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**Transport of chemical components in sea ice and under-ice water during melting in the seasonally ice-covered Saroma-ko Lagoon, Hokkaido, Japan**

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## Abstract

Physico-chemical properties in the brine and under-ice water were measured in Saroma-ko Lagoon on the northeastern coast of Hokkaido, Japan, which is connected to the Sea of Okhotsk, during the period from mid-February through mid-March 2006. The brine within brine channels of the sea ice was collected with a new sampling method examined in this study. Salinity, dissolved inorganic carbon (DIC), total alkalinity (TA), dissolved oxygen (DO), nutrients and oxygen isotopic ratio ( $\delta^{18}\text{O}$ ) contained in the brine within brine channels of the sea ice and in the under-ice water varied largely in both time and space during the ice melt period, when discharge from Saromabetsu River located on the southeast of the lagoon increased markedly due to the onset of snow melting. The under-ice plume expands as far as 4.5 km from the river mouth at mid-March 2006, transporting chemical components supplied from the river into the lagoon. The under-ice river water was likely transported into the sea ice through well developed brine channels in the sea ice due to upward flushing of water through brine channels occurred by loading of snowfalls deposited over the sea ice. These results suggest that the river water plume plays an important role in supplying chemical components into the sea ice, which may be a key process influencing the biogeochemical cycle in the seasonally ice-covered Saroma-ko Lagoon.

Keywords: Sea ice; River water plume; Biogeochemistry; Coastal oceanography; Sea of Okhotsk; Saroma-ko Lagoon

## 1. Introduction

Saroma-ko Lagoon is located on the northeast coast of Hokkaido, Japan, which is connected to the Sea of Okhotsk through two inlets (Fig. 1). The surface area of the lagoon is 149.2 km<sup>2</sup> with the mean depth of 14.5 m. The water mass on the eastern part of the lagoon consists mainly of the Okhotsk Sea water and the freshwater input from Saromabetsu River (Shirasawa and Leppäranta, 2003). Almost the entire surface of Saroma-ko Lagoon is generally covered with sea ice from early January through early April with a large year-to-year variability. A river water plume develops under the sea ice in the lagoon in association with the increase of inflow of snow melt water during the ice melt period (Shirasawa and Leppäranta, 2003).

An extensive field campaign on physical and biological studies of the sea ice and under-ice water in Saroma-ko Lagoon was performed in the winter of 1992 during the SARES (Saroma-Resolute Studies) project (e.g., Fukuchi et al., 1997; Shirasawa et al., 1997; Taguchi et al., 1997; Robineau et al., 1997). One of the interesting results from the project was that the low-salinity and low-nutrient (silicate) water was formed at the bottom of the sea ice due to melting of sea ice, which caused reduction of photosynthetic activity of ice algae and consequently led to decrease Chl. *a* concentrations (Taguchi et al., 1997). As ice algae at the bottom of the sea ice exposed to the under-ice river water, they might recover from the osmotic damage when the intermediate-salinity and nutrient-rich river water developed under the sea ice (Taguchi et al., 1997). Ice bottom salinity explained the meso- and small-scale patchiness of ice algae, and salinity of underlying waters probably controlled the spatial heterogeneity of salinity and microalgal biomass in the ice bottom (Robineau et al., 1997).

Although extensive field experiments on physical and biological studies of sea ice and under-ice water were performed during the SARES project, studies on geochemical cycles, especially on the interaction of chemical substances between sea ice and underlying water, were not made.

In southeastern Hudson Bay, as in Saroma-ko Lagoon, salinity of the under-ice water and in the ice bottom was controlled by hydrographic conditions of the freshwater plume supplied by the river (Ingram, 1981; Legendre et al., 1992). In the coastal area of the Baltic Sea the salinity gradient towards offshore from the river mouth controlled the horizontal heterogeneity of biogeochemical properties in the ice bottom as well as of the under-ice plume (Granskog et al., 2005).

Those results from Saroma-ko Lagoon, southeastern Hudson Bay and Baltic Sea suggest that the under-ice river plume obviously transports freshwater, chemical substances and heat from the river into the lagoon, and salinity of the plume is hydrographically controlled by discharge of the river; e.g., the increase of snow melt river water. Physical processes of transporting the under-ice water into the sea ice were also studied in Saroma-ko Lagoon during the SARES, and it was found that upward flushing of the under-ice water through brine channels in sea ice occurred due to loading of snowfalls deposited over sea ice (Hudier et al., 1995). However, transport processes of chemical substances in the under-ice water into brine channels of the sea ice have not been studied in Saroma-ko Lagoon, since the conventional sampling technique for collecting the brine in brine channels of the sea ice was not appropriate to thinner and warmer sea ice in Saroma-ko Lagoon (Taguchi et al., 1997).

The purpose of the present study is to examine and apply a new sampling method for collecting the brine within brine channels of the sea ice for relatively thinner and warmer sea ice, and to measure spatial and temporal distributions of physico-chemical properties of the

brine in the sea ice and of under-ice water in Saroma-ko Lagoon. Discussion will be also made on how chemical substances contained in the under-ice plume water are transported into the sea ice during the period of snow melting, which induces the increase in discharge of river water. It must be a key process to understand the biogeochemical cycle in the seasonally ice-covered Saroma-ko Lagoon.

## 2. Materials and Methods

### 2.1 Observation sites and sampling methods

Field observations were carried out in Saroma-ko Lagoon on the Okhotsk Sea coast of Hokkaido, Japan during mid-February through mid-March 2006 (Fig. 1). A total of seven sampling sites were chosen; one (St. Main) as a representative station of the eastern lagoon, located at approximately 1.5 km offshore, and other six stations (St. River Mouth and Sts. 1 to 5) along the transect between the mouth of Saromabetsu River and the second (east) inlet (Fig. 1 and Table 1). Samples of sea ice cores, brine in sea ice and under-ice water were collected from each station during the sampling period (Table 1).

Sea ice cores were collected with a SIPRE (Snow, Ice, and Permafrost Research Establishment) ice corer with an inner diameter of 7.5 cm. Immediately after ice cores were collected, temperatures of ice cores were measured at 2 cm below the top of the core, the center of the core and 2 cm above the bottom of the core by inserting a needle-like thermometer sensor (SK-250WP, Sato Keiryoki Mfg., Co., Ltd., Japan) into a drilled hole of the core. Then, each ice core was packed in a polyethylene bag and kept horizontally in a cooler box with snow as a coolant. Thereafter, the ice cores were transported to the Saroma

Research Center of Aquaculture (SRCA) (Fig. 1) to store in a deep freezer at  $-30^{\circ}\text{C}$ . The ice cores were later used for further analysis of salinity and oxygen isotopic ratio ( $\delta^{18}\text{O}$ ) of the ice cores in a laboratory of Hokkaido University in Sapporo.

The thickness of sea ice cores ranged from 32 to 50 cm with the average of 42 cm during the sampling period. The snow depth deposited over sea ice at St. Main decreased from 4.5 cm on 18 February to 0 cm on 1 March due to snow melting and increased to 17.5 cm on 3 March 2006 after heavy snowfalls. The snow depth at Sts. 1-5 was within the range of 0-16 cm, which was almost the same range at St. Main.

Samples of the brine in the sea ice were collected by a gravity drainage method (Fig. 2). This method is new for collecting the brine in the sea ice and applicable to relatively thinner sea ice especially under such environmental circumstances that air and ice temperatures are higher and the brine volume fraction is higher during the ice melting season. During the experiment period, the thickness of sea ice cores ranged from 32 to 50 cm, and it was in the process of warming and melting. Immediately after the two pieces of ice core were collected from sea ice, they were kept in two plastic pipes, and 200 ml sample bottles collecting the brine extracted through brine channels of the ice core by gravity were placed at the end of funnels over the period for approximately 15 min (Fig. 2).

Reliability to apply the gravity drainage method to Saroma-ko Lagoon sea ice was further confirmed by examining temporal variability in the volume and salinity of the extracted brine from brine channels of the ice core at St. Main during the period from 26 February to 3 March 2008. Immediately after the ice core was taken out of the *in situ* sea ice, it was kept in the plastic pipe. Then, the brine filled within brine channels of the sea ice was extracted into the sample bottle. The sample bottle was kept for 3 min, and another bottle was replaced at every 3 min. This procedure was repeated until 27 min. The results from this

examination will be discussed later in the chapter of Results and Discussion.

The brine extracted from the ice core into the 200 ml sample bottles during the 2006 experiment was divided into a 10 ml glass vial as a sub-sample for measuring salinity and  $\delta^{18}\text{O}$  and into a 120 ml glass vial for measuring dissolved inorganic carbon (DIC) and total alkalinity (TA). The 50  $\mu\text{l}$  mercuric chloride ( $\text{HgCl}_2$ ) in volume was added to the DIC sample to cease from biological activity. The sample of dissolved oxygen (DO) was placed into a 100 ml authorized vial, and oxygen was fixed with reagents according to the JGOFS (Joint Global Ocean Flux Study) protocols (Knap et al., 1996). For measurements of Chl. *a* concentration, the 116 ml sample was filtered through a 47 mm GF/F filter under the low pressure (< 100 mmHg). The filter was immediately soaked in N, N-dimethylformamide (DMF) and was stored in a deep freezer at  $-30^\circ\text{C}$  (Suzuki and Ishimaru, 1990). For analysis of the nutrients, the brine sample was placed in a 10 ml polyethylene screw vial and stored also in the deep freezer.

