

Carbon and nitrogen zooplankton isoscapes in West Antarctica reflect oceanographic transitions

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ABSTRACT: Antarctic marine ecosystems are spatially and temporally dynamic. Regional climate change is significantly altering the patterns and magnitudes of this dynamism with cascading impacts on biogeochemistry, productivity, and food web architecture. Isoscapes (or isotopic maps) provide a valuable analytical framework to characterize ecosystem processes and address questions about trophic dynamics, animal movement, and elemental cycling. Applications of stable isotope methods to Antarctic ecosystems are currently limited by a paucity of information on geo-spatial isotope characteristics within the Southern Ocean. In response, we have created the first empirically derived zooplankton isoscapes for West Antarctica based on analysis of bulk nitrogen and carbon isotope values ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$) in 94 zooplankton specimens from the Drake Passage, West Antarctic Peninsula (WAP), and Amundsen and Ross Seas. The zooplankton $\delta^{15}\text{N}$ values increased by 3‰ from north of the Polar Front ($3.3 \pm 0.6\text{‰}$, mean \pm SD) to the Ross Sea ($6.2 \pm 0.8\text{‰}$), reflecting a productivity gradient across this region. Abundant open water polynyas in the Amundsen and Ross Seas exhibit strong nitrate drawdown, resulting in more ^{15}N -enriched phytoplankton and zooplankton relative to those from the generally less productive WAP and Drake Passage. Zooplankton $\delta^{13}\text{C}$ values decreased by 3‰ from north of the Polar Front ($-24.2 \pm 0.9\text{‰}$) to the Ross Sea ($-27.5 \pm 1.6\text{‰}$), likely driven by decreasing sea surface temperatures with increasing latitude. Our isoscapes are a valuable first step in establishing isotopic spatial patterns in West Antarctica and are critical for addressing numerous ecosystem questions.

KEY WORDS: Isoscape · Antarctica · Zooplankton · Biogeochemistry · Animal migration · Food web · ENSO

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INTRODUCTION

The Southern Ocean is one of the largest, most dynamic ecosystems on Earth, playing a critical role in ocean primary productivity and fisheries production, biogeochemical cycling, and global climate (Falkowski et al. 1998, Gille 2002, Croxall & Nicol 2004, Marinov et al. 2006). It consists of the waters south of the Subtropical Front, including the Antarc-

tic Circumpolar Current and high latitude waters surrounding the Antarctic continent. West Antarctica, the Southern Ocean region between the Ross and Weddell Seas, is experiencing some of the most profound and rapid regional climate change on Earth (Meredith & King 2005, Ducklow et al. 2007, 2012, Stammerjohn et al. 2012). Warming is predicted to result in increased upper ocean stratification and altered phytoplankton assemblages with unknown

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long-term ecosystem consequences (Arrigo et al. 2000, Jacobs et al. 2002, Tortell et al. 2008). Climate change impacts on a range of taxa have been documented in the Southern Ocean over the past 50 yr, including phytoplankton (Montes-Hugo et al. 2009), Antarctic krill and other pelagic invertebrates at the base of the food web (Atkinson et al. 2004), and upper trophic level consumers, including sea birds, penguins, and marine mammals (Trathan et al. 2007, Nicol et al. 2008, Siniff et al. 2008, Forcada & Trathan 2009). Given the rapid physical, chemical, and biological changes occurring in West Antarctica, it is critical to understand the underlying biogeochemical cycling that supports the base of Antarctic food webs and ultimately controls the ecological response to climate change.

Stable isotope analysis is now a routine tool to characterize elemental cycling and trophic dynamics (Boecklen et al. 2011). Stable nitrogen (N) isotope values ($\delta^{15}\text{N}$) are typically used to determine the number of trophic transfers between a consumer and the base of the food web, while stable carbon (C) isotope values ($\delta^{13}\text{C}$) are often used to infer sources of primary production fueling food webs (Peterson & Fry 1987). Ecological applications of stable isotope data, termed ecogeochemistry, require careful consideration of the spatio-temporal dynamics of isotope values at the base of the food web (Graham et al. 2010, McMahon et al. 2013a).

Geospatial maps of isotopic values, termed isoscapes, provide an analytical framework for understanding regional biogeochemical processes (Bowen 2010, West et al. 2010, McMahon et al. 2013a). Isoscapes generated from organisms at the base of the food web provide an integrated view of the spatial gradients in stable isotope values within a system. A number of factors can influence baseline stable nitrogen isotope ($\delta^{15}\text{N}_{\text{baseline}}$) and carbon isotope ($\delta^{13}\text{C}_{\text{baseline}}$) values (Wainright & Fry 1994, Needoba et al. 2003, Montoya 2007, 2008, Chikaraishi et al. 2009, Graham et al. 2010). For instance, phytoplankton $\delta^{15}\text{N}$ values are set by their nutrient source (i.e. nitrate, ammonium, or N_2), biological transformations (e.g. N_2 -fixation and denitrification), isotopic fractionation during N assimilation, and nutrient pool size (or the extent of nitrogen pool drawdown) (reviewed by McMahon et al. 2013a). For carbon, variability in the $\delta^{13}\text{C}$ value of phytoplankton reflects dissolved inorganic carbon $\delta^{13}\text{C}$ values, $[\text{CO}_2]_{\text{aq}}$, temperature, cell size and geometry, internal biological parameters (e.g. growth rate), and CO_2 drawdown (reviewed by McMahon et al. 2013a). Spatial and temporal variations in these driving forces (e.g. sea-

sonal or latitudinal gradients in temperature) will in turn create spatial and temporal variations in phytoplankton isotope values (e.g. Schell et al. 1998). Phytoplankton $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values at the base of the food web are subsequently passed on, with modifications associated with trophic transfer, to upper trophic level consumers (e.g. Lorrain et al. 2009, Graham et al. 2010, Jaeger et al. 2010a).

In recent years, researchers have established baseline isoscapes for a number of regions and spatial scales (e.g. McMahon et al. 2013a, MacKenzie et al. 2014, Vokhshoori et al. 2014, Vokhshoori & McCarthy 2014), and these efforts have produced profound insights into animal movement and foraging ecology, habitat use, and regional biogeochemical cycling (e.g. Graham et al. 2010, Jaeger et al. 2010b, MacKenzie et al. 2011). The Southern Ocean has the potential for significant geospatial isotope dynamics, which would facilitate similar studies in this critical ecosystem. Three major fronts separate the Southern Ocean into 4 distinct biogeographic zones (from north to south): Subantarctic Zone (SAZ), Polar Front Zone (PFZ), Antarctic Zone (AZ), and Antarctic Continental Zone (ACZ) (Fig. 1). ACZ, the zone south of the southern boundary of the Antarctic Circumpolar Current (ACC), in West Antarctica, may be divided into 3 regions: the West Antarctic Peninsula (WAP), the Amundsen Sea, and the Ross Sea. Baseline isotope values have not yet been determined for all major frontal zones and seas, such as the Amundsen and Ross Seas in the Pacific Sector. Where available, isotopic baselines are proving useful in interpreting broad ecosystem dynamics.

Off East Antarctica (the portion of the continent largely within the Eastern Hemisphere), DiFiore et al. (2006) determined summer and winter $\delta^{15}\text{N}_{\text{NO}_3^-}$ values for the STZ, SAZ, and PFZ. They described a seasonal increase in $\delta^{15}\text{N}_{\text{NO}_3^-}$ values in surface waters, which are greatest in the summer and associated with a decrease in NO_3^- concentration $[\text{NO}_3^-]$. The authors attributed the inverse relationship between $\delta^{15}\text{N}_{\text{NO}_3^-}$ value and $[\text{NO}_3^-]$ and the resulting seasonal pattern in $\delta^{15}\text{N}_{\text{NO}_3^-}$ values to phytoplankton NO_3^- consumption, which increases the $\delta^{15}\text{N}$ value of the residual NO_3^- pool. DiFiore et al. (2006) also reported decreasing surface water $\delta^{15}\text{N}_{\text{NO}_3^-}$ values with increasing latitude from $\sim 13.5\text{‰}$ at 42°S to $\sim 7.5\text{‰}$ at 54°S , which may have resulted from decreasing productivity between the STZ and PFZ. DiFiore et al. (2009) also measured $\delta^{15}\text{N}_{\text{NO}_3^-}$ values in 3 regions along the East Antarctic continental margin and in the Ross Sea polynya, all sites within the ACZ and at latitudes between about 65 and 80°S . The

authors reported surface water $\delta^{15}\text{N}_{\text{NO}_3^-}$ values ranging from about 5 to 8‰, with the highest values at productivity 'hot spots' that have the highest surface NO_3^- depletions. The surface water $\delta^{15}\text{N}_{\text{NO}_3^-}$ values of hot spot locations were similar to those measured in the PFZ at $\sim 54^\circ\text{S}$, conflicting with prior work suggesting a consistent decrease in $\delta^{15}\text{N}_{\text{NO}_3^-}$ with increasing latitude (DiFiore et al. 2006). Somes et al. (2010) used a marine ecosystem model with N isotopes to construct a global map of $\delta^{15}\text{N}_{\text{NO}_3^-}$ values, which they compared to a global database of $\delta^{15}\text{N}_{\text{NO}_3^-}$ values. From their model, $\delta^{15}\text{N}_{\text{NO}_3^-}$ values decrease with increasing latitude in the Southern Ocean, likely due to increasing $[\text{NO}_3^-]$ (Somes et al. 2010). Jaeger et al. (2010a) defined the isotopic baseline in open waters of the southwest Indian Ocean by measuring isotopic values in the feathers of seabirds. They reported decreases in both $\delta^{15}\text{N}$ (12.9 to 8.2‰) and $\delta^{13}\text{C}$ (−19.0 to −23.7‰) values of light-mantled sooty albatross *Phoebastria palpebrata* from the STZ towards the AZ.

