



HOKKAIDO UNIVERSITY

Title	Incorporation of nitrogen compounds into sea ice from atmospheric deposition
Author(s)	Nomura, Daiki; McMin, Andrew; Hattori, Hiroshi et al.
Citation	Marine Chemistry, 127(1-4), 90-99 https://doi.org/10.1016/j.marchem.2011.08.002
Issue Date	2011-12-20
Doc URL	https://hdl.handle.net/2115/70581
Rights	© 2011. This manuscript version is made available under the CC-BY-NC-ND 4.0 license https://creativecommons.org/licenses/by-nc-nd/4.0/
Rights(URL)	https://creativecommons.org/licenses/by-nc-sa/4.0/
Type	journal article
File Information	MarineChemistry_127(1-4)_2011.pdf



Incorporation of nitrogen compounds into sea ice from atmospheric deposition

Daiki Nomura ^{a,*}, Andrew McMinn ^{b,1}, Hiroshi Hattori ^{c,2}, Shigeru Aoki ^{d,3},
Mitsuo Fukuchi ^{a,4}

^a National Institute of Polar Research, 10-3 Midori-cho, Tachikawa-shi, Tokyo, Japan

^b Institute of Antarctic and Southern Ocean Studies, University of Tasmania, Hobart,
Tasmania, Australia

^c Tokai University, Minamisawa, Minami-ku, Sapporo, Japan

^d Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan

*Corresponding author (Daiki Nomura)

Present address: Norwegian Polar Institute, The Polar Environmental Centre, Tromsø 9296,
Norway

e-mail: daiki.nomura@npolar.no

phone: +47-77-75-06-42

fax: +47-77-75-05-01

¹ Andrew McMinn (e-mail: andrew.mcminn@utas.edu.au)

phone: +61-3-6226-2980

² Hiroshi Hattori (e-mail: hattori@tspirit.tokai-u.jp)

phone: +81-11-571-5111

³ Shigeru Aoki (e-mail: shigeru@lowtem.hokudai.ac.jp)

phone: +81-11-706-7430

⁴ Mitsuo Fukuchi (e-mail: fukuchi@nipr.ac.jp)

phone: +81-42-512-0740

ABSTRACT

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

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

1. Introduction

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

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

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

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

2. Materials and methods

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

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

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

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

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

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

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

Snow samples, integrated over the whole snow depth, were collected with an acid-washed polycarbonate shovel, placed into polyethylene zipper storage bags and then kept in a freezer (−30 °C). Snow temperatures were measured with a needle-type temperature sensor (Testo 110 NTC, Brandt Instruments, Inc., Prairieville, USA). To minimize spatial heterogeneity, we collected ice cores, under-ice water and snow within a 5-m × 5-m area during the study period.

2.3. Sample analysis

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

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

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

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

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

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

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

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

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

3. Results

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

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

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

3.2. Ice structure

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

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

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

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

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

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

During the study period, the concentrations of nitrogen compounds in the snow ranged from 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 were higher than those of the sea ice and under-ice water (Fig. 4d, e). The vertical profiles of $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ concentrations in the sea ice were similar to those of salinity, with high concentrations at the top and bottom and low concentrations in the middle. In contrast,

PO₄³⁻ concentrations were higher in the upper part of the sea ice and in the snow than in the bottom of the sea ice and in the under-ice water (Fig. 4f).

The concentrations of NO₃⁻ + NO₂⁻ and NH₄⁺ were highest in the snow (e.g., NO₃⁻ + NO₂⁻ was 2.2–7.9 times as high in the snow as in the under-ice water, and NH₄⁺ was 3.0–7.6 times as high) (Table 2). Snow-ice had higher NO₃⁻ + NO₂⁻ and NH₄⁺ concentrations than did the sea ice (frazil + columnar ice). The trends for the PO₄³⁻ concentrations differed from the trends for the NO₃⁻ + NO₂⁻ and NH₄⁺ concentrations in all categories. PO₄³⁻ concentrations in the snow-ice were lower than those in the sea ice and under-ice water. The PO₄³⁻ concentrations in the snow were generally low, ranging from 0.1 to 0.2 µmol L⁻¹, except on 1 March (1.5 µmol L⁻¹) and 2 March (1.1 µmol L⁻¹).

The nutrient concentrations in the snow-ice were plotted against salinity, and the plots were compared with the theoretical dilution line (Fig. 5). For NO₃⁻ + NO₂⁻ and NH₄⁺ concentrations, most of the data plotted well above and deviated widely from the theoretical line. The PO₄³⁻ concentration data, however, plotted mostly along or slightly above the theoretical line. The ratios of the nutrient concentrations in snow-ice to the concentrations in water diluted to the salinity of snow-ice were 4.5 ± 1.7 (mean ± standard deviation) for NO₃⁻ + NO₂⁻, 5.3 ± 2.4 for NH₄⁺ and 2.3 ± 1.7 for PO₄³⁻. The relationship between salinity and nutrient concentrations in the snow-ice indicated that the NO₃⁻ + NO₂⁻ and NH₄⁺ concentrations were correlated with salinity ($R^2 = 0.78$, $P < 0.0001$ for NO₃⁻ + NO₂⁻; $R^2 = 0.37$, $P < 0.0001$ for NH₄⁺). However, salinity and PO₄³⁻ concentrations showed no correlation ($R^2 = 0.001$, $P = 0.809$).

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

Chlorophyll *a* concentrations were high at the bottom of the sea ice (139 times as high as the concentration in under-ice water; 0.4 µg L⁻¹) (Fig. 6). Chlorophyll *a* concentration increased with ice depth, from 5.4 µg L⁻¹ at the top of the ice to 55.4 µg L⁻¹ at the bottom.

3.6. Mass fraction of snow in snow-ice

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

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

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

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

4. Discussion

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

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

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

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

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

NH_4^+ concentrations is likely to have been the biological activity in the sea ice (e.g., Thomas et al., 2010 and references cited therein). During photosynthesis by ice algae, concentrations of dissolved nutrients in sea ice decrease owing to algal uptake (e.g., Gleiz et al., 1995). In addition, remineralization of organic matter by heterotrophic organisms and bacteria redistributes the nutrients in sea ice (Thomas et al., 1995). This reaction usually occurs in highly productive parts of sea ice, where the content of particulate organic compounds is high throughout the ice (Nomura et al., 2010a). However, our results indicate that the chlorophyll *a* concentration at the top of the sea ice was low (Fig. 6). Chlorophyll *a* concentrations at the top of the sea ice are generally low in Saroma-ko Lagoon (M.A. Granskog, unpublished results). At low chlorophyll *a* concentrations, regeneration of the particulate organic compounds by heterotrophic organisms and bacteria was probably inhibited, which suggests that biological activity was only a minor factor in the nutrient modification at the top of the 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 were higher than in the middle (Fig. 4), suggesting that the regeneration of the particulate organic compounds occurred at the bottom of the sea ice, where chlorophyll *a* concentrations were high (Fig. 6). In addition, at the bottom of sea ice, salinity and temperature were high (Fig. 4), indicating that the brine volumes were also high. These results suggest that higher nutrients were present at the bottom of sea ice than in the middle of sea ice.

