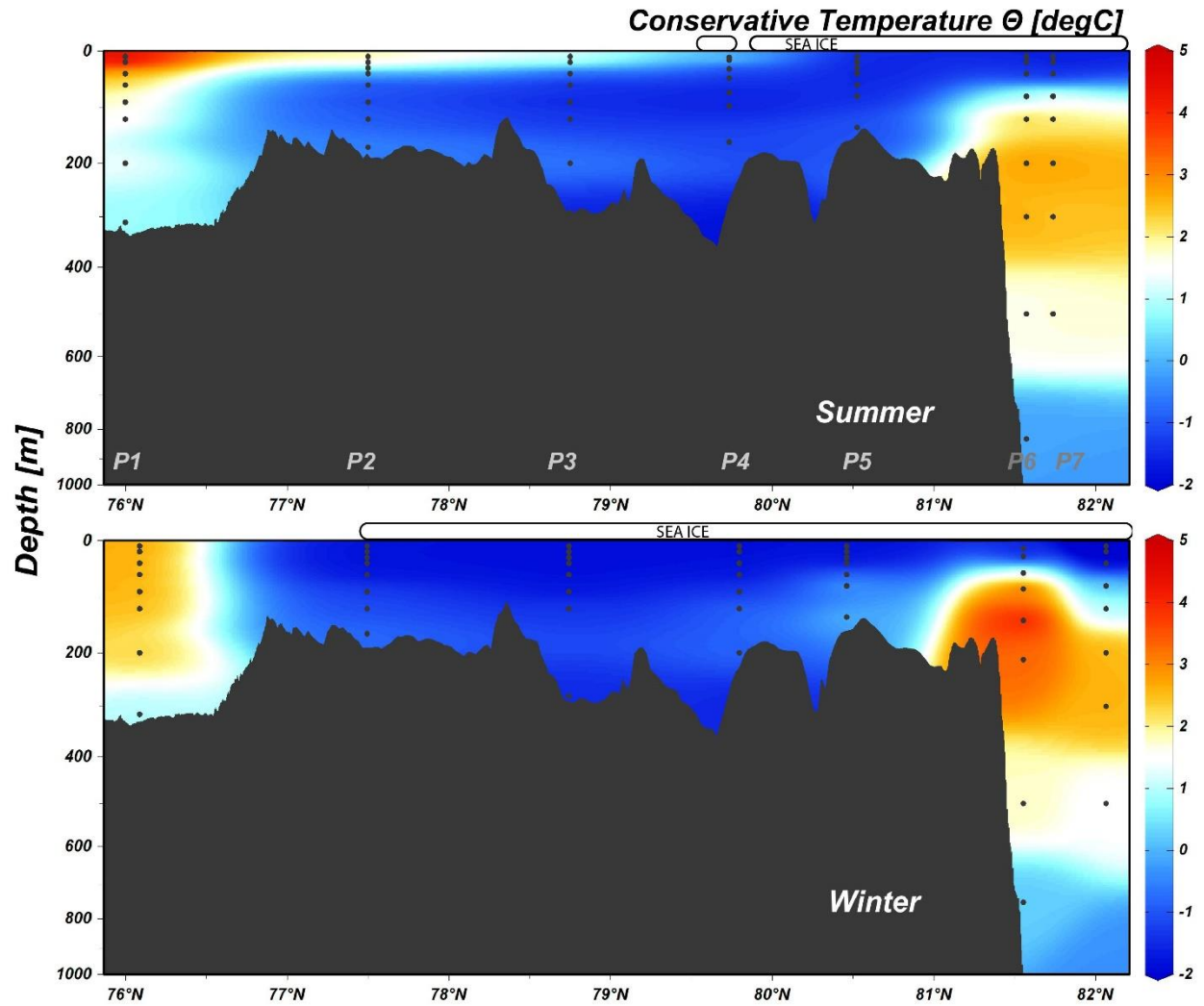
467 55 Schlitzer, R. Ocean Data View. [odv.awi.de](http://odv.awi.de) (2021).

468 56 Kohler, S. G. *et al.* Concentrations of total mercury, total methylated mercury, and  
469 selected trace elements in the northern Barents Sea as part of the Nansen Legacy project,  
470 Cruise 2019706 Q3. Norwegian Marine Data Centre [https://doi.org/10.21335/NMDC-](https://doi.org/10.21335/NMDC-416151559)  
471 [416151559](https://doi.org/10.21335/NMDC-416151559) (2022).

