Ice melt influence on summertime net community production along the Western Antarctic Peninsula


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A B S T R A C T

The Western Antarctic Peninsula (WAP) is a highly productive marine environment that is undergoing rapid change, with consequences for productivity and total ecosystem carbon cycling. We present continuous underway O2/Ar estimates of net community production (NCPO2Ar) in austral summer 2012, 2013 and 2014 at sub-kilometer horizontal resolution within the Palmer Long-Term Ecological Research (Pal-LTER) grid region of the WAP. Substantial spatial variability is observed with NCPO2Ar ranging from 0 to 790 mmol O2 m⁻² d⁻¹ and considerable interannual variability with mean values in the grid region of 54.4 ± 48.5, 44.6 ± 40.5, and 85.6 ± 75.9 mmol O2 m⁻² d⁻¹ in 2012, 2013 and 2014 respectively. Based on a strong correlation (r² = 0.83) between residence time integrated NCPO2Ar and NCPDIC derived from seasonal DIC drawdown, we find the observed NCPO2Ar spatial and interannual variability to be consistent with the December–January NCPDIC magnitude. Seeking to explain the mechanistic drivers of NCP in the WAP, we observe a linear relationship between NCPO2Ar and meteoric water content derived from δ¹⁸O and salinity. This correlation may be due to Fe supply from glacial melt and/or strengthening of stratification and relief of light limitation. Elevated surface Fe availability, as indicated by Fv/Fm and measurements of surface water dissolved Fe and Mn (a rough proxy for recent potential Fe availability), and shallower, more stable mixed layers are present where meteoric water and/or sea ice melt is high near the coast. Light limitation is evident in the WAP when mixed layer depths are greater than ~40 m. Additionally we document hotspots of NCP associated with submarine canyons along the WAP. While it is difficult to predict how the physical-biological system might evolve under changing climatic conditions, it is evident that NCP, and potentially carbon flux out of the mixed layer, along the WAP will be sensitive to shifts in meltwater input and timing.

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1. Introduction

The climate of the Western Antarctic Peninsula (WAP) is changing rapidly, with July air temperatures increasing 6.3 °C since 1951 (Ducklow et al., 2007), sea ice duration decreasing by approximately 3 days each year (Stammerjohn et al., 2008), retreat of the majority of glaciers (Vaughan, 2006) and shifting ecological structures (Ducklow et al., 2013; Montes-Hugo et al., 2009). With such pronounced climatic changes we would likely expect accompanying impacts on net community production (NCP, gross photosynthesis minus community respiration) and regional carbon export production that could in turn feed back on the climate and ecosystem.

Predictive skill requires mechanistic understanding of the controlling processes. Since 1993, primary production has been estimated discretely in the WAP region as part of the Palmer Long-Term Ecological Research (Pal-LTER) program (Ducklow et al., 2013). These previous studies have broadly identified water column stability (thus light) and Fe supply as the likely main controls on primary production in the WAP (Dierssen et al., 2002; Ducklow et al., 2007; Smith et al., 1998; Vernet et al., 2008) consistent with other seasonal ice zones in the Southern Ocean, however no Fe measurements were available in the region prior to our study. The physical environment of the Pal-LTER study region is diverse, including offshore (northwest of the shelf break), shelf and coastal...
zones, deep glacially-scoured canyons that act as conduits of heat and nutrients via deep water intrusions onto the shelf, and pronounced latitudinal gradients. Across this varied seascape we might expect the relative importance of light and Fe limitation to change, yet currently this variability is not well understood. Additionally, the physical underpinnings of seasonal stratification and Fe supply including sea ice, winds, horizontal and vertical advection and mixing, and freshwater supply are complex and poorly resolved.

Few studies have documented NCP in the WAP, hence little is known about its magnitude, interannual variability, spatial variability and drivers. Huang et al. (2012) presented O₂/Ar-based NCP measurements in the Pal-LTER study region and found evidence of Fe and light limitation. Consistent with the prior discrete incubation NCP studies in the WAP (Carrillo et al., 2004), they document declining NCP with increasing distance from shore consistent with onshore-offshore gradients in primary production but, limited to only 46 discrete observations, could not resolve variability embedded within this gradient. Tortell et al. (2014) captured continuous time series of the pCO₂ and O₂/Ar spring-summer season within this gradient. Tortell et al. (2014) captured continuous time series of the pCO₂ and O₂/Ar spring-summer seasonal cycle at Palmer Station that showed a seasonal progression closely tied to water column stability and mixed layer depth. This well-resolved seasonal cycle provides a valuable context for broad-scale spatial surveys, such as presented here, but does not inform our understanding of variability across the WAP region. Recently, Tortell et al. (2015) presented underway O₂/Ar measurements in the Pal-LTER grid region in the austral summer 2011. Here we resolve additional interannual variability with three years of spatial surveys.

Three years of summertime high spatial resolution (<1 km) underway NCP data along the WAP are presented. We estimate NCP from Equilibrator Inlet Mass Spectrometry (EIMS) measured O₂/Ar (NCP_{O₂/Ar}) and NCP from underway pCO₂ (NCP_{DIC}) and use their relationship to elucidate the January contribution of NCP to the elapsing growing season. In a companion paper (Eveleth et al., 2017) we show that biological processes primarily control O₂ and pCO₂ in the WAP and that there is substantial mesoscale horizontal variability across the region. Here we seek to explain which underlying mechanisms are setting this biological variability, with a focus on glacial and sea-ice melt water influences.

