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1 **Bromoform concentrations in slush-layer water in Antarctic fast ice**

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28 Abstract:

29 Bromoform concentrations in water of the slush layer that developed at the interface  
30 between snow and sea ice were measured during the seasonal warming in Lützow-Holm  
31 Bay, Eastern Antarctica. Mean bromoform concentration was  $5.5 \pm 2.4 \text{ pmol l}^{-1}$ , which  
32 was lower than that of the under-ice water ( $10.9 \pm 3.5 \text{ pmol l}^{-1}$ ). Temporal decrease in  
33 bromoform concentrations and salinity with increasing in temperature of the slush water  
34 suggest that the bromoform concentrations were reduced through dilution with  
35 meltwater input from the upper surface of sea ice. In contrast, bromoform  
36 concentrations in the under-ice water increased during this period while the salinity of  
37 the under-ice water decreased. It is speculated that the sea ice meltwater input contained  
38 high bromoform concentrations from the brine channels within the sea ice and from the  
39 bottom of the ice that were contributed to the increased bromoform concentrations in  
40 the under-ice water.

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43 Key words: bromoform, sea ice, slush layer, under-ice water, Lützow-Holm Bay

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46

47 **Introduction**

48

49 Bromoform (CHBr<sub>3</sub>) is one of the volatile organic compounds (VOCs) originating with  
50 macroalgal and planktonic sources in the ocean, and bromoform is emitted from the  
51 ocean surface to the atmosphere (Quack & Wallace 2003). Bromoform is an important  
52 carrier of bromine to the troposphere, and its lifetime in the atmosphere is one to four  
53 weeks (Quack & Wallace 2003 and references therein). Although bromoform  
54 concentrations in the ocean have been measured widely, there is a lack of information  
55 regarding measurements of bromoform in the ice-covered seas. Sea ice may be a  
56 significant platform for the production of bromine compounds and a source for the  
57 atmosphere (Sturges *et al.* 1992, 1993, 1997, Carpenter *et al.* 2007). For example, polar  
58 ice algae is known to produce significant quantities of bromoform (Sturges *et al.* 1992).

59

60 A surface slush layer (gap layer) is found extensively in Antarctic sea ice during the ice  
61 melting season (Haas *et al.* 2001, Kattner *et al.* 2004, Ackley *et al.* 2008, Zemmeling *et al.*  
62 *et al.* 2008, Papadimitriou *et al.* 2009). Snow accumulation over sea ice and the formation  
63 of superimposed ice leads to the formation of a slush layer below sea level (Haas *et al.*  
64 2001). High biological activity has been found in this layer (Kattner *et al.* 2004),  
65 suggesting that bromoform production could also be high in this layer. In addition,  
66 bromoform produced in the slush layer would accumulate because of limited gas  
67 diffusion through the snow and superimposed ice (Delille 2006, Nomura *et al.* 2010).

68

69 The bromoform dynamics in the sea ice column has been well studied (Sturges *et al.*  
70 1993, 1997). From these studies, it is clear that the biogenic production of bromoform  
71 by ice algae could be an important contributor to atmospheric bromoform levels in the  
72 polar regions (e.g., Sturges *et al.* 1992). However, although slush water is expected to  
73 potentially include the highest levels of bromoform in surface ice, bromoform  
74 concentrations in slush water have not yet been examined. In addition, it is not clear  
75 which processes dominate the temporal variability of bromoform concentrations in  
76 slush water.

77

78 In this study, we examined for the first time the magnitude and temporal variations of  
79 bromoform concentrations in slush water, and their links to the physical and  
80 biogeochemical parameters of slush water and sea ice. Our results should provide an  
81 important insight into the organic bromine cycle in ice-covered seas.

82

83

#### 84 **Materials and methods**

85

86 Slush-water samples were collected in the austral spring/summer (26 December 2009 to  
87 5 February 2010) from the multi-year land-fast ice in Lützow-Holm Bay, Eastern  
88 Antarctica (Fig. 1). During this period, several sampling stations were established  
89 within a 0.5-km<sup>2</sup> area. Under-ice water was also collected from the same area.

