

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

Anonymous Referee #2

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The manuscript by Hemming et al. describes a deployment of a seaglider in the Mediterranean Sea equipped with an experimental pH sensor. The performance of this pH sensor is evaluated against shipboard carbonate system parameter measurements of A_T and DIC and the authors suggest a number of corrections to make their data fit their expectations. This is an instructive example of the challenges of implementing and field testing new sensor technology and represents one of the first reports on pH measurements from gliders.

I have some general comments:

The presentation of the data manipulations and suggested corrections appear very diagnostic and data-driven. At the same time, there are plausible physical causes to most of them, which the authors present, too (e.g., ambient light effect on FETs;

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temperature effect on E^*). It's likely mainly a question of style, but my preference would be to always start from the sensor knowledge to explain an observed mismatch and then suggest corrections, rather than an "our data didn't fit, so we made it fit" approach and then defending these corrections with theory after the fact.

More importantly, the goal of most (all?) the corrections seems to be to reduce the glider pH variability to the level seen in shipboard pH samples? This misses the point. Continuous, autonomous observations can very well be more variable than discrete measurements, in particular if the continuous measurement series captures time/spatial scales of variability or events that simply go undetected with coarser discrete sampling.

In that regard, the drift correction to pH(@14 °C) is a critical point that needs more detail and potentially a second look (details further below).

There is a lack of detail on the sensor used and its handling. This limits the utility and impact of the present study. Relevant information need to be added.

Specific comments:

P1L4: "Northwestern Mediterranean Sea" suggests a basin scale study and is maybe a bit a too generic description of the deployment location, i.e., a transect of just 100 km off the Sardinian coast?

Similarly, P1L14 and P1L16: "this region" is not well defined (I didn't know what it actually refers to), so I would suggest to closer specify the study region.

P2L9: Why not use ppm for the mole fraction?

P2L16: Potentially add the relevance of pH changes/anthropogenic CO₂ invasion to the study region/Northwestern Mediterranean?

P2L17: What is stochastic variability?

P3L11: Last sentence is irrelevant to the presented study.

P3 ISFET and glider sensors: What was the source of the sensor? Is it commercial/semi-commercial/custom-built? Was the ISFET unit a commercial product (Honeywell)? On what material support is it mounted (important to assess the pressure tolerance)? Is the packaging of the ISFET into a sensor a commercial/semi-commercial/custom-built one?

This is essential information to put it into context of other studies with (other) ISFET pH sensors and directly affects the impact of this study.

P3 ISFET and glider sensors: The handling of the pH sensor needs to be described in detail. Was there any temperature or pressure compensation/calibration (in particular on E^*) other than described later in the manuscript? Were salinity/ Cl^- changes taken into account (as suggested by equation 1) for the calculations? How was the ISFET and the reference electrode stored before deployment: in NaCl solution, artificial seawater, Mediterranean seawater, at what salinity, how long before deployment? ...

P3L16: "the [other] retrieved data were of very poor quality". Any ideas why?

P4L18: I don't understand the figures. "DIC and A_T differed by 3.1 and 2.5 $\mu\text{mol kg}^{-1}$, respectively" means that the second sample was always higher than the first one? I would hope that the difference between replicates would average around zero, otherwise this sounds like a serious methodological issue? I assume the authors refer either to the average absolute difference between replicates or the standard deviation between replicates?

P4 last sentence and first sentence on P5: This is unclear:

- How many casts were performed? (Should probably be mentioned in section 2.3 and/or P5L18)
- Why are there several standard deviations for a "standard deviation of the mean DIC/ A_T (averages over all casts)"?

I kind of get the idea to split it into surface (top 150 m) and deep values, but

that only gives me two values. Instead, I see two ranges of standard deviations? Looking at the figures (4d), it seems like the data were aggregated into depth bins and – likely – the ranges are the numbers for the respective depth bins shallower than 150 m and deeper?

(a) This has to be explained in the text.

(b) Depending on the size of the depth bin, the depth gradient can become an important contributor to the standard deviation. Say all glider dives are identical, the standard deviation of the top 150 m would still be much higher than the bottom 150 m because of the higher depth variability near the surface compared to depth. Same for P5L9 and other statements like this (e.g., P7)

P5L14: What about the magnitude of diel variations? Because that's essentially what is looked at here.

P6L6-9: Is there experience from other autonomous deployments (floats?) in the literature that could be used?

Section 3.3 Correcting pH for drift, temperature, and pressure: Can you give more details about your corrections (equations, magnitude/values of m and c) to make it reproducible for others? Please also comment whether the temperature and pressure slopes are comparable to other findings (in particular P6L24 and Johnson et al. 2016)?

P6L27: "unrealistic scale" is unclear. Please specify or rephrase (large range?). In addition, scale is ambiguous here since it could refer to the different pH scales (total, seawater, ...).

P6L28/P6L30/P7L4/P1L8: What is it, a time-varying or a constant offset? Please be consistent to avoid confusion (or simply remove the constant in P6L30/P7L4?).

P6L28: "depth-constant" (uniform with depth) instead of "constant-depth" (applied to the same depth level)?

P6L30: The density gradient was weak, the pH gradient, too? You don't want to have

a gradient in your variable..

Can the depth of $\theta = 14$ °C be made visible in one of the plots to get an idea of the depth range?

