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Nitrogen uptake regime regulated by ice melting during austral summer in the Prydz Bay, Antarctica

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Abstract

Using a combination of stable isotope (^{15}N) and radionuclide (^{226}Ra) analyses, we examine possible controls on the interactions between melting ice and the uptake of nitrogen in the Prydz Bay during the 2006 austral summer. We find that specific rates of uptake for nitrate and ammonium correlate positively to their concentrations, thus suggesting a substrate effect. In the study area, we observe that regions along open, oceanic water have high *f*-ratios (nitrate uptake/nitrate+ammonium uptake), while areas near the Amery Ice Shelf have significantly low *f*-ratios. Further analysis reveals a negative correlation between the *f*-ratio and the melt water fraction, thus implying that the melting of ice plays an essential role in regulating pelagic N dynamics in the Southern Ocean (SO). Stratification, produced by melting ice, should profoundly affect the efficiency of the SO's biological pump and consequently affect the concentration of CO_2 in the atmosphere. Results presented in this study add information to an already significant base of understanding of the controls on pelagic C and N dynamics in the SO. This provides unique insights for either interpreting past changes in geologic records or for predicting future climate change trends.

Key words: nitrogen uptake regime, ice melting, Prydz Bay, Antarctica

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1 Introduction

The Southern Ocean (SO) plays an important role in the sequestration of carbon dioxide (CO_2) in the global carbon cycle (Arrigo et al., 1999; DiTullio et al., 2000); therefore, it is vulnerable to change in carbon import and export caused by anthropogenic climate change. Biogeochemistry in the SO is highly diverse and dynamic. In the SO, nitrogen uptake processes play an essential role in biogeochemical cycles and the sequestration of atmospheric CO_2 (Cochlan, 2008). Concepts of new and regenerated production have been widely used to link surface nitrogen dynamics with biogenic particle flux (Eppley and Peterson, 1979). Although nitrogen is not a limiting factor for primary production in the SO (Cochlan, 2008), the nitrogen uptake regime, represented by the well-known parameter *f*-ratio, regulates the majority of the net oceanic sequestration of atmospheric CO_2. In other words, the *f*-ratio can be used as a measure of the efficiency of the "biological pump". The efficiency of the biological pump is expressed as the amount of carbon exported from the surface layer divided by the total amount produced through photosynthesis (Ducklow et al., 2001). Generally, a relatively small portion of net primary production is exported from the euphotic zone (De La Rocha and Passow, 2007, and references therein), which should equal the new production sustained by external nutrients (Eppley and Peterson, 1979). Understanding nitrogen uptake regime in the SO, particularly for high latitude Antarctic waters, will provide important information to understand the changes occurring in the SO as a whole. However, currently, the controlling factors on nitrogen uptake in the SO have not been resolved.

The melting of ice is a prominent physical process for hydrodynamics, and has important implications for phytoplankton bloom processes in the high latitude SO during the austral summer (Smith et al., 2000; Smith and Nelson, 1986; Zhang et al., 2014). The injection of low-salinity melt water increases vertical stratification in the upper water column, which may create a favorable environment for phytoplankton growth and aggregation (Smith and Nelson, 1986; Zhang et al., 2014). Examining the possible relationships between the melting of ice and the nitrogen uptake regime will provide unique insights to understand C and N biogeochemistry and their interactions with climate in the past, present and future.

Unfortunately, there are scarce direct results that integrate the nitrogen uptake regime and ice melt in the SO, within these data, the influence of melting ice is not clear in Antarctic waters (Cochlan, 2008). On the other hand, significant changes in ice-sheet dynamics are occurring in the high latitude SO (Massom and Stammerjohn, 2010). To understand climate change in the past, present and future, there is an urgent need to appropriately understand the nitrogen uptake regime and the manner in which the melting of ice influences the nitrogen uptake regime in the SO. There are several factors that indicate that melting ice exerts

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*Corresponding author, E-mail: mchen@xmu.edu.cn a significant impact on the nitrogen uptake regime in the SO during the austral summer. First, despite depleted sea surface nutrients throughout the SO, relatively high primary production was only observed in areas (MIZ, polynya) that were highly impacted by ice melting during the austral summer (Arrigo and van Dijken, 2003; Smith et al., 2000; Zhang et al., 2014). Second, based on δ^{15}N analyses, the isotope fractionation factor (ε) of nitrate assimilation decreases poleward and correlates strongly with the mixed layer depth (MLD) across the SO (DiFiore et al., 2010; Kemeny et al., 2016). This indicates the increasing influence that melting ice has on the nitrogen uptake regime. Third, physical forcing in Antarctic waters significantly affects the dynamics of phytoplankton. Ice melting events play a major role during the low wind stress austral summer (Arrigo et al., 1999; Arrigo and van Dijken, 2003; Smith et al., 2000).