5. Conclusions

Taken together, our results suggest that nitrogen compounds originating from the atmosphere were incorporated into the sea ice via snow-ice formation. The increase in the mass fraction of snow in the snow-ice over time (Fig. 7) provides a clear picture of the incorporation of nitrogen compounds into the sea ice (Fig. 9a). The temporal cross-section of $\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$ concentration in the sea ice indicates that the nitrogen compounds penetrated downward with time and that concentrations in the middle part of the sea ice (about 0.2-m depth) were twice as high at the end of the period (4 March) as at the beginning of the period (25 February) (Fig. 9a). These variations were coincident with those of the mass fraction of snow in snow-ice (Fig. 9b). Furthermore, because of the large daily variations in air temperature (Fig. 2a), it is likely that a melt-freeze cycle occurred at the top of sea ice and it is possible that this freezing for snow-ice formation led to an increase in the nutrient concentrations by solute exclusion which was enhanced by vertical mixing in the brine-channel. These

processes also might increase the penetration of nitrogen compounds downward.

Based on field experiments focused on the temporal variation of nutrient concentrations in sea ice, incorporation processes were identified, particularly relating to the incorporation of nitrogen compounds during snow-ice formation at the top of the sea ice. Spatial measurements of nutrient concentrations in sea ice in the southernmost part of the Sea of Okhotsk indicated that there were high concentrations of nitrogen at the top of the sea ice in all ice cores (Nomura et al., 2010a), suggesting that these high concentrations might be widespread in the southern parts of the Sea of Okhotsk.

Incorporation of nitrogen compounds into the sea ice may make an important contribution to biological productivity, although the potential contribution was not measured here. The accumulation of high nutrient snow over sea ice supplied the nutrients to the under-ice water at one time during the melting season, which might be a important supply of nutrient to the subsequent ice edge bloom, suggesting that there is a remarkable difference for the direct snow deposition to seawater. The results presented here indicate the presence of novel chemical cycles in sea ice, which are affected by polluted precipitation (snow). The ice-covered area north of Hokkaido (southernmost part of the Sea of Okhotsk) is a highly productive area and supports a wide range of species (Sakurai, 2007). These species could be sustained by a food chain that starts with the sea ice-related organic matter at the before melt (Hiwatari et al., 2008). Although the effect of melting of snow and sea ice is to reduce the salinity and cause either no change or only a minor enrichment in nitrogen species in the mixed layer in spring and early summer in the southernmost part of the Sea of Okhotsk (Nomura et al., 2010a), results presented here indicate that snow/ice meltwater with different nutrient ratios to those from under-ice water and with a different Redfield ratio is supplied to under-ice water during melt season in April/May in the southern Sea of Okhotsk. In addition, sea-ice formation in the Sea of Okhotsk drives the transport of nutrients (e.g., iron) as far away from the Sea of Okhotsk as the North Pacific Intermediate Water (Talley, 1991; Yasuda, 1997; Nishioka et al., 2007). Therefore, sea ice-related chemical cycles that occur in the Sea of Okhotsk affect not only the marginal sea but also the broad open ocean in the North Pacific. Although the degree to which nutrient supply from the atmosphere to sea ice contributes to biological productivity and subsequent nutrient cycles in the Sea of Okhotsk remains unclear, our results may provide useful information for further studies of the marginal sea-ice zone.

Acknowledgments

We thank Ms. K. Nakamura, Dr. K. Shirasawa, Dr. T. Toyota, Dr. M. A. Granskog, Dr. S. Nihashi, Professor H. Y. Inoue, Dr. J. Nishioka and Ms. A. Murayama for assistance in sampling and analyzing samples, for providing access to instruments and for useful comments. This work was supported partly by a Research Fellowship of the Japan Society for the Promotion of Science (#195968).

References

- Aga, H., Noguchi, I., Sakata, K, 2001. Aquatic chemistry of a reservoir during the thaw season. *Water, Air and Soil Pollut.* 130, 811–816.
- Arrigo, K.R., Mock, T., Lizotte, M.P. 2010. Primary producers and sea ice. In Thomas, D. N. and Dieckmann G. S. eds. *Sea ice: Second edition*. Oxford, Wiley-Blackwell. 283–325.
- Dieckmann, G.S., Lange, M.A., Ackley, S.F., Jennings Jr., J.C. 1991. The nutrient status in sea ice of the Weddell Sea during winter: effects of sea ice texture and algae. *Polar Biol.* 11, 449–456.
- Eicken, H., Lange, M. 1989. Development and properties of sea ice in the coastal regime of the southern Weddell Sea. *J. Geophys. Res.* 94, 8193–8206.
- Eicken, H., Lange, M.A., Hubberten, H.-W., Wadhams, P. 1994. Characteristics and distribution patterns of snow and meteoric ice in the Weddell Sea and their contribution to the mass balance of sea ice. *Ann. Geophys.* 12, 80–93.
- Furuya, K., Hayashi, M., Yabushita, Y. 1998. HPLC determination of phytoplankton pigments using N, N-Dimethylformamide. *J. Oceanogr.* 54, 199–203.
- Garrison, D.L., Buck, K. 1988. Organism losses during ice melting - a serious bias in sea ice community studies. *Polar Biol.* 6, 263–269.

543

544 Gleiz, M., Rutgers v.d. Loeff, M., Thomas, D.N., Dieckmann, G.S. and Millero, F.J. 1995.

545 Comparison of summer and winter inorganic carbon, oxygen and nutrient concentrations in

546 Antarctic sea ice brine. *Mar. Chem.* 51, 81–91.

547

548 Granskog, M.A., Kaartokallio, H., Shirasawa, K. 2003. Nutrient status of Baltic Sea ice:

549 Evidence for control by snow-ice formation, ice permeability, and ice algae. *J. Geophys. Res.*

550 108, C8, 3253, doi:10.1029/2002JC001386.