P6/P7 offset drift correction: How does the time evolution of the offset look like? Is it linear, exponential, or at least smooth (could be added to Figure 7)? If not, then what the authors measure is in fact not the pH but a pH anomaly relative to $\text{pH}_s(14$ °C), i.e., they remove the environmental variability of $\text{pH}_s(14$ °C) from their pH_g data.

P7L5: If you derive the temperature correction from a subset with similar temperature gradients in the surface, is it applicable for the entire deployment/dives with different temperature gradients? Temperature certainly plays a role for these dives, too, but does it follow along the same relation? A look at figure 6 suggests that the selected stations cluster on one side of the corrected profiles, i.e., there is a bias? (Which might also cause some portion of the high surface variability in $\text{pH}_{g\text{TPC}}$?)

P7L13: And excluding daytime dives?

P7L14 vs. P7L21: in situ or potential temperature??

P7L28: "to achieve a match within the pH repeatability of the discrete samples"

That's not the point of continuous vs. discrete measurements. A higher variability in continuous data can easily be real.

P7L26: Indeed. Did you try any laboratory experiments with your pH sensor to confirm a temperature dependence (and salinity- and pressure dependence, if possible)? At least the temperature aspect should be easily feasible and would add significantly to solidify the correction approach.

P7L29: Can you comment on the uncertainty of your corrections and how that might affect your data? A linear temperature correction for ISFETs seems to be well-established, pressure corrections seem to be handled differently (e.g., this work, Johnson et al. 2016)?

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P8L3: "at some locations": Imprecise, please specify (East/West/coastal/...?)

P8L5: Don't you have any data to support the DCM depth for your study? It seems like there were (at least) 12 gliders and two research vessels deployed..it should be possible to find (even an uncalibrated) Chlorophyll a fluorometer on a CTD among them..?

P8L17: "The spatial variability of these two regions differed for each time period" is unclear. Can you extend on this (what time periods; any relation of changing extend with displacement of isopycnals/water masses/SSHA)?

P8L18: "at a range of depths": Please specify. Were values similar along isopycnals E/W and the depth differences are just inclined density surfaces?

P8L23: Which time periods? (Maybe specify in section 2.1?)

P8L28: Sentence unclear to me. (Intrusion instead of encroachment?)

P8, section 3.4: This section describes the data and depth structure (first paragraph), it describes the East-West differences in the transect (second paragraph), and it discusses circulation aspects to explain mainly the physical oceanography data (third paragraph). What I think is missing in a section entitled "pH variability" is a biogeochemical discussion how to interpret the East West differences in pH. Is it related to a coastal/offshore gradient, to different preformed pH/DIC/A_T/O₂ concentrations in the respective water masses, to a gradient in nutrient supply and/or respiration (again: coastal/offshore gradient or likely water mass effect), ...? All these questions remain unanswered. (Potentially, part of the depth structure discussion of the first paragraph could be merged with this "fourth" paragraph.)

P9L4: Do you have any ideas/reason/speculation what caused the drift? The ISFET unit? E*? How could you reduce the drift in the first place or is it impossible to avoid?

P9L7-9: Again, a lab temperature study would solidify this result.

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Fig 1: A distance scale in the left figure, too, would be nice.

Fig 1: What about the ca. 15 km North/South displacement between water samples and glider path for the match of water samples to glider dives?

I might have missed it, but did you describe in your methodology how you matched glider dives to ship hydrocasts? Shortest distance? Along equal longitude? The bathymetry suggests quite some difference at the same longitude close to the coast, so that a "distance from the coast" or "equal bottom depth" might be more adequate/give a better match?

Fig 4: What about a left/right grouping of water samples (DIC, A_T , pH_s ; left top to bottom) and CTD/GLIDER data (θ , S , pH_g ; right top to bottom)? This would avoid confusion about the legend next to 4c. Also, the legends could be placed inside the subpanels to gain some space (in particular to better see the subsurface maximum in pH_s)?

Fig 5: Maybe rename the y axis labels of panels b-e and the variables in the figure caption by ΔX instead of X to emphasize the anomaly?

Fig 6: "offset drift correction" and 40 m?

(Fig 7: Make consistent with in situ / potential temperature of the correction description.)

Fig 8 and 9: Why did you split the plots into two figures? In my view, they would be more sensible as one (pH data together with its context). If space is a concern, you could think about removing the x axis labels and ticklabels for the upper panels since they are identical (as you did for the y axis labels and ticklabels for the center and right panels).

Minor: I would also appreciate a distinction between "the sensor"/"the ISFET sensor"/"the ISFET pH sensor" and "the ISFET". The first refers to the ISFET including the packaging (housing, electronics, ...) the authors used (i.e., their experimental sensor)

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while the second refers to the type of sensing probe (a transistor)/its working principle that can be shared by many different pH sensors but the one discussed here. It seems that in quite a few instances where "The ISFET ..." is used, it merely refers to "Our ISFET pH sensor ..." rather than to all ISFETs.

Typos:

P4L15: ...Scripps Insitution of Oceanography, USA, ...

P5L33: FET-based sensors

P7: "Tc" is sometimes italic and sometimes not

[Interactive comment on Ocean Sci. Discuss., doi:10.5194/os-2016-78, 2016.](#)

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