472 57 Kohler, S. G. *et al.* Concentrations of total mercury, total methylated mercury, and  
473 selected trace elements in the northern Barents Sea as part of the Nansen Legacy project,  
474 Cruise 2019711 Q4. Norwegian Marine Data Centre [https://doi.org/10.21335/NMDC-](https://doi.org/10.21335/NMDC-1871554897)  
475 [1871554897](https://doi.org/10.21335/NMDC-1871554897) (2022).

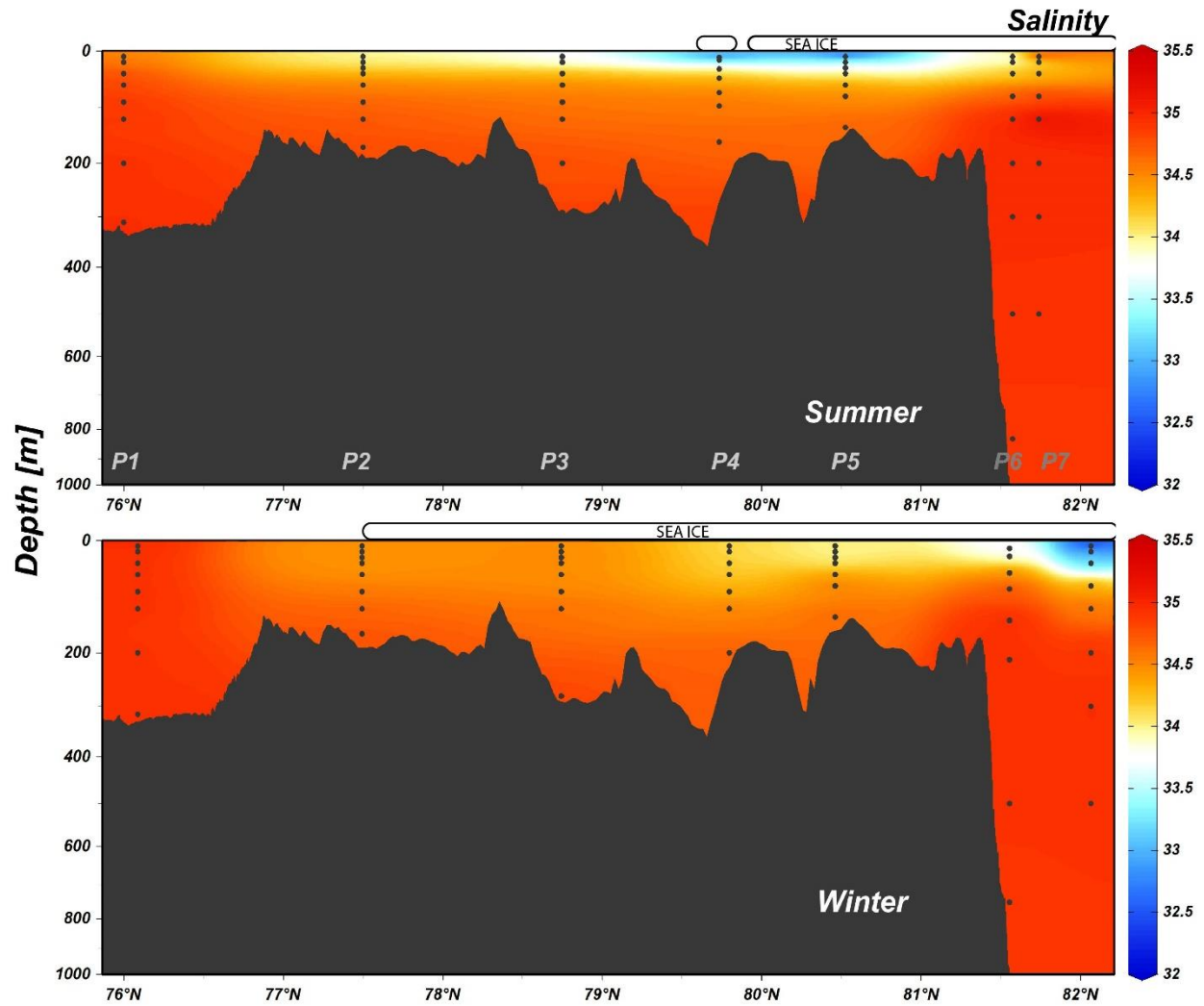
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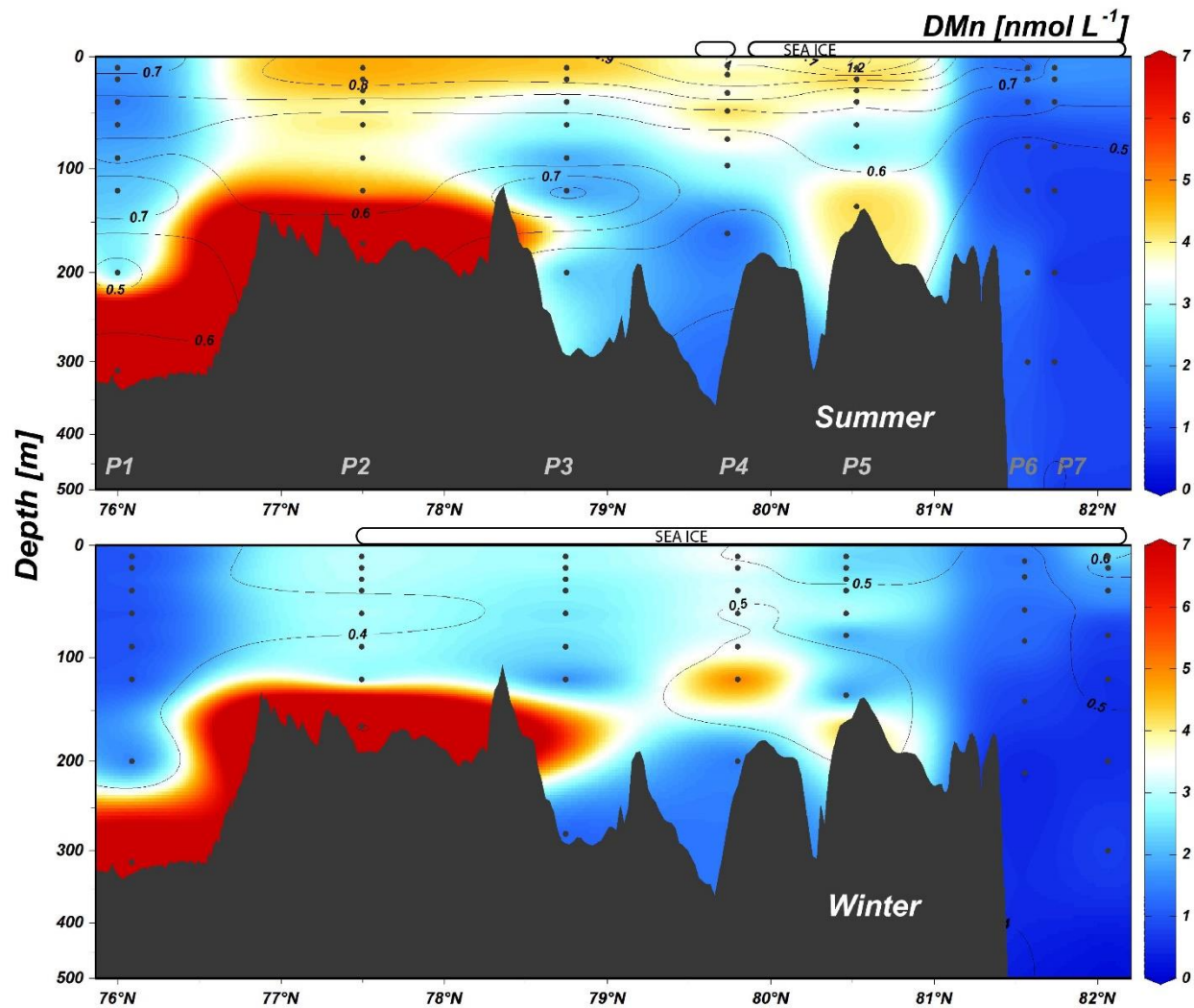
478