Despite the potential for strong isotope gradients in the West Antarctic and the clear value of quantifying and understanding regional geospatial isotope dynamics here, no isoscapes have been generated for this critical region. This is particularly troubling given the rapid warming and associated ecological and environmental changes this system is experiencing. In this study, we generated the first empirical isoscapes for the West Antarctic region by measuring the $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values of multiple taxa of zooplankton and phytoplankton. These isoscapes cover an expansive area of the West Antarctic: from the tip of South America to the Antarctic Peninsula, and along the West Antarctic coast from the Peninsula to the Ross Sea.

This study focuses on isoscapes of West Antarctic continental margins because these systems are ecologically critical zones for fisheries, seabirds, and marine mammals and have not been fully assessed in prior isoscapes. The isoscapes generated in this study will serve as an important first step to quantifying the geospatial isotope dynamics of this critical ecosystem and understanding the underlying mechanisms generating these patterns. Our work also highlights key gaps in data needed to realize the full potential of this powerful isotope approach to understanding movement, foraging ecology, and biogeochemical cycling in the Southern Ocean. In particular, we discuss the need for additional research to carefully examine temporal variability in isotopic baselines as a result of physical conditions fluctuating across seasons and climate modes, as well as to increase the

data coverage in certain West Antarctic regions, such as the Bellingshausen Sea. This work not only provides an initial framework for understanding baseline variability in Antarctic food webs, past and present, but also serves as a benchmark for evaluating future ecological and biogeochemical changes associated with rapid climate change.

MATERIALS AND METHODS

Sampling sites

Plankton samples were collected between 2007 and 2015 adjacent to the shore over the continental shelves in the ACZ of the WAP, Amundsen Sea, and Ross Sea, as well as from open water off the continental shelf in the AZ and from the PFZ and SAZ between the WAP and South America (Fig. 1). Ninety-four discrete samples, comprising a variety of zooplankton taxa (average of 4 taxa per station; Table S1 in the Supplement at www.int-res.com/articles/suppl/m593/p029_supp.pdf), were collected at 34 stations over this region, including: 5 stations across the PFZ and SAZ waters, 5 stations within the AZ, 10 nearshore stations off the WAP in the ACZ, 7 stations in the Amundsen Sea, and 7 stations in the Ross Sea.

Within the Palmer Long-Term Ecological Research (PAL-LTER) study area along the WAP and on the continental shelf, phytoplankton and Antarctic krill were collected during austral summers between 2007 and 2011: phytoplankton, December and January of 2009/10 and 2010/11 and krill, January of 2007/08 and 2010/11. We incorporated $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values of PAL-LTER krill samples reported by Brault (2012) into our isoscapes.

Amundsen and Ross Sea zooplankton and phytoplankton were collected on the 2007/08 and 2010/11 RV 'Oden' austral summer (December to January) cruises. All Ross Sea samples were obtained on the continental shelf. For the Amundsen Sea samples, 4 samples were collected on the continental shelf and the other 3 samples were collected within the continental margin. Zooplankton samples were taken from the ACZ, AZ, PFZ, and SAZ during the early austral fall (March to April) 2015 cruise of the SV 'Lawrence M. Gould.' Of these samples, only sampling within the ACZ was on the continental shelf. Mixed phytoplankton and zooplankton samples were obtained from the western Ross Sea during the 2011/2012 austral summer (January to February) cruise of the RV 'Nathaniel B. Palmer.' All samples in this region were from sites on the continental shelf.

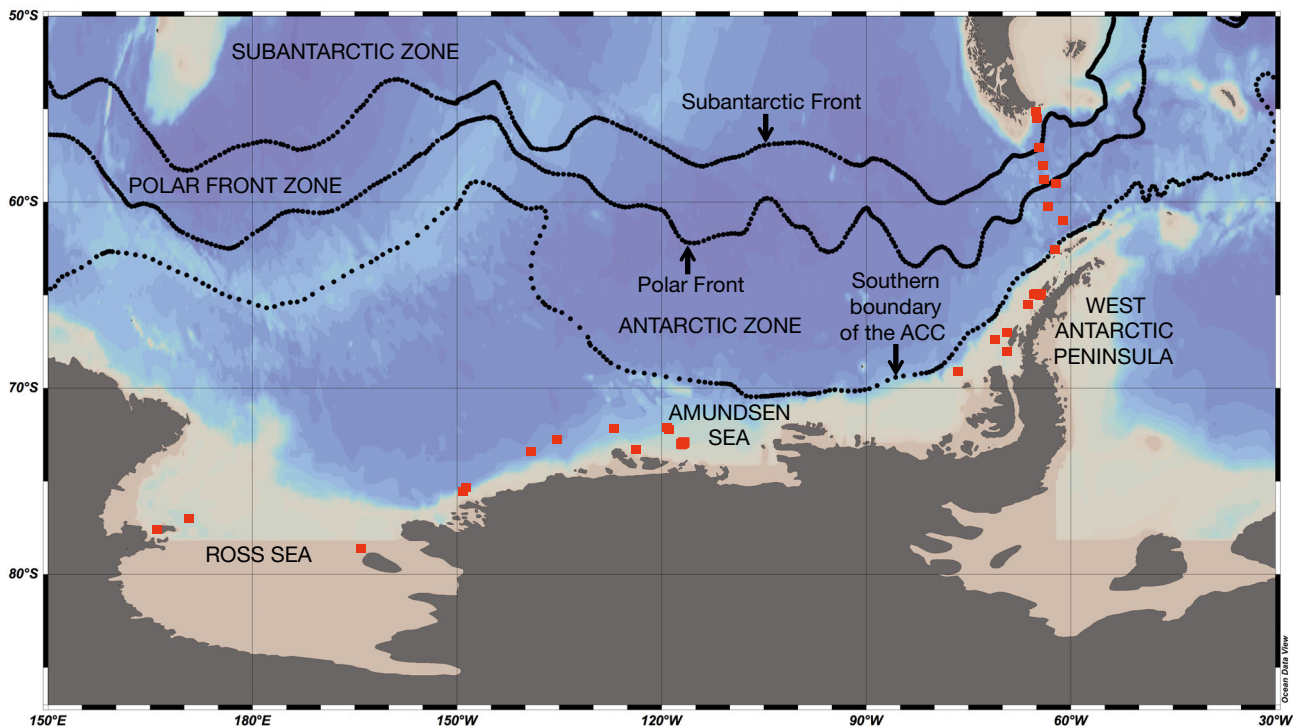


Fig. 1. Zooplankton sampling locations (red squares) for developing $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ isoscapes across 5 Southern Ocean biogeographic zones. Major fronts are indicated with black dotted lines, according to Orsi et al. (1995). ACC: Antarctic Circumpolar Current. Ocean bathymetry is shown with increasing depth below sea level from light brown to dark blue

Sample collection

Phytoplankton samples from the PAL-LTER surveys were collected using an 80 μm ring net towed through the upper water column (≤ 50 m depth) for ~30 min. The sample were rinsed into a pre-cleaned plastic tub, re-concentrated by sieving through a 25 μm mesh, and then frozen at -80°C . A sub-sample of each tow was examined under a compound microscope to determine the dominant species (diatoms in all cases) and any microzooplankton were removed manually. During the 'Oden' cruises of 2007/08 and 2010/11, phytoplankton were collected via vertical tows from depths of ~20 m with a 30 μm ring net. Samples were similarly re-concentrated and frozen at -80°C . The 2010/11 samples were dominated by the prymnesiophyte *Phaeocystis antarctica* according to onboard microscopy of tow sub-samples and once again any microzooplankton were discarded manually. The 2007/08 samples were not evaluated under a microscope to identify the dominant phytoplankton species.

Krill obtained during the PAL-LTER sampling, mixed zooplankton samples collected during the 'Oden' cruise in 2010/11, and 1 sample of *Clione limacina* from a 2007/08 'Oden' cruise were derived from oblique tows (700 μm square-frame net) in 120 and

400 m depth for PAL-LTER and 'Oden' cruises, respectively. Samples were transferred from the cod end into pre-cleaned buckets, re-concentrated by sieving through 700 μm mesh (saving the retentate), and frozen at -80°C . Samples were identified to the lowest taxonomic group possible prior to freezing. Zooplankton samples from the 'L. M. Gould' cruise were obtained with open oblique hauls of a 505 μm mesh net from ~150 m to the surface using a 1.8 m Isaacs-Kidd midwater trawl. Samples were filtered through a 505 μm mesh sieve, sorted by species, and frozen at -20°C . Mixed phytoplankton and zooplankton samples from the 2011/2012 cruise aboard the RV 'Nathaniel B. Palmer' were collected with 200 μm bongo net tows in the upper water column (0–200 m). The samples were stored in a 4 % formaldehyde-sea-water mixture at 4°C .

