Physical and Biological Drivers of Biogeochemical Tracers Within the Seasonal Sea Ice Zone of the Southern Ocean From Profiling Floats

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Abstract Here we present initial findings from nine profiling floats equipped with pH, O2, NO3, and other biogeochemical sensors that were deployed in the seasonal ice zone (SIZ) of the Southern Ocean in 2014 and 2015 through the Southern Ocean Carbon and Climate Observations and Modelling (SOCCOM) project. A large springtime phytoplankton bloom was observed that coincided with sea ice melt for all nine floats. We argue this bloom results from a shoaling of the mixed layer depth, increased vertical stability, and enhanced nutrient and light availability as the sea ice melts. This interpretation is supported by the absence of a springtime bloom when one of the floats left the SIZ in the second year of observations. During the sea ice covered period, net heterotrophic conditions were observed. The rate of uptake of O2 and release of dissolved inorganic carbon (derived from pH and estimated total alkalinity) and NO3 is reminiscent of biogeochemical respiration and is nearly Redfieldian for the nine floats. A simple model of mixed layer physics was developed to separate the physical and biological components of the signal in pH and O2 over one annual cycle for a float in the Ross Sea SIZ. The resulting annual net community production suggests that seasonal respiration during the ice covered period of the year nearly balances the production in the euphotic layer of up to 5 mol C m−2 during the ice free period leading to a net of near zero carbon exported to depth for this one float.

1. Introduction

Sea ice cover has strong influence on the air-sea gas exchange, vertical stability, and biological production, which are critical to understanding the Southern Ocean’s central role in oceanic biogeochemical cycling, heat, and carbon uptake under a changing climate (Delille et al., 2014; Majkut et al., 2014). For example, the Southern Ocean is responsible for up to 50% of the ocean’s uptake of human induced carbon dioxide (CO2) emissions (Khatiwala et al., 2009; Majkut et al., 2014; Sabine et al., 2004). However, there is great uncertainty and disagreement between models over the regional variability in the sign and magnitude of CO2 exchange due to the combination of natural and anthropogenic CO2 contributions (Gruber et al., 2009).

The upper ocean carbon cycle is governed by a combination of physical and biological processes. The biological carbon pump involves photosynthetic production of organic carbon within the euphotic layer of the upper ocean and removal of CO2 from direct contact with the atmosphere (Volk & Hoffert, 1985). A fraction of the organic carbon is exported to the interior of the ocean where it is respired to CO2 and remains sequestered for weeks to millions of years. Physical processes such as upwelling can bring these CO2 rich waters back up in contact with the atmosphere. In regions of sea ice cover, CO2 uptake can also be driven by brine rejection during ice formation through the sinking of carbon rich brine, gas exchange can be inhibited during ice cover, CO2 depleted ice melt enhances gas exchange, and ice enhanced biological production may increase CO2 uptake (Delille et al., 2014; Rysgaard et al., 2011). However, the relative influence of physical versus biological processes in this hard-to-study region is poorly understood due to limited observations particularly in the seasonal ice zone where substantial biological activity is known to occur (Eveleth et al., 2016; Li et al., 2016; Shadwick et al., 2014, 2015; Smith & Nelson, 1986; Tortell et al., 2015).

Large phytoplankton blooms have been observed at ice edges in high latitude regions (Arrigo & van Dijken, 2003, 2004). Springtime sea ice melt stratifies the upper water column, i.e., that sea-ice mainly consists of
freshwater which strongly lowers the surface ocean salinity when it melts and as the density stratification in this region is mainly determined by salinity, it has profound effects on the density stratification (Haumann et al., 2016). This increased stratification causes the depth of the surface mixed layer to shoal which in turn promotes conditions that trigger a phytoplankton bloom following Sverdrup’s hypothesis where greater density of phytoplankton is within the euphotic zone (Smith & Nelson, 1986; Sverdrup, 1953). Other factors affecting the timing or magnitude of an ice edge phytoplankton bloom include release of iron and nutrients stored in ice upon ice melt (Lannuzel et al., 2016) as well as wind forcing (Fitch & Moore, 2007) and thermal convection (Ferrari et al., 2015).

Profiling floats equipped with oxygen (O$_2$) and nitrate (NO$_3$) sensors have been valuable in quantifying marine biogeochemical processes over multiyear time scales (Bushinsky & Emerson, 2015; Hennon et al., 2016; Johnson et al., 2010; Juranek et al., 2011; Martz et al., 2008; Plant et al., 2016). As organic matter is broken down into inorganic matter (mineralization) or inorganic matter is transformed into organics (production), a constant stoichiometry is observed between elemental carbon, nitrogen, and oxygen, known as the Redfield ratio, where C:N:O = 106:16:138–150 (Anderson & Sarmiento, 1994). These ratios are derived from the average composition of organic matter and can vary depending on the phytoplankton community structure (Li & Peng, 2002). Estimates of net primary production (NPP), net community production (NCP), and export production (EP) from O$_2$ or NO$_3$ data rely on these Redfield relationships to convert reported rates into carbon.

