



# Sea ice and mixed layer depth influence on nitrate depletion and associated isotopic effects in the Drake Passage – Weddell Sea region, Southern Ocean

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17 Abstract. The regions near the Antarctic Peninsula in the Southern Ocean are highly productive, with notable 18 phytoplanktonic blooms in the ice-free season. The primary productivity is sustained by the supply of nutrients from 19 convective mixing with nitrate-rich subsurface waters, which promotes rapid phytoplankton growth as the sea ice 20 melts in spring and summer. Surface waters are marked by the contrast between the warmer Drake Passage and the 21 colder Weddell Sea, and seasonal duration of sea ice cover varies accordingly. Sea ice exerts multiple controls over 22 primary production, by shading the light entering the ocean and stratifying the upper ocean with freshening by ice 23 melt. However, the interaction between sea ice and productivity remains poorly characterized because satellites are 24 unable to quantify biomass in partially ice-covered ocean, and direct measurements are too scarce to characterize the 25 seasonally varying productivity. Here we evaluate productivity by assessing removal of nitrate from surface waters by biological nutrient utilization, and study the associated change in  $\delta^{15}$ N of nitrate. We use a combination of bottle 26 27 samples and in situ nitrate measurements from published databases, completed by two transects with isotopic 28 measurements. The timing of sea ice melt date conditions the initiation of nitrate drawdown, but the annual minimum 29 of nitrate only weakly correlates with sea ice concentration. As previously reported, we observe that  $\delta^{15}N$  of nitrate 30 increases with nitrate depletion. Interestingly, the lowest nitrate depletion and  $\delta^{15}N$  values are found in the central 31 region of N-S transects, where intermediate temperature and sea ice conditions prevail. Deeper mixing in waters that 32 passed through the northern Bransfield Strait may explain higher nitrate concentration due to both a greater nitrate 33 resupply and reduced productivity under light limitation in deeply mixed waters, confirmed by isotopic fractionation 34 effects during nitrate uptake and nitrogen isotope modelling. This highlights the importance of oceanographic controls 35 on productivity patterns in sea-iced regions in the Southern Ocean.

# 36 1. Introduction

37 In the Southern Ocean (SO), phytoplanktonic blooms develop near the Antarctic continent, in the seasonally ice-38 covered region and in coastal polynyas (Soppa et al., 2016). The marginal ice zone, where sea ice is present but 39 scattered, contributes to a large part of SO productivity (Arrigo et al., 1998; Savidge et al., 1996). Coastal regions 40 around the Antarctic Peninsula are particularly productive as apparent from satellite-based ocean color scanning 41 (Arrigo et al., 2008; Moreau et al., 2020), which stands out from the low-chlorophyll and high-nutrients waters that 42 characterize most of the SO. Oceanic regions south of the Polar Front play an important role in carbon sequestration, 43 due to the high efficiency of carbon export in areas of deepwater formation (DeVries et al., 2012; Gruber et al., 2009; 44 Huang and Fassbender, 2024; Sabine et al., 2004; Wang et al., 2023). Understanding productivity patterns and

45 limitations in the seasonally ice-covered SO is thus an important aspect of the global climate.





46 The Antarctic Peninsula and surrounding oceans constitute one of the fastest warming regions in the Southern 47 Hemisphere (Fan et al., 2014; Jones et al., 2016), and yet challenges remain to understand how primary productivity 48 will react to such warming. Although increase of surface water chlorophyll concentration may hint towards increased 49 open-water productivity (Moreau et al., 2015), this method does not account for productivity within the marginal ice 50 zone and may primarily reflect the shift from marginal ice zone productivity to open-water productivity due to longer 51 ice-free season. The presence of sea ice prevents the estimation of chlorophyll concentration from satellites, 52 hampering our ability to remotely evaluate the productivity of seasonally ice-covered regions (Bélanger et al., 2007). 53 While in situ quantification of chlorophyll concentration may be useful to estimate biomass of primary producers, it 54 only provides information at a given date, and because such measurements are rarely repeated throughout a growth 55 season, they cannot be used to quantify seasonal productivity and export. Indeed, blooming phases in the SO are 56 marked by a high renewal rate of phytoplankton, with turnover rate of phytoplankton reaching 1 day<sup>-1</sup> (Arteaga et al., 57 2020). Alternative productivity estimates have been proposed, relying on the quantification of nutrient uptake by 58 primary producers to estimate production and export in the SO (Moreau et al., 2020). This quantification relies on the 59 seasonal dynamics of nutrient resupply: deep mixing in winter replenishes the nutrient pool, whereas surface 60 stratification during productive season limits exchanges with underlying water, creating a nutrient budget that will be 61 consumed by primary producers (Codispoti et al., 2013). This method does not account for regenerated nutrients 62 within the surface layer by heterotrophic activity during growth season (Fripiat et al., 2015), but is useful to quantify 63 the seasonal export of organic matter as sinking particles (Flynn et al., 2021; Mdutyana et al., 2020).

64 In the SO, upwelling of nutrient-rich Circumpolar Deep Water at the Antarctic divergence supplies substantial amount 65 of nitrate and phosphate, so phytoplanktonic growth may rather be limited by iron and silicate (M. Franck et al., 2000; 66 Moore et al., 2002). In the coastal regions around the Antarctic Peninsula and nearby islands, dissolved iron is 67 abundantly supplied by desorption from sediment on the shelves or the coasts, glacier melt, and dust deposition 68 (Ardelan et al., 2010; Jiang et al., 2019; Sherrell et al., 2018). Therefore, contrary to the largest part of the SO, iron is 69 not the limiting factor on phytoplanktonic growth in coastal areas such as in the Bransfield Strait (hereafter abbreviated 70 BS, Frants et al., 2013; Measures et al., 2013). Rather, light availability, controlled by ice shading and vertical mixing, limits phytoplankton growth in these areas (Gonçalves-Araujo et al., 2015), which is especially true for winter when 71 72 light intensity is low (Hatta et al., 2013).

73 Sea ice has two opposite effects on light availability: ice shades underlying water when it is present, but its melting 74 releases buoyant freshwater that stabilizes the density structure of upper water column and maintains phytoplankton 75 community in euphotic zone (Taylor et al., 2013). We thus hypothesize that sea ice melt contributes to thinning the 76 mixed layer above which the water is actively mixed by winds. Besides, in areas of sea ice formation, brine rejection 77 favorizes winter convective mixing and nutrient influx from nitrate-rich subsurface waters. This replenishes surface 78 water nutrients, which may then be used next growing season by primary producers. While some algae also develop 79 within brines and pools of sea ice, their contribution to seasonal biomass productivity is relatively small (Arrigo, 2017). 80 Due to its complexity and opposite effects, the influence of sea ice on seasonally integrated phytoplankton productivity 81 remains poorly characterized.