551

552 Granskog, M.A., Kaartokallio, H. 2004. An estimation of the potential fluxes of nitrogen,

553 phosphorus, cadmium and lead from sea ice and snow in the northern Baltic Sea. *Water Air*

554 *and Soil Pollut* 154, 331–347.

555

556 Granskog, M.A., Leppäranta, M, Kawamura, T., Ehn, J., Shirasawa, K. 2004. Seasonal

557 development of the properties and composition of landfast sea ice in the Gulf of Finland, the

558 Baltic Sea. *J. Geophys. Res.* 109(C2), C02020, doi:10.1029/2003JC001874.

559

560 Hiwatari, T. Shirasawa, K., Fukamachi, Y., Nagata, R., Koizumi, T., Koshikawa, H., Kohata,

561 K. 2008. Vertical material flux under seasonal sea ice in the Okhotsk Sea north of Hokkaido,

562 Japan. *Polar Sci.* 2, 41–54.

563

564 Jeffries, M., Shaw, R., Morris, K., Veazey, A., Krouse, H. 1994. Crystal structure, stable

565 isotopes ($\delta^{18}\text{O}$), and development of sea ice in the Ross, Amundsen, and Bellingshausen seas,

566 Antarctica. *J. Geophys. Res.* 99(C1), 985–995.

567

568 Jeffries, M.O., Krouse, H.R., Hurst-Cushing, B., Maksym, T. 2001. Snow-ice accretion and

569 snow-cover depletion on Antarctic first-year sea-ice floes. *Ann. Glaciol.* 33, 51–60.

570

571 JGOFS, 1994. Protocols for the Joint Global Ocean Flux Study core measurements.

572 International JGOFS Report Series, 19, 174 pp.

573

574 Kaartokallio, H. 2001. Evidence for active microbial nitrogen transformations in sea ice (Gulf

575 of Bothnia, Baltic Sea) in midwinter. *Polar Biol.* 24, 21–28.

576

577 Kawamura, T., Shirasawa, K., Ishikawa, N., Lindfors, A., Rasmus, K., Granskog, M.A., Ehn,
 578 J., Leppäranta, M., Martma, T., Vaikmäe, R. 2001. Time-series observations of the structure
 579 and properties of brackish ice in the Gulf of Finland. *Ann. Glaciol.* 33. 1–4.
 580
 581 Kodama, Y., Takizawa, A., Ishikawa, N., Shirasawa, K., Ishikawa, M., Ikeda, M., Takatsuka,
 582 T., Daibou, T., Aota, M., Fujiyoshi, Y. 1999. Comparison of the meteorological conditions
 583 between the two sites. *Low temp. sci. Ser. A, Data report*, 57. 81–98.
 584
 585 Krell, A., Ummenhofer, C., Kattner, G., Naumov, A., Evans, D., Dieckmann, G.S., Thomas,
 586 D.N. 2003. The biology and chemistry of land fast ice in the White Sea, Russia-A comparison
 587 of winter and spring conditions, *Polar Biol.* 26, 707–719.
 588
 589 Kudoh, S., Robineau, B., Suzuki, Y., Fujiyoshi, Y., Takahashi, M. 1997. Photosynthetic
 590 acclimation and the estimation of temperature ice algal primary production in Saroma-ko
 591 Lagoon, Japan. *J. Mar. Syst.* 11, 93-109.
 592
 593 Lange, M.A., Schlosser, P., Ackley, S.F., Wadhams, P., Dieckmann, G.S. 1990. ^{18}O
 594 concentrations in sea ice of the Weddell Sea, Antarctica. *J. Glaciol.* 36, 124, 315–323.
 595
 596 McMinn, A., Skerratt, J., Trull, T., Ashworth, C., Lizotte, M. 1999. Nutrient stress gradient in
 597 the bottom 5 cm of fast ice, McMurdo Sound, Antarctica. *Polar Biol.* 21, 220–227.
 598
 599 Nishioka, J., Ono, T., Saito, H., Nakatsuka, T., Takeda, S., Yoshimura, T., Suzuki, K., Kuma,
 600 K., Nakabayashi, S., Tsumune, D., Mitsudera, H., Johnson, W.K., Tsuda, A. 2007. Iron input
 601 into the western subarctic Pacific, importance of iron export from the Sea of Okhotsk. *J.*
 602 *Geophys. Res.* 112, C10012, doi:10.1029/2006JC004055.
 603
 604 Nomura, D., Inoue H.Y., and Toyota, T. 2006. The effect of sea ice growth on air-sea CO_2
 605 flux in a tank experiment. *Tellus* 58B, 418–426.
 606
 607 Nomura, D., Takatsuka, T., Ishikawa, M., Kawamura, T., Shirasawa, K., Inoue, H.Y. 2009.
 608 Transport of chemical components in sea ice and under-ice water during melting in the
 609 seasonally ice-covered Saroma-ko Lagoon, Hokkaido, Japan. *Est. Coast. Shelf Sci.* 81,
 610 201–209.

611

612 Nomura, D., Nishioka, J. Granskog, M.A., Krell, A., Matoba, S., Toyota, T., Hattori, H.,
 613 Shirasawa, K. 2010a. Nutrient distributions associated with snow and sediment-laden layers
 614 in sea ice of the southern Sea of Okhotsk. *Mar. Chem.*, 119, 1–8.

615

616 Nomura, D., Inoue-Yoshikawa, H., Toyota, T., Shirasawa, K. 2010b. Effects of snow,
 617 snowmelting and refreezing processes on air-sea-ice CO₂ flux. *J. Glaciol.* 56, 196, 262–270.

618

619 O’Neil, J. 1968. Hydrogen and oxygen isotope fractionation between ice and water. *J. Phys.*
 620 *Chem.* 72, 10, 3683–3684.

621

622 Ooki, A., Uematsu, M. 2005. Chemical interactions between mineral dust particles and acid
 623 gases during Asian dust events, *J. Geophys. Res.* 110, D03201, doi:10.1029/2004JD004737.

624

625 Rahm, L., Håkansson, B., Larsson, P., Fogelqvist, E., Bremle, G., Valderrama, J. 1995.
 626 Nutrient and persistent pollutant deposition on the Bothnian Bay ice and snow fields. *Water*
 627 *Air and Soil Pollut.* 84, 187–201.

628

629 Sakurai, Y. 2007. An overview of Oyashio Ecosystem. *Deep-Sea Res. II* 54, 2525–2542.

630

631 Shirasawa, K., Ingram, R.G., Hudier, E.J.J. 1997. Oceanic heat fluxes under thin sea ice in
 632 Saroma-ko Lagoon, Hokkaido, Japan. *J. Mar. Syst.* 11, 9–19.