Through the Southern Ocean Carbon and Climate Observations and Modelling (SOCCOM) project, approximately 200 profiling floats equipped with O$_2$, pH, NO$_3$, and bio-optical sensors are being deployed in the Southern Ocean. These “Biogeochemical-Argo” (BGC-Argo) floats provide biogeochemical observations during the austral winter and under sea ice, a region that has been inaccessible with traditional platforms. Here we present analyses from the first set of SOCCOM floats deployed within the seasonal ice zone (SIZ) in the Pacific and Atlantic sectors of the Southern Ocean. The relative influence of physical (e.g., mixing and air-sea gas exchange) and biological (e.g., production and respiration) drivers of the carbonate system, O$_2$, and NO$_3$ within the upper ocean are explored during the phases of ice formation, ice cover, and ice melt over a seasonal cycle. In the first and second parts of the manuscript, profiling float observations are used directly to give a qualitative description of the physical and biological processes that occur through the annual cycle in the seasonal ice zone and to quantify remineralization during the period of full ice cover when biological processes dominate the signal over physical drivers. In the third part, a model is adapted to separate the physical from the biological processes over the course of the annual cycle when physical processes cannot be approximated small or negligible.

2. Methods

2.1. BGC-Argo Float Information and Locations

Nine SOCCOM profiling floats deployed in the SIZ between March 2014 and January 2015, observed at least one full annual cycle within the SIZ of the Southern Ocean (Figure 1 and Table 1). As shown in Table 1, most of these floats were equipped with a Deep-Sea DuraFET pH sensor (Johnson et al., 2016; Martz et al., 2010), Aanderaa oxygen optode (Johnson et al., 2015; Tengberg et al., 2006), ISUS nitrate sensor (Johnson et al., 2013), and other bio-optical sensors including chlorophyll a (Chl a) fluorescence and backscatter (Boss et al., 2008). The initial accuracy of the biogeochemical sensor suite is 2 $\mu$mol/kg for oxygen, 1 $\mu$mol/kg for nitrate, and 0.01 for pH. Quality-controlled float data were downloaded from the SOCCOMViz data portal (http://soccom.princeton.edu/soccomviz.php) and no additional adjustments were applied to the data (Williams et al., 2016). Please refer to Johnson et al. (2017) for a detailed summary of sensor calibration and data quality.

Argo and BGC-Argo floats are programmed to profile from 2,000 m to the surface once every 10 days (from a nominal park depth of 1,000 m). Temperature, salinity, pH, O$_2$, NO$_3$, and Chl a fluorescence

Figure 1. Location of SOCCOM floats deployed in the Pacific (2014) and Atlantic (2014/2015) sectors of the Southern Ocean within the seasonal ice zone. Black dots indicate last position as of April 2016 and red dots indicate the float trajectory.
are directly measured. Total alkalinity (TA) is estimated from float temperature, salinity, and O$_2$ using the Linearly Interpolated Alkalinity Regression (LIAR) algorithm (Carter et al., 2016), and these estimated values are made available through the SOCCOM float data repository. Dissolved inorganic carbon (DIC) is then derived from pH and estimated TA. The estimated uncertainty in TA using the LIAR algorithm with inputs of T, S, and O$_2$ is $6.5 \pm 6$ for the global ocean, which translates to an uncertainty in DIC of approximately $6 \pm 10$ $\mu$mol kg$^{-1}$ when computed with float pH with an uncertainty of 0.01. The mixed layer depth (MLD) is defined here as the depth at which potential density ($\rho_h$) changes from the surface by 0.05 kg m$^{-3}$, chosen from visually inspecting individual profiles (see Figure 2; Dong et al., 2008). Chl $\alpha$ was derived from fluorescence data (Boss & Haëntjens, 2016) and is used only qualitatively.

Floats deployed in the SIZ are equipped with sea ice avoidance software in order to protect the sensors from colliding with ice at the surface. When the float measures a temperature below a given threshold near the surface (~20 m) indicative of ice, the float immediately descends to the park depth. The float continues to cycle without surfacing until two consecutive measurements are above the threshold temperature at which point the float surfaces and transmits its data via satellite. Because the float is not surfaced during the under-ice period, the coordinates of the float are unknown. The position of the float is then estimated by linearly interpolating between its last and first known positions. The temperature threshold criterion is only an indicator of ice and gives no information on the sea ice cover or thickness. We used satellite-derived sea ice concentration (Meier et al., 2016) to estimate the sea ice cover at the float locations.