90

91 For slush-water sampling, snow and superimposed ice were removed with a scoop, and  
92 ice crystals in the slush layer were removed with a net. The water in the slush layer was  
93 pumped through a Teflon tube by a diaphragm pump (EWP-01, As One Corporation,  
94 Osaka, Japan) and collected in a 30-ml amber glass vial (Nichiden-Rika Glass Co. Ltd,  
95 Kobe, Japan). Mercuric chloride solution (Saturated-HgCl<sub>2</sub>; 200 µl) was added to the  
96 samples to stop biological activity. Vials were sealed with a Teflon-lined septum  
97 (Nichiden-Rika Glass Co. Ltd) and an aluminum cap (Nichiden-Rika Glass Co. Ltd).  
98 Slush-water samples were stored in a refrigerator (+4 °C) until further analysis. To  
99 check the spatial heterogeneity of slush water, duplicate samplings were carried out for  
100 slush water within 2 m<sup>2</sup> on each sampling day.

101

102 For under-ice water sampling, a hole was made using an ice corer (Geo Tecs Co., Ltd.,  
103 Chiba, Japan) with an internal diameter of 9.0 cm, and under-ice water was collected  
104 with a Teflon water sampler (GL Science Inc., Tokyo, Japan) at 1 and 7 m below the  
105 bottom of the sea ice. Under-ice water samples were collected approximately 30  
106 minutes after drilling of the ice cores to avoid the effects of the disturbance caused by  
107 drilling. Samples were treated and stored in the same manner as for slush-water samples.

108

109 The temperature of the slush and under-ice water was measured using a needle-type  
110 temperature sensor (Testo 110 NTC, Brandt Instruments, Inc., Prairieville, LA, USA).  
111 Slush and under-ice water samples were also collected and placed into 12-ml glass  
112 screw-cap vials (Nichiden-Rika Glass Co. Ltd) for salinity analysis, and into 500-ml  
113 Nalgene polycarbonate bottles (Thermo Fisher Scientific Inc., Waltham, MA, USA) for  
114 chlorophyll *a* (chl-*a*) measurement. Salinity samples were kept in a refrigerator (+4 °C).  
115 The seawater samples for chl-*a* analysis were filtered through 25-mm Whatman GF/F  
116 filters immediately after returning to the laboratory near the sampling station.  
117 Chlorophyll pigments on the filters were extracted in dimethylformamide (Suzuki &  
118 Ishimaru 1990) for 24 h at approximately –80 °C.  
119  
120 The bromoform concentrations were determined by a purge-and-trap (P&T) and gas-  
121 chromatograph–mass spectrometry (GC-MS) method (Yokouchi *et al.* 2006, Ooki &  
122 Yokouchi 2011a, Ooki & Yokouchi 2011b). The total volume of seawater in the sample  
123 bottle was transferred to a custom-made bubbling vessel by helium carrier at 40 ml min<sup>–</sup>  
124 <sup>1</sup>. The dissolved bromoform in the water was purged with the helium carrier at 80 ml  
125 min<sup>–</sup><sup>1</sup> and 45 °C for 30 min, and simultaneously transferred to a pre-concentration-GC-  
126 MS system (Agilent 5973, 6390; Agilent Technologies Inc., Santa Clara, CA, USA)  
127 (Yokouchi *et al.* 2006, Ooki & Yokouchi 2011a, Ooki & Yokouchi 2011b). The purge  
128 efficiency for bromoform was 84%. A diluted standard solution containing bromoform  
129 at 1.2 pmol l<sup>–</sup><sup>1</sup> was introduced to the P&T-GC-MS system every 24 h to calibrate for the  
130 bromoform concentrations in seawater samples. The precision of standard solution  
131 measurements was ±2% (*n* = 4), and the detection limit (S/N = 10) was 0.4 pmol l<sup>–</sup><sup>1</sup>.  
132  
133 Salinity was measured with a salinity analyzer (SAT-210, Toa Electronics Ltd., Tokyo,  
134 Japan). The salinity analyzer was calibrated with International Association for the  
135 Physical Science of the Ocean standard seawater (P series; Ocean Scientific  
136 International Ltd., Hampshire, UK). Chl-*a* concentrations were determined using a  
137 fluorometer (Model 10AU, Turner Designs, Inc., Sunnyvale, CA, USA), following  
138 methods described by Parsons *et al.* (1984).  
139

140

## 141 **Results**

142

### 143 *Bromoform and chl-a concentrations, salinity and temperature*

144

145 Bromoform and chl-*a* concentrations, salinity and temperature in slush and under-ice  
146 water obtained during the study period are summarized in Table 1. The mean  
147 bromoform concentration in slush water was 5.5 pmol l<sup>-1</sup>, which was lower than that of  
148 under-ice water (10.9 pmol l<sup>-1</sup>). In contrast, the mean chl-*a* concentration in slush water  
149 (0.4 µg l<sup>-1</sup>) was approximately double that of under-ice water (0.2 µg l<sup>-1</sup>). The mean  
150 salinity of the slush water (9.7) was approximately one-third that of the under-ice water  
151 (32.5). The mean temperature of the slush water (+0.5 °C) was higher than that of the  
152 under-ice water (-0.4 °C) due to the downward flushing of meltwater from the top,  
153 which was generated by the melting of the snow on sea ice at higher air temperature  
154 (Fig. 2). Although the range of values for some of these parameters includes temporal  
155 variations during the study period, the slush water was consistently characterized by  
156 lower bromoform concentrations and lower salinity compared to the under-ice water  
157 (Table 1).