633

634 Shirasawa, K., Leppäranta, M. 2003. Hydrometeorological and sea ice conditions at
 635 Saroma-ko lagoon, Hokkaido, Japan. In: *Report Series in Geophysics. University of Helsinki,*
 636 *Finland No. 46pp.* 161–168.

637

638 Shirasawa, K., Leppäranta, M., Saloranta, T., Kawamura, T., Polomoshnov, A., Surkov, G.
 639 2005. The thickness of coastal fast ice in the Sea of Okhotsk. *Cold Reg. Sci. Technol.* 42,
 640 25–40.

641

642 Talley, L.D. 1991. An Okhotuk Sea water anomaly: Implications for ventilation in the North
 643 Pacific, *Deep Sea Res. I* 38, 171–190.

644

Thomas, D.N., Lara, R.J., Eicken, H., Kattner, G., Skoog, A. 1995. Dissolved organic matter in Arctic multi-year sea ice during winter: major components and relationships to ice characteristics. *Polar Biol.* 15, 477–483.

Thomas, D.N., Lara, R.J., Haas, C., Schnack-Schiel, S.B., Dieckmann, G.S., Kattner, G., Nöthig, E.-M., Mizdalski, E. 1998. Biological soup within decaying summer sea ice in the Amundsen Sea, Antarctica. In: Lizzote, M., Arrigo, K. (Eds.) *Biological Processes, Interactions and Variability*. American Geophysical Union, Antar. Res. Ser. 73, 161–171.

Thomas, D.N., Papadimitriou, S., Michel, C. 2010. Biogeochemistry of sea ice. In Thomas, D.N. and Dieckmann, G.S. eds. *Sea ice: second edition*. Oxford, Wiley-Blackwell. 425–467.

Yasuda, I. 1997. The origin of the North Pacific Intermediate Water, *J. Geophys. Res.* 102, 893–909.

List of Tables

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

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).

"—" indicates there was only one data point.

Figure Legends

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

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

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

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

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

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

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

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

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

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

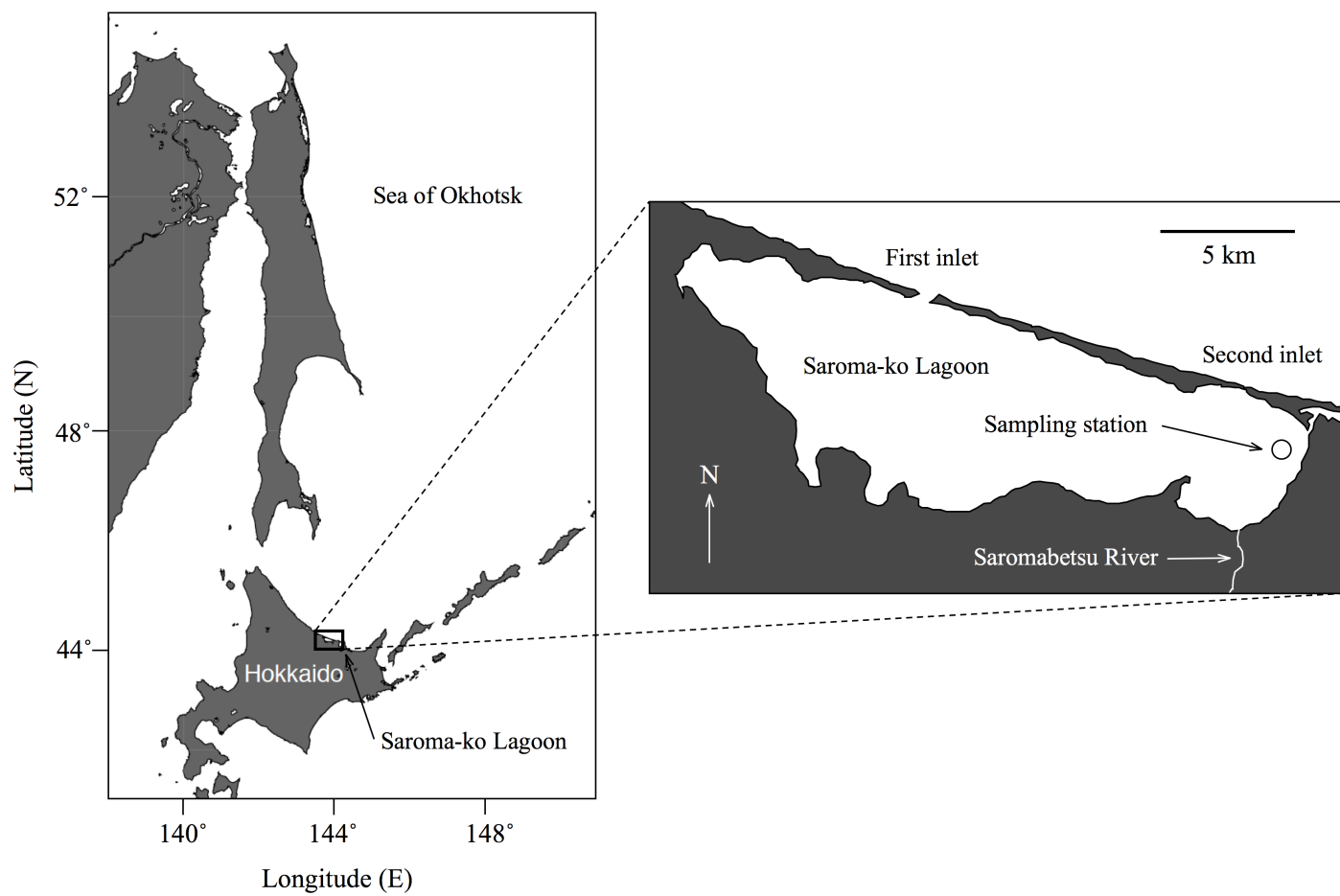


Fig. 1.