As the third largest embayment in the Antarctic, the Prydz Bay, in the Indian sector of the SO, is highly impacted by ice dynamics, thus providing an ideal environment to examine the nitrogen uptake regime under the influence of melting ice. The Prydz Bay and its surrounding regions have large variations in environmental factors and conditions (Chen et al., 2017). For instance, summertime phytoplankton blooms in the polynya are a persistent feature in the Prydz Bay, while open oceanic waters are characterised by a high nutrient low chlorophyll regime (Arrigo and Van Dijken, 2003; Zhao et al., 2014). However, there are very few published results that discuss the state of the nitrogen uptake regime in the Prydz Bay (Mengesha et al., 1998; Cai et al., 2005; Liu et al., 2004), and there are no published results examining the relationships between nitrogen uptake and melting ice in the Prydz Bay. The majority of studies regarding nitrogen uptake regimes were conducted in the Ross Sea, while much less information is available for the Indian sector of the SO (Cochlan, 2008).

Using stable isotope (^{15}N) techniques, we examine the nitrogen uptake regime in the Prydz Bay during the austral summer. We analyse the influence of melting ice, i.e., the fraction of melt water, by using the naturally occurring radionuclide (^{226}Ra) and conservative mixing models. We investigate the relationships between the nitrogen uptake regime and the melt water fraction. Our results add key knowledge for understanding the C and N biogeochemical cycles in the rapidly changing SO.

2 Regional setting

The Prydz Bay is a triangular embayment along the Antarctic margin between 66°E and 79°E that covers an area of ~80 000 km^2 in the Indian sector of the SO (Vaz and Lennon, 1996; Pu and Dong, 2003). It is the third largest Antarctic embayment, just after the Weddell Sea and Ross Sea. It is located between the West Ice Shelf (around 80°E) and Cape Darnley (70°E). Surface circulation in the Prydz Bay is characterized by a closed, cyclonic gyre (the Prydz Gyre) adjacent to the Amery Ice Shelf. Another feature is the inflow of cold water from the east, near the West Ice Shelf and the outflow near Cape Darnley (Vaz and Lennon, 1996; Pu and Dong, 2003). South of 65°N, the Antarctic coastal current (westward) dominates circulation and is the largest ocean current in the world. North of 63°N, the Antarctic circumpolar current dominates circulation. The transition zone between these two currents is named the Antarctic Divergence, which is characterised by a strong upwelling of circumpolar deep water induced by wind forcing (Gao et al., 2008).

3 Materials and methods

3.1 *Sample collection*

Sampling was performed (n=21) aboard the icebreaker R/V *Xuelong* during the 22nd Chinese Antarctic Research Expedition (CHINARE) in the Prydz Bay region (64°–70°S, 68°–76°E), East Antarctica from 16 January to 23 January (austral summer), 2006 (Fig. 1). Surface (~2 m) seawater samples were collected using 10-L Niskin bottles.

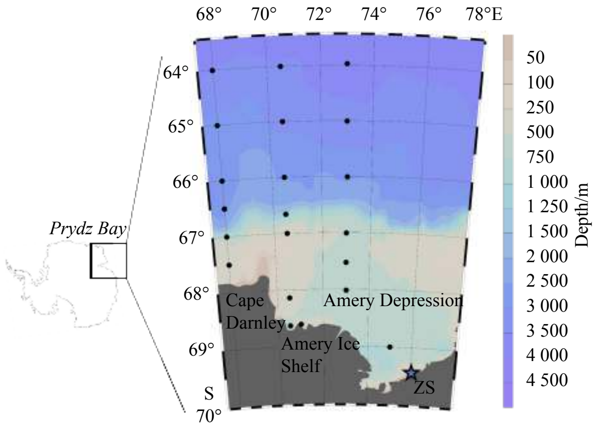

Fig. 1. Sampling locations in the Prydz Bay in 2006. ZS represents the Chinese Antarctic base Zhongshan.

