Response to referee #1

> The authors thank the anonymous referee for their comments. Our responses are follow the referee's comments in the indented text. Corrected text is in quotes.

The paper is well laid out, and is very readable, though often the language is not precise – use of roughly, appearing to, approximately etc.

> The manuscript was checked for imprecise language and corrected throughout.

Specific comments
Line 21, spell [CO2] out in full the first time it is used.

> Line 21 "…in response to elevated concentration of atmospheric carbon dioxide (CO_2), with a decline in pH and an increase in the partial pressure of dissolved CO_2 (pCO_2) over the coming decades."

Line 28, the potentiometric method for measurement of seawater pH can be accurate and precise if appropriate care is taken with temperature control, use of seawater buffers etc. An appropriate reference is required here, (Eg Dickson, A. G., Sabine, C. L., and Christian, J. R.: Guide to best practices for ocean CO2 measurements. PICES Special Publication 3. IOCCP Report No. 8, 191 pp, in: PICES Special Publication 3, 191 2007.)

> Line 28 "Seawater pH has been commonly measured with a potentiometric technique using glass electrodes. While this method can be accurate and precise if appropriate care is taken with temperature control and the use of seawater buffers (Dickson, 2010), this technology suffers from a gradual…".

The spectroscopic method should also be mentioned in this paragraph, as it is now a common method of measuring seawater pH, and indeed is used in the work described here in Lines 102 - 105. Relevant references should be included, such as the Dickson et al. Guide to Best Practices.

> Line 32. "… pers.comm). Spectroscopic techniques for measuring seawater pH use a pH-sensitive dye that assumes different absorbance spectra depending on pH. While the method can provide pH estimates with an uncertainty less than 0.01, variability in the quality of the dye obtained from commercial suppliers can cause the true extinction coefficients associated

> with a particular dye to differ slightly from published extinction coefficient values. Consequently, uncertainty associated with this technique is generally assumed to be about 0.01 pH units (Dickson, in Riebesell et al. 2010)
>
> Reference is “Dickson, A.G. “The carbon dioxide system in seawater: equilibrium chemistry and measurements”. *In* Riebesell, V.J., Fabry, V.J., Hansson, L. and Gattuso, J.-P. 2010. Guide to best practises for ocean acidification research and data reporting. Luxembourg, Publications Office of the European Union.”

Line 48 – specify austral Autumn and Summer.

> “… two multi-day intervals in austral Autumn and Summer”

Line 49 – the alkalinity -salinity relationship determined by Lenton et al (2016) was shown to be valid at the open ocean and coastal IMOS sites. The relationship at the Chowder Bay site is likely to be different due to terrestrial influences, and this should be acknowledged.

> “Electrical conductivity and temperature were also measured, and an approximation for alkalinity was derived from a salinity-alkalinity relationship reported for the Australasian region (Lenton et al. 2016). We acknowledge that the relationship between salinity and alkalinity is subject to terrestrial influence, and consequently our estimate of alkalinity remains an approximation.”

Line 55 – repetitive wording needs editing.

> “Real-time measurements were made of seawater in the Sydney Harbour…”

Line 56 – specify Australia in the description of the location.

> “Chowder Bay, NSW, Australia (-33…”

Line 90 – specify the brand of the “standard buffers”, and what scale the pH is on (pHT, pHNBS or something else).

> “was calibrated against standard buffers (pH 7.02 and 10.06 at 20°C, Amalgamated Instruments Co. Pty Ltd, Australia)

Line 91 – the C1 referring to the measured pH of the first buffer, can be confused with Cl (chloride) used earlier in the line. I suggest using a different symbol for the buffer pH.

> "isotonic to ~34.5 ppt NaCl (*I* = 0.7 M) with B1=8.33 pH and B2=4.00 pH (where B1 and B2 are the measured pH of each of the buffers).

Line 98 – although you did not use tris buffer, because of its adverse effect on the electrode, it is necessary to tie your measurements back to the seawater scale, particularly as you state in line 96 that you are using the (total) pH scale. You should also mention the temperature of your calibration. Was it assumed that everything was at the stable room temperature of 22 oC (line 89), or did you measure the temperature?

> We used the total pH scale as recommendation by Dickson (in Riebesell et al. 2010), who also advised against the use of the seawater pH scale for seawater pH measurements. We selected the total scale when calculating omega values, to ensuret hat the equilibrium constants used to determine seawater carbon chemistry values were consistent with the scale we used to measure and report pH. The room temperature of 22°C was stable during the calibration procedure, and buffer temperature was 22 ± 0.5 °C during the calibration procedure.
>
> Line 98: "We did not use Tris as a buffer as it is known to poison single junction Ag/AgCl electrodes, and report pH in the total hydrogen ion scale (as recommended by Dickson (in Riebesell et al. 2010). Both room and buffer temperature were stable during the calibration procedure at 22°C and 22 ± 0.5 °C, respectively."

Line 100 - how many calibration samples taken during the in situ deployment, and how many samples were taken? These should be noted on Figures 4 and 5.

> Line 100: "At the beginning and end of the *in situ* deployment, water samples were collected adjacent to the submerged pH monitor and transported to the nearby lab at SIMS. At each sampling time, three 200 mL glass jars were completely filled, and lids secured underwater to eliminate air bubbles. This process was repeated at least three times, with approximately 30 minutes between each sampling time.
>
> This information will be added to Figs 4 and 5

Line 101 - specify the actions taken to minimise gas exchange during sampling.

See above

Line 104 - more information here needed here on the validation against the CRMs – the precision and accuracy of your measurements is required.

Line 104: “Spectrophotometric measurements of pH_T were validated using seawater certified reference material (CRM, Dickson Standard Batch 145). The precision of the spectrophotometric technique in our laboratory is typically ±0.006 at temperatures between 17 to 24°C (standard deviation), with an accuracy very much dependent on the dye quality. We did not apply corrections for dye impurities, temperature and salinity variations as discussed in Douglas and Byrne (2017a,b) because obtaining such highly accurate pH values was not an objective of this study.”

Line 106 - replace the term “published” with “certified” .

Line 106: “the CRM using published values (derived from certified standards) for total alkalinity (A_T), dissolved inorganic carbon (DIC) and salinity at the same”

Line110 - how were the corrections applied – an average offset, a drift, or some other method?

Line 110: “Corrections were made against spectrophotometric measurements of the reference samples by calculating two average offsets between values of collected samples measured using the fluorometric device and the spectrophotometric device. One offset was derived for the beginning of the deployment and one for the end. The gradual decline in measured values over time was corrected assuming a constant linear drift.”

Lines 111 – 113, 117-119, and 124-126. These sentences are clumsy – separate into the ex situ and in situ methods.

The sentences have been corrected.

Lines 111-113: “*In situ* measurements were taken ten times per minute and averaged over one minute before analysis. *Ex situ* measurements were taken once per minute and a running average of 10 minutes of the *ex situ* measurements is presented.”

Lines 117-119: *"In situ* measurements were taken ten times per minute and averaged over one minute before analysis. *Ex situ* measurements were taken twice per minute and a running average of 10 minutes of the *ex situ* measurements is presented."

Lines 124-126: *"In situ* measurements were taken ten times per minute and averaged over one minute before analysis. *Ex situ* measurements were taken three times per minute and a running average of 10 minutes of the *ex situ* measurements is presented.

Line 131 - specify what corrections were made to the raw data, and what scale the final pH is on (pHT?).

Line 131: "Drift and offset corrections were made to the raw data as required (described above), and final pH, salinity, temperature and alkalinity values were used…" to calculate Ω_{Ca} and Ω_{Ar} in CO2Sys (V2.1) (Dickson and Millero 1987). The final pH is reported on the total scale."

Line 138 - a reference is required for the influence of photodegradation on fluorophores.

A references is added to Line 138:
"Gradual bleaching is known to influence fluorophores (Lakowicz 2006), contributing to a steady drift."
Reference: Lakowicz J.R. 2006. Principles of Fluorescence Spectroscopy". 3rd edition. Springer.

Line 139 - How was the drift corrected for? Were the bottle samples used for this?

Line 139: see above

Line 146 - Use the symbol oC not the word degrees.

Line 146: "…temperature varied between 1 and 2°C,

Line 157-157 Different symbols used for aragonite and calcite saturation, see Lines 132, 154-157, 181, 201 and Figs 6 and 7.

Consistent use of the term ω_{Ca} and ω_{Ar} throughout text and Figs 6 and 7

Line 163 - a reference is required for this sentence – what values of pH, S and T would be expected?

Line 163: "   would expect for the harbour at that time of year (e.g. pH ~8.0, S=~35 ppt, T= ~18°C, pers.obs.)

Line 162: "Values of pH, salinity and temperature were all within what one would expect for the harbour at that time of year."

See above

Line 167 - what is the variation due to – is it degassing due to pumping, temperature changes or another reason?

Line 167: "However, the dissolved gas content of pumped water can vary relative to the source water due to degassing and temperature changes, making measurements potentially less representative of the water to be sampled"

Fig 1 - it would be useful to include an inset map of Australia with the location noted.