82 Nitrate is a major source of nitrogen for microorganisms (Ohkouchi and Takano, 2014), with additional variable 83 contributions of nitrite, ammonium, and urea throughout the season (Goevens et al., 1995; Mengesha et al., 1998). 84 While N<sub>2</sub> fixation can be an alternative nitrogen source in oligotrophic subtropical seas, this contribution is negligible 85 in the SO (Zehr and Capone, 2021). In winter between the ice edge and the Polar Front, nitrification is an important 86 source of regenerated nitrate (Smart et al., 2015), causing the net primary productivity and net nitrogen uptake to be 87 decoupled (Mdutyana et al., 2020). In summer, however, primary productivity is primarily supported by nitrate both 88 in the ice-free SO (Mdutyana et al., 2020) and the seasonally ice-covered zone (DiFiore et al., 2009). In the Weddell 89 Sea (WS), where sea ice concentration (SIC) is usually high, nitrification is slower, suggesting that nitrate utilization 90 may reflect directly net primary productivity (Flynn et al., 2021). Quantifying nitrate depletion in surface water can 91 therefore be used to estimate productivity in summer, or at least organic matter exported to deeper waters.

92 In this study, we explore the relationship between nitrate concentration and sea ice characteristics in the SO near the 93 tip of the Antarctic Peninsula, to clarify the impact of sea ice on phytoplankton productivity. We first compare satellite-94 derived estimations of SIC by area, available year-round, to numerous nutrient concentration that has been widely





- 95 measured in the SO both with regular sampling (Olsen et al., 2016) and automated *in situ* quantification (Johnson et
- al., 2017). We also describe in further detail a transect of nitrate concentration and its nitrogen isotope, which is
- 97 expected to record isotopic effects during nitrate consumption by primary producers (DiFiore et al., 2009; Sigman et 98 al. 1000) The summarized data is then explained with an isotopic explanation model
- al., 1999). The summarized data is then explained with an isotope-enabled ecosystem model.
  - 65°W 60°W 55°W 50°W 2582 58°S Drake Passage evation relative to sea level (m) 2000 LB 60°5 1000 Ele 500 200 62°S -1000 -1500 2000 64°S 3000 ш Weddell Sea 4000 5000 66°S -5712

# 99 **2. Oceanographic setting**

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Figure 1. Regional map of the northern Antarctic Peninsula, Bransfield Strait, South Shetland Islands (SSI), Elephant
 Island (EI), and parts of the Weddell Sea and Drake Passage. Arrows highlight the surface water circulation, orange for
 water originating from the west side, and red for water exiting the Weddell Gyre (Moffat and Meredith, 2018; Thompson
 et al., 2009). DP and LB refer to two transects discussed in Sect. 4.1; black dots represent the location of bottle sampling
 stations. Elevation from ETOPO 2022 (NOAA, 2022).

106 North of the Antarctic Peninsula, two surface water masses with distinct properties converge in the BS (Fig. 1; Sangrà 107 et al., 2011). Transitional Zonal Water with Weddell Sea influence (TWW) enters BS from the southeast via the 108 westward coastal current, running along the tip of the Antarctic Peninsula. In the northwest of the BS, Transitional 109 Zonal Water with Bellingshausen influence (TBW) enters via a branching derived from the Antarctic Circumpolar 110 Current, and flows northeastward in the Bransfield Current along the South Shetland Islands (SSI). Further east, this 111 current divides into a return current north of SSI (Moffat and Meredith, 2018) and an eastward branch passing south 112 of Elephant Island (Gordon et al., 2000; Thompson et al., 2009). TBW and TWW are separated by a front with a 113 surface gradient of temperature extending to 50-100 m depth, the Peninsula Front, and subsurface gradient, the 114 Bransfield Front, located further north beneath the Bransfield Current jet at depths of 150 to 500 m (Sangrà et al., 115 2011). The Bransfield Current is associated with TWB-containing anticyclonic eddies in the upper 80 m at its southern 116 boundary (Thompson et al., 2009). The colder TWW supports the persistence of sea ice for a longer part of the year 117 in the southeast of the Antarctic Peninsula (Fig. 2). Relative contribution of these two surface water masses to BS, and 118 the position of the front separating them, has been suspected to vary with westerly wind intensity (Vorrath et al., 2020). 119 The water masses properties condition the development of primary producers. Previous studies have found higher 120 concentration of chlorophyll in the TWB, that was interpreted as warm waters with a shallow pycnocline being more 121 productive (Gonçalves-Araujo et al., 2015; La et al., 2019; Pereira Granja Russo et al., 2018).







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Figure 2. Map of sea ice seasonality in the Southern Ocean and nitrate data location. Duration of sea ice presence in months per year, defined as the number of months where sea ice concentration is greater than 15% by area (color scale, with black contour lines at 1, 4, and 8 months). Sea ice in coastal areas is reportedly inaccurate due to the coarse resolution of the sensor (Lavergne 2023). Symbols indicate the location of nitrate concentration data used in this study, classified by data source.

### 128 **3. Material and methods**

A large number of measurements have been made publicly available in recent years through data repositories. We
 briefly describe the datasets used, and additional original data presented in this study. We use a regional subsection of
 the datasets around the Antarctic Peninsula (Fig. 2).

### 132 **3.1 KARP-20 Nitrate concentrations and isotopes**

133 The Korea Antarctic Research Program 20<sup>th</sup> expedition (KARP-20) conducted Conductivity-Temperature-Depth 134 (CTD) profile using SBE CTD 911plus along three transects in the DP region between the 1<sup>st</sup> and the 31<sup>st</sup> of December 135 2006. Water bottle samples were collected for nitrate analysis at 13 stations (black circles on Fig. 2) with 12 water 136 depth sampled at each location. Salinity and temperature from CTD were used to determine the potential density 137 anomaly,  $\sigma_0$ .

Nitrate concentration of each bottle was determined after reduction of nitrate and nitrite to nitric oxide using a V(III) reagent, then quantified by chemiluminescence (Braman and Hendrix, 1989). Our concentration measurements include nitrite, whose contribution is expected to be small in the SO in summer (Thomas et al., 2024). In addition to nitrate concentration,  $\delta^{15}N$  of nitrates were analyzed using the "denitrifier method", where nitrate is converted to nitrous oxide gas by modified denitrifying bacteria lacking nitrous oxide reductase activity (Sigman et al., 2001). After transformation of nitrate to nitrous oxide, the nitrogen isotopic composition of resulting nitrous oxide is analyzed with gas chromatography-isotope ratio mass spectrometry (GC-IRMS) at Princeton University (USA).

# 145 **3.2 Glodapv2 nitrate concentrations**

- 146 The Global Ocean Data Analysis Project Version 2 (GLODAPv2; Olsen et al., 2016) is a collection of biogeochemical
- 147 bottle data, extending from the World Ocean Circulation Experiment database with quality-controlled additions from
- 148 more recent cruises. A thorough description of the GLODAPv2.2022 used here is given by Lauvset et al. (2022).