3.2 *Environmental parameters*

Temperature, salinity and density data were recorded using a SeaBird CTD system. Concentrations of dissolved inorganic nutrients (NO_3^-, NO_2^-, NH_4^+, PO_4^{3-} and $Si(OH)_4$) were determined via standard methods. Onboard, immediately after filtering seawater samples through 0.45-μm cellulose acetate membranes, nitrate, phosphate and silicate concentrations were measured using the standard pink azodye method and the molybdenum blue method, respectively (Grasshoff et al., 1999). Both the CTD and nutrient data originate from the CHINARE program.

3.3 *Fraction of ice melt water*

To test the effect that melting ice has on the stratification of the upper water column, the fraction of ice melt water in surface waters was estimated from both constraints on the naturally occurring long-lived radium radionuclide (^{226}Ra, $T_{1/2}$=1 600 a) and salinity, which was measured during the cruise. Briefly, surface waters in the Prydz Bay during the austral summer are divided into the following three groups: (1) Antarctic surface water, (2) the Prydz Bay intermediate/deep water and (3) melt water (Zhang et al., 2014; references therein). Melt water has distinct properties, low salinity and low ^{226}Ra activity, when compared with the other two water masses. The Antarctic surface water has high salinity and high ^{226}Ra activity and the Prydz Bay intermediate/deep water has high salinity and intermediate ^{226}Ra activity. We can estimate the fraction of melt water using a conservative mixing (mass and isotope balance) model. More details on the conservative mixing model can be found in Zhang et al. (2014).

3.4 *Nitrogen uptake rate*

Nitrate and ammonium uptake by phytoplankton were measured using a ^{15}N tracer assay (Dugdale and Wilkerson, 1986). Water samples, placed in l-L incubation bottles, were enriched with either 1 μmol $^{15}NO_3^-$ (98.5 atom percentage) or $^{15}NH_4^+$ (98.5% atom percentage) and were incubated for 24 h in an on-deck incubator connected to a surface water flowing system under natural light. At the end of incubation, particulate matter was filtered onto pre-combusted (450°C, 2 h) Whatman GF/F glass fibre membranes that were dried and stored in a frozen state while at sea. After the cruise, PON concentrations and ^{15}N abundance were measured on a Thermo Finnigan MAT Delta$^{\text{plus}}$XP isotope ratio mass spectrometer interfaced with a Carlo Erba NC2500 elemental analyser. Reproducibility for nitrogen isotopic compositional (using the notation δ^{15}N, the abundance of ^{15}N relative to air, N_2, in per mil) measurements was better than ±0.2‰.

Specific and absolute uptake rates were calculated for each nutrient (Dugdale and Wilkerson, 1986). Specific uptake rates (V, h^{-1}) represent the PON-normalised turnover rates for cell nitrogen, while absolute uptake rates (ρ_N, μmol/(m^3·h)) represent the amount of nitrogen consumed by the phytoplankton during the incubation period (1 d).

3.5 *f*-ratio

As a measure of the "new" production that was contributed by primary production, the *f*-ratio was calculated as a measure of new (nitrate) against regenerated production (Eppley and Peterson, 1979):

$$f\text{-ratio} = \frac{\text{Uptake rate of nitrate}}{\text{Uptake rate of nitrate} + \text{Uptake rate of ammonium}}$$

4 Results

4.1 *Hydrographic features*

The study area was essentially free of sea ice during the sampling period, observable on satellite images (https://seaice.uni-bremen.de) (Fig. 2). High ammonium concentrations and marked nitrate drawdown indicate enhanced biological activity in the vicinity of the Amery Ice Shelf. The continental shelf break at 67°S (~1 000 m isobath) serves as a boundary between the subregions of the open oceanic zone (OOZ) and the coastal and continental shelf zone (CCSZ), which have distinct environmental conditions. Surface waters in the OOZ are characterised by high nutrient low chlorophyll (HNLC) conditions. By contrast, high chlorophyll concentrations (bloom condition) are confined to areas of low salinity in the coastal zone of the Prydz Bay, which coincides spatially with the greatest nutrient depletion. More details can be found in Zhang et al. (2014).