479 **Extended Data Fig. 1. Conservative temperature ( $\Theta$ ) in degrees Celsius ( $^{\circ}\text{C}$ ) along the shelf-**  
 480 **deep basin gradient.** Stations P1 – P7, (Latitude) are on the x-axis for summer 2019 (top) and  
 481 winter 2019 cruises (bottom). Data retrieved from the Norwegian Marine Data Centre<sup>53,54</sup>.



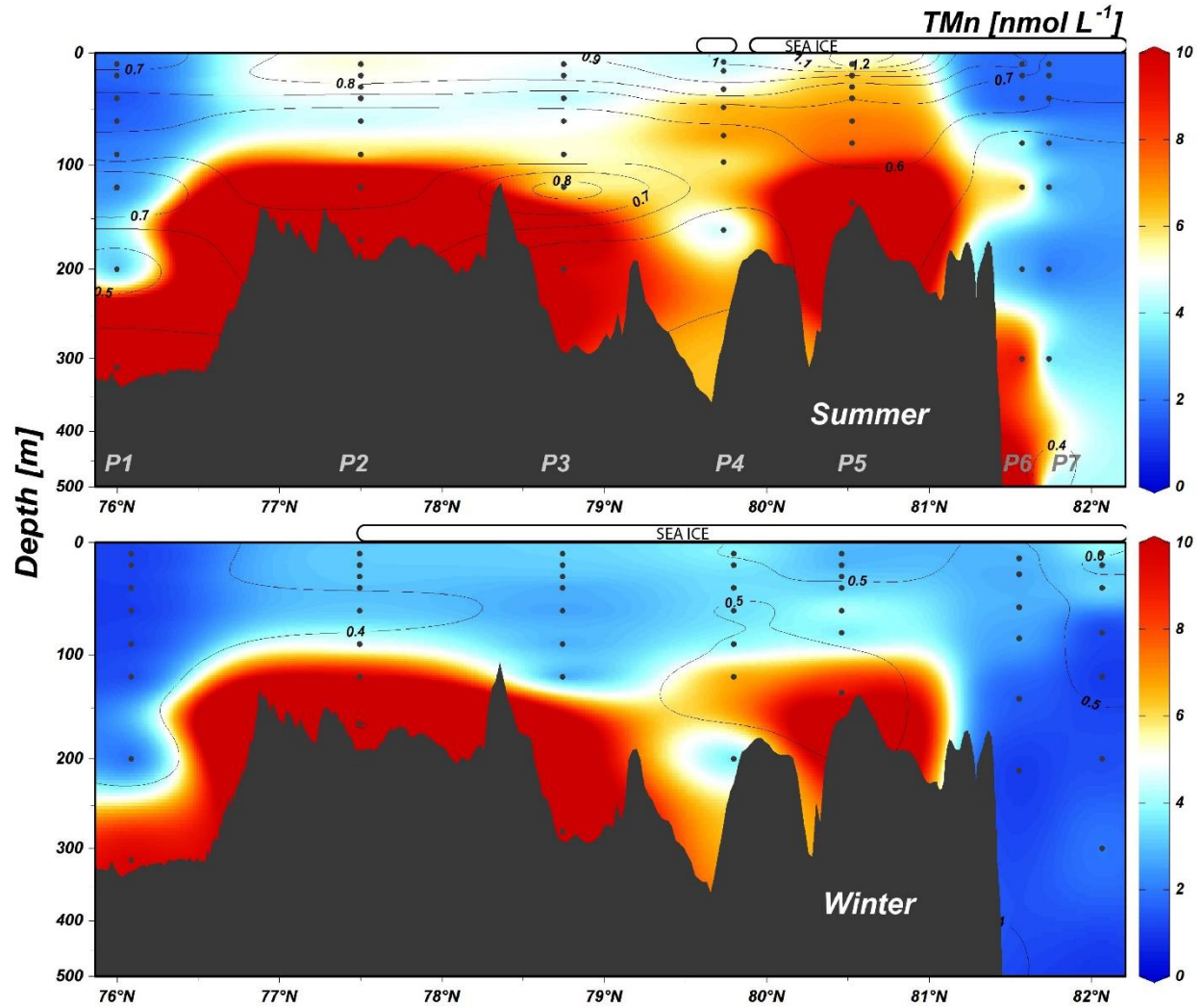
482

483 **Extended Data Fig. 2. Salinity along the shelf-deep basin gradient.** Stations P1 – P7, (Latitude)  
 484 are on the x-axis for summer 2019 (top) and winter 2019 cruises (bottom). Data retrieved from the  
 485 Norwegian Marine Data Centre<sup>53,54</sup>.



486

487 **Extended Data Fig. 3. Dissolved manganese (DMn) concentrations ( $\text{nmol L}^{-1}$ ) along the shelf-**  
 488 **deep basin gradient.** Stations P1 – P7, (Latitude) are on the x-axis for summer 2019 (top) and  
 489 winter 2019 cruises (bottom). Black contour lines for THg ( $\text{pmol L}^{-1}$ ) from each corresponding  
 490 season are overlain. Concentrations greater than the presented range ( $7 \text{ nmol L}^{-1}$ ) are plotted as the  
 491 maximum.