Nitrate concentrations in bottle samples are typically determined using the colorimetric absorbance measurement after
 reduction to nitrite (Armstrong et al., 1967). Measurements included in GLODAPv2 database were quality checked

- and outliers are removed from the published dataset (Key et al., 2015). Here we only briefly describe how we selected
- 152 samples used in our study. We defined a regional subset around the Antarctic Peninsula with  $45 \text{ }^{\circ}\text{W}-78 \text{ }^{\circ}\text{W}$  and  $56 \text{ }^{\circ}\text{S}-78 \text{ }^{\circ}\text{W}$
- 153 66 °S boundaries, and selected stations where sea ice was present in the year prior to sampling, thus excluding the 154 permanently open ocean zone (see Sect. 3.5 for sea ice data used). Bottles included in this subset were collected
- between September 1989 and January 2016. In addition to the nitrate value, we use the potential density anomaly ( $\sigma_0$ )
- 156 for definition of mixed layer depth (MLD). In the subregion defined for the present study, a total of 187 stations with
- 157 at least one nitrate measurement above MLD were used (the calculation of MLD used here is given in Section 3.4).
- 158 While nitrate concentration measurements are very precise with around 0.2% uncertainty, comparison of deep bottles
- 159 (>1000 m) with nearby (<250 km) measurements give variations usually lower than 2% of the measured value
- 160 (Aoyama, 2020), which can provide a base estimate of consistency of repeat nitrate measurements, and adjustment
- 161 were made in GLODAPv2 which resulted in a similar consistency level (Lauvset et al., 2022), even if it is not
- 162 uncertainty in the strict sense.

# 163 **3.3 SOCCOM Argo floats** *in situ* nitrate estimation

164 Recent developments of ultraviolet spectrophotometers nitrate sensors provide in situ quantification of nitrate 165 concentrations using its absorbance in the ultraviolet band, without requiring chemical transformation (Johnson et al., 166 2013; Johnson and Coletti, 2002; MacIntyre et al., 2009). When mounted on profiling floats, they can profile the 167 nitrate content of the water column, and are set to measure 300 profiles at a rate of one profile every ~5 days which 168 can make the battery last for a couple of years (Johnson et al., 2013). The SO Carbon and Climate Observations and Modeling (SOCCOM) has deployed 295 floats in the SO, equipped with biogeochemistry sensors including 169 170 submersible nitrate (as of May 2024. sensor source: 171 https://www3.mbari.org/soccom/tables/SOCCOM float performance.html). A description and evaluation of 172 accuracy of nitrate sensors used on SOCCOM floats is given in Wanninkhof et al. (2016). We use a quality-controlled 173 dataset where nitrate sensors were calibrated prior to deployment, and offset and drift were adjusted throughout the 174 float service time using known concentration at depths below 1000 m as a reference for calibration (Maurer et al., 175 2021). This lowers the uncertainty on nitrate concentrations to 0.5 µmol kg<sup>-1</sup>. SOCCOM floats have previously been 176 used to assess nitrate drawdown and net community production (Johnson et al., 2017), and hereafter we specifically 177 assess the influence of sea ice on nitrate drawdown. We use a total of 194 profiles from 16 floats, all measured in the 178 regional subset previously defined, dated between January 2016 and June 2022.

### 179 **3.4 Definition of mixed layer depth and surface nitrate depletion**

180 The surface mixed layer depicts a layer actively mixed by wind activity, leading to homogenous physical and chemical 181 properties. Its depth is controlled by the strength of winds and the density gradients, such as a change of temperature 182 or an increase of density indicates the MLD. In the SO, it is preferable to use a density criterion due to the low 183 temperatures throughout the year and significant contribution of meltwater to salinity changes. Therefore, we define 184 the MLD as the depth with a density increased by  $\Delta \sigma = 0.03$  kg m<sup>-3</sup> relative to the reference density taken at 10-m 185 depth (de Boyer Montégut et al., 2004).

186 Surface nitrate concentrations presented in this study are an average of all available measurement points in the mixed 187 layer. For summer samples, we also use nitrate depletion, defined as the difference in nitrate concentration between 188 the surface mixed layer and a subsurface water referred to as Winter Water (WW; Goeyens et al., 1995). WW describes 189 water that was last mixed during the previous winter, when cold surface temperature leads to higher density, thereby 190 increasing the depth of mixing. Similarly to Flynn et al. (2021), we define the WW layer as the layer between the MLD and the depth of the temperature minimum within 20 to 200 m below the MLD. WW serves as a reference for 191 192 ocean conditions before the seasonal growth of phytoplankton, therefore nitrate depletion is defined as the difference 193 between nitrate concentration in the WW (average of all measurements in the depth range) minus surface nitrate 194 concentration.

195 Input of meltwater from sea ice with low nitrate concentration could bias this depletion value due to the dilution of 196 nitrate in surface waters. We corrected for this dilution effect following the method of Flynn et al. (2021), proposed





197 for the WS. To evaluate the maximum dilution potential, we also use the minimal value for nitrate concentration in 198 sea ice of 1 µmol kg<sup>-1</sup> reported for the Bellingshausen and Weddell Seas (Fripiat et al., 2014). Note that, as in the 199 original study by Flynn et al. (2021), this correction only marginally affects the depletion values; in the samples considered here, the average summer salinity decrease is 0.18 PSU (1st decile - 9th decile range: 0.04-0.36 PSU), and 200 result in an average dilution correction of 0.18  $\mu$ Mol kg<sup>-1</sup> (1<sup>st</sup> decile – 9<sup>th</sup> decile range: 0.04–0.37  $\mu$ mol kg<sup>-1</sup>) for nitrate 201 202 depletions. The slightly greater dilution effect for strong salinity decrease is due to the higher seawater nitrate 203 concentration with high sea ice meltwater contribution. Therefore, the interpretations that we would make in this 204 article do not differ. We hereafter refer to meltwater-dilution corrected nitrate depletion as "nitrate depletion 205 (corrected)".

### 206 **3.5 Sea ice concentration**

We use daily SIC retrieved from version 3 of the EUMETSAT Ocean and Sea Ice Satellite Application Facility seaice products for the 1979-2022 period (OSI SAF 2022a, 2022b; updated from Lavergne et al., 2019). This 25 km resolution reconstruction is based on microwave emissivity of surface ocean, with SIC calculated from brightness temperature. Accuracy of SIC by area was evaluated to 8 % in version 2 of this dataset (Lavergne et al. 2019). Updated processing chain and auxiliary climate fields in version 3 used here result in a reduced bias (Lavergne et al., 2023).

For each nitrate concentration measurement, we extracted the SIC on the grid cell corresponding to measurement location, at daily resolution on the year preceding the measurement date. We therefore retrieve the sea ice condition in the time leading up to nitrate measurement. This approach enables monitoring the anomalies in SIC on the year of measurement, since sea ice conditions at the measurement location may substantially differ from average due to the

216 high international variability (Parkinson and Cavalieri, 2012; Wang and Wu, 2021).