The under-ice water sample was collected through an ice core hole with a 500 ml Teflon water sampler (GL Science Inc., Japan) at the depths of 1, 3, 5, 7 and 9 m below the surface of sea ice. Under-ice water samples were collected at 1 m depth at Sts. 1 and River Mouth, since the water depth was approximately 1.5 m at both stations. Those water samples were collected after approximately 15 min of drilling of ice cores so as to avoid disturbance caused by drilling. The under-ice water samples were kept in the same manner as that for the brine samples for further analysis.

Temperature and salinity profiles under sea ice were measured by a Conductivity-Temperature-Depth profiler (SBE-19, Sea-Bird Electr. Inc., USA) through a 30 cm x 30 cm hole in sea ice at St. 5 on 14 February, at Sts. 2, 3 and 4 on 16 February, at Sts. 4 and 5 on 7 March, and at Sts. 2 and 3 on 8 March 2006 (Table 1).

Air temperature was measured at the height of 150 cm above the ice surface, and ice temperatures were measured at the depths of 5, 10, 20 and 30 cm below the ice surface, with thermistor probes (Grant Instruments Ltd., UK) at every 30 min during the entire experiment period at St. Main (Fig. 3).

Sea surface water was collected at St. 8 (44° 20'N and 143° 50'E) during the icebreaker *P/V Soya*'s cruise in the southern Sea of Okhotsk on 12 February 2006 for further analysis of salinity and  $\delta^{18}\text{O}$  (Fig. 1). A water sample was collected through cracks between sea ice floes with a bucket, and the sample was stored in vials for salinity and  $\delta^{18}\text{O}$  measurements in the same manner as for the under-ice water samples in Saroma-ko Lagoon.

## 2.2 Sample analysis

Salinity of the brine and under-ice water was measured using a salt analyzer (SAT-210, Toa Electronics Ltd., Japan). A standard deviation calculated from the fifteen sub-samples taken from a single sample bottle was 0.03 in salinity. DIC was determined by the coulometry technique (Johnson et al., 1985). DIC measurements were calibrated with working seawater standards traceable to the Certified Reference Material distributed by Prof. A. G. Dickson (Scripps Institution of Oceanography, USA). The precision of DIC analysis from duplicate determinations was within  $\pm 0.1\%$  (Wakita et al., 2005). TA was analyzed by the improved single point titration method (Culberson et al., 1970). We measured TA using a glass electrode calibrated with Tris buffer and 2-aminopyridine buffer (DOE, 1994). The precision of the TA analysis from duplicate determinations was within  $\pm 0.2\%$  (Wakita et al., 2005). DO was determined by the standard Winkler techniques with the potentiometric titration

using an autoburette (751 GPD Titrino, Metrohm Ltd. Switzerland). The precision of the DO analysis from duplicate determinations was better than  $\pm 0.2\%$  (Wakita et al., 2005). Nutrients (Dissolved Inorganic Nitrogen: DIN-N,  $\text{Si(OH)}_4$ -Si and  $\text{PO}_4$ -P) were determined by an auto-analyzing system (AACS II, Bran+Luebbe, Germany) according to the JGOFS spectrophotometric method (JGOFS, 1994). DIN-N refers to the sum of the concentration of  $\text{NO}_3$ -N,  $\text{NO}_2$ -N and  $\text{NH}_4$ -N.  $\delta^{18}\text{O}$  was determined with a mass spectrometer (DELTA plus, Finnigan MAT, USA). The  $\delta^{18}\text{O}$  in per mil was defined as the deviation of  $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$  ratio of the measured sample to that of the international standard water (SMOW). The precision of  $\delta^{18}\text{O}$  analysis from duplicate determinations was within  $\pm 0.02\text{‰}$  (Toyota et al., 2007). Chl. *a* concentration was determined using a spectrofluorometer (RF-5300PC, Shimadzu, Japan), and estimated using equations proposed by MacKinney (1941) and Moran (1982). For estimation of the brine volume fraction, the ice core sample was cut to 4.5 cm x 2.5 cm in plane size by a band saw and then sliced into the 3 cm thick section in the cold room at  $-15^\circ\text{C}$ . The bulk volume and mass of the 3 cm thick sea ice section was measured to calculate density of sea ice. The sea ice sections were then melted to measure salinity and  $\delta^{18}\text{O}$ , and finally the brine volume fraction of sea ice was calculated using the equations by Eicken (2003).

Fraction of the Okhotsk Sea water, river water and ice meltwater to the total water was estimated on the basis of salinity and  $\delta^{18}\text{O}$ , which can be considered as conservative properties (Östlund and Hut, 1984; Macdonald et al., 1999; Yamamoto-Kawai et al., 2005). The fraction of each source to the total water is defined as the part of the mixture consisting of the Okhotsk Sea water, the Saromabetsu River water and sea ice meltwater. Fraction (F) can be estimated from the following equations:

$$F_{sea} + F_{river} + F_{ice} = 1 \quad (1)$$

$$F_{sea} S_{sea} + F_{river} S_{river} + F_{ice} S_{ice} = S_{obs} \quad (2)$$

$$F_{sea} \delta_{sea} + F_{river} \delta_{river} + F_{ice} \delta_{ice} = \delta_{obs} \quad (3)$$

where  $S$  and  $\delta$  represent salinity and  $\delta^{18}\text{O}$ , respectively. The subscripts, “sea”, “river”, “ice” and “obs”, refer to the Okhotsk Sea water, river water, sea ice meltwater and observed bulk values, respectively. The end-member values of salinity and  $\delta^{18}\text{O}$  for each source used in this study are listed in Table 2. The end-member value of  $\delta^{18}\text{O}$  for the Okhotsk Sea water obtained at St. 8 (Fig.1) was  $-0.75\text{‰}$ , which was within  $-0.96 \pm 0.24\text{‰}$  (mean  $\pm$  standard deviation) obtained from the water in the southern Sea of Okhotsk at mid-February (Toyota et al., 2007). The end-member value of  $\delta^{18}\text{O}$  for the river water as determined at St. River Mouth (Fig. 1) was  $-11.21\text{‰}$ , which was within the range of  $-10.5$  to  $-12.0\text{‰}$  during the period from December 2005 to April 2006 (Morimoto pers. comm.). The end-member values of the ice meltwater obtained from all ice cores were  $3.83 \pm 2.41$  (mean  $\pm$  standard deviation) for salinity and  $-2.62 \pm 0.52\text{‰}$  (mean  $\pm$  standard deviation) for  $\delta^{18}\text{O}$ . The calculated fractions of the ice meltwater varied within  $\pm 0.10$  for  $S_{ice}$  and  $\pm 0.06$  for  $\delta_{ice}$  in changing of the values within the standard deviation. As in the same manner, the calculated fractions varied within  $\pm 0.14$  for  $S_{sea}$ ,  $\pm 0.09$  for  $\delta_{sea}$ ,  $\pm 0.09$  for  $S_{river}$  and  $\pm 0.07$  for  $\delta_{river}$  in changing of the values within the standard deviation.

### 3. Results and Discussion

#### 3.1. Applicability of the gravity drainage method to Saroma-ko Lagoon sea ice

In Fig. 4, the relationship of brine salinity collected by the gravity drainage method in 2006 with that calculated from the empirical equation based on ice temperatures (Cox and Weeks, 1983) shows well agreement, suggesting the applicability of the gravity drainage method to sea ice in Saroma-ko Lagoon. The regression line between measured and calculated values from the equation based on the mean ice temperatures shows slightly higher than the 1:1 line within 8% in difference. It can be considered that as measured brine salinity is lower than that calculated from the equation, the former appears to be more contributed from the lower brine salinity at/near the bottom of the ice core, where the temperature and brine volume fraction are highest throughout the entire ice core.

The measured brine volume and salinity are shown as a function of elapsed time in Figs. 5(a) and (b). The volume of the brine decreased with the increase of the elapsed time for each experiment. After the elapsed time of approximately 15 min, the volume of the brine was almost constant or slightly decreased throughout the entire experiment period for 27 min. Salinity of the brine increased with the increase of the elapsed time, showing that the property of the brine changed with the increase of the elapsed time, correspondingly with changing the ice temperature from at higher at the ice bottom to at lower at the upper part of the ice core. These results correspond to those appeared in the relation of salinity of the brine from the gravity drainage method with that from the empirical equation in Fig. 4.

It might be nearly impossible to collect completely the brine flushed out of brine channels when the ice core is taken out of the *in situ* sea ice sheet. In Fig. 5(a), assuming that the ice core is placed in the plastic pipe within 3 sec after being taken out of the sea ice sheet, approximate 1% of the total amount of the brine (within 27 min) might be lost within the first 3 sec, according to the same attenuation rate for the first 3 min of the elapsed time. This

implies that the loss of the brine can be negligible.

In the polar seas and laboratory experiments, the brine in thicker sea ice has been collected by the sack hole method under colder circumstances (Gleitz et al., 1995; Papadimitriou et al., 2003; Trevena and Jones, 2006; Lannuzel et al., 2007). Once a hole in sea ice is made, the brine in sea ice and under-ice water can be percolated into the hole through brine channels of sea ice, obviously much effectively occurring in the melting season, where brine channels of sea ice have well developed (Kawamura et al., 2006). Since Saroma-ko Lagoon is located on the southernmost area in the seasonal sea ice zone, where air temperature is too moderate to grow sea ice thicker, sea ice grows generally as thick as 50 cm by the end of the ice growing season, that was the case for this study. The brine volume fraction of sea ice at Saroma-ko Lagoon is higher especially during the ice melting season than that in the polar seas and the Baltic Sea (Kawamura et al., 2006). As a result, the gravity drainage method can be recommended to use for thinner and warmer sea ice in the melting season so that most of the brine in the ice core should be kept in the ice core at the time that the ice core was taken out from *in situ* sea ice.