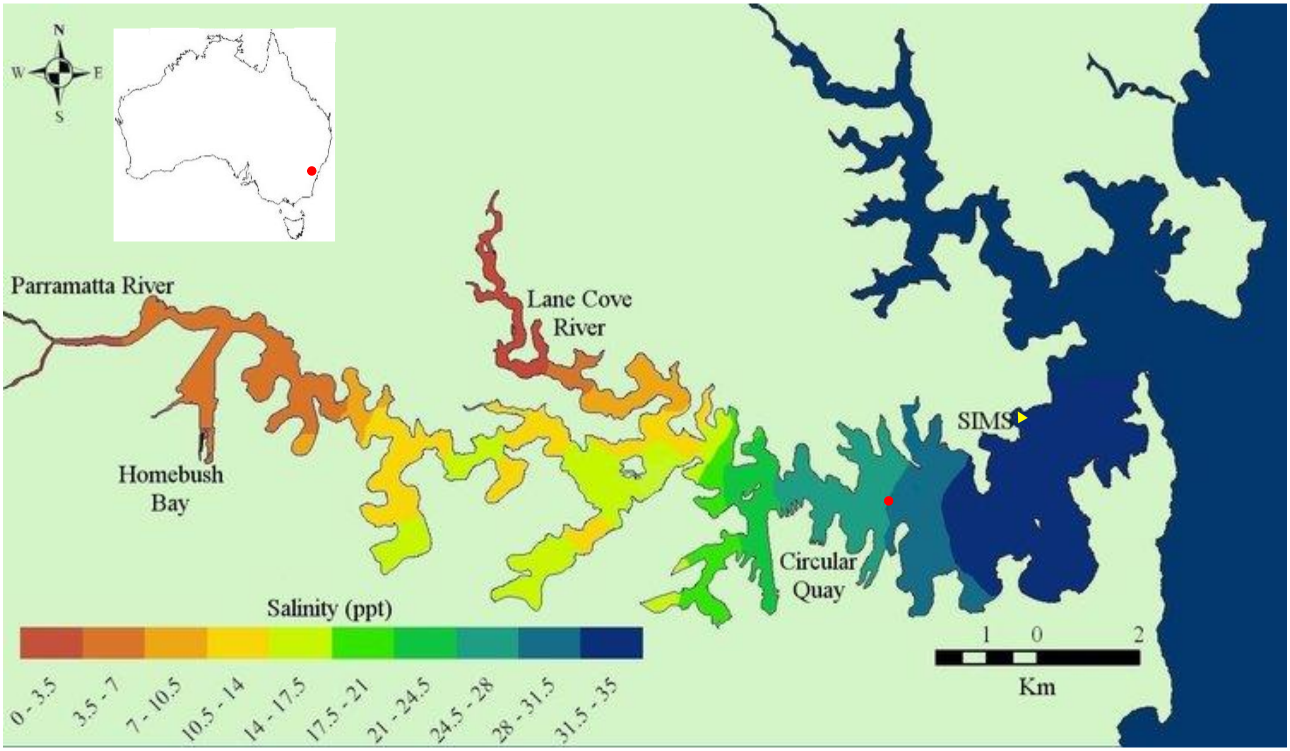

Fig 3 caption - It would be useful to specify in the caption that the red arrow show light conveyed to the spot is indicated by the red arrow, and light emitted from the spot is indicated by the blue arrows. Eg The insert shows light conveyed through the transparent vessel wall to the spot (red arrow) , and fluorescent light emitted from he spot back along the fibre (blue arrows).

> Figure 3. Schematic of pH monitoring system with EOM-pH-mini (left), and fibre optic conveying light to fluorescent spot attached to inside of vessel (right). The insert shows light conveyed through the transparent vessel wall to the spot (red arrow), and fluorescent light emitted from the spot back along the fibre (blue arrows).

Figs 4 and 5– Specify the pH scale, and mark the pH of the bottle samples on the plot.

> Ok this will be done.

Figs 6 and 7 captions, delete the sentence “Values below unity represent dissolution.”

> Ok this will be done.

Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-222, 2017.

Response to referee (A. Dickson)

The authors thank Professor Dickson for his comments. Please note responses are indented and follow the referee's comment.

Although I was interested to see the application of the Presens pH-sensitive spots to looking at seawater pH variability, I am not comfortable recommending this manuscript for publication in its present form.
The title, and the abstract, indicate that this paper is to be considered as an assessment of using this technique to monitor estuarine pH, and hence (when used in conjunction with salinity information) to provide information about the time-dependent variation of the seawater CO2 properties, and in particular the aragonite and calcite saturation states. The authors however fail to make clear the likely overall uncertainty of their measurements, a key parameter when assessing a measurement technique. Also, the data provided do not really cover a sufficient range of salinity to plausibly assess likely behaviour in an estuary.

> The intent of the work was to determine the utility of the Presens sensor for use in shallow inshore marine systems to detect variability in seawater carbonate chemistry over timescales of minutes to hours. While accuracy was an important factor, our intention, with proof-of-concept data, was to demonstrate that this technique is capable of showing clear patterns of variability.
>
> To avoid confusion, we propose changing the title to:
> "Continuous fluorescence-based monitoring of seawater pH *in situ*." This excludes the word estuary and will hopefully avoid any implication that the research is generally applicable to estuaries. While the study location can be said to be in the estuary, in reality it is close to the ocean and is primarily influenced by the ocean.
>
> The abstract is also modified to now include an estimate of uncertainty.
> Line 13: "…background variability. While the stated phase angle resolution of the lifetimes fluorometer translated into pH units was +/- 0.0028 pH units, the precision of calculated pH was +/- 0.022, indicating error associated with calibrating the device against known reference samples. Diel variability…"
>
> Further:
> Line 45: "…in the setting of an ocean-water dominated estuarine environment."

> Line 52: "… in surface waters. The study focussed on natural fluctuations in seawater pH and the capability of the fluorescence technique to address these fluctuations. Determining the accuracy of pH values obtaining from the fluorescence device was not an objective, as correct determinations would require considerable resources that were not available at the time of study."

The calibration of the Presens sensor for use in seawater media seems odd, and is insufficiently described. In principle, a calibration curve was prepared documenting the instrument response as a function of the pH of a series of buffer solutions: phosphate buffers in a NaCl background (I = 0.7 M) . The pH values for the various buffer solutions -at a temperature of _22 _C - were themselves measured directly using a pH cell that had itself been calibrated against low ionic strength buffers (_0.1 M I suspect). The authors note that validation samples were collected and their pH measured spectrophotometrically (using m-cresol purple - though not purified), but the paper does not really show the direct comparison but simply comments that a "drift" in the fluorescence based pH sensor was thus corrected for.

> We now show a direct comparison of data obtained using the spectrophotometric technique and the fluorometric technique as indicated by the data points in Figures 4 and 5.

There is, I feel, so much wrong with this approach. First, it is not at all clear what really is being measured as pH (and this will cause a mismatch with the equilibrium constants used when the various saturation states are calculated),

> Our initial measurement of pH was conducted using the potentiometric technique, where we calibrated the glass electrode using standard buffers to ensure the electrode provided a reasonable estimate of pH, notwithstanding any effect of increased salinity on subsequent measurements. The phosphate buffers then enabled us to characterise the relationship across a range of pH values (with salinities similar to seawater) and various values of fluorescence lifetime. From this relationship we could then interpolate and use the fluorescence lifetime to indicate the "pH". However, only when the fluorescence sensor was directly compared with the spectrophotometric measurements of a collected sample were we able to apply corrections to the fluorescence-derived values for pH, and refer to them as "pH_T" in line with the spectrophotometric pH_T values.
>
> We also discuss the use of constants when calculating the seawater saturation state

second I would have imagined that the response of the sensor dot would depend (at least to some extent) on temperature and salinity - this is not even mentioned.

> This will be mentioned in the introduction.
> L 44 "…changes in fluorescence intensity. As the fluorophores used in this study are sensitive to changes in temperature and salinity, careful measurement of these parameters remains essential.".

Furthermore, the simple calibration of the conductivity sensor with a pure NaCl solution will likely affect the accuracy of estimated salinity values, and ultimately the accuracy of alkalinity values estimated from these.

> We agree that the use of NaCl to calibrate the salinity sensor is not ideal. However the aim of the exercise was to demonstrate the ability of the fluorescence-based technique to show diel variability in seawater carbonate chemistry.

Other notes (linked to line numbers)
103,4 The text refers to a commercial dye (Acros, and to the calibration for a purified dye. I would note that Acros was one of the worst commercial dyes, and that a recent paper in Marine Chemistry by Douglas & Byrne, suggests how to convert the behaviour of the impure dye to approximate that of a pure dye.

> In the introduction we now make it clear that our rationale was to demonstrate that the fluorescence method that can show natural variability of pH within an estuary over time scales of minutes to hours rather than provide highly accurate pH data.
>
> Line 52: "… in surface waters. The study has focussed on natural fluctuations in seawater pH and the capability of the fluorescence technique to address these fluctuations. Determining the accuracy of pH values obtained from the fluorescence device to the third decimal place was not an objective.
>
> While we did not correct for dye impurities - we agree that these new papers are important to cite.
>
> Line 104: "and calculations from Liu et al. (2011). No attempt was made to correct for dye impurities (Douglas and Byrne 2017a) nor variable salinity and temperature (Douglas and Byrne

2017b), where uncertainty attributable to these combined factors is within approximately ± 0.004 (Douglas and Byrne 2017b).”

123 It is stated that the conductivity probe was calibrated with a sodium chloride solution of known concentration. Surely one also needs a value for its conductivity, and a process for inferring seawater salinity from conductivity (rather than conductivity ratio - as implied by the definition of Practical Salinity).

A value for salinity in psu was sufficient to calculate seawater carbonate chemistry, and no attempt was made to infer conductivity from the sensor.

Line 123: The sensor was calibrated directly against a pure NaCl solution across a range of concentrations (0 to 40 ppt) at temperatures similar to that expected of seawater at the sampling location (23°C).

133 Why “pCO2” here? It is not a measurement, nor is it discussed anywhere as a calculated value

Alll reference to pCO2 has been removed from the text.

133 The citation to “Dickson and Millero (1987) does not make clear which constants were chosen. The usual ones are those of Mehrbach, converted to the total hydrogen ion concentration pH scale, but a more explicit statement would be appropriate

Line 132: “Corrections were made to the raw data if required, and final pH, pCO2, temperature and alkalinity values were used (with equilibrium constants from Mehrbach et al., 1973 refit by Dickson and Millero, 1987) to calculate Ω_{Ca} and Ω_{Ar} in CO2Sys (V2.1).”

136 The “precision” of the pH value is given as 0.022 - assuming this is some form of standard deviation, it is not clear how it was computed.

Suitable text describing the method for determining the precision of measurements has been added to the methods section:

Line 108: An additional series of continuous measurements were made in a static constant-temperature 20 L seawater system over an approximately three-hour period to determine the variability in measured pH. The resolution attributable to the lifetimes decay fluorometer (as

> stated by the manufacturer) can be matched with corresponding values of pH to provide resolution of pH measurement at the instrument level.