2. Methods

Data presented here were collected in January-February 2012, 2013 and 2014 onboard the ARSV Laurence M Gould in conjunction with the Pal-LTER annual cruises. The Pal-LTER sampling scheme spans a ∼700 km x 250 km grid with discrete surface sampling every 20 km along 100 km spaced grid lines (Fig. 1). Conductivity-temperature-depth (CTD) casts were conducted at selected stations every 40-100 km with a SeaBird 911plus instrument (temperature sensor model 3plus with accuracy ±0.001 °C, conductivity sensor model 4C with accuracy ±0.002 S/m). Mixed layer depth (MLD) was determined as the depth at which the potential density increased by 0.125 kg m⁻³ relative to the surface value (Monterey and Levitus, 1997). Photochemical efficiency of photosystem II (Fv/Fm) measurements were taken discretely with a fluorescence induction relaxation system (FIRe) following standard published protocol (Gorbunov et al., 1999). Raw surface values have been re-calibrated to account for sampling artifacts using FPR02 but should still be treated as qualitative. Some variability in Fv/Fm may be due to diel cycles but we discuss all data here. We do not observe any relationship between time of day or surface irradiance and Fv/Fm (Fig. S1), indicating that the spatial variability may be overwhelming the diurnal cycle. We do additionally show a subset of nighttime Fv/Fm data from the expected peak window of photochemical efficiency defined here as between midnight and 4 a.m. (Huang et al., 2012). Sea surface salinity and temperature (SSS and SST respectively) here refer to two-minute averages of these properties measured continuously in the ship’s underway seawater supply by a flow-through thermosalinograph (SBE 45 MicroTSG accuracy ±0.0003 S/m, ±0.002 °C intake at 5 m depth). Gases (O₂/Ar and pCO₂) were also measured underway. Continuous (2-min averaged) underway O₂/Ar measurements were performed using Equilibrator Inlet Mass Spectrometry (EIMS) (Cassar et al., 2009) (method also detailed in companion paper [Eveleth et al., 2017]). In this method, gasses are equilibrated from seawater flowing through the ship’s underway lines using a gas permeable membrane contactor cartridge, and the ratio of O₂ to Ar is analyzed using a quadrupole mass spectrometer (Pfeiffer Prisma model QMG 220 M1). Seawater samples are calibrated against the stable atmospheric O₂/Ar ratio every four hours. The instrument precision is ±0.3%. Respiration in the ship’s seawater lines is likely negligible as Juranek et al. (2010) show that respiration is slow at low temperatures (0.5%) and water residence time in the lines is ~1 min. Sink and Niskin bottle comparisons were performed using potentiometric Winkler titrations in January, 2016. The data show no significant difference between the underway lines of the LMG and Niskin bottles closed at the surface (0.06%, n=9). Surface pCO₂ (pCO₂_{meas} ) was measured every 2.5 min (the approximate integration time of the equilibration system) using a 30L shower-type air-water equilibrator and an IR CO₂ analyzer (Munro et al., 2015). Underway data were time matched to station data, as an average of all data measured within 15 min of discrete sampling.

Surface chlorophyll concentration was measured ~weekly from ~November–March at Station B and E near Palmer Station and from ~October–May at the British Antarctic Survey’s Rothera Research Station's oceanographic and biological time series site.
(RatS) as described in Saba et al. (2014) and Clarke et al. (2008) respectively (station locations indicated on Fig. 1). Chlorophyll a concentration was also measured discretely on the cruise track. Seawater samples were filtered and extracted in 90% acetone, frozen and stored for 24 h, then measured using a digital Turner Designs fluorometer following standard protocol (Smith et al., 1981).

2.1. Fe and Mn concentration

Surface water was collected for trace metal analysis during the January 2012 expedition, using a non-contaminating towfish deployed from a laterally-extended crane off the starboard side of the ship, avoiding contamination from the ship’s hull. Seawater was pumped through an acid-cleaned plastic tube, attached to the fish and collecting water at −2 m depth, to a HEPA-filtered clean lab built within the ship’s main science lab, where it was filtered at 0.2 μm through acid-cleaned capsule filters (Acropak 200, Pall®). The surfaces contacted by seawater in this system were Teﬂon, polypropylene, polyethylene and polyethersulfone only. Filtered water samples in acid-cleaned low density polyethylene bottles (Nalgene) were acidified at sea to pH ~2.0 using ultraclean HCl (Fisher Optima HCl, concentration in seawater 0.012 M) in order to prevent adsorptive loss of metals to container walls and to prevent biological growth. Seawater samples were analyzed at Rutgers University for dissolved Fe and Mn (in addition to Zn, Cu and Ni; reported elsewhere) using an automated flow injection ICP-MS method developed in R. Sherrell’s laboratory (Lagerström et al., 2013). Briefly, the automated device loaded a 9 mL aliquot of seawater, buffered online to pH 7.0 with 3 mL of acetic acid/ammonium hydroxide buffer, onto a column packed with Nobias PA1 chelating resin (Hitachi High-Technologies). The column was eluted with 1.5 M nitric acid directly into the nebulizer of an Element-1 sector field ICP-MS (Thermo-Finnigan, Bremen, Germany). The eluate, a 200-fold concentrate of the sample but with greatly reduced major ion concentration, was analyzed in medium resolution and temporal peak integration was performed using custom software coded in Matlab. Quantification was carried out using internal isotope dilution (Fe) for each sample or matrix matched external standards in seawater (Mn), the latter pre-concentrated through the chelating column at the beginning and end of each analytical session, and corrected for instrumental sensitivity drift.

Analytical duplicates were measured every sixth sample and typically displayed 1–3% deviation about the mean. The long-term precision over many analytical runs runs over a period of months, as demonstrated by repeated analysis of a large-volume in-house seawater standard from the Ross Sea (analyzed 5–6 times during each analytical session), was 3% for Fe (RSD; see Table 3 in Lagerström et al., 2013). Accuracy was verified by repeated analysis of reference seawater materials (SAFe S and D2, GEOTRACES S and D), which showed agreement within one standard deviation of the consensus values for almost all reference seawaters (see Table 5 in Lagerström et al., 2013).

Methods for the collection and analysis of particulate Fe (pFe) followed Planquette and Sherrell (2012). Briefly, particles were filtered from towfish-collected seawater onto 0.45 μm pore size filters (Supor; Pall®) within the shipboard clean lab. Filters were then frozen for shipping and subjected to complete acid digestion in nitric and hydroﬂuoric acid, followed by analysis by ICP-MS at Rutgers University.

2.2. δ18O freshwater fraction determination

Discrete sampling for the ratio of stable isotopes of oxygen in seawater (δ18O) was conducted from the underway water supply at 5 m depth on the Pal-LTER cruises. Additionally, samples were drawn from Niskin bottles closed at various depths during the station-based CTD proﬁling on the cruises. Samples were collected in 50 ml glass vials that were sealed with stoppers and aluminum crimps, and were transported by dark cool stow to the Natural Environment Research Council Isotope Geochemistry Laboratory (NERC) at the British Geophysical Survey, U.K., for analysis using the equilibration method for oxygen (Epstein and Mayeda, 1953). Samples were run on a VG Iso6pre 18 and SIRA 10 mass spectrometer, with random duplicates indicating a precision better than ± 0.02‰ was attained. To obtain quantitative details on the freshwater sources from these data, they were used alongside salinity in a simple 3-endmember mass balance, whereby each water sample is presumed to be a three component mixture of CDW, sea ice melt and meteoric water, and the relative proportions of each derived. We use end-member salinity and δ18O values of 34.73 and 0.1‰ respectively for CDW, 7 and +2.1‰ for sea ice melt and 0 and −16‰ for meteoric water. Full details of the methodology are given in Meredith et al. (2013).