#### 217 **3.6 Nitrogen isotope modelling**

218 We simulated the nitrogen cycle in the surface ocean using an isotope enabled ecosystem model. This model has six 219 compartments, phytoplankton (PHY), zooplankton (ZOO), particulate organic nitrogen (PON), dissolved organic 220 nitrogen (DON), nitrate (NO<sub>3</sub><sup>-</sup>), and ammonium (NH<sub>4</sub><sup>+</sup>). The prognostic variables are the N and <sup>15</sup>N concentrations. 221 The equations and parameters excluding nitrification are the same as those used by Yoshikawa et al., (2005), which 222 successfully simulated nitrogen isotope observations in the Sea of Okhotsk, a high-latitude marginal sea. The 223 equations and parameters for nitrification are the same as those used by Yoshikawa et al. (2022), which includes 224 photoinhibition terms. The nitrogen isotope fractionation parameters are the same as those used by Yoshikawa et al. 225 (2024).

226 We applied the model to the ocean environment in three locations around the Antarctic Peninsula: Drake Passage (DP: 227 60 °S, 60 °W), Eastern Bransfield Strait (BS: 62 °S, 55 °W) and Weddell Sea (WS: 64 °S, 50 °W). This model has 228 two vertical layers (surface layer: 0-20 m; subsurface layer: 20-120 m). Light intensity at the surface was taken from 229 long term mean daily net shortwave radiation fluxes of NCEP-NCAR Reanalysis (Kalnay et al., 1996). Water temperature at upper and lower layers and MLD were taken from the World Ocean Atlas 2018 (Garcia et al., 2019). 230 231 Water exchange between the surface and subsurface layers, and between the subsurface layer and the layer deeper 232 than 120 m are changed seasonally in conjunction with the MLD. Boundary conditions at 120 m depth for the nitrate 233 concentration were taken from the World Ocean Atlas 2018 (Garcia et al., 2019) and its  $\delta^{15}$ N value was fixed to 5‰ 234 which is in the range of the observations at 120 m during KARP-20 (Sect. 4.2). The model was integrated for a 4-year 235 spin-up period, and then used to simulate a period of 1 year.

#### 236 4. Results and Discussion

#### 237 4.1 Sea ice impact on nitrate depletion

In this section we assess the impact of sea ice on nitrate depletion, to verify the hypothesis that large seasonal variations in sea ice could contribute to stratification of the surface water, as sea ice retreat enhances light availability and

240 nutrient consumption by primary producers (Sallée et al., 2010) while reducing the available nutrient pool due to the

thinning of the surface mixed layer (Smith, and Nelson, 1986; Taylor et al., 2013).





242 We use the sea ice seasonality at the location where the nitrate concentration was measured. We did not backtrack the 243 water parcel or the sea ice. Also, we assume that sea ice seasonality at the point of nitrate measurement is similar to 244 that of the water parcel present at the time of nitrate sampling, *i.e.* not resolving the effects of ocean circulation or

245 drifted ice over the course of a season. A parcel-tracking approach would be technically possible using coupled ocean-

246 sea ice model, but we do not expect significant improvement of our results due to limitations in modelled ice drift

247 (Uotila et al., 2014).

#### 248 4.1.1 Spatial patterns



249

250 Figure 3. (a) Map of summer surface water nitrate concentration (color scale) classified by data source (symbol type). 251 Contour lines indicate the 1979-2022 average sea ice presence duration in months per year. (b) same as (a), but for summer 252 nitrate depletion (corrected). The definition of summer depletion and its correction are given in Sect. 3.4. The lower number 253 of points for nitrate depletion results from the absence of nitrate concentration data in the subsurface layer of winter water.

254 Spatial patterns of summer (December, January, and February: DJF) nitrate concentration (Fig. 3a) and depletion (Fig. 255 3b) do not particularly match the sea ice presence gradient (Fig. 2). Nitrate depletion is intense in the western BS and 256 Gerlache Strait, with values consistently exceeding 5 µmol kg<sup>-1</sup>, as described by Castro et al. (2002) which first 257 described this data included in Glodap.v2. They attributed this strong depletion to thriving phytoplankton blooms in 258 the very stable surface waters. In addition, strong depletion values close to 10 µmol kg<sup>-1</sup> are observed in the WS around 259 50 °W, contrasting with lower depletion values further east, of profiles on the same cruise (Fahrbach, 1993). KARP-20 nitrate concentrations east of Elephant Island (61 °S, 54 °W to 62 °S, 52 °W) are among the highest nitrate 260 261 concentrations measured for summertime, with values exceeding 30 µmol kg<sup>-1</sup>. KARP-20 stations also reveal that 262 nitrate is not depleted relative to subsurface waters in the outlet of the BS (discussed in further detail in Sect. 4.1). 263 Generally, nitrate concentration or depletion do not correspond spatially to sea ice duration (Fig. 2).

#### 264 4.1.2 Timing of ice melt

265 The biological activity in the SO is restricted in the austral spring by light, both from low incident light angle and from the shading effect of remaining sea ice. Near the Antarctic Peninsula, the duration of sea ice cover varies latitudinally 266 from the quasi-permanently ice-covered WS to the open ocean in the center of DP (Fig. 2). As the sea ice retreats, the 2.67 268 light limitation is expected to be reduced, and the water column is stabilized by release of low-density meltwater

269 (Taylor et al., 2013). This would favor phytoplanktonic growth and nitrate consumption.

270 To visualize the effect of ice retreat on nutrient drawdown, we show how nitrate depletion (surface minus subsurface 271 concentration, see Sect. 3.4) varies during the season, and relative to the day of ice melt at different locations around 272 the Antarctic Peninsula (Fig. 4). In September and October, the surface nitrate depletion is minimal, owing to deep 273 mixing and limited nitrate utilization. In late spring to early summer (November-December), the surface nitrate is 274 more depleted, although approximately half of the waters sampled during these months have nitrate depletion of less 275 than 3 µmol kg<sup>-1</sup>. In January and February, the surface nitrate is depleted by more than 5 µmol kg<sup>-1</sup> at most sampling 276 stations. Nitrate depletion exceeding 5 µmol kg<sup>-1</sup> is encountered throughout the summer. In March, the deepening of





MLD vertically homogenizes the nitrate concentrations, and in conjunction with the slowing of biological uptake in autumn, the nitrate depletion in surface water decreases.

279 Timing of ice melt controls the initiation of phytoplankton bloom and associated nutrient uptake through the formation 280 of buoyant surface meltwater (Fig. 4). Although few samples were recovered prior to complete ice melt, the nitrate 281 concentrations measured before ice melt are marginally depleted relative to subsurface waters, with less than 5 282 µmol kg<sup>-1</sup> difference. The highest of these pre-ice melt depletions comes from the profiles measured in July when the 283 water column may not have been homogenized, and the depletion is probably a remnant of the previous year. Low 284 nitrate depletions prior to ice melt results from the low biological activity, the larger nutrient resupply due to non-285 segregated surface waters, or a combination of both. After sea ice melts, depletion greater than 5 µmol kg<sup>-1</sup> is frequent, 286 but not observed in all samples. More than half of nitrate depletion values are still lower than 5 µmol kg<sup>-1</sup>. Although 287 there is a large spread of nitrate depletion values at any time after the ice melt, the highest depletions are reached after 288 about 50 days, which may reflect the entire duration of the phytoplankton bloom following ice melt, with the lowest 289 nutrient values after the bloom phase ends (Arteaga et al., 2020, and supplement therein). Later in the season, 290 phytoplankton growth slows down (Arteaga et al., 2020), and the relative contribution of regenerated nutrients to 291 biological production increases (decrease in the f-ratio, Fripiat et al., 2015; Mdutyana et al., 2020). Additionally, 292 weakening of the stratification in later season can lead to decrease in surface nitrate depletion, as mixed layer gradually 293 deepens and incorporates nitrate-rich water from the subsurface.

