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Macronutrient supply, uptake and recycling in the coastal ocean of the west Antarctic Peninsula

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ABSTRACT

Nutrient supply, uptake and cycling underpin high primary productivity over the continental shelf of the west Antarctic Peninsula (WAP). Here we use a suite of biogeochemical and isotopic data collected over five years in northern Marguerite Bay to examine these macronutrient dynamics and their controlling biological and physical processes in the WAP coastal ocean.

We show pronounced nutrient drawdown over the summer months by primary production which drives a net seasonal nitrate uptake of $1.83 \text{ mol N m}^{-2} \text{ yr}^{-1}$, equivalent to net carbon uptake of $146 \text{ g C m}^{-2} \text{ yr}^{-1}$. High primary production fuelled primarily by deep-sourced macronutrients is diatom-dominated, but non-siliceous phytoplankton also play a role. Strong nutrient drawdown in the uppermost surface ocean has the potential to cause transient nitrogen limitation before nutrient resupply and/or regeneration. Interannual variability in nutrient utilisation corresponds to winter sea ice duration and the degree of upper ocean mixing, implying susceptibility to physical climate change.

The nitrogen isotope composition of nitrate ($\delta^{15}\text{N}_{\text{NO}_3}$) shows a utilisation signal during the growing seasons with a community-level net isotope effect of $4.19 \pm 0.29\text{‰}$. We also observe significant deviation of our data from modelled and observed utilisation trends, and argue that this is driven primarily by water column nitrification and meltwater dilution of surface nitrate.

This study is important because it provides a detailed description of the nutrient biogeochemistry underlying high primary productivity at the WAP, and shows that surface ocean nutrient inventories in the Antarctic sea ice zone can be affected by intense recycling in the water column, meltwater dilution and sea ice processes, in addition to utilisation in the upper ocean.

1. Introduction

1.1. Nutrients, primary production and CO_2 in the Southern Ocean

The Southern Ocean plays a crucial role in air-sea CO_2 exchange and consequently global climate over annual to glacial-interglacial timescales (Caldeira and Duffy, 2000; Fletcher et al., 2006; Gruber et al., 2009; Lenton et al., 2013; Sarmiento and LeQuere, 1996; Sigman and Boyle, 2000). The Antarctic continental shelves are particularly important for biological CO_2 uptake during photosynthesis by phytoplankton because area-normalised primary production rates here are greater than for any other Southern Ocean region (Arrigo et al., 2008a).

As such, these shelf regions play a disproportionately strong role in the Southern Ocean carbon system and air-sea exchange of CO_2 , such that changes here may have implications for large-scale biogeochemical cycles and climate (Arrigo et al., 2008b).

The west Antarctic Peninsula (WAP) continental shelf is an ecologically-important region of high primary productivity, strong air-sea CO_2 fluxes and a large and productive food web (Carrillo et al., 2004; Clarke et al., 2008; Ducklow et al., 2007; Legge et al., 2015; Montes-Hugo et al., 2010; Ruiz-Halpern et al., 2014; Schofield et al., 2010). Primary production is regulated by the annual sea ice cycle, because the timing and distribution of phytoplankton blooms is modulated by ice extent and duration, coupled upper-ocean processes

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and their impact on light availability (Smith and Comiso, 2008; Venables et al., 2013; Vernet et al., 2008). Primary production and biological CO₂ uptake are minimal during austral winter, due to extensive sea ice cover and low irradiance levels. As ice cover retreats in spring/early summer, large phytoplankton blooms can develop due to increased light availability, stratification of the upper water column by sea-ice meltwater and other freshwater inputs, and possible seeding of surface water blooms by sea-ice algae (Clarke et al., 2008; Smith and Nelson, 1985). In WAP coastal regions, summer chlorophyll levels often exceed 20 µg L⁻¹ (Ducklow et al., 2013; Venables et al., 2013) and this high production and resultant uptake of CO₂ into organic matter is sufficient to create a seasonal biological sink for CO₂ (Carrillo et al., 2004; Legge et al., 2015; Montes-Hugo et al., 2010; Ruiz-Halpern et al., 2014). Throughout autumn, primary production and biomass decrease to low winter levels due to shorter day-length, deepening of the mixed layer and decreasing phytoplankton growth rates, as well as high loss rates driven by zooplankton grazing, scavenging by sea ice, cell lysis and sedimentation (Vernet et al., 2012). Life cycles of the majority of Antarctic marine species and consequently the functioning of the entire marine ecosystem are paced by the annual advance and retreat of the ice pack, and its control of the key phytoplankton food source for higher organisms (Clarke et al., 2008; Ducklow et al., 2007). Efficient carbon export (> 10% of net primary production) at the WAP also delivers a source of organic matter to subsurface and benthic food webs and may lead to longer-term CO₂ sequestration (Buesseler et al., 2010; Smith et al., 2012).

The supply and biogeochemical cycling of nutrients is critical for phytoplankton production, ecosystem function and their relationship to CO₂ dynamics (Deutsch and Weber, 2012). In the Southern Ocean, and specifically over the WAP continental shelf, nutrients and CO₂ are supplied to the upper ocean via upwelling and mixing of Circumpolar Deep Waters (CDW) from the Antarctic Circumpolar Current (ACC) (Carrillo et al., 2004; Martinson et al., 2008; Prezelin et al., 2000; Serebrennikova and Fanning, 2004). Macronutrient supply from atmospheric, glacial or terrigenous inputs is thought to be negligible at the WAP, such that these deeper waters are the predominant nutrient source to phytoplankton blooms (Dierssen et al., 2002; Karl et al., 2002; Pedulli et al., 2014). These deep-sourced nutrients fuel primary production and biological uptake of CO₂, such that the large phytoplankton blooms observed at the WAP drive a substantial drawdown of macronutrients and CO₂ in surface waters over the summer months (Clarke et al., 2008; Ducklow et al., 2007). The principal objective of this study is to provide a detailed description of the supply, uptake and cycling of macronutrients and their controlling biological and physical processes in northern Marguerite Bay in the WAP coastal sea ice zone, based on a five-year high-resolution time-series of biogeochemical and isotopic data.