2.3. NCP/O2Ar

Neglecting vertical mixing, the net biological oxygen flux is a function of the net community production (NCP) and gas exchange of biologically-produced oxygen ([O2]bio) with the atmosphere (Cassar et al., 2011)

\[
\frac{d[O_2]}{dt} = NCP_{O2Ar} - k_{O2}[O_2]_{bio} 
\]

where \( k_{O2} \) is the piston velocity (m d⁻¹), and

\[
[O_2]_{bio} = [O_2]_{total} - [O_2]_{phys} \approx \frac{\Delta[Ar]}{[Ar]_{sat}}[O_2]_{sat}\Delta(O_2/Ar) 
\]

In steady state, NCP/O2Ar (mmol O₂ m⁻² d⁻¹) in the mixed layer over the residence time of oxygen (~10 days in this region) is commonly approximated by

\[
NCP_{O2Ar} \approx k_{O2}[O_2]_{sat}\Delta(O_2/Ar) 
\]

where

\[
\Delta(O_2/Ar) = \left(\frac{[O_2]/[Ar]}{[O_2]/[Ar]_{sat}}\right)_{meas} - 1 .
\]

\([O_2]/[Ar]_{meas}\) is the measured O₂/Ar ratio from EIMs. The equilibrium saturation concentrations of O₂ ([O₂]_{sat}) and Ar ([Ar]_{sat}) were calculated using underwater temperature and salinity measurements and the equations of Garcia and Gordon (1992) and Hamme and Emerson (2004) respectively. In this region, O₂ is often undersaturated below the mixed layer. Negative NCP/O2Ar could reflect surface heterotrophy, or vertical mixing of oxygen-undersaturated waters. In regions where vertical mixing is significant, NCP/O2Ar represents a lower bound on true NCP (Cassar et al., 2014), but here we assume that negative O₂/Ar supersaturation (and thus negative NCP/O2Ar) values are contaminated by vertical mixing and remove them (~10% of sampled points) from our NCP analysis and treat NCP/O2Ar as a conservative estimate of NCP magnitude (Cassar et al., 2007; Giesbrecht et al., 2012; Reuer et al., 2007). The approximation of NCP/O2Ar assumes that [Ar]/[Ar]_{sat} equals unity. By making this assumption we are introducing an error in NCP/O2Ar that is equal to the observed Ar saturation. This is an important note for calculations of NCP/O2Ar when Ar concentration deviates substantially from the equilibrium saturation concentration (Evelleth et al., 2014) (e.g. brine where Ar undersaturation may be as low as 45% (Top et al., 1988)). Argon supersaturation ranged from ~5.3% to 2.8% in 2012 in the WAP, as is explored in the companion paper (Evelleth et al., 2017). Under these conditions, the error associated with this assumption is negligible compared to the error in wind speed.
parameterization of the piston velocity (~40%) (Bender et al., 2011). We estimate piston velocity using four-times daily NCEP/NCAR reanalysis wind speed and the parameterization of Wanninkhof (1992). Piston velocity is weighted as in Reuer et al. (2007) to account for wind speed history prior to sampling.

Sufficient time series measurements of dissolved organic carbon (DOC) across the grid are not available to assess accumulation in the mixed layer. NCP is commonly taken to estimate carbon export from the mixed layer in the Southern Ocean where DOC in the mixed layer is low relative to the observed NCP rates (e.g. Allison et al., 2010; Carlson et al., 2002; Hansell and Carlson, 1998; Ishii et al., 2002; Sweeney et al., 2000), as specifically shown in the WAP by Huang et al. (2012). However if significant dissolved or particulate organic carbon accumulation did occur, NCP<sub>DOC</sub> would overestimate carbon flux out of the mixed layer (Sweeney et al., 2000).

### 2.4. NCP<sub>DIC</sub>

DIC was determined from pCO<sub>2</sub>, salinity-based total alkalinity (TA) estimates, and underway temperature, salinity and pressure using CO2SYS (van Heuven et al., 2011) and dissociation constants for carbonic acid by Lueker et al. (2000) and for boric acid by Dickson (1990). The following salinity-TA algorithm for the LTER grid region was determined by Hauri et al. (2015) from linear least squares fits of historical discrete surface measurements of alkalinity and salinity from 1993–2013:

\[
TA_{\text{LTER}} = 58.5 S + 322.1
\]

(Hauri et al., 2015).

\[TA_{\text{LTER}}\] has a root mean square error (RMSE) of 16.8 μeq kg<sup>−1</sup> (Hauri et al., 2015). Salinity-predicted TA appears to underestimate TA by as much as 25 μeq kg<sup>−1</sup> in the northern portion of the Palmer-LTER grid region, as seen by comparison with discrete TA measurements in 2012 (Fig. S2a). This leads to a local DIC underestimation of up to 50 μmol kg<sup>−1</sup> (root mean squared error ±15.21 μmol kg<sup>−1</sup> (~0.7%), Fig. S2b). Discrete measurements are not available for comparison in 2013 and 2014. DIC was salinity normalized (nDIC) to 35 to account for dilution by meteoric water and sea-ice meltwater input.

Average winter DIC in the WAP was calculated from a climatology of all winter (June–August) underway pCO<sub>2</sub> and salinity measurements between 1998–2013 (http://www.ldeo.columbia.edu/res/pi/CO2/). Winter pCO<sub>2</sub> does not show any significant long-term trend over this time (Hauri et al., 2015). We calculated nDIC the same way as for the summer months. Mean winter nDIC was 2272 ± 8 μmol kg<sup>−1</sup> (SE 0.04 μmol kg<sup>−1</sup>). While there is some regional variability across the grid, data were too sparse to resolve a spatial climatology.

The seasonal mixed layer integrated NCP rate (mmol C m<sup>−2</sup> d<sup>−1</sup>) can be calculated from the DIC drawdown as follows:

\[
\text{NCP}_{\text{DIC}} = \frac{nDIC_w \cdot \rho_w - nDIC_s \cdot \rho_s \cdot MLD}{\Delta t}
\]

where nDIC<sub>w</sub> is the mean winter nDIC (2272 μmol kg<sup>−1</sup>), nDIC<sub>s</sub> is the winter pCO<sub>2</sub> value derived from pCO<sub>2</sub> measured in this study, ρ<sub>w</sub> and ρ<sub>s</sub> are the prescribed winter (~−1.85 °C; 33.88 (Martinson et al., 2008) and measured summer water densities respectively, MLD (m) is the mixed layer depth from the nearest CTD cast, and Δt is the length of the growing season in days. The length of the growing season could be approximated from satellite chlorophyll data, relative sea-ice retreat timing or in situ Chl a time series records at Palmer Station and Rothera Station (Fig. 2), but is not required here as we present growing season integrated NCP<sub>DIC</sub> (see Section 3.2). Very likely, MLDs shoaled during the growing season, but because of a lack of December data across the grid region we use the measured January MLD. This probably leads to an underestimation of NCP<sub>DIC</sub> but significant primary production likely does not occur until after mixed layer shoaling (Tortell et al., 2014; Venables et al., 2013). Additional uncertainties as they relate to the data interpretation are discussed in Section 3.2.