> Line 136: "The precision of calculated pH_T (defined as the standard deviation of three hours of consecutive measurements of a static seawater solution) was ± 0.022 pH units. The phase angle resolution of the lifetimes fluorometer was stated by the manufacturer as 0.05 degrees, and this translated to an instrument resolution of 0.0028 pH units.

149 "psu" is not an appropriate unit abbreviation. The Practical Salinity Scale has the unit "1" I note in Figs. 4 and 5 that salinity is apparently in "ppt" - this may be a closer reflection of the calibration approach

> Line 149: "and ranged from 33.0 to 34.3 ppt…"

155 two not "three" parameters?

> Line 155: "smoothed approximation of diel variation in these two parameters (Fig. 6).

156 The comment is made that the saturation state of aragonite has less "variability" than that of calcite. This is a necessary consequence of the definitions of saturation state whereby the ion product [Ca][CO3] is multiplied by 1/Ksp, and as the Ksp is different for aragonite and for calcite, so too is the multiplier with that for calcite being the larger.

> Thankyou for your insight
> Line 156 "As a consequence of the definitions of saturation state, and form-specific values of K_{sp} for aragonite and calcite, Ω_{ara} was slightly less variable than Ω_{cal} (with values between 2.5 and 3.1, or 3.8 to 5.4 units respectively, Fig. 6).

182 The comment is made that temperature and salinity play an important role in seawater chemistry. This is, in part, because the various equilibrium constants are themselves function of T & S. But also, here alkalinity (the 2nd CO2 parameter required for calculations) is itself a function of salinity. - the m/s does not make this clear.

> Line 182: "These data show the important role that temperature and salinity play in determining seawater carbonate chemistry (Millero 1995). Further, as the saturation state in this study is in part derived from alkalinity which is in turn derived from salinity and

temperature, the importance of obtaining accurate measurements of temperature and salinity is to be emphasised.

Figures I was surprised to see that the night/day cycle is identical in both April and December The time axis on the figures is hard to read (and needlessly varies from one frame to another

Good spotting - we corrected this error in Figures 4 to 7 and the time axis is larger and now uniform across all figures.

Additional references to add (Douglas and Byrne 2017a, and 2017b, Dickson 2010 [in Guide to best practises… edited by Riebesell et al])

Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-222, 2017

Continuous fluorescence-based monitoring of seawater pH *in* ~~a temperate estuary~~*situ*.

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Abstract. Electrical conductivity (salinity), temperature and fluorescence-based measurements of pH were employed to examine diel fluctuations in seawater carbonate chemistry of surface waters in Sydney Harbour over two multiple-day periods. The fluorescence-based technique provided a useful time-series for pH. Alkalinity with pH and temperature were used to calculate the degree of aragonite and calcite saturation (Ω_{Ca} and Ω_{Ar} respectively). Alkalinity was determined from an alkalinity-salinity relationship. Variation in pH over minute- to hour-long periods was distinguishable from background variability. ~~Diel variability in pH, Ω_{ara} and Ω_{cal}~~While the stated phase angle resolution of the lifetimes fluorometer translated into pH units was ± 0.0028 pH units, the precision of calculated pH was ± 0.022, indicating error associated with calibrating the device against known reference samples. Diel variability in pH, Ω_{Ar} and Ω_{Ca} showed a clear pattern that appeared to correlate with both salinity and temperature. Drift due to photodegradation of the fluorophore was minimised by reducing exposure to ambient light. Ω_{Ca} and Ω_{Ar} fluctuated ~~approximately~~ on a daily cycle. The net result of changes in pH, salinity and temperature combined to influence seawater carbonate chemistry. The fluorescence-based pH monitoring technique is simple, provides good resolution and is unaffected by moving parts or leaching of solutions over time. The use of optics is pressure insensitive, making this approach to ocean acidification monitoring well suited to deepwater applications.

1 Introduction

Ocean carbon chemistry is predicted to vary in response to elevated concentration of atmospheric ~~[~~carbon dioxide (CO_2~~],~~), with a decline in pH and an increase in the partial pressure of dissolved CO_2 (pCO_2) over the coming decades. However, short-term diel changes in seawater pH and pCO_2 at the scale of an embayment are unlikely to represent predicted globally increasing trends. Seawater carbonate chemistry in shallow nearshore environments is more likely driven by a combination of biological (photosynthesis, respiration) and local hydrodynamic (tidal, low salinity surface- and/or ground-water input) processes (Santos et al. 2012) with typical variation at time scales ranging from minutes to days. Capturing these short-term fluctuations requires virtually-continuous monitoring of water chemistry.

Seawater pH has ~~until recently~~ been ~~largely~~commonly measured with a potentiometric technique using glass electrodes. While this method can be accurate and precise~~,~~, if appropriate care is taken with temperature control and the use of seawater buffers (Dickson, 2010), this technology suffers from a gradual loss of electrolyte and consequent drift, requiring recalibration. In addition, ion selective electrodes are susceptible to poisoning, in particular by sulphide released when conditions become anoxic. However, recent advances in electrode design including the incorporation of more internal salt bridges have enabled the continuous use of glass pH electrodes in shallow marine waters for over 12 months (Ionode Pty Ltd, Australia, pers. comm).

Spectroscopic techniques for measuring seawater pH use a pH-sensitive dye that assumes different absorbance spectra depending on pH. While the method can provide pH estimates with an uncertainty less than 0.01, variability in the quality of the dye obtained from commercial suppliers can cause the true extinction coefficients associated with a particular dye to differ slightly from published extinction coefficient values. Consequently, uncertainty associated with this technique is generally assumed to be about 0.01 pH units (Dickson 2010).

Ion selective field effect transistor (ISFET) technology is becoming more widely used to measure pH in seawater. pH sensors using ISFET technology comprise the ISFET sensor itself - a solid-state device with a H+ ion sensitive material, a counter electrode and a reference electrode. In pH monitoring systems such as the SeaFET (Martz et al. 2010, Takeshita et al. 2015, Johnson et al, 2016) a chloride electrode is used as reference as chloride ion activity is relatively constant in deep water. However this introduces problems in locations where chloride concentrations fluctuate, such as euryhaline estuarine environments.

Optical fluorescence-based approaches to pH sensing offer an alternative to glass electrodes, spectrophotometric techniques and ISFET sensors. Optical fluorescence-based methods do not require electrolyte solutions or gels which gradually lose ions, nor do they require reference electrodes and their accompanying susceptibility to varying environmental conditions. Optical methods are also impervious to high pressure~~, only~~. Only the housing for the device and the window through which the optical signal is passed must be pressure resistant. The use of fluorescence lifetimes measurements provides the additional advantage of being insensitive to changes in fluorescence intensity. As the fluorophores used in this study are sensitive to changes in temperature and salinity, careful measurement of these parameters remains essential.

In this study we explore a new approach to logging pH in seawater ~~and~~ in the setting of an ocean-water dominated estuarine environment. We incorporated a commercially available fluorescence-based pH sensing system (Presens GmbH) in a submersible continuous monitoring device (Aquation Pty Ltd) to measure short~~-~~-term changes in seawater pH in surface waters in Sydney Harbour over two multi-day intervals in austral Autumn and Summer. Electrical conductivity and temperature were also measured, and an approximation for alkalinity was derived from a salinity-alkalinity relationship reported for the Australasian region (Lenton et al. 2016). We acknowledge that the relationship between salinity and alkalinity is subject to terrestrial influence, and consequently our estimate of alkalinity remains an approximation. With these data we estimated changes in seawater carbonate chemistry during the deployments. The objectives of the study were a) to ~~a)~~ characterise the fluorescence-based pH monitoring system in seawater in terms of stability and resolution, and b) to characterise diel fluctuations of pH and aragonite/calcite saturation state in surface waters. The study focussed on natural fluctuations in seawater pH and the capability of the fluorescence technique to address these fluctuations. Determining the accuracy of pH values obtaining from the fluorescence device was not an objective, as highly accurate determinations would require considerable resources that were not available at the time of study.

2 Methods

2.1 Study site and sampling arrangements

Real-time ~~seawater~~ measurements were made of seawater in the Sydney Harbour estuary at the Sydney Institute of Marine Sciences (SIMS), Chowder Bay, NSW, Australia (-33.839357 °S, 151.254587 °E) (Fig. 1). Chowder Bay is a shallow (5 to 10 m) embayment located on the northern shore of Sydney Harbour some 3 km from the ocean. Tides in Sydney Harbour (depths typically ~20 m) are semi-diurnal, with a maximum difference of 1.95 m at the estuary entrance. Tidal fluctuation during the deployment intervals is referenced to measurements made at nearby Fort Denison (Caldwell et al. 2015). Seawater chemistry was measured from ~~approximately~~ ~1 m below sea level at low tide below the SIMS pier at Chowder Bay.

Two field deployments were conducted. Firstly, water was collected ~~some~~ ~1~~-2~~ m below ~~sea level at~~ low tide and pumped 3-5 m up into a 2 L reservoir in an enclosed structure at the end of the ~~wharf~~pier. Water exited the reservoir through a narrow tube located below an overflow pipe at the upper part of the reservoir, passing through a clear polycarbonate tube for optical measurement (*ex situ* measurements, Autumn, 8th-19th April 2016). Fluorescence spots were attached to the inside of this tube and a plastic optical fibre was positioned perpendicular to the outside of the tube and directed to the spot. To avoid photobleaching the system was covered in black plastic eliminating most light. Waste water was directed back into the harbour at least 5 m away from the intake location. This preliminary series of tests enabled us to make frequent measurements as the system could use a constant supply of mains power. The primary objective of the *ex situ* measurements was to assess the stability of the system.