Taxonomic groups

All of the phytoplankton samples were treated together as 'phytoplankton.' Zooplankton taxonomic samples from the Ross and Amundsen Seas were categorized into (1) copepods, (2) gammarid and hyperiid amphipods, (3) euphausiids (larval, juvenile,

adult), (4) *Salpa thompsoni*, and (5) pteropods *Clione limacina* (naked) and *Limacina helicina* (shelled) (Table S1). The WAP and Drake Passage samples consisted of euphausiid species *Euphausia superba*, *E. crystallorophias*, *E. frigida*, *E. triacantha*, and *Thysanoessa macrura*, hyperiid amphipod species *Themisto gaudichaudii*, *Vibilia antarctica*, and *Primno macropa*, *Salpa thompsoni*, and the pteropod *Spongiobranchia australis* (naked) (Table S1).

Sample preparation

All samples were kept frozen until laboratory preparation, except for the formaldehyde-preserved plankton samples. Phytoplankton collected on the 'Oden' cruises and phytoplankton and krill from the PAL-LTER cruises were freeze-dried at the Virginia Institute of Marine Science (VIMS, Gloucester Point, VA) with a Labconco Freezone Plus 6 at -80°C for ~ 72 h. Krill were homogenized with a Virtis '45' tissue homogenizer before freeze-drying. Phytoplankton samples were manually homogenized after freeze-drying. Zooplankton from the 'Oden' and 'L. M. Gould' cruises, sorted by taxon at each station, were freeze-dried at the University of California, Santa Cruz (UCSC) using a Labconco Freeze Dry System (Lyph Lock 4.5) at -40°C for ~ 48 h and then manually homogenized. All freeze-dried phytoplankton and zooplankton samples were stored in a desiccator after drying.

Sub-samples of all zooplankton samples were lipid-extracted, except for the Antarctic shelled pteropods, to account for lipid ^{13}C -depletion relative to other biochemical classes. Lipid removal decreased atomic C:N ratios by about 2 for zooplankton. We note that a few specimens for 2 taxa have anomalously high atomic C:N ratios for lipid-free material (Table S1). The effect of chitin content on $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values is poorly understood, but given zooplankton chitin contents (Ventura 2006) and isotopic offsets between protein and chitin (Perkins et al. 2013), the presence of chitin in whole zooplankton material may result in lower $\delta^{15}\text{N}$ values and higher $\delta^{13}\text{C}$ values by up to about 2 and 1‰, correspondingly, relative to those of pure protein. Since the magnitude of the chitin content effect on $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values is uncertain and such an effect would either be negligible or amplify our observed pattern, we have not removed zooplankton data with anomalously high atomic C:N ratios from our analyses.

Carbonate shells of the pteropod *Limacina helicina* were acidified and decarbonated with a 10% HCl solution. After HCl treatment, the samples were neu-

tralized with Milli-Q water (Thermo Fisher Scientific) and freeze-dried in the UCSC Labconco Freeze Dry System as described above. These samples were not lipid-extracted due to sample size limitations but are considered lipid-poor (Kattner et al. 1998).

The PAL-LTER krill were lipid-extracted at the VIMS over 3 d using a chloroform:methanol (1:2; v:v) mixture via Soxhlet extraction (Bligh & Dyer 1959). After lipid extraction, samples were dried and frozen at -80°C until stable isotope analysis. While non-lipid extracted material was not retained for $\delta^{15}\text{N}$ analysis, we found no significant difference in the $\delta^{15}\text{N}$ value of the lipid-extracted and lipid-intact krill from PAL-LTER. A portion of each zooplankton sample from the 'Oden' and 'L. M. Gould' cruises was lipid-extracted via accelerated solvent extraction (1500 psi; 60°C ; 3 cycles) with petroleum ether, according to a lab-established protocol at the UC Santa Cruz (Dobush et al. 1985, Kurle & Worthy 2002). For these zooplankton samples, $\delta^{13}\text{C}$ values were obtained from lipid-extracted material, and $\delta^{15}\text{N}$ values were obtained from the non-extracted material.

To remove the formaldehyde-seawater solution from the Ross Sea mixed plankton samples, samples were transferred to 50 ml BD Falcon centrifuge tubes, centrifuged (15 min, 10000 rpm), and decanted. The pellet was rinsed with Milli-Q water and centrifuged (15 min, 10000 rpm) 3 times, discarding the supernatant between rinses. Samples were then transferred to 10 ml borosilicate vials and dried at 60°C . We acknowledge that prior research has shown that formalin-preservation may affect $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values (Sarakinis et al. 2002, González-Bergonzoni et al. 2015). From analysis of fish tissues, González-Bergonzoni et al. (2015) suggested that the formalin preservation effect (4% formalin solution) on $\delta^{15}\text{N}$ values is ecologically insignificant relative to the range of values in our system. Formalin-fixed $\delta^{13}\text{C}$ values were $\sim 0.9\%$ less than those of fresh material. Since formalin may affect isotope values, we produced separate nitrogen and carbon isoscapes for the formalin-preserved samples in this study (Table S2 in the Supplement).

Isotopic analyses

For $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ analyses, ~ 1 mg of sample was weighed into tin cups (Costech, 3×5 mm) for elemental analysis-isotope ratio mass spectrometry (EA-IRMS). The PAL-LTER krill were analyzed at VIMS on a Costech ECS 4010 CHNS-O Elemental Analyzer (EA) (Costech Analytical Technologies) coupled to a

Delta V Advantage Isotope Ratio Mass Spectrometer (IRMS) with a ConFlo IV Interface (Thermo Electron North America). The $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values were referenced to atmospheric air (AIR) and Vienna-Pee Dee belemnite (V-PDB) standards, respectively. Blanks and international standards—USGS 40 (L-glutamic acid with $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values of -4.5 and -26.4 ‰, respectively) and USGS 41 (enriched L-glutamic acid with $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values of 47.6 and 37.6 ‰, correspondingly)—were analyzed on the EA-IRMS after every 10 samples (standard deviations were <0.1 ‰ for both $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$). All other phytoplankton and zooplankton samples were analyzed at the Stable Isotope Lab at UC Santa Cruz using a Carlo Erba EA 1108 EA coupled to a Thermo-Finnigan Delta^{plus} XP IRMS referenced to AIR and V-PDB standards for N and C, respectively. Seven PUGel standards were analyzed at the start of each session and a PUGel and an acetanilide standard were analyzed after every 8 samples during an analysis session. Across 11 analytical sessions, the standard deviations were <0.1 ‰ ($n = 103$) for $\delta^{13}\text{C}$, <0.1 ‰ ($n = 103$) for $\delta^{15}\text{N}$, and <0.02 ‰ ($n = 103$) for C:N (atomic) for PUGel, and <0.2 ‰ ($n = 68$) for $\delta^{13}\text{C}$, <0.1 ‰ ($n = 68$) for $\delta^{15}\text{N}$, and <0.06 ‰ ($n = 68$) for C:N (atomic) for acetanilide.

Data analyses

Analyses of spatial patterns in the $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values of phytoplankton and zooplankton taxa were performed with Ocean Data View (ODV) version 4.7.4 (Schlitzer 2015) using Data Interpolating Variational Analysis (DIVA) gridding software (Barth et al. 2010). DIVA gridding is highly optimized and relies on a finite-element resolution that takes into account the distance between analysis and data (observation constraint), the regularity of the analysis (smoothness constraint), and physical laws (behavior constraint). DIVA also takes into account coastlines, sub-basins, and advection. Color-shaded contour maps were produced to display $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values using DIVA gridding for phytoplankton and zooplankton taxa. In cases where multiple phytoplankton tows or zooplankton taxa were collected at a given site, the mean isotope value was calculated for that location and used for the isoscapes of 'all phytoplankton' or 'all zooplankton.' Since sampling of 2 major zooplankton taxonomic groups (euphausiids and amphipods) spanned our entire study area, we generated taxon-specific isoscapes for these taxa, again using mean values for euphausiids or amphipods if multiple replicates were sampled at a given station.

Prior to applying a statistical test, conformance with the test's assumptions was evaluated. Any violations of test assumptions and subsequent data transformations are indicated below. Statistical comparisons of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values for phytoplankton, all zooplankton taxa, euphausiids, and amphipods of different regions and sampling periods were performed with separate 2-way ANOVAs with post hoc pairwise comparisons. Samples were clustered into 5 geographic regions: Ross Sea, Amundsen Sea, WAP (all 3 of the preceding regions are in the ACZ), AZ, and combined PFZ and SAZ (PFZ/SAZ). Model II linear regression analysis was used to examine relationships between zooplankton $\delta^{15}\text{N}$ values and surface $[\text{NO}_3^-]$. Since we performed isotopic analysis on homogenized whole organisms, the $\delta^{15}\text{N}$ values integrate the oceanographic conditions experienced by the organism over multiple preceding months, not the physical environment at the exact moment and site when the organism was sampled. Thus, we averaged surface $[\text{NO}_3^-]$ over a 6 mo period encompassing the spring and summer, obtaining values of $[\text{NO}_3^-]$ from the literature (Table S3), as our samples predominately were collected during the summer. Linear regression analysis was used to assess the relationship between all zooplankton $\delta^{13}\text{C}$ values and latitude after log transformation of the data. Similarly, linear regression analysis with square root-transformed data was used to investigate the relationship between all zooplankton $\delta^{13}\text{C}$ values and sea surface temperature (SST). As with $\delta^{15}\text{N}$ values, the $\delta^{13}\text{C}$ values in our study represent an integration of the oceanographic conditions experienced by the zooplankton over several months. Therefore, we used SSTs derived from Gouretski & Koltermann (2004), who used multiple datasets to construct SSTs across the West Antarctic from the Drake Passage to the Ross Sea. All statistical tests were performed in R (R Core Team 2014).

