Comment on os-2021-126
Anonymous Referee #2

Referee comment on "Technical Note: Calibration-Free pH Sensing of Ocean and Estuarine Waters" by Monica Miranda Mugica et al., Ocean Sci. Discuss., https://doi.org/10.5194/os-2021-126-RC2, 2022

This manuscript is badly organized with a lot of important information left out. There are a lot of issues with the experiment, and the results do not support the author’s points at all. This manuscript should be rejected. The authors need to re-design and re-do all the experiments, and follow the instructions of Ocean Science journal to re-write the manuscript in the correction structure (Introduction, Experimental, Results and Discussion, Conclusion).

- The background info about the importance of pH in the ocean (line 1 – line 48) seems to be a bit tedious, which needs to be consolidated.
- In the introduction section, it’d be very useful to list the accuracy requirements of each application (e.g. ocean acidification research, routine water monitoring, aquarium management, and aquaculture).
- The author should mentioned that the state-of-the-art lab method for seawater pH measurement is the indicator dye-based spectrophotometric method. A table of the accuracy and precision of each method (i.e. lab based spectrophotometric method, spectrophotometry-based sensors, potentiometry-based sensors, and the solid state sensor) would be very useful here.
- The author should write about the chemistry behind the solid state pH sensor either in the ‘Introduction’ section, which is important for a technic note like this.
- Some contents of the ‘Technology’ section belongs to the ‘Introduction’, and the rest should be moved to the ‘Result and Discussion’.
- Line 91 – Line 92: Do you mean the ‘peak height’ changes for reference tracker electrode?
- The titles of Figure 2 need to be consistent with the figure caption ( ‘(a) pH sensing electrode’, ‘(b) reference tracking electrode’).
- Figure 3(a): Need to add parameter name and unit for Y-axis.
- How is experiment done for Figure 3? What pH buffer solution was used? Was it a fresh water buffer or seawater buffer? How was the temperature controlled? What was the temperature?
- Need to use a smaller Y-range in Figure 3b. I don’t know how the experiments was
done, but such pH variation is actually too big for most ocean acidification research.

- Line 120: You need to use pH buffer solution for such experiment. Such as tris-buffer in synthetic seawater. How is the temperature controlled?
- Line 124: It is wrong to use a glass electrode as the gold-standard for such experiment, since the glass electrode itself could be drifting. You need to use the state-of-the-art lab-based spectrophotometric method for the validation. And the validation measurements need to be taken throughout the whole period.
- Figure 4: Use time rather than measurements as the X-axis
- If the temperature and the pH of the testing solution were stable, the result in Figure 4 shows: (1) there are really big and non-consistent differences between the two solid state sensors; and (2) for an individual sensor the readings were not stable at all. And the conclusion will be this solid-state sensor is really bad and not suitable for ocean acidification research.
- The ‘Experimental’ section should be right behind the ‘Introduction’ Section.
- Some contents of the ‘Demonstration of deployments’ should be in the ‘Experimental’ section, and the rest should be part of ‘Result and Discussion’ section.
- Section 3.1 and 4.1: Again, it is wrong to use a glass electrode as the gold-standard for such experiment, since the glass electrode itself could be drifting. You need to use the state-of-the-art lab-based spectrophotometric method for the validation.
- Figure 5 is unnecessary.
- Texts in Figure 6 are very blurry.
- Section 4.1: What is the point to change sensors during the long-term experiment? It’d be better to use all three sensors for the entire experiment period so that both accuracy and the reproducibility of different sensors can be evaluated.
- Figure 7: It would be more useful to plot the sensor values against the pH measured by standard method, do a linear regression and give the statistics (e.g. slope, intersect, r square, and RMSE).
- Section 4.2: It is wrong to use a glass electrode as the gold-standard for such experiment, since the glass electrode itself could be drifting. You need to use the state-of-the-art lab-based spectrophotometric method for the validation.
- Figure 8: only one validation point is far from enough. Validation measurements need to be taken throughout the entire period.
- Figure 9: This figure doesn’t mean anything. First of all, there is no validation and we don’t know if the solid state sensor or the glass electrode are correct. Secondly, ‘more stable’ doesn’t mean it is correct. In contrast, it could mean it is not sensitive enough.
- Section 5: The experiments don’t support the author’s claims at all. Based on the data presented in this manuscript, it seems that this sensor is not suitable for ocean acidification research.