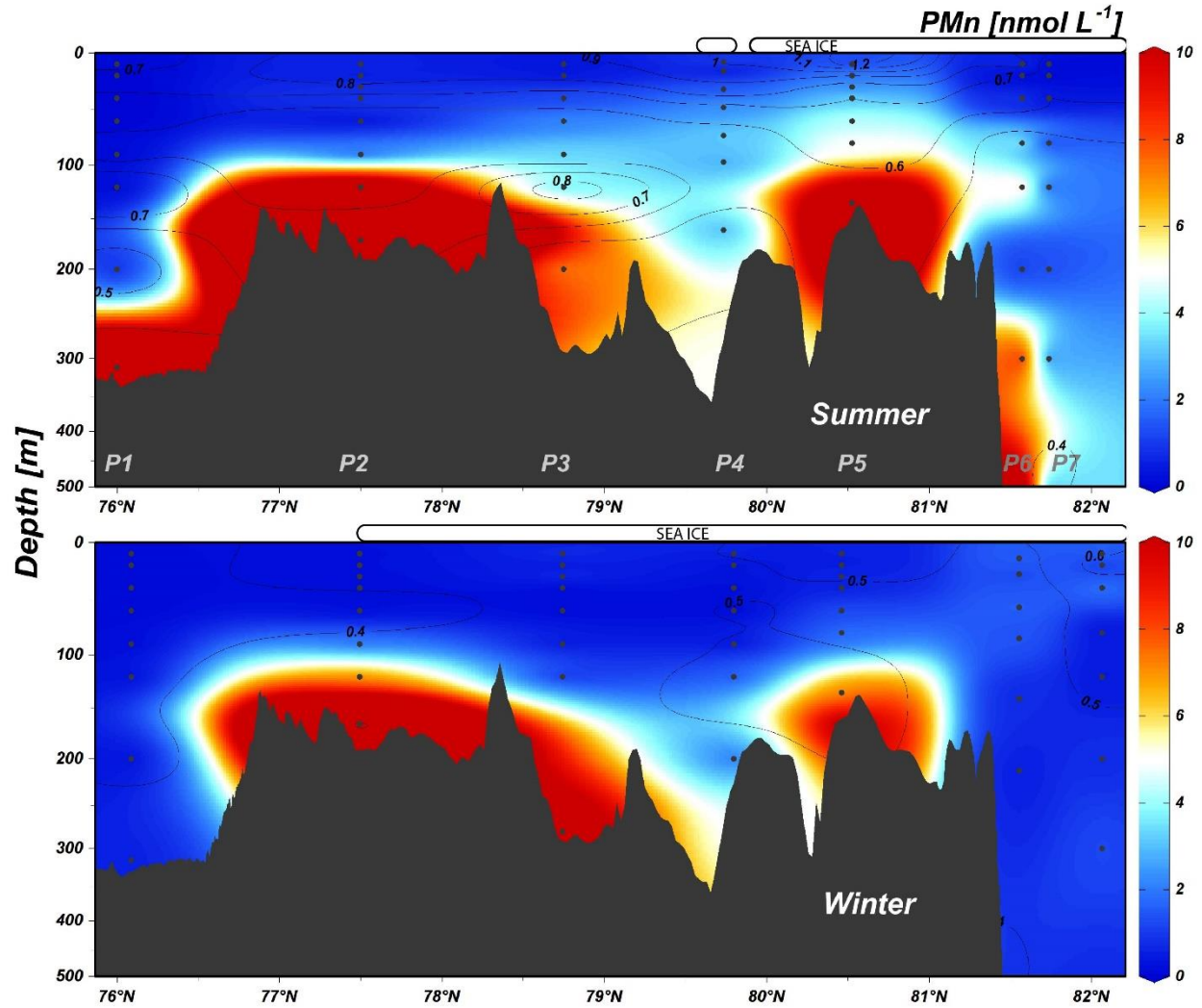


492

493 **Extended Data Fig. 4. Total acid-leachable manganese (TMn) concentrations (nmol L<sup>-1</sup>)**  
 494 **along the shelf-deep basin gradient.** Stations P1 – P7, (Latitude) are on the x-axis for summer  
 495 2019 (top) and winter 2019 cruises (bottom). Black contour lines for THg (pmol L<sup>-1</sup>) from each  
 496 corresponding season are overlain. Concentrations greater than the presented range (10 nmol L<sup>-1</sup>)  
 497 are plotted as the maximum.