RESULTS

$\delta^{15}\text{N}$ isoscapes

Zooplankton $\delta^{15}\text{N}$ values varied significantly across the West Antarctic ($p < 0.001$, ANOVA), and sampling period had no significant effect on the observed gradient. Ross Sea and Amundsen Sea zooplankton had significantly higher $\delta^{15}\text{N}$ values (mean \pm SD: 6.2 ± 0.8 ‰ and 6.2 ± 0.6 ‰, respectively; $n = 7$ for both regions) than those from the WAP (4.1 ± 0.7 ‰, $n = 10$), AZ (3.7 ± 0.6 ‰, $n = 5$), and PFZ/SAZ (3.3 ± 0.6 ‰,

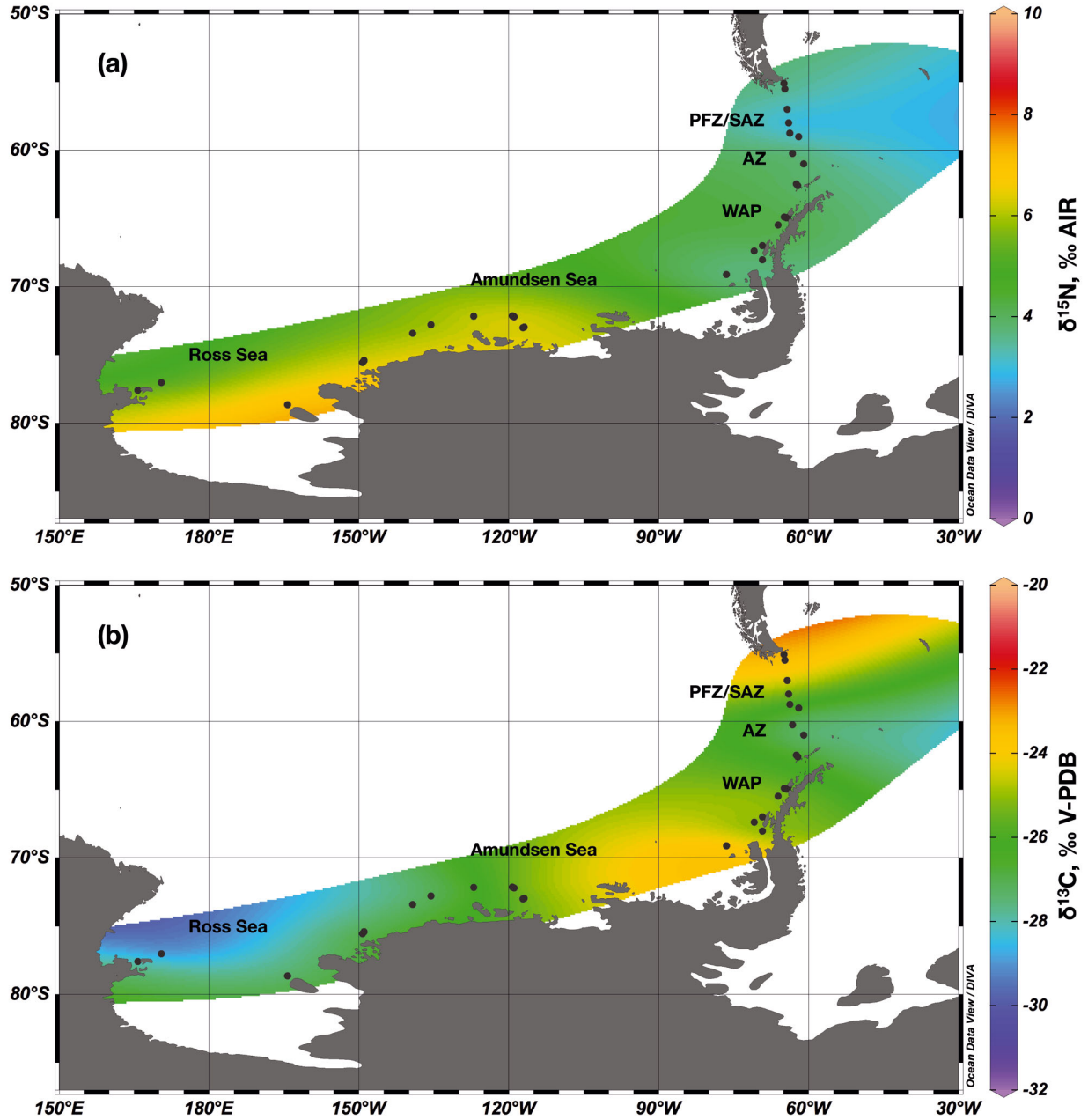


Fig. 2. (a) $\delta^{15}\text{N}$ and (b) $\delta^{13}\text{C}$ values of all zooplankton taxa from West Antarctica. These isoscapes include data for all zooplankton from all sampling periods. PFZ/SAZ: Polar Front Zone/Subantarctic Zone, AZ: Antarctic Zone, WAP: West Antarctic Peninsula. Isoscapes were produced in ODV 4.7.4 (Schlitzer 2015) using Data Interpolating Variational Analysis (DIVA) gridding software (Barth et al. 2010). Sampling locations are indicated by black dots

$n = 5$; Fig. 2a, and see Fig. S1 and Table S1 in the Supplement; $p < 0.001$ for all Bonferroni post hoc pairwise comparisons). Interestingly, these isotope gradients were not reflected in the phytoplankton $\delta^{15}\text{N}$ values across this region, which did not vary significantly across region but did vary significantly among sampling periods ($p = 0.004$, ANOVA, Fig. S2a, Table S4).

The $\delta^{15}\text{N}$ isoscapes for euphausiids and amphipods were similar to the composite iscape of all zooplankton. The $\delta^{15}\text{N}$ values of euphausiids varied significantly among the regions ($p < 0.001$, ANOVA), with euphausiid $\delta^{15}\text{N}$ values significantly higher in the Ross Sea ($6.5 \pm 0.4\text{‰}$, $n = 6$) and Amundsen Sea ($6.7 \pm 0.9\text{‰}$, $n = 6$) than in the WAP ($4.1 \pm 0.8\text{‰}$, $n = 10$), AZ ($4.8 \pm 0.9\text{‰}$, $n = 5$), and PFZ/SAZ ($3.8 \pm 1.0\text{‰}$,

$n = 5$) based on Bonferroni post hoc tests ($p < 0.001$ in all cases, except $p = 0.02$ and 0.004 for the Ross Sea versus AZ and Amundsen Sea versus AZ, correspondingly, Fig. 3a). Although sample sizes were low, the $\delta^{15}\text{N}$ pattern of amphipods across the 5 regions (Fig. 4a) was similar to that of all zooplankton: the $\delta^{15}\text{N}$ values of amphipods in the Ross ($6.9 \pm 0.8\text{‰}$, $n = 3$) and Amundsen ($6.2 \pm 1.2\text{‰}$, $n = 3$) Seas were higher than those in the WAP ($3.8 \pm 2.7\text{‰}$, $n = 2$),

AZ ($3.4 \pm 1.2\text{‰}$, $n = 4$), and PFZ/SAZ ($3.4 \pm 1.4\text{‰}$, $n = 4$). Spatial coverage was poor for the other taxa, but the $\delta^{15}\text{N}$ patterns for pteropods, salps, copepods, and mixed plankton (0–200 μm , 4 % formaldehyde-seawater mixture) were consistent with the significant patterns of all zooplankton taxa and euphausiids (Figs. S3a, S4a, S5a, & S6a, Tables S1 & S2). The $\delta^{15}\text{N}$ values of zooplankton were inversely related to the surface $[\text{NO}_3^-]$ ($p = 0.05$, $R^2 = 0.8$, Fig. S7).

