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RESEARCH ARTICLE

Macro-nutrient concentrations in Antarctic pack ice: Overall patterns and overlooked processes

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Antarctic pack ice is inhabited by a diverse and active microbial community reliant on nutrients for growth. Seeking patterns and overlooked processes, we performed a large-scale compilation of macro-nutrient data (hereafter termed nutrients) in Antarctic pack ice (306 ice-cores collected from 19 research cruises). Dissolved inorganic nitrogen and silicic acid concentrations change with time, as expected from a seasonally productive ecosystem. In winter, salinity-normalized nitrate and silicic acid concentrations (C^*) in sea ice are close to seawater concentrations (C_w), indicating little or no biological activity. In spring, nitrate and silicic acid concentrations become partially depleted with respect to seawater ($C^* < C_w$), commensurate with the seasonal build-up of ice microalgae promoted by increased insolation. Stronger and earlier nitrate than silicic acid consumption suggests that a significant fraction of the primary productivity in sea ice is sustained by flagellates. By both consuming and producing ammonium and nitrite, the microbial community maintains these nutrients at relatively low concentrations in spring. With the decrease in insolation beginning in late summer, dissolved inorganic nitrogen and silicic acid concentrations increase, indicating imbalance between their production (increasing or unchanged) and consumption (decreasing) in sea ice. Unlike the depleted concentrations of both nitrate and silicic acid from spring to summer, phosphate accumulates in sea ice ($C^* > C_w$). The phosphate excess could be explained by a greater allocation to phosphorus-rich biomolecules during ice algal blooms coupled with convective loss of excess dissolved nitrogen, preferential remineralization of phosphorus, and/or phosphate adsorption onto metal-organic complexes. Ammonium also appears to be efficiently adsorbed onto organic matter, with likely consequences to nitrogen mobility and availability. This dataset supports the view that the sea ice microbial community is highly efficient at processing nutrients but with a dynamic quite different from that in oceanic surface waters calling for focused future investigations.

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1. Introduction

Antarctic sea ice is one of the largest and most dynamic ecosystems on Earth, with a maximum aerial extent of $19 \times 10^6 \text{ km}^2$ in winter and a minimum of $3 \times 10^6 \text{ km}^2$ in summer (Parkinson and Cavalieri, 2012). Measurements of primary production in Antarctic pack ice are scarce (Roukaerts et al., 2016), but the available evidence suggests that Antarctic pack ice contributes to a small, but significant, fraction of the primary production of the Southern Ocean (Legendre et al., 1992; Arrigo and Thomas, 2004; Saenz and Arrigo, 2014). Sea ice is a semi-solid medium permeated by a network of channels and pores that are variably connected with seawater (Weeks, 2010). These brine-filled spaces can be heavily colonized by a sympagic (ice-associated) microbial community that is taxonomically diverse and metabolically active (Arrigo et al., 2010; Caron and Gast, 2010; Deming, 2010; and references therein). During its incorporation into the ice, the microbial community is exposed to major biogeochemical and physical changes in its habitat, including fluctuations in temperature, salinity, dissolved oxygen, light, pH, the surrounding organic matrix, and nutrients. These conditions change further during consolidation and melting of the sea ice (Thomas et al., 2010; Fransson et al., 2013; Vancoppenolle et al., 2013).

All organisms must obtain essential elements, termed nutrients, from their external environment to grow. The macro-nutrients (i.e., needed in large amounts) include dissolved inorganic nitrogen (DIN) in the form of nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+), and dissolved inorganic phosphorus (mostly phosphate; PO_4^{3-}). These nutrients provide structural and functional components to all organisms (Gruber, 2007; Paytan and McLaughlin, 2007). By contrast, dissolved silicon [mostly silicic acid; $\text{Si}(\text{OH})_4$] is a macro-nutrient predominantly used by diatoms to build their frustules (biogenic silica; bSiO_2) and to a lesser extent by radiolarians and silicoflagellates (Tréguer and De La Rocha, 2013). Since primary production in sea ice is thought to be dominated by diatoms (Arrigo et al., 2010), $\text{Si}(\text{OH})_4$ has also been suggested as a potentially limiting nutrient in this ecosystem (Gosselin et al., 1990; Smith et al., 1990).

Although many nutrient transformations (e.g., converting one form to another) have been either documented or inferred in Antarctic pack ice, the overall pattern of nutrient concentrations has remained elusive (Arrigo et al., 1995; Gleitz et al., 1995; Rysgaard et al., 2004, 2008; Fransson et al. 2011; Fripiat et al., 2014a, 2014b; Baer et al., 2015; Roukaerts et al., 2016). Previous studies are based on a few ice cores only, limited in space and time (e.g., Thomas et al., 1998; Becquevort et al., 2009). Hence, the high spatial and temporal variability that characterizes pack ice (e.g., Eicken et al., 1991; Rysgaard et al., 2001) has never really been accounted for. We performed a large-scale compilation of nutrient concentration data for pack ice from the Southern Ocean, using both previously published and

unpublished data. We describe the patterns that are elucidated by such a large dataset and discuss several associated underlying processes. The information compiled here will also aid in a better parameterization of models representing sea ice algal production (Steiner et al., 2016).

2. Description of data and methods

This compilation gathers much of the currently available nutrient data (concentrations of NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-} , and $\text{Si}(\text{OH})_4$) from the Antarctic pack ice. The data were derived from peer-reviewed publications, cruise reports, and direct contributions by field-research teams. The dataset is based on nutrient analyses performed on 2639 ice sections from 306 ice cores and on 93 samples of sackhole brines, all collected in the course of 19 cruises (see Table S1). The locations of these studies are shown in **Figure 1**.

2.1. Sea ice nutrient measurements

During most of the cruises, bulk ice nutrient concentrations (in $\mu\text{mol L}^{-1}$) were measured in melted ice core sections ($n = 2487$). The general procedure consists of collecting a core, dividing it into sections (average section thickness = $0.09 \pm 0.04 \text{ m}$) using a clean stainless steel saw, followed by the melting of the ice sections in the dark at ambient temperature or $< 4^\circ\text{C}$ (see Miller et al., 2015). Nutrient concentrations in brine were obtained either from measurements in samples extracted from centrifuged ice sections ($n = 152$; average section thickness = $0.14 \pm 0.05 \text{ m}$) (Arrigo et al., 2003; Munro et al., 2010), or using the sackhole technique ($n = 93$), i.e., drilling partial core holes to a desired depth within the ice and allowing brines from the surrounding ice to drain into the hole (Gleitz et al., 1995). These methods have been shown to be robust for nutrient sampling (Miller et al., 2015). In the following discussion, both centrifuged and bulk melted ice sections are presented together after salinity-normalization (i.e., equivalent nutrient concentration at seawater salinity; section 3.2). Sackhole data are used only for comparison with corresponding ice cores taken during the same cruises (section 3.4).

Nutrient concentrations were measured in filtered and unfiltered samples (**Table 1**), either in field laboratories soon after melting (ice core sections) or collection (brines) (52% of the analyses), or at home-based laboratories following storage either at $\leq -18^\circ\text{C}$ or by poisoning with HgCl_2 and refrigeration (Dore et al., 1996; Kattner et al., 1999; Hydes et al., 2008). No significant differences have been reported in the literature between samples stored frozen or poisoned and samples treated immediately (Dore et al., 1996; Kattner et al., 1999; Wurl, 2009; Fawcett et al., 2014). The only exception is NH_4^+ in poisoned samples, for which a systematic enrichment has been reported (Kattner et al., 1999). This type of storage was applied to 27% of the NH_4^+ samples from this dataset (Thomas et al., 1998; Kennedy et al., 2002; Nomura et al., 2016), a potential bias discussed further (Section 3.2). No differences have been

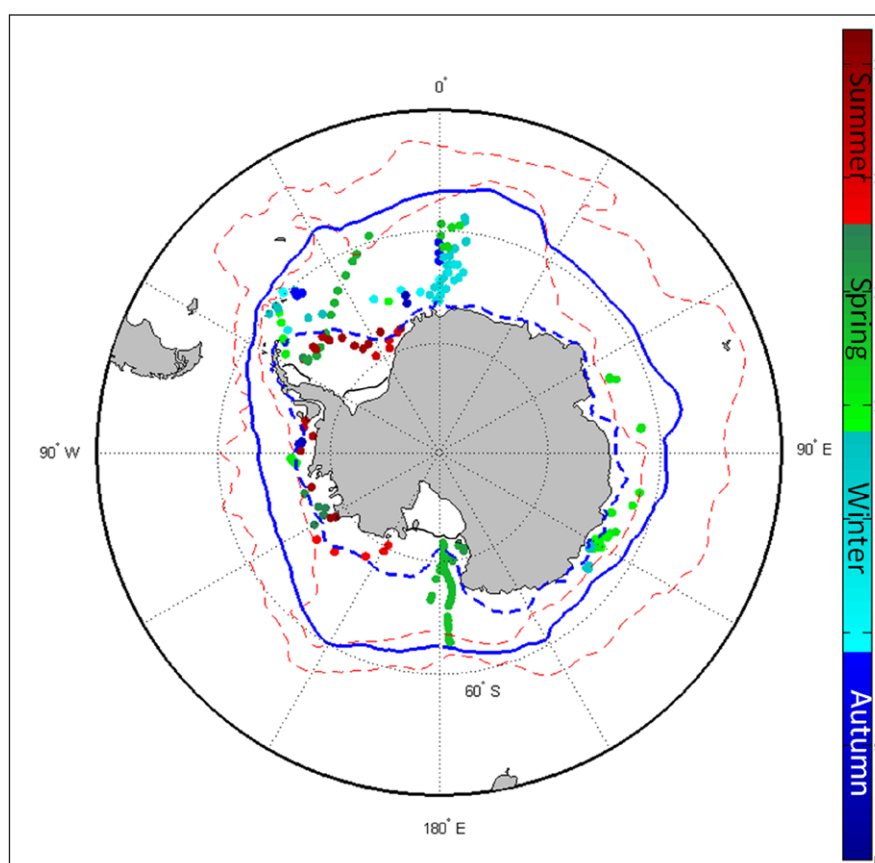


Figure 1: Map showing the location of sampling sites for sea ice cores and sackhole brines. The colors correspond to the seasons. The solid and dashed blue lines represent mean maximal and mean minimal sea ice extent (1979–2008, $\geq 15\%$ ice cover; Raymond, 2014). The position of the Polar Front and the southern boundary of the Antarctic Circumpolar Current are indicated by the dashed red lines (Orsi et al., 1995). DOI: <https://doi.org/10.1525/elementa.217.f1>

reported between filtered and unfiltered samples during storage (Dore et al., 1996; Kattner et al., 1999; Fawcett et al., 2014). Another concern is $\text{Si}(\text{OH})_4$ polymerization during freezing storage and its slow depolymerization when the sample is thawed for analysis, potentially resulting in underestimation of the actual $\text{Si}(\text{OH})_4$ concentration (e.g., Hydes et al., 2010). Prolonged thawing has been applied for $\text{Si}(\text{OH})_4$ determination in this dataset, which has been proven suitable for the recovery of the polymerized forms of silicic acid during analysis (Dore et al., 1998).