Table 1

<table>
<thead>
<tr>
<th>Float ID</th>
<th>Deployment date</th>
<th>Initial coordinates</th>
<th>O$_2$</th>
<th>pH</th>
<th>NO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5904180</td>
<td>3/31/2014</td>
<td>67°S, 156°W</td>
<td>+</td>
<td>−</td>
<td>+</td>
</tr>
<tr>
<td>5904183</td>
<td>4/1/2014</td>
<td>67°S, 150°W</td>
<td>+</td>
<td>−</td>
<td>±</td>
</tr>
<tr>
<td>5904184</td>
<td>4/3/2014</td>
<td>64°S, 150°W</td>
<td>+</td>
<td>+</td>
<td>±</td>
</tr>
<tr>
<td>5904182</td>
<td>4/10/2014</td>
<td>66°S, 162°W</td>
<td>+</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>5904467</td>
<td>12/14/2014</td>
<td>60°S, 0°E</td>
<td>+</td>
<td>−</td>
<td>±</td>
</tr>
<tr>
<td>5904471</td>
<td>12/21/2014</td>
<td>67°S, 0°E</td>
<td>±</td>
<td>±</td>
<td>+</td>
</tr>
<tr>
<td>5904472</td>
<td>1/18/2015</td>
<td>68°S, 2°W</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>5904468</td>
<td>1/19/2015</td>
<td>66°S, 0°E</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>5904397</td>
<td>1/22/2015</td>
<td>61°S, 0°E</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Note. Sensors marked (+) are onboard and fully operational, (−) not onboard, and (∓) onboard but data have been flagged poor.

Figure 2. Contour plots of in situ O$_2$, T, S, and $\rho_h$ for Ross Sea float 5904184 deployed in April 2014, over a 22 month period showing one season with near complete sea ice cover and one season with patchy to no ice cover. Black dots at the surface indicate when the float did not surface. The black line indicates the MLD. Fractional ice concentration, derived from satellite data, is shown in the top panels where 0 is no ice cover and 1 is complete cover.
Float 5904184, deployed April 2014 in the northern Ross Sea in the Pacific sector of the Southern Ocean (Table 1), is the central focus of this study because it displayed a very clean signal under ice and has pH and O₂ sensors. This float was in the SIZ for one annual cycle; the next year the float skirted the ice edge and never went under complete ice cover (see supporting information Movie MS01), which serves as a useful comparison for the influence of sea ice on the underlying ocean physical and biogeochemical processes. Unfortunately, the NO₃ sensor on this float became biofouled and the NO₃ data are flagged poor.

2.2. Under-Ice Remineralization Rates

O₂, NO₃, and DIC inventories were calculated for the under sea ice period (indicated by the ice avoidance software) for seven of the nine floats by integrating the surface (20 m) to 300 m depth range. This range of depth was chosen based on the observation that seven of the floats in this analysis returned no significant temporal changes in density below 300 m. Integrating below the MLD to flat isopycnals was done to minimize effects of vertical processes such as entrainment, detrainment, and advective transport in an attempt to best conserve the biogeochemical tracers. Floats 5904468 and 5904471 in the Atlantic sector, however, did not have constant isopycnals over time at depth and the inventories were calculated by integrating down to 70 m where a potentially clearer remineralization signal was observed for these two floats rather than primarily a physical signal.

Remineralization rates were then calculated from the slopes in O₂, NO₃, and DIC inventories using linear regression analysis during the period of ice cover. The elemental ratio of C:N:O was then computed from the remineralization rates. It was assumed that ice cover acted as a cap between the ocean and atmosphere such that air-sea gas exchange was negligible for ice concentration greater than 70% (Butterworth & Miller, 2016). The first and last 2–3 under-ice profiles were removed from the fit based on visual inspection of the surface O₂ and temperature because of the conservative nature of the ice avoidance software and hence likelihood of little to no ice cover.

In an effort to apply the same treatment across the floats, caution was taken to integrate to a depth greater than the deepest MLD of the suite of floats where flat isopycnals were observed with the exception of floats 5904468 and 5904471. When building the inventories, sensitivity to integration depth did not affect the resultant remineralization rates between 200 and 300 m. Integrating down to the MLD seemed to provide a similar result but increased noise in the signal.

2.3. One-Dimensional Physical Mixed Layer Model

In an attempt to separate the biological and physical changes captured in the observations, a simple one-dimensional bulk mixed layer model of the top 300 m was used to simulate the physical component of the signal. The residual of the float observations minus the physical model output is then estimated to be the biological component assuming horizontal fluxes are small:

\[ \text{float data} - \text{physical output} = \text{biological component} \]  

This model is forced from the surface and any contribution due to intrusion of tracers from below 300 m as well as horizontal fluxes and errors in simulating the physical processes would appear in the residual interpreted as the biological component.

Expanding upon work by Plant et al. (2016), the Price-Weller-Pinkel (PWP) model of mixed layer physics (Price et al., 1986) was modified to include air-sea gas exchange of O₂ and CO₂, ice formation and melt, and biogeochemical tracers including O₂, NO₃, DIC, and TA (Baehr & DeGrandpre, 2004; Glover et al., 2011; Martz et al., 2008). Biological processes were not incorporated into the model and the biogeochemical tracers were treated as biologically inert. Plant et al. (2016) were followed directly with the exception of using Liang et al. (2013) for gas exchange parameterization, tuning the vertical eddy diffusivity coefficient, \( K_z \), for the Southern Ocean, integrating a simplified ice production model, and adding additional biogeochemical tracers (DIC, TA, and pCO₂). (Please refer to Plant et al. (2016) for a more detailed description of the model.) This analysis was an initial test to see if PWP can be applied to under-ice regions with profiling float observations; the model was specifically tuned for Ross Sea float 5904184 and only applied to this one float.