158

159

### 160 *Temporal variations in bromoform and chl-a concentrations, salinity and temperature*

161

162 Sampling occurred from late spring (26 December) to mid summer (5 February),  
163 providing an opportunity to observe temporal variations of physico-chemical properties  
164 during warming and ice-melting conditions (Fig. 2). The snow depth over the sea ice  
165 decreased from 100 cm at the beginning of this period to less than 10 cm at the end,  
166 whereas ice thickness was almost constant during the period (176 ± 25 cm). There was a  
167 layer of superimposed ice (about 10 cm thick) between the snow and slush layers during  
168 the sampling period.

169

170 Temporal variations in bromoform and chl-*a* concentration, salinity and temperature in  
171 slush and under-ice water were shown in Figure 3. Bromoform concentrations in the  
172 slush water were relatively constant (8–9 pmol l<sup>-1</sup>) until 5 January, and then they  
173 decreased to below 5 pmol l<sup>-1</sup> and remained constant for the rest of the sampling period  
174 (Fig. 3a). The salinity of the slush water decreased dramatically from 28.6 on 26  
175 December to 0.8 on 2 February (Fig. 3e). On the other hand, the slush-water  
176 temperature increased from -1.9 °C to +2.6 °C during the study period (Fig. 3g). The  
177 trends of decrease in salinity and increase in temperature of slush water were similar to  
178 that of bromoform concentrations during this period (Figs. 3a, e & g), with the  
179 bromoform concentrations being correlated with the salinity (shown in Figure 4), and  
180 with the temperature of slush water ( $r = 0.78$ ,  $P < 0.0001$ ,  $n = 22$ ). For the relationship  
181 between salinity and bromoform concentrations in slush water (Fig. 4), there were two  
182 different regimes: 1) the decrease in bromoform concentrations in the slush water only  
183 holds until a decrease in salinity to around 5, 2) at lower salinity (salinity < 5), the  
184 bromoform concentration in slush water increased to 5.9 pmol l<sup>-1</sup> with decreasing  
185 salinity. Chl-*a* concentrations in slush water varied between 0.0 and 1.1 µg l<sup>-1</sup> (Fig. 3c),  
186 and were not correlated with the changes in bromoform concentrations ( $r = 0.09$ ,  $P =$   
187  $0.68$ ,  $n = 22$ ).

188  
189 Concentrations of bromoform in under-ice water (5–18 pmol l<sup>-1</sup>) were higher compared  
190 with the slush-water concentrations (Figs. 3a & b). Chl-*a* concentrations in under-ice  
191 water remained low (<0.3 pmol l<sup>-1</sup>) until 14 January, and then they gradually increased  
192 (Fig. 3d). Salinity of under-ice water decreased from about 34 early in the study period  
193 (26 December–5 January) to below 30 at the end (29 January–5 February) (Fig. 3f). The  
194 temperature of under-ice water increased slightly during the study period (Fig. 3h).  
195 There were no notable differences between the under-ice water at 1 m and 7 m for any  
196 of the parameters during the study period (Figs. 3b, d, f & h).

197  
198  
199  
200

## Discussion

201 The bromoform concentrations in under-ice water measured in this study (5.9–18.3  
202 pmol l<sup>-1</sup>) were lower than those of Arctic under-ice water in spring (about 80 pmol l<sup>-1</sup>;  
203 Sturges *et al.* 1997) and coastal Antarctic surface water in spring/summer (about 57  
204 pmol l<sup>-1</sup>; Carpenter *et al.* 2007). The higher bromoform concentrations previously  
205 measured in polar seawater were caused by inputs of ice meltwater containing high  
206 levels of bromoform produced by ice algae, or by *in situ* production of bromoform in  
207 the seawater during algae blooms (e.g., Sturges *et al.* 1992, Carpenter *et al.* 2007). The  
208 increasing levels of bromoform in the ocean have generally been associated with the  
209 increasing abundance of diatoms (Klick & Abrahamsson 1992, Baker *et al.* 1999). An  
210 *in situ* culture experiment has shown that Arctic ice algae have the potential to produce  
211 substantial quantities of bromoform at high chl-*a* concentrations (>700 µg l<sup>-1</sup>) within  
212 the bottom layer of sea ice (Sturges *et al.* 1992). However, because chl-*a* concentrations  
213 were generally low during our study (mean, 0.2 µg l<sup>-1</sup>), the contribution of ice algae to  
214 bromoform production would have been minor. This is likely to be one of reasons why  
215 bromoform concentration in under-ice water in this study were so much lower than  
216 those of previous studies (Sturges *et al.* 1992, Carpenter *et al.* 2007).