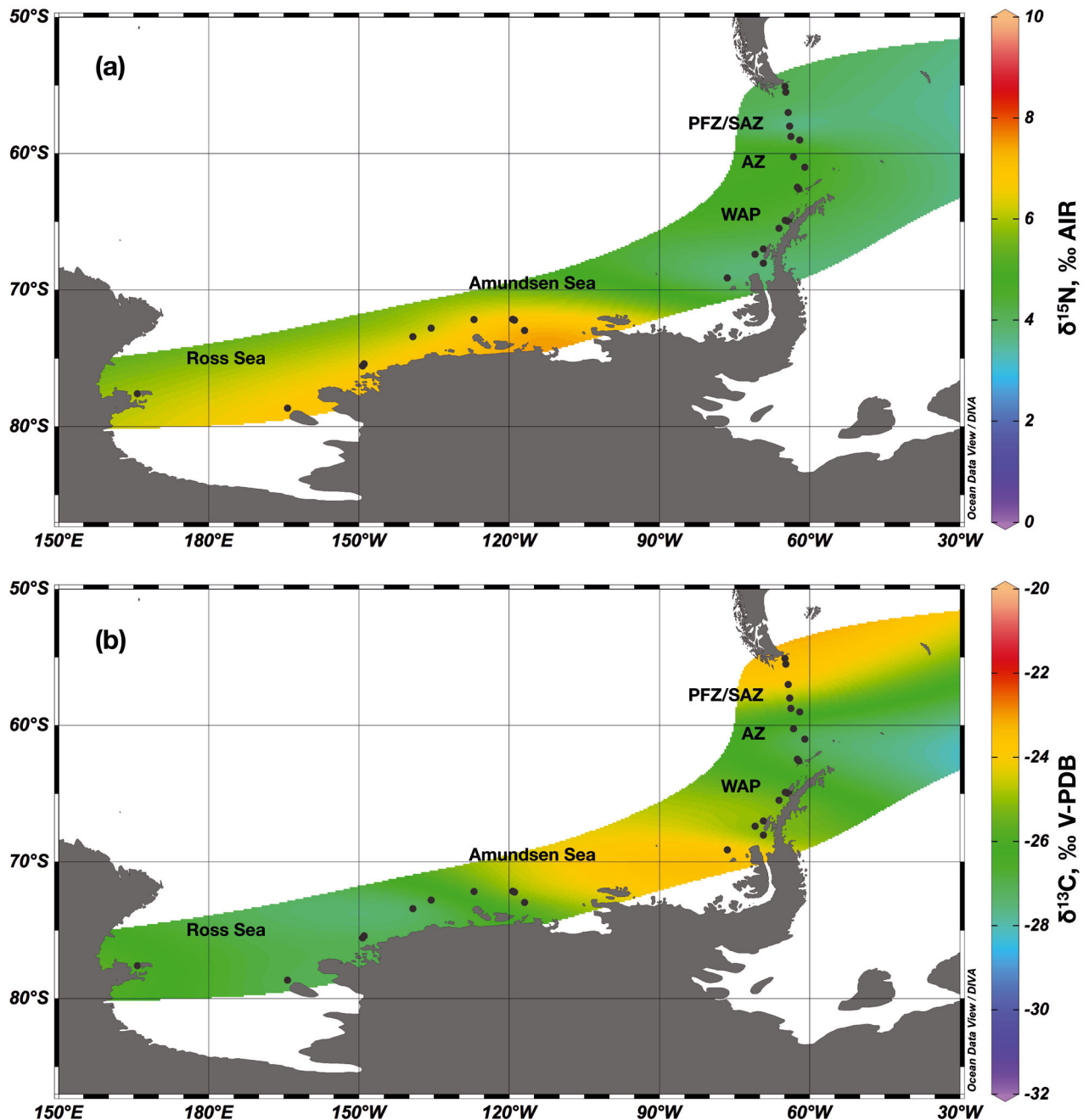


Fig. 3. (a) $\delta^{15}\text{N}$ and (b) $\delta^{13}\text{C}$ values of all euphausiids from West Antarctica. Details as in Fig. 2

$\delta^{13}\text{C}$ isoscapes

The $\delta^{13}\text{C}$ values for all zooplankton taxa varied significantly across the West Antarctic ($p < 0.001$, ANOVA), and sampling period did not significantly affect these patterns (Fig. 2b & S1, Table S1). Zooplankton from the Ross Sea had significantly lower $\delta^{13}\text{C}$ values ($-27.5 \pm 1.6\text{‰}$, $n = 7$) than those from the WAP ($-25.1 \pm 1.7\text{‰}$, $n = 10$) and the PFZ/SAZ ($-24.2 \pm$

0.9‰ , $n = 5$) (Bonferroni post hoc test $p = 0.01$ and 0.002 , respectively). Additionally, all zooplankton $\delta^{13}\text{C}$ values from AZ waters ($-27.1 \pm 0.7\text{‰}$, $n = 5$) were significantly lower than those of the PFZ/SAZ ($p = 0.01$ in Bonferroni post hoc test). All zooplankton from the Amundsen Sea had $\delta^{13}\text{C}$ values ($-26.1 \pm 1.1\text{‰}$, $n = 7$) similar to those from the Ross Sea. Similar to the $\delta^{15}\text{N}$ patterns, phytoplankton $\delta^{13}\text{C}$ values were not significantly different among these regions,

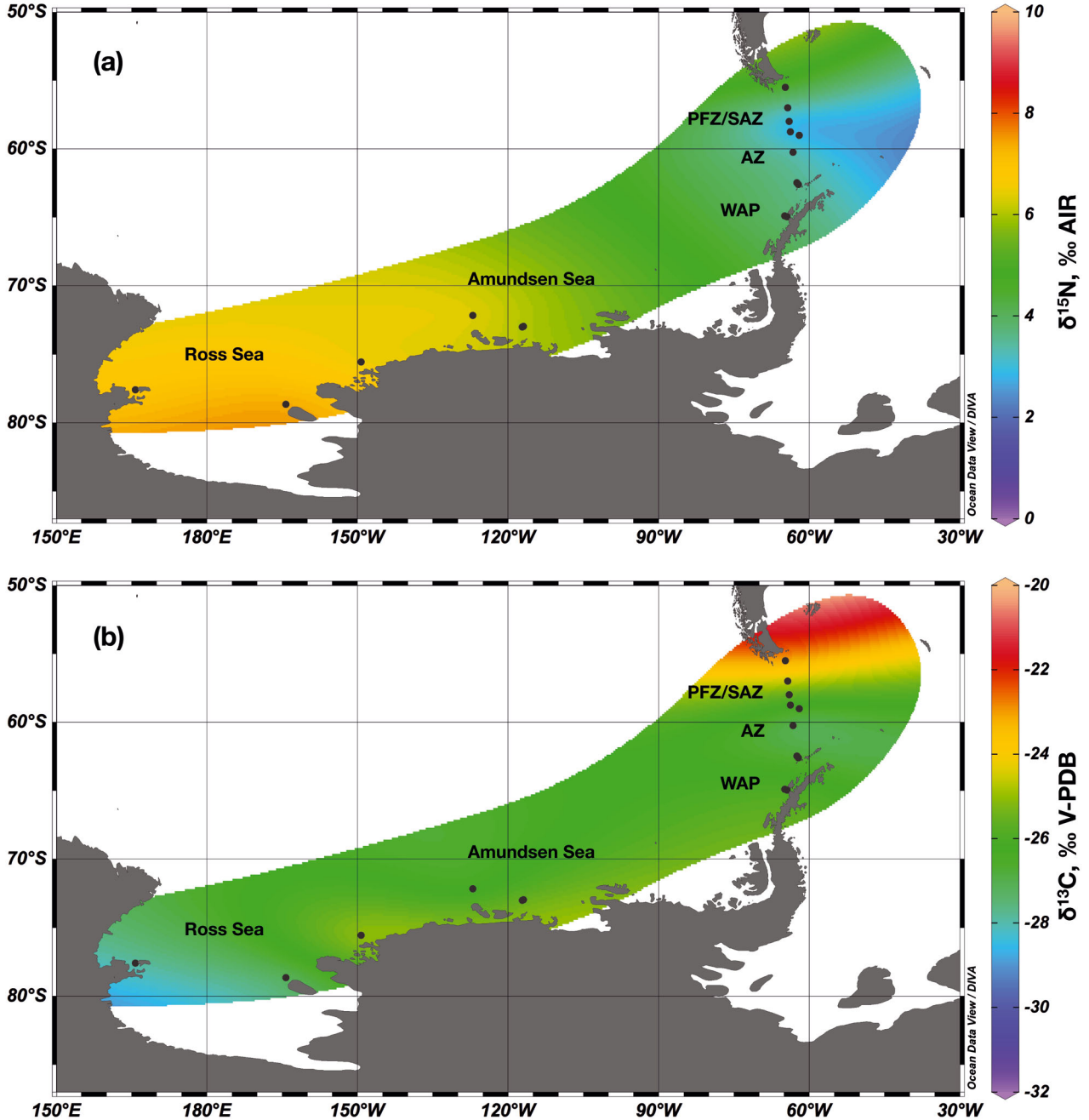


Fig. 4. (a) $\delta^{15}\text{N}$ and (b) $\delta^{13}\text{C}$ values of all amphipods from West Antarctica. Details as in Fig. 2

in contrast with the zooplankton $\delta^{13}\text{C}$ pattern (Fig. S2b). Additionally, phytoplankton $\delta^{13}\text{C}$ values did not vary significantly among sampling time periods (Table S4).

