

Interactive comment on “Continuous fluorescence-based monitoring of seawater pH in a temperate estuary” by John W. Runcie et al.

Anonymous Referee #1

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General Comments

This manuscript describes the development and testing of a sensor for monitoring seawater pH, suitable for coastal and estuarine locations, and potentially deployable at depth. A relatively low cost, sensor that is simple to deploy and accurate and precise enough to detect changes on diurnal time scales has many potential applications. However, such a sensor needs to be very well characterised and its reliability assessed under a variety of conditions.

The sensor described in this paper potentially meets these criteria, however this is difficult to assess because not enough information is given. The presentation at The Oceans in a High CO₂ World conference was good in that context, however more detail and more validation is required in a journal paper.

C1

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

Specific comments

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

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.)

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 48 – specify 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.

Line 55 – repetitive wording needs editing.

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

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

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

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pH.

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 °C (line 89), or did you measure the temperature?

Line 199 - 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 101 - specify the actions taken to minimise gas exchange during sampling.

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

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

Line 110 - how were the corrections applied – an average offset, a drift, or some other method?

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

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

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

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

Line 146 - Use the symbol °C not the word degrees.

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

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

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be expected?

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

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 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.

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

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