

RESEARCH/REVIEW ARTICLE

Multi-frequency observations of seawater carbonate chemistry on the central coast of the western Antarctic Peninsula

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Abstract

Assessments of benthic coastal seawater carbonate chemistry in Antarctica are sparse. The studies have generally been short in duration, during the austral spring/summer, under sea ice, or offshore in ice-free water. Herein we present multi-frequency measurements for seawater collected from the shallow coastal benthos on a weekly schedule over one year (May 2012–May 2013), daily schedule over three months (March–May 2013) and semidiurnal schedule over five weeks (March–April 2013). A notable pH increase (max pH = 8.62) occurred in the late austral spring/summer (November–December 2012), coinciding with sea-ice break-out and subsequent increase in primary productivity. We detected semidiurnal variation in seawater pH with a maximum variation of 0.13 pH units during the day and 0.11 pH units during the night. Daily variation in pH is likely related to biological activity, consistent with previous research. We calculated the variation in dissolved inorganic carbon (DIC) over each seawater measurement frequency, focusing on the primary DIC drivers in the Palmer Station region. From this, we estimated net biological activity and found it accounts for the greatest variations in DIC. Our seasonal data suggest that this coastal region tends to act as a carbon dioxide source during austral winter months and as a strong sink during the summer. These data characterize present-day seawater carbonate chemistry and the extent to which these measures vary over multiple time scales. This information will inform future experiments designed to evaluate the vulnerability of coastal benthic Antarctic marine organisms to ocean acidification.

To access the supplementary material for this article, please see supplementary files under Article Tools online.

Patterns in pH and carbonate chemistry of seawater in coastal and offshore regions of the world's oceans have become increasingly relevant in the face of ocean acidification, a process defined as the decrease in oceanic pH driven by the absorption of increasing anthropogenic atmospheric carbon dioxide (CO₂; Caldeira & Wickett 2003). High-latitude marine environments are particularly susceptible to ocean acidification due to the naturally lower buffer capacity (higher Revelle factor) associated with cold, high-latitude waters (Sabine et al. 2004). This in turn contributes to a reduction in carbonate ion concentration that can challenge the ability of marine

organisms to produce and maintain calcium carbonate (CaCO₃) skeletal structures comprised of aragonite or calcite (Orr et al. 2005). Seawater carbonate models developed for high latitudes predict that regions such as the Southern Ocean will approach undersaturation thresholds for aragonite and calcite ($\Omega \leq 1$) sooner than temperate and tropical regions (McNeil & Matear 2008). Large seasonal fluctuations in aragonite saturation have already been detected in coastal regions of eastern Antarctica (McNeil et al. 2010), fostering predictions that aragonite undersaturation may occur within the next 25 years (McNeil & Matear 2008).

Understanding the chemical properties of present-day seawater experienced by coastal Antarctic organisms is critical to understanding and interpreting their susceptibility to ocean acidification. To date pH, total alkalinity (TA) or carbonate saturation states in the Southern Ocean have been measured primarily under sea ice (Gibson & Trull 1999; Matson et al. 2011; Roden et al. 2013; Matson et al. 2014), in pelagic open water environments (Takahashi et al. 2012; Björk et al. 2014), or at a combination of both open water and under-ice locations (Gibson & Trull 1999; Roden et al. 2013). These studies have largely focused on East Antarctica and the Ross Sea, which are experiencing slower rates of climate variation than the western Antarctic Peninsula (Stammerjohn, Martinson, Smith & Iannuzzi 2008).

The rapid warming and concomitant reduction in the extent and duration of the annual sea ice along the Antarctic Peninsula (Martinson et al. 2008) make studies of the prospective additive or synergistic impacts of ocean acidification on marine organisms in this region important (Fabry et al. 2009). As the Antarctic Peninsula runs north–south in its geographic orientation it is directly exposed to westerly atmospheric and oceanic circulation patterns. These processes facilitate an influx of warmer water from the nutrient rich upper circumpolar deep-water (UCDW) current system and reinforce atmospheric variations that induce frequent upwelling of warmer waters along the western Antarctic Peninsular shelf (Ducklow et al. 2013).

There is limited information on the fluctuations of temperature or carbonate chemistry of the coastal benthic waters of the western Antarctic Peninsula. Fluctuations of seawater chemistry variables have the potential to increase with climate forcing induced by increased atmospheric $p\text{CO}_2$ levels, resulting in concomitant decreases in pH. A variety of calcified and non-calcified marine organisms are susceptible to ocean acidification (Byrne 2011). However, it is important to first understand ambient carbonate chemistry parameters to which these organisms are regularly exposed. In the present study, we have three main goals: (1) to present measurements of seawater pH, TA and carbonate system parameters at three sampling frequencies over three overlapping time periods ranging from one year to five weeks; (2) to compare these measurements and the variation between repeat measurements recorded at our three sampling frequencies to observations from other coastal regions of Antarctica; (3) to discuss the role of biological activity in the variations in seawater chemistry presented here. The present study represents the first assessment of these seawater parameters for a coastal benthic site representative of regional bays along the central western Antarctic Peninsula.

Materials and methods

Seawater sampling

The site of seawater collection was Arthur Harbor, located adjacent to the US Antarctic Program (USAP) research facility, Palmer Station, on the central western Antarctic Peninsula ($64^{\circ}46' \text{ S}$, $64^{\circ}03' \text{ W}$). Seawater was collected at three sampling frequencies over three overlapping time periods: weekly over one year (4 May 2012–31 May 2013), once daily in the early morning over approximately three months (3 March–30 May 2013) and semidiurnally—at approximately 08:00 local time and after 17:00 local time every day over the course of five weeks (3 March–10 April 2013). Unfiltered seawater was collected from a hose plumbed off the main seawater intake pipe, resting on the seafloor (approximately 6 m depth) in Arthur Harbor adjacent to Palmer Station. The sampling hose siphoned seawater off prior to any treatment (filters, bubblers, etc.) and before entering the main seawater system that provides seawater for the Palmer Station aquarium facility. The intake pipe was approximately 45 m in length; the intake point was submerged and screened 10 m from shore. The seawater intake system is back-flushed daily to minimize algal and invertebrate growth and has been used to sample natural seawater year round or when sea ice makes sampling unfeasible from small boats (e.g., Vernet et al. 2012; Tortell et al. 2014). There were no discernible differences between pH, TA, temperature and salinity of seawater samples hand-collected along the shore of Arthur Harbor and seawater sampled from the hose plumbed to the seawater intake line (differences fell within the recorded range of experimenter/instrument error).

Seawater samples were collected and processed in accordance with methods presented by Dickson et al. (2007). Prior to each sample collection, both the hose and sample bottles were thoroughly flushed (flow rate = 37.5 L min^{-1}) for a minimum of five minutes to ensure that seawater samples for pH and TA analysis had been pumped immediately from the benthos and had stabilized at ambient seawater temperature prior to collection. During flushing, seawater temperature was measured at the outflow location of sample collection using a DigiSense® ThermoLogR Thermister (resolution of 0.01°C ; Cole-Parmer, Vernon Hills, IL). Seawater samples for pH and TA for each given time point were collected in the same 300 ml borosilicate bottles fitted with ground glass stoppers. The pH was analysed immediately following the first opening of each sample bottle after collection. The remaining seawater was used for TA titrations. When it was impossible to conduct this two-step analysis within four hours, the sample was fixed with 0.10 ml of a 50%

saturated mercuric chloride solution to halt biological activity. Bottles were sealed with a greased glass stopper and further secured with electrical tape and stored in a cool dark location until subsequent pH and TA analysis. Samples analysed within four hours were not preserved, but were held in a cool dark location until analysis.