In situ measurements were later made ~1 m below low tide during 14th-22nd December 2016, with the self-contained instrument attached vertically to a ~~pier~~post under the ~~wharf~~pier and the fluorescence spot facing downwards to minimise sunlight-induced photobleaching (Fig. 2). In this arrangement the plastic optical fibre within the clear polycarbonate cylindrical housing of the instrument was oriented perpendicular to the faceplate. To ensure that the spot could not peel off, a non-fluorescent mesh was held in place over the spot with a plastic ring. This arrangement ensured that the spot was fixed in position and water could easily reach the fluorophore and respond to ambient pH. A small hole was drilled partway into the inside of the faceplate to bring the fibre tip closer to the spot, which was affixed to the external surface of the faceplate. This was necessary to increase signal strength to an acceptable level. During the *in situ* measurements, water samples were collected adjacent to the instrument and removed to the laboratory for measurement of pH_T (see below) within 30 minutes of sampling. The instrument contained three NiMH battery packs in series comprising 14 cells each with a total of 13.5 Ah at 16.8 volts.

Sunrise and sunset at the study site on the 9th April 2016 was 06:14 and 17:38 respectively. Sunrise and sunset on the 18th December 2016 was 05:40 and 20:02 respectively.

2.2 pH measurements

The fluorescence-based pH measurement uses a dual-luminophore frequency-domain fluorescence decay technique (Huber et al. 2001). A pH sensitive dye with short fluorescence decay time which changes its fluorescence intensity dramatically with pH is mixed together with an inert reference dye with long decay time. Both dyes are immobilized in particles which are dispersed in a hydrophilic membrane. This sensing membrane is in contact with the ambient water and a light guide is brought to the opposite site of the membrane to read the pH (Fig. 3). The read out unit (EOM-pH-mini) sends sine-wave modulated blue light to excite both dyes simultaneously (the “spot”) and measures the average decay time of the sum of returned fluorescence light from both dyes.

Calibration was performed prior to deployment of the instrument. All glassware, buffers, seawater and the instrument were left overnight in an air-conditioned room to reach a stable temperature of 22 °C. An Ag/AgCl pH electrode (Ionode Pty Ltd) was calibrated against standard buffers (pH 7.02 and 10.06 at 20° ~~C).~~C, Amalgamated Instruments Co. Pty Ltd, Australia). A pair of phosphate buffer solutions were also prepared, isotonic to ~34.5 ppt NaCl ($I = 0.7$ M) with ~~C1~~B1=8.33 pH and ~~C2~~B2=4.00 pH (where ~~C1~~B1 and ~~C2~~B2 are the measured pH of each of the buffers). A small volume (e.g. 0.25 mL) of ~~C1~~B1 was added to 10 mL of ~~C2~~B2 until the combined buffer reach a pH of 4.45 as measured by the Ag/AgCl electrode. An aliquot (approx. 1 mL) of this combined buffer solution of known pH was pipetted onto the fluorescence spot (fixed to the inside of the clear polycarbonate tube, or fixed to the faceplate of the instrument) and the fluorescence phase measured. Settling time of the phase value for each aliquot could take at least 10 minutes. Then, more ~~C1~~B1 was added to the combined buffer and the process repeated at pH 5.66, 6.81, 7.23, 7.72, 8.02 and 8.30. The relationship between measured phase and (total) pH was determined with a non-linear Boltzman sigmoid model using the software provided by the manufacturer. We did not use Tris as a buffer as it is known to poison single junction Ag/AgCl electrodes, and report pH in the total hydrogen ion scale (as recommended by Dickson 2010). Both room and buffer temperature were stable during the calibration procedure at 22°C and 22 ± 0.5 °C, respectively.

~~During~~At the beginning and end of the *in situ* deployment, water samples were collected ~~by swimmer~~ adjacent to the submerged pH monitor ~~when underwater~~ and transported to the nearby lab at SIMS~~ in~~. At each sampling time, three 200 mL glass jars~~.~~ were completely filled, and lids secured underwater to eliminate air bubbles. This process was repeated at least three times, with approximately 30 minutes between each sampling time. Within 30 minutes of collection, pH was measured spectrophotometrically with *m*-cresol purple indicator dye (Acros Organics, Lot # A0321770) using a custom-built automated system with a USB4000 fibre optic spectrophotometer (Ocean Optics) following SOP 6b from ~~(~~Dickson et al~~.,~~. (2007) and calculations from Liu et al. (2011). Spectrophotometric measurements of pH$_T$ were validated using seawater certified reference material (CRM, Dickson Standard Batch 145). The precision of the spectrophotometric technique in our laboratory is typically ±0.006 at temperatures between 17 to 24°C (standard deviation), with an accuracy very much dependent on the dye quality. We did not apply corrections for dye impurities, temperature and salinity variations as discussed in Douglas and Byrne (2017a,b) because obtaining such highly accurate pH values was not an objective of this study. The uncertainty attributable to these combined factors is within approximately ±0.004 (Douglas and Byrne (2017b). The measured pH$_T$ was compared to the calculated pH$_T$ of the CRM using published values for total alkalinity (A$_T$), dissolved inorganic carbon (DIC) and salinity at the same temperature.

~~The gradual drift experienced with the fluorescence-based pH sensor was then corrected assuming a linear decline in measured pH corresponding with photodegradation of the fluorophore spot, which was shaded but not in the dark. Corrections were made against the reference samples measured spectrophotometrically, as described previously.~~

An additional series of continuous measurements were made in a static constant-temperature 20 L seawater system over an approximately three-hour period to determine the variability in measured pH. The resolution attributable to the lifetimes decay fluorometer (as stated by the manufacturer) can be matched with corresponding values of pH to provide resolution of pH measurement at the instrument level. Corrections for the *in situ* measurements were made against spectrophotometric measurements of the reference samples by calculating two average offsets between values of collected samples measured using the fluorometric device and the spectrophotometric device. One offset was derived for the beginning of the deployment and one for the end. The gradual decline in measured values over time was corrected assuming a constant linear drift.

In situ measurements were taken ten times per minute and averaged over one minute before analysis. *Ex situ* ~~and *in situ*~~ measurements were taken once per minute ~~or 10 times in one minute every 10 minutes, respectively,~~ and a running average of 10 minutes of the *ex situ* measurements is presented.~~ *In situ* measurements taken over one minute were averaged before analysis.~~

2.3 Temperature

PT100 sensors were either suspended in the 2L reservoir that received seawater immediately prior to ~~measurement~~*ex situ* measurements, or were simply positioned up against the inside of the housing wall when deployed *in situ*. Initial temperature data during the *in situ* deployment were ignored until the sensors reached equilibrium with ambient water. ~~*Ex situ* and *in*~~*In* *situ* measurements were taken ~~twice every~~ten times per minute~~, or 10 times in~~ and averaged over one minute ~~every 10 minutes, respectively. Sets of two or 10 measurements were averaged~~ before analysis. *Ex situ* measurements were taken twice per minute and a running average of 10 minutes of the *ex situ* measurements is presented.

2.4 Salinity

Electrical conductivity was measured using a Hanna HI3001 four ring potentiometric conductivity probe designed for flow-through sensing wired to a custom circuit board. Millivolt values were converted to salinity assuming a linear relationship between sensor readings and salt content. The sensor was calibrated directly against a pure NaCl solution across a range of ~~known concentration~~concentrations (0 to 40 ppt) at temperatures similar to that expected of seawater at the sampling location~~. *Ex situ* and *in*~~ (23°C). *In* *situ* measurements were taken ~~three~~ten times per minute ~~every minute, or 10 times in~~and averaged over one minute ~~every 10 minutes, respectively, and these sets of three or 10 measurements were averaged~~ before analysis. ~~A~~ *Ex situ* measurements were taken three times per minute and a running average of 10 minutes of the *ex situ* measurements is presented.

2.5 Datalogging and calculations

Both flow-through and *in situ* deployments were conducted using a custom datalogger/controller system based on a Submersible Datalogger (Aquation Pty Ltd, Australia). All data were saved on board and downloaded to PC after retrieval of the instrument. Alkalinity was calculated from salinity data according to a linear salinity-alkalinity relationship for Australasian waters described by Lenton et al. (2016). ~~Corrections~~Drift and offset corrections were made to the raw data ~~if~~as required~~,~~ (described above), and final pH, ~~pCO2~~salinity, temperature and alkalinity values were used (with equilibrium constants from Mehrbach et al., 1973 refit by Dickson and Millero, 1987) to calculate Ω_{Ca} and Ω_{Ar} in CO2Sys (V2.1) (Dickson and Millero 1987). The final pH is reported on the total scale.

3.0 Results

3.1 pH

Seawater collected and pumped to the sensor varied by 0.08 pH units from 7.97 to 8.05 over the three-day interval in Autumn (Fig. 4). The ~~precision~~phase angle resolution of ~~calculated pH~~the lifetimes fluorometer was stated by the manufacturer as 0.~~022~~05 degrees, and this translated to an instrument resolution of 0.0028 pH units. This is constrained by the resolution (0.01°) and precision (0.05°) of the lifetimes-decay fluorometer. The precision of calculated pH_T (defined as the standard deviation of three hours of consecutive measurements of a static seawater solution) was ± 0.022 pH units. The best precision can be achieved by averaging multiple measurements. Gradual ~~photodegradation~~bleaching is known to influence fluorophores~~,~~ (Lakowicz 2006), contributing to a steady drift. This was accounted for with corrections based on samples collected *in situ* as described above. In this case, the decline in pH was 0.0136 pH units per day. pH measured over summer ranged from 7.95 to almost 8.15 units, some 0.1 units more basic than Autumn values (Fig. 5).

3.2 Temperature

~~Temperature~~Surface seawater temperature fluctuated between 21.6°C and 22.6°C in April (*ex situ* measurements, Fig. 4), and 21.0 to 23.6 in December (*in situ* measurements, Fig. 5). The stated resolution of the PT100 temperature sensors was 0.01°C and concurrent readings were within 0.05 °C of each other. Over the three day period, temperature showed a consistent pattern of declining at night and then rapidly increasing again around the middle of the day, reaching a maximum value around mid-afternoon. During the *in situ* deployment, diel fluctuations in ambient seawater temperature varied between 1 and 2~~ degrees~~°C, and increased to 23.6°C in the last two days of the measuring interval (Fig. 5).