The sea ice nutrient measurements presented here (Table 1) are mostly based on automated or manual colorimetric analysis (e.g., Hydes et al., 2010). In some studies, NH_4^+ concentrations were measured using the fluorometric method (“OPA”) described in Holmes et al. (1999). To avoid analytical salinity effects given the wide range of salinities in sea ice samples, from melted ice sections to high-salinity brines, the calibration standards were prepared in artificial seawater solutions with salinities similar to those of the samples analysed. The measuring technique for DIN targets individual chemical species: NO_3^- , NO_2^- , or $\text{NH}_4^+/\text{NH}_3$. Soluble reactive phosphorus is defined as the dissolved P fraction that reacts in an acid solution containing molybdate ions to form a complex

that can be coloured by further reduction with ascorbic acid. This fraction includes mostly dissolved inorganic PO_4^{3-} (HPO_4^{2-} and PO_4^{3-}) but also some easily hydrolysable inorganic and organic P forms (Paytan and McLaughlin, 2007). Over the pH range that characterizes both sea ice and seawater, non-ionized $\text{Si}(\text{OH})_4$ is the dominant form of dissolved silicon, with the remainder being largely $\text{SiO}(\text{OH})_3^-$ (Sjöberg et al., 1981). Hereafter, soluble reactive phosphorus and dissolved silicon are referred to as phosphate (PO_4^{3-}) and silicic acid ($\text{Si}(\text{OH})_4$), respectively. When NO_2^- concentrations were unavailable, the available $\text{NO}_3^- + \text{NO}_2^-$ concentrations are presented as NO_3^- only. This assumption is reasonable given the small and relatively constant contribution of NO_2^- to the $\text{NO}_3^- + \text{NO}_2^-$ pool (median contribution of 5% in this dataset; Table S1).

2.2. Comment on nutrient contributions from cell lysis during bulk melting

There are concerns that the salinity change during the melting of ice core sections may induce osmotic shock to the ice-associated microbial cells, causing cell lysis and release of the intracellular nutrient content into solution. Significant differences in cell counts between melting treatments have been reported for samples containing

Table 1: Analytical treatments for ice core sections and sackhole brine samples. DOI: <https://doi.org/10.1525/elementa.217.t1>

Method	Analysis	Filtration	Storage	# Cores ^a	# Sackholes ^a
Colorimetric ^b	on ship	no	none	83(31)	32
Colorimetric ^c	on ship	yes	none	38(14)	19
Colorimetric + OPA ^d	on ship	yes	none	38	14
Colorimetric ^e	home laboratory	yes	< -18°C; < 18 months	22	0
Colorimetric + OPA ^f	home laboratory	yes	< -18°C; < 6 months	34	0
Colorimetric + OPA ^g	home laboratory	yes	HgCl ₂ poisoning; 4°C; < 3 years ^h	53	17(17)
Colorimetric ⁱ	home laboratory	no	< -20°C; < 3 months	17(17)	0
Colorimetric ^j	home laboratory	no	-80°C; < 6 months	12	0
Colorimetric ^k	home laboratory	no	HgCl ₂ poisoning; -20°C; < 3 months	3(3)	0
Colorimetric ^l	home laboratory	no	HgCl ₂ poisoning; 4°C; < 8 months	6	11

^a In parentheses are the number of cores or sackholes with no data for ammonium concentration.

^b ANTARKTIS V/2; ANTARKTIS X/3; ROAV98; NBP06-08; SIMBA (Dieckmann et al., 1991; Gleitz and Thomas, 1993; Gleitz et al., 1995; Arrigo et al., 2001; Munro et al., 2010).

^c WEPOLX; ANTARKTIS VIII/2; AURORA2003-V1; OSO 08-09 (Clarke and Ackley, 1984; Becquevort et al., 2009; Fransson et al., 2011).

^d ANTARKTIS XXII/2 (Papadimitriou et al., 2007; Tison et al., 2008).

^e SIPEX2; ANTARKTIS XXIX/6 (Meiners et al., 2016; Lannuzel et al., 2016).

^f ANTARKTIS XXIII/7; SIPEX (Meiners et al., 2009, 2011; Lannuzel et al., 2011).

^g ANTARKTIS IX/3; ANTARKTIS XI/3; ANTARKTIS XIV-3 (Gleitz et al., 1995; Thomas et al., 1998; Kennedy et al., 2002).

^h For sackhole data only; for cores, storage was < 6 months.

ⁱ AURORA1997-V2 Trevena et al., 2000).

^j AMERIEZ 88 (Garrisson et al., 1993).

^k ANTARKTIS XVIII/5b (Meiners et al., 2004).

^l SIPEX2 (Nomura et al., 2016).

flagellates and ciliates, which are considered to be particularly susceptible to osmotic shock (Garrison and Buck, 1986; Michelsen and Witkowski, 2010; Rintala et al., 2014), but also for bacteria in winter ice with brine salinities > 100 (Ewert et al., 2013). The changing conditions during melting could also induce stress to live cells, resulting in efflux of intracellular nutrients to the external medium. Measured nutrient concentrations would be expected to increase with increasing biomass if contribution by cell lysis or nutrient efflux from stressed live cells were significant (Thomas et al., 1998). The absence of a significant correlation between bulk nutrient and chlorophyll-*a* concentrations in bulk sea ice suggests minimal contribution of intracellular nutrients from algal cells to the measured concentrations (range of variability was 450-fold for bulk chlorophyll-*a* concentration and 40-fold for bulk nitrate concentration; Table S1).

High intracellular concentrations have been reported for all nutrients in flagellates and ciliates, with intracellular NO₃⁻ and NH₄⁺ concentrations ranging from

undetectable to 47.4 mmol L⁻¹ (Dortch et al., 1984; Lomas and Glibert, 2000; Kamp et al., 2015). Using these values and focusing on cell lysis, the typical upper range for algal cell abundance in Antarctic pack ice (10⁷ cell L⁻¹), and maximum sea ice flagellate cell volume (370 μm³) (Garrison and Buck, 1989), we estimated the maximum potential contribution of cell lysis to the dissolved nutrient pool of melted ice core sections. We further assumed Redfield N:P ratio to estimate the intracellular PO₄³⁻ pool (Sterner and Elser, 2002). Because only flagellates appear to be susceptible to cell lysis during sample melting, the melting effect on measured Si(OH)₄ concentrations was assumed to be negligible. This calculation shows that the maximum contribution of the intracellular nutrient pool would be equivalent to 0.18 μmol L⁻¹ for both NH₄⁺ and NO₃⁻, and 0.02 μmol L⁻¹ for PO₄³⁻. Such contributions from cell lysis are marginal as they are lower than most of the measured nutrient concentrations in melted bulk sea ice (**Figure 2**). During a recent Baltic sea ice study, where direct and salinity-buffered melting were compared, no

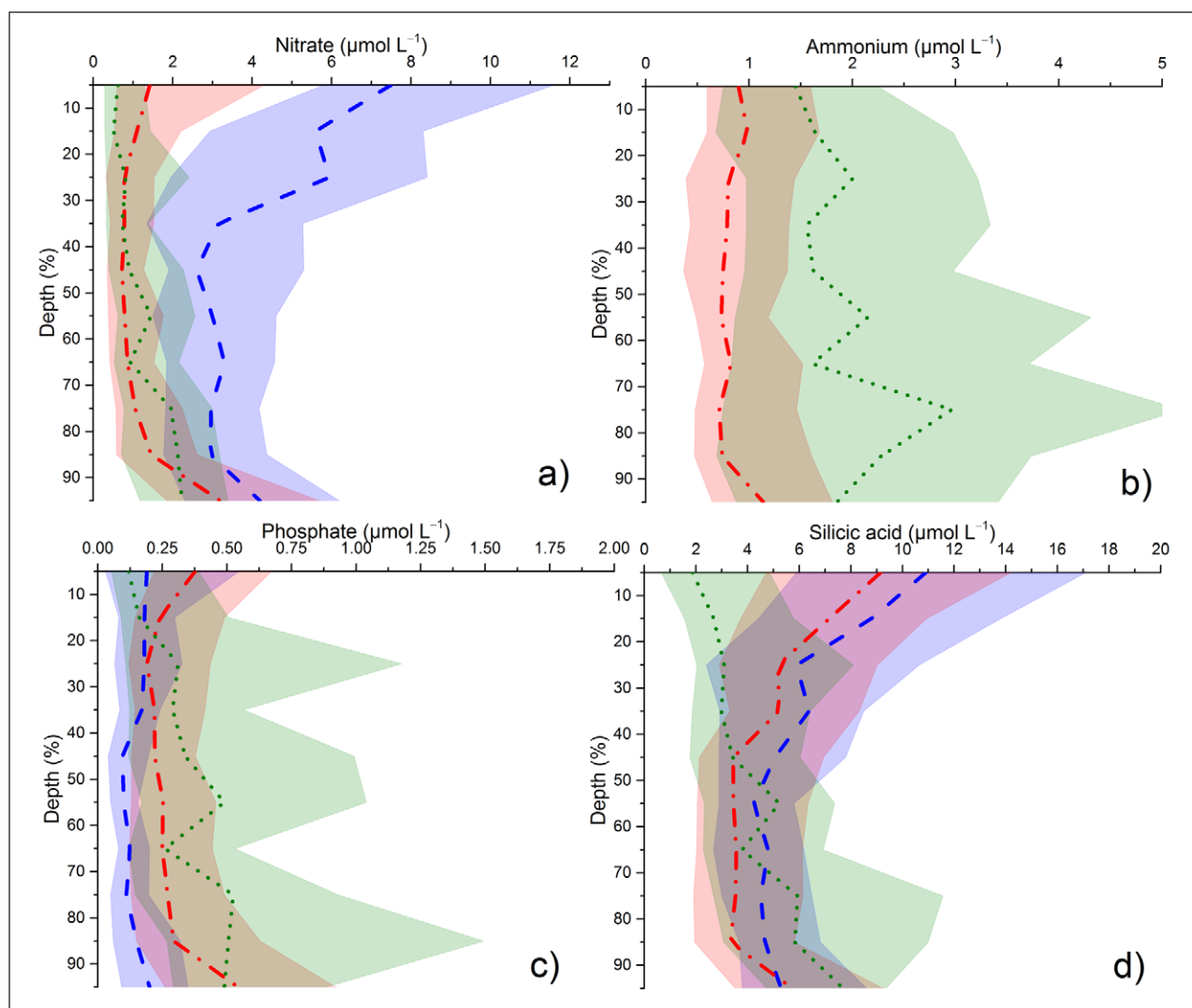


Figure 2: Vertical profiles for bulk nutrient concentrations in sea ice cores. Vertical profiles for bulk concentrations ($\mu\text{mol L}^{-1}$) of (a) NO_3^- (or $\text{NO}_3^- + \text{NO}_2^-$), (b) NH_4^+ , (c) PO_4^{3-} , and (d) Si(OH)_4 as a function of normalized ice core depth (i.e., $100 \times \text{sampling depth} / \text{total ice thickness}$). Median concentrations are indicated by the blue dashed, red dashed-dotted, and green dotted lines for winter, spring, and summer, respectively. The data have been binned into 10% depth intervals. The interquartile ranges are represented by the colored-corresponding envelopes. Insufficient data were available for ammonium in winter (~12 per 10% depth intervals, collected in late winter only). DOI: <https://doi.org/10.1525/elementa.217.f2>

significant differences in nutrient concentrations were observed (Rintala et al., 2014). However, as pointed out by Miller et al. (2015), a more systematic investigation is required of the different sample treatments, including centrifugation of ice sections.

3. Results and discussion

As with any literature compilation and given what could be viewed as a relatively small amount of data (306 ice cores from 19 cruises), there are inevitable biases in our dataset in terms of both spatial and temporal coverage. Most of the data (53%) were obtained from sea ice in the Atlantic sector of the Southern Ocean, while 26% of the data were obtained from sea ice in the Bellingshausen, Amundsen, and Ross Seas, and 21% from Eastern Antarctic sea ice (Table 2). A large proportion of the Antarctic pack ice not represented here is therefore still

undocumented. Spring (21 September to 20 December) is the most represented season (55%), followed by summer (21 December to 20 March; 22%), winter (21 June to 20 September; 16%), and autumn (21 March to 20 June; 6%) (Figures 1 and 3; Table 2).