Seawater analysis

Seawater carbonate chemistry was analysed following the methods outlined by Dickson et al. (2007). We recorded pH, TA, temperature and salinity for each seawater sample collected. Seawater pH was determined spectrophotometrically on the total hydrogen scale (pH_T) using an ultraviolet-visible spectrophotometry Spectrometer Lambda 40P (Perkin Elmer, Waltham, MA, USA) equipped with temperature-controlled cell plumbed to a water bath (Digital One RTE 17 Chiller Recirculating Water Bath, Neslab, Portsmouth, NH, USA). We used *m*-cresol purple as our pH sensitive indicator dye (SOP 6b; Dickson et al., 2007). Analysis of replicate seawater samples collected over the year, as well as certified reference material (CRM) provided by A. Dickson at Scripps Institute of Oceanography, University of California at San Diego, indicated instrument and technician precision of 0.03 pH units (mean SD, $N=11$). We used certified TA, dissolved inorganic carbon (DIC), temperature and salinity data provided, to calculate corresponding CRM pH_T levels. We then compared these calculated levels to spectrophotometrically measured pH_T for CRMs to confirm calibration because certified pH levels are not included in provided CRM data. Spectrophotometer calibration diagnostics were also run to determine measurement precision and accuracy.

Seawater TA was determined by open cell potentiometric titration, outlined in SOP 3b of Dickson et al. (2007), using a T50 open cell titrator equipped with a pH probe (Model DGI115-SC, Mettler-Toledo, Greifensee, Switzerland). All seawater samples were held in a jacketed beaker plumbed to a water bath (Digital One RTE 17 Chiller Recirculating Water Bath, Neslab) to maintain constant sample temperature during titration. Titrant volumes were recorded in real time using Mettler-Toledo LabX[®] software. All TA determinations were based on formulas described by Dickson et al. (2007). We confirmed TA calibration and precision through replicate analysis of individual seawater samples and CRMs. We established instrument and technician precision of $4.02 \mu\text{mol kg}^{-1}$ SW (mean SD, $N=17$).

Carbonate system parameters were calculated based on pH_T , TA, temperature and salinity data using CO2calc software (Robbins et al. 2010). For these calculations, we

used CO_2 constants from Roy et al. (1993) and a KHSO_4 acidity constant from Dickson (1990) for carbonate chemistry calculations. The use of appropriate CO_2 constants has been previously discussed and assessed in the literature (Wanninkhof et al. 1999). There is good general agreement between predicted carbonate chemistry based on multiple models when seawater samples are below 5°C (see Wanninkhof et al. 1999). To maintain consistency with previous assessments of Antarctic seawater carbonate chemistry (Gibson & Trull 1999; Wang et al. 2010; Roden et al. 2013), CO_2 constants determined between 0 and 45°C by Roy et al. (1993) were used.

While temperature was digitally recorded immediately at the time of seawater collections, salinity was measured later when samples were subsequently processed for pH_T and TA analysis. A salinity probe equipped with a Model 3200 conductivity instrument (YSI, Yellow Springs, OH, USA) with conductivity cell (3253 Model B, YSI) with precision of ± 0.1 ppt was used for seawater samples collected during May 2012 and March–April 2013 samples. The samples collected from May 2012 to February 2013 were measured using a refractometer (1.000–1.070 specific gravity, Model A366ATC, Vista, Kirkland, WA, USA) with precision of ± 1 ppt zeroed with distilled water prior to each measurement. We used the salinity data to normalize TA and DIC measurements to isolate influences associated with variations in salinity (e.g., mixing, ice formation/melt, glacial melt, precipitation or other freshwater input) from biological activity. As sea ice forms, salts are rejected, leading to the creation of brines that can increase TA, DIC and salinity. Inverse changes in these parameters occur with ice melt. Therefore, salinity normalization of TA values assumes that these changes occur in proportion to each other, isolating the effects of hydrographic changes in TA values. To calculate salinity normalized total alkalinity (nTA), we multiplied each TA measurement by the ratio of the annual mean salinity (35) by the salinity (S_{TA}) of a given measurement based on the traditional salinity normalization calculation method.

$$\text{nTA} = \text{TA} + \left(\frac{35}{S_{\text{TA}}} \right) \quad (1)$$

Chlorophyll *a* and sea ice

To evaluate the potential influence of local autotrophic biological activity on the seawater chemical parameters measured, we report chlorophyll (chl) *a* concentrations from Arthur Harbor, Palmer Station, recorded and analysed as a part of the Palmer Long-Term Ecological

Research (PAL-LTER) programme (data repository ID: 197, www.oceaninformatics.ucsd.edu/datazoo/data/pallter/datasets). All seawater samples collected for the PAL-LTER chl *a* analysis were collected at the same time and from the same source as samples collected for weekly analysis in the present study. The chl *a* samples were collected and processed in accordance with PAL-LTER protocols, briefly summarized here (Schofield & PAL-LTER 2014, data repository ID: 197). Seawater samples were collected after seawater was flushed for 2–3 min from the sampling line. Each discrete sample was filtered using 0.45 HA. The filters were placed at -70°C for at least 24 h prior to extraction in 90% acetone (Schofield & PAL-LTER 2014). Fluorescence was read on a digital Turner fluorometer and resultant chl *a* was calculated following Smith et al. (1981).

Additionally, annual sea-ice development and melt can influence seawater chemistry, therefore we also report sea-ice conditions derived from satellite observations conducted by the PAL-LTER programme (Stammerjohn & PAL-LTER 2014; data repository ID: 151, www.oceaninformatics.ucsd.edu/datazoo/data/pallter/datasets). Sea-ice data are collected and analysed in accordance with PAL-LTER protocols and briefly summarized here (Stammerjohn & PAL-LTER 2014). Sea-ice advance, retreat, duration and concentrations were derived from satellite images using version 2 of the Bootstrap sea-ice concentrations from Nimbus-7 SMMR and DMSP SSM/I. Sea-ice duration was defined as the time between the first sea-ice advance and final retreat within a given region over the course of a year. Sea-ice concentration was derived from grid superimposition (Stammerjohn & PAL-LTER 2014). In the present study, we have combined the percent sea-ice coverage with the annual data sets to illustrate the influence of sea-ice duration and coverage on local Palmer area seawater chemistry.

Drivers of DIC variability

The seawater sampling location, Arthur Harbor, is a relatively shallow, protected bay which experiences wind driven mixing. Therefore we presumed sea-ice formation and melt, air–sea CO_2 gas exchange and biological activity to be the major drivers of variations in local DIC concentrations. We calculated the drivers of DIC variability from salinity normalized DIC values. To calculate nDIC values, we utilized the same basic equation (Eqn. 1), substituting DIC for TA values (Wang et al. 2010). From the calculated variation in nDIC ($\Delta\text{DIC}_{\text{obs}}$), we calculated variations due to air–sea CO_2 flux ($\Delta\text{DIC}_{\text{as}}$) and biological activity ($\Delta\text{DIC}_{\text{bio}}$).

$$\Delta\text{DIC}_{\text{obs}} = \Delta\text{DIC}_{\text{as}} + \Delta\text{DIC}_{\text{bio}} \quad (2)$$

It is possible for local air–sea CO_2 flux to exert a prominent influence on DIC fluxes in the Palmer Station area due to the sea remaining largely ice-free for the majority of the year (Ducklow et al. 2013). A positive air–sea CO_2 flux value implies a net absorption of CO_2 from the atmosphere into surface waters, indicating that local waters may be acting as a CO_2 sink during these time periods. To calculate the local air–sea CO_2 flux at each sampling frequency ($\text{mmol C m}^{-2} \text{ d}^{-1}$ – weekly and daily sampling or $\text{mmol C m}^{-2} \text{ h}^{-1}$ – semidiurnal sampling), we utilized CO2calc software (Robbins et al. 2010) with the air–sea flux transfer velocity equation of Wanninkhof (1992). For the calculation of the gas transfer velocity, we obtained average wind speeds recorded for each sampling day at Palmer Station as part of PAL-LTER weather monitoring (data repository ID: 28, www.oceaninformatics.ucsd.edu/datazoo/data/pallter/datasets). To obtain atmospheric $p\text{CO}_2$, we utilized measurements made of atmospheric $p\text{CO}_2$ at South Pole Station after comparing measurements taken at Palmer Station (www.scrippsco2.ucsd.edu/data/psa.html; Graven et al. 2012) from March 2005 to September 2007 with samples taken over the same time period at South Pole Station (www.scrippsco2.ucsd.edu/data/spo.html; Keeling et al. 2001). Measurements made over the same time period at each location showed little monthly variation (mean \pm SD – South Pole Station = 378.7 ± 1.5 μatm ; Palmer Station = 379.0 ± 2.0 μatm), indicating that measurements made at South Pole Station are representative of atmospheric $p\text{CO}_2$ at Palmer Station.