A simple thermodynamic ice production model was implemented by creating ice when the surface temperature fell below the freezing point of the surface seawater. Following Hyatt (2006), equation (2) is used to calculate \( F_i \), the rate at which ice is created. \( F_i \) is then used to solve for the salt flux (\( \Delta S / \Delta t \)) into the surface.
ocean in equation (3), where \( c_p \) is the specific heat of seawater (4,183.3 J/kg°C), \( L_f \) is the latent heat of fusion of sea ice (333 kJ/kg), \( T_{frz} \) is the freezing point of seawater, \( T_{surf} \) is the surface temperature, \( \rho_o \) (1,024 kg m\(^{-3}\)) and \( \rho_i \) (920 kg m\(^{-3}\)) refer to the density of seawater and ice, respectively, \( S_{surf} \) is the surface salinity, \( S_{ice} \) is set to 4, and \( \Delta z \) is the vertical change in depth. The surface temperature is set to \( T_{frz} \) plus a fraction of the surface heat flux into the ocean on the next time step.

\[
\rho_i L_f F_i = \rho_o c_p \frac{\Delta T}{\Delta t} T_{frz} - T_{surf} \Delta z \tag{2}
\]

\[
\frac{\Delta S}{\Delta t} = F_i (S_{surf} - S_{ice})/\Delta z \tag{3}
\]

To account for ice melt, an influx of fresh water was supplied to the surface to best fit the observations during the austral spring. The equations used by Hyatt (2006) describe ice formation only (not melting). Due to our perceived difficulty in using a model to predict the onset of melting, we chose to add an influx of fresh water to best fit the observed salinity data during the austral spring. This approach could have been used to describe ice formation with little consequence to biogeochemical model results and, due to its simplicity, may be the preferred choice in future versions of under-ice models for SOCCOM float data. More complex thermodynamic ice models exist, for example Maykut and Untersteiner (1971), however, this simple ice production model is believed to capture the essential components of ice production and corresponding brine rejection on shorter time scales relevant to this study.

During the period of ice cover, air-sea gas exchange was neglected for ice concentrations greater than 70% and the effective air-sea gas transfer velocity \( \left( k_{air} \right) \) was scaled linearly to the open ocean value for ice cover from 0 to 70% (Butterworth & Miller, 2016). The momentum imparted by the wind and heat fluxes were partitioned between the ice and the ocean. During the entire under-ice period, wind momentum and heat fluxes were reduced by a single factor to qualitatively best fit the data under the ice (reduced by 45% and 50%, respectively). During ice melt and ice formation as well as precipitation and evaporation, all tracers were diluted or concentrated correspondingly (see supporting information Figure S4). A similar approach was taken by Baehr and DeGrandpre (2004) to evaluate under-ice CO\(_2\) observations in a lake by adding ice to the PWP model; however, all air-sea gas exchange and wind momentum were turned off during ice cover in their approach.

The top 300 m profiling float data were interpolated onto a 1 m spaced vertical grid and the surface was assumed homogenous between the surface most measurement to 0 m. The model was initialized with each profile and driven by 6 h heat flux, winds, and net atmospheric freshwater flux data from the NCEP/NCAR Reanalysis at the float location (Kalnay et al., 1996). Two-dimensional vertical advection was accounted for following Plant et al. (2016). Four times daily wind stress curl data were obtained from the Environmental Research Division (ERD) of NOAA through their web site at http://las.pfeg.noaa.gov/thredds/dodsC/Model/FNMOC/ to compute upwelling velocities. The wind stress curl was calculated by ERD from analyzed fields of sea level pressure from the Fleet Numerical Meteorology and Oceanography Center (http://www.usno.navy.mil/FNMOC). As outlined in Plant et al. (2016), Ekman depth and vertical velocity attenuation were calculated following the approach of Signorini et al. (2001).

The model was then tuned by adjusting the background vertical eddy diffusivity, \( K_v \), from 1 to 20 \( \times 10^{-5} \) m\(^2\) s\(^{-1}\). Heat and salt offsets and a wind scaling factor were also optimized to minimize the residual between float and model temperature, salinity, and MLD (see supporting information Figures S4–S6). (Please refer to Glover et al. (2011) for a detailed description of the effect of adjusting these tuning parameters on model output.) All tuning parameters are time invariant and intend to remove the mean bias in order to capture the temporal seasonal variability which is not being tuned. The ability of the tuned model to reproduce the physical processes was assessed by initializing the model with only the first profile and running the model out over 1 year. The tuned model was then run reinitializing with each profile and the NCP at each depth was calculated by subtracting the model output from the float data using O\(_2\) and DIC. The remineralization ratio determined during the under-ice period was used to convert O\(_2\) into carbon. Sea-
2.4. Advective Processes

The magnitude of O2 changes from divergence of vertical and horizontal advection was estimated in order to validate the claim that biological processes dominate the signal during the under sea ice period and to assess the validity of some of the assumptions in using a 1-D vertical model. The observed signal in O2 and other biogeochemical tracers is the sum of a biological term and physical processes including advection. The advection term, shown in equation (4), is the sum of a vertical component where $w$ is the Ekman velocity and a horizontal component in the $x$ and $y$ directions with $u$ and $v$ as the corresponding horizontal velocities.