The average thickness of ice (0.85 ± 0.65 m; $n = 306$) and snow (0.17 ± 0.18 m; $n = 150$) are indistinguishable from that estimated by the ASPeCt (Antarctic Sea ice Processes and Climate) dataset built from ship-based observations around Antarctica (0.87 ± 0.91 and 0.16 ± 0.20 m, respectively; $n = 23373$) (Worby et al., 2008). However, thinner ice types have been under-sampled in our dataset, especially in autumn and winter when the pack ice expands. The evolution from thinner to thicker ice from autumn through to summer is roughly reproduced in our dataset (Figure 3), which is nevertheless biased towards thicker ice. Pressure ridges make up a significant fraction of the Antarctic pack

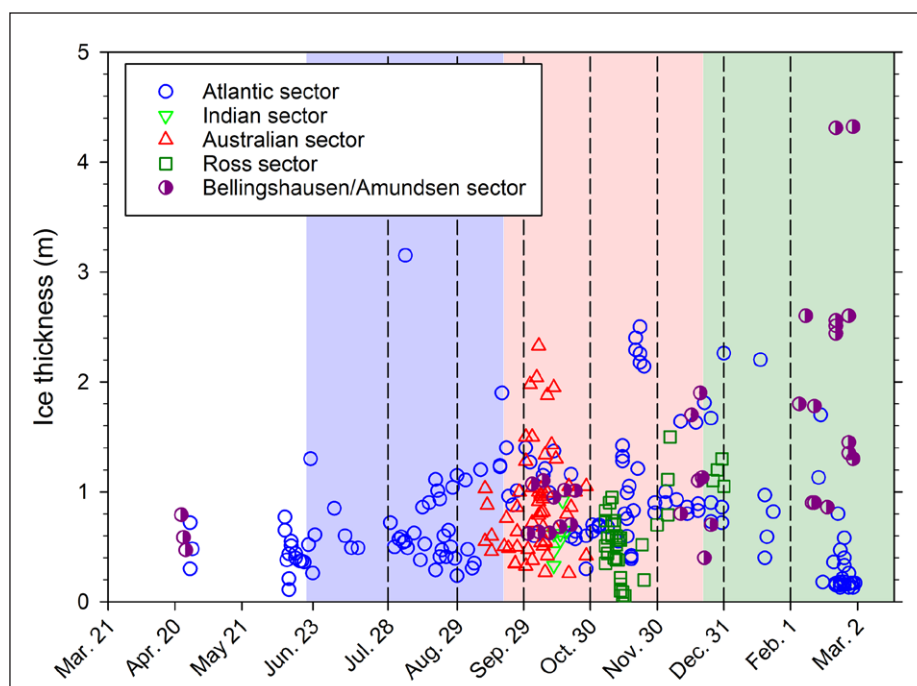


Figure 3: Sea ice thickness as function of time. Ice thickness in different sectors of the circumpolar Southern Ocean (Table 2). The vertical dashed lines represent the time period that was used to compute the seasonal evolution in Figures 6 and 7. The colored areas represent winter (blue), spring (red), and summer (green), as also used for vertical profiles in Figures 2, 4, 5, and 8. DOI: <https://doi.org/10.1525/elementa.217.f3>

Table 2: Ice core and sackhole sampling sites according to Antarctic sector and season. DOI: <https://doi.org/10.1525/elementa.217.t2>

Sector	Longitude	# Cores	# Sackholes	Time frame	Ice thickness (m)
Atlantic	60°W/20°E	161	31	27 April–02 March	0.1–4.3
Indian	20°E/90°E	11	0	13–19 October	0.3–0.9
Australian	90°E/160°E	55	23	27 September–28 October	0.3–2.3
Ross	160°E/130°W	43	4	6 November–1 January	0.1–1.5
Bellingshausen/Amundsen	60°W/130°W	36	3	23 April–1 March	0.4–4.3

ice cover (with surface ridging covering 12 ± 15 %; Worby et al., 2008), but none of the compiled ice cores falls in this category. Based on autonomous underwater vehicle retrievals, Williams et al. (2015) recently estimated that deformed ice comprised an average of 57 % (volumetric) of the investigated floes, far exceeding that estimated from previous shipboard observations and drilling data.

For all these reasons, our discussion will be focused on level ice and associated nutrient transformations from late winter to late summer, i.e., the most represented time periods in the current data compilation. We do not make the distinction between first-year and multi-year ice because no clear differences in nutrient concentrations were observed, and only 9 of the 306 cores have been identified as multi-year ice (in peer-reviewed publications or cruise reports).

3.1. Nutrient sources and exchange

Seawater is the main source of nutrients in Antarctic pack ice (Gleitz et al., 1995), with a minor contribution expected from atmospheric deposition. Nutrient-rich Circumpolar Deep Water ascends into the surface of the Antarctic Zone of the Southern Ocean (south of the Polar Front; Figure 1). Upwelled waters are either transported northward or southward to form the upper and lower branches of the meridional overturning circulation, before the available nutrient pools can be fully utilized by phytoplankton (Speer et al., 2000; Sarmiento et al., 2004; Rintoul et al., 2009). The inability to strip nutrients out of the surface oceanic water has been attributed to light and iron co-limitation (Martin et al., 1990; Mitchell et al., 1991) and results in high macro-nutrient concentrations year-round in the Antarctic Zone (Garcia et al.,

2014): specifically, the NO_3^- concentrations range from 30–35 $\mu\text{mol L}^{-1}$ to 20–25 $\mu\text{mol L}^{-1}$, the PO_4^{3-} concentrations from 2.0–2.4 to 1.4–2.0 $\mu\text{mol L}^{-1}$, and the Si(OH)_4 concentrations from 50–90 to 40–75 $\mu\text{mol L}^{-1}$ during winter and summer, respectively. The higher Si(OH)_4 compared to NO_3^- and PO_4^{3-} depletion in the surface waters has been attributed to the influence of iron-limited diatom growth that dramatically increases their Si to nutrient assimilation ratios (where ‘nutrient’ refers to both N and P; Hutchins and Bruland, 1998; Takeda, 1998; Claquin et al., 2002), along with processes involved in the so-called “silicate pump” (i.e., deeper remineralization of Si relative to C, N, and P; Dugdale et al., 1995). Both NH_4^+ and NO_2^- are intermediaries in the biological N cycle (assimilation, ammonification, and nitrification). By producing and consuming both NH_4^+ and NO_2^- , the microbial community maintains low and relatively constant concentrations of these compounds (usually below 0.4 $\mu\text{mol L}^{-1}$) year-round in the surface waters (Gruber, 2007).

Nutrient dynamics in sea ice are driven by biologically-mediated consumption and assimilation into biomass and by production via remineralization, as well as by brine transport. Because they are expelled from the ice crystal lattice, dissolved sea salts are mostly concentrated in the interstitial brine (Vancoppenolle et al., 2013). Controlled by the same physical processes, nutrients in sea ice would behave like major dissolved sea salts when biological activity is negligible. Upon freezing, dissolved sea salts are partly incorporated in the sea ice but they are quickly lost due to desalination processes within a few days (Notz and Worster, 2009). Hence, pack ice has a typical bulk salinity (S_{bulk}) of ~ 5 , whereas seawater in the sea-ice covered

Antarctic Zone has a salinity of ~ 34 (**Figure 4**). During ice growth, exchange with seawater occurs nearly continuously in a thin layer near the ice-ocean interface (Rees-Jones and Worster, 2013). In this process, the downward temperature gradient generates an upward brine salinity gradient, destabilizing the brine column and forcing brine convection with seawater (Notz and Worster, 2009; Wells et al., 2011). Full-depth brine convective events may also occur episodically, once the ice has warmed sufficiently in spring to make the entire ice thickness permeable to fluid transport (Griewank and Notz, 2013; Jardon et al., 2013). Seawater flooding of the snow base increases the salt and nutrient content near the ice surface. Seawater flooding is commonly observed in Southern Ocean pack ice characterized by high snow accumulation (up to 3 m) on relatively thin ice (Worby et al., 2008). As a result, the snow-ice interface often sinks below sea level, resulting in a negative ice freeboard (the elevation of the snow-ice interface relative to the local sea surface) and hydraulically forcing the infiltration of seawater and brine into snow, with slush and snow ice forming in the process (Jeffries et al., 1997, 2001; Haas et al., 2001; Maksym and Markus, 2008; Papadimitriou et al., 2009).

The combination of these processes explains the different salinity profiles observed in winter and spring pack ice (C- and S-shaped profiles; **Figure 4**) (Eicken, 1992), compared to summer pack ice which exhibits lower near-surface salinities than in the underlying layers (?- and i-shaped profiles) due to surface melting in summer (Eicken, 1992; Haas et al., 2001; Weeks, 2010). The effect of fluid transport through sea ice is discernible in profiles of nutrient concentrations in sea ice. If biological activity were

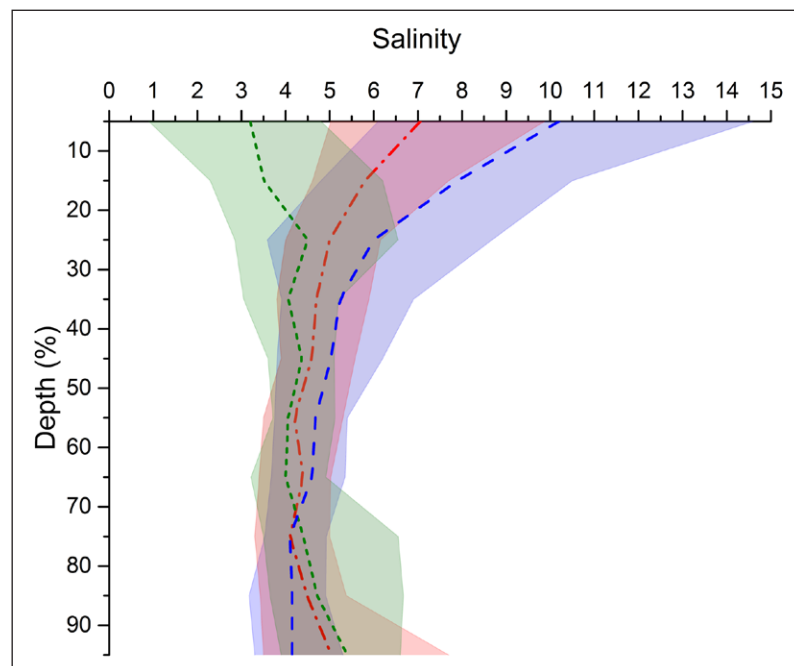


Figure 4: Vertical profiles for bulk salinity in sea ice cores. Vertical profiles of the salinity of bulk sea ice as a function of normalized ice core depth. Median values are indicated by the blue dashed, red dashed-dotted, and green dotted lines for winter, spring and summer, respectively. The data have been binned into 10% depth intervals. The interquartile ranges are represented by the colored-corresponding envelopes. DOI: <https://doi.org/10.1525/elementa.217.f4>

negligible, bulk nutrient concentrations would follow the conservative trend of the major dissolved salts as measured by bulk salinity. Seawater-derived nutrients (NO_3^- , PO_4^{3-} , and Si(OH)_4) present a distribution roughly similar to salinity, with both C-shaped and S-shaped profiles in both winter and spring, as well as ?-shaped and i-shaped profiles in summer (Figures 2 and 4). Despite large scatter, the correlation between bulk nutrient concentrations and bulk salinity is significant in all seasons (p-value < 0.05; not shown). Winter NO_3^- and Si(OH)_4 concentrations are the most highly correlated with salinity (slope of 0.7 and 1.1, R^2 of 0.45 and 0.62, p-value < 0.001, respectively). The large scatter can be attributed to variability in biological nutrient transformations (section 3.2). Similar to salinity, bulk nutrient concentrations in sea ice are lower than those in seawater. This difference indicates that, following

incorporation into sea ice, nutrients are partly expelled out of the growing sea ice during desalination.