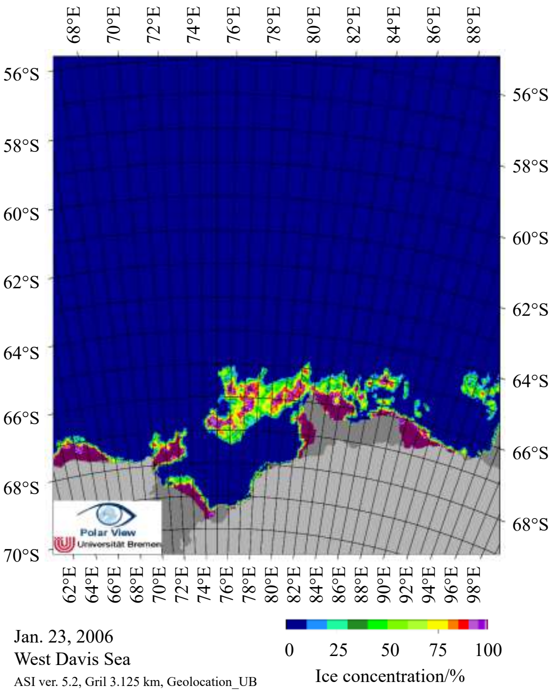

Fig. 2. Sea ice concentration from satellite remote sensing in the Prydz Bay during the sampling period. Data source: https://seaice.uni-bremen.de/databrowser/.

4.2 *Fraction of meltwater*

The fraction of melt water in surface waters ranged between 1.6% and 11.9%, with an average of 4.1% (n=19; also see Zhang et al. (2014)). Generally, the fraction of melt water in surface waters did not exceed 2% north of 67°S. Melt water fractions were elevated in coastal and continental shelf waters (south of 67°S), thus resulting in mixed layers that were both much shallower and more strongly stratified compared to water above 67°S (Fig. 3). Despite having a relatively low concentration, the fraction of melt water can generate both significant changes in the density field of the upper water column and in biogeochemical processes. A spatial correlation between seawater salinity, temperature and the density of the upper water column exists, thus suggesting that the injection of melt water has changed the density field.

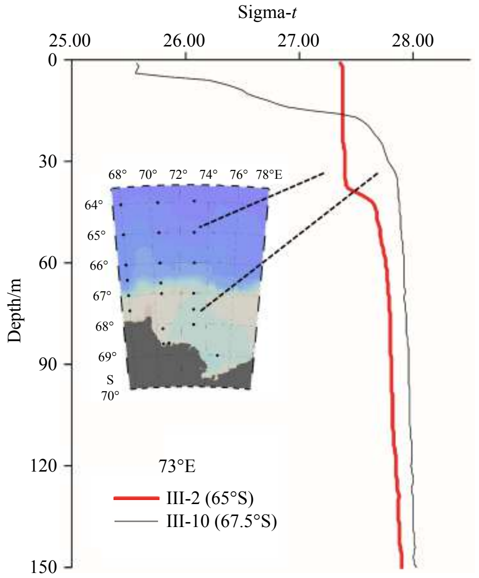

Fig. 3. Profiles of seawater density anomaly (sigma-t) at two typical stations (III-2 and III-10) along 73°E. Stations III-2 (65°S) and III-10 (67.5°S) are located in the coastal continental shelf zone (CCSZ) and the open oceanic zone (OOZ), respectively.

4.3 *Surface mixed layer depth*

The study area was characterised by MLDs shallower than 50 m, showing an onshore–offshore gradient (Fig. 3). Water columns were mixed more in the slope and basin (30–40 m) than in the coastal and continental shelf zone (5–15 m). The distinct water column stability can be seen by the density anomaly depth profiles for stations in the CCSZ and OOZ (Fig. 3).

4.4 *Nitrogen uptake rates*

Specific nitrate uptake rates (V_{NO_3}) ranged between 0.000 2 and 0.006 9 h^{-1} (mean=0.003 6 h^{-1}). Specific ammonium uptake rates (V_{NH_4}) ranged between 0.0004 and 0.001 4 h^{-1} (mean=0.000 8 h^{-1}).

