

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 (CO₂), with a decline in pH and an increase in the partial pressure of dissolved CO₂ (pCO₂) 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 ensure that 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”

Line 110 - 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 reference 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 °C 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.

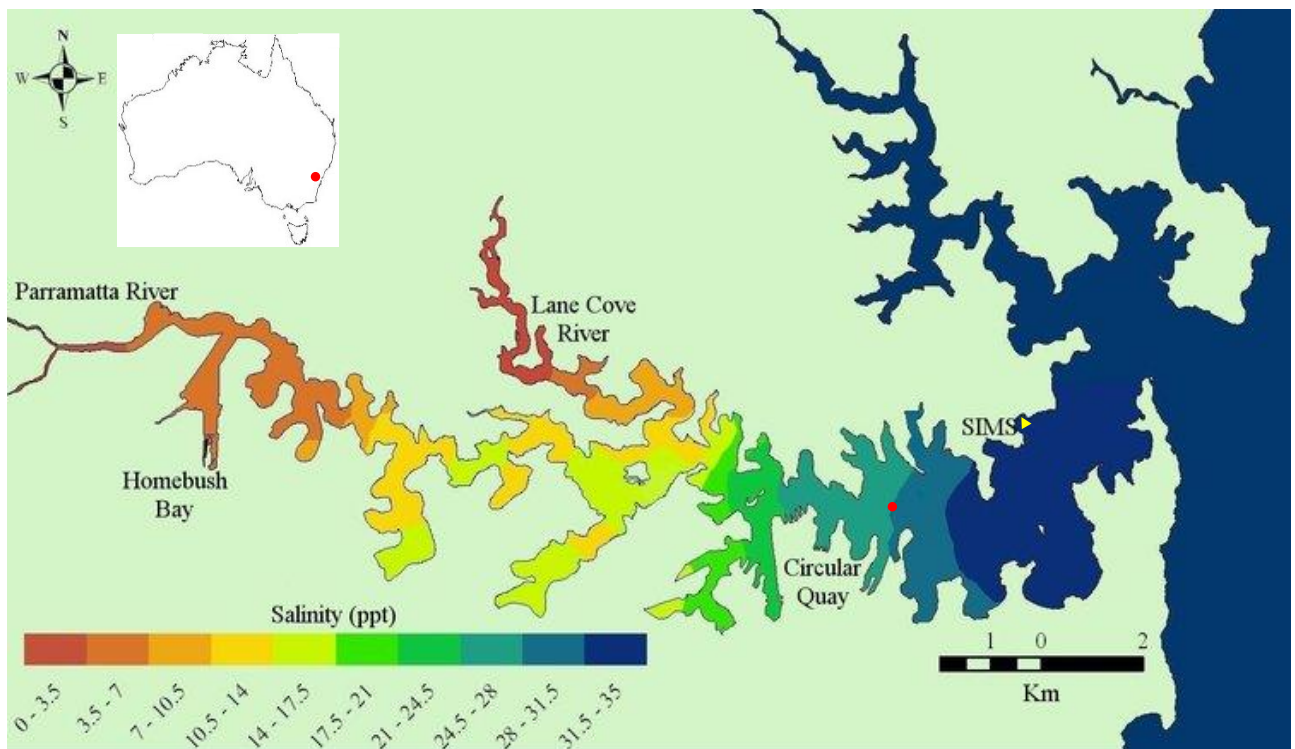


Fig 3 caption - It would be useful to specify in the caption that the red arrow show light conveyed to the spot is indicated by the red arrow, and light emitted from the spot is indicated by the blue arrows. Eg The insert shows light conveyed through the transparent vessel wall to the spot (red arrow)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