Net consumption of nutrients during microalgal growth is associated with their assimilation into organic matter during the spring–summer bloom (Figure 5). Total concentrations (organic + inorganic) are only available for nitrogen, for which data on particulate N (PN; n = 606), dissolved organic N (DON; n = 858) and DIN are available (Figure 5; Table S1 in supplementary materials; mainly from spring to summer). No data are available for organic P and only Fripiat et al. (2007) reported measurements of biogenic silica concentrations in Antarctic pack ice. Most of the observations indicate lower total N concentrations in summer, and even more so in spring, than in seawater (Figure 5d). However, the concentration of total N is higher than would be predicted from the salinity of

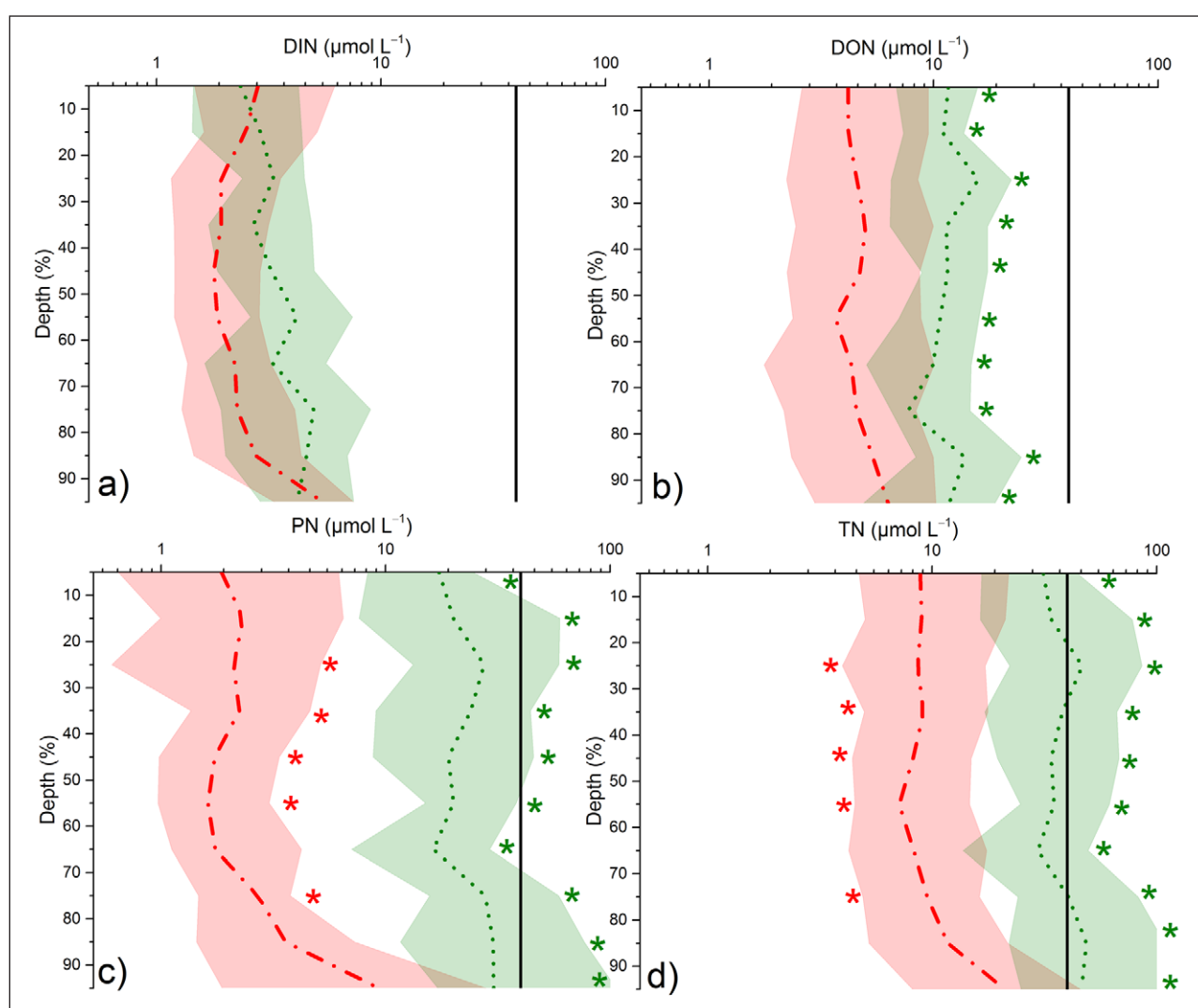


Figure 5: Vertical profiles for bulk N concentrations in sea ice cores. Vertical profiles of bulk N concentrations as a function of normalized ice core depth: **(a)** dissolved inorganic nitrogen (DIN), **(b)** dissolved organic nitrogen (DON), **(c)** particulate nitrogen (PN), and **(d)** total nitrogen (TN). Median concentrations are indicated by the red dashed-dotted and green dotted lines for spring and summer, respectively. The data have been binned into 10% depth intervals. The interquartile ranges are represented by the corresponding colored envelopes. Seawater TN is indicated by the solid black line (value estimated for Antarctic pack ice in Fripiat et al., 2014a). Insufficient data were available in winter (~ 12 per 10% depth interval, collected mainly in late winter). The symbol * indicates depth intervals with less than 30 data points available. DOI: <https://doi.org/10.1525/elementa.217.f5>

the melted sample ($\sim 5 \mu\text{mol L}^{-1}$) and consists mostly of organic N (**Figure 5**). Higher bulk total N concentrations than in seawater are commonly observed in the bottom sea ice layer in spring and at all depths in summer, with maximum PN, DON, and DIN concentrations of 616, 78, and $81 \mu\text{mol L}^{-1}$, respectively. These concentrations are equivalent to ~ 15 – 20 times the concentration in seawater. The mass balance of nutrients in sea ice is controlled by desalination and microbial activity. During ice growth, desalination results in nutrient expulsion from the ice but the activity of ice-associated organisms will generate an interior sink for nutrients via assimilation into biomass. This biologically-mediated sink can be higher than the net removal of nutrients from the system via desalination. It is still uncertain whether the bulk of organic matter produced in situ or scavenged from the seawater is degraded and respired within sea ice or in surface waters after melting, or if it is exported to the deep ocean (Smith and Nelson, 1985; Riebesell et al., 1991; Boetius et al., 2013). The overall balance amongst these processes will determine the fraction of the nutrients (and carbon) removed from surface oceanic water through the sea ice biological pump.

3.2. Nutrient seasonal trends and processes

As discussed above, bulk salinities and solute concentrations are affected by the fluid transport, while brine salinity and nutrient concentrations are affected by temperature-driven concentration and dilution. To tease apart these physical effects, the *salinity-normalized nutrient concentration* C^* is calculated as follows:

$$C^* = C \cdot \frac{S_w}{S} \quad (1)$$

where C is the measured nutrient concentration (bulk ice or brine), S_w is the salinity of seawater, and S the corresponding measured salinity in the sample (bulk ice or brine). We use a constant initial seawater salinity of 34.3, as surface salinity values in the polar Antarctic zone range from 33.5 to 35 (World Ocean Atlas 2013), which implies a maximum uncertainty of 5% in the estimates of C^* . This level of uncertainty is below the analytical precision of nutrient measurements (relative standard deviation of $\sim 10\%$). Normalization to salinity filters out the effect of physical processes and allows us to focus on the effects of biogeochemical processes, which are the topics of the following sections. This assumption is valid as long as nutrients come from seawater; it could be invalidated either when nutrient-loaded meltwater from snow infiltrates sea ice or when infiltrated seawater passes through intermediate ice layers where biogeochemical processes have altered the original seawater nutrient-to-salinity ratio. In order to better assess the effect of nutrient-loaded snow, we recommend that, in future, researchers systematically measure nutrient concentrations in the overlying snow.

The annual cycle of nutrients in pack ice was investigated here by grouping the data into seven periods of about one month each (**Figures 3, 6 and 7**). Given the small amount of data available for austral autumn and early winter, those data were binned into a single time

period (from March to July) and will be discussed briefly at the end of this section. Results are also presented as a function of depth (surface, 0.0–0.2 m from the ice surface; bottom, 0.0–0.1 m from the bottom; and interior, between the surface and bottom layers), reflecting the main sea ice habitats (Arrigo and Thomas, 2004). In support of the circumpolar seasonal trends, the seasonal evolution for the Atlantic sector (between 60°W and 8°E) is shown for comparison and is in good agreement with the circumpolar trends (**Figures S1 and S2**). At any given time, a large variability in salinity-normalized nutrient concentrations is evident (**Figures 6 and 7**), most likely due to the large spatial variability common to many sea ice properties (Eicken et al., 1991; Arrigo and Thomas, 2004). Despite this variability, clear and contrasting seasonal trends for the different nutrients were discernible (**Figures 6 and 7**), as also represented in vertical profiles (**Figure 8**).

The $^*\text{NO}_3^-$ concentrations in winter sea ice are indistinguishable from seawater concentrations (**Figures 6a and 8a**), suggesting either little or balanced NO_3^- production (nitrification) and consumption (assimilation) during this period. Following the increase in solar radiation in spring and the resulting algal bloom, $^*\text{NO}_3^-$ tends to be depleted significantly in comparison to seawater at all depths within sea ice from September to March (**Figures 6a and 8a**; see Table S2 for pairwise multiple comparison; Gleitz et al., 1995; Thomas et al., 2010). The $^*\text{NO}_3^-$ concentrations tend to be higher at the bottom of the ice due to replenishment by nutrient-rich underlying seawater (**Figures 6a and 8a**).

Together with the decrease in solar radiation, $^*\text{NO}_3^-$ concentrations tend to increase in February (significantly only in the interior of sea ice; Table S2). During this time, sea ice around Antarctica is at its annual minimal areal extent, with a perennial ice cover remaining in the western Weddell Sea and in coastal regions along the Bellingshausen, Amundsen, and Ross Seas (**Figure 1**; Parkinson and Cavalieri, 2012). Two processes can be responsible for such an increase in $^*\text{NO}_3^-$ concentrations: (i) an increase in the exchange with nutrient-rich seawater in porous decaying sea ice (Fritsen et al., 1994; Kattner et al., 2004; Haas et al., 2001), or (ii) an imbalance between the processes of NO_3^- production (nitrification, partly light-inhibited) and consumption (assimilation, light-dependent) with the decrease in solar radiation. Nitrification has been shown to be significant in sea ice (Priscu et al., 1990; Fripiat et al., 2014a, 2015; Baer et al., 2015; Firth et al., 2016), with the microbial community being embedded in biofilms and exposed to both low-light and high NH_4^+ concentrations from decaying organic matter (Hagopian and Riley, 1998; Meiners et al., 2004; Ward, 2007; Deming, 2010).