217

218 A surface slush layer is found widely distributed in Antarctic sea ice during the ice  
219 melting season (Haas *et al.* 2001, Kattner *et al.* 2004, Ackley *et al.* 2008, Zemmeling *et al.*  
220 *et al.* 2008, Papadimitriou *et al.* 2009). Snow accumulation over sea ice and the formation  
221 of superimposed ice leads to the formation of a slush layer below sea level (Haas *et al.*  
222 2001). In this layer, high biological activity has been found (Kattner *et al.* 2004),  
223 suggesting that the biogenic production of bromoform should also be high in this layer.  
224 However, in this study we found chl-*a* concentrations in the slush layer (mean 0.4 µg l<sup>-1</sup>  
225 l<sup>-1</sup>; Table 1) to be much lower than those in the productive slush layer in the Weddell Sea,  
226 Antarctica (3.1–16.5 µg l<sup>-1</sup>; Kattner *et al.* 2004). Snow depth was basically high (mean  
227 24 cm) compared to those in the Weddell Sea, Antarctica (mean 16 cm; Kattner *et al.*  
228 2004). These results suggest the reduction of the light intensity in the slush layer,  
229 thereby reducing the light available for growth of ice algae living in slush water. In  
230 addition, the salinity of slush water was lower than under-ice water, reflecting the  
231 dilution of all slush-water components including nutrients. Therefore, it was considered

232 that available nutrient concentration in the slush water was also low and depleted for  
233 growth of ice algae. Although measures of the light intensity and nutrient concentrations  
234 in slush layer were not examined in this study, these may be one of the factors  
235 controlling biological productivity in slush water.

236

237 The temporal decrease of bromoform concentrations in slush water was correlated with  
238 that of salinity when the salinity was higher than 5 (Fig. 4), suggesting that bromoform  
239 concentrations in the slush water decreased because of dilution by the meltwater input  
240 from the upper surface of sea ice in accordance with the increase of temperature (Figs. 2  
241 & 3g). Therefore, the decrease in bromoform concentrations in slush water should  
242 closely reflect the effects of dilution. Same dilution process was observed for  
243 hexachlorocyclohexane in sea ice brine in the Canadian western Arctic in spring due to  
244 the melting of the ice crystal matrix and replenishment of brine with seawater (Pucko *et al.*  
245 *et al.* 2010). On the other hand, at lower salinity (salinity < 5), the bromoform  
246 concentrations in the slush water increased with decreasing salinity (Fig. 4). It is  
247 speculated that the bromoform in the slush layer tended to remain even if the large  
248 volume of meltwater was added to the slush layer and diluted the bromoform because of  
249 the limited gas diffusion to the atmosphere through the snow and superimposed ice  
250 (Delille 2006, Nomura *et al.* 2010).

251

252 In contrast to the changes in slush water, bromoform concentrations in under-ice water  
253 increased during the study period, tracking the increase in chl-*a* concentrations, whereas  
254 the salinity decreased (Figs. 3b, d & f). These results for salinity suggest that the under-  
255 ice water included a proportion of meltwater from the sea ice. This phenomenon is  
256 similar to the process occurring in the slush water, but there are some differences in the  
257 effects on bromoform and chl-*a* concentrations. Previously, bromoform and chl-*a*  
258 concentration at the bottom of the sea ice have been found to be higher than in the other  
259 parts of sea ice (Sturges *et al.* 1997). During ice melting, the impurities in sea-ice brine  
260 channels are flushed out before the melting of the ice itself, therefore these components  
261 were added to the under-ice water with meltwater. The temporal changes of each  
262 component in under-ice water reflect the input of the high-bromoform and chl-*a*, low-

263 salinity meltwater during the study period (Figs. 3b, d & f). These changes would be  
264 also enhanced by the horizontal advection of under-ice water from offshore that  
265 accumulates in Lützow-Holm Bay (Ohshima et al., 1996).