3.3 Salinity

Salinity was calculated from electrical conductivity, and ranged from 33.0 to 34.3 ~~psu~~ppt during the *ex situ* measurements, and 34.6 to 37.7 during the *in situ* measurements with a mean value of ~~approximately~~ 36.5 ~~psu~~ppt during the *in situ* measurements (Figs 4 and 5 respectively). Diel variation ~~roughly~~ tracked the tidal cycle with higher salinity driven by the incoming tide~~.~~ (Fig. 4). However, the amplitude of the salinity signal was not ~~driven by~~consistently coincident with the tidal amplitude (Fig. ~~4~~5).

3.4 Saturation states

Both Ω~~$_{ara}$~~$_{Ca}$ and Ω~~$_{cal}$~~$_{Ar}$ calculated from water in the *ex situ* trial fluctuated over the course of three days, ~~appearing to provide~~providing a smoothed approximation of diel variation in these ~~three~~two parameters (Fig. 6). Most striking is the noise associated with the calculated values, reaching as high as 1 Ω units. As a consequence of the definitions of saturation state, and from specific values of K_{sp} for aragonite and calcite, Ω_{Ar} was slightly less variable than Ω_{Ca} (with values between 2.5 and 3.1, or 3.8 to 5.4 units respectively, Fig. 6). ~~Ω_{ara}~~Ω_{Ar} appeared to have slightly less variability than Ω~~$_{cal}$. Ω_{ara}~~$_{Ca}$. Ω_{Ar} varied between ~~approximately~~ 2.5 and 3.1 units, while Ω~~$_{cal}$~~$_{Ca}$ varied from ~~approximately 3.8 to 5.4 units (Fig.~~ 3.8 to 5.4 units (Fig.~~6). Saturation state values also shifted approximately on a 24 hour cycle, with higher values roughly synchronising with 1800 hours (Figs~~ 6 ~~and 7~~).

4.0 Discussion

4.1 Instrumentation

The fluorescence-based pH measurements provide sufficient resolution to observe and predict diel changes in nearshore system pH, and indicated significant changes in seawater /carbonate chemistry at timescales of hours to days. Values of pH, salinity and temperature were all within what one would expect for the harbour at that time of year~~.~~ (e.g. pH ~8.0, S=~35 ppt, T= ~18°C, pers. obs.). Further, the average magnitude of both Ω~~$_{cal}$~~$_{Ca}$ and Ω~~$_{ara}$~~$_{Ar}$ were within the bounds of expected values for current-day marine surface waters.

The mains-powered instrument designed to measure water pumped up from the harbour had the advantage of unlimited power and the capacity to make multiple measurements several times per minute. However, the dissolved gas content of pumped water can vary relative to the source water due to degassing and temperature changes, making measurements potentially less representative of the water to be sampled. We kept this to a minimum by pumping water over a short distance. Further, the need to use a suitable secure location with a constant power source is a limitation with respect to field deployments. ~~On the other hand~~In contrast, the self-powered instrument tested during December 2016 had sufficient power to operate unattended for several weeks, and with a decrease in sampling frequency the lifetime of the unit could be extended to several months. For even longer periods the device could be constructed using a longer cylinder, a separate battery pack, with lithium ion batteries, or combinations of these. With this approach, the unit could be powered to operate unattended for over 12 months.

The housing used in this study was constructed from 5 mm thick acrylic. However, calculations indicate failure of the housing at depths exceeding 100 m. A metal housing with regular bulkheads along its length would increase pressure resistance and provide an instrument capable of withstanding deep ocean pressures.

4.2 Data and significance

While there was a clear diel fluctuation in temperature of about 1 °C both in December and April, the gradual increase in temperature during the 20th and 21st of December (austral Summer) was coincident with a decline in salinity and tidal amplitude (Fig. 5). This suggests an influx of warmer freshwater into the estuary coupled with weaker tidal pumping, where pumping corresponds with flushing of the harbour with higher-salinity seawater from the ocean. pH, $\Omega_{\cancel{\mathrm{cal}}\mathrm{Ca}}$ and $\Omega_{\cancel{\mathrm{ara}}\mathrm{Ar}}$ also declined during these last two days of the deployment. These data show the important role that temperature and salinity play ~~an important role~~ in determining seawater carbonate chemistry~~, as is well known~~ (Millero 1995). Further, as the saturation state in this study is in part derived from alkalinity which is in turn derived from salinity and temperature, the importance of obtaining accurate measurements of temperature and salinity is to be emphasised. As a consequence of these physical factors (and presumably photosynthesis and respiration; Schulz and Riebesell, 2013), nearshore coastal waters and estuaries experience changes in $\Omega_{\cancel{\mathrm{cal}}\mathrm{Ca}}$ and $\Omega_{\cancel{\mathrm{ara}}\mathrm{Ar}}$ not only over the course of several days, but also over a 24 hour period. This contrasts with oceanic marine waters that maintain relatively constant values of saturation state. Models used to forecast seawater carbonate chemistry, such as those employed in the IPCC reports are typically based on the open ocean. The projections for the open ocean do not incorporate the short-term fluctuations typical of coastal waters (Hendriks et al. 2015).

~~However, when~~When assessing nearshore shallow-water marine coastal and estuarine environments, these short-term fluctuations in seawater carbonate chemistry can be significant, as found in this study, and are best accounted for and included in predictive models. Perhaps most important is to determine the capacity for organisms that live in these highly fluctuating environments to withstand or thrive in spite of such a regular chemistry change. ~~Here~~In this study we generated a targeted data set to assess the application of the fluorescence based method~~.~~ for measuring seawater pH. Our results show the influence of fluctuating temperature and salinity on calcium carbonate saturation state in an estuarine environment. More research is needed to determine in detail these and other drivers of fluctuating saturation states (e.g. photosynthesis and respiration), and the actual consequences of these changes to key resident marine species.

4.3 Conclusion

We observed pH of surface water at Chowder Bay in Sydney Harbour to vary significantly across a diel cycle, influenced by temperature, salinity and tidal height /alternating freshwater or saline dominance. The fluorescence-based pH monitoring technique used here could resolve changes in pH to 0.022 pH units. Corresponding saturations states of calcite and aragonite ($\Omega_{\cancel{\text{cal}}\text{Ca}}$ and $\Omega_{\cancel{\text{ara}}\text{Ar}}$), calculated from pH, temperature and salinity-derived alkalinity values showed diel fluctuations in seawater carbonate chemistry that can be interpreted as the combined effect of pH, temperature and salinity. Variability in saturation state over such short time scales in this shallow ecosystem indicates the importance of high temporal and spatial resolution measurements of seawater carbonate chemistry when determining the impact of ocean acidification on shallow nearshore marine and estuarine ecosystems.

Competing Interests

JWR is a director of Aquation Pty Ltd.

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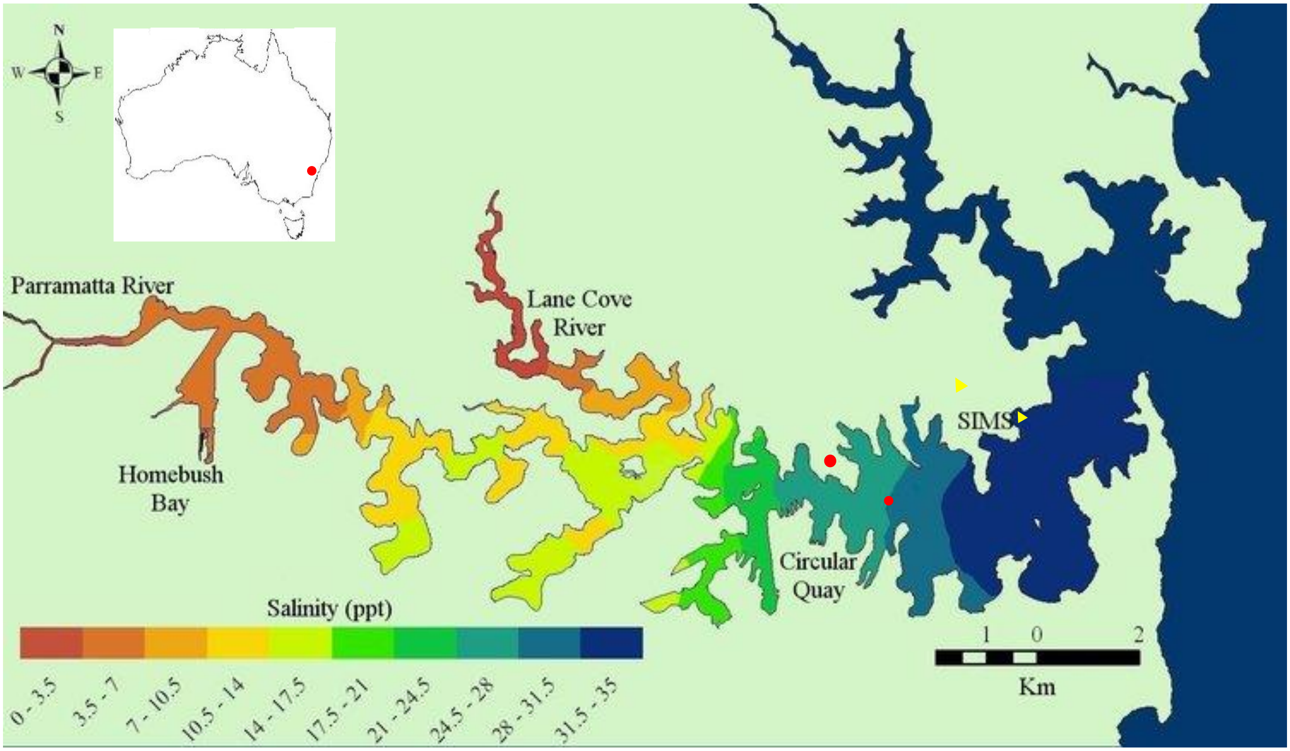

N
W
E
S
Parramatta River
Lane Cove River
Homebush Bay
Circular Quay
SIMS
Salinity (ppt)
0 - 3.5
3.5 - 7
7 - 10.5
10.5 - 14
14 - 17.5
17.5 - 21
21 - 24.5
24.5 - 28
28 - 31.5
31.5 - 35
1
0
2
Km

Figure 1. Port Jackson (Sydney Harbour) with sampling site (SIMS, yellow triangle) and Fort Denison tide reference station (red circle). **The red dot on the insert map indicates Sydney's location.** **Map courtesy of http://www.sydneyharbourobservatory.org/.**

Figure 2. Submersible logging pH monitor. The fluorescence spot is located on the upper faceplate between and forward of the two submersible connectors, beneath a clear plastic ring.