In agreement with *in situ* production, $^*\text{NH}_4^+$ and $^*\text{NO}_2^-$ typically accumulated within pack ice at all times and all depths (**Figures 6b, 6c and 8b**). The $^*\text{NH}_4^+$ concentrations are relatively constant in spring (from September to December; see Table S2 for pairwise multiple comparison). In the pelagic euphotic zone, NH_4^+ produced by remineralization is swiftly assimilated back into biomass, maintaining low and constant concentrations in the surface waters (Gruber, 2007). Such a scenario is likely to

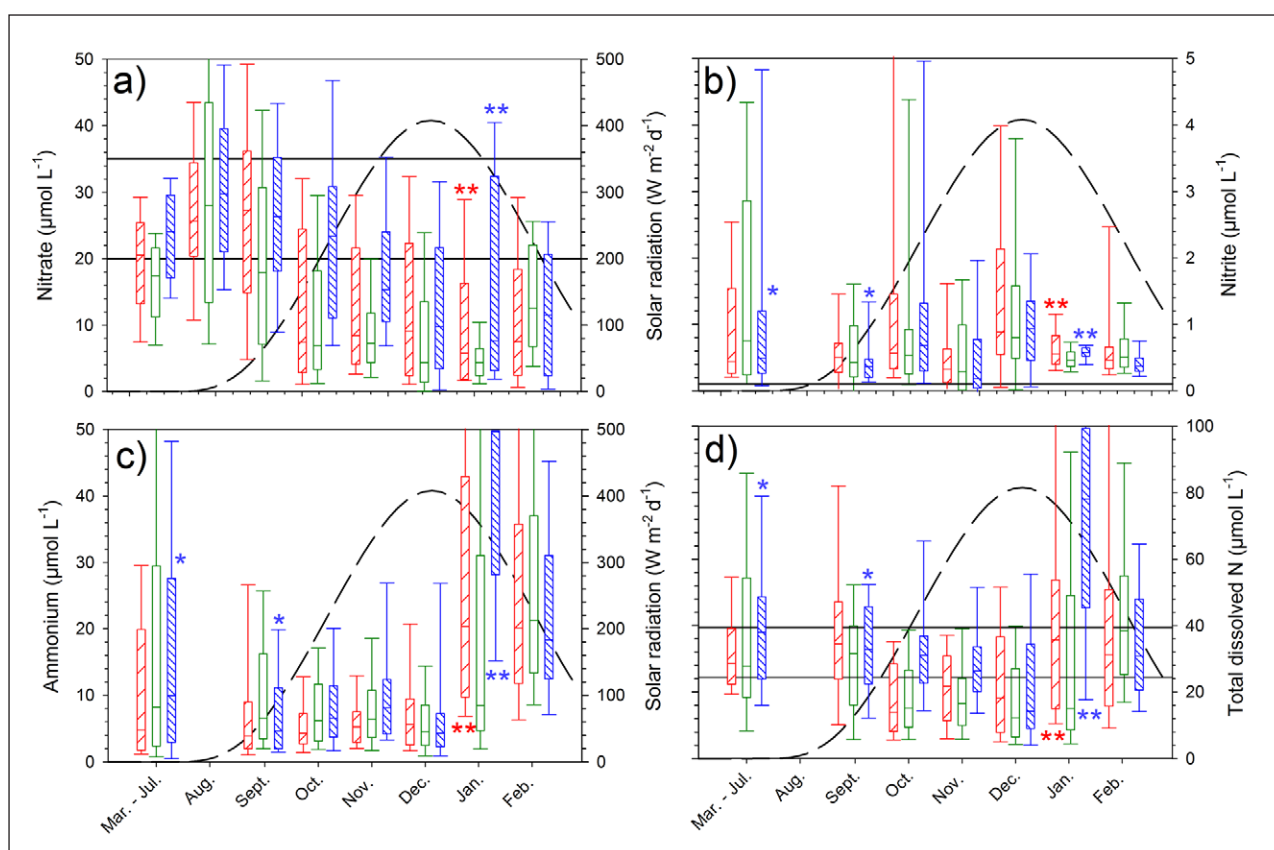


Figure 6: Salinity-normalized concentrations for dissolved inorganic N in sea ice cores as a function of time.

Panels show salinity-normalized concentrations for (a) NO_3^- (or $\text{NO}_3^- + \text{NO}_2^-$ for samples with no NO_2^- measurements), (b) NO_2^- , (c) NH_4^+ , and (d) total dissolved inorganic N. The coarsely red hatched, empty green, and finely blue hatched boxes indicate the concentration ranges in surface (0–0.2 m), interior, and bottom-most 0.1-m layers in sea ice, respectively. In all panels, the concentration range in seawater is indicated by the solid line (the range for ammonium in seawater is too low to be discernible, $< 0.4 \mu\text{mol L}^{-1}$), and the average solar radiation by the dashed line. The symbols * and ** indicate occasions with less than 30 and 15 data points, respectively, in a depth interval. DOI: <https://doi.org/10.1525/elementa.217>f6

occur within productive sea ice in spring, implying a balance between NH_4^+ production (rem mineralization) and consumption (assimilation and nitrification) processes.

The NH_4^+ concentrations increase significantly in summer (January – February; see Table S2 for pairwise multiple comparison; **Figures 6b** and **8b**). This increase cannot be explained by an increase in the exchange with NH_4^+ -poor seawater ($< 0.4 \mu\text{mol L}^{-1}$), as this process would dilute instead of concentrate the NH_4^+ pool. Similar to NO_3^- , remineralization is not directly affected by light but assimilation by (algal) primary producers is light-dependent. When light decreases (**Figure 6c**), such assimilation is likely to decrease while the unaffected remineralization rates will result in a net increase in the NH_4^+ concentration. The build-up of a large pool of ice-trapped organic matter from spring to summer and its subsequent remineralization will further accentuate this trend. The available data in both January and February, however, have been measured only on poisoned samples (HgCl_2 ; Thomas et al., 1998; Kennedy et al., 2002). Such preservation has been shown to have an effect on NH_4^+ concentrations, being systematically higher than for samples analyzed immediately onboard ship (Kattner et al., 1999). By taking the NH_4^+ relationship between poisoned and immediately

treated samples in Kattner et al. (1999), a median of $2.3 \mu\text{mol L}^{-1}$ measured on poisoned samples in bulk summer sea ice (**Figure 2**) will give a concentration of $\sim 1.5 \mu\text{mol L}^{-1}$ in immediately treated samples, implying a correction in salinity-normalized concentrations from 18 to $12 \mu\text{mol L}^{-1}$ for a bulk salinity of 4.5 (Equation 1). This corrected value is still higher than spring NH_4^+ concentrations, being closer to $6 \mu\text{mol L}^{-1}$, in agreement with the hypothesis described above. We recommend freezing as a better mode for preservation in future studies (Dore et al., 1998; Wurl, 2009; Fawcett et al., 2014).

The NO_2^- concentrations remain relatively low and constant in spring–summer (with median NO_2^- concentrations between 0.2 and $0.8 \mu\text{mol L}^{-1}$; **Figure 6b**; see Table S2 for pairwise multiple comparison), also implying a balance between production (NH_4^+ oxidation, i.e., first step in the nitrification process) and consumption (NO_2^- oxidation, i.e., second step of nitrification, and assimilation). To conclude, DIN appears to be actively assimilated and regenerated within pack ice, supporting the view that the sympagic microbial community is efficient in processing fixed nitrogen either to synthesize new biomass or to use as a source of energy for growth (e.g., Fripiat et al., 2015).

Silicic acid is mainly required for the growth of diatoms, with likely minor consumption by silicoflagellates and radiolarians, to form their cell walls (i.e., biogenic silica, bSiO_2) (Tréguer and De La Rocha, 2013). Despite the growing recognition of the role played by flagellates in sea ice habitats (Caron and Gast, 2010; Torstensson et al., 2015), diatoms are thought to dominate primary production in Antarctic sea ice (Arrigo et al., 2010). Silicon is therefore a potentially limiting element for diatom-based primary

production in sea ice (as suggested for Arctic sea ice by Gosselin et al., 1990, and Smith et al., 1990).

In Antarctic pack ice, $^*\text{Si}(\text{OH})_4$ is partially depleted in comparison to seawater at all depths in December and January during the spring–summer transition (see Table S2 for pairwise multiple comparison; **Figure 7c**). Such partial depletion is poorly represented in vertical profiles (**Figures 2 and 8**) when regrouped as spring and summer sea ice. The strongest depletion occurs in January during the most

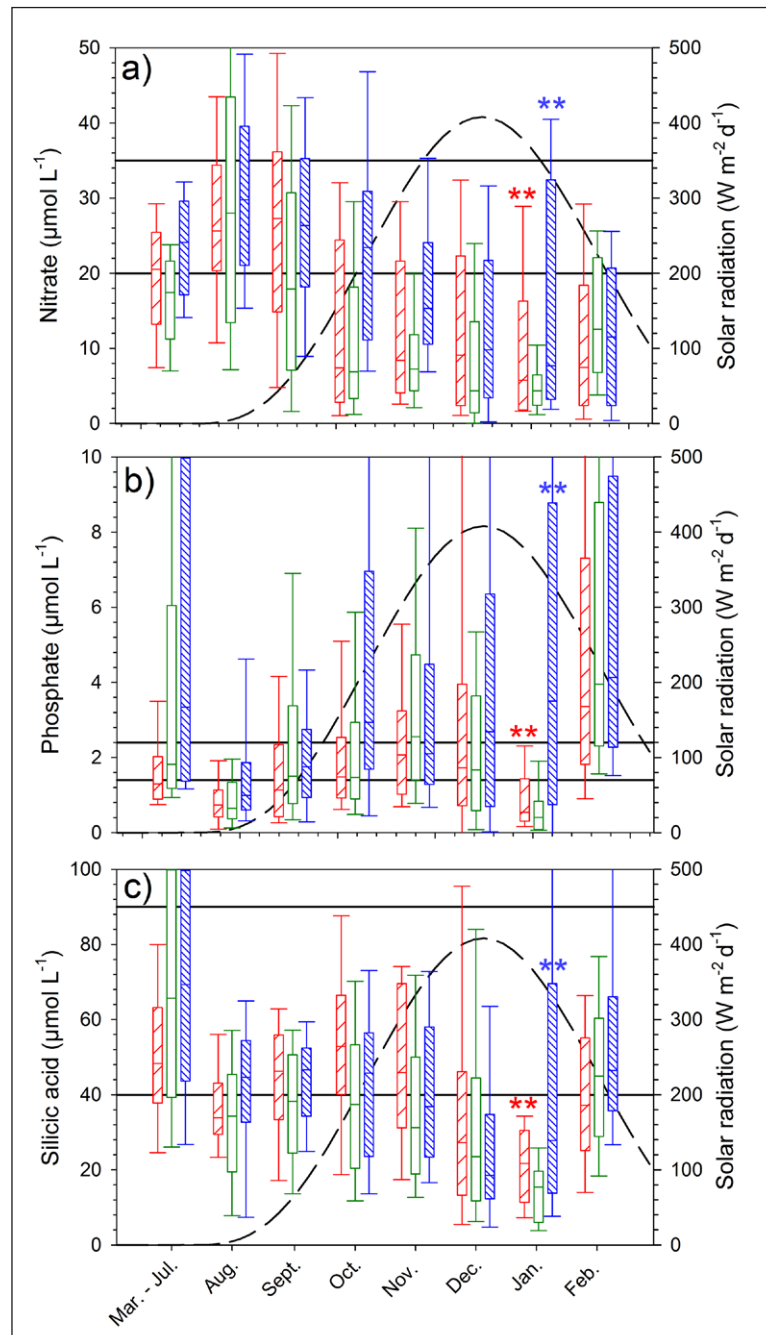


Figure 7: Salinity-normalized concentrations for nutrients in sea ice cores as a function of time. Panels show salinity-normalized concentrations for **(a)** NO_3^- (or $\text{NO}_3^- + \text{NO}_2^-$ for samples with no NO_2^- measurements), **(b)** PO_4^{3-} , and **(c)** $\text{Si}(\text{OH})_4$. The coarsely red hatched, empty green, and finely blue hatched boxes indicate the concentration ranges in surface (0–0.2 m), interior, and bottom-most 0.1-m layers in sea ice, respectively. In all panels, the concentration range in seawater is indicated by the solid line, and the average solar radiation by the dashed line. The symbols * and ** indicate occasions with less than 30 and 15 data points, respectively, in a depth interval. DOI: <https://doi.org/10.1525/elementa.217.f7>