![Fig. 2. Near surface (5 m) Chl a concentration time series in 2012 (top), 2013 (middle) and 2014 (bottom) at Palmer Station B (blue line, purple star Fig. 1), Station E (red-orange line, red star Fig. 1) and RATS (yellow line, yellow star Fig. 1). Shaded box indicates time window of Pal-LTER annual cruise sampling. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)
3. Results and discussion

3.1. NCP_{O2Ar}

NCP_{O2Ar} in the Pal-LTER grid of the WAP (Fig. 3) averaged 54.4 ± 48.5 mmol O$_2$ m$^{-2}$ d$^{-1}$ in 2012, 44.6 ± 40.5 mmol O$_2$ m$^{-2}$ d$^{-1}$ in 2013 and 85.6 ± 75.9 mmol O$_2$ m$^{-2}$ d$^{-1}$ in 2014, neglecting negative values and noting that spatial surveys in each year vary so full-grid averaging could be biased by the cruise track. Means by sub-region are presented in Fig. 4 with offshore, southern onshore and northern onshore regions roughly dividing the shelf and coast from the slope and latitudinally separating regions known to have hydrographic, sea ice and other biological distinctions (Bernard et al., 2012; Martinson et al., 2008; Stammerjohn et al., 2008; Steinberg et al., 2015) but these sub-regions cannot fully resolve the gradients in observations. If we consider only a subset of stations (those which were occupied in all three years), NCP_{O2Ar} averaged 37.3 ± 28.5 mmol O$_2$ m$^{-2}$ d$^{-1}$ in 2012, 12.3 ± 17.5 mmol O$_2$ m$^{-2}$ d$^{-1}$ in 2013 and 50.8 ± 63.0 mmol O$_2$ m$^{-2}$ d$^{-1}$ in 2014, consistent with the interannual variability documented in full grid averages. The interannual variability in in situ observations clearly shown in Fig. 3 is also supported by mean January satellite NCP estimates in the grid region, with 2014 being anomalously productive. Satellite NCP estimates were derived from a WAP specific satellite Chl algorithm and in situ comparisons of NCP_{O2Ar} and Chl concentration from 2008–2014 (Li et al., in review). There is relatively high production near the coast, decreasing offshore in all years (Figs. 3 and 4). In addition to the higher overall magnitude, NCP in the onshore region (including shelf and coastal regions roughly defined as east of grid station 100 (Fig. 3)) is also more spatially variable than offshore (Eveleth et al., 2017). This onshore-offshore trend is consistent with previous studies of NCP (Huang et al., 2012), chlorophyll and primary production (Garibotti et al., 2005; Smith et al., 1998; Vernet et al., 2008) and bacterial activity (Ducklow et al., 2012).

We also noted negative biological O$_2$ flux (NCP_{O2Ar} estimates including negative values) in the coastal straits north of the traditional Pal-LTER sampling region (Fig. S3), specifically persistent negative ΔO$_2$/Ar in the Gerlache Strait in all crossings save one in 2014. While it is possible that this area is net heterotrophic in the summer, the values could alternatively be exposing a limitation of our methodology. We assume that there is no vertical mixing across the lower mixed layer interface, however the Gerlache Strait and adjacent inner bays have been shown to be strongly influenced by upwelling of modified upper CDW (UCDW) routed through the strait via a deep canyon (Espinasse et al., 2012).

Fig. 3. NCP_{O2Ar} in austral summer 2012 (left), 2013 (center) and 2014 (right) on the Pal-LTER grid. Thin gray line is the 500 m isobath. Black, blue and red boxes mark the designated offshore, northern onshore and southern onshore sub-regions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Mean NCP_{O2Ar} (±1σ) in three regions of the Pal-LTER grid in 2012 (black), 2013 (gray) and 2014 (white). Regions defined as in Fig. 3.
Upwelling would bring O₂-undersaturated water to the surface, influencing our NCP estimate. Modified UCDW, possibly influenced by Fe inputs from shelf sediments (Sherrell et al., 2015), may also be a source of Fe in the region, so this upwelling may promote high NCP. The Gerlache Strait and surrounding inner bays have been shown to be significantly productive in the summer (carbon fluxes up to 800 mg C m⁻² d⁻¹ (Anadon et al., 2002; Karl, 1991), supporting extremely high krill and whale density in the austral fall (Nowacek et al., 2011). In February 2014 (Fig. S3), there was a very large bloom in the Gerlache Strait with NCPO₂Ar reaching ~175 mmol O₂ m⁻³ d⁻¹. ~20 days after the region was O₂/Ar undersaturated, giving support to the prominent role of upwelling controlled productivity in the straits. Unfortunately, this area is outside of the traditional Pal-LTER sampling grid, thus we have no depth information and are limited in our ability to further explain our Δ(O₂/Ar) observations. The following analysis will first explore the validity of the O₂/Ar-based NCP measurements in the grid region and then attempt to develop a mechanistic understanding of the onshore-offshore NCP gradient and coastal hot spots, especially as they relate to meltwater input. Negative NCPO₂Ar values are not considered in the remainder of the discussion, as they may be reflective of upwelling processes rather than net heterotrophy.

3.2. Biological oxygen and DIC inventories

NCPO₂Ar has a memory of production over the relatively short ~10 day residence time of O₂ in the mixed layer. This short residence time makes it difficult to discriminate between spatial and temporal variability when interpreting observed O₂/Ar signals alone. For example, high NCPO₂Ar in a particular location could indicate a region of persistently high productivity or our sampling time might have simply coincided with the peak of a short lived bloom in that location. Further, interannual variability in NCPO₂Ar may reflect variability in overall summer NCP magnitude, or instead a shifting phenology relative to sampling date, for example in the far south where we encounter ice-edge blooms in some years but miss them in others. We employ estimates of recent and seasonal organic carbon production from NCPO₂Ar and NCPDIC respectively to investigate these issues as well as to corroborate our NCPO₂Ar estimates with an independent measurement. This approach builds on Carrillo et al. (2004) and Tortell et al. (2015) in the WAP, as well as the discussion of O₂ and CO₂ gas fluxes presented in the companion paper (Eveleth et al., 2017). In order to properly assess timing and the biologically-driven relationship between O₂ and CO₂ we need to isolate the biological components (e.g. utilizing Ar in conjunction with O₂ and salinity normalizing derived DIC) and compare time-integrated inventories rather than fluxes.