266

267

## 268 **Conclusions**

269

270 Bromoform concentrations in slush-layer water in Antarctic fast ice were measured  
271 during the seasonal warming in Lützow-Holm Bay. Mean bromoform concentration was  
272  $5.5 \pm 2.4 \text{ pmol l}^{-1}$ , which was lower than that of the under-ice water ( $10.9 \pm 3.5 \text{ pmol l}^{-1}$ ).  
273 Temporal decrease in bromoform concentrations and salinity with increasing in  
274 temperature of the slush water, suggesting that bromoform concentrations in the slush  
275 water decreased because of dilution by the meltwater input from the upper surface of  
276 sea ice in accordance with the increase of temperature. However, at lower salinity of  
277 slush water (salinity < 5), the bromoform concentrations in the slush water increased  
278 with decreasing salinity. It is speculated that the bromoform in the slush layer tended to  
279 remain even if the large volume of meltwater were added to the slush layer and diluted  
280 bromoform in slush water because of the limited gas diffusion to the atmosphere  
281 through the snow and superimposed ice (Delille 2006, Nomura *et al.* 2010).

282

283 In contrast to the changes in slush water, bromoform concentrations in under-ice water  
284 increased during the study period, tracking the increase in chl-*a* concentrations, whereas  
285 the salinity decreased. These results suggest that the temporal changes of each  
286 component in under-ice water reflect the input of the high-bromoform and chl-*a*, low-  
287 salinity meltwater during the study period.

288

289

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291

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296 MS).

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381  
382  
383

384 **Figure captions**

385

386 Fig 1 Map showing the location of sampling area in Lützow-Holm Bay, Eastern  
387 Antarctica.

388

389 Fig 2 Time series of daily mean air temperatures at the sampling station. Gray band  
390 indicates the sampling period.

391

392 Fig 3 Time series values for (a, b) bromoform concentration, (c, d) chl-*a* concentration,  
393 (e, f) salinity and (g, h) temperature, for slush water (a, c, e & g) and under-ice water (b,  
394 d, f & h). Error bars for slush water data (a, c, e & g) indicate the range of duplicate  
395 measurements. Error bars are only shown if they extend beyond the symbols.

396

397 Fig 4 Relationships between salinity and bromoform concentrations in slush water.  
398 Solid and dashed line represents the linear regression line. Bromoform concentrations in  
399 slush water were correlated with the salinity in slush water for salinity > 5 ( $r = 0.93$ ,  $P$   
400 < 0.0001,  $n = 12$ ) and for salinity < 5 ( $r = 0.64$ ,  $P < 0.046$ ,  $n = 10$ ).

401

402

403 **Table captions**

404

405 Table 1. Mean, minimum, Q1 (25 percentile), median, Q3 (75 percentile) and maximum  
406 of bromoform and chl-*a* concentrations, and salinity and temperature for slush water  
407 (n=22) and under-ice water (n=30 to 32) as measured during the study period.