To account for sea-ice cover influences in our air–sea flux calculations we scaled all calculated fluxes using a multiplier estimating the proportion of open, ice-free water (I_F). This is equal to one minus the fraction of local sea surface covered by ice (P_i), allowing us to calculate free air–sea CO_2 gas exchange (Eqn. 3; Bates 2006).

$$I_F = 1 - P_i \quad (3)$$

We utilized this method based on the assumption that the sea ice present during a given sampling period acted as an effective barrier to air–sea CO_2 exchange (Bates 2006; Roden et al. 2013). The variation in DIC due to biological processes ($\Delta\text{DIC}_{\text{bio}}$) was estimated by calculating the difference between $\Delta\text{DIC}_{\text{obs}}$ and $\Delta\text{DIC}_{\text{as}}$ (Eqn. 2).

The variations in DIC due to the potential drivers ($\Delta\text{DIC}_{\text{bio}}$ and $\Delta\text{DIC}_{\text{as}}$) were estimated for samples collected for each sampling frequency previously described. In the weekly and daily samples, variations in DIC were calculated as daily fluctuation ($\text{mmol C m}^{-2} \text{ d}^{-1}$). Samples for the present study were collected weekly with few exceptions when it was not possible to collect seawater samples on the same day every week. For samples collected

semidiurnally, we calculated the hourly variations in DIC that developed during the day (08:00–17:00) and during the night (17:00–08:00).

Error analysis

The propagated uncertainty associated with calculated carbonate parameters based on the propagation of error associated with each measured parameter input into CO2calc (pH_T , TA, temperature and salinity) was estimated by calculating the quadratic sum of partial uncertainties. The ΔDIC_{obs} was estimated from the quadratic sum of partial uncertainty associated with the ΔDIC and salinity. The ΔDIC_{as} has an approximate 20% uncertainty associated with its calculation (discussed further by Watson et al. 2009), due in large part to the uncertainty associated with the gas transfer velocity used in equations provided by Wanninkhof (1992) to calculate the CO_2 air–sea flux in CO2calc. The overall uncertainty associated with the CO_2 air–sea flux estimated in the present study may have been increased by an additional ca. 10% because phosphate and silicic acid were not included in our calculations of carbonate chemistry parameters. Therefore, to be conservative, we report 30% uncertainty for the estimated ΔDIC_{as} reported here. The ΔDIC_{bio} uncertainty was estimated from the quadratic sum of partial uncertainty associated with ΔDIC_{obs} and ΔDIC_{as} .

Statistics

In semidiurnal sampling, we calculated the variation for seawater chemistry values that occurred between morning and evening sampling within the 24 h period. For the changes calculated to have occurred during the day and night, we used a 2×3 contingency table to test whether the relative frequency of the direction of net change was independent of the time of sampling. Similarly, we also calculated the ΔDIC_{obs} , ΔDIC_{as} and ΔDIC_{bio} for each day and night pair with a 2×3 contingency table to test whether the frequency of the direction of net change (the same values recorded for both measurement time points) was independent of the time of observation.

Results

Weekly measurements

There was a gradual increase in seawater pH that began in October and peaked in mid-November, continuing through early December (Fig. 1a). There was an increase from an annual median baseline pH of 8.09 to a maximum of pH 8.62. Following this peak, seawater pH rapidly

returned to a spring/summer (Nov–Dec/Jan–Feb) median of 8.22 and remained at this level until the beginning of March (Fig. 1a, Supplementary Table S1). The TA and nTA values for this same period remained relatively constant (Fig. 1b, c, Supplementary Table S1). However, there was a general decline in TA and nTA beginning in January 2013, prior to the beginning of the daily sampling in March, following the decline of the pH to its spring/summer median of 8.22 (Fig. 1b, c, Supplementary Table S1).

The median temperature of seawater was approximately $0.9^\circ C$ over the course of the one-year sampling period (May 2012–May 2013). Temperatures reached a seasonal minimum of $-1.54^\circ C$ by August and September 2012 (Fig. 1d, Supplementary Table S1). Seawater temperatures returned to levels above $0^\circ C$ by December 2012 and climbed to a high of $2.2^\circ C$ by January 2013. Coincident with the pH pattern described above for this spring/summer period, seawater temperature increased rapidly from approximately $-1.0^\circ C$ to approximately $2.5^\circ C$ (Fig. 1d). This warming occurred as the sea ice transitioned from thicker, more extensive areal coverage to thinner, reduced coverage prior to the subsequent spring break-out (Fig. 1a–d). Salinity during this time period remained stable (Fig. 2a, Supplementary Table S1). However it should be noted that the use of a refractometer to measure salinity of seawater samples collected between May 2012 and February 2013 reduced the resolution of these measurements.

Calcite and aragonite saturation states (Ω_{cal} and Ω_{arg}) mirrored the annual pattern of seawater pH, with a gradual increase in October, followed by a peak in mid-November through early December (Fig. 2b, c). The minimum Ω_{cal} and Ω_{arg} recorded were 2.08 and 1.31, respectively, both occurring during the late austral autumn/winter (September 2012). The Ω_{arg} and Ω_{cal} approached undersaturation levels during the austral autumn/winter (median $\Omega_{arg} = 1.52$, Figs. 2, 3, Supplementary Table S1) and remained saturated during the spring/summer period (median $\Omega_{arg} = 2.19$, Supplementary Table S1). The pCO_2 levels over the austral winter remained relatively stable until the spring sea-ice break-out when levels dramatically decreased. In the austral 2013 autumn months, pCO_2 levels returned to levels similar to those observed during the 2012 autumn/winter season (Fig. 2d). Additionally, the median seawater pCO_2 value was approximately 42% higher in autumn/winter ($340 \mu atm$) than in spring/summer ($240 \mu atm$). We recorded maximum pCO_2 levels during the austral winter up to $418 \mu atm$. During this time the atmospheric pCO_2 levels were approximately 389 – $391 \mu atm$ for the same time period (recorded at South Pole Station,