$$ADV = -w \frac{dO_2}{dz} - \left( u \frac{dO_2}{dx} + v \frac{dO_2}{dy} \right)$$  

Horizontal O2 gradients are estimated using O2 values from World Ocean Atlas 2013 (WOA13) (Garcia et al., 2014). The gradient of O2 along the $x$ and $y$ planes was computed for the upper 300 m at the mean location for float 5904184 over 6° spacing in longitude ($x$) and latitude ($y$). While WOA13 fields are smooth, we expect the missing high wavenumber structure to not result in a mean bias of oxygen change over the year. In other words, the missing eddy contribution is expected to be multidirectional, and thus unlike the one directional decrease in O2 in the austral winter and increase in the austral spring that we observe. Horizontal velocities ($u$ and $v$) were estimated to be 0.01 m s$^{-1}$ which is likely an overestimate when considering the float is quasi Lagrangian with a mean velocity of 0.01 m s$^{-1}$ over 1 year. The mean horizontal advective contribution over the top 300 m was estimated to be 12 mmol O2 m$^{-2}$ d$^{-1}$ compared to the observed signal of 52 mmol O2 m$^{-2}$ d$^{-1}$. This corresponds to an upper bound of horizontal advective flux divergence accounting for up to 23% of the observed signal.

The Ekman velocity was computed using the ERA-Interim reanalysis product (Dee et al., 2011) for all nine floats and ranged from $1 \times 10^{-6}$ m s$^{-1}$ for the floats in the Atlantic sector and $2 \times 10^{-7}$ to $5 \times 10^{-8}$ m s$^{-1}$ for floats in the Pacific sector of the Southern Ocean. Vertical advection at the base of 300 m is estimated to account for 2 mmol O2 m$^{-2}$ d$^{-1}$ compared to the observed signal of 52 mmol O2 m$^{-2}$ d$^{-1}$ for float 5904184 which is only 3% of the observed signal. This is also an upper bound because much of the Ekman
velocity would diminish by 300 m. For the floats in the Atlantic sector, vertical advection may play a greater role because the Ekman velocities are an order of magnitude greater in this region. The estimated upper bound of the role of both vertical and horizontal advection is 14 mmol O$_2$ m$^{-2}$ d$^{-1}$ or 27% of the observed signal for float 5904184.

3. Results

3.1. Seasonal Ice Zone Cycle

Physical and biogeochemical contour plots for Ross Sea float 5904184 are shown in Figures 2 and 3, demonstrating a typical seasonal cycle of float data in the SIZ. Note that the second winter shown in the record had only partial ice cover and is thus not as representative of the SIZ but is instructive for observing the significance of sea ice influence on physical and biogeochemical processes. As austral winter approaches, the temperature drops and ice begins to form. Oxygen concentration increases to retain saturation as the water temperature drops, and salinity increases due to brine rejection. Increase in salinity could also be due to deepening of the MLD and mixing with higher saline deep water. Salt inventories computed down to flat isopycnals (300 m) during the onset of ice cover, however, suggest an increase of salinity due to brine rejection. Vertical advection, addressed in section 2.4, is estimated to account for 3% of the observed change in O$_2$ for float 5908184. This suggests vertical advection only plays a minor role for the upper 300 m in this region. During the period of ice cover, oxygen is drawn down and pH decreases due to biological respiration. As austral spring approaches, the surface temperature warms and the ice begins to melt. Freshening due to ice melt stratifies the upper water column at the ice edge causing the MLD to shoal from 100 to 50 m. During sea ice melting at the ice edge, a phytoplankton bloom is observed in Chl a data, with a corresponding increase in pH and O$_2$ supersaturation consistent with biological production.

3.2. Remineralization Ratios During the Sea Ice Covered Period

The O$_2$ and DIC inventories for the first annual cycle of float 5904184 are shown in Figure 4. The float did not surface between early June and early December; however, ice formation appears to have begun by early July and melt had begun by early November. The decrease in O$_2$ and corresponding increase in DIC during the under sea ice period is attributed to remineralization. At the ice melt edge in December, the drawdown of DIC and increase in O$_2$ are due to a combination of biological production and physical processes such as gas exchange. It is estimated from satellite data that all floats in this study experienced nearly complete ice cover over the duration of one austral winter (see supporting information Movies MS01 and MS02). The remineralization rates are calculated for all the floats in this study and goodness of fit ($R^2$) as well as the C:N:O ratios and are listed in Table 2 (see supporting information Figures S1–S3 for the remaining float inventories). In cases where no pH sensor was available, ratios have been reported as N:O. Near-Redfieldian remineralization ratios (106:18:275$^{\pm}$95) were observed for several of the floats; however, there was in all cases but one (float 5904180) greater consumption of oxygen relative to production of DIC and NO$_3$ compared to the theoretical Redfield ratio. The mean ratio of C:N:O is 106:18:285$^{\pm}$104 and N:O is 16:276$^{\pm}$95.