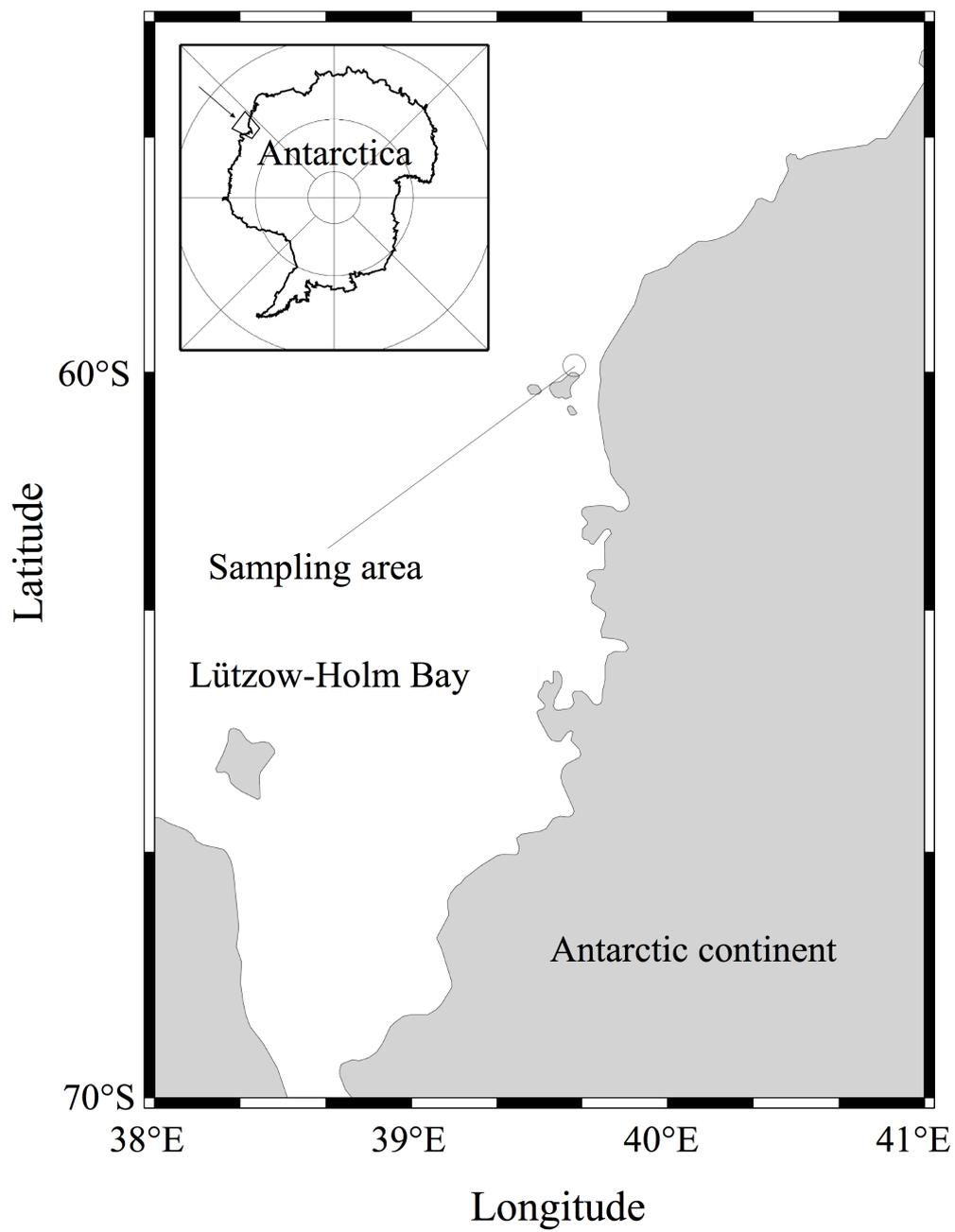


Figure 1. Nomura et al.

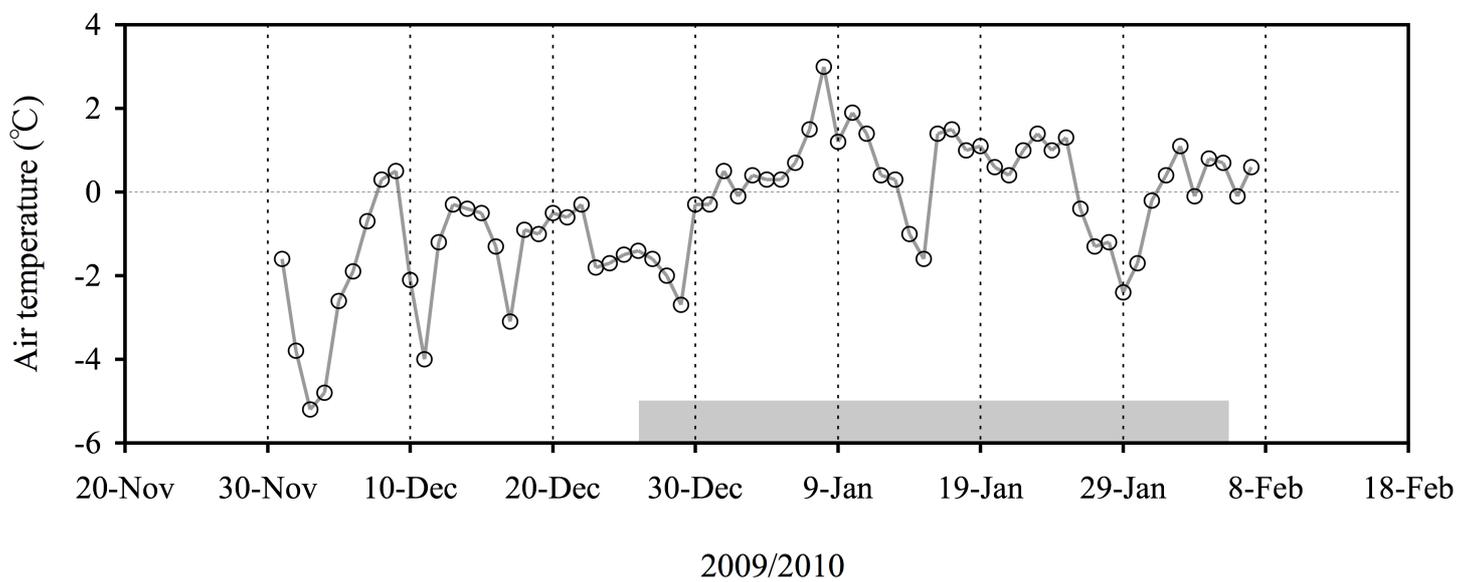


Figure 2. Nomura et al.