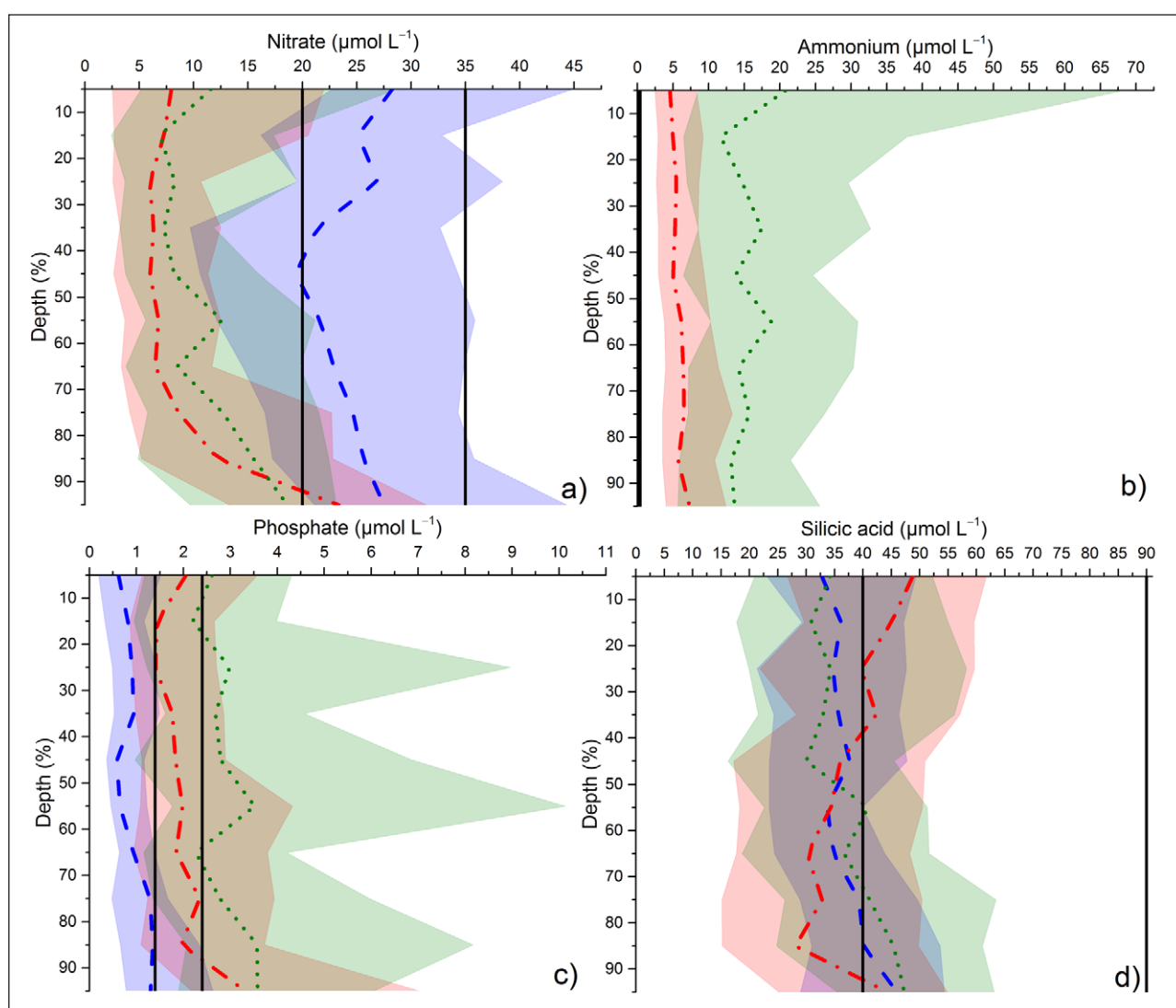


Figure 8: Vertical profiles for salinity-normalized nutrient concentrations in sea ice cores. Vertical profiles of salinity-normalized concentrations ($\mu\text{mol L}^{-1}$) for (a) NO_3^- (or $\text{NO}_3^- + \text{NO}_2^-$ for samples with no NO_2^- measurements), (b) NH_4^+ , (c) PO_4^{3-} , and (d) Si(OH)_4 as a function of normalized ice core depth. Median concentrations are indicated by the dashed blue, red dashed-dotted and green dotted lines for winter, spring and summer, respectively. The data have been binned into 10% depth intervals. The interquartile ranges are indicated by the colored-corresponding envelopes. In all panels, the vertical solid lines indicate the concentration range in seawater (Section 3.1). Note that the concentration range of ammonium in seawater is too low to be discernible ($< 0.4 \mu\text{mol L}^{-1}$). Insufficient data were available for ammonium in winter (~ 12 per 10% depth intervals, collected in later winter only). DOI: <https://doi.org/10.1525/elementa.217.f8>

under-sampled time period in our data set (one cruise in the Weddell Sea, five ice cores; Kennedy et al., 2002). Relative to NO_3^- , the small depletion in Si(OH)_4 concentrations from winter to summer is at odds with the idea that sea ice primary production is dominated by diatoms (Thomas and Arrigo, 2004). The average Si:N ratio for a broad range of diatom species growing under nutrient-replete conditions is 1.0, and this ratio increases during light, N, P or Fe-limited growth (Brzezinski, 1985; Hutchins and Bruland, 1998; Takeda, 1998; Claquin et al., 2002). Further, the Si(OH)_4 concentrations tend to be depleted later than NO_3^- , with a time lag of approximately 1–2 months (Figure 7c). These findings suggest that a significant fraction of primary productivity in sea ice is sustained by flagellates (e.g., Becquevort et al., 2009; Arrigo et al., 2014; Torstensson et al., 2015).

Similar to NO_3^- , the Si(OH)_4 concentrations increase in January – February (see Table S2 for pairwise multiple comparison), indicating either an increase in the exchange with the nutrient-rich seawater or a net increase in biogenic silica dissolution relative to its production. The temporal trend of increasing concentrations of *NH_4^+ in sea ice suggests that dilution by infiltration of seawater rich in Si(OH)_4 but poor in NH_4^+ cannot account for the observed increase in *Si(OH)_4 concentration in summer sea ice and that the more likely explanation is dissolution of biogenic silica in the ice. It is generally assumed that biogenic silica dissolution rates are low under sea ice conditions, especially due to low temperatures. However, biogenic particles tend to remain trapped in the brine network, implying a much longer residence time for detrital biogenic silica in sea ice (weeks to months)

compared to that of detritus in the euphotic zone of the ocean (days to weeks). Assuming that the specific dissolution rates (V_d) measured in the Ross Sea (0.01 to 0.19 d⁻¹; Nelson et al., 1991) are representative of sea ice, half of the detrital biogenic silica in sea ice, i.e., $\ln(2)/V_d$, can be dissolved in 4 to 70 days. In addition, the often high bacterial population density in sea ice (Deming, 2010) should promote efficient removal of the organic coating from diatom frustules, exposing naked frustules to the ambient brine environment under-saturated with respect to bSiO₂ (Bidle and Azam, 1999). Biogenic silica dissolution is therefore likely to be significant in Antarctic sea ice (Fripiat et al., 2014b), as manifested in the increasing concentrations of *Si(OH)₄ in late summer.

In contrast to the NO₃⁻-depleted sea ice, *PO₄³⁻ concentrations in sea ice increase progressively in spring–summer to values higher than in seawater (see Table S2 for pairwise multiple comparison; **Figures 7b** and **8c**), except for two outliers on 15 January at the surface and interior of the ice, which were the lowest *PO₄³⁻ concentrations of this dataset. This time period is under-represented in our data set (one cruise in the Weddell Sea, five ice cores; Kennedy et al., 2002) so that we cannot rule out a bias in terms of how representative the available data are in January. Excess PO₄³⁻ has been observed in several instances in Antarctic pack ice (Clarke and Ackley, 1984; Arrigo et al., 2003; Kattner et al. 2004; Papadimitriou et al., 2007; Becquevort et al., 2009; Munro et al., 2010; Meiners et al., 2011). The unique behavior of PO₄³⁻ in sea ice relative to that in the pelagic realm is discussed further in Section 3.5. Intriguingly, *PO₄³⁻ is depleted relative to seawater in winter with a tendency to lower concentrations in the interior and at the surface of the ice (see Table S2 for pairwise multiple comparison; **Figures 7b** and **8c**). Hu et al. (2014) reported PO₄³⁻ co-precipitation with ikaite (CaCO₃·6H₂O) in laboratory experiments. Ikaite has been mainly extracted from the surface and interior of the ice where low temperature, high brine salinity, and low porosity prevail (Dieckmann et al., 2008; Papadimitriou et al., 2013; Rysgaard et al., 2014; Moreau et al., 2015); these conditions are expected to prevail in Antarctic pack ice in winter.

Although usually overlooked, autumn blooms have been documented in Antarctic sea ice (Fritsen et al., 1994; Delille et al., 2002; Meiners et al., 2012). Such blooms can explain the observed partial *NO₃⁻ depletion with a concomitant accumulation in both *NH₄⁺ and *NO₂⁻ in autumn–early winter (**Figure 6**). The *PO₄³⁻ concentrations indicated accumulation in sea ice to concentrations higher than those in seawater, but *Si(OH)₄, rather than being depleted, was in the range of seawater concentrations (**Figure 7**). As in early spring, NO₃⁻ depletion and the closeness of Si(OH)₄ concentrations to seawater values together suggest that diatoms are also not the dominant primary producers in sea ice in autumn. Additional studies are needed in this time period, which likely contributes a significant, if small, fraction of the total primary production in Antarctic sea ice (Saenz and Arrigo, 2014; Lieser et al., 2015).

3.3. Nutrient limitation in sea ice

Together with light, nutrients likely limit primary production in Antarctic sea ice (Arrigo and Thomas, 2004; Vancooppenolle et al., 2013). Co-limitation occurs when one or

several specific nutrients are at insufficient concentrations to sustain maximum growth rates. Inhibited growth at high salinity has also been suggested to influence the distribution of primary productivity within sea ice (Arrigo and Sullivan, 1992). Iron and other trace metals are usually found at high concentrations in Antarctic sea ice (Lannuzel et al., 2016), in strong contrast with Southern Ocean surface waters (Martin et al., 1990).

In the present dataset, the most likely limiting nutrient in pack ice is DIN, although the lowest median *DIN concentrations are still significant (> 12 μmol L⁻¹; **Figure 6**). For comparison, phytoplankton in the euphotic zone are usually N-limited when DIN is significantly below 2 μmol L⁻¹ (Moore et al., 2013). This consideration arises by the observation that *PO₄³⁻ is present at higher concentrations in sea ice than in the deep ocean and that *Si(OH)₄ is depleted to a lower extent than *DIN (> 15 μmol L⁻¹; **Figure 7**). However, salinity-normalized concentrations do not represent the concentrations available to the sympagic organisms in individual brine pockets and channels. To estimate brine concentrations from measurements in bulk (melted) sea ice, the brine volume fraction must be estimated from bulk ice salinity and temperature, assuming ice-brine (thermal) equilibrium (Cox and Weeks, 1983). Unfortunately, temperature measurements were seldom available for most of the ice sections compiled in this investigation (which future studies need to rectify, as urged by Miller et al., 2015). By dividing the median bulk concentrations for DIN, PO₄³⁻, and Si(OH)₄, binned by time period, by the maximum expected ice porosity (0.2) characteristic of warm and saline Antarctic pack ice (e.g., Tison et al., 2008), the median nutrient concentrations in brines for the time periods derived from the lowest concentrations in bulk sea ice were estimated at 7.2, 0.3, and 7.9 μmol L⁻¹, respectively, concentrations still much higher than those encountered in the oligotrophic ocean. In comparison, the median concentrations for DIN, PO₄³⁻, and Si(OH)₄ for the sackhole brines in spring–summer (n = 57) are 1.1, 0.3, and 32.8 μmol L⁻¹, respectively. The latter analysis is based on a much smaller amount of data, so that the representativeness both in space and time should be taken with caution.

