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1 **Incorporation of nitrogen compounds into sea ice from atmospheric deposition**

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33

34 ABSTRACT

35

36 Temporal measurements of temperature, salinity, water-oxygen isotopic ratio and nutrient
37 concentrations at Saroma-ko Lagoon, southern Sea of Okhotsk, were made in
38 February–March 2008 to examine the processes by which nitrogen compounds from the
39 atmosphere were incorporated via snowfall into sea ice. Granular ice made up more than half
40 the ice thickness, and the mass fraction of snow in the snow-ice layer on top of the ice ranged
41 from 0.8% to 46.9%. The high concentrations of $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ observed in the snow
42 and snow-ice throughout the study period were likely due to the proximity of the study site, in
43 northern Japan, to the east coast of the Asian continent. Pollutants containing high NO_3^- and
44 NH_4^+ concentrations are transported from east Asia and deposited in snowfall over the sea ice
45 in the southern part of the Sea of Okhotsk. Compared with $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+
46 concentrations, PO_4^{3-} concentrations in the snow and snow-ice were low. The strong
47 correlation between the $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ concentrations in the snow-ice and the mass
48 fraction of snow indicates that the nitrogen compounds on top of the sea ice was controlled
49 mainly by the snow contribution to the sea ice when snow-ice predominated. Our results
50 indicate that chemical cycles in sea ice can be affected by polluted precipitation (snow)
51 originating from a nonpolar sea.

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54 Keywords: Nutrient, Sea ice, Snow, Melting, Sea of Okhotsk

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68 1. Introduction

69

70 In sea ice, the ice and brine-channel network system contains abundant microorganisms such
71 as ice algae and bacteria (e.g., Arrigo et al., 2010). Photosynthesis by ice algae causes the low
72 concentrations of nutrients that are observed in sea ice (Dieckmann et al., 1991; McMinn et
73 al., 1999). Nutrients are re-supplied by oxidative remineralization of organic matter by
74 heterotrophic organisms and bacteria (Thomas et al., 1995) and sometimes by replenishment
75 from under-ice seawater (Nomura et al., 2009; Thomas et al., 2010). The atmospheric transfer
76 and deposition of nutrients onto sea ice is an important source of nutrients for potentially
77 nutrient-depleted sea-ice surfaces (Rahm et al., 1995; Kaartokallio, 2000; Granskog et al.,
78 2003; Krell et al., 2003; Granskog and Kaartokallio, 2004; Nomura et al., 2010a). In the
79 Northern Hemisphere, snow on sea ice contains high concentrations of nutrients, which are
80 incorporated into the ice during snow-ice formation. The flooding of sea ice by seawater and
81 the resulting formation of snow-ice are widespread and important ice-thickening processes
82 (Lange et al., 1990; Eicken et al., 1994; Jeffries et al., 2001). When sufficient snow has been
83 deposited on sea ice, the ice surface is depressed below sea level and flooding occurs at the
84 snow–sea ice interface. Subsequent freezing of the snow and water leads to the formation of
85 snow-ice. These processes strongly affect the heat budget, biological productivity and
86 chemical composition of polar oceans. However, the contribution of nutrient loading from the
87 atmosphere has not been studied in detail (Thomas et al., 2010).

88

89 In sea ice of the southern Sea of Okhotsk, concentrations of nitrogen compounds, especially
90 NO_3^- and NH_4^+ , in snow and snow-ice are high, which implies that these compounds are
91 supplied from the atmosphere by snowfall and are incorporated into the sea ice through
92 snow-ice formation (Nomura et al., 2010a). The high concentrations may be due to the
93 location of the study area, off the east coast of the Asian continent; particulate pollutants from
94 that area contain high NO_3^- and NH_4^+ concentrations (Ooki and Uematsu, 2005). In a
95 previous study (Nomura et al., 2010a), we focused on the spatial distribution of nutrients in
96 sea ice in the southern Sea of Okhotsk, but no information on the temporal variation of
97 nutrient concentrations in the sea ice in this area is available. In particular, there are no data
98 on the incorporation of nitrogen compounds ($\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+) into the sea ice.

99

100 In this study, we investigated the temporal variation of nutrient concentrations in sea ice in
101 Saroma-ko Lagoon to determine the incorporation processes, particularly the incorporation of

102 nitrogen compounds during snow-ice formation at the top of the sea ice. We hope that our
103 results will improve our understanding of the role of sea ice in biogeochemical cycling in the
104 southern Sea of Okhotsk and beyond.

105

106

107 **2. Materials and methods**

108

109 *2.1. Sampling date and general information of Saroma-ko Lagoon*

110

111 Sea ice, under-ice water, and snow were sampled at a fixed station on Saroma-ko Lagoon
112 between 25 February and 4 March 2008. The lagoon (surface area, 149 km²; mean depth, 14.5
113 m) is located on the northeast coast of Hokkaido, Japan, and is connected to the Sea of
114 Okhotsk by two inlets (Fig. 1). The water mass of the eastern part of the lagoon consists
115 mainly of Okhotsk Sea water with freshwater input from the Saromabetsu River (Shirasawa
116 and Leppäranta, 2003; Nomura et al., 2009; Nomura et al., 2010b). Generally, freezing started
117 at the beginning of January, and the whole surface of the lagoon was covered with sea ice
118 from early February through early April (Shirasawa et al., 2005). The maximum annual
119 thickness of ice was 35–60 cm in the eastern lagoon, and on average, the growth to 34 cm
120 took 1 month, to mid-February, and thereafter the ice grew a further 8 cm (Shirasawa et al.,
121 2005). The average snow thickness on the ice was 11 cm (standard deviation of 10 cm) in
122 mid-February (Shirasawa et al., 2005). Northwesterly winds were dominant in the ice-covered
123 season in this area (Kodama et al., 1999). Because the sea ice grows in a semi-enclosed
124 lagoon, the conditions are stable and thus provide an opportunity to examine the temporal
125 change in the physico-chemical properties of the sea ice at a fixed location (Kudoh et al.,
126 1997; Shirasawa et al., 1997; Nomura et al., 2009).

127

128

129 *2.2. Sampling of sea ice, under-ice water, and snow*

130

131 A subset of sea ice cores per day of the study was collected with a SIPRE (Snow, Ice, and
132 Permafrost Research Establishment) ice corer with an internal diameter of 7.5 cm.
133 Immediately after collecting a core, we measured the ice temperature by inserting a
134 needle-type temperature sensor (Testo 110 NTC, Brandt Instruments, Inc., Prairieville, USA)
135 into holes drilled into the core. To avoid contamination from the temperature sensor, we then

136 collected a new core for nutrient analysis. Then sea ice core was packed it in a polyethylene
137 bag and kept it horizontal in a cooler box with snow as a coolant to avoid the loss of brine
138 from ice core. We did not see any liquid in the plastic bag after storage, supporting low brine
139 drainage. However, it is likely that brine drainage occurred when collecting the sea ice cores
140 from the sea ice, in practice this cannot be avoided, especially for the lowest parts of the ice,
141 as some is lost when a core is retrieved (moved upward). Even though special care was taken
142 and the cores were collected quickly, some brine loss from the sea ice would have occurred.
143 Therefore, these results would have led to a small underestimation of the nutrient
144 concentration in sea ice. However, it is difficult to quantify the nutrient loss during this
145 process.

146

147 Thereafter, the ice core was transported to the nearby SRCA (Saroma Research Center of
148 Aquaculture) and stored in a deep freezer at $-30\text{ }^{\circ}\text{C}$ for further analysis of ice texture, salinity,
149 nutrients and water-oxygen isotopic ratio (water- $\delta^{18}\text{O}$) at Hokkaido University, Sapporo. For
150 measurement of chlorophyll *a* concentrations, a third core was collected on 4 March as
151 described for the second ice core. Immediately upon arrival at the SRCA, this third core was
152 cut into 10–14-cm sections and melted into 200-ml artificial seawater (40 g NaCl in 1 L
153 Milli-Q water) in polyethylene cups to avoid the loss of intracellular organic solute due to cell
154 rupture under osmotic stress (Garrison and Buck 1988). Melted core samples of known
155 volume were filtered through Whatman GF/F glass-fiber filters (nominal pore size $0.7\text{ }\mu\text{m}$)
156 under low vacuum, and the meltwater was put into cryo-vials, which were placed in liquid
157 nitrogen for analysis at Tokai University, Sapporo.

158

159 Under-ice water samples were collected through the ice core holes with a 500-ml Teflon
160 water sampler (GL Science Inc., Tokyo, Japan) at depths of 1 and 3 m below the surface of
161 the ice. We collected these water samples approximately 15 min after the drilling of the ice
162 cores to avoid disturbance caused by the drilling. Under-ice water for salinity and water- $\delta^{18}\text{O}$
163 measurements was subsampled into 10-ml glass vials; water for inorganic nutrient
164 concentration measurements was subsampled into 10-ml polyethylene screw-cap vials; and
165 water for chlorophyll *a* concentration measurements was subsampled into 100-ml
166 polyethylene screw-cap vials (only on 4 March). Nutrient samples were immediately placed
167 in a freezer ($-30\text{ }^{\circ}\text{C}$). Salinity and water- $\delta^{18}\text{O}$ samples were kept at room temperature
168 ($+15\text{ }^{\circ}\text{C}$). Chlorophyll *a* samples were treated in the same manner as ice-melt water and were
169 then stored for further analysis.