To obtain a mixed layer inventory of biological oxygen we integrate Eq. (1) with respect to time and multiply by MLD to obtain

\[
\text{MLD} \cdot \text{O}_2 \text{bio(O)} = \text{MLD} \cdot \frac{\text{NCPO}_2 \text{Ar}}{k_{O_2}} + \text{MLD} \cdot C_e \cdot \text{MLD} \cdot \text{Ce}^{-t_{MLD}}
\]

(7)

where C is an arbitrary constant of integration. Thus, under steady-state conditions

\[
\text{MLD} \cdot \text{O}_2 \text{bio(O)} = \tau_{O_2} \cdot \text{NCPO}_2 \text{Ar}.
\]

(8)

Converting to carbon units using a stoichiometric C/O₂ of 1:1.4 (Laws, 1991), we obtain the mixed layer organic carbon production inventory (mmol C m⁻²) during τO₂, the residence time of O₂ in the mixed layer (~10 days). The growing season carbon production (mmol C m⁻²) is approximated by

\[
\int_0^t \text{NCPDIC} = \Delta t \cdot \text{NCPO}_2 \text{Ar} = (\text{nDICw} \cdot \rho_{w} - \text{nDIC} \cdot \rho_{s}) \cdot \text{MLD}.
\]

(9)

where Δt is the length of the growing season and NCPO₂Ar is as given in Eq. 6. This is equivalent to a mixed layer inventory of seasonal biological DIC drawdown independent of the length of the growing season. NCPO₂Ar represents seasonal biological carbon drawdown here because the residence time of pCO₂ in the mixed layer is months to years. Our tentative estimate for the uncertainty in the seasonal biological DIC drawdown, adding uncertainties in quadrature, is ±8% not including any error associated with our use of the summer mixed layer depth here which may lead to significant underestimation of NCPDIC.

The time-integrated NCP properties τO₂NCPO₂Ar and ΔtNCPO₂Ar are highly correlated with a slope of 0.37 and an r² of 0.83 (Model II least squares bisector regression, p < 0.0001, Fig. 5). If NCP does not change over the growing season (i.e. NCPO₂Ar = NCPDIC), the slope of the regression should reflect the ratio of the residence time of O₂ at the ocean surface to the length of the growing season. The average τO₂ during this study was ~10 days (MLD/kO₂) and the length of the growing season Δt was ~30 days, as first ice retreat from the region was no more than 36 days before sampling and chlorophyll time series at Palmer Station and RaTS show bloom activity starting in late November–December (Fig. 2). Thus the slope of 0.37 is approximately what would be expected for the ratio of τO₂ to Δt. The slope may indicate that NCPO₂Ar and NCPDIC are near equal and O₂/Ar estimates are capturing persistent December–January spatial variability in the WAP rather than reflecting the impact of short-lived blooms. However, we cannot rule out any other combination of τO₂NCPO₂Ar; ΔtNCPO₂Ar that leads to a ~1/3 ratio such as a longer growing season and higher recent NCP than the growing season average. Interestingly, all three years display the same relationship between τO₂NCPO₂Ar and ΔtNCPO₂Ar (slope 0.36 ± 0.005, 0.36 ± 0.004, 0.37 ± 0.002 in 2012, 2013 and 2014, respectively), suggesting that we are capturing interannual variability in December–January NCP magnitude with the O₂/Ar...
approach. Of course this correlation does not fully capture the full growing season’s organic carbon production; chlorophyll concentration time series at Palmer Station (stations B and E) and RaTS as well as satellite data show that blooms occur until late March. In fact, based on the RaTS time series, chlorophyll concentration did not peak in Ryder Bay until March in 2012 and 2013 (Fig. 2). Li et al. (in press) use satellite derived NCP climatologies to show that in the productive onshore region of the WAP, peak annual NCP is observed in January.

It is possible that deviations from the observed \( \tau_{O2,NCP_{O2/Ar}}: \Delta NCP_{DIC} \) relationship could indicate local bloom timing since \( O2/Ar \) re-equilibrates with the atmosphere much faster than pCO2. \( \tau_{O2,NCP_{O2/Ar}}: \Delta NCP_{DIC} \) significantly less than 0.37 might indicate that the recent rate capture with \( O2/Ar \) is much lower than the rate earlier in the season (i.e. the peak bloom occurred prior to sampling) while a ratio much greater than 0.37 would indicate that the current rate is higher than the seasonal average and we are capturing a more recent bloom. We assessed the validity of the \( \tau_{O2,NCP_{O2/Ar}}: \Delta NCP_{DIC} \) ratio as a tracer of bloom timing by comparing it to satellite derived NCP (Li et al. in press) at the time of cruise sampling relative to NCP in the months prior. No clear relationship exists between \( \tau_{O2,NCP_{O2/Ar}}: \Delta NCP_{DIC} \) and \( NCP_{sat} \), the 32 day integrated \( NCP_{sat} \) (Fig. 3). Additionally we see no relationship between the difference between \( \tau_{O2,NCP_{O2/Ar}} \) and \( \Delta NCP_{DIC} \) and the days of open water prior to sampling, which may be an indicator of bloom timing. Because of all the uncertainties discussed herein, scatter about the \( \tau_{O2}/\Delta t \) slope is not a reliable indicator of bloom timing in the WAP. More likely, deviations from 0.37 could arise from limitations in both NCP estimation methods. Error in NCPDIC may arise from errors in DIC reconstruction from pCO2, horizontal and vertical transport, calcium carbonate dissolution/precipitation, gas exchange (2-10% underestimation likely based on Sweeney et al., 2000) or by using an nDICw climatology that does not represent true winter DIC in a particular location or year. NCP from \( O2/Ar \) may be biased due to vertical mixing. Ar supersaturation, non-steady state conditions over the residence time of O2 variability in piston velocity (for example due to partial ice cover, which is not accounted for here) or a stoichiometric C/O2 different from 1.14. Tortell et al. (2014) suggest, for example, that the WAP quotient may be closer to 1:1. Both NCP estimates would likely be biased low if vertical mixing were significant, though the extent would likely differ depending on vertical gradients of O2 and DIC and the timing of the mixing. There may also be geographical variations in \( \tau_{O2}/\Delta t \). Additionally, it is important to note that this is inherently an Eulerian (not Lagrangian) study and as a result of the differing residence times of O2 and pCO2, NCP_{O2/Ar} and NCP_{DIC} are not necessarily reflecting production in the same water parcel over time. NCP_{DIC} reflects larger spatial and temporal footprints.