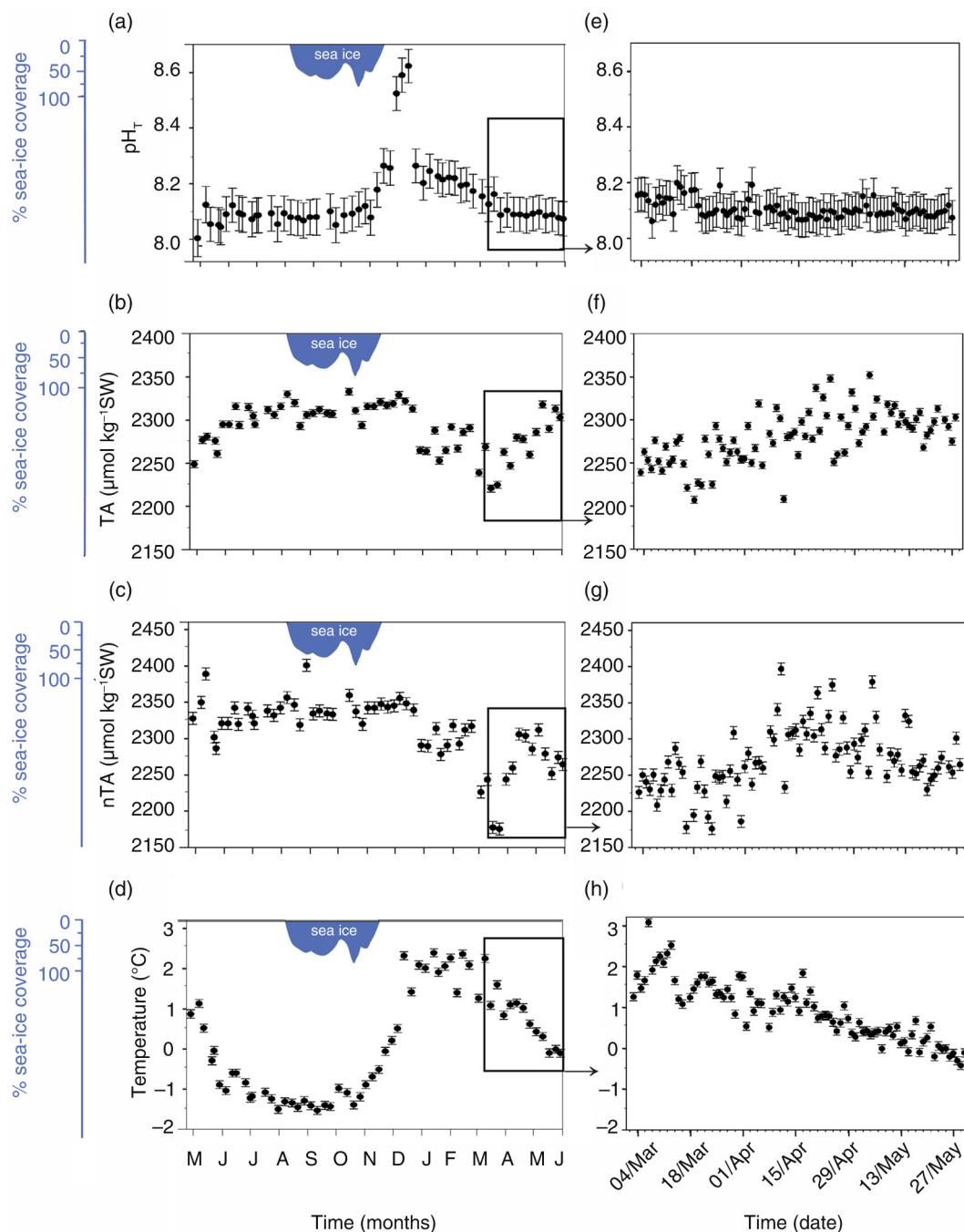


Fig. 1 Graphs depict multi-frequency seawater sampling measurements. (a)–(d) Weekly seawater samples were collected from Arthur Harbor adjacent to Palmer Station, Antarctica over the course of one year (May 2012–May 2013). (e)–(h) Daily measurements were performed for the last three months of the observation period (March–May 2013). Boxed sections in (a)–(d) represent the same time period represented by the corresponding graphs on the right, (e)–(h). Maximum sea-ice coverage depicted in annual seawater chemistry figure panels was 76%. Error bars represent measurement and propagated uncertainties associated with each parameter.

www.scrippsco2.ucsd.edu/data/spo.html; Keeling et al. 2001). In contrast, we recorded the lowest seawater $p\text{CO}_2$ levels during the austral summer, with a median

seawater $p\text{CO}_2$ level of $334 \mu\text{atm}$. This is well below the atmospheric $p\text{CO}_2$ range ($390\text{--}391 \mu\text{atm}$) recorded at South Pole Station over the same period.

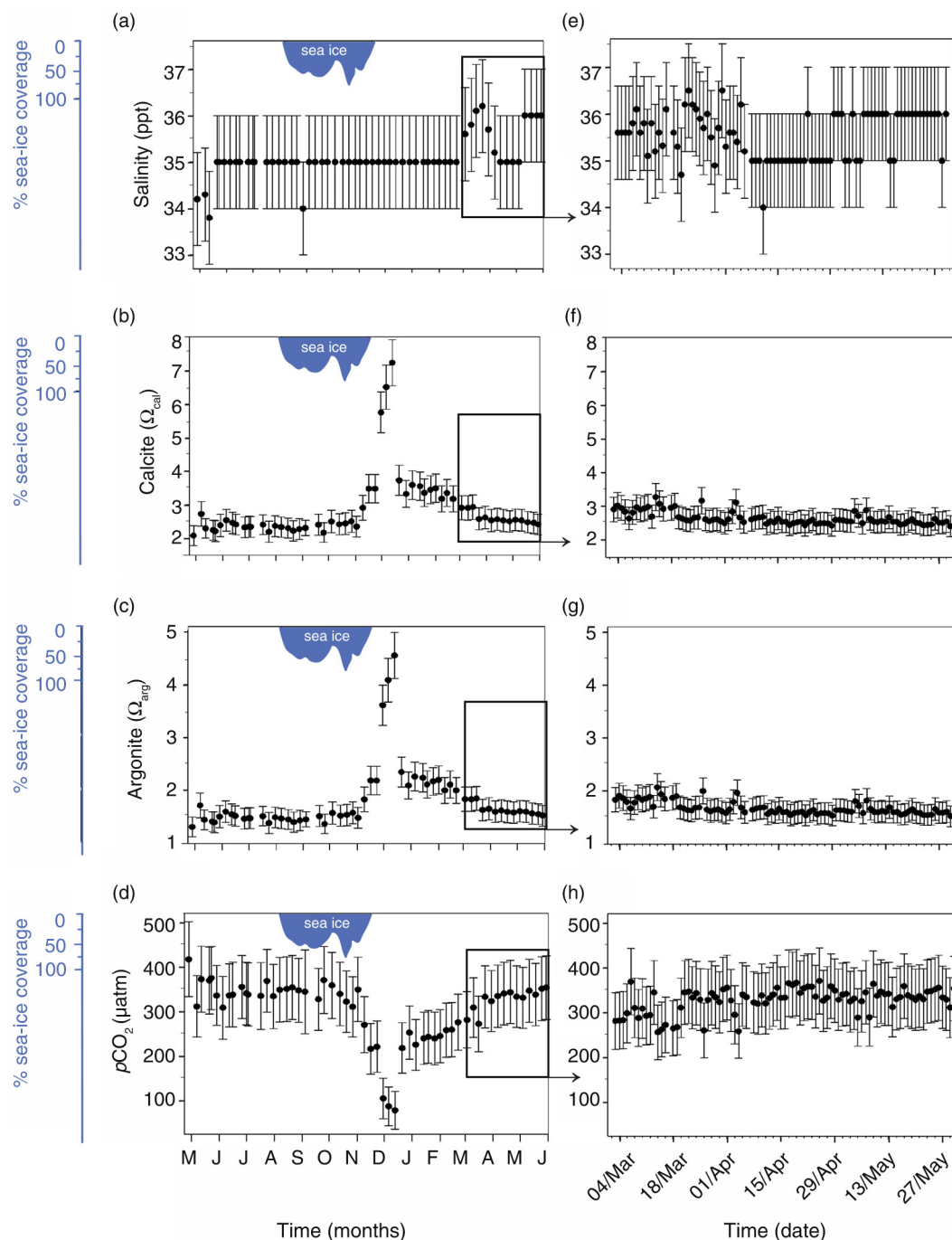


Fig. 2 Graphs depict multi-frequency seawater sampling measurements. (a)–(d) Weekly seawater samples were collected from Arthur Harbor adjacent to Palmer Station, Antarctica over the course of one year (May 2012–May 2013). (e)–(h) Daily measurements were performed for the last three months of the observation period (March–May 2013). Boxed sections in (a)–(d) represent the same time period represented by the corresponding graphs on the right, (e)–(h). Maximum sea-ice coverage depicted in annual seawater chemistry figure panels was 76%. Error bars represent measurement and propagated uncertainties associated with each parameter.

Daily measurements

Daily sampling during the austral autumn (March–May 2013) revealed substantial variability in seawater

pH (Fig. 1e). Daily measures of TA revealed greater variability than that observed by sampling weekly (see above) during the three-month sampling period (Fig. 1b, f,