170

171 Snow samples, integrated over the whole snow depth, were collected with an acid-washed
172 polycarbonate shovel, placed into polyethylene zipper storage bags and then kept in a freezer
173 ($-30\text{ }^{\circ}\text{C}$). Snow temperatures were measured with a needle-type temperature sensor (Testo
174 110 NTC, Brandt Instruments, Inc., Prairieville, USA). To minimize spatial heterogeneity, we
175 collected ice cores, under-ice water and snow within a $5\text{-m} \times 5\text{-m}$ area during the study
176 period.

177

178

179 *2.3. Sample analysis*

180

181 Ice cores were split in half lengthwise with an electric band saw, and photographs of the ice
182 sections were taken under transmitted light in a cold room ($-16\text{ }^{\circ}\text{C}$) at Hokkaido University.
183 One half of each core was thin-sectioned for ice texture analysis, and the other half was used
184 for measurement of ice salinity, water- $\delta^{18}\text{O}$ and nutrient concentrations. For thin-section
185 analysis, ice sections of 0.7-cm thickness were attached to a glass plate and cut to a thickness
186 of 0.1 cm with a microtome (Model SM2400, Leica Microsystems, Wetzlar, Germany). We
187 photographed ice crystallographic structures by illuminating the thin sections under polarized
188 light. For measurement of ice salinity, water- $\delta^{18}\text{O}$ and nutrient concentrations, the other half
189 of the core was trimmed to a rectangle with a $4.5\text{-cm} \times 2.5\text{-cm}$ cross-section and then sliced
190 into 3.0–4.0-cm-thick sections. To avoid contamination during sampling and handling, we
191 removed 0.3 cm of the outside of the ice sections with a stainless steel plane. In addition, to
192 minimize impact from the loss of brine on the outer margins of the ice core, only the inner
193 sections of the ice cores were used for analysis in this study. The trimmed sections were put
194 into polyethylene zipper storage bags for melting. These samples were melted shortly before
195 analysis at room temperature, as were the snow samples. During the melting of the bulk ice
196 samples, organisms were released from a high salinity to a much lower salinity. This may
197 have resulted in the loss of intracellular organic solutes. However, for nutrient samples, it was
198 important not to contaminate the samples with the addition of the filtered or artificial seawater.
199 Thomas et al. (1998) examined the effect of the loss of intracellular organic solutes on the
200 nutrient concentration in melted water during ice melting. Their results indicated that these
201 amounts was low and could be neglected. Therefore, no filtered or artificial seawater was
202 added to the nutrient samples during ice melting in this study. In addition, melted-ice and

203 water samples for nutrients analysis were not filtered prior to analysis because of the
204 sufficiently short time (30 minutes) of melting and analysis to avoid the remineralization.

205

206 The salinity of the melted snow and sea ice and under-ice water was measured with a salt
207 analyzer (SAT-210; Toa Electronics, Tokyo, Japan). The standard deviation (SD) for salinity,
208 calculated from 15 subsamples taken from a reference water sample ($S = 10.00$), was 0.03
209 (Nomura et al., 2006). The concentrations of nutrients ($\text{NO}_3^- + \text{NO}_2^-$, NH_4^+ and PO_4^{3-}) were
210 determined with an auto-analyzer system (Quattro; Bran+Luebbe, Norderstedt, Germany)
211 according to the spectrophotometric method reported by the Joint Global Ocean Flux Study
212 (JGOFS, 1994). SDs for nutrient concentrations calculated from 10 subsamples taken from a
213 reference water sample with $\text{NO}_3^- + \text{NO}_2^-$, NH_4^+ and PO_4^{3-} concentrations of 52.53, 9.99 and
214 $5.00 \mu\text{mol L}^{-1}$, respectively, were 0.53, 0.18 and $0.07 \mu\text{mol L}^{-1}$, respectively. Water- $\delta^{18}\text{O}$ was
215 determined with a mass spectrometer (DELTA plus; Finnigan MAT, San Jose, CA, USA).
216 Water- $\delta^{18}\text{O}$ in per mil (‰) was defined as the deviation of the $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ ratio of the
217 measured sample from the ratio of the standard mean ocean water. SD for water- $\delta^{18}\text{O}$,
218 calculated from 10 subsamples taken from a reference water sample with water- $\delta^{18}\text{O}$ value of
219 0.241‰, was 0.026‰.

220

221 Chlorophyll *a* concentrations of sea ice and under-ice water were measured by means of
222 high-performance liquid chromatography (Shimadzu SPD-M10AVVP with Class-VP Multi
223 Workstation) according to the method of Furuya et al. (1998).

224

225 To examine ice growth processes, we used thin-section analysis to classify the ice cores into
226 granular ice, columnar ice or mixed granular and columnar ice (Eicken and Lange, 1989). The
227 granular ice was subdivided into frazil ice and snow-ice (or superimposed ice) on the basis of
228 the water- $\delta^{18}\text{O}$ value. For the purposes of this study, snow-ice was defined as granular ice
229 with a water- $\delta^{18}\text{O}$ value that was lower than that of the parent seawater (see Jeffries et al.,
230 1994; Granskog et al., 2004). The amount of each ice type is presented as a proportion of the
231 total length of the ice core.

232

233 To determine the mass fraction of snow in the snow-ice, we used a mass balance equation
234 model (Jeffries et al., 1994; 2001):

235

236 $f_{\text{snow}} + f_{\text{sea}} = 1$ (1)

237

$$238 \quad f_{\text{snow}}\delta_{\text{snow}} + f_{\text{sea}}\delta_{\text{sea}} = \delta_{\text{obs}}, \quad (2)$$

239

240 where f represents the mass fraction of snow or seawater, δ represents the water- $\delta^{18}\text{O}$ value,
241 and the subscripts “snow,” “sea” and “obs” refer to snow, under-ice seawater and observed
242 bulk ice, respectively. For δ_{sea} , we used the parent water- $\delta^{18}\text{O}$ seawater values rather than the
243 value that includes the fractionation factor during seawater freezing (see Jeffries et al., 1994;
244 2001), because we assumed that all the granular ice with a value smaller than that of under-ice
245 water was snow-ice (Jeffries et al., 1994; Granskog et al., 2004). On the basis of the results
246 obtained on each sampling day, the δ_{snow} and δ_{sea} values used for calculation were $-14.2\text{‰} \pm$
247 2.5‰ (mean \pm SD) and $-1.3\text{‰} \pm 0.1\text{‰}$, respectively. The calculated fractions varied within
248 11.3% for δ_{snow} and 1.1% for δ_{sea} in changing the standard deviation values.

249

250

251 **3. Results**

252

253 *3.1. Air temperature, snow depth, slush layer thickness and sea ice thickness*

254

255 During the study period, air temperature ranged from -21.9 to $+2.5$ °C, with a mean of
256 -6.7 °C (Fig. 2a). Westerly winds were dominant during the study period, except on 29
257 February (Fig. 2a). At the onset of the study, snow depth was 0.10 m. Snow depth increased
258 from 0.10 m to a maximum of 0.19 m on 26 February due to an overnight snowfall event (Fig.
259 2b), although the exact time of the event is not known. The snow depth decreased slightly
260 from 28 February to 4 March (Fig. 2b). The slush layer thickness during the study period
261 ranged from 0.01 to 0.11 m (Fig. 2c) owing to the loading of snow on the sea ice, indicating
262 that the sea ice surface was below sea level (negative freeboard). Sea ice thickness increased
263 from 0.37 to 0.55 m during the study period (Fig. 2d). Because the difference in the ice
264 thickness of the two cores collected for the measurement of ice temperature and nutrient
265 analysis for each day was only $0.026 \text{ m} \pm 0.021 \text{ m}$ (mean \pm SD), the sea ice thickness in study
266 area was considered uniform. These results indicated that the increase in ice thickness during
267 the study period (0.18 m) resulted from the temporal increase in ice thickness. These results
268 suggest that the variation in other sea ice parameters (e.g., ice structure, salinity, water- $\delta^{18}\text{O}$
269 and nutrients in sea ice) also indicated the temporal development of the sea ice during the
270 study period. However, the results obtained in this study might be affected by short-range

271 spatial variability in sea ice properties (e.g., Granskog et al., 2004). No data was collected that
272 would allow an evaluation of the heterogeneity of these sea ice parameters.

273

274 *3.2. Ice structure*

275

276 The vertical thin-section photographs of the sea ice cores indicated that granular ice (snow-ice
277 plus frazil ice) made up more than half the ice thickness in the upper parts of all the ice cores,
278 and columnar ice dominated the lower parts of the cores (Fig. 3, Table 1). The fraction of
279 snow-ice increased from 23.0% on 25 February to 59.6% on 3 March, and the fraction of
280 columnar ice varied between 10.3% and 36.2% of the total.

281

282 *3.3. Vertical profiles of temperature, salinity and water- $\delta^{18}O$ of snow, sea ice and under-ice* 283 *water*

284

285 During the study period, snow temperature varied between -5.7 and -0.8 °C. In contrast,
286 throughout the ice core, the sea ice temperature held nearly constant at the same temperature
287 as the under-ice water (Fig. 4a).