We are not aware of any studies reporting the affinity of sea ice algae for nutrients, defined for phytoplankton as the efficiency with which the cell exploits low nutrient concentrations. Nutrient affinity is usually inferred from the half saturation constant in a Michaelis-Menten saturation function. In the ocean, relatively large variations in nutrient affinity are reported, with half-saturation constants varying from 0.02 to 10.3, 0.01 to 8.9, and 0.2 to 61 μmol L⁻¹ for DIN, PO₄³⁻ and Si(OH)₄, respectively (Eppley et al., 1969; Nelson et al., 2001; Sarthou et al., 2005). Given this variability, it is difficult to assess accurately which nutrients may limit primary production in Antarctic sea ice. Nutrient affinity is affected by cell size (Eppley et al., 1969; Timmermans et al., 2005), temperature (Nedwell et al., 1999; Reay et al., 1999), and salinity (Aslam et al., 1984; Martinez et al., 1994). Given the biotic conditions encountered in sea ice brines (low temperatures and high salinity), the affinity for nutrients is likely to differ from that in seawater and requires further investigation (Thomas and

Dieckmann, 2002). Investigation of potential systematic differences in cell properties (e.g., cell size, surface-to-volume ratio) between sea ice and pelagic microorganisms are also crucially needed. For the ocean, incubation experiments involving nutrient additions have typically been used to assess which nutrients are limiting, allowing also the determination of kinetic uptake parameters (i.e., half saturation constant and maximum specific uptake rate). However, we acknowledge the inherent difficulties in performing similar incubation experiments for sea ice (Miller et al., 2015). The utilization of protein biomarkers of nutrient limitation could be valuable in this regard (Saito et al., 2014), as this approach does not require manipulation of the microorganisms.

3.4. Nutrient adsorption within sea ice

Adsorption here refers to the accumulation of chemicals at the solid-liquid interface. Nutrient adsorption is still overlooked in sea ice. To consider this process in more detail, a comparison was made between sackhole and adjacent bulk ice core data. It is recognized that the spatial variability of sea ice properties might partially invalidate such a comparison, as adjacent cores can have very different biogeochemical compositions (Eicken et al., 1991), and brine collected in the holes integrates the biogeochemical properties of numerous individual brine structures from an undefined volume of ice (over several tens of centimeters; Miller et al., 2015). For these reasons, only qualita-

tive comparisons of large differences are considered. No clear differences in salinity-normalized concentrations for either $\text{NO}_3^- + \text{NO}_2^-$ or $\text{Si}(\text{OH})_4$ were evident. In contrast, higher salinity-normalized concentrations are observed in bulk-melted ice sections for NH_4^+ and, to a lesser extent, for PO_4^{3-} (Figure 9).

NH_4^+ adsorption onto organic matter is a well-known process within soils (Sollins et al., 1988; Spotiso, 2008; Thompson, 2012), sediments (Blackburn and Henriksen, 1983; Seitzinger et al., 1991), and biofilms (Kurniawan et al., 2012). This adsorption results from the presence of ionizable functional groups (carboxyl and hydroxyl groups being the most important) that confer a negative net charge to organic matter following deprotonation at pH values also typically encountered in sea ice. Sea ice contains a large amount of organic matter, both living and detrital, that remains trapped within the ice (Thomas et al., 1998, 2001; Kattner et al., 2004; Dumont et al., 2009; Underwood et al. 2013). Organic matter is under-represented in sackhole samples (Weissenberger, 1992; Becquevort et al., 2009), likely due to preferential adsorption onto the ice walls, 'filtration' by the brine channel network, and the impeded transport of sticky, gelatinous biofilms (Miller et al., 2015). Any NH_4^+ adsorbed onto organic matter will not be completely collected with the sackhole technique, while, to be measured in bulk-melted ice sections, NH_4^+ desorption must occur. It is likely that the melting of ice core sections induces desorption of

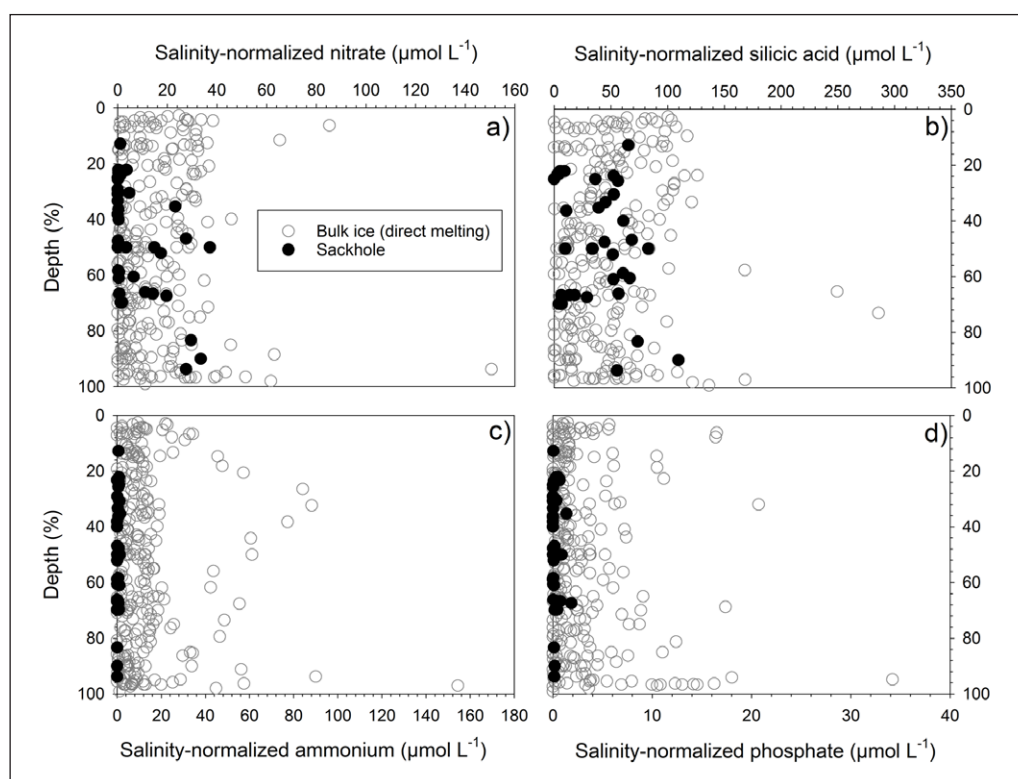


Figure 9: Comparative vertical distributions for salinity-normalized nutrient concentrations in sea ice cores and sackhole brines. Panels show salinity-normalized concentrations for (a) NO_3^- (or $\text{NO}_3^- + \text{NO}_2^-$ for samples with no NO_2^- measurements), (b) $\text{Si}(\text{OH})_4$, (c) NH_4^+ , and (d) PO_4^{3-} as a function of normalized ice depth (i.e., $100 \times$ sampling depth/total ice thickness) in bulk melted ice (open gray circles) and in sackhole brines (solid black circles) collected contemporaneously. The data are from the ANTARKTIS IX/3, X/3, XXII/2, AURORA2003-V1, OSO 08–09, and SIPEX2 cruises (see Tables 1 and S1). DOI: <https://doi.org/10.1525/elementa.217.f9>

this easily exchangeable pool via dilution by meltwater and the associated change in the ionic strength and pH of the melting medium (Spotiso, 2008; Thompson, 2012; Kurniawan et al., 2012). Clearly, further work is required to better characterize NH_4^+ adsorption in sea ice, which potentially immobilizes the NH_4^+ produced by remineralization in close proximity to the microbial community.

The comparison of PO_4^{3-} concentrations between sackholes and bulk-melted ice sections also suggests some adsorption within sea ice but to a lesser extent than for NH_4^+ (Figure 9). PO_4^{3-} adsorption is a well-known process in soils (Sollins et al., 1988; Spotiso, 2008) and sediments (Paytan and McLaughlin, 2007) but mainly on minerals, such as clays and metal (oxy-hydro) oxides. However, such minerals are not likely to be abundant in Antarctic pack ice, nor does PO_4^{3-} react directly with organic matter, likely the main adsorbent within sea ice. However, PO_4^{3-} does react with Fe and Al associated with organic matter (metal-DOM complexes; Yuan and Lavkulich, 1994; Zhou et al., 1997; Maranger and Pullin, 2003). The presence of both large quantities of organic matter and trace metals in sea ice may promote this adsorption pathway (Thomas et al., 2001; Dumont et al., 2009; Lannuzel et al., 2011), as suggested in Becquevort et al. (2009). It should be noted that concentration differences between sackhole brines and melted bulk sea ice are also reported for dissolved Fe in Antarctic sea ice, suggesting potential Fe adsorption within sea ice in agreement with our hypothesis (Lannuzel et al., 2016).

3.5. Phosphorus excess in sea ice

Both DIN and Si(OH)_4 were found to be partially depleted in spring–summer while PO_4^{3-} tended to accumulate in Antarctic sea ice, all relative to a simple physical concentration-dilution process upon incorporation of surface seawater nutrients into sea ice as reflected in salinity changes (Figures 6, 7 and 8). These patterns are also reflected in the ratios of DIN to PO_4^{3-} and Si(OH)_4 to PO_4^{3-} , which both decrease from late winter to spring–summer, with median values relatively close to seawater (~16 and 35) in winter decreasing to 4.7 and 7.6, respectively, in spring–summer (Figure 10). Accumulation of PO_4^{3-} has been reported in many instances in Antarctic pack ice (Clarke and Ackley, 1984; Arrigo et al., 2003; Kattner et al. 2004; Papadimitriou et al., 2007; Becquevort et al., 2009; Munro et al., 2010; Meiners et al., 2011), as well as in land-fast sea ice (Arrigo et al., 1995; Cozzi, 2008).

To accumulate to salinity-normalized concentrations higher than in seawater, nutrients must be trapped within sea ice. Exchange with the nutrient pool of surface seawater and nutrient assimilation into biomass can lead to the build-up of a large interior pool of biomass-associated nutrients that can be trapped in the narrow brine channel system of sea ice. Bacterial colonization, algal mortality, cell lysis, and sloppy feeding can mobilize the ice-trapped organic matter and promote its remineralization (Günther et al., 1999; Thomas and Dieckmann, 2002), allowing the accumulation of excess nutrient concentrations relative to surface seawater. Assimilation and remineralization at constant N:P:Si cannot lead to preferential accumulation

of a single nutrient as observed for PO_4^{3-} . Excess PO_4^{3-} will develop only if phosphorus is preferentially assimilated or remineralized relative to DIN and Si(OH)_4 .

(i) *Preferential P assimilation.* The stoichiometric composition of algae is species-specific and depends on the biochemical allocation of resources for different growth strategies (Geider and La Roche, 2002; Sterner and Elser, 2002; Klausmeier et al., 2004; Arrigo, 2005). Klausmeier et al. (2004) and Arrigo (2005) defined two categories of phytoplankton: the bloomers, allocating more resources into the growth machinery such as ribosomal RNA (enriched in both N and P; “growth rate hypothesis”; optimal N:P = 8.2), and the survivalists, allocating more resources to acquisition machinery (light or nutrients) such as proteins and chlorophyll (enriched in N but not in P; optimal N:P = 45). Following this view, sea ice algae during the bloom period could allocate a significant share of resources into the growth machinery, accumulating P-rich biomass. Diatoms, often observed to dominate primary productivity in sea ice, are known to have low cell N:P, further accentuating this trend (Arrigo et al., 1999; Martiny et al., 2013). In a closed system, the ratio of DIN: PO_4^{3-} would increase following assimilation and return to the initial DIN: PO_4^{3-} ratio upon remineralization. A decrease in the DIN: PO_4^{3-} ratio, as observed, would require removal of excess DIN from sea ice during the bloom, which can occur via exchange with seawater if the P-rich biomass is retained in the ice microstructure. Subsequent remineralization of the retained P-rich, diatom-dominated organic pool could then release sufficient PO_4^{3-} to cause the observed decrease in the ratios of DIN: PO_4^{3-} and Si(OH)_4 : PO_4^{3-} . This effect could be further accentuated by the preferential assimilation of N accompanying the switch from bloomers (low N:P) to survivalists (high N:P) when conditions become less favorable for growth and light is decreasing (Klausmeier et al., 2004; Arrigo, 2005). This scenario is likely to occur at the bottom of ice floes, when continuous brine convection provides an efficient mechanism to fractionate P from N across the ice-seawater interface during the ice algal bloom. The observed higher accumulation of PO_4^{3-} towards the ice-ocean interface appears consistent with this hypothesis (Figures 7b and 8c).