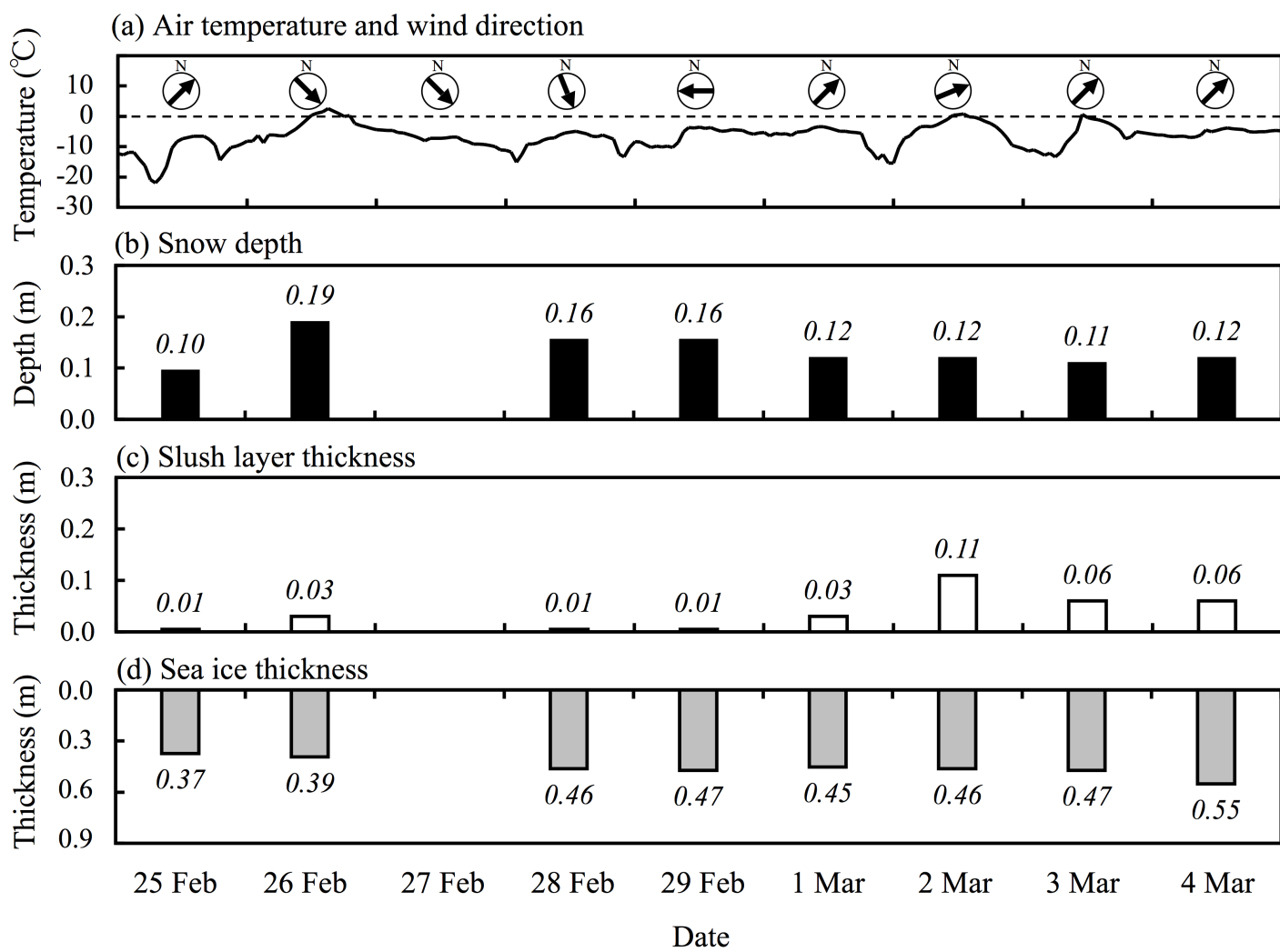


Fig. 2.

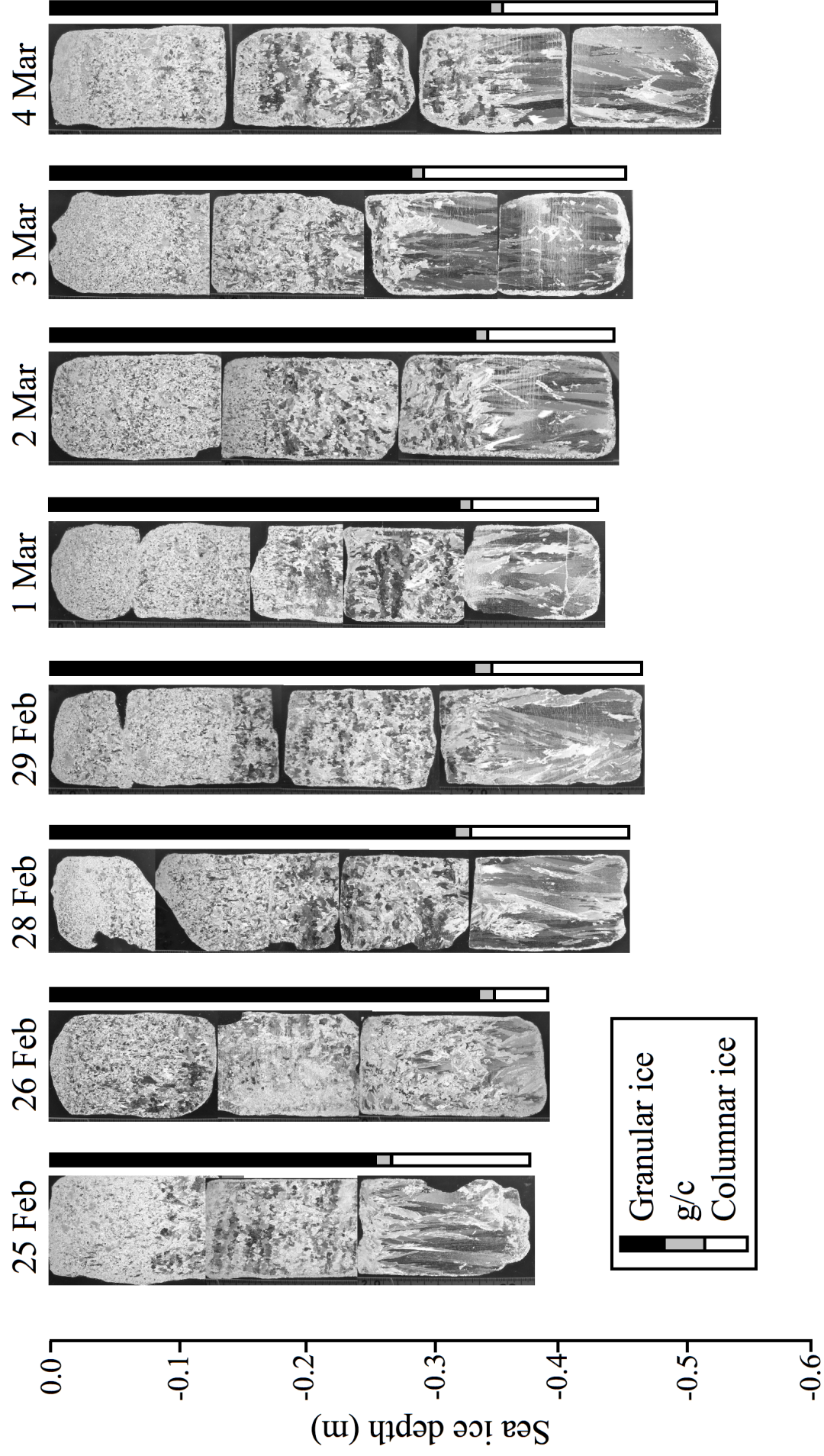


Fig. 3.