288

289 The snow salinity was zero, and the vertical profile of the sea ice salinity was C-shaped, with
290 higher salinities in the upper and lower parts of ice core than in the middle (Fig. 4b), except
291 on 3 and 4 March, when a high sea-ice salinity (up to 6.0) was measured in the middle of the
292 ice core. The salinity of the under-ice water was constant at 32.0 ± 0.3 (mean \pm SD).

293

294 The snow water- $\delta^{18}O$ varied between -18.0‰ and -11.8‰ during the study period (Fig. 4c).
295 At the top of the sea ice, the minimum water- $\delta^{18}O$ was found on 1 March (-7.3‰). The
296 water- $\delta^{18}O$ of the under-ice water was constant at $-1.3\text{‰} \pm 0.1\text{‰}$ (mean \pm SD).

297

298 *3.4. Nutrient concentrations in snow, sea ice and under-ice water*

299

300 During the study period, the concentrations of nitrogen compounds in the snow ranged from
301 15.7 to $57.6 \mu\text{mol L}^{-1}$ for $\text{NO}_3^- + \text{NO}_2^-$ and from 7.2 to $17.6 \mu\text{mol L}^{-1}$ for NH_4^+ ; these values
302 were higher than those of the sea ice and under-ice water (Fig. 4d, e). The vertical profiles of
303 $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ concentrations in the sea ice were similar to those of salinity, with
304 high concentrations at the top and bottom and low concentrations in the middle. In contrast,

305 PO_4^{3-} concentrations were higher in the upper part of the sea ice and in the snow than in the
306 bottom of the sea ice and in the under-ice water (Fig. 4f).

307

308 The concentrations of $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ were highest in the snow (e.g., $\text{NO}_3^- + \text{NO}_2^-$
309 was 2.2–7.9 times as high in the snow as in the under-ice water, and NH_4^+ was 3.0–7.6 times
310 as high) (Table 2). Snow-ice had higher $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ concentrations than did the
311 sea ice (frazil + columnar ice). The trends for the PO_4^{3-} concentrations differed from the
312 trends for the $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ concentrations in all categories. PO_4^{3-} concentrations in
313 the snow-ice were lower than those in the sea ice and under-ice water. The PO_4^{3-}
314 concentrations in the snow were generally low, ranging from 0.1 to 0.2 $\mu\text{mol L}^{-1}$, except on 1
315 March (1.5 $\mu\text{mol L}^{-1}$) and 2 March (1.1 $\mu\text{mol L}^{-1}$).

316

317 The nutrient concentrations in the snow-ice were plotted against salinity, and the plots were
318 compared with the theoretical dilution line (Fig. 5). For $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+
319 concentrations, most of the data plotted well above and deviated widely from the theoretical
320 line. The PO_4^{3-} concentration data, however, plotted mostly along or slightly above the
321 theoretical line. The ratios of the nutrient concentrations in snow-ice to the concentrations in
322 water diluted to the salinity of snow-ice were 4.5 ± 1.7 (mean \pm standard deviation) for NO_3^-
323 $+ \text{NO}_2^-$, 5.3 ± 2.4 for NH_4^+ and 2.3 ± 1.7 for PO_4^{3-} . The relationship between salinity and
324 nutrient concentrations in the snow-ice indicated that the $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+
325 concentrations were correlated with salinity ($R^2 = 0.78$, $P < 0.0001$ for $\text{NO}_3^- + \text{NO}_2^-$; $R^2 =$
326 0.37 , $P < 0.0001$ for NH_4^+). However, salinity and PO_4^{3-} concentrations showed no
327 correlation ($R^2 = 0.001$, $P = 0.809$).

328

329 *3.5. Chlorophyll a concentrations in sea ice and under-ice water*

330

331 Chlorophyll *a* concentrations were high at the bottom of the sea ice (139 times as high as the
332 concentration in under-ice water; 0.4 $\mu\text{g L}^{-1}$) (Fig. 6). Chlorophyll *a* concentration increased
333 with ice depth, from 5.4 $\mu\text{g L}^{-1}$ at the top of the ice to 55.4 $\mu\text{g L}^{-1}$ at the bottom.

334

335 *3.6. Mass fraction of snow in snow-ice*

336

337 The mass fractions of snow in the snow-ice layer at the top of the sea ice ranged from 0.8% to
338 46.9% (Fig. 7). Higher snow fractions (12.6%–46.9%) were found in the top layer (0–3 cm

339 from the ice surface) than in the deeper layers (3–6 and 6–9 cm from the surface). The snow
340 fraction of each snow-ice layer increased with time and reached a maximum of 46.9% in the
341 top 0–3 cm on 1 March.

342

343 *3.7. Relationship between nutrient concentrations and mass fraction of snow in snow-ice*

344

345 The relationship between nutrient concentrations and the mass fraction of snow in the
346 snow-ice is shown in Figure 8. The $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ concentrations were highly
347 correlated with increasing snow fraction ($R^2 = 0.77$, $P < 0.0001$ for $\text{NO}_3^- + \text{NO}_2^-$; $R^2 = 0.74$, P
348 < 0.0001 for NH_4^+). However, snow fraction and PO_4^{3-} concentration showed no correlation
349 ($R^2 = 0.003$, $P = 0.661$).

350

351

352 **4. Discussion**

353

354 That no vertical gradients of sea ice temperature were seen during the study period (Fig. 4a)
355 suggests that no ice growth occurred at the bottom of sea ice. The ice texture (Fig. 3) and the
356 fraction of each ice type in the ice cores (Table 1) also suggest that snow-ice formation
357 contributed to the increase of ice thickness during the study period (Fig. 2d). Sudden
358 decreases of air temperature to lower than -10°C were sometimes observed, particularly
359 during the nighttime (Fig. 2a). Therefore, it was possible for freezing to occur at the top of sea
360 ice as snow-ice formation during the study period. Because the field experiments were done
361 during daytime (usually max temperature and high solar radiation), the fingerprint of the
362 nighttime cooling did not persist to the sampling time due to the daily variation of the
363 temperature in the snow and at the top of sea ice. The study area in Saroma-ko Lagoon is
364 located in the southernmost part of the seasonal sea-ice zone, where the sea ice is relatively
365 thin and the snowfall is high. Therefore, snow-ice formation is likely to have been an
366 important part of the ice-growth process in this area (Shirasawa et al., 2005). Our results are
367 consistent with previously reported field data and thermodynamic modeling results for
368 Saroma-ko Lagoon (Shirasawa et al., 2005). According to these earlier results, the snow-ice
369 fraction contributes more than 50% of the ice thickness during the ice-melting season in
370 Saroma-ko Lagoon.

371

372 High concentrations of NO_3^- (up to $49.2 \mu\text{mol L}^{-1}$) and NH_4^+ (up to $16.9 \mu\text{mol L}^{-1}$) in snow

373 deposited on sea ice in the southern Sea of Okhotsk have been reported (Nomura et al.,
374 2010a). Furthermore, snow deposited on land on the Japan Sea side of Hokkaido also has high
375 concentrations of NO_3^- (~9–24 $\mu\text{mol L}^{-1}$) and NH_4^+ (~3–18 $\mu\text{mol L}^{-1}$) (Aga et al., 2001).
376 These high concentrations were attributed to the proximity of the northern part of Japan to the
377 east coast of the Asian continent: particulate pollutants from the continent contain high NO_3^-
378 and NH_4^+ concentrations (Ooki and Uematsu, 2005), and the pollutants are deposited along
379 with snowfall on the sea ice and land in the southern part of the Sea of Okhotsk. Although we
380 collected samples at only one station in our study, the NO_3^- and NH_4^+ concentrations were of
381 the same order of magnitude as concentrations previously found elsewhere in the southern
382 Sea of Okhotsk and Hokkaido (Aga et al., 2001; Nomura et al., 2010a). This similarity
383 suggest that our data were not affected by local anthropogenic effects near the station and
384 could therefore be applied to a wide area near the southern Sea of Okhotsk.

385

386 Our results suggest that the high concentrations of $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ in the upper part of
387 the sea ice (Fig. 4d, e) were due mostly to atmospheric supply via snowfall and that these
388 compounds were incorporated into the ice by snow-ice formation. This possibility is
389 supported by the fact that the $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ concentrations in the snow-ice were
390 clearly higher than the concentrations expected from the nutrient-to-salinity ratios of the ice
391 (Fig. 5a, b). Furthermore, snow-ice with a high snow contribution had a higher salinity at the
392 top of the sea ice (Fig. 4b and 7) because of the capacity of snow to retain seawater during
393 snow-ice formation. Therefore, it is reasonable to suggest that both the $\text{NO}_3^- + \text{NO}_2^-$ and
394 NH_4^+ concentrations and the salinity in the snow-ice were dependent on the snow contribution,
395 illustrating the correlation between the nutrient concentrations and salinity in snow-ice
396 (Section 3.4).

397

398 High concentrations of $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ in the snow (Fig. 4, Table 2) maintained the
399 supply of nutrients to the upper part of the sea ice. (Note, however, that we did not obtain
400 samples of snow or precipitation before it was deposited over the sea ice.) In addition to
401 snow-ice formation, the melting of snow due to warming (Fig. 2b) also contributed to the
402 increase of $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ concentrations because high-nutrient snow-meltwater
403 ($\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+) was imported into the upper parts of the sea ice. That the
404 concentrations of PO_4^{3-} in the snow and the upper part of the sea ice were low (Fig. 4f)
405 indicates that snowfall and snow-ice formation made only a minor contribution to the
406 phosphorus levels in the upper part of the sea ice.