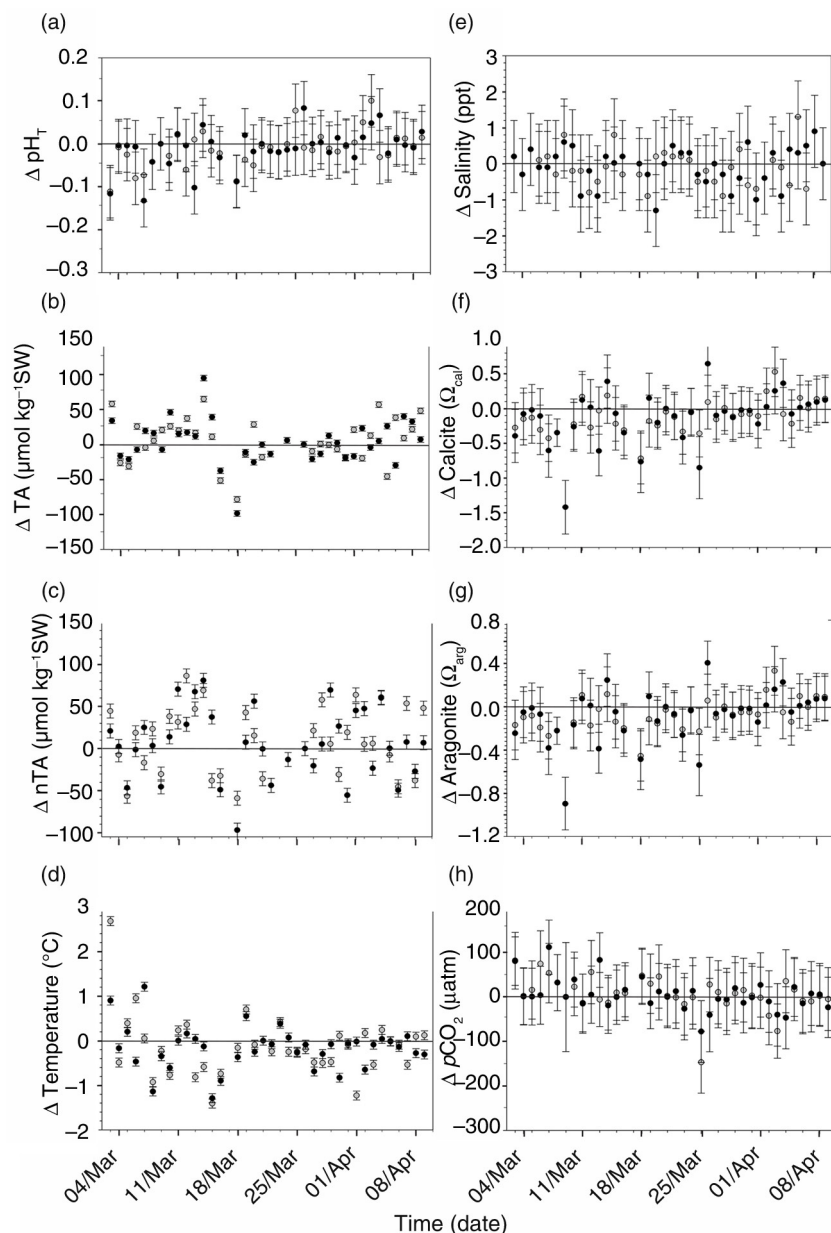


Fig. 3 Graphs depict semidiurnal seawater sampling measurements. Twice daily samples were collected from Arthur Harbor adjacent to Palmer Station, Antarctica to quantify local seawater pH_T , total alkalinity (TA), temperature and salinity semidiurnal fluctuations (March–April 2013). Also included are the salinity normalized total alkalinity (nTA), calcium (Ω_{cal}) and aragonite (Ω_{arg}) saturation states and pCO_2 . Open circles represent semidiurnal seawater variations calculated for the day (Δ_{day}) and filled circles represent seawater variations calculated for the night (Δ_{night}). Horizontal lines at zero indicate no net change. Error bars represent measurement and propagated uncertainties associated with each parameter.

Supplementary Table S1). The high degree of variation in TA (Fig. 1f) is reflected and augmented in calculated nTA (Fig. 1g, Supplementary Table S1). There was decreased variation in gradually declining seawater temperature (Fig. 1h, Supplementary Table S1). There was little difference in temperature patterns between weekly (Fig. 1d) or

daily (Fig. 1h) sampling data sets. In contrast to temperature, salinity measurements were more variable with no clear pattern, remaining primarily between 34.5 and 36.5 ppt over the sampling period (Fig. 2e). Daily measurements revealed little variation in Ω_{cal} , Ω_{arg} and pCO_2 from day to day (Fig. 2f–h, Supplementary Table S1).

Semidiurnal measurements

For seawater samples collected semidiurnally it was possible to determine daily variation in all measured and calculated seawater parameters occurring during the day and night. Semidiurnal seawater measurements revealed similar patterns in variability across most day time periods, during which there was less than 0.05 unit variation in pH. However there were intermittent days of considerable pH variability (median semidiurnal variation $-\Delta = 0.02$; max $\Delta_{\text{day}} = 0.13$, $\Delta_{\text{night}} = 0.11$ pH units; Fig. 3a, Supplementary Table S2). For the variations in pH that occurred during the day and night, there was a significant difference in the frequency of the direction of net change (2×3 contingency table, $X^2 = 8.5$, $df = 2$, $P = 0.01$). This result indicates that the magnitude and direction (positive or negative) of variation in pH recorded depended on the time of sampling.

Semidiurnal variation in TA was high most days, resulting in $50\text{-}\mu\text{mol kg}^{-1}$ SW variation (median $\Delta_{\text{day}} = 16$, $\Delta_{\text{night}} = 21\text{ }\mu\text{mol kg}^{-1}$ SW; maximum $\Delta_{\text{day}} = 99$, $\Delta_{\text{night}} = 79\text{ }\mu\text{mol kg}^{-1}$ SW; Fig. 3b, Supplementary Table S2). The absolute variation in TA tended to be greater during the day than at night (Fig. 3b; Supplementary Table S2), with the TA increasing 56% and decreasing 44% of the days observed. Similarly, TA increased 56%, decreased 41% and no net change for 3% of the nights observed (Supplementary Table S2). However, there was no significant difference in the frequency of the direction of net change (2×3 contingency table, $X^2 = 2.3$, $df = 2$, $P = 0.31$). The trends in the variations in recorded TA values were therefore independent of the time of sampling.

The same pattern of semidiurnal variation observed for TA was also observed with nTA (Fig. 3c). However, overall median and maximum semidiurnal variation in nTA was greater than that observed with TA (Fig. 3c, Supplementary Table S2). Overall, there was no significant difference in the frequency of the direction of net change in nTA over the day and night (2×3 contingency table, $X^2 = 4.4$, $df = 2$, $P = 0.11$).

Seawater temperature generally decreased over the five-week semidiurnal sampling period (Fig. 3d) and decreased over the observation period (median $\Delta_{\text{day}} = 0.25^\circ\text{C}$, $\Delta_{\text{day}} = 0.36^\circ\text{C}$; Fig. 3d, Supplementary Table S2) and there was not a significant difference in the frequency of the direction of net change (2×3 contingency table, $X^2 = 0.6$, $df = 2$, $P = 0.75$). Therefore, it was independent of the time of sampling.

There were no discernible patterns in the salinity variation. Most of the observed variation in salinity fell in the range of 0.3 ± 0.5 ppt (median \pm SD) over the course of the observation period (Fig. 3e, Supplementary

Table S2). However, there were days and nights during which there was increased semidiurnal variability in salinity, changing up to 1.3 units (Fig. 3e, Supplementary Table S2). This increased variability occurred during or followed periods of greater accumulated rainfall by an average of 2 ± 1.2 days ($N = 6$). The mean accumulated rainfall during these periods of increased precipitation was 2.0 ± 1.3 mm ($N = 28$; PAL-LTER weather monitoring data, data repository ID: 28, www.oceaninformatics.ucsd.edu/datazoo/data/pallter/datasets). Despite these occasional increases in salinity variations, there was no significant difference in the frequency of the direction of net change (2×3 contingency table, $X^2 = 2.2$, $df = 2$, $P = 0.33$), indicating that the temporal trends in variations in salinity were independent of the time of sampling.

Semidiurnal measurements of carbonate chemistry indicated that the frequency of the direction of net change in Ω_{cal} (Fig. 3f, Supplementary Table S2) and Ω_{arg} (Fig. 3g, Supplementary Table S2) calculated for day or night were significantly different (2×3 contingency table, $X^2 = 10.5$, $df = 2$, $P = 0.01$ for both Ω_{cal} and Ω_{arg}). However, the saturation states displayed substantial variability within a given day (max day $\Delta\Omega_{\text{cal}} = 1.42$, $\Delta\Omega_{\text{arg}} = 0.90$; Supplementary Table S2) and generally less variation over the night (max night $\Delta\Omega_{\text{cal}} = 0.72$, $\Delta\Omega_{\text{arg}} = 0.45$; Supplementary Table S2). There was also substantial semidiurnal variation in $p\text{CO}_2$ (max $\Delta_{\text{day}} = 112$, $\Delta_{\text{night}} = 146\text{ }\mu\text{atm}$; Supplementary Table S2) but no distinct pattern of differences between day and night (Fig. 3h, Supplementary Table S2) or significant difference in the frequency of the direction of net change in $p\text{CO}_2$ based on the time of observation (2×3 contingency table, $X^2 = 4.9$, $df = 2$, $P = 0.08$).