Absolute nitrate uptake rates (new production, $\rho_{\mathrm{NO_3}}$) ranged between 4.3 and 28.1 μmol/(m^3·h) (mean=11.0 μmol/(m^3·h)). Absolute ammonium uptake rates ($\rho_{\mathrm{NH_4}}$) ranged between 0.7 and 10.7 μmol/(m^3·h) (mean=3.1 μmol/(m^3·h)). Specific uptake rates of NO_3 were an order of magnitude higher than those for NH_4, thus suggesting that NO_3 is the dominant inorganic N source for phytoplankton growth (Fig. 4). The absolute uptake rate generally showed a distinct pattern to that of specific uptake rate (Fig. 5).

4.5 *f-ratio*

As a measure of nitrate uptake relative to total N uptake, the *f*-ratio varied between 0.37 and 0.89 (mean=0.76) for total inorganic nitrogen (nitrate plus ammonium) uptake, thus suggesting that phytoplankton primary production was mainly supplied by the “new” nitrate. Spatially, *f*-ratios tend to decrease with an increase in proximity to the Amery Ice Shelf (Fig. 6). However, the OOZ is characterised by much higher *f*-ratios than those in the Amery Ice Shelf.

5 Discussion

5.1 *Spatial patterns of the nitrogen uptake regime in the Prydz Bay*

Nitrogen uptake rates and *f*-ratios generally are consistent with values previously published in the SO (Bury et al., 1995; Cochlan, 2008; Mengesha et al., 1998; Cai et al., 2005; Liu et al., 2004). The open oceanic zone (OOZ, north of ~67°S) is characterised by higher specific nitrate uptake rates compared to the coastal continental shelf zone (CCZZ, south of ~67°S) (Fig. 4). This is consistent with published results in previous studies for the Prdyz Bay region during the austral summer (Mengesha et al., 1998; Cai et al., 2005; Liu et al., 2004). We find that there is a relationship between the specific uptake rate and the substrate concentration for nitrate and ammonium (Fig. 7). This explains the distinct patterns of specific nitrate uptake rates observed in Fig. 5. The OOZ is characterised by HNLC conditions even during the austral summer, and occurrences of nitrate drawdown are rarely observed. In contrast, the CCSZ is quite productive during the

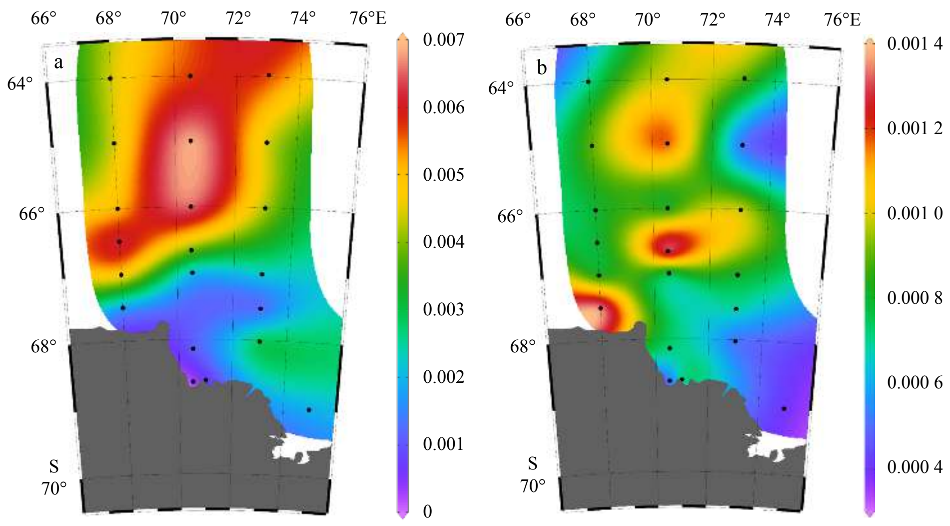

Fig. 4. Specific uptake rate (h^{-1}) of nitrate (a) and ammonium (b) in surface waters.