407

408 Similar results were observed in studies conducted in the Baltic Sea (Kaartokallio, 2001;
409 Granskog et al., 2003) and the White Sea (Krell et al., 2003), in the Northern Hemisphere. For
410 example, in the Baltic Sea, high NO_3^- and NH_4^+ concentrations ($5.5\text{--}12.2 \mu\text{mol L}^{-1} \text{NO}_3^-$;
411 $1.7\text{--}7.6 \mu\text{mol L}^{-1} \text{NH}_4^+$) were observed in the upper part of the sea ice (Kaartokallio, 2001).
412 These previous investigators concluded that the atmospheric supply of nutrients plays an
413 important role in many ice-covered regions.

414

415 The mass fractions of snow in the snow-ice obtained in this study (0.8%–46.9%) were
416 consistent with the fractions for Baltic Sea sea ice (0%–74%; Kawamura et al., 2001;
417 Granskog et al., 2004) but were considerably higher than the fractions in Antarctic sea ice
418 (4%–18%; Eicken et al., 1994; Jeffries et al., 2001). These results suggest that the snow
419 fraction of snow-ice varies considerably with time and location. However, any particular
420 value would depend on the accumulation of snow on the sea ice (Kawamura et al., 2001). At
421 Saroma-ko Lagoon, the snow depth was high with respect to the sea ice thickness (Fig. 2b, d),
422 and the relatively deep snow was one reason why the snow fraction was so high during the
423 study period. In this study, the mass fractions of snow in the snow-ice were calculated by
424 equations 1 and 2 assuming no isotopic fractionation during ice freezing (Jeffries et al., 1994;
425 2001). Some isotopic fractionation occurs during ice formation (e.g., O'Neil, 1968), causing,
426 the water- $\delta^{18}\text{O}$ of sea ice to be greater than that of the under-ice water. Generally, the isotopic
427 fractionation was evaluated from the difference between columnar ice and under-ice water
428 water- $\delta^{18}\text{O}$ (Kawamura et al., 2001). However, because the freezing speed of granular ice is
429 faster than columnar ice, the isotopic fractionation of granular ice is smaller than in columnar
430 ice. In particular, in this study, snow-ice formation might have occurred at nighttime, when
431 the freezing speed was likely to have been very fast, resulting in, minimum isotopic
432 fractionation. Furthermore, the extent of isotopic fractionation in the snow-ice during the
433 formation was unknown and difficult to evaluate. Therefore, in this study the mass fractions
434 of snow in the snow-ice were calculated assuming no isotopic fractionation during ice
435 formation (Jeffries et al., 1994; 2001).

436

437 The strong correlation between the $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ concentrations in the snow-ice and
438 the snow fraction of the snow-ice (Fig. 8) indicates that the concentrations of $\text{NO}_3^- + \text{NO}_2^-$
439 and NH_4^+ at the top of the sea ice, which was mostly snow-ice, were controlled by the
440 contribution of snow falling onto the sea ice. Another factor controlling the $\text{NO}_3^- + \text{NO}_2^-$ and

441 NH_4^+ concentrations is likely to have been the biological activity in the sea ice (e.g., Thomas
442 et al., 2010 and references cited therein). During photosynthesis by ice algae, concentrations
443 of dissolved nutrients in sea ice decrease owing to algal uptake (e.g., Gleiz et al., 1995). In
444 addition, remineralization of organic matter by heterotrophic organisms and bacteria
445 redistributes the nutrients in sea ice (Thomas et al., 1995). This reaction usually occurs in
446 highly productive parts of sea ice, where the content of particulate organic compounds is high
447 throughout the ice (Nomura et al., 2010a). However, our results indicate that the chlorophyll *a*
448 concentration at the top of the sea ice was low (Fig. 6). Chlorophyll *a* concentrations at the
449 top of the sea ice are generally low in Saroma-ko Lagoon (M.A. Granskog, unpublished
450 results). At low chlorophyll *a* concentrations, regeneration of the particulate organic
451 compounds by heterotrophic organisms and bacteria was probably inhibited, which suggests
452 that biological activity was only a minor factor in the nutrient modification at the top of the
453 sea ice in this study. $\text{NO}_3^- + \text{NO}_2^-$, NH_4^+ and PO_4^{3-} concentrations at the bottom of the sea ice
454 were higher than in the middle (Fig. 4), suggesting that the regeneration of the particulate
455 organic compounds occurred at the bottom of the sea ice, where chlorophyll *a* concentrations
456 were high (Fig. 6). In addition, at the bottom of sea ice, salinity and temperature were high
457 (Fig. 4), indicating that the brine volumes were also high. These results suggest that higher
458 nutrients were present at the bottom of sea ice than in the middle of sea ice.

459

460

461 **5. Conclusions**

462

463 Taken together, our results suggest that nitrogen compounds originating from the atmosphere
464 were incorporated into the sea ice via snow-ice formation. The increase in the mass fraction of
465 snow in the snow-ice over time (Fig. 7) provides a clear picture of the incorporation of
466 nitrogen compounds into the sea ice (Fig. 9a). The temporal cross-section of $\text{NO}_3^- + \text{NO}_2^- +$
467 NH_4^+ concentration in the sea ice indicates that the nitrogen compounds penetrated downward
468 with time and that concentrations in the middle part of the sea ice (about 0.2-m depth) were
469 twice as high at the end of the period (4 March) as at the beginning of the period (25
470 February) (Fig. 9a). These variations were coincident with those of the mass fraction of snow
471 in snow-ice (Fig. 9b). Furthermore, because of the large daily variations in air temperature
472 (Fig. 2a), it is likely that a melt-freeze cycle occurred at the top of sea ice and it is possible
473 that this freezing for snow-ice formation led to an increase in the nutrient concentrations by
474 solute exclusion which was enhanced by vertical mixing in the brine-channel. These

475 processes also might increase the penetration of nitrogen compounds downward.
476
477 Based on field experiments focused on the temporal variation of nutrient concentrations in sea
478 ice, incorporation processes were identified, particularly relating to the incorporation of
479 nitrogen compounds during snow-ice formation at the top of the sea ice. Spatial
480 measurements of nutrient concentrations in sea ice in the southernmost part of the Sea of
481 Okhotsk indicated that there were high concentrations of nitrogen at the top of the sea ice in
482 all ice cores (Nomura et al., 2010a), suggesting that these high concentrations might be
483 widespread in the southern parts of the Sea of Okhotsk.
484
485 Incorporation of nitrogen compounds into the sea ice may make an important contribution to
486 biological productivity, although the potential contribution was not measured here. The
487 accumulation of high nutrient snow over sea ice supplied the nutrients to the under-ice water
488 at one time during the melting season, which might be a important supply of nutrient to the
489 subsequent ice edge bloom, suggesting that there is a remarkable difference for the direct
490 snow deposition to seawater. The results presented here indicate the presence of novel
491 chemical cycles in sea ice, which are affected by polluted precipitation (snow). The
492 ice-covered area north of Hokkaido (southernmost part of the Sea of Okhotsk) is a highly
493 productive area and supports a wide range of species (Sakurai, 2007). These species could be
494 sustained by a food chain that starts with the sea ice–related organic matter at the before melt
495 (Hiwatari et al., 2008). Although the effect of melting of snow and sea ice is to reduce the
496 salinity and cause either no change or only a minor enrichment in nitrogen species in the
497 mixed layer in spring and early summer in the southernmost part of the Sea of Okhotsk
498 (Nomura et al, 2010a), results presented here indicate that snow/ice meltwater with different
499 nutrient ratios to those from under-ice water and with a different Redfield ratio is supplied to
500 under-ice water during melt season in April/May in the southern Sea of Okhotsk. In addition,
501 sea-ice formation in the Sea of Okhotsk drives the transport of nutrients (e.g., iron) as far
502 away from the Sea of Okhotsk as the North Pacific Intermediate Water (Talley, 1991; Yasuda,
503 1997; Nishioka et al., 2007). Therefore, sea ice–related chemical cycles that occur in the Sea
504 of Okhotsk affect not only the marginal sea but also the broad open ocean in the North Pacific.
505 Although the degree to which nutrient supply from the atmosphere to sea ice contributes to
506 biological productivity and subsequent nutrient cycles in the Sea of Okhotsk remains unclear,
507 our results may provide useful information for further studies of the marginal sea-ice zone.
508

509

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511

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517

518

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659

660

661 **List of Tables**

662

663 Table 1. Fraction of ice type for total length of ice core.

664

665 g/c indicates the mixture of granular and columnar ice.

666

667

668 Table 2. Mean nutrient concentrations and ranges for snow, snow-ice and sea ice
669 (frazil+columnar ice).

670

671 "—" indicates there was only one data point.