Given the multitude of uncertainties and assumptions, the strong correlation (\( r^2 = 0.83 \)) could be fortuitous (i.e. multiple factors canceling each other), or instead may indicate that those factors are of second-order importance. If the latter is true, it notably implies that the assumptions for estimating NCP based on \( O2/Ar \) in this region are generally valid, although we cannot rule out that they contribute to some of the noise around the regression. Two main limitations of the \( O2/Ar \) method are the necessary assumptions of insignificant vertical mixing and steady-state conditions (Cassar et al., 2009; Jonsson et al., 2013). Cassar et al. (2014) recently showed that the influence of vertical mixing on biological oxygen can be addressed by taking concurrent measurements of N2O and using a composite \( ^{N2}O_3:O2/Ar \) tracer that is conservative with respect to water mass obduction (any vertical mixing into the mixed layer including upwelling, entrainment, and diapycnal mixing). Others have addressed the steady-state assumptions with Lagrangian studies (Hamme et al., 2012). Here we are able to indirectly assess the steady-state assumption by comparing \( \tau_{O2,NCP_{O2/Ar}} \) to \( \Delta NCP_{DIC} \). Such observations in other regions may allow us to determine whether the large discrepancies between biological \( O2 \) flux and NCP in the modeling study of Jonsson et al. (2013) are significant.

### 3.3. Drivers of NCP

In the remainder of the discussion we refer to the \( O2/Ar \)-derived mixed-layer integrated NCP_{O2/Ar} rates (mmol O2 m\(^{-2} \) d\(^{-1} \)), with the understanding that these are broadly consistent with December–January production rates and the timescale of NCP_{O2/Ar} displays a significant linear correlation with surface chlorophyll concentration (\( n=129, r^2 = 0.54 \) \( p < 0.0001 \), Fig. 6) and gross primary production (Huang et al., 2012). With replete macronutrients (Ducklow et al., 2007; Garibotti et al., 2005; Huang et al., 2012), the primary candidates for bottom-up control on NCP_{O2/Ar} are light and iron. While the following discussion focuses on physical drivers it is important to note that top-down controls on primary production likely also have significant influences on NCP_{O2/Ar}. Lin et al. (submitted) examine NCP_{O2/Ar} variability in the WAP from a community perspective including top-down controls.

#### 3.3.1. Light limitation and freshwater input

We document a non-linear negative response of NCP_{O2/Ar} to mixed layer depth whereby NCP_{O2/Ar} is consistently low when MLDS are greater than ~40 m and NCP_{O2/Ar} is elevated and more variable when MLDS are shallower than 40 m (Fig. 7a). Several studies in this region and throughout the Southern Ocean have documented a consistent non-linear negative relationship between the summer MLD and primary production (Garibotti et al., 2005; Mitchell et al., 1991; Mitchell and Holmhansen, 1991; Vernet et al., 2008) and MLD and NCP_{O2/Ar} (Cassar et al., 2011; Huang et al., 2012; Tortell et al., 2015) with thresholds at 25–50 m. This suggests light limitation, at least locally, at the WAP. We document independently this ~40 m threshold here by comparing seasonal DIC drawdown (nDICw - \( \rho_w - nDIC_s - \rho_s \)) to mixed layer depth (Fig. S5).

![Fig. 6. NCP_{O2/Ar} vs. surface (~5 m) Chl a concentration in the Pal-LTER grid region with least squares regression (\( r^2 = 0.54 \)). Symbols denote grid region as defined in Fig. 3.](image-url)
Freshwater input (meteoric and sea-ice meltwater) is a primary control on summertime upper water column stability in the WAP (Dierssen et al., 2002; Garibotti et al., 2005; Meredith et al., 2013; Venables et al., 2013; Vernet et al., 2008). MLDs are generally shallower than when total meteoric and sea-ice meltwater content is greater than 3.5% in the surface. While it is clearly the case that freshwater inputs add buoyancy and lead to shallow mixed layers, it should be noted that the nature of the relationship is also controlled by deep mixing events diluting the surface freshwater fractions. Shallower mixed layers are also more strongly stratified as indicated by the negative correlation between MLD and $\Delta\sigma\theta_{T_{\text{min}}-0}$ ($n=152$, $r^2=0.29$, $p<0.0001$) where $\Delta\sigma\theta_{T_{\text{min}}-0}$ is the potential density difference between the winter water (defined by the water column temperature minimum) and the surface (Saba et al., 2014).

Elevated meteoric water fraction and accompanying shallower, more stable mixed layers are correlated with NCP$_{O_{2}}$Ar in the WAP ($n=124$, $r^2=0.33$, $p<0.0001$, Fig. 7b). These correlations are indicative of a bottom-up controlled, light-limited system that is critically sensitive to freshwater inputs. Meteoric water, mixed layer depth, $\Delta\sigma\theta_{T_{\text{min}}-0}$ and NCP$_{O_{2}}$Ar all exhibit onshore-offshore gradients. The correlation could be an artifact of a corresponding spatial gradient in an additional covarying property, such as Fe availability. The correlation between NCP$_{O_{2}}$Ar and

![Figure 7](image1)

Fig. 7. a) NCP$_{O_{2}}$Ar vs. MLD colored by grid station (low values coastal, high values offshore) in all years with regional symbol shape as in c, b) NCP$_{O_{2}}$Ar vs. near surface meteoric water fraction with color indicating upper water column stratification and symbol size representing relative MLD with larger symbols for deeper MLDs.

![Figure 8](image2)

Fig. 8. Surface (5 m) dissolved Fe (left), particulate Fe (middle) and dissolved Mn (right) concentrations in 2012. Maximum pFe concentration was 21.05 nmol kg$^{-1}$. R. Eveleth et al. / Deep-Sea Research II 139 (2017) 89–102
meteoric water fraction is stronger than that between NCPO2Ar and sea-ice meltwater fraction, which may indicate the importance of glacial Fe input, as discussed below.