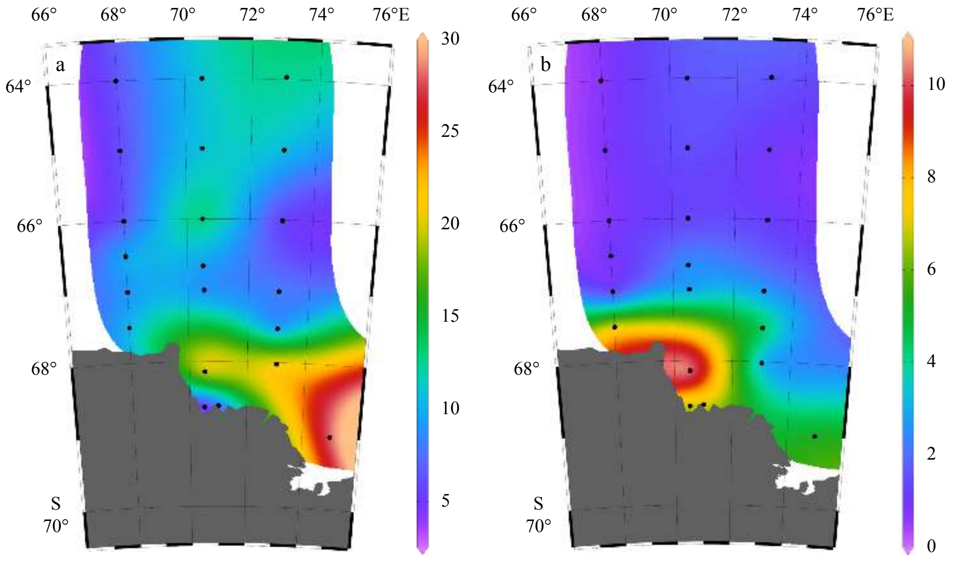

Fig. 5. Absolute uptake rate (μmol/(m^3·h)) of nitrate (a) and ammonium (b) in surface waters.

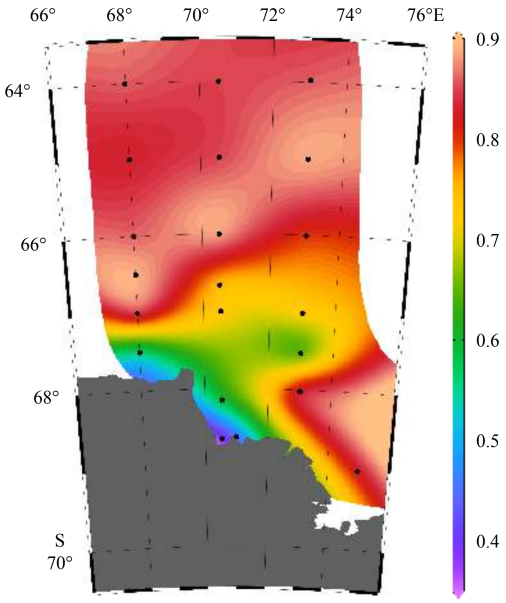

Fig. 6. The *f*-ratios in surface waters.

austral summer when environmental conditions are in favour of phytoplankton growth, thus inducing nitrate drawdown. Indeed, the absolute uptake rates in the CCSZ are much higher, implying much more active biological drawdown of macronutrients. Variability of nutrient consumption would be reflected in phytoplankton biomass in the Prydz Bay during summer (Han et al., 2011; Zhao et al., 2014). The highly dynamic nitrogen uptake regime cause variability of the stable isotope composition (δ^{15}N) of suspended particulate organic matter (Ren et al., 2015) and nitrate (DiFiore et al., 2010) in the Prydz Bay. This is of important implications for interpreting past changes in nitrate utilization and CO_2 level from sediment records.

At most stations, *f*-ratios are higher than 0.5, reaching as high as 0.9, thus suggesting that nitrate is the dominant N source for phytoplankton nutrition. This is consistent with past studies in the SO (Cochlan, 2008). The *f*-ratio was as low as 0.4 near the Amery Ice Shelf, thus suggesting that ammonium surpasses nitrate as the primary support for phytoplankton primary production. This is accompanied by a dramatic depletion of nitrate ($[NO_3]\approx2$ μmol/L) at the marginal ice stations. Uptake of ammonium is less energetically costly than nitrate, because the assimilation of nitrate requires the synthesis of the nitrate and nitrite reductase (Hurd et al., 1995). Thus, changes in the SO's *f*-ratio are in response to the changing nutrient structure during the austral summer, particularly for sub-regions highly impacted by melting ice.