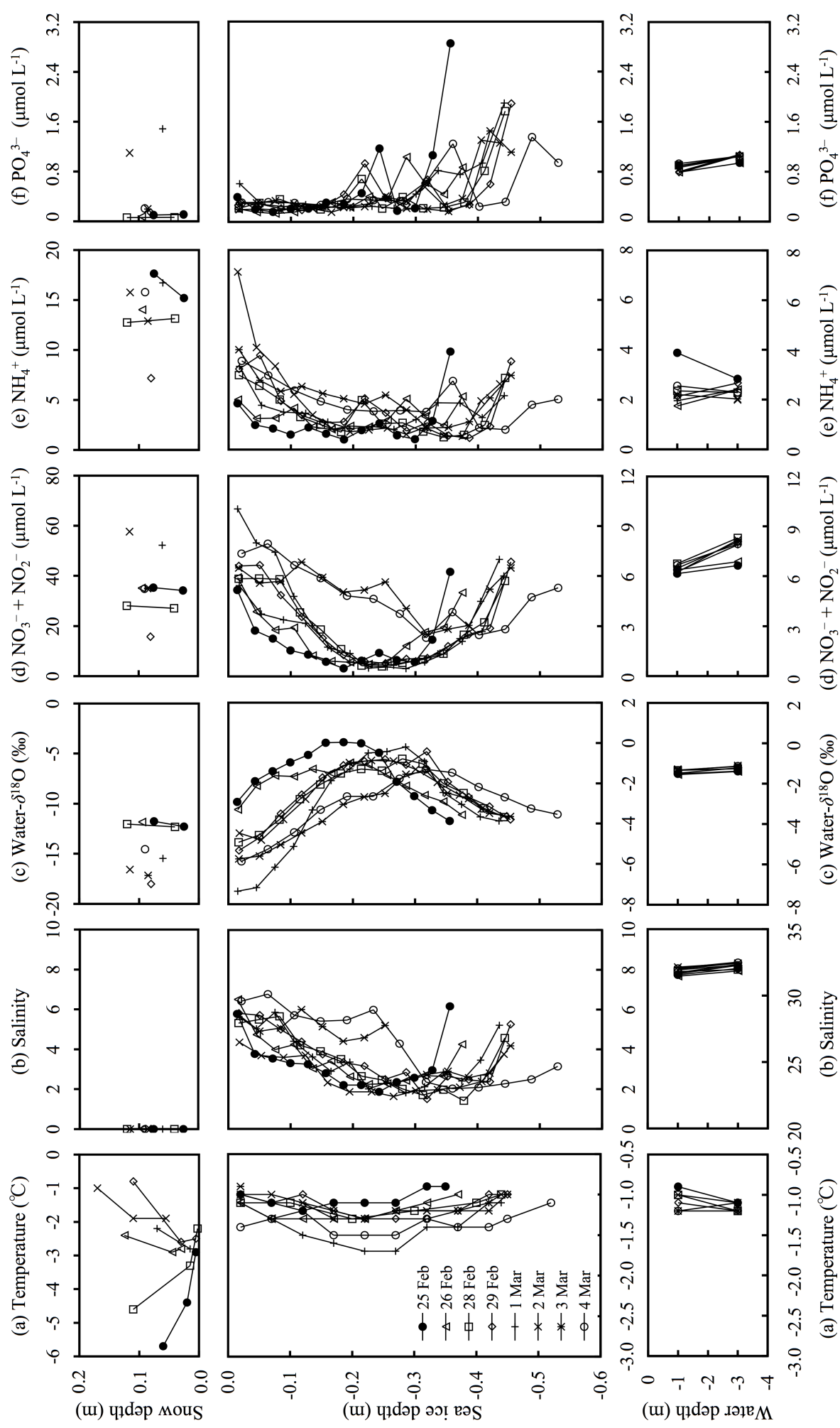


Fig. 4.

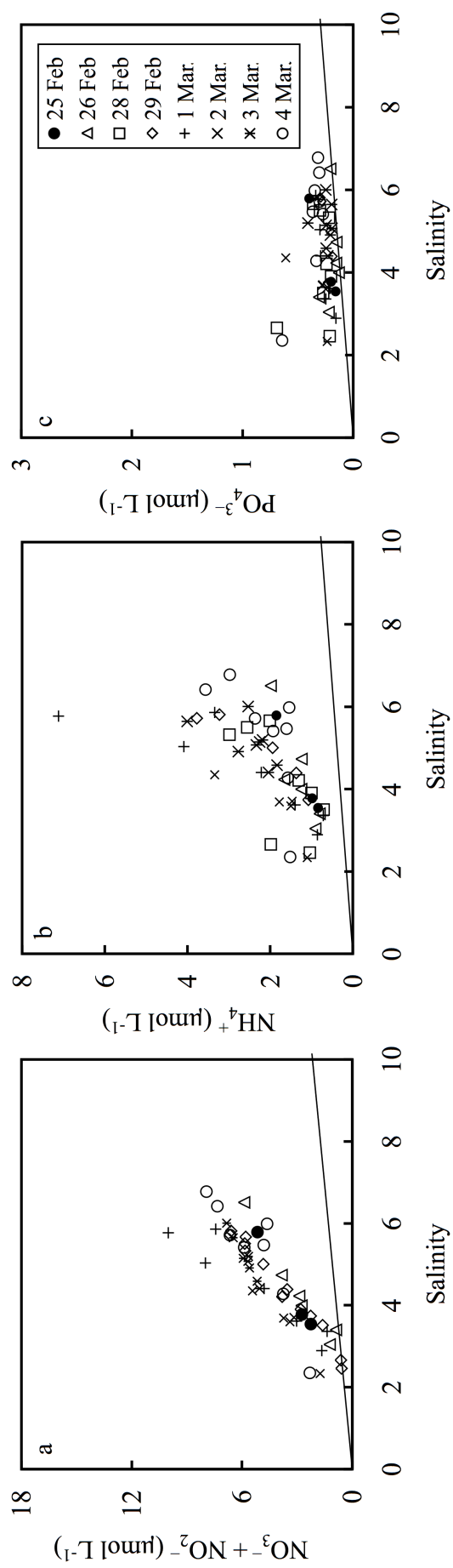


Fig. 5.