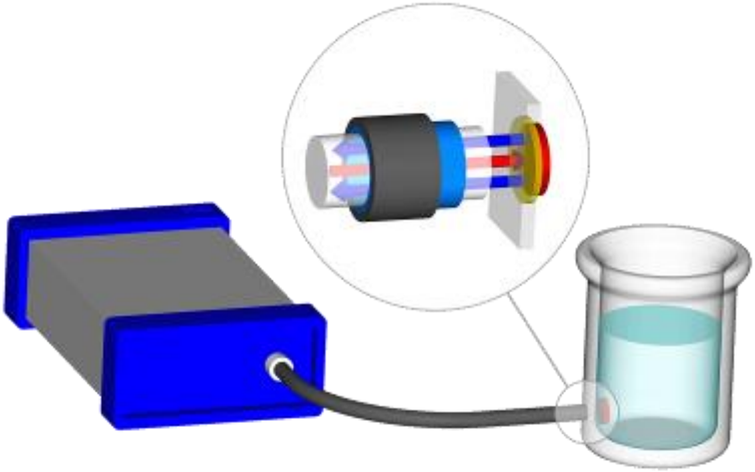
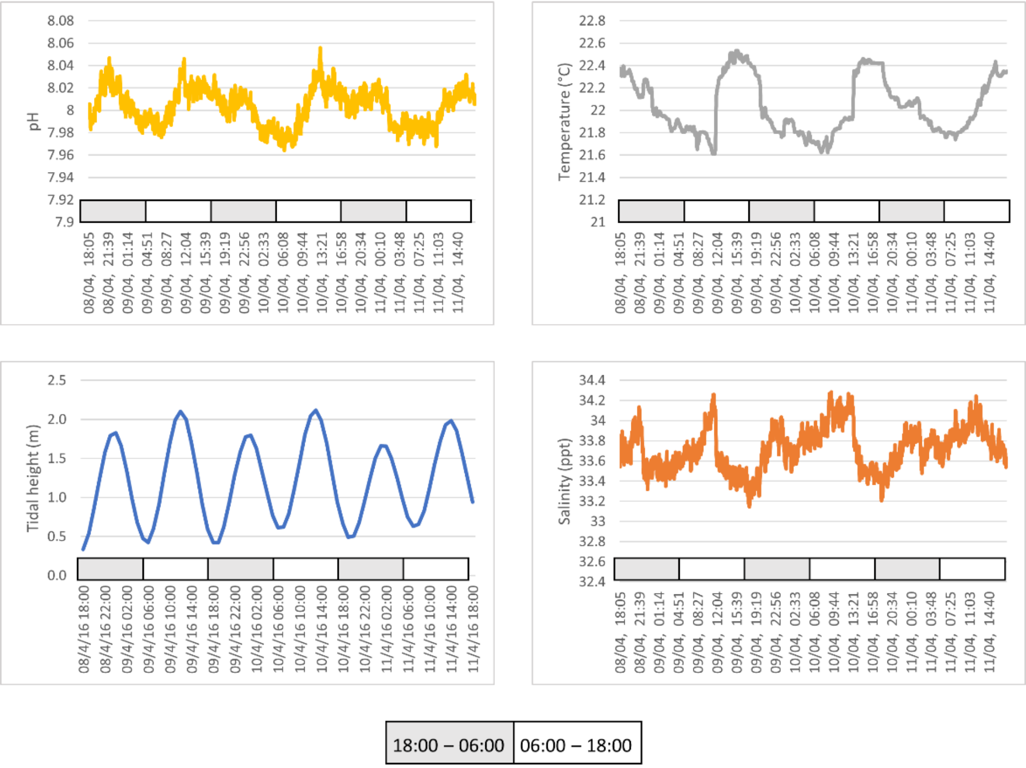


Figure 3. Schematic of pH monitoring system with EOM-pH-mini (left), and fibre optic conveying light to fluorescent spot attached to inside of vessel (right). The insert shows light conveyed through the transparent vessel wall to the spot~~,~~ (red arrow), and fluorescent light emitted from the spot back along the fibre~~.~~ (blue arrows).


pH
8.08
8.06
8.04
8.02
8
7.98
7.96
7.94
7.92
7.9
08/04, 18:05
08/04, 21:39
09/04, 01:14
09/04, 04:51
09/04, 08:27
09/04, 12:04
09/04, 15:39
09/04, 19:19
09/04, 22:56
10/04, 02:33
10/04, 06:08
10/04, 09:44
10/04, 13:21
10/04, 16:58
10/04, 20:34
11/04, 00:10
11/04, 03:48
11/04, 07:25
11/04, 11:03
11/04, 14:40
Temperature (°C)
22.8
22.6
22.4
22.2
22
21.8
21.6
21.4
21.2
21
Tidal height (m)
2.5
2.0
1.5
1.0
0.5
0.0
08/4/16 18:00
08/4/16 22:00
09/4/16 02:00
09/4/16 06:00
09/4/16 10:00
09/4/16 14:00
09/4/16 18:00
09/4/16 22:00
10/4/16 02:00
10/4/16 06:00
10/4/16 10:00
10/4/16 14:00
10/4/16 18:00
10/4/16 22:00
11/4/16 02:00
11/4/16 06:00
11/4/16 10:00
11/4/16 14:00
11/4/16 18:00
Salinity (ppt)
34.4
34.2
34
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33.4
33.2
33
32.8
32.6
32.4
18:00 – 06:00
06:00 – 18:00

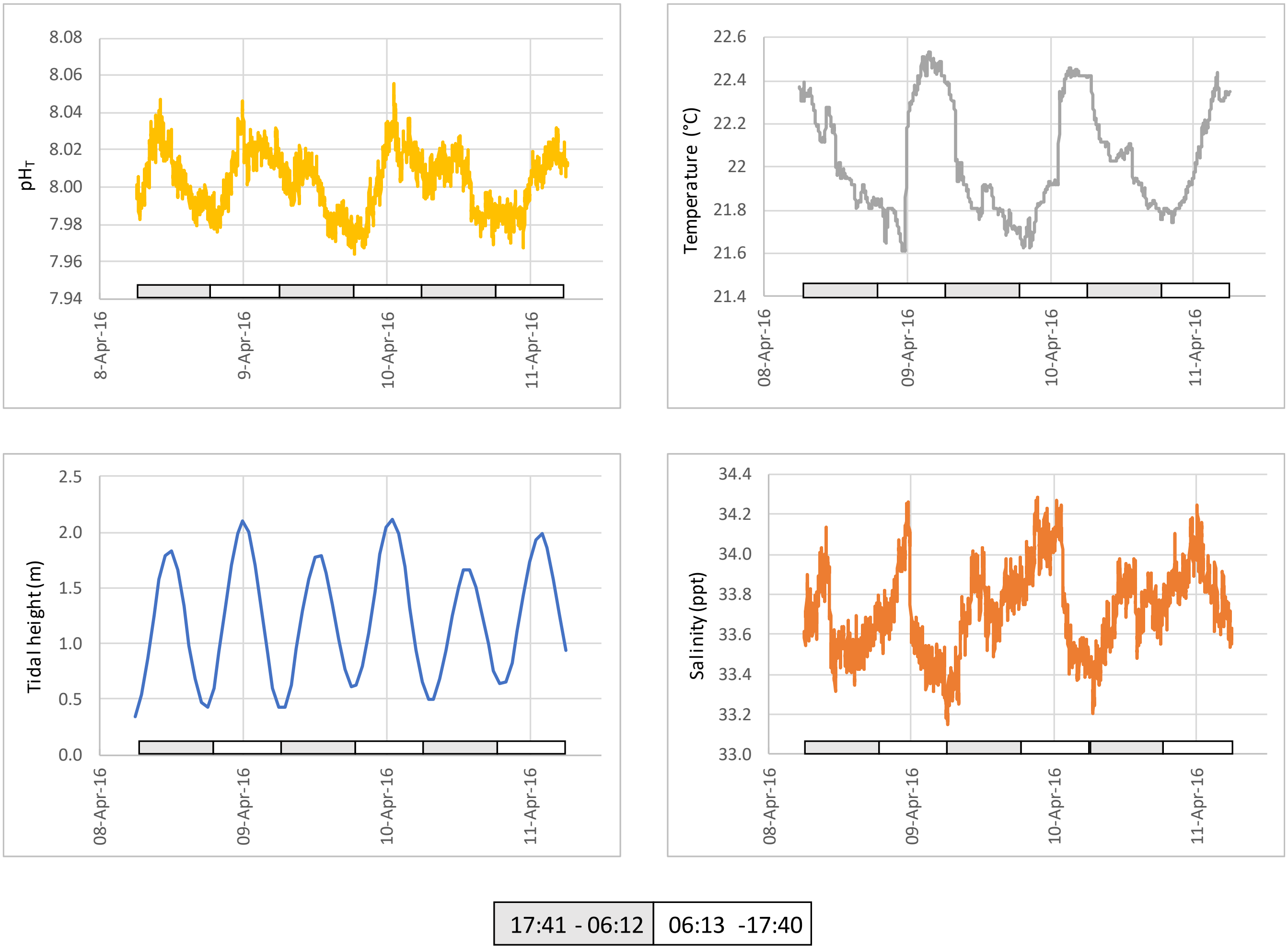
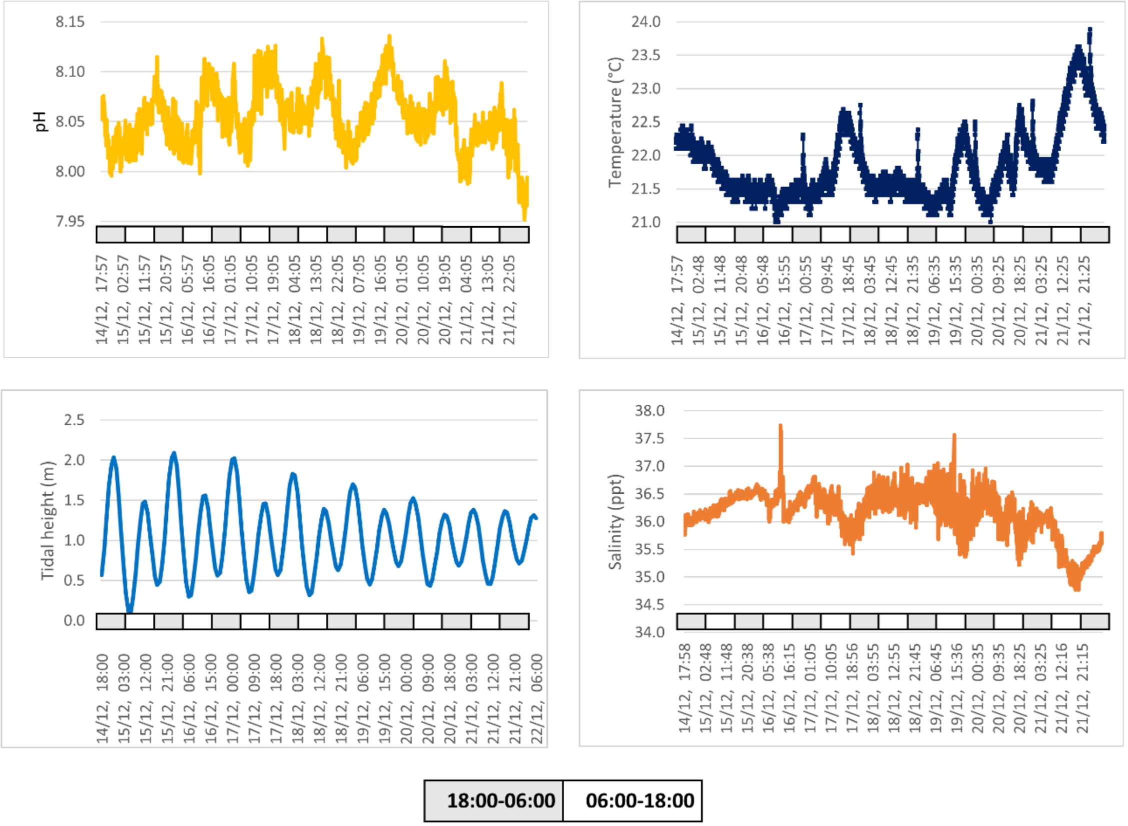


