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Ocean Science Discussions

Interactive comment on "Measuring pH variability using an experimental sensor on an underwater glider" *by* Michael P. Hemming et al.

Anonymous Referee #3

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This manuscript describes the deployment of an ISFET-pH sensor on a glider in the Mediterranean as part of the REP14-MED experiment. Shipboard carbonate measurements of dissolved inorganic carbon and total alkalinity were used to evaluate the sensor performance. The authors suggested a number of corrections to the ISFET data to make it fit with the shipboard measurements.

One of the major concerns I have with this paper, is that the author's main aim appears to be to reduce the variability of the glider samples to match the significantly lower resolution CTD samples. The much higher temporal resolution and greater sampling area of the glider will give greater variability in the pHg compared to the pHCTD. Therefore, I am concerned that the authors may be misguided in their application of corrections – perhaps the difference in resolution could be commented on and the corrections discussed further, or the data presented in such a way that the pHCTD measurements

are used as a guide rather than an elimination benchmark. This is discussed briefly in section 3.5 of Bresnahan et al., 2014. I understand that this correction of the sensor is based on the similarity of observed temperature and salinity measurements between CTD and glider – however, measurement techniques for these parameters are well established, with similar accuracy levels, and care should be taken when using the same standards for the ISFET pH sensor and pH calculated from bottled sampels.

The difference in variability could also be addressed with more information in the introduction on expected regional pH variability as seen from previous work in the Mediterranean (as briefly mentioned on page 5 line 14). This would demonstrate that temporal variability over the length of the deployment is minimal. Therefore, the procedures in the manuscript – correcting the data using 16 of the glider profiles, along with the pH of the bottled reference samples collected before the ISFET deployment time are valid for quality controlling the sensor.

Overall, I think this paper should be published with minor corrections. The manuscript gives an indication of the challenges when field testing new sensor technology, and is one of the first demonstrations of pH measurements a mobile platform.

Specific Points: P3 Section 2.2: More information on the ISFET-sensor used would be useful – specifically the calibration. It would also be interesting to know what the authors mean by poor quality –was this caused by integration into the glider electronics, or did the sensors malfunction? A brief sentence on this would also be useful – given that the paper is based around discussing challenges when field-testing sensors. The authors specify that they used a Cl-ISE. How long was this conditioned for? Previous studies (Bresnahan et al., 2014, Takeshita et al., 2014) both recommended conditioning in seawater levels of bromide ions before deployment to prevent reference electrode drifts.

What was the ionic strength of the two buffers used on deck to calibrate the ISFET? You also specify the pH of these solutions to a 4 decimal point (5 sig. figs). This is

very accurate for a pH sensor – particularly when the accuracy of the pH sensor you deploy is only 0.005. What pH system did you use to get this accurate buffer pH to calibrate your solutions? Was the deployed ISFET-measured pH of the buffer solutions the same before and after (i.e. was there any drift?)? Were the same solutions used – was there any drift in the solutions? Was there any noticeable biofouling on the ISFET sensor during the deployment?

Was there any lab-based temperature calibration done prior to deployment? Bresnahan et al., 2014 discuss a temperature error of <0.015 in their calibration of the sensors – this is greater than the specified accuracy of the deployed ISFET sensors. You mention the air temperature when calibrating with the buffer solutions, a measurement of the temperature of the buffer solutions would also be useful, particularly as you later correct for temperature dependence of the sensor. This is important, as the temperature of the solution may change the buffer pH (particularly when using such accurate pH figures) between the pre-deployment measurement and post-deployment measurement.

Finally, you provide a reference to Fukuba et al., 2008. This particular ISFET sensor does not have details of correction using buffers before and after deployment, but rather buffer solutions deployed with the sensor itself, allowing for in situ referencing. This is not the same procedure as the sentence is suggesting, nor does it provide an example of the converting the raw output to pH. Unless the ISFET sensor deployed had a similar "self-calibration" system, I would suggest removing this reference.

P4 Line 18: the difference in the DIC and the TA quoted from replicate samples – is this calculated from the standard deviation for each replicate? You state, in the previous sentence, there were two to three replicates collected per CTD cast – If this is not the standard deviation, how was this difference calculated between the three samples.

P4 Line 20: Please also state the borate-chlorinity ratio and the sulphate constants that were applied when using CO2SYS- with appropriate references. I realise these

may be quoted in the best practices section in the paper by Orr et al (2015), however it would be best if they were also specified here for clear understanding.

P4 Line 32: I find the range of standard deviations quoted throughout the manuscript to be confusing. For each specified bin (top 150m and below 150m) there is range of standard deviations quoted instead of one number for each bin. Is the standard deviation not calculated over the whole 150m? Is it further subdivided into smaller bins, and in which case what size are these bins and how many are there? I feel this should be clarified at the start of this section as the ranges are applied throughout the remainder of the manuscript. I assume these bins are the same as those specified in the caption for figure 5, but should be mentioned in the text for clarity.

P5 Line3: The authors refer to environmental variability when referring to the range of pH observed. This is not further discussed - What is the expected natural variability for the region? How much extra variability was observed and can be attributed to instrumental error? I realise that this is mentioned briefly in line 12, however numbers specifying the expected pH range and variability would be useful for those of us with little knowledge of the region. Furthermore, the instrumental error is not discussed in section 2.3. I think the authors meant sections 3.2 and 3.3.

P5 Line 22: Please specify if the same subtraction was performed on the salinity, dissolved oxygen and potential temperature.

P6 Line5: Does the ISFET have a constant offset caused by light? Or an offset changing with irradiance time/strength? Could you give some indication of the size of the offset based on your experiments.

P6 Line 28: I find it confusing when you discuss a constant depth –time varying offset, and then subsequently refer to, what I assume is the same correction, as a constant offset. It is not a constant offset as it varies with time. It also presumably varies with depth, as the correction was determined from the depth where the potential temperature was 14°C.

P7 Line 9: It would be good if the authors could specify the slope and the intercept of the linear regression in the text. This will allow better comparison with other studies.

P7 Line 27: The authors say poor-accuracy, is this relative to previous deployment? How did they determine the accuracy if the paper is based around correcting the pH sensor to the bottle samples? The best accuracy quotable for the sensor is that related to the reference samples.

P8 Line 7: Remove “there being”

Conclusions: The conclusion could be improved by summarising the findings of the paper including the biogeochemical variability (similar to the abstract). The authors also specify that the corrections they performed are not generally recommended or valid. A brief discussion of why these corrections are valid in this study, and under what other conditions they may not be valid would be good for future work by other studies.

Figures: (in general) seem to have a grey line around the edges. This is particularly on figure 8 where it looks like another figure was cropped out.

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