498

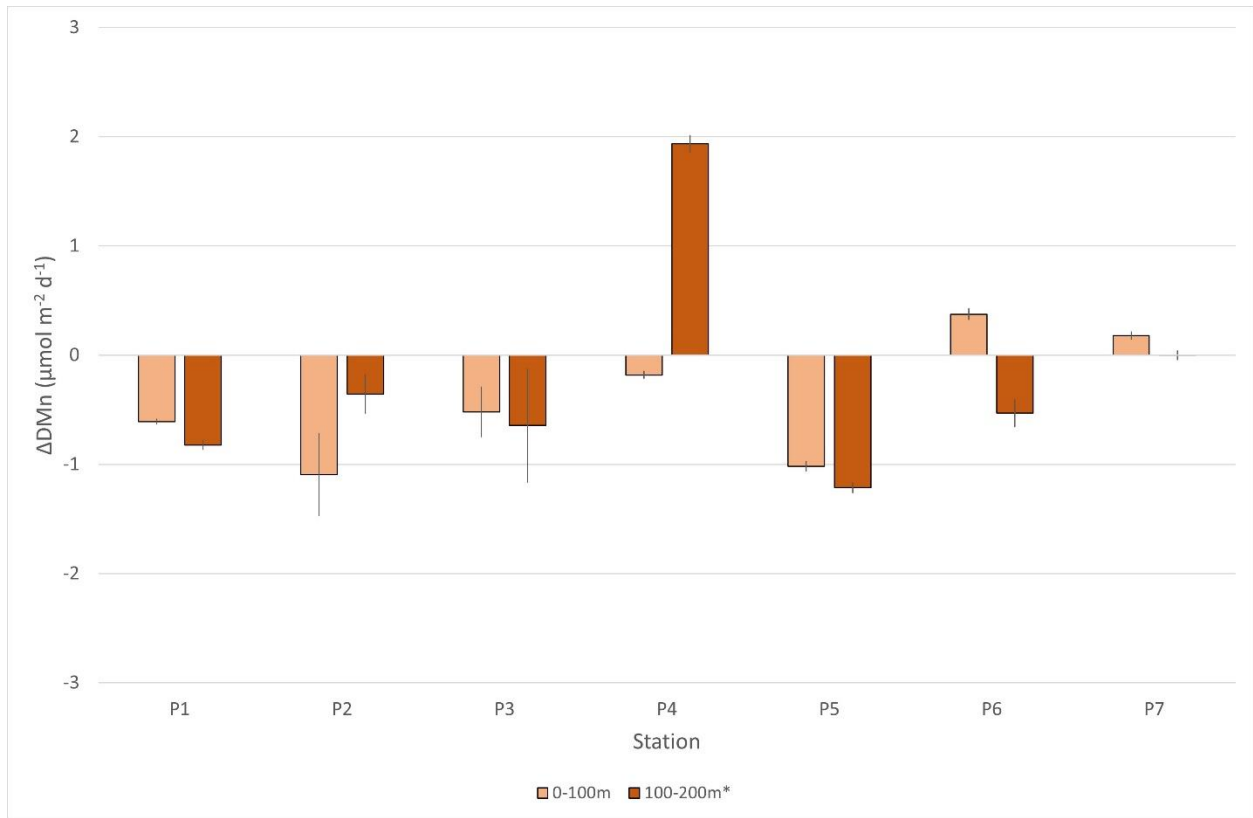




499

500 **Extended Data Fig. 5. Particulate manganese (PMn) concentrations (nmol L<sup>-1</sup>) along the**  
 501 **shelf-deep basin gradient.** Stations P1 – P7, (Latitude) are on the x-axis for summer 2019 (top)  
 502 and winter 2019 cruises (bottom). Black contour lines for THg (pmol L<sup>-1</sup>) from each corresponding  
 503 season are overlain. Concentrations greater than the presented range (10 nmol L<sup>-1</sup>) are plotted as  
 504 the maximum.