Figure 4. pH, temperature, tidal height and salinity of seawater pumped from ~1 m below low water at Chowder Bay, Sydney over a three-day period. Grey and white boxes indicate the time ~~of day, with grey representing 1800 to 0600 and white representing 0600 to 1800~~between sunset and sunrise.


pH
8.15
8.10
8.05
8.00
7.95
14/12, 17:57
15/12, 02:57
15/12, 11:57
15/12, 20:57
16/12, 05:57
16/12, 16:05
17/12, 01:05
17/12, 10:05
17/12, 19:05
18/12, 04:05
18/12, 13:05
18/12, 22:05
19/12, 07:05
19/12, 16:05
20/12, 01:05
20/12, 10:05
20/12, 19:05
21/12, 04:05
21/12, 13:05
21/12, 22:05
Temperature (°C)
24.0
23.5
23.0
22.5
22.0
21.5
21.0
14/12, 17:57
15/12, 02:48
15/12, 11:48
15/12, 20:48
16/12, 05:48
16/12, 15:55
17/12, 00:55
17/12, 09:45
17/12, 18:45
18/12, 03:45
18/12, 12:45
18/12, 21:35
19/12, 06:35
19/12, 15:35
20/12, 00:35
20/12, 09:25
20/12, 18:25
21/12, 03:25
21/12, 12:25
21/12, 21:25
Tidal height (m)
2.5
2.0
1.5
1.0
0.5
0.0
14/12, 18:00
15/12, 03:00
15/12, 12:00
15/12, 21:00
16/12, 06:00
16/12, 15:00
17/12, 00:00
17/12, 09:00
17/12, 18:00
18/12, 03:00
18/12, 12:00
18/12, 21:00
19/12, 06:00
19/12, 15:00
20/12, 00:00
20/12, 09:00
20/12, 18:00
21/12, 03:00
21/12, 12:00
21/12, 21:00
22/12, 06:00
Salinity (ppt)
38.0
37.5
37.0
36.5
36.0
35.5
35.0
34.5
34.0
14/12, 17:58
15/12, 02:48
15/12, 11:48
15/12, 20:38
16/12, 05:38
16/12, 16:15
17/12, 01:05
17/12, 10:05
17/12, 18:56
18/12, 03:55
18/12, 12:55
18/12, 21:45
19/12, 06:45
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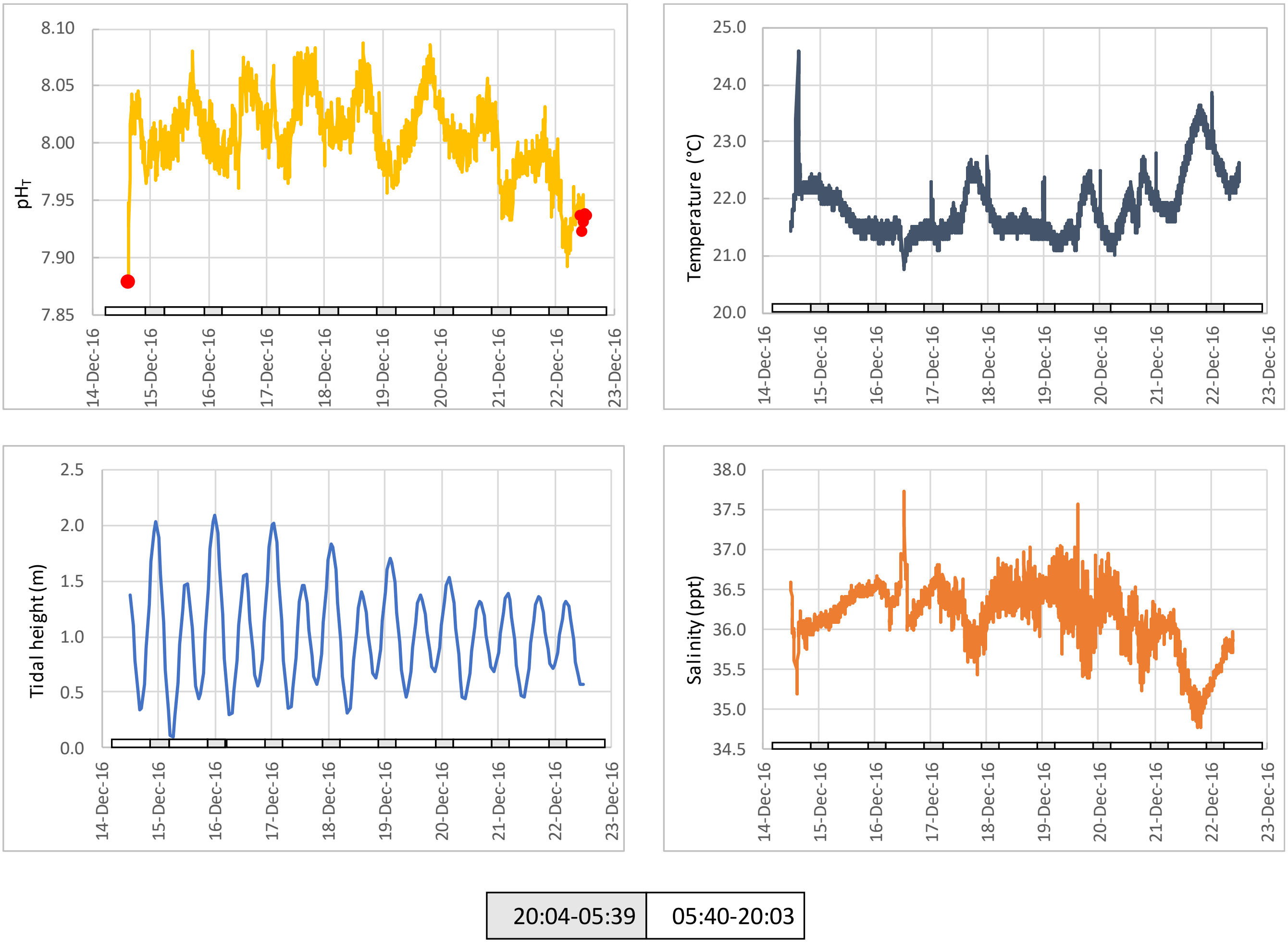


Figure 5. pH, temperature, tidal height and salinity of seawater measured *in situ* at ~1 m below low water at Chowder Bay, Sydney over a multi-day period. Grey and white boxes indicate the time ~~of day, with grey representing 1800 to 0600 and white representing 0600 to 1800.~~

between sunset and sunrise. Red dots indicate values of reference samples collected adjacent to the device and measured using spectrophotometry.