(ii) *Preferential P remineralization.* Organic matter is trapped in great quantities within sea ice for weeks to months and cold-adapted bacteria are known to thrive in this specific environment (Thomas et al., 1998, 2001; Hudson et al., 2000; Junge et al., 2004; Meiners et al., 2004; Deming, 2010; Bowman, 2015). An excess of phosphorus can also be explained by preferential remineralization of phosphorus with respect to N and Si. This process has already been suggested to occur in the ocean (Dugdale et al., 1995; Clark et al., 1998, 1999; Loh and Bauer, 2000; Paytan and McLaughlin, 2007; Letscher and Moore, 2015). The large organic pool within sea ice is mostly produced by the *in situ* microbial community and, at least initially, should represent relatively fresh material. Over time, the selective remineralization of organic P will decrease the DIN: PO_4^{3-} and Si(OH)_4 : PO_4^{3-} ratios in the brine.

(iii) *Phosphate adsorption.* As previously discussed in Section 3.4, phosphate adsorption, most probably onto

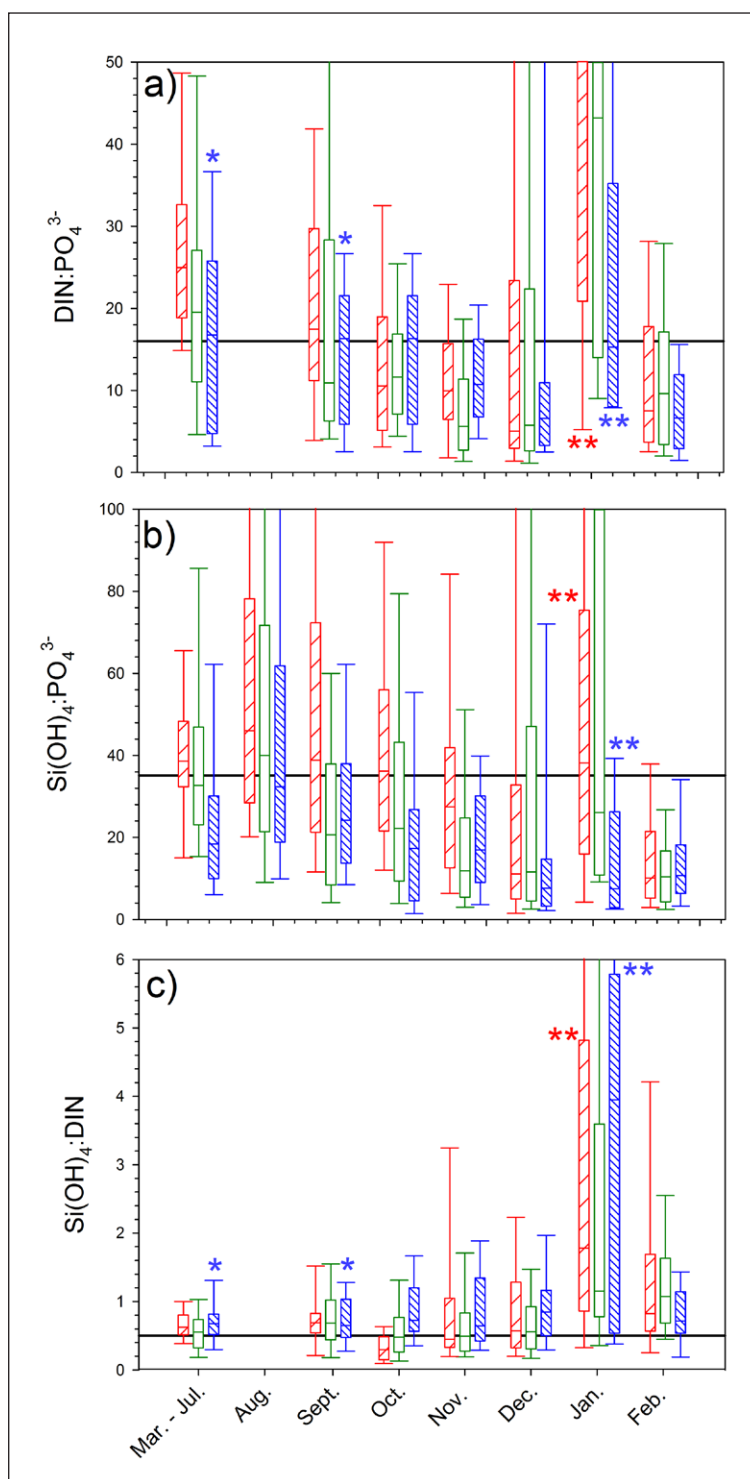


Figure 10: Stoichiometric nutrient ratios in sea ice cores as a function of time. Panels show ratios for **(a)** $\text{DIN}:\text{PO}_4^{3-}$, **(b)** $\text{Si(OH)}_4:\text{PO}_4^{3-}$, and **(c)** $\text{Si(OH)}_4:\text{DIN}$. The coarsely red hatched, empty green, and finely blue hatched boxes indicate the concentration ranges in surface (0–0.2 m), interior, and bottom-most 0.1-m layers in sea ice. In all panels, the symbols * and ** indicate occasions with less than 30 and 15 data points, respectively, in a depth interval. The distribution for data from 15 January falls outside of trends. This time period is under-represented in this dataset (one cruise in the Weddell Sea, five ice cores). DOI: <https://doi.org/10.1525/elementa.217>

metal-organic matter complexes (Yuan and Lavkulich, 1994; Zhou et al., 1997; Maranger and Pullin, 2003), could provide an alternative mechanism to a change in the metabolic stoichiometry (assimilation and remineralization) described above. Surface waters in the Southern Ocean are enriched in PO_4^{3-} due to the upwelling of

nutrient-rich Circumpolar Deep Water (Sarmiento et al., 2004). Over time, and additionally with brine convection, adsorption will result in accumulation of PO_4^{3-} within sea ice, which will also be consistent with a higher accumulation of PO_4^{3-} toward the ice-ocean interface (Figures 7b and 8c).

All three hypotheses, (i) to (iii), need further testing. Clearly, the phosphorus cycle in sea ice has been overlooked and is differently constrained from the one known to occur in the open ocean. Studies investigating the C:N:P stoichiometric composition of particulate and dissolved organic matter will be useful to elucidate the pathways described in the above hypotheses: low PON:POP will support the growth hypothesis (Klausmeier et al., 2004; Arrigo, 2005), while high DON:DOP will support the remineralization hypothesis (Letscher and Moore, 2015). PO_4^{3-} adsorption will have no effect on either PON:POP or DON:DOP, but ligand formation with metal-organic complexes implies that adsorbed PO_4^{3-} is not readily exchangeable and special care should be taken to desorb PO_4^{3-} prior to organic matter analysis.

4. Conclusion

The current compilation of data on dissolved inorganic nitrogen, phosphate, and silicic acid concentrations from a large expanse of the ice pack of the Southern Ocean considerably improves our understanding of the overall nutrient dynamics in sea ice and has identified several overlooked aspects of it. Ice growth is accompanied by a net loss of nutrients from sea ice via desalination. During the first stages of sea ice growth, its bulk nutrient concentrations correlate the most with salinity, indicating that nutrients behave like the major dissolved sea salts. After incorporation, biologically-mediated nutrient consumption and production result in the decoupling of nutrient concentrations from salinity. Depending on the magnitude of primary production and exchange with seawater, nutrient assimilation into ice-trapped biomass generates an interior nutrient store in sea ice, which, upon remineralization, may serve to either counteract or overcome the loss of nutrients by desalination.

The salinity-normalized concentrations (C^*) of DIN and Si(OH)_4 in Antarctic pack ice follow the general trends expected for productive ecosystems. With increased insolation in spring–summer, NO_3^- and Si(OH)_4 are partially assimilated into biomass and biogenic silica, respectively. Nitrate is more depleted than Si(OH)_4 in comparison to seawater concentrations (C_w) and earlier in the growing season, suggesting a significant contribution of flagellates to sea ice primary production. Intermediate nutrients (NH_4^+ and NO_2^-) accumulate in sea ice ($C^* > C_w$) to relatively invariable concentrations that indicate an overall balance between production and consumption processes. Following the decrease in solar radiation in late summer and the build-up of a large pool of ice-trapped organic matter during the preceding growing period, the DIN and Si(OH)_4 concentrations (C^*) increase (especially for NH_4^+) in sea ice likely due to an imbalance between nutrient production (light-independent or light-inhibited) and consumption (largely light-dependent) processes, and faster remineralization (dissolution for biogenic silica) rates in late summer. For both NO_3^- and Si(OH)_4 , we cannot rule out that an increase in the exchange with seawater in decaying sea ice may replenish these nutrients in the brine network. In contrast to the trends for both DIN and Si(OH)_4 , a large accumulation in sea ice is observed in spring–summer for PO_4^{3-} ($C^* > C_w$). The excess PO_4^{3-} could be explained by a greater allocation to P-rich biomolecules during ice algal blooms

coupled with removal of the residual excess DIN with brine convection, a preferential remineralization of phosphorus, and/or retention in sea ice via PO_4^{3-} adsorption onto metal-organic complexes. Additional studies are needed to test these hypotheses and resolve previously overlooked aspects of the phosphorus cycle with respect to its speciation and abundance relative to N, C and Si.

We suggest that differences in nutrient concentrations obtained by the sackhole and bulk ice collection methods provide evidence for the adsorption of NH_4^+ , and to a lesser extent, PO_4^{3-} within sea ice. The involved mechanism has, as yet, unaccounted-for consequences for both nutrient mobility and availability in sea ice. A better understanding of the affinity of sea ice algae for nutrients is also required to decipher accurately which nutrients limit sea ice primary productivity and, therefore, affect the structure of the sympagic microbial community in both space and time.

Data accessibility statement

The data are accessible in the supplementary Table S1.

Supplemental Files

The supplemental files for this article can be found as follows:

- **Text file.** One .txt file including the explanation for the three different supplementary materials: S1 on all data presented in this manuscript (Table S1, provided separately); S2 on the seasonal trends for the Atlantic sector only (Figures S1 and S2, provided separately); and S3 on the statistical tests (Table S2, provided in this file) to compare the different time periods in Figures 6 and 7. DOI: <https://doi.org/10.1525/elementa.217.s1>
- **Table S1.** One .xls file (Table S1) with all data within one worksheet for ice sections and one for sackhole samples. DOI: <https://doi.org/10.1525/elementa.217.s2>
- **Figures S1 and S2.** Showing the seasonal trends for the Atlantic sector only. DOI: <https://doi.org/10.1525/elementa.217.s3>

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Competing Interests

The authors have no competing interests to declare.

Contributions

- FF wrote the first draft and coordinated and synthesized the contribution from the other authors.
- KMM and MV coordinated the task group managing the compilation of biogeochemical parameters in sea ice, in the framework of the SCOR working group 140 BEPSII.
- FF, KMM, MV, SP and DNT contributed significantly to draft and the revision of the manuscript.
- All authors contributed materials and in the acquisition of data.

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