Chlorophyll *a* and sea ice

The chl *a* concentrations remained low for most of the year with an abrupt increase occurring during the final sea-ice break-out in the early austral spring (late November 2012-, Fig. 4). The peak in chl *a* mirrored that of pH, reaching the highest recorded level (pH 8.62) approximately one week after the highest recorded chl *a* concentration of the year (Fig. 4, Supplementary Table S1). These increases in chl *a* coincide with increases in day length and light availability as previously demonstrated by Tortell et al. (2014). Sea ice was present for a total of 89 days with an average coverage of 47% for this time period. The majority of the sea ice had broken up and been blown out of the Palmer Station region by 11 November 2012, with the last of the ice blown out on 28 November 2012.

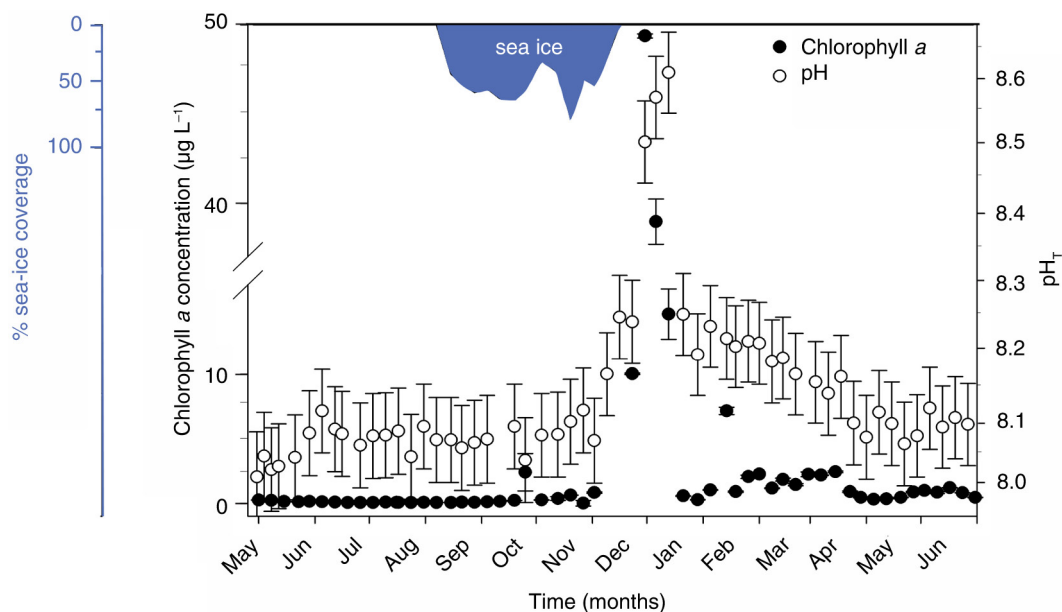


Fig. 4 Comparison of dynamics of chl *a* concentrations and pH measured from the immediate vicinity of Palmer Station by month for one year (May 2012–May 2013, compiled from the Palmer LTER Data Repository). Maximum sea-ice coverage was 76%. Error bars represent measurement uncertainties.

Drivers of DIC variability

We calculated ΔDIC values due to air–sea CO_2 flux and biological activity for weekly and daily samples to determine and compare the drivers of changes in DIC. The $\Delta\text{DIC}_{\text{bio}}$ were frequently positive from May 2012 to October 2012 (Fig. 5a, Supplementary Table S3). During this same time period, the $\Delta\text{DIC}_{\text{as}}$ was frequently negative (Fig. 5a). In November, $\Delta\text{DIC}_{\text{bio}}$ was positive and $\Delta\text{DIC}_{\text{as}}$ was more negative, resulting in an overall negative $\Delta\text{DIC}_{\text{obs}}$ until January 2013 (Fig. 5a, Supplementary Table S3). The variation calculated for weekly sample collections underestimates the variation in DIC for the overlapping three months (March–May 2013; Fig. 5a, b, Supplementary Table S3).

We calculated ΔDIC values reflecting hourly variations in the drivers of DIC variability during day and night (Fig. 6, Supplementary Table S3). We did not find a significant difference in the frequency of the direction of net change during the day or night (2×3 contingency table, $\chi^2 = 4.1$, $\text{df} = 2$, $P = 0.13$). Therefore the semidiurnal $\Delta\text{DIC}_{\text{obs}}$ are independent of the time of sampling (day or night). In contrast, there was a significant difference in the frequency of the direction of net change for $\Delta\text{DIC}_{\text{as}}$ (2×3 contingency table, $\chi^2 = 4.1$, $\text{df} = 2$, $P = 0.13$). This indicates that the $\Delta\text{DIC}_{\text{as}}$ is dependent on time of sampling (day or night), potentially a result of the high proportion of neutral changes in $\Delta\text{DIC}_{\text{as}}$ observed during the day compared to the night (Fig. 6, Supplementary Table S3).

The DIC tended to decrease during the day (more negative ΔDIC values; Fig. 6a), and increase during the nighttime hours (more positive ΔDIC values; Fig. 6b). Despite these patterns, we found that the frequency of the direction of net change in $\Delta\text{DIC}_{\text{bio}}$ was independent of the time of sampling (2×3 contingency table, $\chi^2 = 4.0$, $\text{df} = 2$, $P = 0.14$).

Discussion

pH and carbonate chemistry dynamics

This is one of the first studies to report natural patterns of seawater pH, TA, temperature and associated carbonate system chemistry over multiple time scales from the benthos along the Antarctic Peninsula. Our measure of a maximal semidiurnal variation of 0.13 in pH over five weeks in Arthur Harbor is within a similar range of the maximum semidiurnal variation (0.043–0.115 pH_T units) reported by Matson et al. (2011) from McMurdo Sound. We observed a similar magnitude of semidiurnal variation in pH during both the day and night. Previous research has demonstrated that the adaptive and acclimation potential of marine organisms increases in regions of higher seawater chemistry variability (Hofmann et al. 2014). Baseline documentation of variations in seawater pH in conjunction with complementary studies will facilitate the identification of specific regions where Antarctic organisms may experience and influence seawater pH