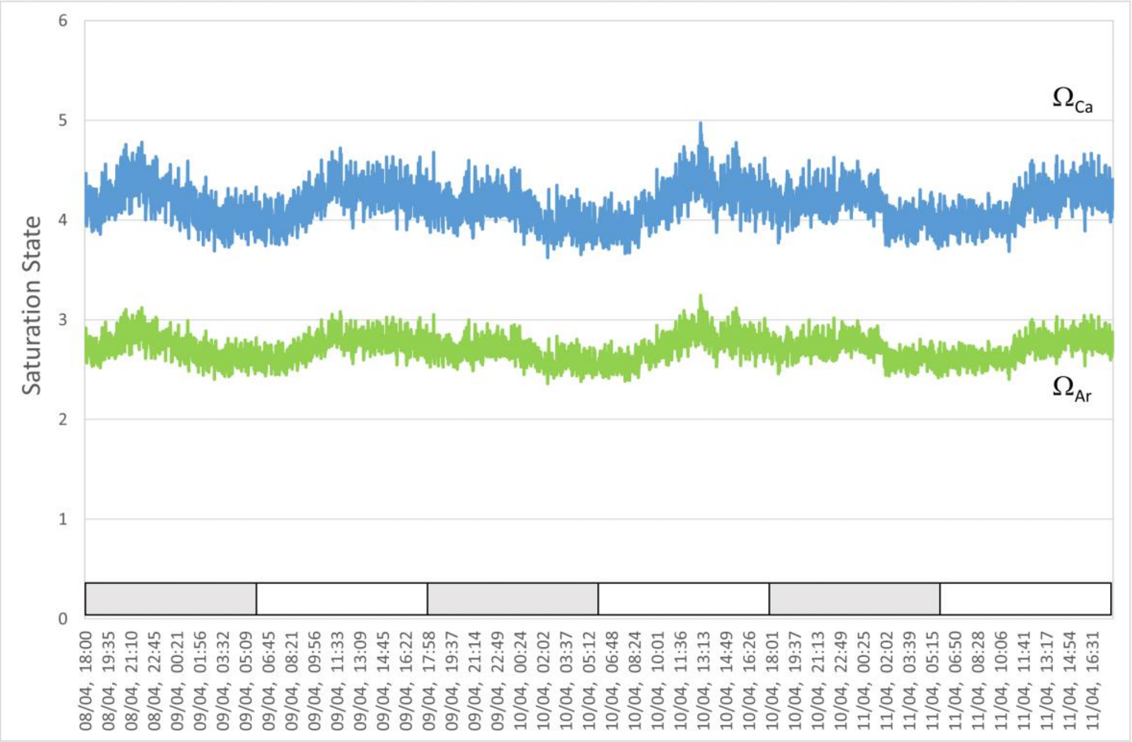
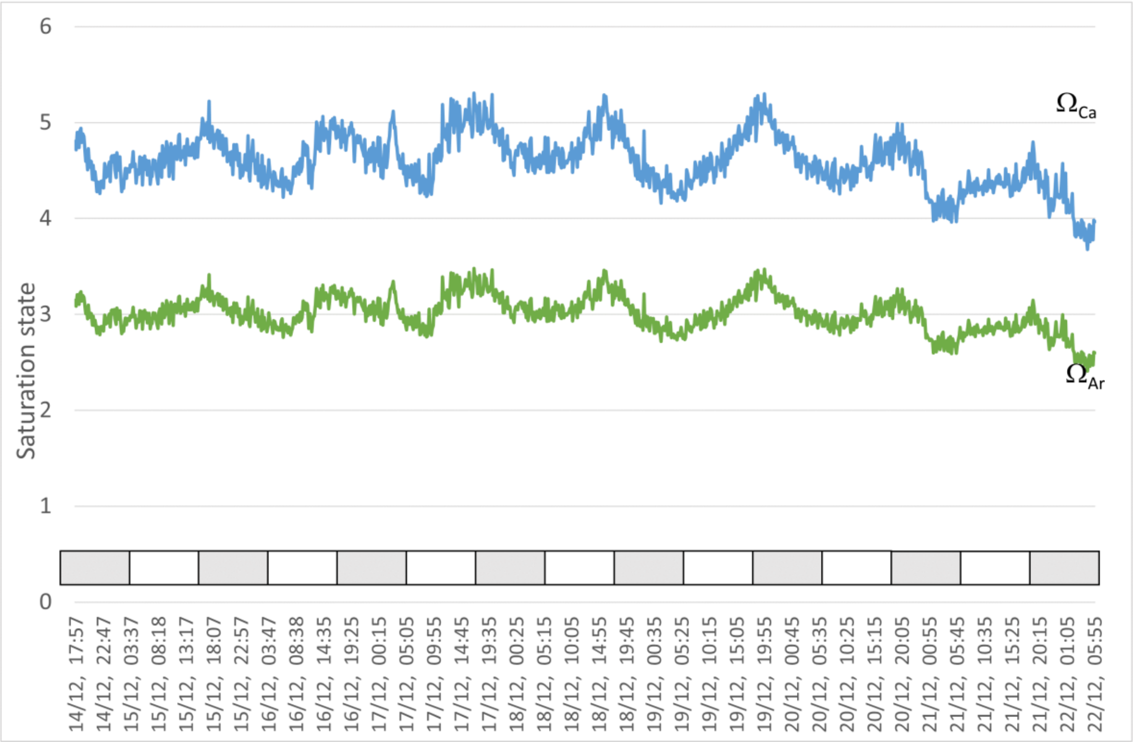


Figure 6. Aragonite and calcite saturation values calculated from data presented in Fig. ~~2. Values below unity represent dissolution.~~ 4. Grey and white boxes indicate the time ~~of day, with grey representing 1800 to 0600~~between sunset and ~~white representing 0600 to 1800.~~sunrise.


6
5
4
3
2
1
0
Saturation state
Ω_{Ca}
Ω_{Ar}
14/12, 17:57
14/12, 22:47
15/12, 03:37
15/12, 08:18
15/12, 13:17
15/12, 18:07
15/12, 22:57
16/12, 03:47
16/12, 08:38
16/12, 14:35
16/12, 19:25
17/12, 00:15
17/12, 05:05
17/12, 09:55
17/12, 14:45
17/12, 19:35
18/12, 00:25
18/12, 05:15
18/12, 10:05
18/12, 14:55
18/12, 19:45
19/12, 00:35
19/12, 05:25
19/12, 10:15
19/12, 15:05
19/12, 19:55
20/12, 00:45
20/12, 05:35
20/12, 10:25
20/12, 15:15
20/12, 20:05
21/12, 00:55
21/12, 05:45
21/12, 10:35
21/12, 15:25
21/12, 20:15
22/12, 01:05
22/12, 05:55

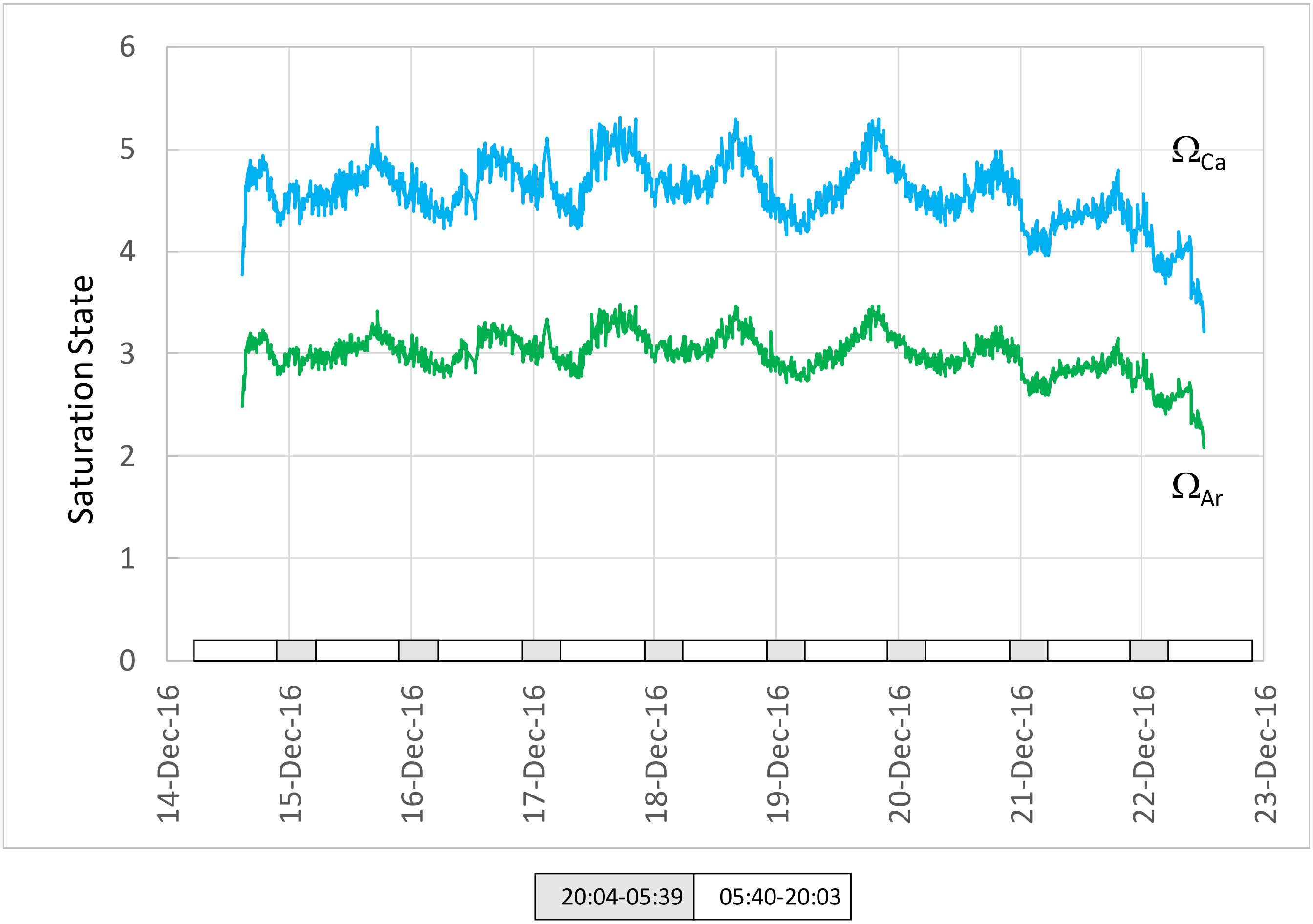


Figure 7. Aragonite and calcite saturation values calculated from data presented in Fig. ~~4. Values below unity represent dissolution.~~5. Grey and white boxes indicate the time ~~of day, with grey representing 1800 to 0600~~between sunset and ~~white representing 0600 to 1800~~sunrise.