294 In summary, nitrate depletion is strongest when the sea ice melting precedes light maximum by about 50 days (Fig. 295 4a). It points out the high nutrient utilization in well-lit buoyant lens of meltwater, supporting the hypothesis of sea 296 ice control on nutrient utilization. However, the large variability of nitrate depletion noted at any point in time indicates 297 that while nutrient utilization may be optimal at a certain timing after ice melts, nutrient depletion will not necessarily 298 occur at this time. Three-season monitoring near Palmer Station suggests that stratification by surface temperature 299 increase after sea ice has melted is the main condition for bloom initiation (Moline and Prézelin, 1996), which can 300 explain the equivocal relationship between sea ice retreat and bloom initiation: temperature remains low as long as 301 sea ice remains, but sea ice melt is not necessarily immediately followed by a temperature increase. Temperature rise 302 may trigger the bloom initiation at a delay with ice melt by enhancing both stratification and productivity.







303

304Figure 4. Nitrate depletion as a function of day of year (a) and day since ice melt (b). The annual cycle of insolation is given305as daily average irradiance at the top of atmosphere at 60 °S (green dashed line). The color of points in (b) indicates the306timing in the year.

<sup>307 4.1.3</sup> Seasonal range of ice concentration









Figure 5. (a) Summer (December, January, and February: DJF) nitrate depletion as a function of sea ice seasonal range estimated with yearly standard deviation of sea ice concentration. (b) summer (DJF) mixed layer depth (MLD) as a function of sea ice seasonal range. Data source is indicated by symbols, consistently with previous figures.

312 In this section we investigate whether an increased seasonal variation of the SIC (area covered) would favor nitrate 313 depletion, through the shoaling of the MLD which improves the light availability while reducing the amount of 314 nutrients. Although volume or mass of sea ice would be more suited for this comparison, parameters relying on 315 thickness are poorly constrained in the SO (Kwok and Kacimi, 2018; Williams et al., 2015). We thus rely on satellite 316 data to estimate the area of sea ice coverage. We use standard deviation of SIC (SDsic) over the year leading up to the 317 sampling to evaluate the range of seasonal changes in sea ice cover. It is preferred over average sea ice to rule out high sea ice cover grid points such as in the WS, where SIC is high year-round, leading to high average and low 318 319 variability sea ice cover.





320 Summer nitrate depletion varies widely at the regional scale studied here, with values ranging from 0 up to 321 12.5  $\mu$ mol kg<sup>-1</sup>. While most nitrate depletion greater than 5  $\mu$ mol kg<sup>-1</sup> occurs at SD<sub>sic</sub> higher than 10%, there is nevertheless a wide range of nitrate depletion encountered at any SD<sub>SIC</sub> (Fig. 5a). Notably, non-depleted (depletion < 322 1  $\mu$ mol kg<sup>-1</sup>) waters are observed regardless of the SIC. A weak positive correlation (r<sup>2</sup> = 0.179, p<sub>value</sub> < 0.01) between 323 nitrate depletion and SD<sub>SIC</sub> suggests that about 18 % of the variability of both sea ice and nitrate depletion is shared. 324 325 Although we cannot conclude on a causal relationship, changes in SIC may at most be responsible for 18% of the 326 variability in nitrate depletion. This low correlation indicates that seasonal amplitude of sea ice alone cannot explain 327 all the variability found in the surface nitrate depletion in summer.

328 We also tested if high yearly SIC leads to reduced MLD, through the meltwater supply to the surface (sample locations 329 are mostly ice-free in summer, except for a few locations with partial ice cover). Because we analyze the sea ice 330 seasonality at a fixed location for simplicity, this relies on the assumption that sea ice melts locally, ignoring possible 331 ice drift and/or meltwater horizontal transport. Comparing summer MLD with yearly SIC (Fig. 5b) reveals that while 332 stations with yearly SIC exceeding 20 % have a MLD consistently shallower than 60 m, a wide range of MLD is 333 encountered at stations with low SIC, implying control of MLD by additional factors. Indeed, sea ice melting controls 334 freshwater inputs and salinity, but temperature is also an important factor of stability in the sea ice covered section of the SO (Pellichero et al., 2017). Consequently, despite being significantly correlated ( $p_{value} < 0.01$ ), MLD and SIC 335 336 only share 5.7 % variability ( $r^2 = 0.057$ ). At the regional scale, sea ice seasonality has a limited influence on MLD. In 337 turn, the summer nitrate depletion is mostly independent of sea ice cover, although it is less frequently depleted in 338 waters with scarce sea ice cover.

339 Reasons to why sea ice seasonality does not control nitrate depletion at the regional scale likely emerge from the 340 variety of settings across fronts and basins around the Antarctic Peninsula. Light limitation is often indirectly linked 341 to sea ice: the removal of shading is not sufficient to trigger bloom and nutrient drawdown (Fig. 4). It is possible that 342 light limitation is relieved with stratification of the upper ocean layer, which can occur with a delay after ice melts. 343 Density profile and MLD are more likely to be controlled by temperature rather than salinity in the seawaters north of 344 the Peninsula Front (Goncalves-Araujo et al., 2015), where low inputs of freshwater are compensated by stronger 345 temperature-driven stratification. On the contrary in the WS and southern half of BS, sea ice provides freshwater 346 lowering salinity, but it also buffers the temperature and maintains a cool surface even in the summer.

### 347 4.2 Observation and modelling of <sup>15</sup>N enrichment

Nitrate uptake by phytoplankton is associated with an increase of  $\delta^{15}N$  of the nitrate remaining in seawater (following the  $\delta$  notation relative to the ratio  ${}^{15}N/{}^{14}N$  in atmospheric N<sub>2</sub>), due to the preferential uptake of  ${}^{14}N$  by the microorganisms (Sigman et al., 1999). The uptaken nitrate is transformed into organic molecules with an average biosynthetic nitrogen isotope effect  $\varepsilon$  of around 5‰ (Altabet and Francois, 2001; Sigman et al., 1999; Waser et al., 1998), given by the difference in kinetics of reaction rates between  ${}^{14}N$  and  ${}^{15}N$ :  $\varepsilon = {}^{14}k/{}^{15}k - 1$ . Applied in a Rayleigh distillation, isotope effect can be approximated by:

354 
$$\varepsilon = \frac{\delta^{15} N_{initial} - \delta^{15} N}{\ln(NO_3^-) - \ln(NO_3^-)}$$
(1)

355 (Mariotti et al., 1981; Sigman et al., 1999;  $\varepsilon$  is defined as positive if  $\delta^{15}$ N of remaining nitrate increases when nitrate 356 concentration decreases).