### 3.2. Temporal variations in physico-chemical properties in the brine and under-ice water

Temporal variations in physico-chemical properties of the brine in sea ice and of the under-ice water column at St. Main during the period from 18 February through 7 March 2006 are shown in Fig. 6. Salinity of the brine in sea ice at the depth of 0.2 m (Fig. 6(a)) decreased drastically from 36-38 on 18-19 February to 8 on 3 and 7 March, showing that a significant desalination occurred during this period. Salinity of the under-ice water at 1 m

below the surface of sea ice also decreased significantly from approximately 30 to 5 over the same period. On the other hand, salinity of the water column below 5 m was almost constant at  $31.3 \pm 0.9$ . The brine remained at higher salinity of 36-38 during the cold period of 18-19 February, and desalination started as air temperature started to increase correspondingly with the increase of ice temperatures (Fig. 3). Air temperature started to frequently exceed above  $0^{\circ}\text{C}$  from 19 February and reached  $7.1^{\circ}\text{C}$  at maximum on 21 February (Fig. 3). Ice temperatures varied correspondingly to air temperature and gradually increased to  $0^{\circ}\text{C}$  at the depth of 30 cm on 1 March, indicating sea ice started to melt at the ice bottom. The entire experiment period can be divided into two periods from this time series; the cold period for the first half and the warm or melting period for the second half.

Variations in concentrations of DIC and TA were similar to those of salinity, which decreased significantly in the brine and the upper layer of under-ice water column during the warm period (Figs. 6(b) and (c)). The DO concentration in the brine and water just below sea ice increased, showing the opposite trend to that of salinity, DIC and TA (Fig. 6(d)). The DO concentration in the water column below 3 m depth was constant at  $361.2 \pm 3.6 \mu\text{mol kg}^{-1}$ . The nutrients (DIN-N,  $\text{Si}(\text{OH})_4\text{-Si}$  and  $\text{PO}_4\text{-P}$ ) also increased significantly in the brine and upper layer water like the DO (Figs. 6(e), (f) and (g)). The DIN-N and  $\text{Si}(\text{OH})_4\text{-Si}$  increased slightly in the water column below 3 m depth. The Chl. *a* concentration was higher in the brine in sea ice than in the under-ice water (Fig. 6(h)). The  $\delta^{18}\text{O}$  in the brine and upper layer water decreased towards the warm period of the experiment, whereas those in the water column below 3 m were almost constant at  $-1.81 \pm 0.5\text{‰}$  (Fig. 6(i)). It was indicated, as a result, that such physico-chemical properties as measured at St. Main varied significantly in the brine and in the water just below sea ice in accordance with changing in air and ice temperatures, whereas those in the water column below 3 m depth were rather constant

throughout the entire experiment period.

The DIC decreased significantly in the brine and the upper layer of under-ice water column, while the DO and nutrients increased (Figs. 6(b), (d), (e), (f) and (g)). The DIC and nutrients decrease due to photosynthetic activity of ice algae, and subsequently, the DO increases in the brine (Gleitz et al., 1995). However, in this study, the DIC decreased with the increase in the DO, while the nutrients increased. These results suggested that biological activity was little, although the existence of ice algae is seen in higher Chl. *a* concentrations in the brine (Fig. 6(h)).

It appears that during the period from 25 to 28 February 2006 Chl. *a* concentration in the brine decreased significantly from 5.5 to 1.2  $\mu\text{g l}^{-1}$ , and concurrently the brine salinity decreased from 25.4 to 17.0, respectively (Figs. 6(a) and (h)). Thereafter, during the period from 28 February to 7 March, the brine salinity decreased to 8.5, while Chl. *a* concentration in the brine increased to 2.3  $\mu\text{g l}^{-1}$ . Those results suggest that during the period from 25 to 28 February ice algal communities (as indicated by Chl. *a*) was ablated or lost; the osmotic damage was caused due to desalination (Taguchi et al., 1997); and the sudden decrease in salinity led to decrease the photosynthetic rate in sea ice (Lizotte, 2003). Thereafter, activity of ice algal communities might be optimized even at low salinity due to acclimation and species-specific difference (Lizotte, 2003), as seen in the increase of Chl. *a* concentration during the period from 3 to 7 March.

Based on the equations (1)-(3), the fraction of river water at 1 m below the ice surface increased from approximately 0.4 in the cold to 0.8 in the warm periods at St. Main (not shown here). The fraction of ice meltwater in the under-ice water was less than 0.1 and that of seawater in the water column below 3 m was almost 1.0, throughout the entire experiment period. As a result, only the river water increased significantly just below sea ice from the

cold through warm periods, while the underlying seawater and ice meltwater did not change throughout the entire experiment period. It is, therefore, suggested that variations in physico-chemical properties in the brine and water just under sea ice were most likely caused by changes in the freshwater supplied from Saromabetsu River.

### 3.3. Spatial variations in physico-chemical properties in the brine and under-ice water

The fraction of river water and ice meltwater at 1 m below the ice surface is shown along the transect between Sts. River Mouth and 5 during the warm period of the experiment, in Fig. 7. The fraction of river water decreased from 1.0 at St. River Mouth to 0.4 at St. 5, whereas the fraction of ice meltwater was almost zero along the transect. It was indicated that the under-ice water just below sea ice was mostly controlled by the river water supplied from Saromabetsu River. The contribution of the ice meltwater to the under-ice water just below sea ice was negligible. The fraction of river water underlying 3 m below the river water plume was approximately 0.1 along the transect (not shown here). It is, therefore, appeared that the river water most likely spreads just below sea ice as far as to St. 5 from the river mouth.

The configuration of the river water plume from Saromabetsu River can be seen in the cold and warm periods in Figs. 8(a) and (b), respectively. Approximately 2 m thick less saline water layer was distinctly observed as far as approximately 2.5 km from St. River Mouth in the cold period (Fig. 8(a)), and this plume layer expanded as far as approximately 4.5 km from St. River Mouth in the warm period (Fig. 8(b)). It can be considered that the under-ice plume might expand by the increase in the river water during the period from mid-February through early March. In the earlier work by Shirasawa et al. (2002), it was observed that the

freshwater input from Saromabetsu River began to increase largely on average from  $0.8 \text{ m}^3 \text{ s}^{-1}$  in February to  $6.1 \text{ m}^3 \text{ s}^{-1}$  in mid-March due to the onset of snow melt. Assuming that the river water spreads radially from the river mouth and the radius of the fan-shaped plume is defined as the distance between Sts. River Mouth and 4, where the fraction of river water at 1 m below the ice surface is more than 0.8 (Fig. 7), the area of the plume can be estimated as approximately  $20 \text{ km}^2$  during the warm period of the experiment. As the southeastern part of the lagoon can be considered as a small bay (Fig. 1), the under-ice river water might develop enough to maintain the plume configuration obtained from this study (Fig. 8). The less saline under-ice water was observed near St. Main, which might be affected by less saline coastal steady currents along the east coast of the lagoon (Shirasawa and Leppäranta, 2003). Therefore, the less saline water can be considered to exist under sea ice near St. Main during the ice-covered season. Such under-ice plume configuration was also observed near the mouth of River Siikajoki in the Baltic Sea, and its plume area was roughly  $150\text{-}350 \text{ km}^2$  at discharge of approximately  $110 \text{ m}^3 \text{ s}^{-1}$  on average during the period from March to May (Granskog et al., 2005), which is 18 times larger than those of Saromabetsu River.

Physico-chemical properties in the under-ice water at 1 m below the ice surface are shown along the transect during the period between 24 February and 1 March, in Fig. 9. Salinity, DIC and TA increased from St. River Mouth towards Sts. 5 and 8 (Figs. 9(a) and (b)). Nutrients, oppositely to them, decreased towards offshore; namely, DIN-N concentration was approximately 16 times higher, and  $\text{Si(OH)}_4\text{-Si}$  and  $\text{PO}_4\text{-P}$  were 4-5 times higher, at St. River Mouth, than those at St. 8 (Fig. 9(c)). DO was  $462.9 \text{ } \mu\text{mol kg}^{-1}$  at maximum at St. 4 and  $290.0 \text{ } \mu\text{mol kg}^{-1}$  at minimum at St. 1 (Fig. 9(d)). Chl. *a* was  $3.9 \text{ } \mu\text{g l}^{-1}$  at maximum at St. 5 and  $0.3 \text{ } \mu\text{g l}^{-1}$  at minimum at St. 1 (Fig. 9(e)). It is indicated from those results that nutrients can be transported by the river water plume as far as approximately 4.5 km from the river mouth at

mid-March 2006.

### 3.4. Water exchange through brine channels

The relations of salinity, DIN-N and Si(OH)<sub>4</sub>-Si between in the brine in sea ice and in the under-ice water at 1 m below the ice surface, show well agreements with the squared correlation coefficients of  $R^2 = 0.78, 0.91$  and  $0.78$ , respectively, in Fig. 10. It is suggested that the brine in sea ice and under-ice water exchanges well through brine channels in sea ice.

The fraction of the brine volume in sea ice calculated from all sixteen ice cores obtained from the experiment in 2006 ranged from 2.0 to 27.2% with the mean of 10.9%. The permeability of the brine in sea ice tends to increase as the brine volume is larger than 5% (Golden et al., 1998). Since most of the brine volume fraction in Saroma-ko Lagoon is larger than 5% throughout the entire ice core, sea ice can be considered as well permeable materials for transporting the brine in sea ice as well as the under-ice water through larger volume of brine channels in sea ice.

Snowfalls deposited over sea ice cover can be also considered to play an important role in exchanging of water through brine channels; e.g., by upward flushing of water through brine channels, which occurred by loading of snowfalls deposited over sea ice cover at Saroma-ko Lagoon in the melting season (Hudier et al., 1995). It is likely that chemical components might be transported through well developed brine channels by upward flushing, since flooding has already occurred over sea ice by snow loading in the warm period at early March in this study.