672

673

674 **Figure Legends**

675

676 Fig. 1 Location of sampling station in Saroma-ko Lagoon in the southern Sea of Okhotsk.

677

678 Fig. 2 Temporal variations of (a) air temperature and wind direction, (b) snow depth, (c) slush

679 layer thickness and (d) sea ice thickness. Air temperature and wind direction data were
680 measured at Tokoro and Yubetsu, respectively (Japan Meteorological Agency;
681 <http://www.data.jma.go.jp/obd/stats/etrn/index.php>).

682

683 Fig. 3 Photographs of ice core thin sections in polarized light, 25 February to 4 March. g/c =
684 mixture of granular and columnar ice.

685

686 Fig. 4 Vertical profiles of (a) temperature, (b) salinity, (c) water- $\delta^{18}\text{O}$, (d) $\text{NO}_3^- + \text{NO}_2^-$
687 concentration, (e) NH_4^+ concentration and (f) PO_4^{3-} concentration in snow, sea ice and
688 under-ice water.

689

690 Fig. 5 Plots of (a) $\text{NO}_3^- + \text{NO}_2^-$, (b) NH_4^+ and (c) PO_4^{3-} concentrations versus salinity in
691 snow-ice. The solid lines indicate dilution lines predicted from the salinity of the under-ice
692 water. For comparison of the deviations from the dilution lines for the three nutrients, the
693 y -axis scales were adjusted.

694

695 Fig. 6 Vertical profile of chlorophyll a concentration for each layer of sea ice and under-ice
696 water on 4 March.

697

698 Fig. 7 Temporal variation in mass fraction of snow in snow-ice in each layer. Error bars
699 indicate the calculated fractions varied in changing of the δ_{snow} and δ_{sea} values within the
700 standard deviation.

701

702 Fig. 8 Plots of (a) $\text{NO}_3^- + \text{NO}_2^-$, (b) NH_4^+ and (c) PO_4^{3-} concentrations versus mass fraction
703 of snow in snow-ice.

704

705 Fig. 9 Temporal variations in vertical profiles of (a) sea-ice $\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$
706 concentrations and (b) mass fraction of snow in snow-ice. The bar in (a) indicates the
707 snow-ice thickness for each day. The boxed numerals indicate the concentration and percent
708 for the various lines.

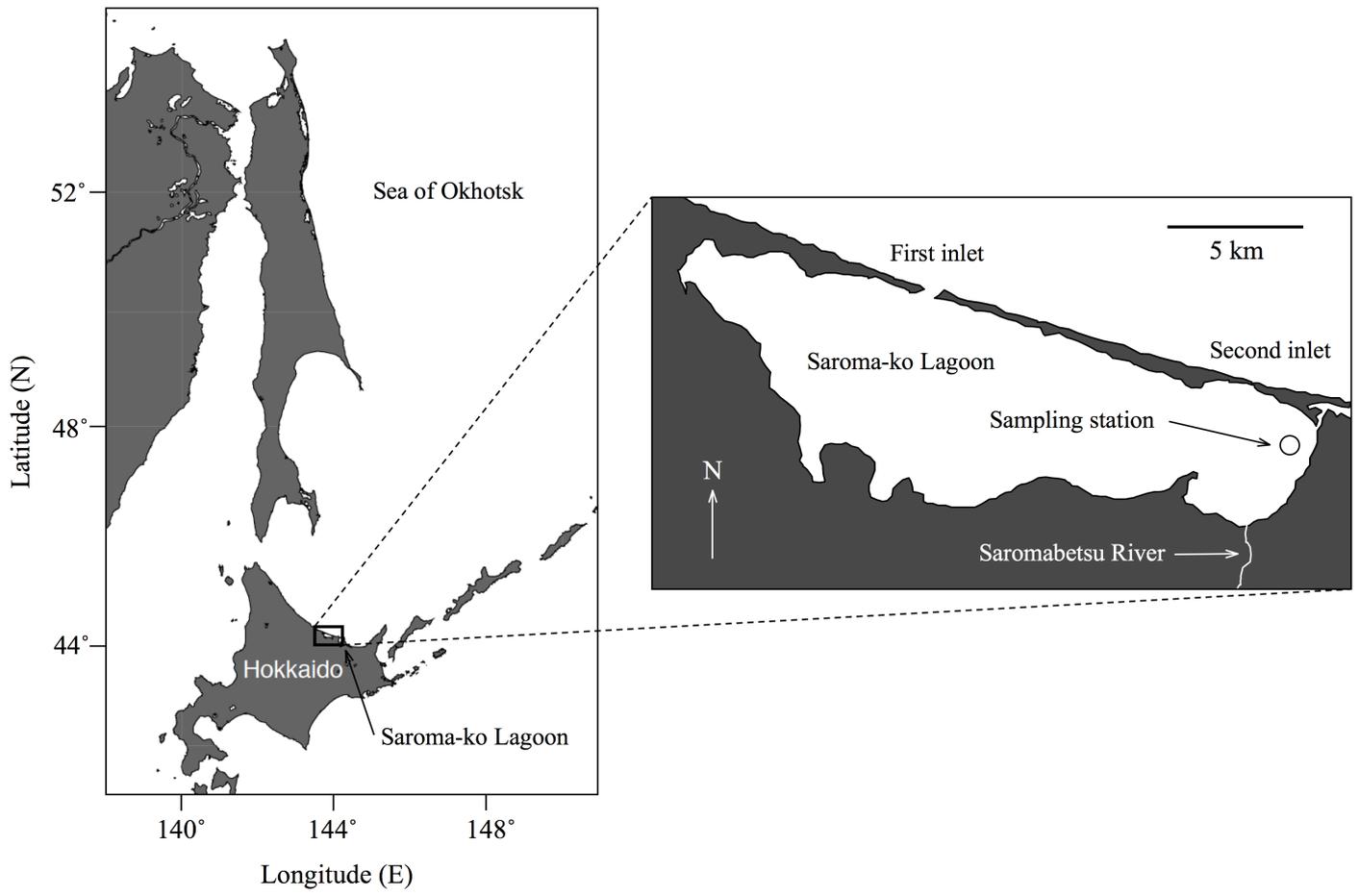


Fig. 1.

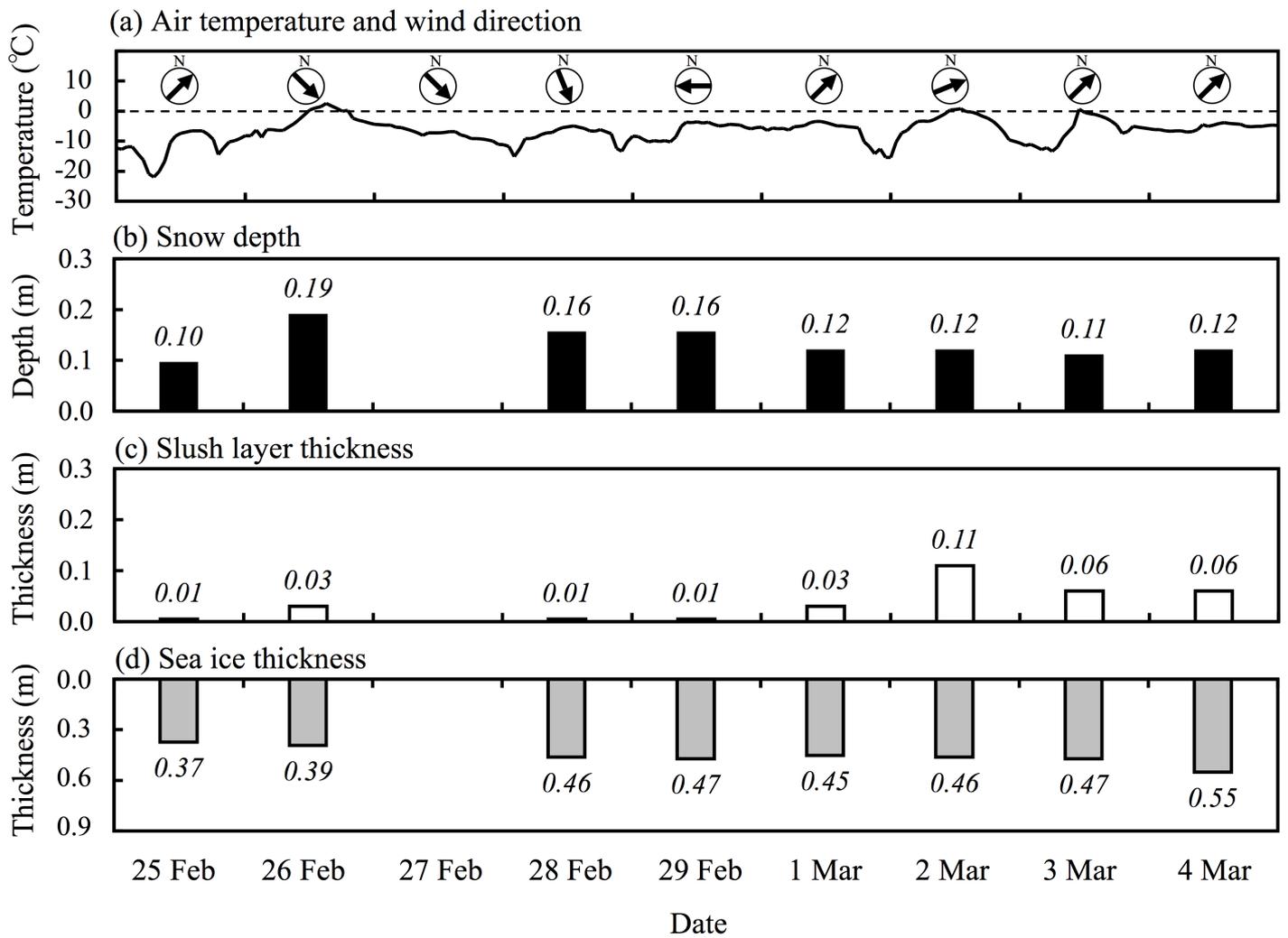


Fig. 2.