3.3. Model Output and NCP

Surface T, S, $\sigma_{\circ}$, and MLD model output versus surface float data are shown in Figure 5 for the model initialized with only the first profile over 1 year beginning in April 2014, for float 5904184. The model was

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Table 2

<table>
<thead>
<tr>
<th>Float</th>
<th>DIC</th>
<th>NO$_3$</th>
<th>O$_2$</th>
<th>C:N:O</th>
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<tbody>
<tr>
<td>Pacific</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>5904184</td>
<td>27.0 (0.94)</td>
<td>s/f</td>
<td>52.0 (0.98)</td>
<td>106:204</td>
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<td>1.7 (0.66)</td>
<td>16.6 (0.80)</td>
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<td>s/f</td>
<td>25.2 (0.77)</td>
<td>n/a</td>
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<td>5904182</td>
<td>n/a</td>
<td>n/a</td>
<td>15.3 (0.61)</td>
<td>n/a</td>
</tr>
<tr>
<td>Atlantic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5904468*</td>
<td>3.4 (0.71)</td>
<td>0.65 (0.91)</td>
<td>8.7 (0.79)</td>
<td>106:20271</td>
</tr>
<tr>
<td>5904472</td>
<td>6.8 (0.26)</td>
<td>0.96 (0.86)</td>
<td>15.5 (0.81)</td>
<td>106:15:242</td>
</tr>
<tr>
<td>5904397</td>
<td>9.2 (0.63)</td>
<td>1.8 (0.85)</td>
<td>36.8 (0.82)</td>
<td>106:20:424</td>
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<tr>
<td>5904467</td>
<td>n/a</td>
<td>1.6 (0.76)</td>
<td>45.6 (0.82)</td>
<td>16:456</td>
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<tr>
<td>5904471*</td>
<td>s/f</td>
<td>0.5 (0.84)</td>
<td>7.7 (0.43)</td>
<td>16:246</td>
</tr>
<tr>
<td>Redfield</td>
<td></td>
<td></td>
<td></td>
<td>106:16:150</td>
</tr>
</tbody>
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*Note. Rates for floats 5904468 and 5904471 (marked *) were computed down to 70 m. s/f indicates the sensors flagged with poor data.
then reinitialized with each profile using similar tuning parameters in further optimizing the model. Optimal tuning parameters were determined to be $250 \text{ W m}^{-2}$ heat offset, 0 salt offset, and a 1.1 wind scaling factor. Table 3 lists the RMS error in the model output from physical observations (T, S, $\rho$, and MLD) for values of $K_z$ ranging from 1 to $20 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. A cost function, 

$$J(K_z) = \sum (T_{\text{model}} - T_{\text{obs}})^2 E_T^{-1} + (S_{\text{model}} - S_{\text{obs}})^2 E_S^{-1} + (\text{MLD}_{\text{model}} - \text{MLD}_{\text{obs}})^2 E_M^{-1}$$

was used to determine an optimal $K_z$ for float 5904184. $E_T$, $E_S$, and $E_M$ were taken as 0.7 times the standard deviation of $T_{\text{obs}}$, $S_{\text{obs}}$, and MLD respectively, which assumes the model is able to fit 51% of the variance in observed T, S, and MLD. An ensemble of five model runs were used to determine an optimal value of $K_z = 5 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. The values of $J(K_z)$ imply the likelihood that $K_z$ is optimal, and weighting the ensemble members by exp($-J$) and taking the second moment gives an uncertainty for our estimate of $K_z$ of $7 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$.

The seasonal cycle of NCP is shown in Figure 6 where net respiration is observed for half the year during sea ice cover and the springtime bloom dominates the production signal. Table 4 lists the seasonal NCP computed during the austral winter (under-ice) and austral summer (ice free) periods of the year (2014/2015) by integrating the NCP rate profiles from the surface to various depths as well as from 100 to 300 m. The seasonal NCP during the ice free period is $1.5$ and $3.6 \text{ mol C m}^{-2}$ and the seasonal NCP during the under sea ice period is $2.4$ and $3.2 \text{ mol C m}^{-2}$ derived from O2 and DIC, respectively, where O2 was translated to carbon using the remineralization ratio determined during the under-ice period of $C:O = 106:204$. Differences in NCP derived from O2 and DIC may be due to error in the gas exchange parameterization of O2 versus CO2 error in DIC derived from pH and estimated TA, and error in the ratio of C:O. NCP computed from O2, which is directly measured, is a more reliable estimate rather than from CO2, a derived variable; however, the faster rate of O2 gas exchange leads to greater error in the parameterization of O2 exchange compared to CO2.

From the seasonal cycle of NCP derived from observations minus model (Figure 6), four distinct regimes are observed in biological productivity and respiration. In the austral fall just prior to ice formation,
there is little net production. Then in winter, during the under-ice period there is low production and respiration dominates (negative NCP). In the austral spring, ice melt gives way to an intense ice edge phytoplankton bloom (Figure 3d) and high productivity is captured by the observations minus model in both O2 and DIC (positive NCP). After the bloom, productivity drops and the net biological activity (ANCP) balances to near zero in the euphotic layer suggesting near zero export production.