357 This effect may be slightly more positive in light-limited environments (DiFiore et al., 2010; Needoba et al., 2004;

Needoba and Harrison, 2004). Consequently, nitrate concentrations are inversely correlated with  $\delta^{15}$ N of nitrate in the

nutrient-rich SO (Lourey et al., 2003; Sigman et al., 1999). In this section, we focus on the KARP-20 transect, with

360 measurements of nitrate concentration and  $\delta^{15}N$ , to gain further insights on nitrate uptake. We then evaluate observed

trends using a nitrogen cycle isotope model with environmental forcings.

#### 362 4.2.1 KARP-20 nitrate concentration and δ<sup>15</sup>N observations





- 363 Here we present the  $\delta^{15}$ N of nitrate collected in the DP and BS (location of transects given in Fig. 1) and discuss the
- 364 environmental factors that can affect nitrate concentration and isotopes. The goal of this section is to confirm that the
- 365 relationship between nitrate concentration and isotopes is respected in this region, and understand the environmental 366 forcings that control them.



367

Figure 6. Leg B and Drake Passage Transects, with color shadings of nitrate concentration (a) and δ<sup>15</sup>N of nitrate (b). Black
 contours represent the CTD potential density anomaly (σ<sub>0</sub> in kg m<sup>-3</sup>). White line highlights the MLD, computed as the depth
 with a potential density increased by 0.03 kg m<sup>-3</sup> relative to the density at 10 m depth.







371

372 Figure 7. Same as Fig. 6, but for potential temperature (a) and salinity (b).

373 Transects of nitrate concentration in the DP and eastern BS (Fig. 6a) depict typical SO summer pattern with partial 374 depletion in the surface waters, down to a minimum of 23 µmol kg<sup>-1</sup> in the DP compared to subsurface waters, where 375 concentrations exceed 31 µmol kg<sup>-1</sup> (profiles also given in Appendix Fig. A1). Isopycnals follow the general SO 376 pattern with deepening at lower latitudes, except for the center section of LB transect (60.7 °S to 61.7 °S) with a 377 shoaling of the 27.7 kg m<sup>-3</sup> isopycnal, indicating the presence of high-density water at relatively shallow depth. The 378 high density is due to higher salinity (>34.45 PSU) of this water rather than temperature (Fig. 7). This center section 379 also has the highest surface nitrate concentration at about 30 µmol kg<sup>-1</sup> and the deepest MLD supported by the vertically homogenous density. In the DP, surface nitrate concentration is generally lower, and the nitrate 380 381 concentration appears low even beneath the MLD (Fig. 6).

382 The center section of LB transect with high surface nitrate concentration and deep mixing is in the prolongation of 383 northern BS current that circulated around the SSI and Elephant Islands (Fig. 1). Although its high salinity could 384 correspond to Weddell Sea Water transported along the slope on the western side of the Powell Basin, its intermediate 385 temperature rather supports a western origin (TWB). Physical ocean modelling supported by tidal stations suggests 386 that tidal interaction on the shelf of the SSI are actively mixes the water, mixing in high salinity from deeper water 387 and homogenizing the density profile (Zhou et al., 2020). The vertical homogeneity of density remains when the water 388 is transported downstream, allowing for the wind mixing to take over and maintain a deep mixed layer, visible in the 389 60.7-61.7 °S section of the LB transect. Activation energy for wind-mixing is lowered in case of lower density 390 gradient (Pollard et al., 1973), which means that a similar wind stress will result in a deeper mixing. Surface nitrate 391 concentration appears closely related to oceanographic circulation.

Two mechanisms may explain higher nitrate concentration in deeply mixed water: (1) quantitatively greater initial nitrate pool, due to a larger volume (or greater resupply) meaning that for an equal uptake per area unit, the concentration remains higher; and (2) lower nitrate uptake due to a limited productivity. Nitrogen isotopes can provide insight onto the latter hypothesis.

396 Generally,  $\delta^{15}$ N of nitrate negatively correlates with its concentrations: there is a visible correspondence between low 397 surface nitrate concentrations (Fig. 6a) and high  $\delta^{15}$ N of nitrates (Fig. 6b).  $\delta^{15}$ N is low (4.5 to 5 ‰) in waters deeper





398 than 125 m, where nitrate concentration exceeds 30 µmol kg<sup>-1</sup>, and reaches high values of up to 6.8 ‰ near the surface 399 in DP where nitrate concentrations are the lowest (23 µmol kg<sup>-1</sup>) of these transects. This negative correlation is consistent with previous works, and reflects the isotopic fractionation during partial uptake of the available nitrate 400 (Altabet, 2006; Lourey et al., 2003; Sigman et al., 1999). While the nitrate reservoir is not strictly isolated in summer, 401 402 exchanges between surface mixed layer and subsurface waters are limited due to the density gradient preventing wind-403 activated mixing (Lewis et al., 1986; Pollard et al., 1973). When approximating surface waters above the MLD as a 404 closed system, fractionation during nitrate uptake follows a Rayleigh-type isotopic distillation (Lourey et al., 2003). 405 In the Rayleigh distillation, the  $\delta^{15}$ N is linearly correlated with the logarithm of nitrate concentration (DiFiore et al., 406 2009; Mariotti et al., 1981). We thus quantify the isotopic effect of nitrate uptake following the linear regression on

407 logarithmic concentration scale method (DiFiore et al., 2009; Appendix Fig. A2).





409

410Figure 8. Nitrogen isotope effect  $\varepsilon$  as a function of the mixed layer depth. Error bars indicate the 95 % confidence interval411for  $\varepsilon$  estimation.

412 Nitrate assimilation has been reported to imprint a nitrogen isotope effect of about 5 ‰ in SO field studies (DiFiore 413 et al., 2009, 2010; Sigman et al., 1999). Under light limitation, the isotope effect shows notable increase, with values 414 exceeding 8 % (DiFiore et al., 2010), which is considered to be the result of continuous active pumping of nitrate to 415 offset nitrate loss by diffusion through cell membrane, when assimilatory nitrate reduction is slowed by light-limited 416 cellular activity (Needoba et al., 2004; Needoba and Harrison, 2004). Here, most profiles support nitrogen isotope 417 effects  $\varepsilon$  of 5 ‰, as long as the MLD is shallower than 50 m (Fig. 8). The two profiles where the MLD is deeper, 418 which are in the central section of LB at 61 °S and 61.7 °S, indicate slightly higher  $\varepsilon$  of 6.5 ± 1.4 ‰ and 6.9 ± 3.5 ‰, 419 respectively. These higher  $\varepsilon$  mark light limitation in deeply mixed surface layers (DiFiore et al., 2010), and therefore 420 support the hypothesis of lower nitrate utilization as a cause for the elevated nitrate concentration in the central section 421 of LB. However, these  $\varepsilon$  values are lower than those previously reported for comparable MLD in the open Antarctic 422 Zone, where sea ice is typically absent (DiFiore et al., 2010). This is likely due to stronger seasonal variability in the 423 MLD related to the presence of seasonal sea ice in our study, suggesting that the MLD may have been shallower at 424 the start of growth season. The data from DiFiore et al. (2010) for ocean zones with sea ice do not support  $\varepsilon$  values 425 exceeding 5 ‰, because summer mixed layers in the Indian sector of SO are generally shallower than 50 m. This is