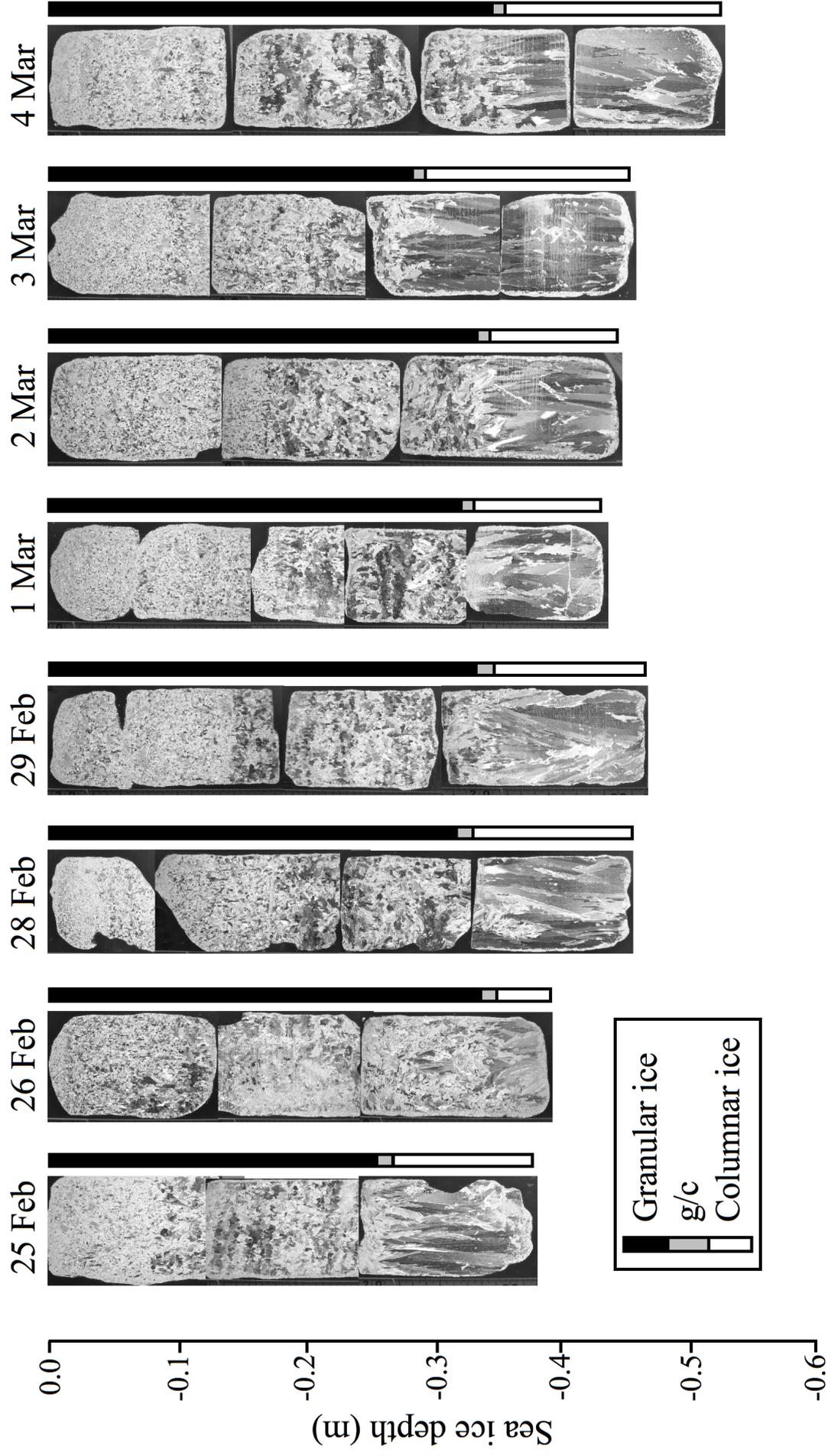


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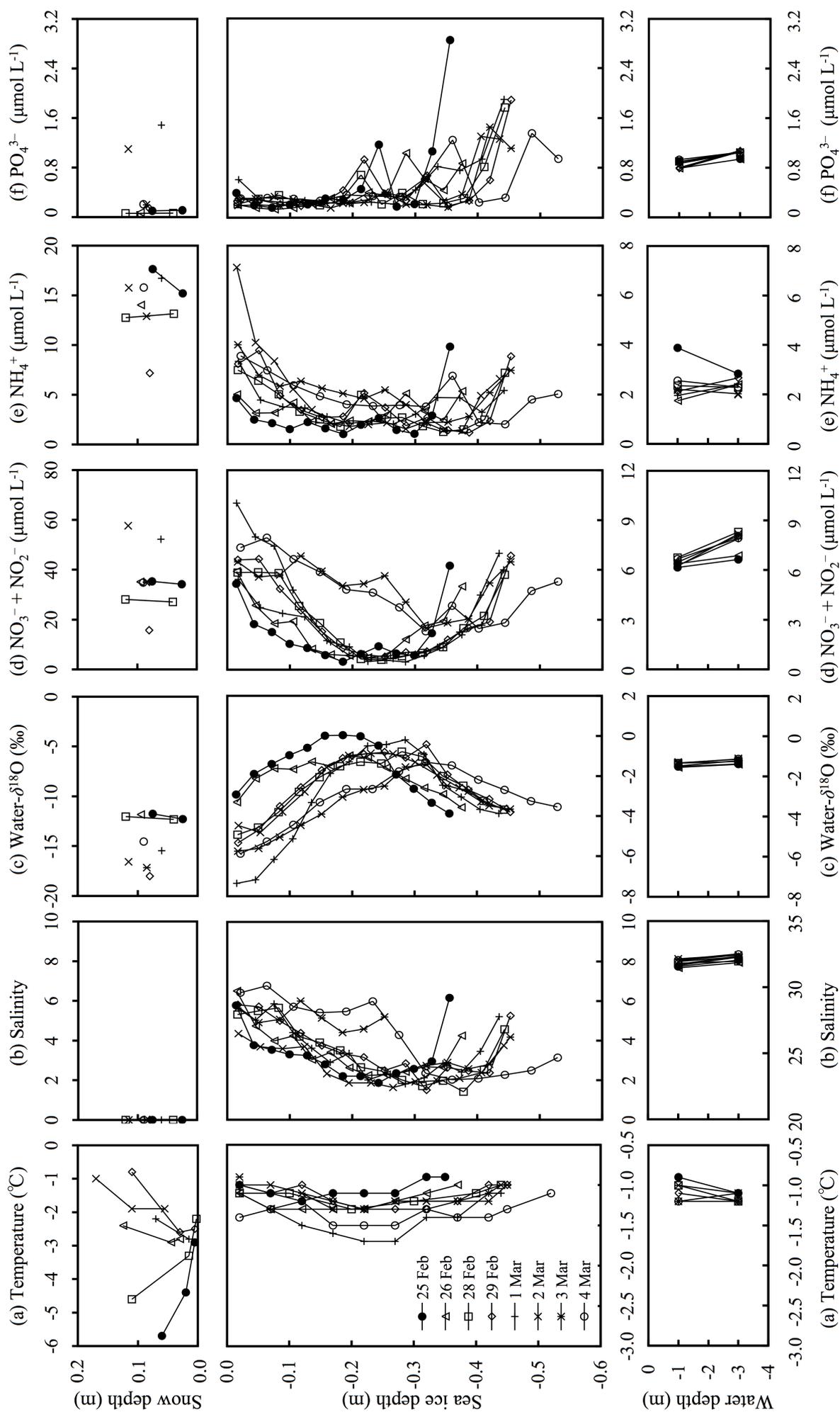