The mean annual NCP (ANCP) derived from O2 and DIC is shown in Figure 7. There is respiration below 100 m that tapers to zero following particle attenuation with depth. The model generated values for gas exchange near zero with an influx of 8 mmol CO2 m$^{-2}$ yr$^{-1}$ and 1.1 mmol O2 m$^{-2}$ yr$^{-1}$ over the annual cycle. Gas flux was set to zero for a portion of the year due to near complete ice cover (>70%) and gas flux estimates from profiling floats are the subject of ongoing work (Williams et al., 2017). During this time of zero gas flux, CO2 produced through the remineralization of organic material cannot escape to the atmosphere. Then in the spring when the sea ice opens up, biological production draws this CO2 down leading to reduced outgassing of CO2 over the annual cycle.

Multiple approaches were taken to estimate error in modeled NCP. An estimate of error was determined to be 14 mmol C m$^{-2}$ d$^{-1}$ by taking the RMS difference of the estimated NCP time series integrated down to the base of the estimated euphotic depth (75 m) derived from DIC versus O2 (Figure 6). This difference in NCP predominantly represents error in the gas exchange parameterization between O2 and CO2. The estimated error in DIC derived from pH data and the TA algorithm is roughly 10 $\mu$mol kg$^{-1}$. By introducing an offset in DIC of 10 $\mu$mol kg$^{-1}$, the model output of ANCP ranges from ±1.3 mmol C m$^{-2}$ yr$^{-1}$.

4. Discussion

4.1. Parsing the Seasonal Cycle

Float 5904184 appeared to go under complete ice cover during its first year (2014). However, even though the float did not surface for a few profiles the next year (2015), temperature, salinity, and O2 as well as satellite data indicate patchy or negligible ice cover. This demonstrates the conservative nature of the ice avoidance software in predicting ice, which is essential for prolonging the life of the float in the SIZ. Without the support of the sea ice edge processes (i.e., shoaling of the MLD, increased vertical stability, and timing of nutrient availability with light throughput as ice melts), a springtime phytoplankton bloom was not observed the second year. There does appear to be a relation between the timing of ice melt and initiation of the phytoplankton bloom in the SIZ. The vertical extent of the bloom observed from O2, pH, and Chl a data, as well as derived DIC and in NO$^-3$ where available, follows the MLD and is initiated concurrently with the shoaling of the MLD upon ice melt (Figure 3).

### Table 4

<table>
<thead>
<tr>
<th>Depth</th>
<th>Summer O2 mol C m$^{-2}$</th>
<th>Summer DIC mol m$^{-2}$</th>
<th>Winter O2 mol C m$^{-2}$</th>
<th>Winter DIC mol m$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.6</td>
<td>0.7</td>
<td>−3.9</td>
<td>−0.8</td>
</tr>
<tr>
<td>75</td>
<td>3.6</td>
<td>0.8</td>
<td>−3.2</td>
<td>−1.2</td>
</tr>
<tr>
<td>100</td>
<td>5.0</td>
<td>2.7</td>
<td>0.2</td>
<td>−0.7</td>
</tr>
<tr>
<td>300</td>
<td>2.6</td>
<td>1.4</td>
<td>−3.9</td>
<td>−4.8</td>
</tr>
<tr>
<td>100–300</td>
<td>−2.4</td>
<td>−1.2</td>
<td>−3.9</td>
<td>−4.1</td>
</tr>
</tbody>
</table>

4.2. Under-Ice Remineralization

A very clear remineralization signal ($R^2 > 0.7$) was observed for several of the floats, in particular for float 5904184. In the absence of sea ice cover, the oxygen concentration would have typically increased in order to maintain saturation near 100% as surface water temperature decreases. Due to the absence of air-sea interaction and estimated low influence of advection as outlined in section 2.4, the under-ice decrease in oxygen represents an exquisite and unambiguous observation of the organic matter remineralization rate. Similarly, the corresponding decrease in pH (increase in DIC) and increase in nitrate provide equally useful remineralization rates.
Even though a clear signal indicative of remineralization was observed for floats 5904397 and 5904467 deployed in the northern SIZ of the Atlantic sector, the computed ratio of C:N:O deviated substantially from Redfield. This deviation could be due to physical processes such as horizontal and vertical advection as noted in section 2.4, leads opening up in the ice, or migration of a float into a different water mass. It is important to note that processes with a small horizontal scale, like convection or ice edge processes will be likely be more susceptible to horizontal mixing which has been observed from profiling floats (Kortzinger et al., 2004).

Biogeochemical processes such as ikaite formation, phytoplankton community structure, preferential degradation of organic material, or influences from ice algae communities were also not accounted for and could affect the remineralization ratios. Error in the sensors or TA algorithm may also contribute to some of this deviation; the TA algorithm was likely poorly optimized in this region due to a lack of observations in the SIZ. Because there was a greater drawdown of O2 relative to DIC and NO3, opening of leads in the ice can be ruled out because the opposite trend would have been observed due to uptake of O2 from the atmosphere by the undersaturated surface waters. At this time, the source(s) of the anomalous O2 respiration rate relative to Redfield is an active research question. In spite of broad deviation from Redfield for a couple floats and numerous sources of uncertainty, the mean C:N:O ratios for all the floats are within the error bars Redfieldian.