427 Nitrogen recycling through heterotrophic activity may modify the isotopic repartition between organic and dissolved 428 inorganic nitrogen (Sigman and Fripiat, 2019). Recycling of N through nitrification preferentially converts <sup>14</sup>N and 429 may decrease the apparent  $\varepsilon$  of N uptake (DiFiore et al., 2009). In the summer, however, contribution of regenerated 430 nitrogen to phytoplankton productivity is low, with f-ratio usually higher than 0.6 in the BS (Bode et al., 2002) and 431 WS (Flynn et al., 2021), and nitrate supplied by nitrification accounts for less than 10 % of nitrate uptake (Flynn et 432 al., 2021; Mdutyana et al., 2020). This means that more than half of summer nitrogen consumption consists of new 433 nitrate uptake from the environment. Low regeneration rate is due to reduced heterotrophic activity in cold oceans, 434 while light inhibits nitrification in summer. The nitrogen isotope effect  $\varepsilon$  in KARP-20 profiles is close to or higher

than the reported values for  $\varepsilon$ , so they are in line with low nitrate recycling, not detectible in the nitrogen isotopes.

436 Despite minor changes in  $\varepsilon$  in light-limiting conditions, the relationship between nitrate depletion and  $\delta^{15}$ N elevation

that has been previously described in other regions of the SO (DiFiore et al., 2010; Lourey et al., 2003; Sigman et al.,

438 1999) holds true in the ice-covered region of the Antarctic Peninsula.

# 439 4.2.2 Nitrogen isotope modelling

440 In this final section, we reproduce the  $\delta^{15}$ N signatures of nitrate using a nitrogen isotope box-model (Yoshikawa et al.,

441 2005) in three oceanic locations around the Antarctic Peninsula: the seasonally ice-covered part of DP (60°S, 60°W),

semi-enclosed eastern BS ( $62^{\circ}$ S,  $55^{\circ}$ W), and the northwestern WS ( $64^{\circ}$ S,  $50^{\circ}$ W) where sea ice exits the Weddell Gyre.

443 The model simulates a nitrogen cycle in a sea ice covered ocean, focusing on surface (0-20 m) and subsurface (20-

444 120 m) layers, from inputs of seawater temperature, mixing depth, insolation, and nitrate concentration and its  $\delta^{15}N$ 

445 at the 120 m boundary condition (Fig. 9). The model has a daily time resolution with a simulation length of one year

446 (after 4 years spin-up), and reproduces an ideal annual cycle at equilibrium, *i.e.* repeating itself given the same forcings.



447







#### 450 sinking particulate N export (g), and $\delta^{15}$ N of nitrate in the surface model box (h) in three oceanic locations (DP, BS, and 451 WS).

452 We first give a brief description of environmental parameters used to constrain the model. Temperature variability is 453 strongest in the DP location (60 °S, 60 °W), which averages 1.7 °C in summer, when BS reaches a maximum of around 454 0°C (Fig. 9a, Fig. 10a). The temperature at the WS location is buffered by the presence of sea ice, and remains below 455 -0.5°C year-round. Insolation is roughly similar for the three sites, although slightly lower in the WS due to the higher 456 latitude. MLD follows the typical seasonal variability (Behera et al., 2020), shoaling in the spring and summer and 457 deepening during autumn and winter. It is implemented indirectly in the model, regulating the exchange rates between 458 surface and subsurface layers, rather than modifying the layer thickness in the model. The amplitude of MLD 459 variability is greater for BS and WS, where more sea ice is present (Fig. 9c, Fig. 10d). The MLD in BS remains deeper 460 even in summer, averaging 59 m. BS location has an intermediate temperature and yearly sea ice (Fig. 10a, 10b), but 461 also the greatest sea ice standard deviation (Fig. 10c), used to approximate the seasonal variability of sea ice cover 462 here. Despite greater change in sea ice cover, the summer MLD is still greater in BS location, which goes against the 463 hypothesis of a sea ice meltwater induced summer stratification (Taylor et al., 2013), and confirms that sea ice seasonal 464 variability is not the main control on summer MLD in this region (as discussed in Sect. 4.1). The model simulates the N cycle in the surface ocean and its impact on  $\delta^{15}N$  (Fig. 9d–h, Fig. 10e–k). For DP and BS 465 466 locations, the resulting annual cycle of seawater nitrate has two peaks of nitrate uptake, corresponding to spring and

467 summer phytoplankton blooms. This matches the two-peak chlorophyll seasonality reported for the Antarctic 468 Circumpolar Current (Prend et al., 2022). Consequently, nitrate depletion in the surface waters increases in two steps 469 in spring and summer, with lower minimal concentration at DP location. Although dual blooming is observed in the 470 environment, it usually is not as clear as the idealized cycle produced by the model, with observed maxima overlapping, 471 or double blooms not repeating every year. At the WS location, growth season is shorter due to its onset delayed by 472 the late melting of sea ice, resulting in a single yearly maximum rate of nitrate uptake. Nevertheless, WS has a greater 473 nitrate depletion (Fig. 10j) in the surface layer compared to the two other locations, driven by higher nutrient uptake 474 in the strongly stratified surface ocean (Fig. 10f). The BS location with the deepest mixed layer is characterized by a 475 lower nitrate uptake especially in the later part of summer (Fig. 9e), resulting in a lower depletion and higher concentration relative to the two other locations.  $\delta^{15}$ N of nitrate (Fig. 10i) scales with the net nitrate uptake (Fig. 10f-476 477 h), with maximum <sup>15</sup>N-enrichment at WS location, and minimum at BS location. The model predicts that N export 478 due to sinking particulate organic matter follows the same pattern (Fig. 10k).







479

Figure 10. Summer (December, January, and February) averages of model forcings and results for (a) surface water temperature, (d) mixed layer depth, (e) surface nitrate concentration, (f) nitrate uptake rate by primary producers, (g) nitrate supply rate from subsurface to surface model layer, (h) difference between uptake and supply rates, (i)  $\delta^{15}$ N of nitrate in surface water, (j) nitrate depletion in the surface water, (k) total nitrogen export in the sinking flux in three oceanic locations. Yearly sea ice parameters are given for (b) average and (c) standard deviation, used here to quantify seasonal variability. Upper row plots (a-d) are environmental forcings, with temperature (a) and mixing depth (d) forcing the model. Lower rows (e-k) describe nitrogen cycle model results.