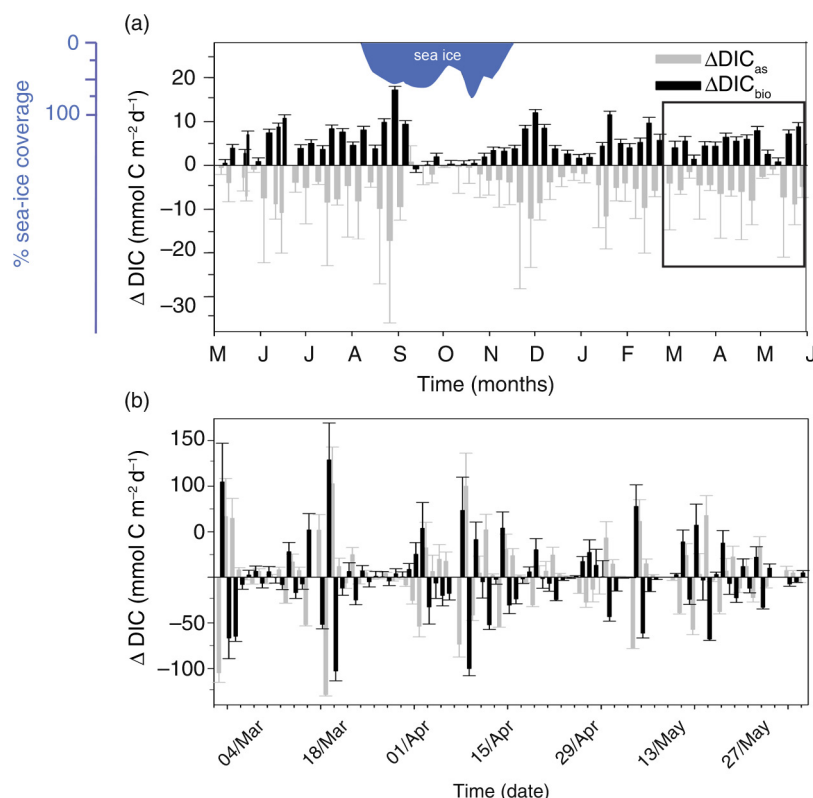


Fig. 5 Drivers of daily dissolved inorganic carbon (DIC) variation calculated for annual and daily DIC ($\Delta\text{DIC}_{\text{as}}$ and $\Delta\text{DIC}_{\text{bio}}$). Negative values represent a decrease in DIC between repeat measurements while positive values denote an increase. (a) Drivers of DIC annual variations in DIC computed over the course of one year (May 2012–May 2013, mean $\Delta\text{DIC}_{\text{obs}} \pm \text{mean uncertainty}$, $-0.003 \pm 0.89 \text{ mmol m}^{-2} \text{ d}^{-1}$). Maximum sea-ice coverage over the course of this year was 76%. (b) Drivers of DIC daily variations in DIC computed for daily measurements were performed for the last three months of the observation period (March–May 2013, mean $\Delta\text{DIC}_{\text{obs}} \pm \text{mean uncertainty}$, $0.85 \pm 0.96 \text{ mmol m}^{-2} \text{ d}^{-1}$). Error bars represent measurement and propagated uncertainties associated with each parameter.

variations that enhance their potential to acclimatize or adapt to changing ocean conditions. Moreover, documentation of coastal seawater chemistry fluctuations may identify regions that serve as more stable refugia for marine organisms unable to acclimatize or adapt to rapid environmental variation (Matson et al. 2011).

The austral summer peak in seawater pH we observed is consistent with the patterns of increased primary production (phytoplankton blooms) that typify Antarctic coastal waters as the annual sea-ice breaks up (Vernet et al. 2008). During phytoplankton blooms, CO_2 is taken up by autotrophs, reducing levels of $p\text{CO}_2$ and overall DIC, while pH and carbonate saturation states increase. In the present study, pH closely tracked seasonal variations in chl *a* (a proxy of phytoplankton productivity and density). Immediately following the break-up of the last winter sea ice in early November, the chl *a* concentration increased abruptly followed a week later by a similar increase in seawater pH (Fig. 5). Recently it has been demonstrated, with a mechanistic model, that phyto-

plankton productivity can drive changes in seawater pH under fast ice in McMurdo Sound (Matson et al. 2014). This suggests that biotic processes associated with phytoplankton productivity are linked to variations observed in a high-frequency pH observation data set.

However, the observed variations in the present study may not be solely related to phytoplankton production since there is a rich and diverse flora of benthic macroalgae along the central western Antarctic Peninsula (Wiencke & Amsler 2012). It is possible that benthic macroalgal production also influenced the rise in pH observed during the austral summer. Previous studies in temperate kelp forests have demonstrated that high densities of macroalgae can drive local variation in dissolved oxygen and pH (Frieder et al. 2012). The sustained elevation of pH, following the first initial peaks in chl *a* and pH (attributed primarily to phytoplankton productivity and biomass) may in part be due to an increase in benthic macroalgal primary productivity through the summer growing season. The relative absence

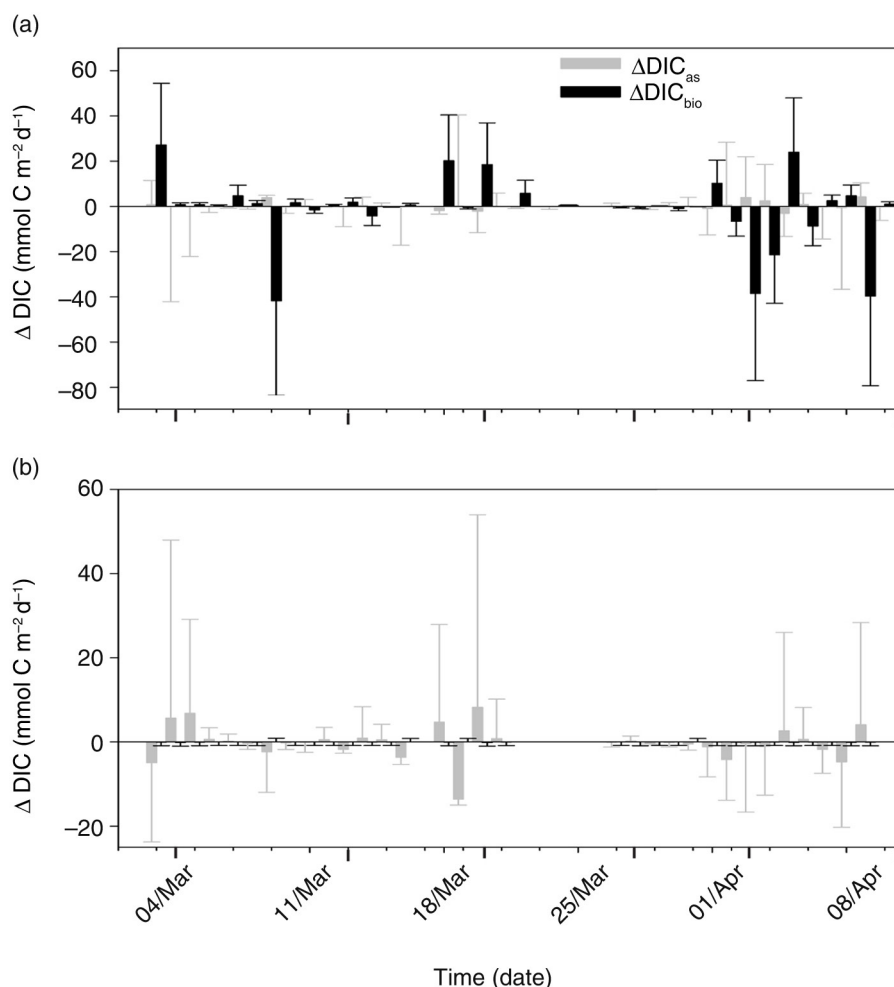


Fig. 6 Controls on semidiurnal variations in dissolved inorganic carbon (DIC; $\Delta \text{DIC}_{\text{as}}$ and $\Delta \text{DIC}_{\text{bio}}$). Negative values represent a decrease in DIC between repeat measurements while positive values denote an increase. (a) Semidiurnal variations in DIC computed to have occurred during the day (mean $\Delta \text{DIC}_{\text{obs}} \pm$ mean uncertainty, $-0.01 \pm 0.88 \text{ mmol m}^{-2} \text{d}^{-1}$). (b) Semidiurnal variations in DIC computed to have occurred during the night (mean $\Delta \text{DIC}_{\text{obs}} \pm$ mean uncertainty, $0.01 \pm 0.88 \text{ mmol m}^{-2} \text{d}^{-1}$). Error bars represent measurement and propagated uncertainties associated with each parameter.

of high chl *a* concentrations in the water column coupled with the elevation in seawater pH may support this hypothesis. The approximate 0.2 pH unit summer pH median elevation above the winter pH median observed in the austral summer exceeds the ± 0.04 pH unit variation predicted from a variation in seawater temperature alone (projections based on pH, TA, salinity and temperature data presented herein). Additionally, we observed a seasonal decline in TA and nTA during the austral summer, probably due to enhanced biological activity, such as calcification, since the influence of freshwater or brine rejection is already accounted for in the nTA calculation.

To put the coastal seawater pH dynamics we have documented in context, it is useful to compare our data

with those from other marine environments. Hofmann et al. (2011) present data for seawater pH dynamics recorded over 15–30-day periods in the open ocean, upwelling regions, estuarine/near shore environments, coral reefs, kelp forests and extreme environments such as CO_2 vents. Overall, the pH patterns we observed in Arthur Harbor on the western Antarctic Peninsula do not appear to be consistent with the more variable coastal upwelling pattern typified by repeated pH declines (Hofmann et al. 2011). Additionally, our one-year seawater pH data were nearly as stable as the steady patterns of pH observed in the open ocean, but not as regular as the oscillatory pH dynamics of coral reefs, kelp forests or estuarine/near shore environments (Hofmann et al. 2011). Rather, our data show seasonal carbonate

chemistry patterns similar to those previously observed in Prydz Bay and the Ross Sea (Gibson & Trull 1999; McNeil et al. 2011; Roden et al. 2013). These data sets are distinguished by low pH variability throughout much of the year, with an abrupt increase in late spring and austral summer months associated with the seasonal sea-ice break-out in the austral spring/summer months. However, in contrast to these Antarctic studies, the multiple frequency measurements employed in the present study revealed a greater degree of local pH variability when measured over shorter time scales, i.e., semidiurnal variation in pH during late summer months and day to day pH variation in autumnal months.