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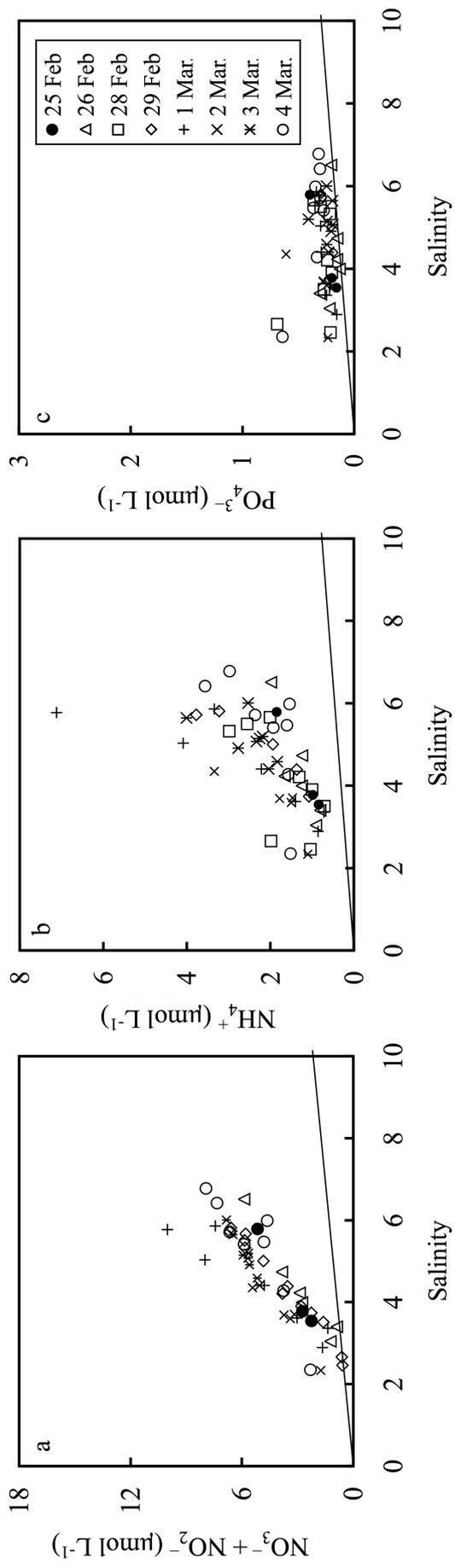


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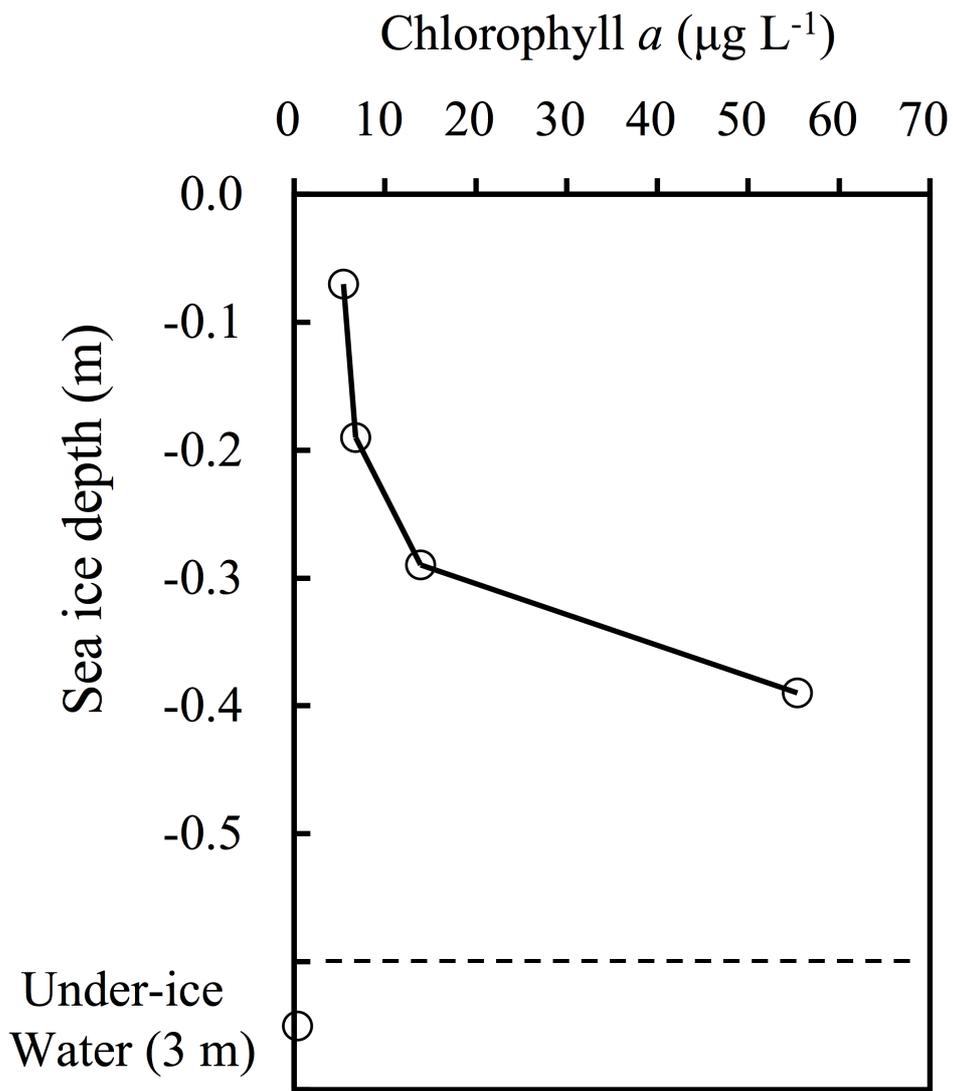


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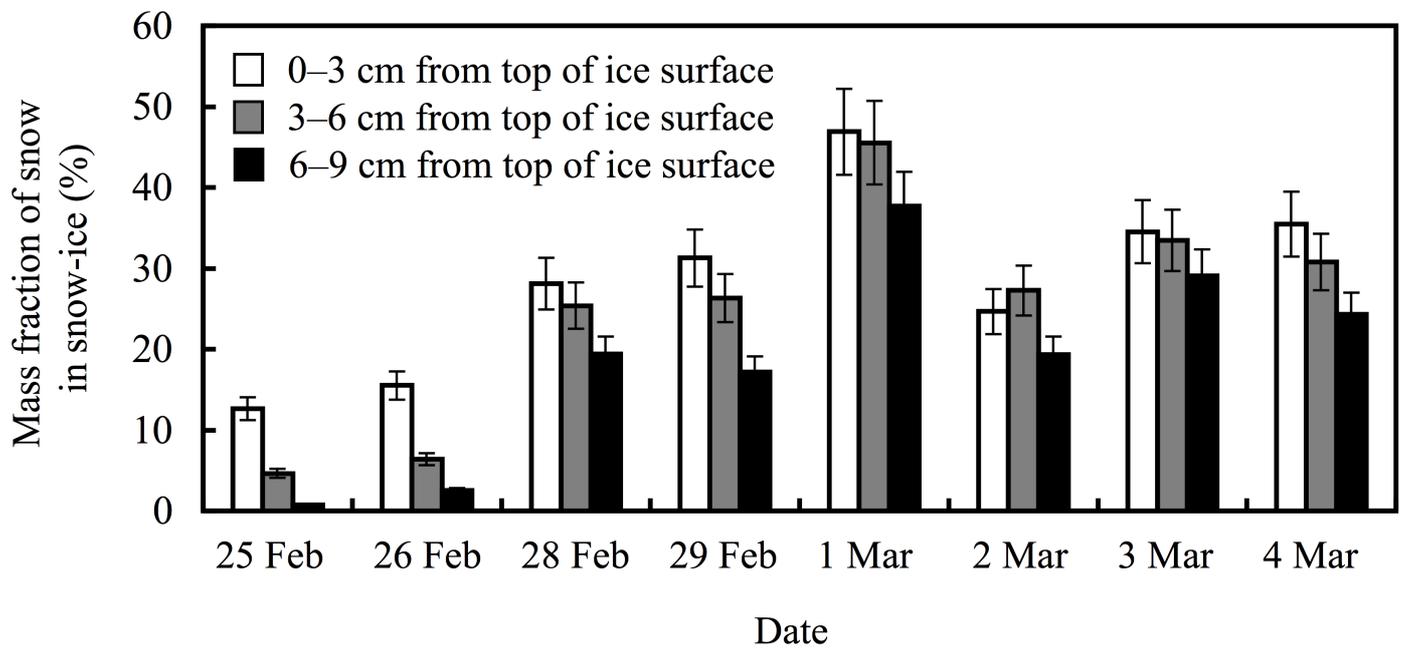


Fig. 7.

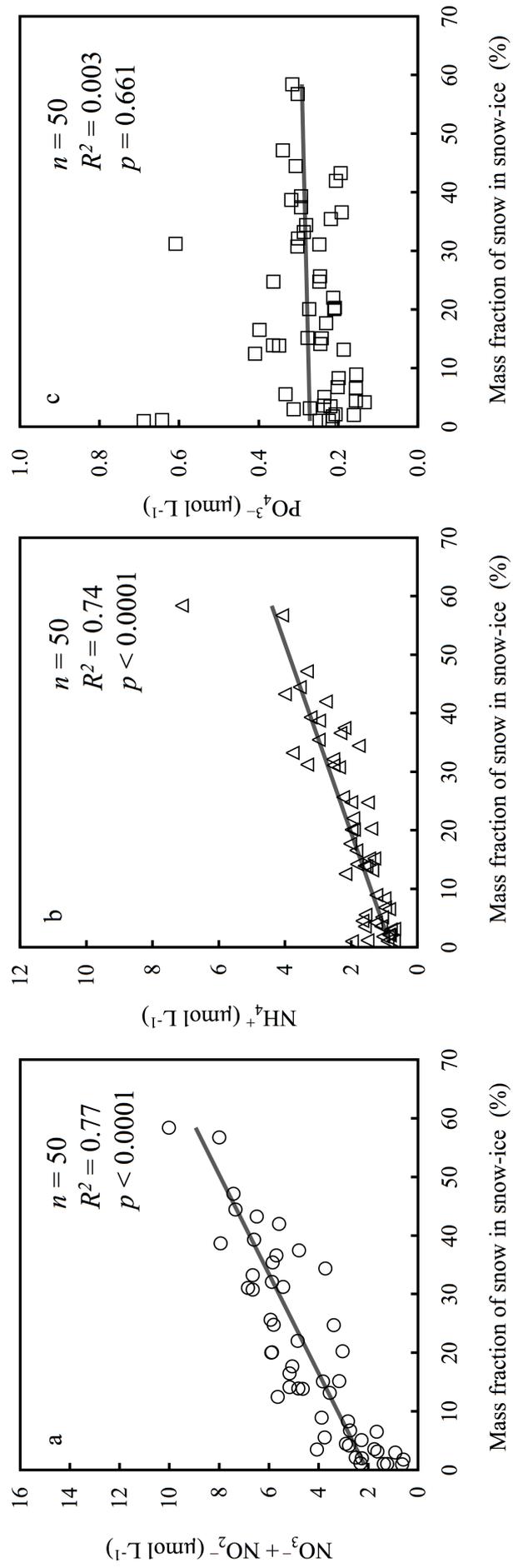


Fig. 8.