4.3. Net Community Production

The ANCP derived from both O2 and DIC in the SIZ is near zero when integrated to the base of the euphotic zone, which differs from other studies at this latitude (DeJong et al., 2017; Ishii et al., 2002; Lee, 2001; Li et al., 2016; Nevison et al., 2012; Thomalla et al., 2015). One potential source of this apparent irregularity might be the large intra-annual variability. For example, if annual bloom intensity is linked to ice cover, then contiguous years may experience vastly different seasonally integrated NCP values, skewing the ANCP that may be determined for any given 12 month period. High frequency multiyear observations have previously not been available and estimates of ANCP that neglect the wintertime component would not account for respiration in the euphotic zone. Integrating to depths shallower than the base of the euphotic layer (upper 75 m) did not significantly change ANCP from zero in O2 though there is greater variability when computed from DIC (Table 4). During the ice free period and phytoplankton bloom, there was a positive NCP that nearly completely balanced with the negative NCP during the period of sea ice cover. This feature may be unique to the SIZ, as the under ice sea ice period of the year is distinctly net-heterotrophic. The phytoplankton bloom was not as intense as observed for other floats in this region from Chl a data (see supporting information Figure S7), which could explain the lower than anticipated ANCP for Ross Sea float 5904184.

Most of the NCP signal, both positive and negative, derived as the difference between observations and the physical model was within the region of the MLD (Figure 7). When integrated down to 300 m, ANCP does not go to zero as anticipated which is likely due to model error in simulating the MLD (see Figure 5) where strong vertical gradients are present, hence mismatch between the model and observations rather than actual biological activity. To help remedy this mismatch, the water column above and below the modeled MLD was stretched or compressed to match the observed MLD from float data, following Plant et al. (2016). However, this introduced more error in T and S around the MLD. Instead, NCP was integrated to the base of the euphotic zone in Figure 6 to remove errors resulting from the MLD region. The Chl-a signal during the springtime bloom does not exceed 75 m; thus, most of the NCP signal below this depth in the model is believed to be primarily due to this mismatch of the model and float data within the MLD region.

The modeled NCP was not very sensitive to both uncertainty in DIC and O2 as well as choice of optimization parameters. Through the range of uncertainty of DIC, the seasonal NCP cycle in the upper ocean varies from net heterotrophic during the under-ice period to net autotrophic during the sea ice free period. There are several sources of error in the model other than just in the estimated DIC and measured O2 including error.
in physical input parameters (heat, wind, and precipitation), sea ice formation/melt, gas parameterization, and horizontal advection; however, the upper and lower bounds on the estimated seasonal NCP fall within a reasonable range. Horizontal advection is estimated to account for up to 23% of the signal as described in section 2.4, however, the contribution would likely not be only one directional unlike the observed signals of drawdown of O$_2$ (release of DIC) during the austral winter and release of O$_2$ (uptake of DIC) during the austral spring into the summer.

The modified PWP model used in this study requires significant float-specific tuning and is thus not easily applied in a bulk analysis of multiple floats and was therefore only applied to one float. There are also several sources of uncertainties; however, the model did help interpret the biological and physical components of the pH and O$_2$ signal for Ross Sea float 5904184. Most noteworthy is that the residual of the model minus float data was able to capture the robust signal of seasonality in NCP that is apparent in the observations and unique to the sea ice zone (see Figure 6).

5. Conclusions

This was a preliminary analysis of the first BGC-Argo profiling floats including a full annual cycle of pH in the SIZ. The significance of the sea ice edge in setting up favorable conditions for a phytoplankton bloom is evident in all nine floats included in this study. In particular, float 5904184 observed an ice edge bloom at the end of its first under sea ice season, but did not experience full ice cover in the subsequent year, with the consequence of no bloom. A clear signal under sea ice indicative of remineralization is observed for most of the floats in this study. Most of the C:NO remineralization ratios were close to Redfieldian, although O$_2$ appeared to have the greatest deviation from C and N and this discrepancy is not yet fully understood. The seasonal NCP for float 5904184 in the SIZ during the time of the phytoplankton bloom depleted up to 5 mol C m$^{-2}$ within the estimated euphotic layer (75 m) based on Chl a data (see Figure 3), which is similar to other studies in this region. However, the under sea ice NCP nearly balances the springtime NCP, drawing the ANCP to near zero suggesting near zero export production in this region. More complex models may be necessary to simulate the mixed layer physics and sea ice interactions in the SIZ. However, a seasonal cycle in NCP was captured in the residual of the model minus float data and net heterotrophy was observed for about half of the year during sea ice cover in the austral winter. As more floats are deployed that acquire a full annual cycle of data in the SIZ, this analysis of remineralization ratios and NCP can be expanded.

References


Acknowledgments

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