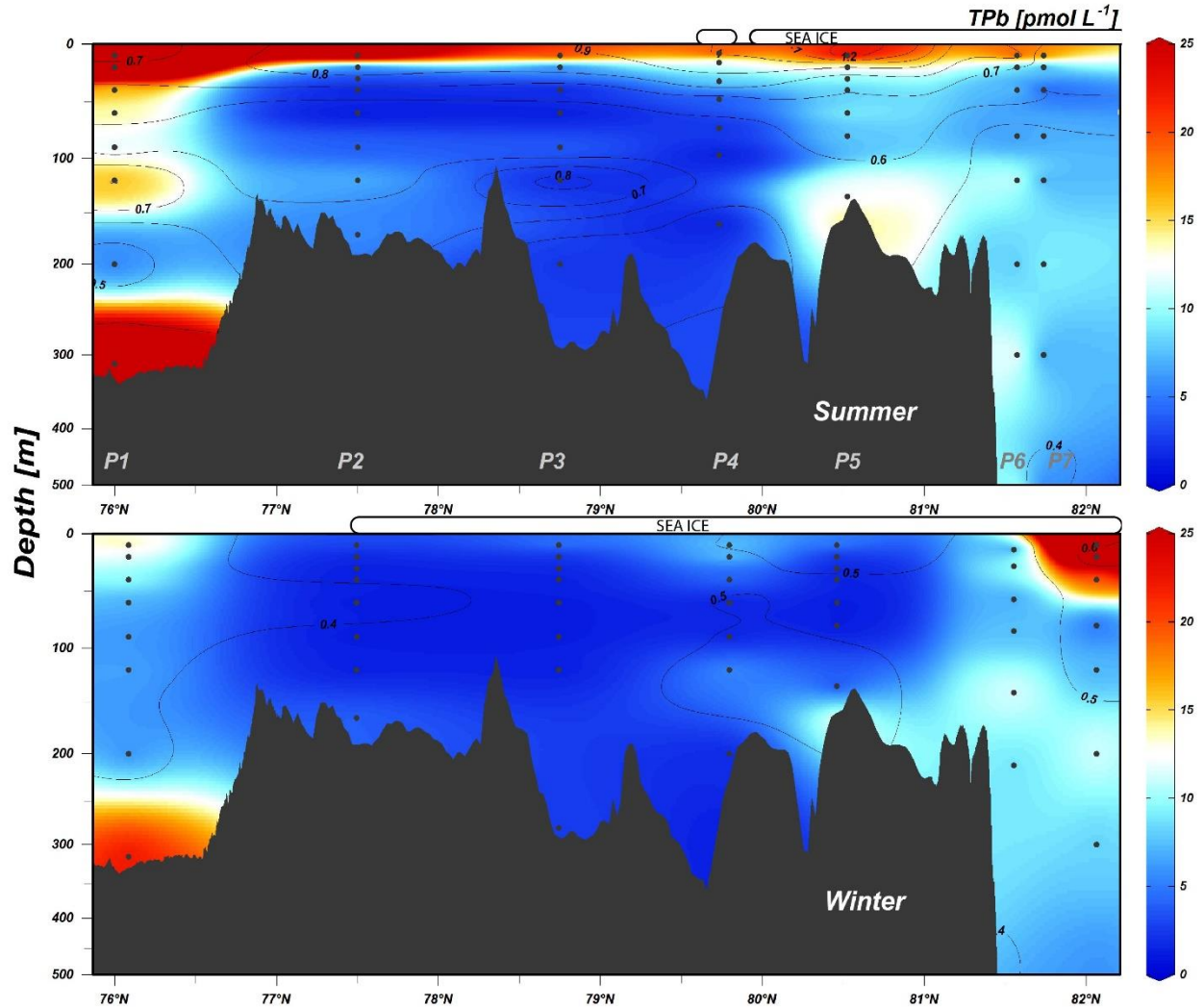
505



506

507 **Extended Data Fig. 6.  $\Delta$ DMn ( $\mu\text{mol m}^{-2} \text{d}^{-1}$ ) at specified depth intervals for each station. A**  
 508 **positive  $\Delta$  value indicates a temporal gain in the DMn pool while a negative  $\Delta$  value indicates a**  
 509 **temporal loss in the DMn pool.  $\Delta$  values are reported with error bars as combined standard**  
 510 **uncertainty ( $\pm 1\sigma$ ). \*Stations P2 and P5 were integrated from 100 m to sample depth less than 200**  
 511 **m.**