In polar seas sea ice is generally thicker at 40 to 150 cm than in Saroma-ko Lagoon, and

in the Baltic Sea the brine volume fraction was lower than 5% due to the brackish surface water of 3.0 to 3.2 in salinity (Gleitz et al., 1995; Granskog et al., 2003). Therefore, as the exchange of the under-ice water with the brine through brine channels in sea ice was likely limited in those seas, biological activity by ice algae in sea ice might be possible only as long as nutrients existed in brine channels in sea ice, not being supplied from the under-ice water, during the ice melting period (Gleitz et al., 1995; Granskog et al., 2003). It appears, oppositely, in Saroma-ko Lagoon in this study, that as nutrients along with the under-ice water might be transported into sea ice through brine channels, biological activity in sea ice continued possibly without depletion of nutrients in sea ice during the ice melting season.

#### 4. Conclusions

Field experiments to examine spatial and temporal changes in physico-chemical properties in the brine in sea ice and the under-ice water were carried out at Saroma-ko Lagoon on the Okhotsk Sea coast of Hokkaido, Japan during the period from mid-February through mid-March 2006. Distinct changes in physico-chemical properties in the brine and under-ice water were observed during the melting period, when discharge from Saromabetsu River into the lagoon increased drastically due to the onset of snow melting. Variations in configuration of the under-ice plume were observed along the transect from the river mouth towards the inlet of the lagoon. Chemical components in the river water can be transported along with the plume water just below sea ice as far as approximately 4.5 km from the river mouth at mid-March 2006, assuming that approximately 20 km<sup>2</sup> in the plume area expanded by the increased river water supplied after snow melting.

Physico-chemical properties in the brine in sea ice were well correlated with those in the water just below sea ice during the warm period of the experiment. It can be considered that brine channels have developed well by early March, since ice temperatures and the brine volume fraction of thinner ice were higher during the warm period. Chemical components transported along with the under-ice plume water are likely exchanged with the brine in sea ice through well developed brine channels, induced by upward flushing caused by loading of snowfalls deposited over sea ice. Those results suggest that the river water plume plays an important role in supplying chemical components into sea ice through brine channels, which may be a key process influencing the biogeochemical cycle in the seasonally ice-covered Saroma-ko Lagoon. Those results from Saroma-ko Lagoon can be applied to understand biogeochemical processes in seasonally ice-covered arctic coastal regions and estuaries, where the variability in river discharge must be an important factor affected by global warming.

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## Figure captions

Fig. 1 Location map of Sts. River Mouth, 1 to 5 and Main in the southeastern part of Saroma-ko Lagoon, Hokkaido, Japan. The water depth for each station is indicated in parenthesis. St. 8 (44° 20'N and 143° 50'E) is shown in the inserted figure.

Fig. 2 A schematic diagram of apparatus for collecting brine samples in sea ice by the gravity drainage method.

Fig. 3 (a) Air temperature at the height of 150 cm above the surface of sea ice, (b) sea ice temperatures at the depths of 5, 10, 20 and 30 cm below the surface of sea ice, at St. Main during the period from 15 February through to 8 March 2006.

Fig. 4 Salinity of the brine in sea ice collected by the gravity drainage method versus values calculated from the equation based on ice temperatures at maximum (open triangle), minimum (open square) and mean (solid circle) through the entire ice core. The regression line is based on ice temperatures at maximum (thick gray line with slope of 0.96 and the squared correlation coefficient,  $R^2 = 0.87$ ), minimum (solid thick line with slope of 1.30 and  $R^2 = 0.94$ ) and mean (dashed line with slope of 1.08 and  $R^2 = 0.96$ ). Thin solid line indicates the 1:1 relation for each axis.

Fig. 5 Temporal variations in volume and salinity of the brine extracted into sample bottles at every 3 min at St. Main during the period from 26 February to 4 March 2008.

Fig. 6 (a) Salinity, (b) DIC, (c) TA, (d) DO, (e) DIN-N, (f)  $\text{Si(OH)}_4\text{-Si}$ , (g)  $\text{PO}_4\text{-P}$ , (h) Chl. *a* and (i)  $\delta^{18}\text{O}$  in the brine in sea ice and under-ice water at St. Main. The property in the brine in sea ice is indicated at the depth of 0.2 m.

Fig. 7 Fraction of sea ice melt water and under-ice water at the depth of 1 m below the surface

of sea ice along the transect during the warm period of the experiment.

Fig. 8 Vertical sections of salinity obtained from CTD data along the transect from Sts. River Mouth to 5 on (a) 14 and 16 February 2006 and (b) 7 and 8 March 2006.

Fig. 9 (a) Salinity, (b) DIC and TA, (c) DIN-N,  $\text{Si(OH)}_4\text{-Si}$  and  $\text{PO}_4\text{-P}$ , (d) DO and (e) Chl. *a*, at the depth of 1 m below the surface of sea ice along the transect. "N.D." means no data.

Fig. 10 Relationships between the brine in sea ice and under-ice water for (a) salinity and (b) nutrients. Those data were obtained at each station during the entire period of the experiment in 2006 in Saroma-ko Lagoon. Dashed lines indicate the 1:1 for each axis. Slopes for each plot were 0.80 for salinity, 1.14 for DIN-N and 1.04 for  $\text{Si(OH)}_4\text{-Si}$ .