The $\delta^{13}\text{C}$ isoscapes for euphausiids and amphipods follow the same pattern as the composite $\delta^{13}\text{C}$ isoscape of all zooplankton. Euphausiid $\delta^{13}\text{C}$ values were $-26.9 \pm 1.0\text{‰}$ ($n = 6$) for the Ross Sea, $-25.9 \pm 1.3\text{‰}$ ($n = 6$) for the Amundsen Sea, $-25.3 \pm 1.7\text{‰}$ ($n = 10$) for the WAP, $-26.9 \pm 0.5\text{‰}$ ($n = 5$) for the AZ, and $-24.1 \pm 0.8\text{‰}$ ($n = 5$) for the PFZ/SAZ (Fig. 3b). Ross Sea and AZ euphausiids had significantly lower $\delta^{13}\text{C}$ values than those from the PFZ/SAZ ($p = 0.01$ and 0.02 , respectively, in Bonferroni post hoc tests). Amphipod $\delta^{13}\text{C}$ values were $-26.5 \pm 2.3\text{‰}$ ($n = 3$), $-26.0 \pm 1.7\text{‰}$ ($n = 3$), $-25.7 \pm 0.2\text{‰}$ ($n = 2$), $-27.2 \pm 0.7\text{‰}$ ($n = 4$), and $-24.4 \pm 1.5\text{‰}$ ($n = 4$) for the Ross Sea, Amundsen Sea, WAP, AZ, and PFZ/SAZ, respectively, and there were no significant differences among the 5 regions (Fig. 4b). Again, the smaller sample sizes of amphipods relative to those of all zooplankton and euphausiids may explain the lack of significant spatial variability. Consistent with the pattern observed for all zooplankton taxa, $\delta^{13}\text{C}$ values of both euphausiids and amphipods increased with decreasing latitude: Ross Sea < Amundsen Sea < WAP < PFZ/SAZ, and $\delta^{13}\text{C}$ values for the AZ were lower than PFZ/SAZ and similar to those of the ACZ regions. The $\delta^{13}\text{C}$ patterns of the other taxa, i.e. pteropods, salps, copepods, and mixed plankton (0–200 μm , 4 % formaldehyde-seawater mixture), were similar to the significant patterns observed in all zooplankton taxa and euphausiids (Figs. S3b, S4b, S5b, & S6b, Table S1 & S2). Zooplankton $\delta^{13}\text{C}$ values significantly decreased with increasing latitude ($p = 0.03$ and $R^2 = 0.1$, Fig. S8) and decreasing SST ($p = 0.04$ and $R^2 = 0.1$ from a linear regression analysis, Fig. S9).

DISCUSSION

Understanding spatial and temporal variations in isotopic baselines is critical to successful application of ecogeochemical approaches to questions of food web architecture, biogeochemical cycling, and animal movement in dynamic marine environments, like the Southern Ocean (Graham et al. 2010, McMahon et al. 2013a). We found strong gradients in both nitrogen and carbon stable isotope values of zooplankton across the 5 geographic regions of the West Antarctic: PFZ/SAZ, AZ, WAP, Amundsen Sea, and Ross Sea (Fig. 2). These geospatial patterns appeared to be driven by regional gradients in biogeochemistry, productivity, and oceanography. Interestingly, we found

no such coherent geospatial gradients in phytoplankton isotope values (Fig. S2). This lack of parallel gradients is likely a function of the short turnover times and fast integration rates (days to weeks) of phytoplankton in this highly dynamic system compared to the longer integration signal from zooplankton (months). Phytoplankton communities are highly dynamic, experiencing considerable variability in species composition, biomass, growth rate, etc., over relatively short scales of time and space (Cloern & Jassby 2010, Zingone et al. 2010). As such, the phytoplankton isotope values represent snapshots of local isotopic baseline signals, and the spatial gradients do not become apparent until the local signals are integrated over longer time periods in the higher trophic level zooplankton (Mullin et al. 1984, Pinkerton et al. 2013). For this reason, we focus on zooplankton for the remainder of this discussion of West Antarctic isoscapes.

$\delta^{15}\text{N}$ isoscapes track productivity gradients

We observed a strong spatial gradient in zooplankton isotope values from low $\delta^{15}\text{N}$ values in the WAP, AZ, and PFZ/SAZ to high values in the Ross and Amundsen Seas. The $\delta^{15}\text{N}$ values of all zooplankton from the Ross and Amundsen Seas were about 2‰ higher than those from the WAP and 3‰ higher than those from the PFZ/SAZ (Fig. 2a). These patterns in zooplankton $\delta^{15}\text{N}$ values are consistent with previously reported data for the region. Pinkerton et al. (2013) reported mean (\pm SD) lipid-extracted zooplankton $\delta^{15}\text{N}$ values of $6.1 \pm 2.3\text{‰}$ across 14 zooplankton taxa from the Ross Sea (austral summer 2008), indistinguishable from the mean for our Ross Sea zooplankton samples ($6.2 \pm 0.8\text{‰}$), despite the fact that our samples had been collected in both the austral summers of 2007/08 ($n = 1$) and 2010/11 ($n = 6$). Similarly, Schmidt et al. (2003) reported mean (\pm SD) $\delta^{15}\text{N}$ values for zooplankton (without lipid extraction) collected from the PFZ/SAZ and 65°S (similar latitude to that of the WAP) of $3.6 \pm 1.1\text{‰}$ (all 15 taxa) and $3.5 \pm 1.1\text{‰}$ (all 4 taxa), respectively, between 1996 and 2000 that are similar to our $\delta^{15}\text{N}$ values for all zooplankton from the PFZ/SAZ ($3.3 \pm 0.6\text{‰}$) and the WAP ($4.1 \pm 0.7\text{‰}$) which had been obtained in the early fall of 2015 and the austral summers of 2007/08 and 2010/11, correspondingly. McMahon et al. (2013b) used meta-analyses of published $\delta^{15}\text{N}$ values to produce a global $\delta^{15}\text{N}$ isoscape. Although much of the West Antarctic is not included in the isoscape due to a paucity of data, their analysis suggests $\delta^{15}\text{N}$ values for the WAP of $\sim 3\text{‰}$, similar to

our measurements, but higher values for the AZ, PFZ, and SAZ (e.g. of 4–6‰) than we observed. However, few data were available for these 3 regions, and thus their isotopic values are largely driven by data for the WAP and South American coast.

The observed patterns in $\delta^{15}\text{N}$ variation within the West Antarctic isoscape likely reflect variable NO_3^- drawdown associated with gradients in productivity (Wada et al. 1987, Altabet & Francois 1994, Waser et al. 2000). The Southern Ocean is the largest high nutrient, low chlorophyll (HNLC) region in the world, with the majority of NO_3^- in the surface waters remaining unused on an annual basis due to iron limitation. As a result, surface $[\text{NO}_3^-]$ is relatively high and phytoplankton and zooplankton $\delta^{15}\text{N}$ values are relatively low (de Baar et al. 1990, Martin et al. 1990, Altabet & Francois 2001). However, localized regions of more complete NO_3^- utilization associated with high rates of primary productivity may result in increased $\delta^{15}\text{N}$ values of phytoplankton and, consequently, zooplankton (DiFiore et al. 2009).

Our $\delta^{15}\text{N}$ spatial pattern suggests lower nutrient utilization and productivity in the pelagic PFZ/SAZ and off the WAP (where the continental shelf is narrow) than on the large continental margins of the Amundsen and Ross Seas, which is consistent with the results of prior studies on West Antarctic productivity. The Ross Sea, where the large Ross Sea and Terra Nova Bay polynyas form each spring, exhibits high annually integrated productivity ($\sim 503 \text{ Tg C yr}^{-1}$) on an annual basis compared to other Southern Ocean sectors (Arrigo et al. 1998, 2008, Smith & Comiso 2008). Smith & Comiso (2008) reported that productivity decreased from the southern Ross Sea ($2.74 \text{ g C m}^{-2} \text{ d}^{-1}$) to the central Ross Sea ($2.26 \text{ g C m}^{-2} \text{ d}^{-1}$) to the WAP ($1.56 \text{ g C m}^{-2} \text{ d}^{-1}$). More recently, the Amundsen Sea has been shown to experience high productivity due to iron inputs and stratification from melting glaciers, with water column productivity ranging from 1.56 (sea ice) to 4.18 (Pine Island polynya) $\text{g C m}^{-2} \text{ d}^{-1}$ (Alderkamp et al. 2012). We hypothesize that the high productivity and NO_3^- drawdown in extensive coastal polynyas of the Ross and Amundsen Seas, resulting from glacial inputs of iron, enhanced light availability, and water column stratification (Gordon et al. 2000, Arrigo et al. 2015), lead to higher $\delta^{15}\text{N}_{\text{baseline}}$ values compared to the WAP and HNLC zones beyond the continental margin.

Our hypothesis that productivity gradients drive the strong gradient in zooplankton $\delta^{15}\text{N}$ values is also supported by work in other sectors of the Southern Ocean. DiFiore et al. (2009) measured the $\delta^{15}\text{N}$ value of suspended particulate organic nitrogen

along the East Antarctic continental margin, including the D'Urville Sea, Davis Sea, and Prydz Bay. They documented a shift in particulate nitrogen $\delta^{15}\text{N}$ values from $<1.5\text{‰}$ for samples from more offshore, pelagic locations to values of $\sim 5\text{‰}$ in persistent coastal polynyas, productivity 'hot spots' where NO_3^- drawdown is extensive (DiFiore et al. 2009). Similarly, Schmidt et al. (2003) reported $\delta^{15}\text{N}$ values of particulate organic matter (POM), *Euphausia superba* furcilia larvae, and copepods (*Metridia gerlachei* and *Calanoides acutus*) that were 4 to 5‰ higher in Marguerite Bay ($67^\circ 30' \text{ S}$, 70° W), in the WAP region than in the Lazarev Sea ($\sim 69^\circ \text{ S}$, 5° W), likely due to differing degrees of NO_3^- utilization by phytoplankton between these 2 sites. During their time of sample collection, phytoplankton abundance in the Lazarev Sea was low ($\sim 0.5 \mu\text{g chl a l}^{-1}$) in contrast with Marguerite Bay, which was experiencing a several-month-long diatom bloom ($7\text{--}10 \mu\text{g chl a l}^{-1}$) (Schmidt et al. 2003). Indeed, visualizations of surface $[\text{NO}_3^-]$ in the WAP during the austral summer revealed pockets of low $[\text{NO}_3^-]$ (e.g. $[\text{NO}_3^-]$ of $\sim 7 \mu\text{mol l}^{-1}$), likely due to phytoplankton NO_3^- consumption, largely along the coast within bays and fjords, while much of the WAP region had surface $[\text{NO}_3^-]$ of 20 to $27 \mu\text{mol l}^{-1}$ (Fig. 5).