3.3.2. Iron

Surface dissolved and particulate Fe data available for 2012 indicate low concentrations offshore and variable concentrations onshore (Fig. 8). Distinct declines in Fe with distance from shore have been documented in the northern tip of the WAP (Ardelan et al., 2010), and more recently in the Pal-LTER grid region (Sherrell et al., in preparation). Because of biological uptake and variable Fe speciation, dissolved Fe (dFe) concentration may however be a poor indicator of Fe availability in the mixed layer (Cassar et al., 2011) and we cannot address the bioavailability of these Fe pools. Here we use dissolved manganese (dMn) concentration as a crude proxy for recent Fe availability. Both dMn and dFe have similar physical supply mechanisms in the Southern Ocean (Measures et al., 2013) but dMn is not scavenged biologically from the water column as rapidly as dFe and thus can serve as a qualitative quasi-conservative indicator of supply and subsequent horizontal dispersal by advection and diffusion in surface waters. We find that dMn shows a strong correlation (Fig. 10b, \( n = 21, r^2 = 0.76, p < 0.0001 \)) with \( F_v/F_m \) (Fig. 9), a qualitative indicator of Fe stress (e.g. Cassar et al., 2011; Hopkinson et al., 2007; Suggett et al., 2009; Trimborn et al., 2015) and a correlation with dFe (\( n = 104, r^2 = 0.36, p < 0.0001 \)). Net community production is positively correlated with dMn (Fig. 10a, \( n = 72, r^2 = 0.26, p < 0.0001 \)). Surface dMn concentration in 2012 displays a pronounced decline from the coastal region to offshore (Fig. 8c). Dissolved Mn is also positively correlated with surface meteoric water fraction (\( n = 48, r^2 = 0.26, p < 0.0005 \)). While it is difficult to conclude whether this is an artifact of coincident onshore-offshore gradients without causal relationship, it is consistent with our current understanding of glacial runoff being an important delivery mechanism of trace metals to the coastal region (Hawkins et al., 2014; Huang et al., 2012; Sherrell et al., 2015; Vernet et al., 2008).

NCPO2Ar is low offshore regardless of light availability as estimated from MLD or stratification (Figs. 2, 7a and b). The consistently-observed low trace metal concentrations offshore suggest Fe to be an important limiting factor for NCPO2Ar in the area. These findings are consistent with other studies that indicate offshore Fe limitation of primary production in the pelagic Southern Ocean (e.g. Cassar et al., 2011; de Baar et al., 2005; Martin et al., 1990; Trimborn et al., 2015). However, these are the first published measurements to show that dissolved Fe in (offshore) continental shelf waters can be as low as in open Southern Ocean surface waters (~0.1 nmol/kg), consistent with Fe limitation of diatoms and other phytoplankton taxonomic groups (Boyd et al., 2000; de Baar et al., 1990; Takeda, 1998). Further, the onshore-offshore gradient in pFe is much stronger and more exponential in character than for dFe (Fig. 8). If some of this pFe is labile, it could be recycled on biologically relevant time scales and contribute to the onshore high NCPO2Ar. \( F_v/F_m \) also shows decreases from onshore to offshore (Fig. 9). High \( F_v/F_m \) supports low Fe stress in the very near shore region especially in Marguerite Bay and near Palmer Station (Fig. 9). While this discussion has focused on meltwater-Fe relationships it is also important to note that sedimentary Fe sources may be important in this region (Sherrell et al., in preparation).

There is evidence of Fe limitation in the onshore regions (landward of grid station 100) as seen by a significant positive correlation between NCPO2Ar and \( F_v/F_m \) (Fig. 10c, \( n = 10, r^2 = 0.31, p = 0.09 \) including only nighttime \( F_v/F_m \) data, Fig. 10d, \( n = 66, r^2 = 0.11, p < 0.01 \) when including all \( F_v/F_m \) data). In these intermediate-status locations Fe and light may be co-limiting or limiting at different times in the growing season with bloom initiation in the spring dictated by stratification and light availability (Tortell et al., 2014; Venables et al., 2013) since Fe is generally replete in January in the coastal region (Sherrell et al., in preparation), but with the ultimate magnitude of the bloom and the timing of the decline linked to Fe availability. Self-shading induced light limitation, grazing pressure (Bernard et al., 2012;
Garzio and Steinberg, 2013) and community structure (Lin et al., submitted) are also likely key players in the bloom decline.

### 3.4. Interannual variability

On average in the Pal-LTER region, ice retreat in 2014 was 11.5 days later than in 2012 and 18.8 days later than in 2013. This later ice retreat is manifested in the form of colder, fresher surface waters with shallower and more stable mixed layers and higher sea-ice meltwater fractions. Average measured NCPO$_{2Ar}$ in 2014 was nearly double the rate in the previous two years. Production was particularly high in Marguerite Bay and near Palmer Station where it reached 413 mmol O$_2$ m$^{-2}$ d$^{-1}$. As documented by Tortell et al. (2015), NCPO$_{2Ar}$ was also this high in Marguerite Bay in January 2011, but it only reached ~140 mmol O$_2$ m$^{-2}$ d$^{-1}$ near Palmer Station at that time. Seasonal cycles of chlorophyll captured in time series sampling at two routinely sampled Pal-LTER sites near Palmer station show that the peak chlorophyll concentration occurred 15–30 days later in 2014 than it did in the 2012 and 2013 (Fig. 2). Peak chlorophyll concentration coincides with the ship sampling time in 2014 (though NCP might peak ~2 weeks later than chlorophyll (Tortell et al., 2014). It is possible that NCPO$_{2Ar}$ only appears highest in 2014 as a result of the bloom phenomenology and alignment with ship occupation. At RaTS, however, maximum chlorophyll concentration occurred at the same time or earlier than the previous years and the concentration had diminished by the time of ship sampling in mid-January. Therefore, timing does not appear to fully explain the observed interannual variability in NCPO$_{2Ar}$ in the southern onshore region. This is supported by satellite-derived NCP estimates that show the mean January NCP in the onshore grid regions of the WAP in 2014 was approximately double that observed in the previous two years (offshore magnitudes were comparable year-to-year). While timing is certainly an important consideration when interpreting our underway data, the $\tau_{O2}$NCPO$_{2Ar}$:$\Delta$NCPDIC comparison (see Section 3.2) also indicates that timing cannot entirely explain the interannual variability at the WAP. Also, the nearshore sampling locations at Palmer and Rothera Stations do not necessarily reflect bloom timing and magnitude on the sampling grid.

Enhanced stability due to high meltwater fractions is a probable driver of elevated NCP. Ice retreat occurs both by melting in situ, and from wind and ocean-driven sea-ice advection (Meredith et al., 2017, 2013) with important implications for regional water column stability. In 2014, winds were such that ice retreat occurred by melting in situ rather than net advection, resulting in more even sea-ice meltwater across the region (Meredith et al., 2017) and lower mean SSS across the Pal-LTER grid. There could have been a more widespread source of Fe from sea ice that was...
not yet depleted at the time of our sampling. Sea ice may act as mobile seasonal reservoir of Fe that is incorporated into the ice during formation in winter then released via meltwater in the spring and summer (Lannuzel et al., 2008; Sedwick and DiTullio, 1997). While dFe data are not available in all years, in 2012 sea-ice meltwater content is correlated with surface dFe ($n=48, r^2=0.4, p<0.0001$), supporting the notion that sea ice acts, at least to some extent, as an Fe delivery mechanism in this region. Fv/Fm data indicate reduced iron stress offshore in 2014 compared to 2012 and 2013. Additionally meteoric water content is high along the coast in 2014 relative to the previous years. Meteoric water is a combination of precipitation and glacial melt water, and both freshwater inputs would have stabilization effects, however glacial melt water would potentially represent a larger and more sustained Fe source.