487 Both in the model results and in the latitudinal transect (Sect. 4.1), it appears that the eastern BS has the lowest 488 productivity due to its deeper mixed layer, despite intermediate temperature and sea ice seasonality. The higher surface 489 nitrate concentration of the model for BS matches the 61-62 °S section with high surface nitrate concentration (Fig. 490 6), although absolute values are slightly lower in the model. Timing-wise, the model tends to predict a larger 491 divergence of nitrate concentration at the BS location in the later part of summer (Fig. 9), but the nitrate concentration 492 already differs in December observations, in part due to a light-limited productivity. The area of low nitrate uptake 493 east of the SSI matches the low chlorophyll area in the climatology of surface ocean color (La et al., 2019). The 494 location of BS point chosen for the model may not be exactly in this low chlorophyll area but closer to the Peninsula 495 Front. However, model results should not differ because the two are characterized with a relatively deep summer 496 mixing and similar ice cover. In addition, the eastern BS is notably characterized with a deepening of isopycnals (Frey 497 et al., 2022; Huneke et al., 2016) and deeper chlorophyll maximum (Pereira Granja Russo et al., 2018), attesting that 498 the MLD increases eastward, and primary producers are likely dragged to deeper waters.

In the SO, despite low temperature, a significant portion of particulate organic matter is remineralized in the water column, and nitrogen loss in surface water by sinking particles is compensated by the upwelling of nutrients, although seasonality of these fluxes is not in phase (Mdutyana et al., 2020). Here, we focused on the summer season, therefore





- 502 the net export of nitrogen that we report does not represent an annual flux. However, the model indicates that 503 productivity decreases with deeper mixing, with reduced flux of sinking particles in the summer. The inferred primary
- 504 productivity changes may also have implications for the carbon cycle and the biological pump.

# 505 5. Conclusions

506 We investigated nitrate dynamics near the Antarctic Peninsula in the Southern Ocean, to better understand 507 environmental controls on primary productivity. We compiled measurements from different databases and new 508 transects for a total of 394 nitrate profiles. In this region seasonally covered by sea ice, nitrate is not limiting 509 productivity, and remains in concentrations above 20 µmol kg<sup>-1</sup> at any time of the year. We evaluated the influence of 510 sea ice on nitrate depletion in the surface water, testing the hypothesis that sea ice melting reduces surface salinity and 511 enhances the stratification propitious to primary producers (Taylor et al., 2013). We used nitrate depletion, defined as 512 surface concentration minus concentration in the Winter Water layer, as an indicator of nutrient uptake and net 513 seasonal productivity. Results do not clearly point to a change in nitrate depletion in regions where sea ice duration 514 differs. Significant nitrate depletion is mostly observed after melting, owing to favorable conditions for blooming after 515 ice melt. However, sea ice melting is not necessarily followed by nitrate depletion. Seasonal amplitude of sea ice only marginally affects nitrate depletion and stratification, opposing the hypothesis that sea ice meltwater controls 516 517 stratification at the regional scale. Diverse oceanographic controls in the water masses properties, density gradients 518 and mixing mask the impact of sea ice on nitrate depletion when comparing a variety of locations.

- 519 Analysis of nitrate along new north-south transects in the DP and Powell basin east of the BS reveals a channel of 520 deeply mixed waters with high surface nitrate concentration. We interpret this channel to be a remnant of actively homogenized water with tidal mixing along the SSI upstream the BS (Zhou et al., 2020).  $\delta^{15}N$  of nitrate in these 521 transects confirm the previously established relationship between nitrate drawdown and <sup>15</sup>N-enrichment in the 522 remaining nitrate. The strong correlation between logarithm of nitrate concentration and  $\delta^{15}$ N indicate that the system 523 524 is well approximated by a Rayleigh distillation, with limited resupply of nitrate during phytoplankton growth. 525 Furthermore, the higher nitrogen isotope effect estimated in the deeply mixed profiles suggests a light limitation during 526 nitrate uptake, contributing to the lower nitrate depletion at these locations. Nitrogen isotope modeling further supports 527 that deeper mixing in the BS induces light limitation, with lower nitrate uptake and  $\delta^{15}$ N compared to both the DP and 528 the WS. Weaker sinking particle flux in the eastern BS equates to weaker organic matter export in summer.
- 529 Strong stratification in the summer surface ocean makes nitrate depletion a seasonal-lasting feature, useful for 530 integrating biological uptake over a growth season. However, variations in MLD makes it difficult to quantify nitrate 531 uptake and productivity based on concentration alone, but hints towards weaker productivity in deeply mixed layer 532 allows the use of nitrate concentration for qualitative estimates. Nitrate utilization appears tied to the MLD, which 533 hardly depends on sea ice meltwater release. Multiple oceanographic features influence the MLD at the regional scale, 534 with varying water masses and mixing dynamics affecting vertical density. Nonetheless, it should be noted that heavily 535 sea-iced areas are comparatively under-sampled, and future efforts may be oriented to fill this knowledge gap.

536 Increasing temperatures with global climate change will likely reduce the extent of sea ice in the future. Summer 537 stratification could shift from a salinity-based density gradient to a temperature-based density gradient. This will 538 probably impact phytoplanktonic activity and ecosystems in a warmer surface layer with a longer ice-free season. A 539 supposed decrease in freshwater supply in the surface ocean would tend to increase MLD inducing light limitation on 540 phytoplanktonic productivity, but this would be counterbalanced by increased productivity in warmer waters and 541 longer growth season. Determining which of these two effects prevails is crucial to understand future changes in the 542 phytoplankton productivity of the high latitude Southern Ocean.

543

### 544 Appendix A: Station-specific profiles and isotope effect





545



546 Figure A1. Station-specific profiles of (a) nitrate concentration and (b)  $\delta^{15}N$  of nitrate.







548

549 Figure A2.  $\delta^{15}$ N of nitrate as a function of nitrate concentration (logarithmic scale) for each KARP-20 profile, used for 550 estimation of nitrate isotope effect  $\varepsilon$  (opposite of the slope value, Eq. (1)).

551 Code availability





- 552 Python code for data processing and figure creation is available on a Zenodo repository 553 (doi:10.5281/zenodo.14221104) for transparency and reproducibility purposes. Potential users should know that it 554 was developed for personal use and has not been cleaned up before distribution. Nitrogen cycle model inquiries should
- 555 be sent to C. Yoshikawa (yoshikawac@jamstec.go.jp).

# 556 Data availability

- 557 KARP-20 data inquiries should be addressed to B.-K. Khim (bkkhim@pusan.ac.kr), and data will be distributed after
- 558 evaluation of the request. GLODAP bottle data is available for download at <u>https://glodap.info/</u> [last access: November
- 559 2024]. SOCCOM float data is available for download at <a href="https://soccom.princeton.edu/float-data-single-float-profiles">https://soccom.princeton.edu/float-data-single-float-profiles</a>
   560 [last access: November 2024]. Sea ice concentration data is available for download at <a href="https://stata.style.org">https://stata.style.org</a>
- 561 <u>https://glodap.info/</u> [last access: November 2024].

#### 562 Sample availability

563 Samples from this study are not available.

#### 564 Author contribution

565 Concept of the study, formal analysis and figure creation were conducted by APMS, as part of project co-led by FJJE 566 and NO. The nitrogen model was developed by CY. Water samples were collected by YJ and BKK. Nitrogen data 567 was obtained and curated by YJ, BKK, YR and DMS at Princeton university. The original manuscript prepared by 568 APMS, YI, and CY, with revisions from BKK, NOO, YR, FJJE and NO.

#### 569 **Competing interests**

570 The authors declare that they have no conflict of interest.

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