In this study, high *f*-ratios indicate a higher contribution of NO_3-uptake compared to total nitrogen. However, high *f*-ratios do not necessarily correspond to high export production. Rather, for the HNLC OOZ, high *f*-ratios are accompanied by decreased new production. However, low *f*-ratios near the ice shelf correspond to increased new production and particulate organic carbon export flux. Our results are also supported by ^{234}Th-based export production estimates during the same cruise (He et al., 2007). This implies that melting ice should have a profound impact on nitrogen uptake regimes in the Prydz Bay during the austral summer.

5.2 *Effects of melting ice on the nitrogen uptake regime: a physical–biological coupling*

We propose that melting ice plays an essential role in regulating the nitrogen uptake regime in the Prydz Bay during the sampling period in the austral summer. This idea is corroborated by a negative correlation between the *f*-ratio and the fraction of melt water (Fig. 8). This is the first direct relationship between the *f*-ratio and the melt water fraction reported in the SO to the best of our knowledge. We suggest that melting ice may have also impacted phytoplankton nutrition dynamics via a physical–biological coupling.

Physical forcing is assumed to be a major factor that influences phytoplankton production regimes in the SO; water column stability is also assumed to be an important factor in phytoplankton production (Arrigo et al., 1999; Smith et al., 2000). The MLD forms during sea ice retreat in the spring and summer and is modified by solar heating and turbulent wind mixing (Arrigo et al., 1999). The MLD correlates to the fraction of melt water in this study (Fig. 9), thus suggesting that melting ice largely controls the vertical stability of the water column. Meanwhile, high production was observed when the fraction of ice melt water in the upper ocean was relatively large. Shallow MLDs have stable water columns, thus creating a favorable environment for phytoplankton growth (Zhang et al., 2014). Increased water column stability will create favorable light environments for phytoplankton photosynthesis and aggregation, as observed in the Ross Sea (Long et al., 2012; Sweeney et al., 2000). New production depends on the transition between the mixed layer and the layer

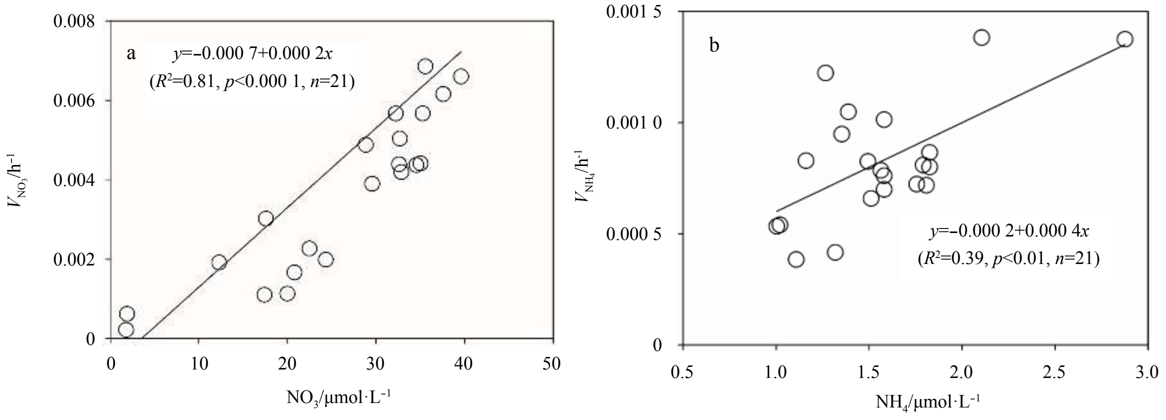

Fig. 7. Specific uptake rate versus nitrogen concentration. a. Nitrate and b.ammonium.

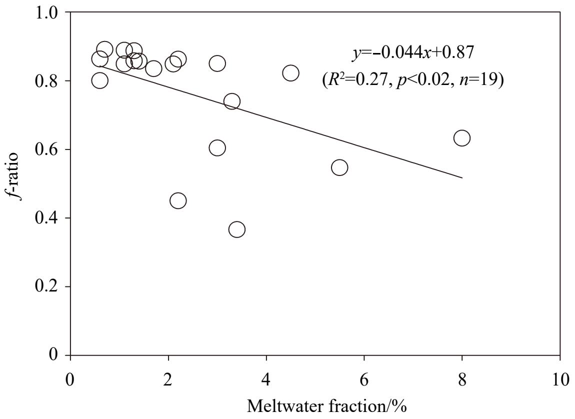

Fig. 8. Relationship between *f*-ratio and fraction of ice-melting water. The *f*-ratio and meltwater fraction (%) were calculated from ^{15}N tracer assay and ^{226}Ra mixing balance, respectively.