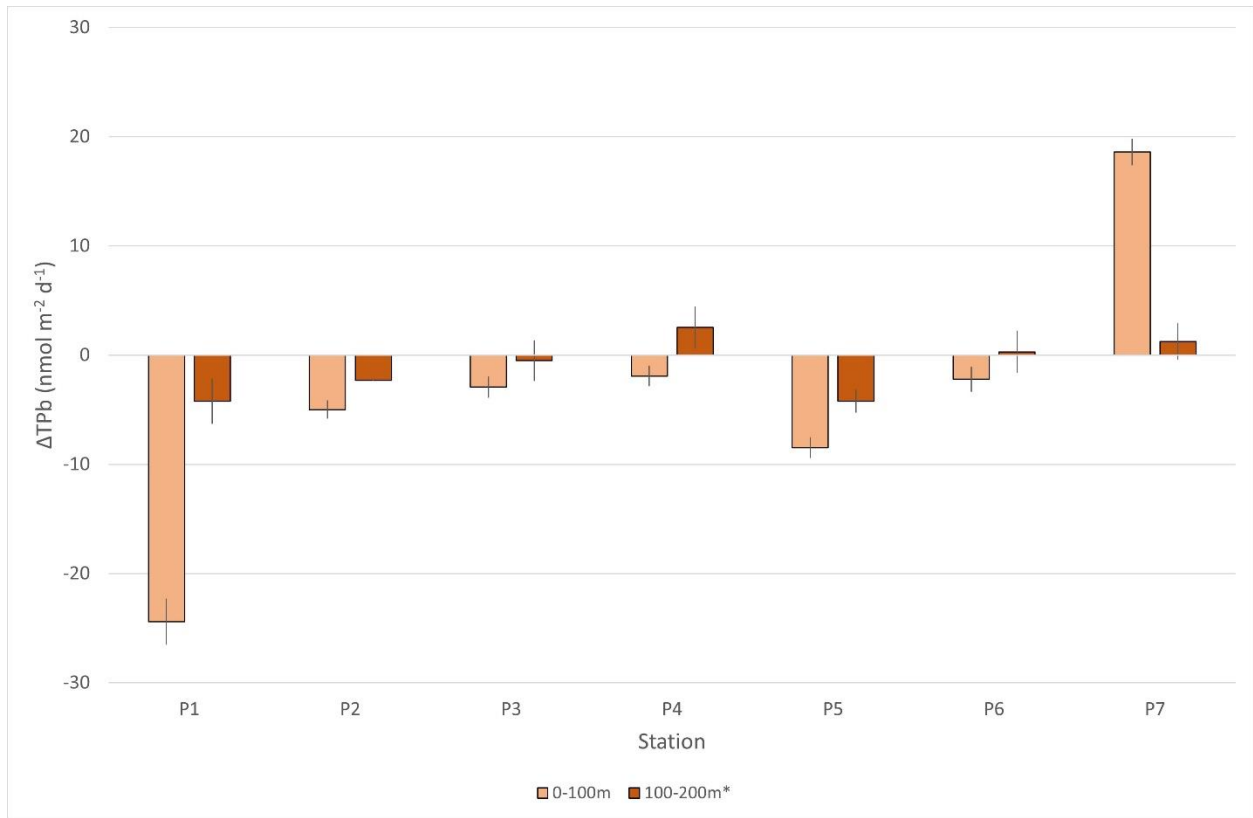




512

513 **Extended Data Fig. 7. Total acid-leachable lead (TPb) concentrations ( $\text{pmol L}^{-1}$ ) along the**  
 514 **shelf-deep basin gradient.** Stations P1 – P7, (Latitude) are on the x-axis for summer 2019 (top)  
 515 and winter 2019 cruises (bottom). Data points at or below the detection limit were assigned the  
 516 value of the detection limit ( $1.08 \text{ pmol L}^{-1}$ ) determined by the seaFAST-pico ICP-MS for plotting  
 517 purposes. Black contour lines for THg ( $\text{pmol L}^{-1}$ ) from each corresponding season are overlain.  
 518 Concentrations greater than the presented range ( $25 \text{ pmol L}^{-1}$ ) are plotted as the maximum.

519



520

521 **Extended Data Fig. 8. Extended Data Figure 8:  $\Delta$ TPb (nmol m<sup>-2</sup> d<sup>-1</sup>) at specified depth**  
 522 **interval for each station.** A positive  $\Delta$  value indicates a temporal gain in the TPb pool while a  
 523 negative  $\Delta$  value indicates a temporal loss in the TPb pool.  $\Delta$  values are reported with error bars  
 524 as combined standard uncertainty ( $\pm 1\sigma$ ). \*Stations P2 and P5 were integrated from 100 m to  
 525 sample depth less than 200 m.

526

527