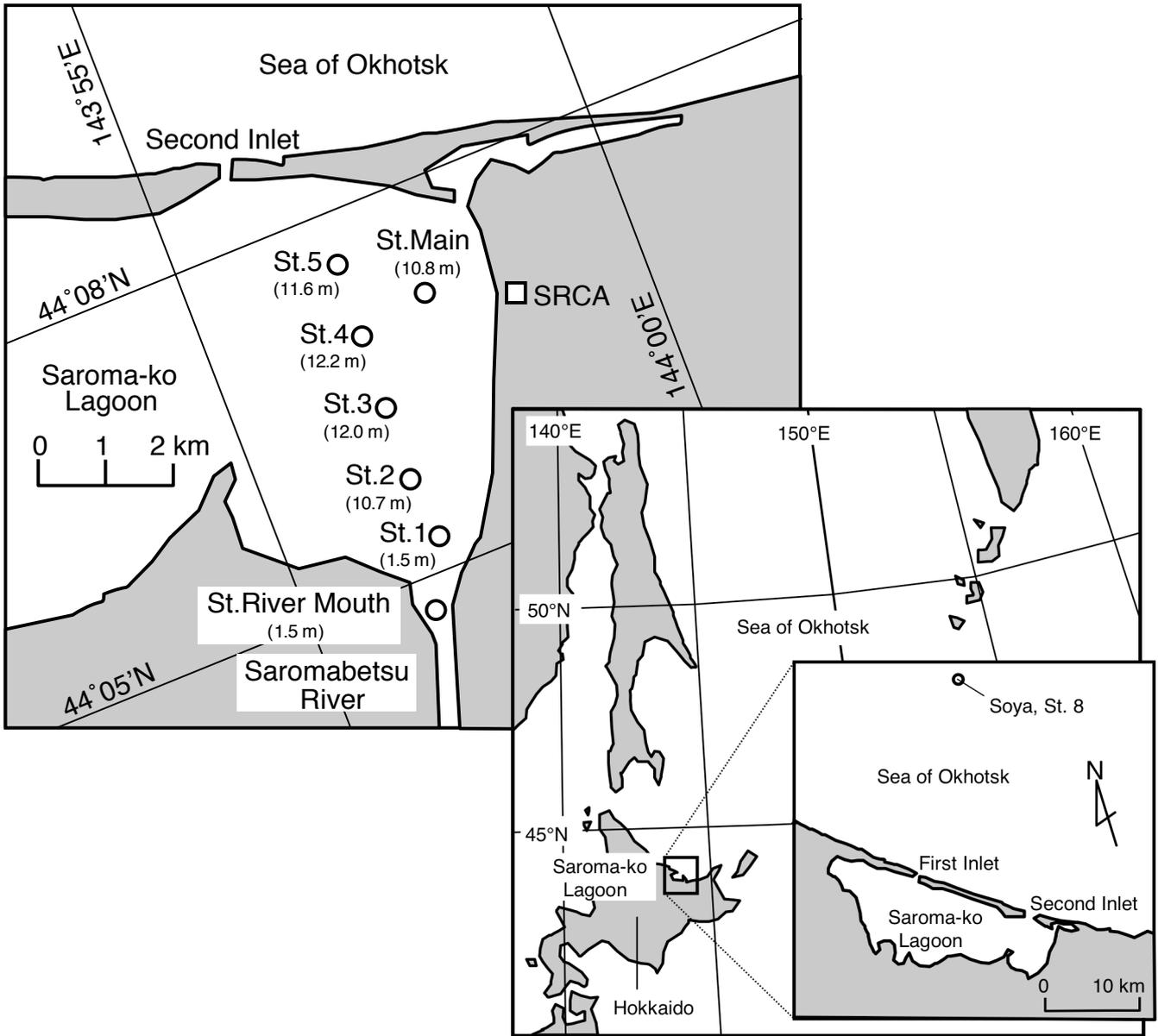


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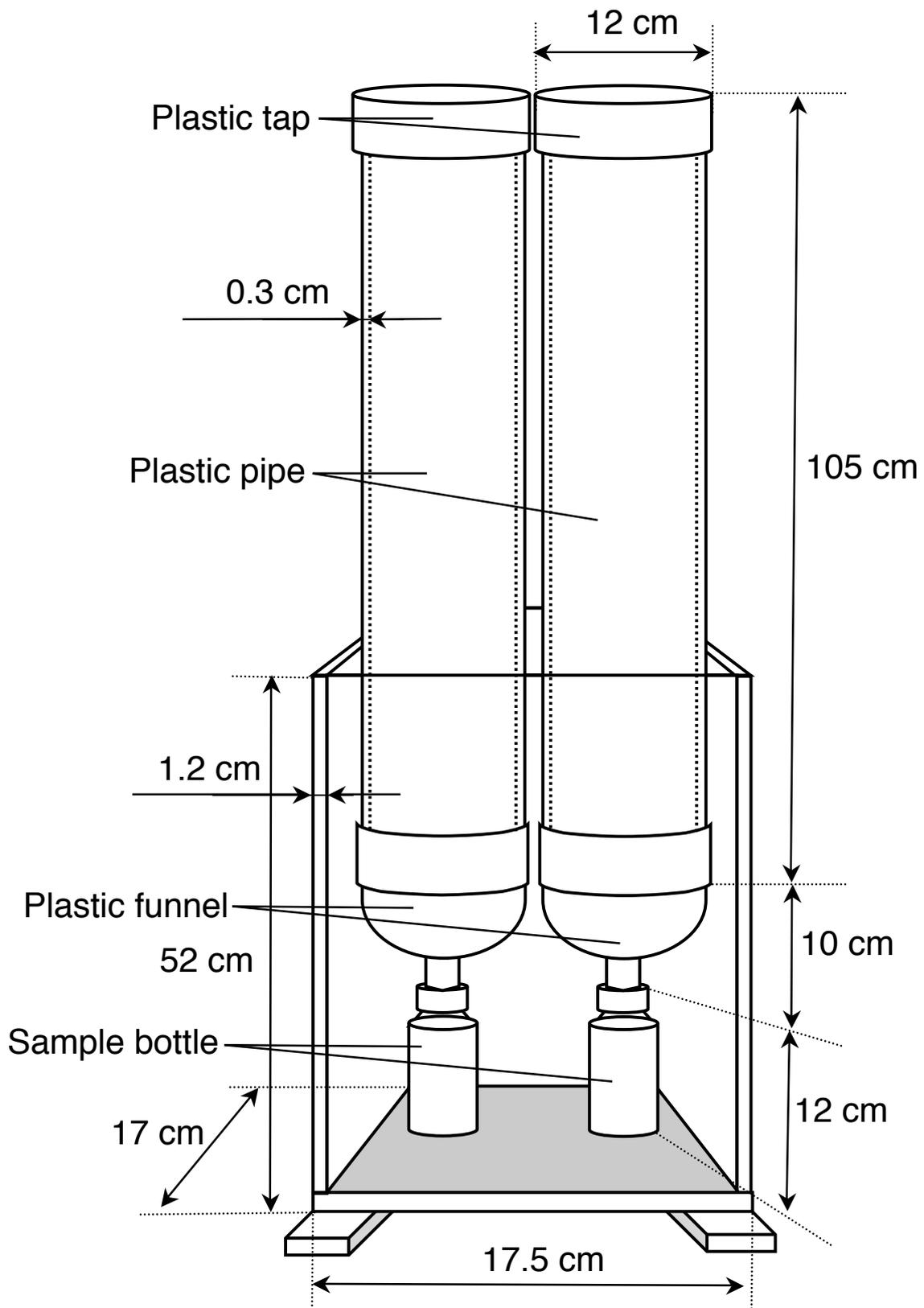


Fig. 2 Nomura et al.

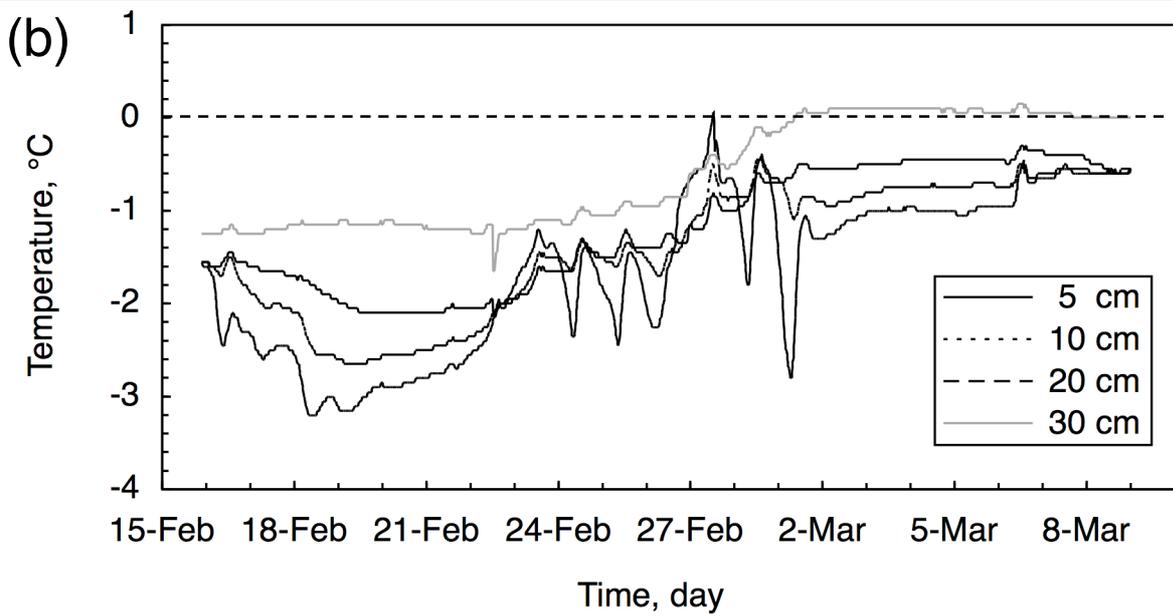
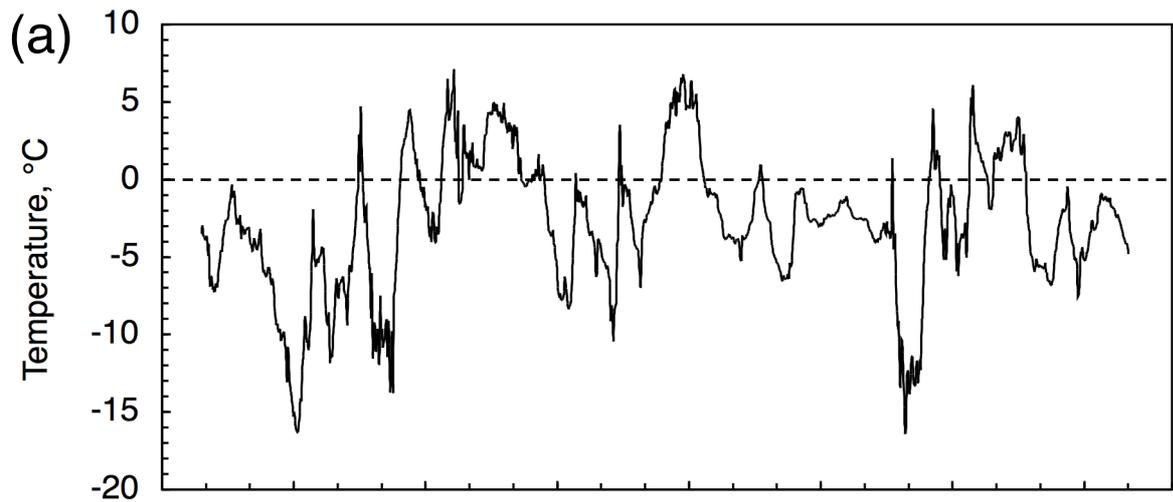


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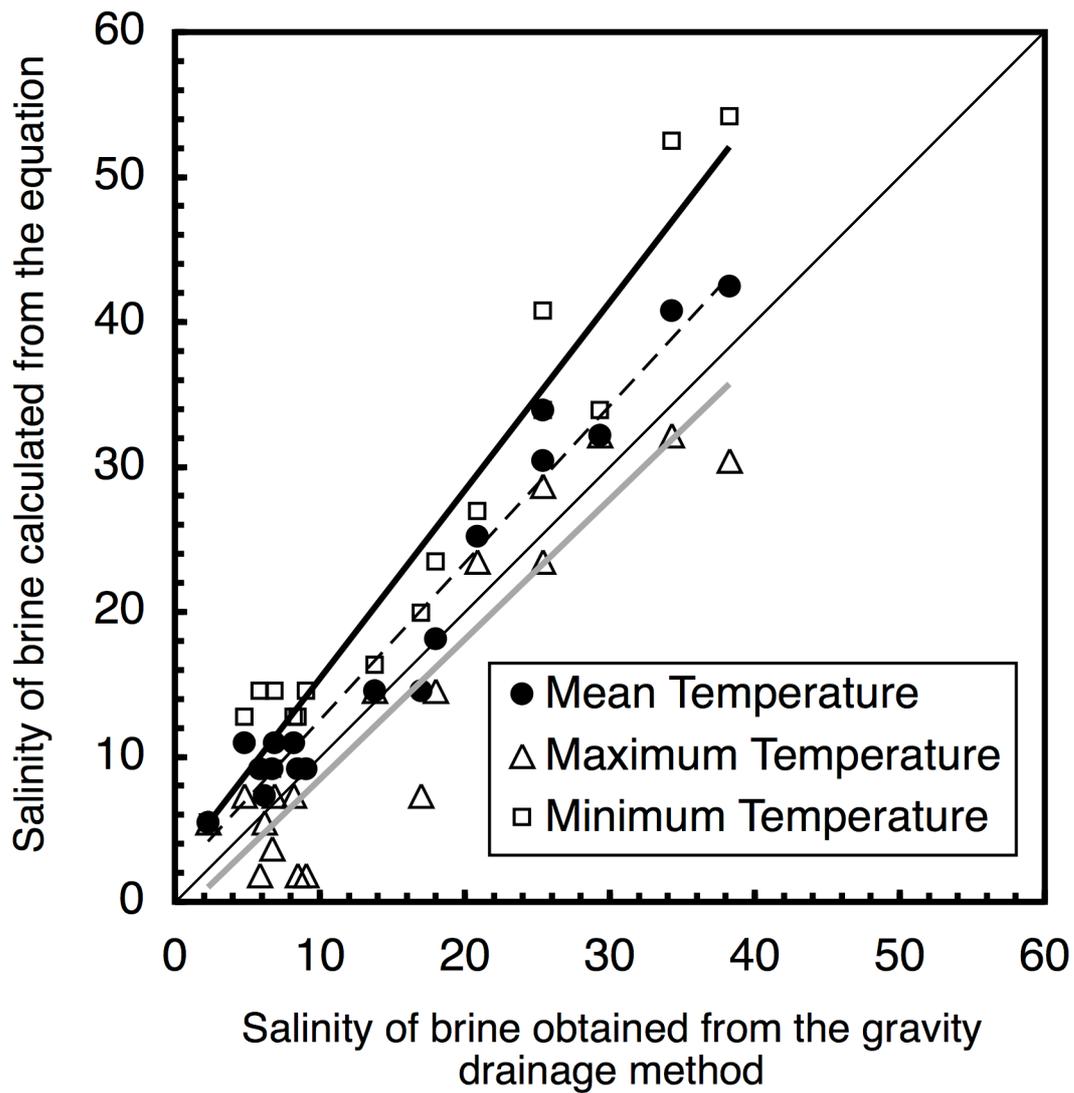