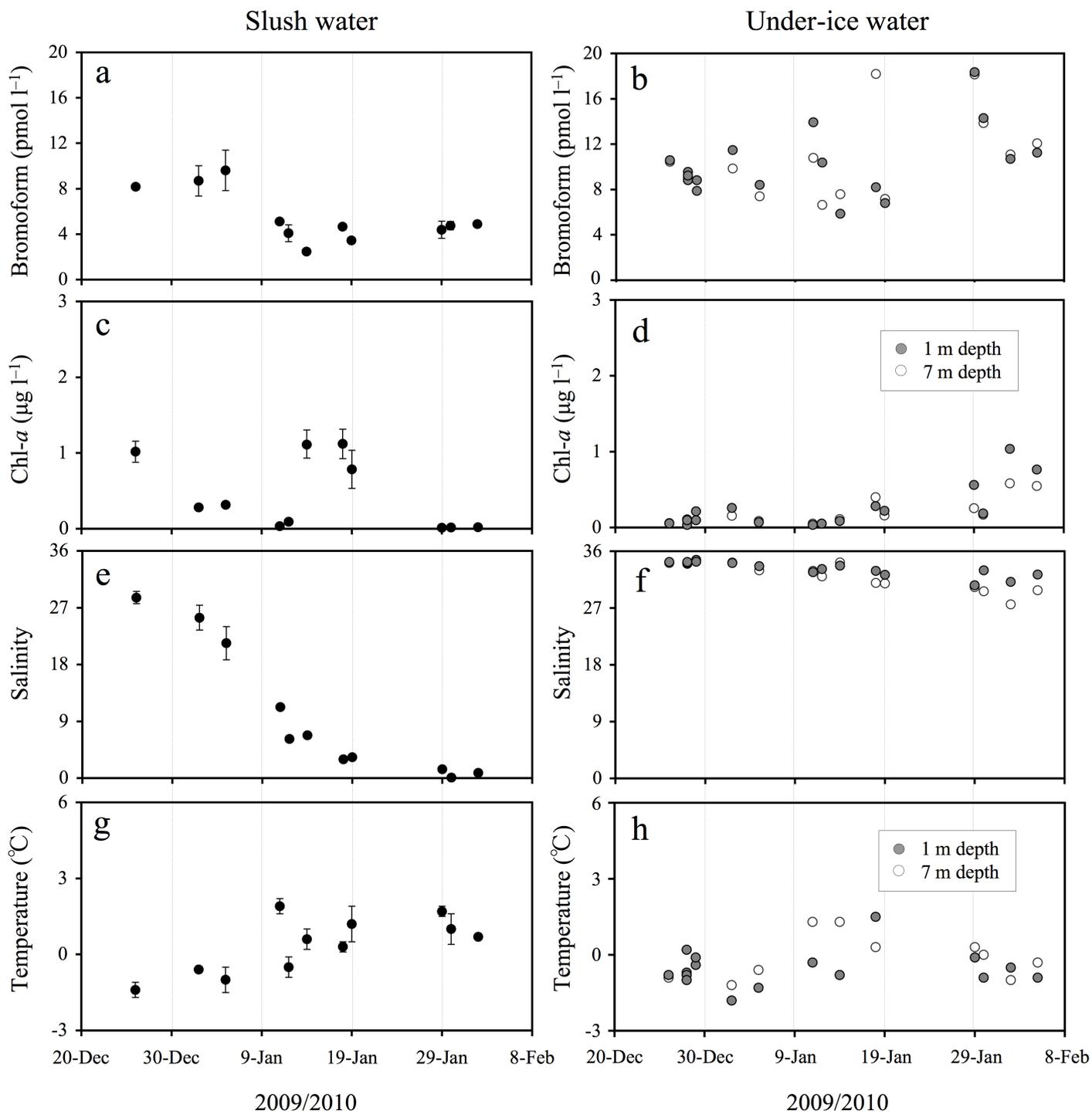


Figure 3. Nomura et al.