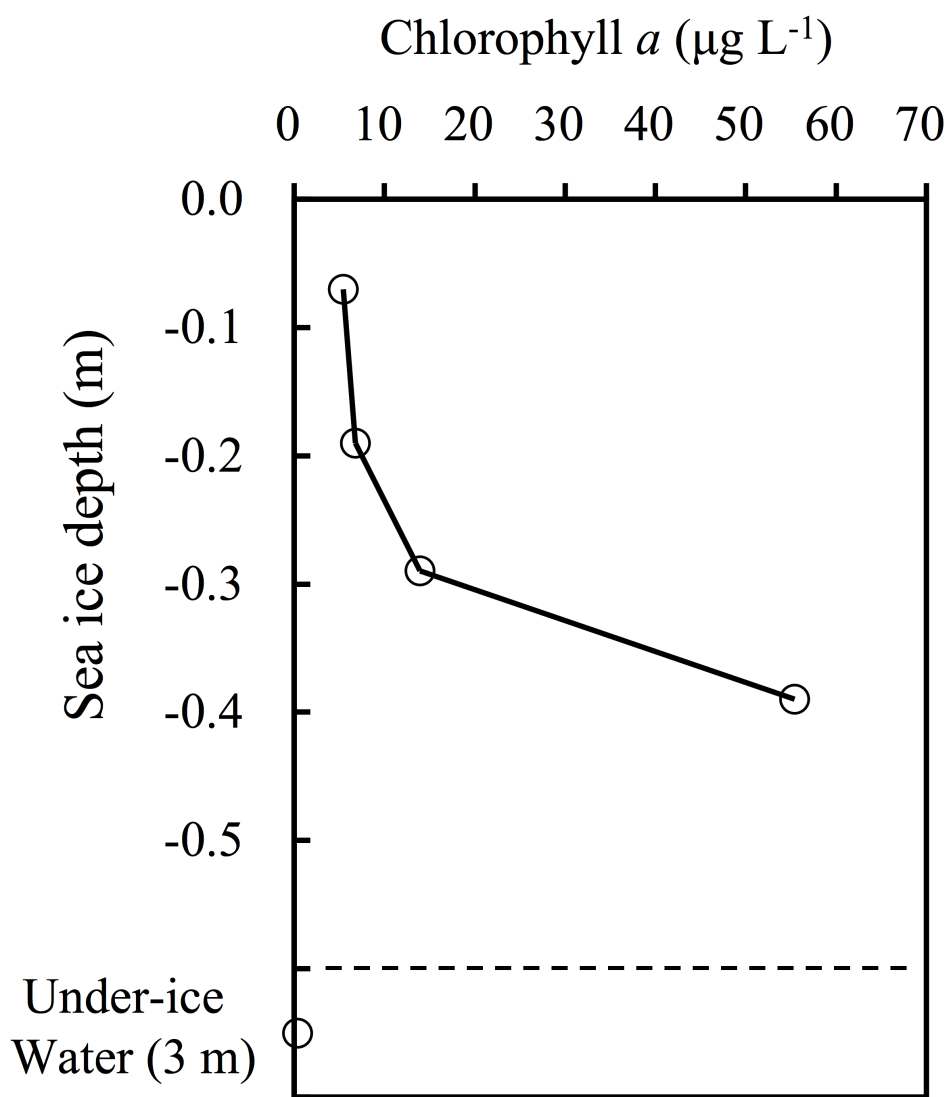


Fig. 6.

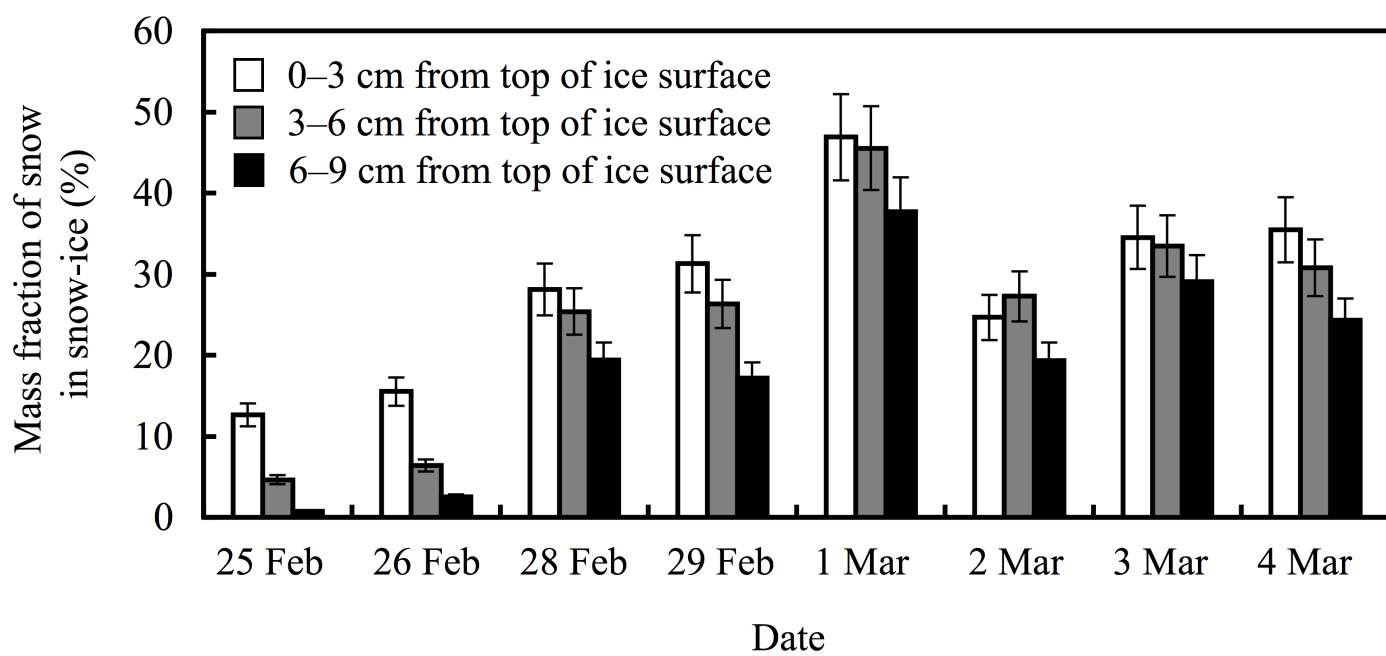


Fig. 7.