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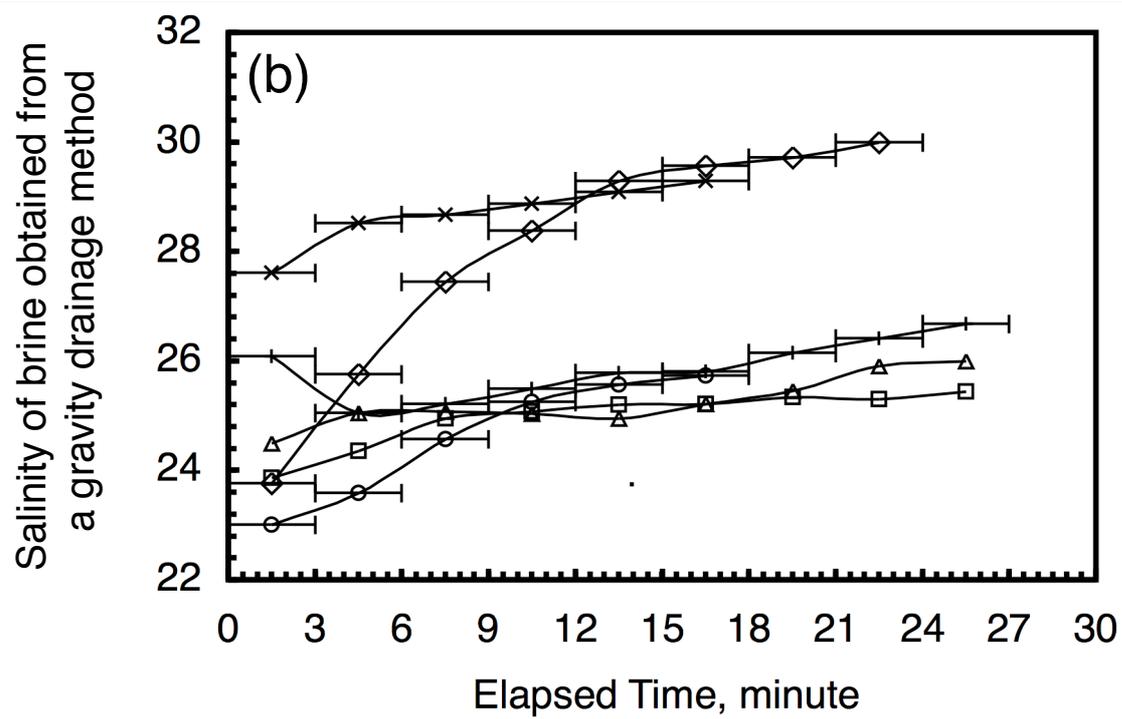
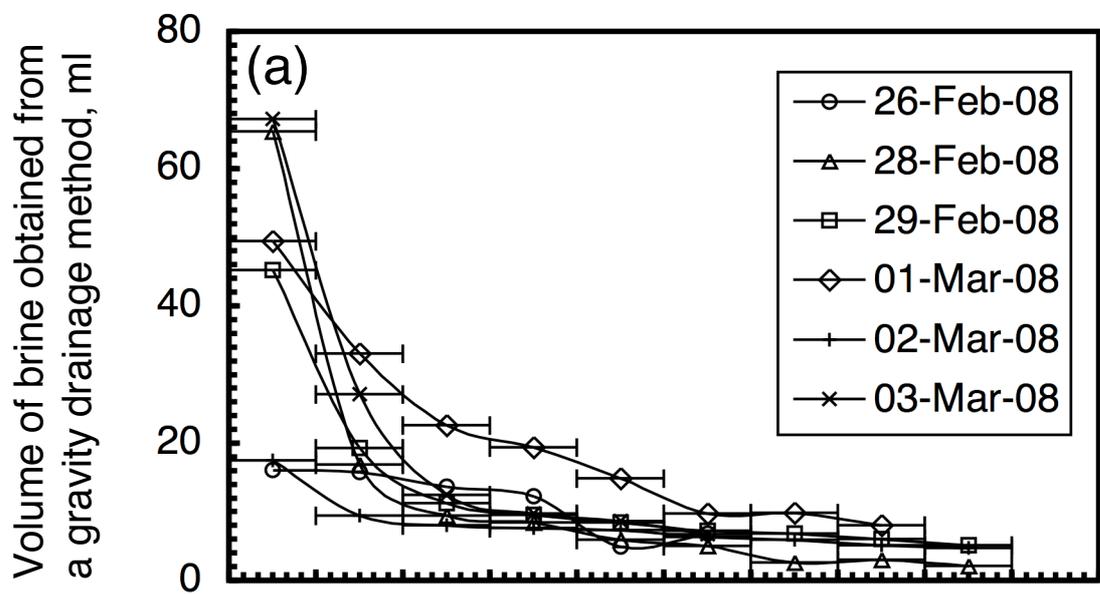


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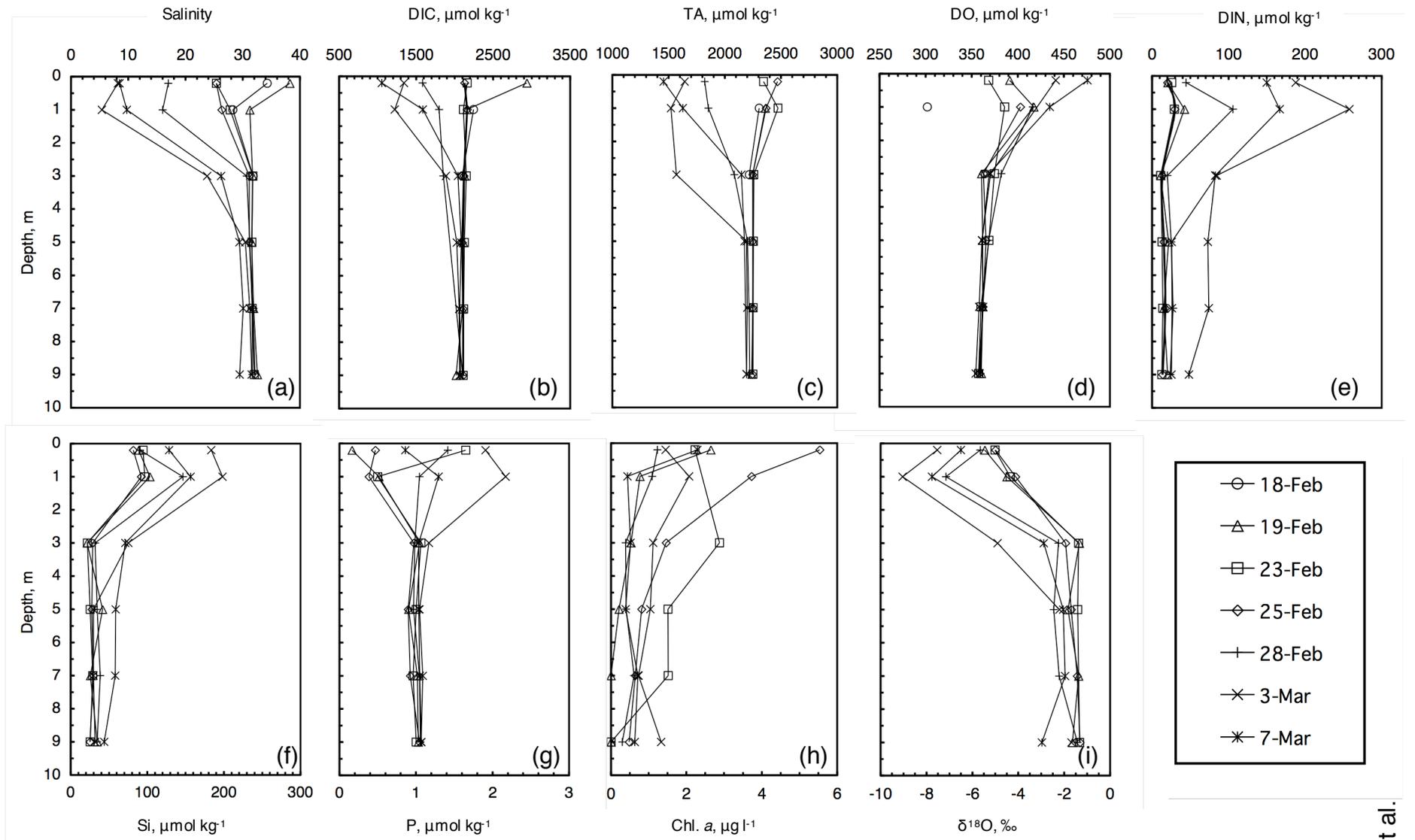