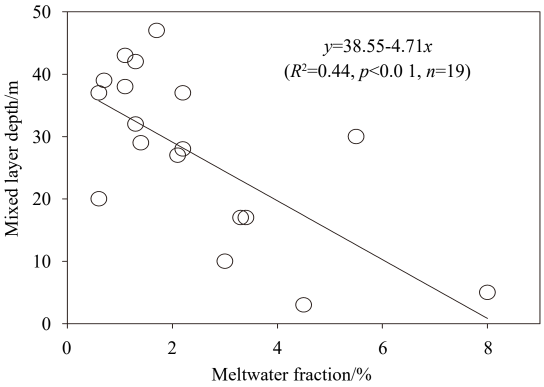

Fig. 9. Relationship between mixed layer depth (MLD) and fraction of ice meltwater.

below (Cochlan, 2008). With an increase in the drawdown of nitrate, an accumulation of ammonium due to increasingly active phytoplankton growth and reduced new nutrient upward flux due to stratification, the nitrogen uptake regime will sustain itself by regenerated forms produced within the mixed layer during the growth season. Thus, we can interpret the *f*-ratio as a measure of the coupling between the mixed layer and the layer below in the polar waters.

The *f*-ratio also represents the efficiency of the biological pump (Eppley and Peterson, 1979); thus, it directly affects the concentration of atmospheric CO_2. The nitrogen uptake regime and the structure of the phytoplankton community are closely related in the SO (Mengesha et al., 1998; Arrigo et al., 1999). The phytoplankton community structure in the SO is controlled by the mixed layer depth (Arrigo et al., 1999). Diatoms act as dominant exporters of organic carbon from the surface to the deep ocean and consequently influence SO nutrient cycles and atmospheric CO_2 concentrations (Smetacek et al., 2012). During this cruise, the dominant phytoplankton species in the bloom were the nanoplanktonic pennate diatom, *Fragilariopsis kerguelensis*, which contains up to 85% of the total cell abundance (Zhu et al., 2007). In fact, *F. kerguelensis* is the most abundant (usually bloom-forming) and widespread species in the SO, reaching 90% of the total diatom assemblage at times (Assmy et al., 2013). However, shifts in the structure of the phytoplankton community (diatom versus *Phaeocystis antarctica*) can occur in response to changes in the vertical stability of the water column. Such shifts can result in changes in the drawdown of nutrients and CO_2 in the SO. Consequently, the biological community's capacity to consume atmospheric CO_2 and to transport it to the deep ocean could dramatically diminish if predicted increases in the stratification of the upper ocean due to climate warming should occur (Arrigo et al., 1999).

Ice conditions in Antarctic waters are constantly and rapidly changing (Massom and Stammerjohn, 2010). Therefore, these changes may affect the stability of the seawater column as well as the nitrogen uptake regime. Future studies need to examine the correlation between the N uptake regime and melting ice, which will help us to understand the changes in the efficiency of the biological pump on a broad scale (Cochlan, 2008; Sarmiento et al., 2004; Wu et al., 2017).

6 Conclusions

In this study, we examined the N uptake regime in the Prdyz Bay during the austral summer in 2006 using the ^{15}N isotope tracer assay. For nitrate as well as ammonium, we found that the specific uptake rates depend on the substrate. The study area is generally characterised by high *f*-ratios (>0.5), thus suggesting that nitrate plays a dominant role in sustaining phytoplankton nutrition. Low *f*-ratios were observed near the Amery Ice Shelf. There is a close correlation between the N uptake regime and the melt water fraction via a physical–biological coupling. Changes in the N uptake regime impact the oceanic sequestration and burial of atmospheric CO_2. Our results highlight the importance of the effects of melting ice on C and N biogeochemistry in the SO. Further studies are needed in the SO, particularly in Antarctic waters, where rapid changes in ice conditions are taking place owing to the effects of climate change.

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