3.5. Spatial variability

3.5.1. Ice retreat

As presented in our companion paper (Eveleth et al., 2017), biologically-produced (or biotic) oxygen and pCO$_2$ display variability on the same spatial scales as salinity, temperature and physical (abiotic) oxygen in the WAP (decorrelation length scale ~4.5 km) bolstering the conclusion that NCP$_{O_2}A$ spatial variability is controlled by physical spatial variability. Some spatial variability across the grid is likely a result of bloom stage at the time of sampling. Ice retreat in our sampling region, defined as the date when sea-ice concentration drops below 15% (Stammerjohn et al., 2008), occurred between 36 days before ship occupation at a given location and 85 days after. While days of open water prior to ship sampling is not significantly correlated to NCP$_{O_2}A$ magnitude at individual sampling points, perhaps because of the relatively low resolution of the satellite ice data, we note large-scale spatial patterns across the grid that are consistent with the well-known ice retreat-primary production progression (Fig. 11). Retreat occurred predominantly from offshore to onshore in 2012 and the NCP$_{O_2}A$ gradient in this direction is prominent. In 2013, ice retreated from north to south and we observe a strong N-S gradient in NCP$_{O_2}A$ with higher values in the southern grid region related to later ice retreat. In 2014, ice retreat was late across most of the region, and there was high NCP$_{O_2}A$ throughout the coastal region. We also note isolated very fresh regions (salinity ~30–32) in 2012 and 2014 that are likely recent freshwater melt lenses that have not yet had time to develop blooms and NCP$_{O_2}A$ is near zero (Fig. S6). As discussed above, while timing is an important consideration, it likely does not fully describe the documented spatial variability. Rather than phenology, the large-scale spatial patterns in NCP$_{O_2}A$ could be a function of sea ice-driven water column stability and/or Fe injection at the site of sea-ice melt (Boyd and Ellwood, 2010; Lannuzel et al., 2008) (See maps of all data Fig. S7).

3.5.2. Canyons

Much attention in the current WAP literature has been paid to productivity at canyon hotspots (Ducklow et al., 2013; Kavanaugh et al., 2015; Oliver et al., 2013; Prezelin et al., 2000; Schofield et al., 2013). Near the 600, 400 and 200 gridlines major penguin breeding colonies on Anvers Island, Renaud Island, and Avian Island have been shown to be co-located with high chlorophyll and krill concentrations and deep cross-shelf cutting canyons (Kavanaugh et al., 2015; Schofield et al., 2013; Smith et al., 1998). By visual inspection, NCP$_{O_2}A$ rates near the canyons also appear elevated relative to the rest of the coastal region. Though this is difficult to show statistically here, it can additionally be seen in the satellite-derived annual NCP$_{O_2}A$ climatology (Li et al., in press). Canyons are believed to act as conduits for the UCDW that carries heat and macro- and micro-nutrients to the near shore region (e.g. Kavanaugh et al., 2015; Martinson et al., 2008; Prezelin et al., 2000; Schofield et al., 2013). The relatively high SST over the canyons is linked to shallower mixed layer depths and localized earlier ice retreat (as seen in 2014, Fig. 11) and longer growing seasons (Kavanaugh et al., 2015). UCDW might pick up additional sedimentary-sourced Fe as it travels across the shelf (Marsay et al., 2014). When these waters obduct to the surface layer, as suggested by the elevated SST (Kavanaugh et al., 2015) and observed

![Fig. 11. Ice retreat for 2012 (left), 2013 (middle) and 2014 (right) in year day defined as the number of days since the previous year's sea ice minimum (~Feb 15). For example, the left plot shows the number of days since Feb 15, 2011 and thus the relevant ice retreat for the 2012 sampling cruise. NCP$_{O_2}A$ (mmol O$_2$ m$^{-2}$ d$^{-1}$) overlaid in gray scale.](image-url)
upwelling from glider transects near Palmer Deep (Schofield et al., 2013), they would likely deliver enhanced concentrations of micronutrients including Fe. Although not conclusive, surface pFe and dMn are elevated in Marguerite Bay (onshore 200 line) and near Palmer Station (onshore 600 line) relative to other coastal areas in 2012. Ongoing horizontal and vertical trace metal surveys being conducted as part of the Pal-LTER program will elucidate Fe supply mechanisms in the WAP including the possible role of canyons as conduits for limiting nutrients.

4. Conclusions

In the austral summers of 2012-2014, the Pal-LTER grid region of the WAP was a net carbon sink with particularly high NCP in the coastal region and at hotspots associated with submarine canyons. Sea ice appears to be an important driver of NCPozoa, likely by stabilizing the summer mixed layer via meltwater input and limiting deep wind-driven winter mixing, and serving as transient Fe storage with seasonal delivery. Meteoric water, both glacial meltwater and precipitation, also acts as a stabilizing force in the region, particularly where input is high along the coast. Glacial meltwater may also be an important source of Fe to the region. Fe stress is widespread in the offshore region, farthest from this meltwater Fe source. In the near coastal zone, Fe stress is low thus high and variable NCPozoa in coastal waters is more related to mixed layer stratification as it controls both light availability and timing. Further from the coast but still on the shelf (~gridlines 20 to 100) we see local indications of both Fe and light limitation.

Controls on summer NCPozoa, are closely tied to sea ice and glacial melt, both of which are changing in the rapidly warming climate (Meredith et al., 2013; Stammerjohn et al., 2008; Vaughan, 2006). If sea ice continues its current trend and melts earlier in the spring, surface water would be exposed to stronger winds and deeper mixing, assuming the winds were strong enough to overcome otherwise warmer more defined surface layers due to increased solar heating. This may distribute the meltwater over a greater depth range, and also promote advection away from input locations (Meredith et al., 2017; Venables et al., 2013). Physical wind mixing and reduction in surface meltwater would both weaken summer stratification, perhaps increasing light limitation but potentially increasing upward mixing of Fe-rich subsurface water. Deeper mixing and weaker stratification due to early sea ice retreat may be countered by enhanced glacial melt water input along the coast (Vaughan, 2006). This melt water may also enhance Fe input and relieve micronutrient limitation onshore. With the multitude of processes involved, it remains challenging to predict how NCP might respond to these potential changes in the WAP and other areas of current and expected future warming in both polar regions. However, given the observed connections with meltwater, stratification and Fe we expect NCP to be sensitive to the changing climate and ongoing sustained observation programs, such as Pal-LTER and RaTS, and high-spatial resolution measurements are critical to developing the needed understanding.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.dsr2.2016.07.016.

References