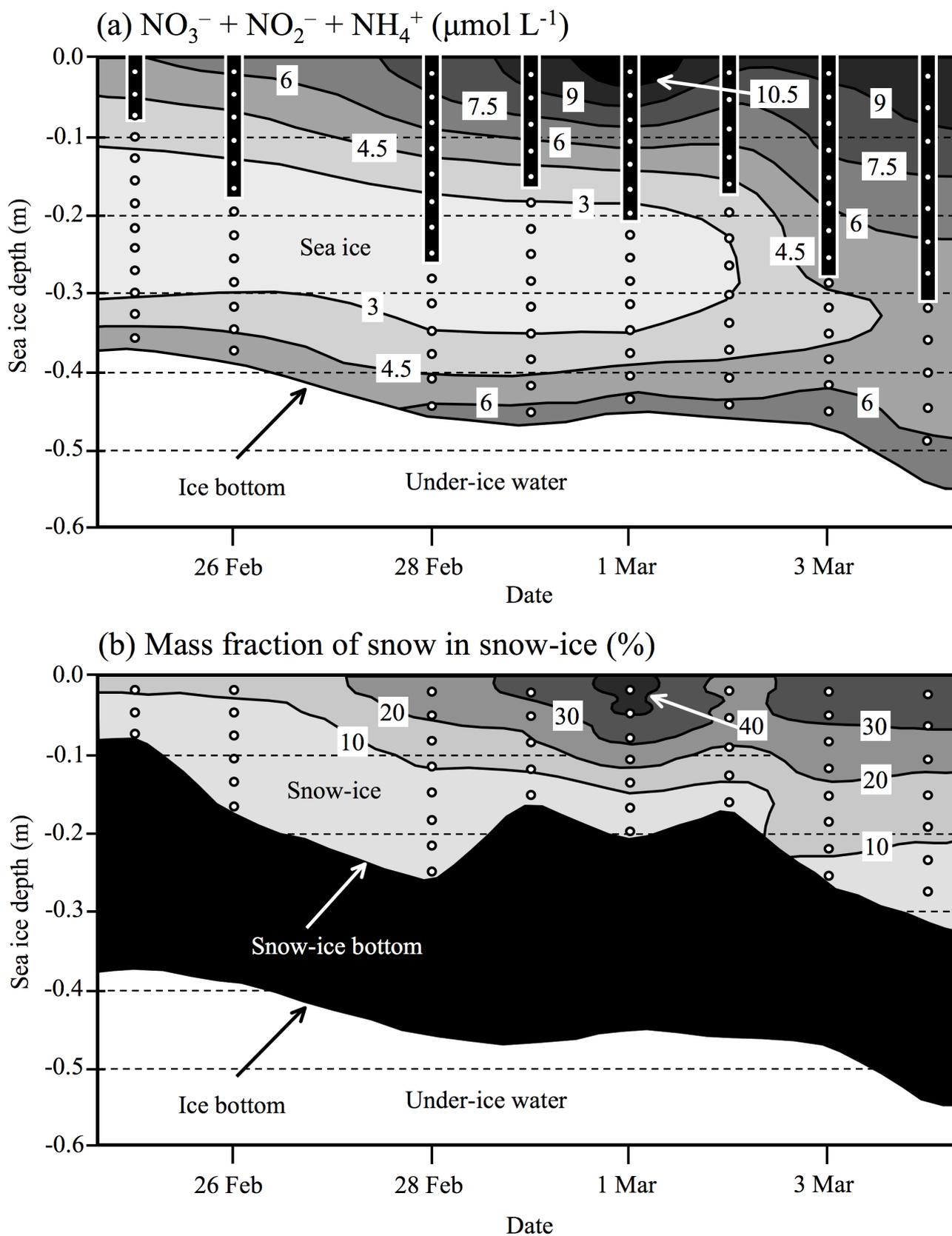


Fig. 9.

Table 1. Fraction of ice type for total length of ice core.

Sampling date	Fraction (%)			
	Snow-ice	Frazil	g/c	Columnar
25 February	23.0	47.3	5.4	24.3
26 February	46.2	41.0	2.6	10.3
28 February	57.2	14.6	2.2	26.1
29 February	35.7	34.5	4.3	25.5
1 March	46.7	24.4	4.4	24.4
2 March	38.5	35.4	2.2	23.9
3 March	59.6	0.0	4.3	36.2
4 March	56.4	7.3	3.6	32.7

g/c indicates the mixture of granular and columnar ice.

Table 2. Mean nutrient concentrations and ranges for snow, snow-ice and sea ice (frazil+columnar ice).

Sampling date	Ice type	NO ₃ ⁻ + NO ₂ ⁻ (μmol L ⁻¹)		NH ₄ ⁺ (μmol L ⁻¹)		PO ₄ ³⁻ (μmol L ⁻¹)	
		Mean	Range	Mean	Range	Mean	Range
25 February	Snow	34.8	34.2–35.4	16.4	15.2–16.7	0.1	0.1–0.1
	Snow-ice	3.4	2.3–5.2	1.2	0.8–1.9	0.3	0.2–0.4
	Sea ice	1.7	0.5–6.3	1.0	0.4–3.9	0.7	0.2–2.9
	Under-ice water	6.6	6.2–6.6	2.8	2.8–3.9	0.9	0.9–0.9
26 February	Snow	35.1	—	14.0	—	0.1	—
	Snow-ice	2.9	0.9–5.9	1.3	0.8–2.0	0.2	0.1–0.3
	Sea ice	2.1	0.7–5.0	1.4	0.9–2.1	0.6	0.2–1.0
	Under-ice water	6.6	6.4–6.9	2.1	1.7–2.4	0.9	0.8–0.9
28 February	Snow	27.6	27.1–28.1	13.0	12.8–13.2	0.1	0.1–0.1
	Snow-ice	3.4	0.6–5.9	1.7	0.7–3.0	0.3	0.2–0.7
	Sea ice	2.4	0.8–5.7	1.1	0.5–2.9	0.6	0.2–1.8
	Under-ice water	7.5	6.8–8.3	2.3	2.4–2.3	1.0	0.9–1.0
29 February	Snow	15.7	—	7.2	—	0.1	—
	Snow-ice	4.8	2.3–6.7	2.3	1.1–3.8	0.2	0.2–0.3
	Sea ice	2.1	0.8–6.9	1.3	0.5–3.5	0.6	0.2–1.9
	Under-ice water	7.3	6.5–8.0	2.4	2.1–2.7	0.9	0.8–1.1
1 March	Snow	52.3	—	16.7	—	1.5	—
	Snow-ice	5.2	1.4–10.0	2.8	0.7–7.1	0.3	0.2–0.3
	Sea ice	2.2	0.5–7.0	1.1	0.5–2.6	0.6	0.3–1.3
	Under-ice water	7.1	6.3–7.9	2.2	2.0–2.4	1.0	0.8–1.0
2 March	Snow	57.6	—	15.7	—	1.1	—
	Snow-ice	3.5	1.8–5.4	1.8	1.1–3.3	0.3	0.2–0.6
	Sea ice	1.9	0.7–6.0	1.4	0.8–2.2	0.7	0.2–1.9
	Under-ice water	7.3	6.5–8.1	2.1	2.0–2.2	1.0	0.9–1.0
3 March	Snow	35.0	—	12.9	—	0.2	—
	Snow-ice	5.8	5.1–6.8	2.5	1.8–4.4	0.2	0.2–0.4
	Sea ice	4.0	2.5–6.5	1.6	0.9–3.0	0.6	0.2–1.5
	Under-ice water	7.2	6.2–8.2	2.1	2.0–2.2	1.0	0.9–1.1
4 March	Snow	34.8	—	15.8	—	0.2	—
	Snow-ice	5.9	3.8–7.9	2.2	1.5–3.6	0.3	0.3–0.4
	Sea ice	3.6	2.3–5.3	1.6	0.8–2.8	0.8	0.2–1.4
	Under-ice water	7.3	6.7–7.9	2.4	2.3–2.6	1.0	0.9–1.1

"—" indicates there was only one data point.