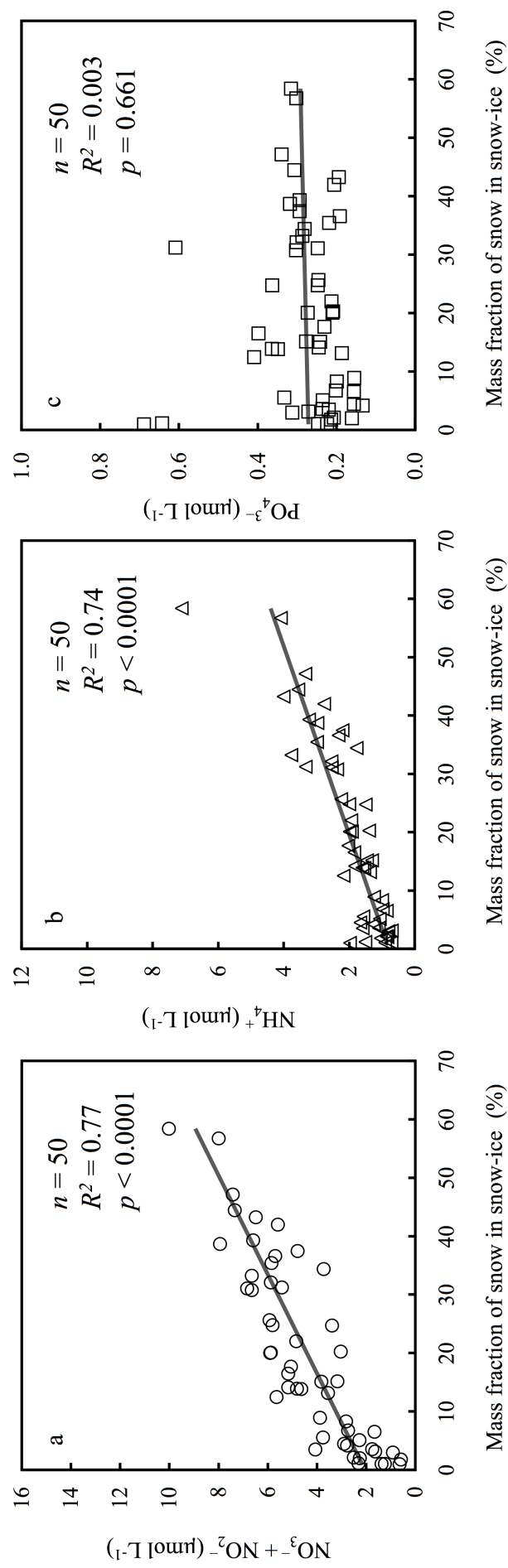


Fig. 8.

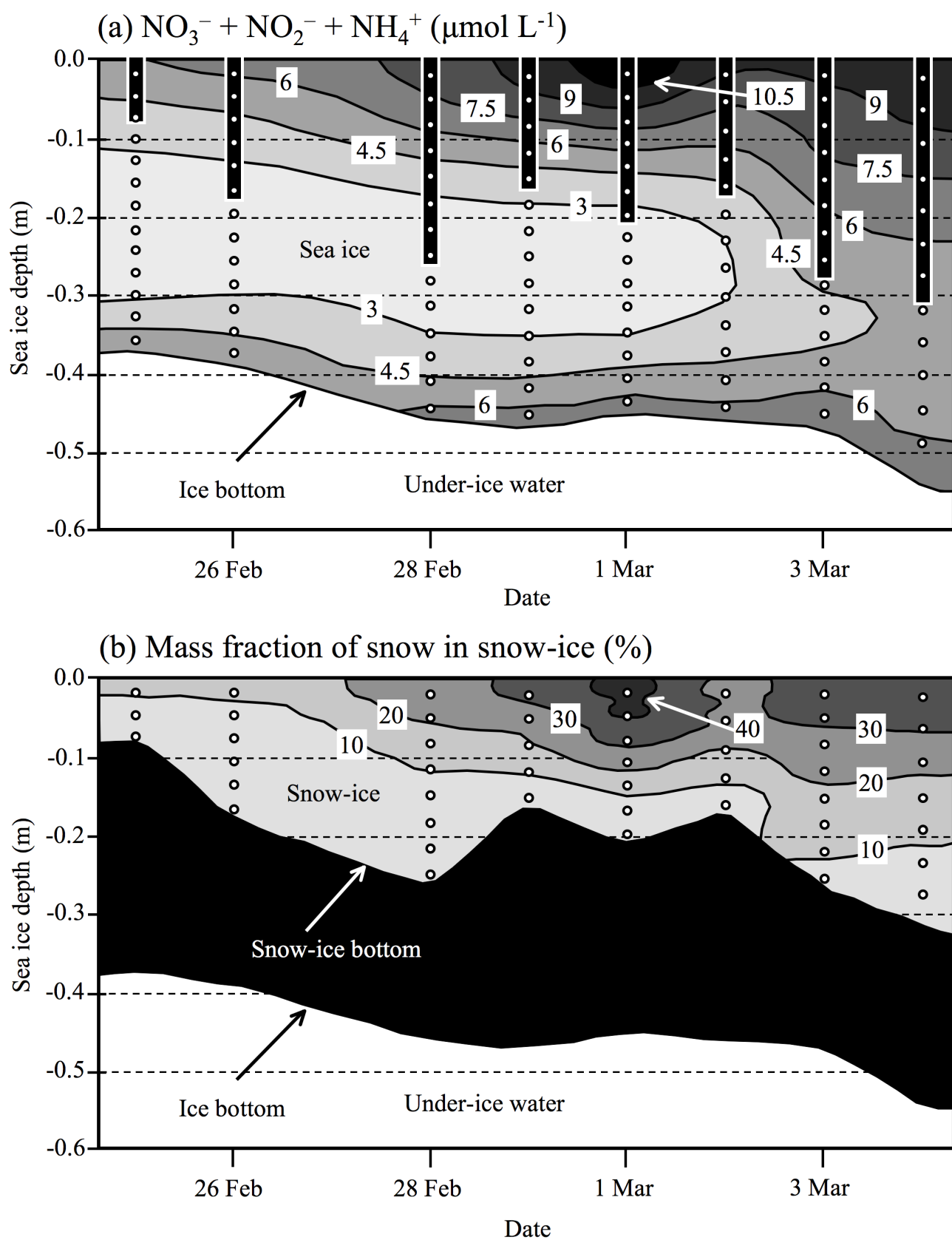


Fig. 9.

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.