In contrast to our observations, previous modeling work by Somes et al. (2010) predicted relatively consistent $\delta^{15}\text{N}_{\text{baseline}}$ values across the West Antarctic, and Jaeger et al. (2010a) modeled a decrease in $\delta^{15}\text{N}_{\text{baseline}}$ values from the STZ towards the AZ. Both the Somes et al. (2010) and Jaeger et al. (2010a) isoscapes focus on oceanic regions, beyond the continental margin, where the NO_3^- pool remains large and underutilized due to apparent iron limitation (Boyd et al. 2012). As such, productivity and associated NO_3^- drawdown, and thus $\delta^{15}\text{N}$ values of POM, decreased from the more productive STZ into the HNLC oceanic area of the Southern Ocean. Our isoscapes include continental margins across the West Antarctic, which are likely to experience higher productivity than oceanic regions due to increased iron inputs and stratification from glacial melting. The WAP has a relatively narrow continental shelf with reduced productivity compared to the wide shelves of the Ross and Amundsen Seas. Thus, our $\delta^{15}\text{N}_{\text{baseline}}$ values increase from the HNLC oceanic area to the continental margins, and this gradient is pronounced in the Amundsen and Ross Sea sectors since they have extensive continental shelves. Additionally, our linear regression analysis revealed increasing zooplankton $\delta^{15}\text{N}$ values with decreasing surface $[\text{NO}_3^-]$ in West Antarctica, indicating that high

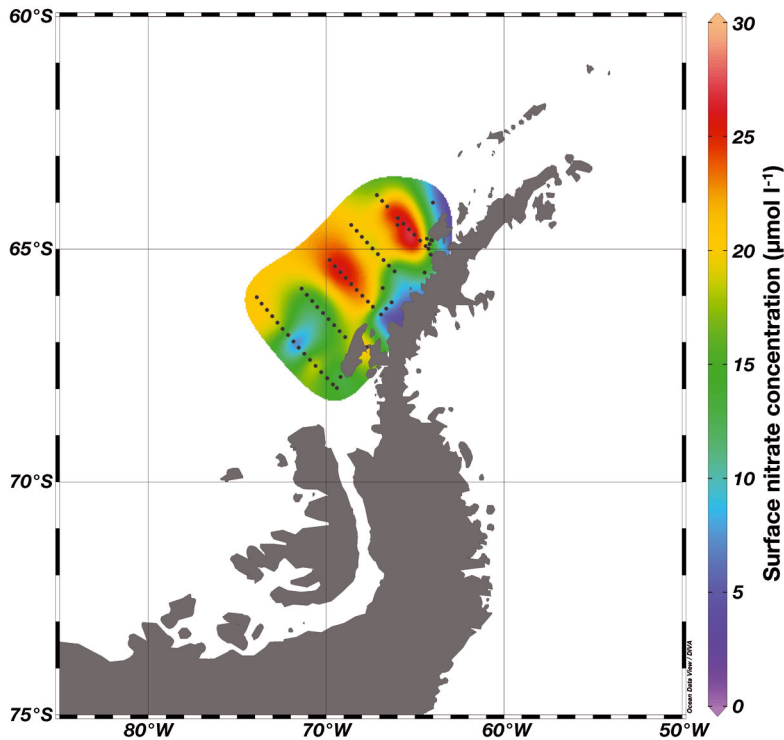


Fig. 5. Surface nitrate concentrations off the West Antarctic Peninsula for the austral summer (January and February) of 2006, a time without a strong El Niño–Southern Oscillation event. Plot produced in Ocean Data View 4.7.4 using a dataset from Ducklow et al. (2017a,b). Sampling locations are indicated by black dots

coastal productivity drives low surface $[\text{NO}_3^-]$ and, consequently, high $\delta^{15}\text{N}_{\text{baseline}}$ values.

The productivity gradient within our systems offers the most parsimonious explanation for the observed $\delta^{15}\text{N}$ isoscape along the continental shelf of the West Antarctic. However, it is possible that either variability in the zooplankton taxa obtained from each region or spatially shifting trophic positions for sampled taxa contribute to the observed nitrogen isoscape patterns. Changes in zooplankton sampling are an unlikely source of the observed pattern because even when analyzed at the level of individual taxon, zooplankton $\delta^{15}\text{N}$ values in the Amundsen and Ross Seas were $\sim 2\%$ higher than those in the WAP (Figs. 3a, 4a, S3a, S4a, S5a, & S6a). While we cannot rule out potential variations in zooplankton trophic position as a contributor to the spatial pattern in $\delta^{15}\text{N}_{\text{baseline}}$ values, it should be noted that the observed $\delta^{15}\text{N}$ gradient would imply nearly a full trophic level change although the $\delta^{15}\text{N}$ gradient is present in the dominantly herbivorous *E. superba* (Siegel & Loeb 1995, Nicol 2006, Pinkerton et al. 2010). Additionally, perhaps spatial variation in the utilization of different nutrient sources (i.e. nitrate and ammo-

nium) by phytoplankton may contribute to our observed $\delta^{15}\text{N}$ gradient (Graham et al. 2010). These possible factors should be explored in future research.

Importantly, the physical conditions affecting primary productivity and nutrient drawdown in West Antarctica vary seasonally and inter-annually as a result of regional and global climate events (Wainright & Fry 1994, Smith et al. 1998, Kwok & Comiso 2002, Arrigo & van Dijken 2004, Arrigo et al. 2008). These temporal dynamics can have a strong impact on the geospatial isotope patterns in this region, depending on organism integration time. For instance, productivity slowly increases in the early austral spring (October) as a result of increased insolation and iron inputs from retreating sea ice (Arrigo & van Dijken 2003), reaching peak bloom in the austral summer, before returning to pre-bloom levels by March or April (Arrigo & van Dijken 2003). The temporal progression of phytoplankton blooms results in a corresponding seasonal pattern of nutrient drawdown and $\delta^{15}\text{N}_{\text{baseline}}$ value shift, whereby the surface layer $[\text{NO}_3^-]$ is low and the $\delta^{15}\text{N}_{\text{baseline}}$ value is high at the bloom peak (DiFiore et al.

2006, 2009). Most of our zooplankton samples were collected during the austral summer, largely between mid-December and late January. Some of our zooplankton samples were obtained during the early austral fall. Sampling period did not significantly affect a region's $\delta^{15}\text{N}$ value for our zooplankton, euphausiid, or amphipod isoscapes. Yet, since our zooplankton sampling occurred predominately within the summer, integrating oceanographic conditions over multiple preceding months, our isoscapes may not fully capture the full seasonal variation in productivity and, consequently, $\delta^{15}\text{N}_{\text{baseline}}$ values. Selection of an isoscape with appropriate time integration for the temporal scale of a research question is important, and our isoscape best represents geospatial gradients in West Antarctica occurring over a period of months and, perhaps, years, not short time scales of weeks or days.

On longer time scales, the dominant climate modes in the Southern Hemisphere, resulting in interannual variation in environmental conditions, are the Southern Annular Mode (SAM) and the El Niño–Southern Oscillation (ENSO) (Arrigo et al. 2008, Stammerjohn et al. 2008), which result in a host of interannual vari-

ations in environmental conditions (e.g. Smith et al. 1999, Croxall et al. 2002). SAM and ENSO co-vary; La Niña (El Niño) is associated with positive (negative) SAM. La Niña and positive SAM events are associated with colder conditions and more sea ice in the Ross and Amundsen Seas, while the WAP experiences warmer conditions and less sea ice (Arrigo et al. 2008, Stammerjohn et al. 2008). The opposite scenario has been observed for El Niño and negative SAM events (Arrigo et al. 2008, Stammerjohn et al. 2008).

Visualizations of surface $[\text{NO}_3^-]$ off the WAP during times of varying ENSO conditions in recent years for which data are available (Ducklow et al. 2017a,b) show possible effects of ENSO events on surface $[\text{NO}_3^-]$ in this region (Figs. 5, S10, & S11). Areas of high NO_3^- drawdown near the WAP coast take place during austral summers with or without a strong ENSO event (Figs. 5, S10, & S11). However, the extent of nearshore NO_3^- drawdown appears low, intermediate, and high during a La Niña event, no strong ENSO event, and an El Niño event, respectively, with presumably opposite (but unmeasured) effects in the Amundsen and Ross Seas. The surface $[\text{NO}_3^-]$ minima along the WAP coast are approximately 12, 7, and 4 $\mu\text{mol l}^{-1}$ during periods with a La Niña event, no strong ENSO event, and an El Niño event, respectively (Figs. 5, S10, & S11).

Our comparison of $\delta^{15}\text{N}_{\text{baseline}}$ values among different West Antarctic regions uses data from zooplankton samples collected during times of La Niña events (periods of December 2007 through January 2008 and December 2010 through January 2011) or an El Niño (early fall 2015) event. While differing ENSO conditions across sampling periods may contribute to some of the observed variation in $\delta^{15}\text{N}_{\text{baseline}}$ values within this isoscape, it should be noted that sampling period did not have a significant effect on zooplankton $\delta^{15}\text{N}$ values. For the WAP, a region sampled during different ENSO conditions, $\delta^{15}\text{N}_{\text{baseline}}$ values of zooplankton collected during strong La Niña events (December 2010 through January 2011 or December 2007 through January 2008) are similar to those collected during a weak-to-moderate El Niño event (early fall 2015). Our findings suggest that the observed nitrogen isotope gradients in the West Antarctic are robust at least over the sampling period of this study. However, future research should further examine the extent of $\delta^{15}\text{N}_{\text{baseline}}$ value variation in West Antarctica resulting from the climate modes over longer time scales.