Semidiurnal variations in pH, Ω_{cal} and Ω_{arg} were observed in the present study. Based on our analysis of the frequency of directional net change in these factors, the biggest difference between day and night dynamics is a tendency for seawater pH, Ω_{cal} and Ω_{arg} levels to decrease during the night. This occurs in conjunction with more net neutral changes in these parameters during the day. These results support our hypothesis that biological activity, through increased respiration drive down pH, Ω_{cal} and Ω_{arg} levels over the night. During the day, autotrophic uptake of CO_2 may have been balanced by heterotrophic respiration, resulting in a general pattern of net neutral variations in pH, Ω_{cal} and Ω_{arg} .

Saturation states for Ω_{arg} over a one-year period have been reported for Prydz Bay, East Antarctica (McNeil et al. 2011; Roden et al. 2013). Values varied from a low Ω_{arg} of 1.20 recorded in September (late austral winter) to a high Ω_{arg} of 1.92 in January at the end of the austral summer. In the present study, we found a similar seasonal pattern in Ω_{arg} levels. The lowest value we recorded was in September ($\Omega_{\text{arg}} = 1.31$) and is higher than that recorded for Prydz Bay, a region with more developed sea ice where photosynthetic activity may be reduced and $p\text{CO}_2$ elevated as a result of respiration. Data sets characterizing seasonal variations in physical and biological environmental variables are an important component of understanding the dynamics experienced by organisms inhabiting an area of interest (Hofmann et al. 2013).

The present data set expands upon a recent study conducted by Wang et al. (2010) investigating levels of inorganic and organic dissolved carbon in Schollaert Channel, bordering the northern end of Anvers Island. Wang et al. (2010) demonstrated that marginal sea-ice zones along the western Antarctic Peninsula act as a source of CO_2 to the atmosphere during austral winter months and a CO_2 sink during summer months.

This pattern is consistent with observations in the present study. The $p\text{CO}_2$ and DIC levels recorded in the present study are within previously reported ranges for the region around Palmer Station ($p\text{CO}_2 = 100\text{--}500 \mu\text{atm}$, $\text{DIC} = 1940\text{--}2210 \mu\text{mol kg}^{-1}$; Tortell et al. 2014) and the Ross Sea ($p\text{CO}_2 = 160\text{--}360 \mu\text{atm}$, $\text{DIC} = 2056\text{--}2250 \mu\text{mol kg}^{-1}$; Bates et al. 1998).

We observed dynamic variations in seawater pH and TA and large fluctuations in the DIC at each of the frequencies measured. Fluctuations in DIC are most likely influenced by biological activity, such as increased carbon fixation by autotrophs during the austral summer through photosynthesis and carbon production in the austral winter due to respiration during periods of low light availability. The resulting build-up of respiration products is subsequently lost to the atmosphere by way of local air–sea CO_2 flux. Our results reveal dramatic variations in coastal Antarctic DIC within a given season or day, on the same scale as previously reported in Prydz Bay ($68 \mu\text{mol kg}^{-1}$ SW seasonal variation; Roden et al. 2013).

During the early austral spring (November) we observed a decline in $\Delta\text{DIC}_{\text{as}}$ as sea-ice cover increased. However, as sea-ice coverage was not complete, $\Delta\text{DIC}_{\text{as}}$ was never completely eliminated. These data are consistent with the DIC dynamics previously observed along the western Antarctic Peninsula in regions with incomplete sea-ice coverage (Carrillo et al. 2004; Wang et al. 2010). Nonetheless, regions with incomplete sea-ice coverage do not remain a perpetual CO_2 sink in contrast to the rectified sink hypothesis (Yager et al. 1995). Wherein hypothetically, regions with marginal sea ice, such as those around polynyas or other high-latitude regions, are generally ice-free. These ice-free regions will continue to absorb CO_2 because melting sea ice creates a thin layer of freshwater near the surface, isolating surface waters from air–sea gas exchange. This isolation of surface waters leads to the creation of a perpetual or “rectified” CO_2 sink (Yager et al. 1995). Observations in the Ross Sea reinforce the potential for the Southern Ocean to act as a net CO_2 sink due to a reduction in CO_2 lost from surface waters to the atmosphere during austral winter months (increased sea-ice coverage), followed by high autotroph CO_2 fixation in austral summer months during intense phytoplankton blooms (Arrigo et al. 2008). The present study demonstrates through multiple pathways (pH, chl *a* concentrations, air–sea CO_2 flux), that coastal seawater in the near vicinity of Palmer Station has the potential to act seasonally as a CO_2 sink (austral summer) and source (austral winter), and less as a rectified sink.

Sea-ice and temperature dynamics

The coastal marine environment of the western Antarctic Peninsula is experiencing unprecedented increases in temperature. Since 1950, air temperatures on the peninsula have risen as much as 7°C (Ducklow et al. 2013). Few data are available to document variations in seawater temperature during this period. However, Meredith & King (2005) compiled hydrographic data collected in the region and estimated an increase of 1°C since the 1950s. The combination of seawater and atmospheric warming along the western Antarctic Peninsula during autumn and winter months is likely contributing to a positive feedback loop of self-reinforcing seawater warming (Stammerjohn, Martinson, Smith, Yuan et al. 2008). Despite high interannual variability in sea-ice coverage, previous records for the Palmer Station region indicate that the winter sea-ice season has been shortened by an average of 92 days between the 1979 and 2012 field seasons (studies cited in Ducklow et al. 2013). This decrease in winter sea ice may exacerbate seawater carbonate chemistry variability associated with periods of open water (Stammerjohn, Martinson, Smith & Iannuzzi 2008; Wang et al. 2010) and could alter the timing of seasonal primary productivity blooms (Ducklow et al. 2013).

The retreat of annual sea ice has been linked to a greater intensity of phytoplankton blooms in coastal regions of the western Antarctic Peninsula (Ducklow et al. 2013). This increased seasonal productivity is attributed to increases in both sea-ice-melt water and light availability (Vernet et al. 2008; Ducklow et al. 2013). In the present study, we detected a strong increase in seawater pH in late November, a likely signal of increased primary production attributable to sea-ice break-out. Similarly, Montes-Hugo et al. (2010) found that increased levels of chl *a*, indicative of greater phytoplankton biomass, corresponded with a depletion of DIC during the spring sea-ice retreat along the central Antarctic Peninsula. Alterations in carbonate chemistry and TA during periods of high austral spring and summer primary production were observed in the present study. Biological activity is the most likely driver of the observed seasonal variations in seawater nTA and associated carbonate system chemistry.

Implications for ocean acidification studies

Few studies have examined the potential impacts of ocean acidification on Antarctic benthic marine organisms. These include studies of ecologically important species including bivalves (*Laternula elliptica* Cummings et al. 2011), sea stars (*Odontaster validus*; Gonzalez-Bernat et al. 2013) and sea urchins (*Sterechinus neumayeri*; Ericson et al. 2011) and have employed experimental *p*CO₂ and

pH levels chosen based on Intergovernmental Panel on Climate Change estimates of current and near future global seawater averages (Riebesell et al. 2010). The present study indicates that some Antarctic marine organisms are already experiencing a wide range of seasonal and semidiurnal fluctuations in seawater carbonate chemistry, in some instances in excess of those predicted from models based on rates of oceanic uptake of anthropogenic CO₂ (also see Roden et al. 2013; Björk et al. 2014). As data such as these become increasingly available, studies of ocean acidification will be better able to evaluate experimental chemical variables in a local context and improve our capacity to evaluate the physiological and behavioural responses of Antarctic benthic marine organisms to rapid climate warming and ocean acidification.

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