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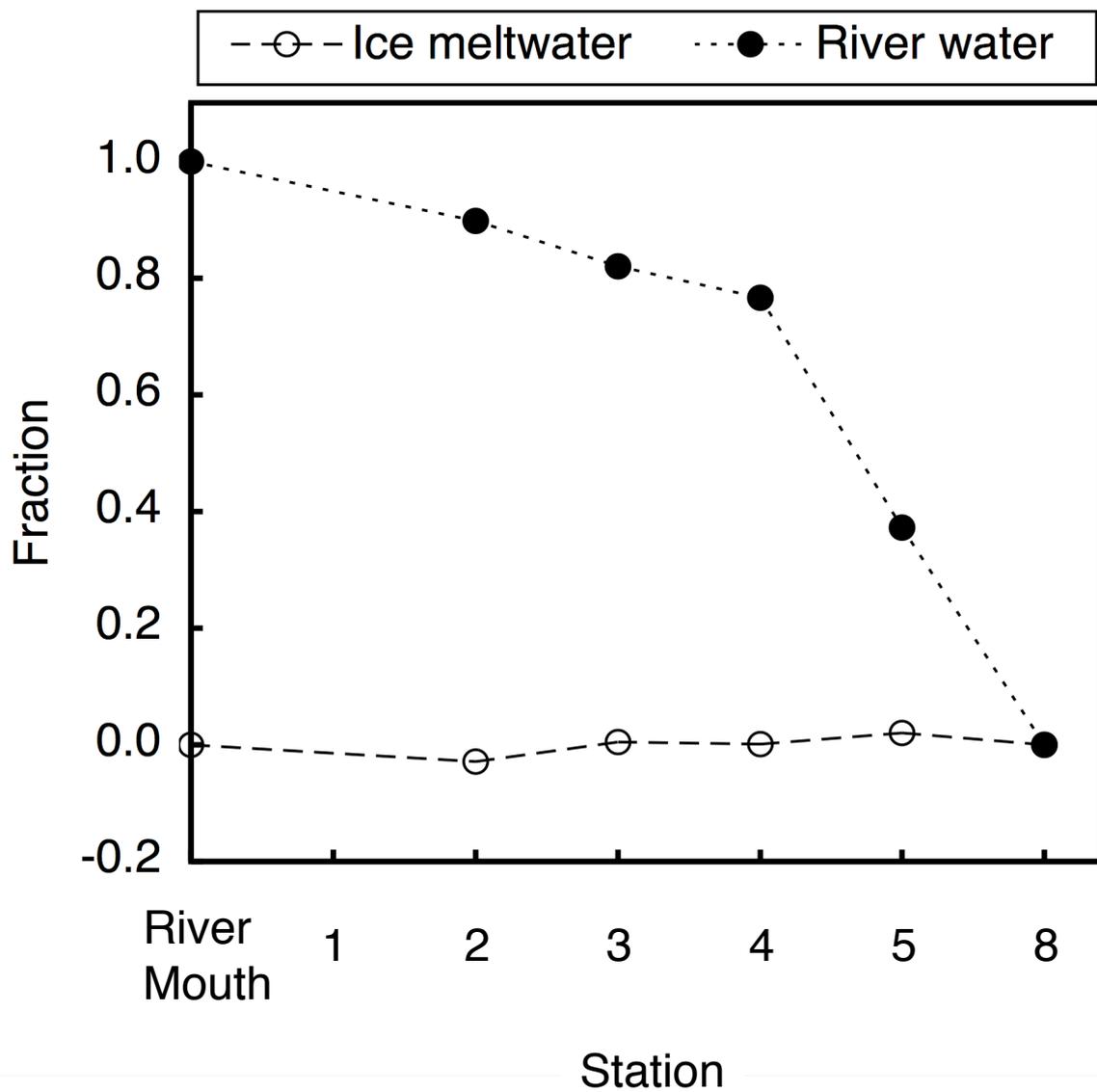


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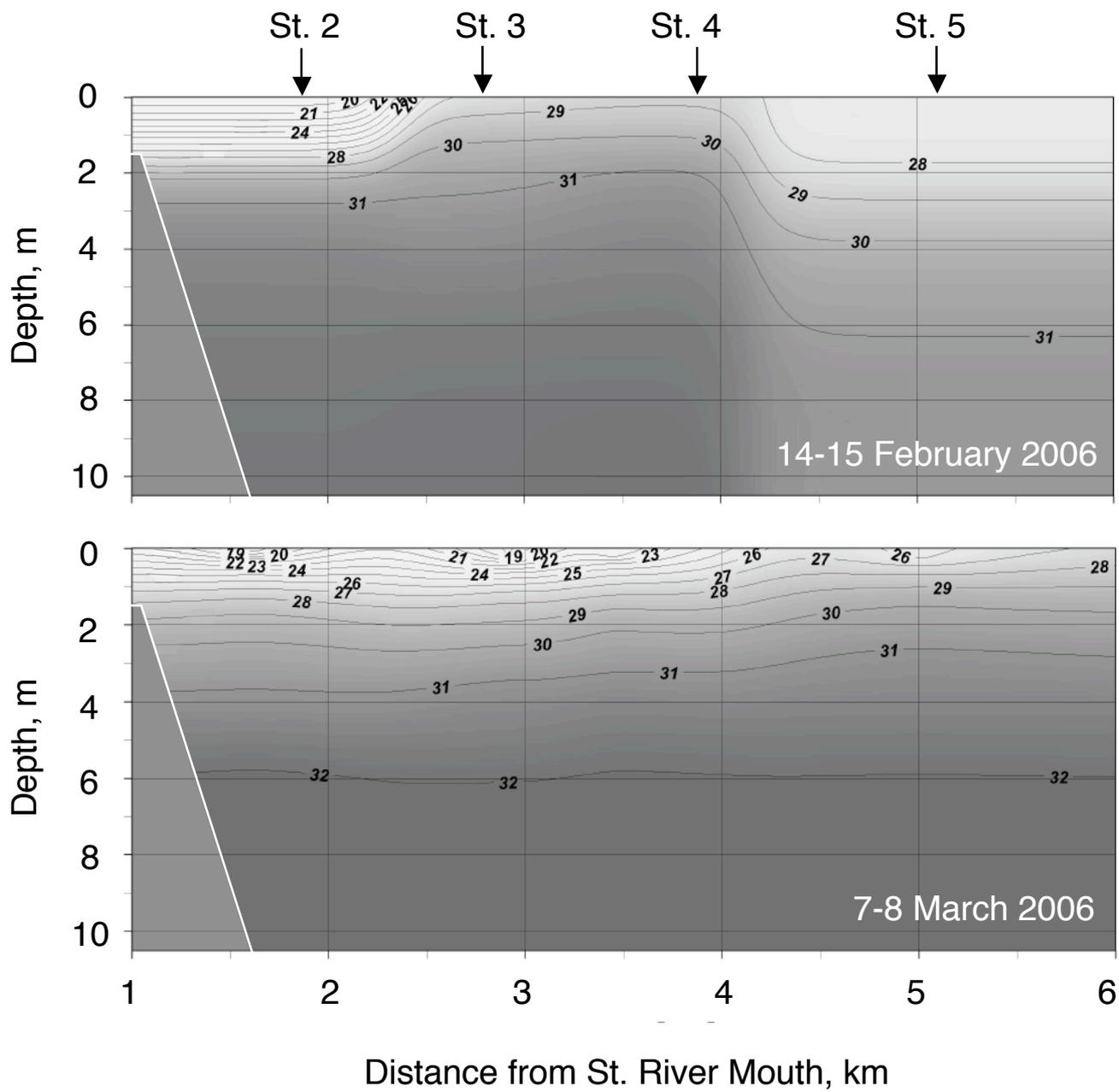