$\delta^{13}\text{C}$ isoscapes track temperature gradients

Our carbon isoscape reveals an inverse relationship between $\delta^{13}\text{C}_{\text{baseline}}$ values and latitude. The Ross Sea (sampling stations at latitudes between 71 and 79° S) has significantly lower $\delta^{13}\text{C}$ values than the WAP and PFZ/SAZ (sampling latitudes between 69 and 55° S) by about 2 and 3‰, respectively (Fig. 2b). These patterns in zooplankton $\delta^{13}\text{C}$ value are generally consistent with previously reported data for the region. Pinkerton et al. (2013) reported that Ross Sea zooplankton have a mean $\delta^{13}\text{C}$ value of $-26.7 \pm 2.0\text{‰}$ (14 taxa), which is similar to that for the composite of all Ross Sea zooplankton in our study ($-27.5 \pm 1.6\text{‰}$). Schmidt et al. (2003) reported a comparable pattern of decreasing zooplankton $\delta^{13}\text{C}$ values from the PFZ/SAZ ($-25.6 \pm 3.3\text{‰}$; 15 taxa) to 65° S ($-30.0 \pm 0.6\text{‰}$; 4 taxa) as we do across a similar latitudinal gradient, although their absolute values are lower than ours. Schmidt et al. (2003) did not lipid-extract their samples, which may explain the lower $\delta^{13}\text{C}$ values they reported. Lastly, McMahon et al. (2013b) produced a global $\delta^{13}\text{C}$ isoscape from meta-analyses of published plankton $\delta^{13}\text{C}$ values. While their global isoscape had limited sample coverage for the area of interest in our study (e.g. no coverage in the Amundsen Sea and only part of the Ross Sea), they found a decrease in plankton $\delta^{13}\text{C}_{\text{baseline}}$ values from -23 to -25‰ in the PFZ/SAZ to values between -25 and -30‰ in the AZ/WAP, similar to the $\delta^{13}\text{C}$ spatial gradient in our study.

The observed inverse relationship between $\delta^{13}\text{C}$ variation and latitude within the West Antarctic isoscape is likely explained by the latitudinal gradient in SST (Cherel & Hobson 2007, Quillfeldt et al. 2010, 2015). This is because the $\delta^{13}\text{C}$ value of primary production is greatly influenced by the CO_2 solubility in the ocean, which increases with decreasing temperature, as the fractionation associated with photosynthetic uptake of CO_2 is strongly expressed in high $[\text{CO}_{2(\text{aq})}]$ environments (Goericke & Fry 1994, Graham et al. 2010). Using SST values for our sampling locations (Gouretski & Koltermann 2004) within these regions (-1.3 , 0.1 , and 4°C for the Ross Sea, WAP, and PFZ/SAZ, correspondingly) and equations derived by Rau et al. (1989) relating SST, $\text{CO}_{2(\text{aq})}$, and phytoplankton $\delta^{13}\text{C}$ values, we correctly predicted an offset between Ross Sea and PFZ/SAZ zooplankton $\delta^{13}\text{C}$ values of 3‰ and an offset of 1‰ between the Ross Sea and WAP zooplankton $\delta^{13}\text{C}$ values. Thus, SST may completely explain the difference in zooplankton $\delta^{13}\text{C}$ values between the Ross Sea and PFZ/SAZ. However, our calculated offset between zooplankton

$\delta^{13}\text{C}$ values from the Ross Sea and WAP was less than our measured offset, suggesting other drivers besides just SST may be influencing this gradient in $\delta^{13}\text{C}_{\text{baseline}}$ values.

Although many studies have indicated that SST and, in association CO_2 solubility, drives variation in phytoplankton $\delta^{13}\text{C}$ values (Rau et al. 1989, 1991, Cherel & Hobson 2007, Quillfeldt et al. 2010, 2015), a number of other potential factors, including dissolved inorganic carbon (DIC) source, growth and photosynthetic rates, and phytoplankton size and geometry, can influence phytoplankton, and therefore zooplankton, $\delta^{13}\text{C}$ values (Descolas-Gros & Fontugne 1985, Falkowski 1991, Popp et al. 1998, 1999, Villinski et al. 2000, Kennedy et al. 2002, Papadimitriou et al. 2009, Kohlbach et al. 2016). Variation in $\delta^{13}\text{C}_{\text{DIC}}$ values is likely not a substantial factor shaping $\delta^{13}\text{C}_{\text{baseline}}$ values in West Antarctica, because prior research has found that areas of the Southern Ocean, such as the Drake Passage, exhibit considerable gradients in phytoplankton $\delta^{13}\text{C}$ values with little change to source DIC values (Rau et al. 1991). However, future work will be needed to determine whether the local regions of plankton $\delta^{13}\text{C}$ offsets are explained by local gradients in cell size or geometry, growth rate, or CO_2 drawdown not directly related to SST.

As was the case with nitrogen, temporal variation in carbon isotope gradients is an important factor to consider when evaluating isoscape structure. SSTs fluctuate seasonally with sea ice conditions, as well as interannually with variation in climate modes (Wainright & Fry 1994, Kwok & Comiso 2002, Arrigo et al. 2008). As described above, La Niña and positive SAM events are associated with colder conditions and more sea ice in the Ross and Amundsen Seas, while the WAP experiences warmer conditions and less sea ice (Arrigo et al. 2008, Stammerjohn et al. 2008). El Niño and negative SAM events experience the reverse situation (Arrigo et al. 2008, Stammerjohn et al. 2008). Prior work has suggested that these climate modes may cause SST anomalies of up to $\pm 0.5^\circ\text{C}$ (Yuan 2004). This temporal variation is less than the SST range spanning our study region, suggesting that the temporal variability will not overpower the spatial gradient signal. For instance, our $\delta^{13}\text{C}$ isoscapes for all zooplankton, euphausiids, amphipods, and phytoplankton are not significantly affected by sampling period. However, our sampling was limited primarily to the austral summer and did not cover several years. Thus, our $\delta^{13}\text{C}_{\text{baseline}}$ may not fully capture the true dynamism of seasonal and interannual patterns, which should be explored more thoroughly in future studies.

CONCLUSIONS

This study presents the first empirically derived zooplankton isoscapes for West Antarctica, reflecting dynamic biogeochemical change across the region. Our isoscapes revealed a $\sim 3\%$ increase in $\delta^{15}\text{N}$ values from HNLC oceanic regions to the continental margins of West Antarctica, which we attribute to increasing productivity and nutrient utilization. Conversely, there was a $\sim 3\%$ decrease in $\delta^{13}\text{C}$ values from the PFZ/SAZ to the Ross Sea, which we attribute primarily to decreasing SST. These isoscapes provide a critical first look at the strong geospatial gradients in stable carbon and nitrogen isotope values across major biogeographic zones of the West Antarctic. Such isoscapes will open new doors for ecological, paleoecological, and oceanographic studies of food web architecture, biogeochemical cycling, and animal migration in the Southern Ocean. Furthermore, these isoscapes will serve as a benchmark for future studies of biogeochemical change in this highly dynamic system, which is experiencing some of the most rapid climate change on Earth.

It is important to recognize the limitations of our $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ isoscapes, which apply to all static isoscape approaches. Our isoscapes were generated from a limited number of opportunistically collected samples, requiring interpolation among data points to generate the smooth gradient contours. The resulting geospatial patterns are strong and consistent across a number of independent taxa, but additional sampling will improve the accuracy and precision of the isoscapes. Our hope is that our isoscapes will encourage more empirical sampling to enhance the evaluation of the geospatial isotope patterns in this critical region and better understand the underlying mechanisms driving those patterns. In addition, our isoscape represents a limited period of time. Temporal variability in regional oceanography (e.g. SST), sources of N or C fueling primary production, phytoplankton growth rate, community composition, etc. can all impact the geospatial distribution of stable isotope values in space and time. In particular, further studies on the role of climate modes (e.g. ENSO) on interannual variation in baseline isotope values will allow for improved construction and application of isoscapes. Future work should advance Southern Ocean isoscapes to better capture temporal variation in baseline isotope values and increase spatial resolution.

Acknowledgements. We thank Deborah Steinberg, Kate Ruck, Heidi Geisz, and Rebecca Dickhut for providing us with an array of samples. We are grateful to Colin Carney

and Dyke Andreassen for laboratory assistance. We also thank the crew and staff on the RV 'Oden' (austral summers of 2007/08 and 2010/11), RV 'Nathaniel B. Palmer' (austral summer 2011/12), and SV 'Lawrence M. Gould' (early fall 2015), as well as the staff of the PAL-LTER (from 2007 through 2011). This project was supported by the National Science Foundation (NSF ANT-1142108 and OPP-1347911). We are grateful to the anonymous reviewers and editor for their valuable guidance in improving this manuscript.

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Editorial responsibility: Keith Hobson,
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Submitted: April 10, 2017; Accepted: February 10, 2018
Proofs received from author(s): April 3, 2018