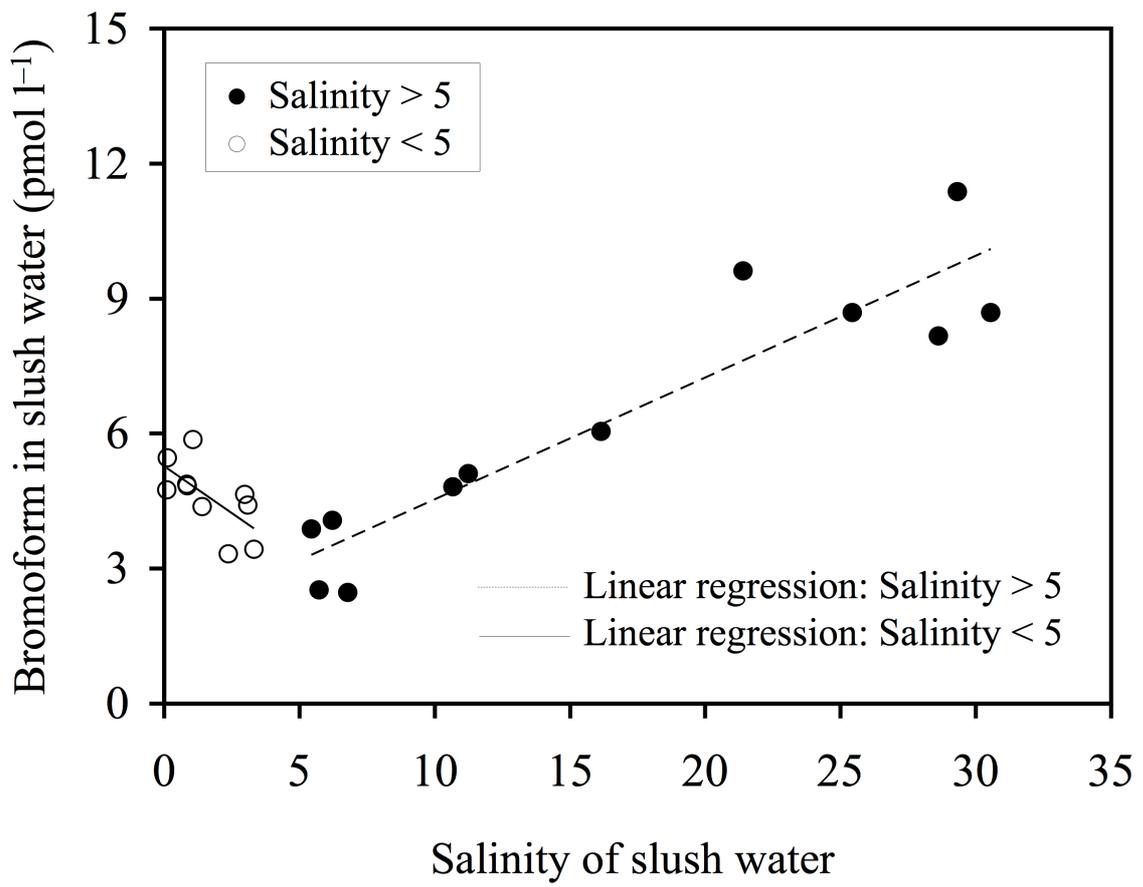


Figure 4. Nomura et al.

Table 1. Mean, minimum, Q1 (25 percentile), median, Q3 (75 percentile) and maximum of bromoform and chl-*a* concentrations, and salinity and temperature for slush water (n=22) and under-ice water (n=30 to 32) as measured during the study period.

Sample	Parameter	Mean	Minimum	Q1	Median	Q3	Maximum
Slush water	Bromoform (pmol l <sup>-1</sup> )	5.5	2.5	4.2	4.8	6.0	11.4
	Chl- <i>a</i> (µg l <sup>-1</sup> )	0.4	0.0	0.0	0.2	0.7	1.1
	Salinity	9.7	0.1	1.6	5.6	14.9	30.6
	Temperature (°C)	+0.5	-1.9	-0.4	+0.6	+1.3	+2.6
Under-ice water	Bromoform (pmol l <sup>-1</sup> )	10.9	5.9	8.4	10.4	12.5	18.3
	Chl- <i>a</i> (µg l <sup>-1</sup> )	0.2	0.0	0.1	0.1	0.3	1.0
	Salinity	32.5	27.6	31.1	32.9	34.1	34.7
	Temperature (°C)	-0.4	-1.8	-0.9	-0.7	-0.1	+1.5