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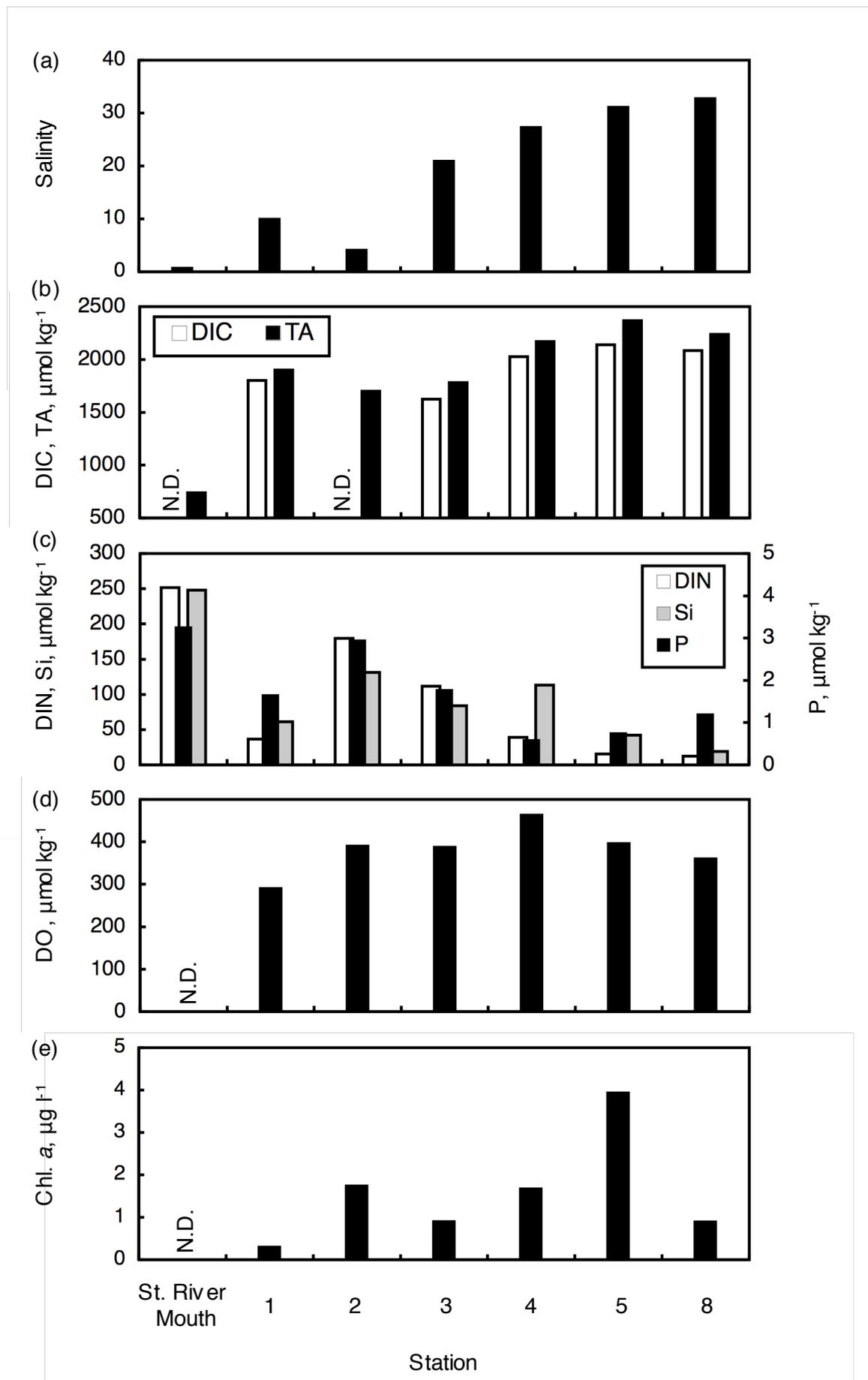


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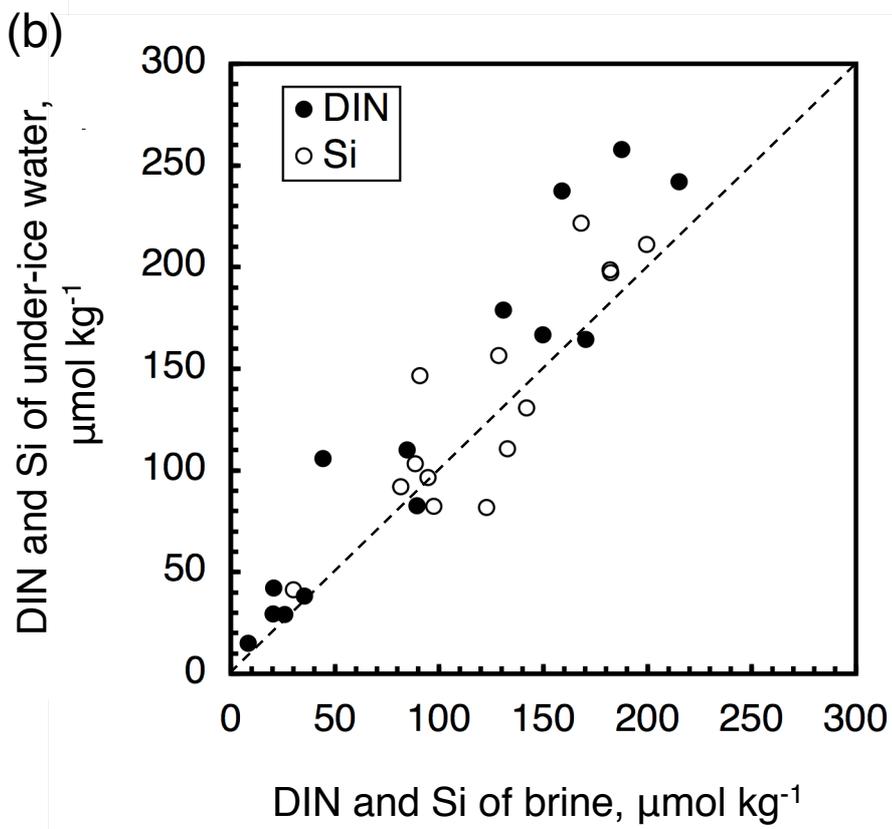
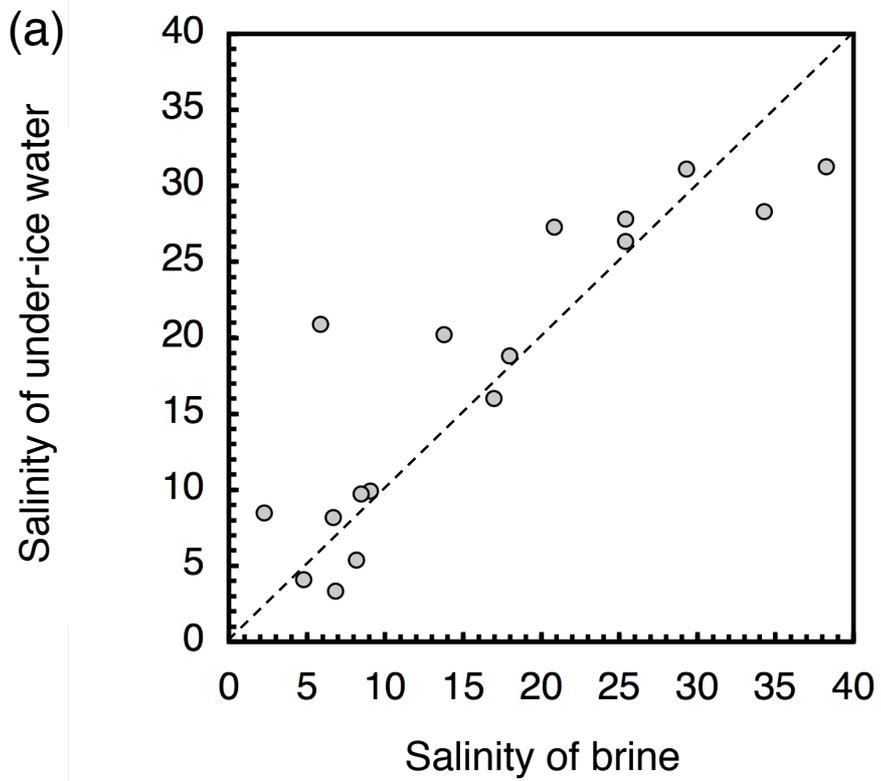


Fig. 10 Nomura et al.

Table 1 Summary of dates, stations and types of samples collected.

Date	<sup>a</sup> Station	CTD profile	Ice core	Brine	Under-ice water
12 February 2006	Soya St. 8	—	—	—	<sup>b</sup> ○
14 February 2006	5	○	—	—	—
16 February 2006	2	○	—	—	—
16 February 2006	3	○	—	—	—
16 February 2006	4	○	—	—	—
18 February 2006	Main	—	○	○	○
19 February 2006	Main	—	○	○	○
23 February 2006	Main	—	○	○	○
23 February 2006	2	—	○	○	○
24 February 2006	1	—	○	○	○
24 February 2006	5	—	○	○	○
25 February 2006	Main	—	○	○	○
26 February 2006	4	—	○	○	○
27 February 2006	River Mouth	—	—	—	○
28 February 2006	3	—	○	○	○
28 February 2006	Main	—	○	○	○
1 March 2006	2	—	○	○	○
3 March 2006	3	—	○	○	○
3 March 2006	Main	—	○	○	○
4 March 2006	4	—	○	○	○
5 March 2006	5	—	○	○	○
7 March 2006	Main	—	○	○	○
7 March 2006	4	○	—	—	—
7 March 2006	5	○	—	—	—
8 March 2006	2	○	—	—	—
8 March 2006	3	○	○	○	○
9 March 2006	2	—	○	○	○
26 February 2008	Main	—	—	○	—
28 February 2008	Main	—	—	○	—
29 February 2008	Main	—	—	○	—
1 March 2008	Main	—	—	○	—
2 March 2008	Main	—	—	○	—
3 March 2008	Main	—	—	○	—

<sup>a</sup> Repeat sample collections was carried out within 15m x 15m area for each station.

<sup>b</sup> Surface water was collected through cracks between sea ice floes during the cruise of the icebreaker *P/V Soya*.

Table 2 End-member values of salinity and  $\delta^{18}\text{O}$  used in this study

End-member	Salinity	$\delta^{18}\text{O}$ , ‰	Date	Station number
Okhotsk Sea water, “sea”	32.73	-0.75	12 February 2006	Soya St. 8
River water, “river”	0.69	-11.21	27 February 2006	St. River Mouth
Ice meltwater, “ice”	$3.83 \pm 2.41$	$-2.62 \pm 0.52$	18 February-8 March 2006	Sts. 1-5 and Main