1.2. Nitrogen isotope systematics and tools

In addition to concentrations of nitrate, phosphate, silicic acid and ammonium, and the relationships between them, we also employ the nitrogen isotopic composition of nitrate ($\delta^{15}\text{N}_{\text{NO}_3}$) as a useful tool for examination of nutrient biogeochemistry and marine nitrogen cycle processes. $\delta^{15}\text{N}$ is the per mille (‰) deviation of the $^{15}\text{N}/^{14}\text{N}$ ratio in the sample from the $^{15}\text{N}/^{14}\text{N}$ ratio in the universal reference standard atmospheric N₂, expressed as

$$\delta^{15}\text{N} (\text{‰}) = \left(\frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}}}{(^{15}\text{N}/^{14}\text{N})_{\text{standard}}} - 1 \right) \times 1000 \quad (1)$$

Biological uptake of nitrate causes a kinetic fractionation between the ^{14}N and ^{15}N isotopes because phytoplankton preferentially assimilate the lighter energetically favoured ^{14}N isotope (Sigman et al., 1999b and references therein). As such, $\delta^{15}\text{N}_{\text{NO}_3}$ increases as nitrate utilisation proceeds according to the fractionation factor or kinetic

isotope effect (ϵ), which is defined by the ratio of the rates at which the two N isotopes are converted from nitrate to organic nitrogen:

$$\epsilon (\text{‰}) = (k^{14}/k^{15} - 1) \times 1000 \quad (2)$$

k^{14} and k^{15} are the rate coefficients of the reaction for ^{14}N - and ^{15}N -containing nitrate. Other nitrogen cycle processes, including organic matter remineralisation (Saino and Hattori, 1980, 1987), ammonium uptake (Waser et al., 1998a, 1998b), nitrification (Casciotti et al., 2003; Casciotti, 2009) and denitrification (Granger et al., 2008 and references therein), also fractionate the ^{14}N and ^{15}N isotopes with characteristic isotope effects, such that $\delta^{15}\text{N}_{\text{NO}_3}$ provides an integrative measure of all of the processes at work. $\delta^{15}\text{N}_{\text{NO}_3}$ is used in this study to examine nutrient supply, uptake and recycling over the summer phytoplankton growing season in the high-productivity Antarctic coastal ocean.

1.3. Oceanographic and climatic context

The WAP is unusual in the Antarctic context, being one of only a few regions where the principal nutrient source water mass, CDW, intrudes onto the continental shelf in a much less modified form than in other Antarctic regions, and exerts a particularly direct influence on shelf ecosystems (Hofmann et al., 1996). The southern edge of the ACC lies adjacent to the WAP shelf break such that CDW penetrates onto the shelf year-round, with the incursions being especially pronounced where glacially-scoured canyons dissect the shelf and reach to the shelf edge (Dinniman and Klinck, 2004; Dinniman et al., 2011; Martinson et al., 2008; Martinson and McKee, 2012; Moffat et al., 2009). Whilst lower circumpolar deep water (LCDW) is restricted to the deep canyons, upper circumpolar deep water (UCDW) bathes the WAP shelf up to shallow depths (below 200 m). Mixing and exchange of UCDW with overlying water masses as it moves across the shelf results in a modified form of this water mass in shelf environments, which is warm, saline and rich in nutrients and CO₂ compared with the overlying Antarctic Surface Water (AASW) (Klinck, 1998; Montes-Hugo et al., 2010; Prezelin et al., 2000; Smith et al., 1999). AASW is substantially fresher and less dense, creating a permanent pycnocline between 150 and 200 m (Beardsley et al., 2004; Hofmann and Klinck, 1998; Smith et al., 1999). During the summer months, meltwater-induced freshening and solar warming of surface waters stratifies the upper ocean and leads to isolation of a remnant cold (< -1°C) layer of AASW, termed winter water (WW), centring on ~100 m depth between AASW and UCDW (Mosby, 1934). Vertical mixing between UCDW, WW and AASW is driven by a range of processes including bathymetric interactions, internal tides, wind-induced shear, and coastal upwelling and downwelling, and permits the delivery of a substantial source of heat, salt, nutrients and CO₂ from UCDW to the productive surface ocean (Howard et al., 2004; Klinck et al., 2004; Martinson, 2012; Montes-Hugo et al., 2010; Prezelin et al., 2000; Smith et al., 1999; Wallace et al., 2008).

ACC waters advect northeastwards adjacent to the shelf slope, such that their incursion onto the shelf drives gyre-like surface water circulation over the shelf (Klinck et al., 2004). In the vicinity of Marguerite Bay and environs, the dominant current at depth is the flow of CDW along the glacially-scoured Marguerite Trough and into the bay itself (Klinck et al., 2004). Inshore, the seasonal buoyancy- and wind-forced Antarctic Peninsula coastal current (APCC) flows at shallow depths southwestwards along the coasts of Adelaide and Alexander Islands, with a presumed cyclonic circulation within Marguerite Bay (Beardsley et al., 2004; Moffat et al., 2008; Savidge and Amft, 2009). Intermittent near-inertial currents have also been observed in Marguerite Bay during ice free periods (Beardsley et al., 2004). Whilst currents and flows at depth are crucial for the supply and distribution of UCDW over the shelf, surface water circulation pathways may be important for the transport of dissolved constituents such as nutrients, and plankton during the ice-free summer season.

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