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Interactive comment on "Technical note: Interpreting pH changes" *by* Andrea J. Fassbender et al.

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First, I think this paper will be an excellent addition to the fields of marine pH and ocean acidification (OA) research. I wholeheartedly agree with the notion to report proton or hydrogen ion concentrations which I have encouraged this with one of my own papers and I hope this paper will stimulate further discussion among scientists and environmental managers in regard the reporting pH and proton concentrations in future OA studies undertaken across a variety of disciplines. However, I think the scope of this technical note is too narrow given it predominantly focuses on measurements collected in open ocean environments whereas reporting proton concentration and pH is just as important in nearshore estuarine and coastal and freshwater systems. Details below.

Abstract - Looks good with no further comments.

Introduction - The authors provide a good overview and summary of the chemical history of pH dating back to the work of Sorenson in the early 19th century up to present day with the development of the three concentration scales and widespread development autonomous chemical sensors capable of measuring pH while sufficiently explaining why pH is important, its use in marine carbonate chemistry and OA, and the relationship/conversion of/between pH and proton concentrations. Literature cited is sufficient.

One suggestion for improvement though is the need to address comparing trends in marine pH across programs, years, and sites that measure pH on different scales and different methods. The need to establish inter-comparability between different pH datasets is necessary before calculating proton concentrations from pH if pH were measured on different scales across years, sites, or programs because the differences between scales would lead to systematic errors in the calculated proton concentrations and its relative changes further complicating the use and interpretation of those data. The manuscript mentions that all pH data are reported on the total scale. Notwithstanding, a couple of sentences explaining this may help scientists and environmental managers with little prior knowledge of the chemical history of pH and pH metrology as I think this type of work holds potential utility for folks working in regulatory environments that do not necessarily have their a finger on the pulse of this particular field.

Discussion

This bulk of this section is conservatively a follow-up to Fassbender et al. (2017) (Lines 281-282) which lays the groundwork for the real-world examples that illustrate why report proton concentrations alongside pH can improve the clarity of studies that aim to evaluate changes in ocean chemistry.

The above mentioned paper explains the need to evaluate non-significant long-term decreasing trends in marine pH measured by ocean time-series programs against the same trends in proton concentrations which are likely to be better metrics given different starting/initial pH values in those systems. I think this section can easily expanded to include a paragraph or two that covers the same dynamic but for nearshore estuarine and coastal systems that experience a range of processes that modulate changes in pH, acidification/basification, and marine carbonate chemistry. Carstensen et al. (2019) pulled pH from 83 coastal ecosystems and calculated annual rates of change in pH between -0.23 and +0.23 pH/year which are consistently an order of magnitude greater than those of ocean time-series programs estimated by Bates et al. (2014) (Lines 194-196). I would recommend the authors draw a small subsample of data presented in that paper to illustrate why reporting proton concentrations and pH can hold just as much if not more utility in nearshore systems given how much larger rates of pH change are there, the inherent variability of background pH conditions and the number, timescale, frequency, and type of processes that impact pH in these systems. Alternatively, data from a paper like Lowe et al. (2019) may work as well since it pulled data from 83 sites in Puget Sound and Washington State's Coastal Estuaries (both in the USA) that experienced a broad spectrum of pH trends over time also greater than what absorption of anthropogenic CO2 alone can explain.

The second example is sufficiently explained but I would recommend that the authors that state that marine organisms respond to proton concentrations or acidity rather pH ti drive their point home (use refs for this cited in Fassbender et al. (2017)).

The third example examining changes across depth is also critically needed moving forward. I would further postulate that the change in proton concentration with depth or proton concentration depth gradients could provide a valuable complement to changes of saturation state with depth/depth gradients as well.

For a fourth example, I would strongly recommend at least including a paragraph on the use a proton concentrations as a means to view acidification in nearshore estuarine and coastal systems through the lens of proton cycling and proton fluxes both within individual systems and across/between interconnected systems. Just as CO2 can out-

gas in transit between the head of a large estuary like Delaware Bay and the Atlantic Ocean, protons are produced and consumed by the range of processes that modulate acidification like dilution by freshwater, photosynthesis, and respiration and in transit as well. It is the net result of these proton consuming- and producing-processes (i.e., proton cycling) that ultimately results in acidification or basification in nearshore estuarine and coastal systems. I understand this is a relatively new application and method for OA studies but it is a simple and straightforward forward one. I have attached a paper (Pettay et. al (2020)) outlining the proof of concept for this application that was done using data from the Murderkill Estuary-Delaware Bay System in Delaware, USA. Essentially, once you convert pH into a proton concentration it can be used and treated just as any other dissolved constituent in aquatic systems (e.g., DIC or TA) would be and from this work we conclude that the Murderkill Estuary is acting as a proton sink and sequestering protons from Delaware Bay on monthly and seasonal timescales and locally buffers portions of the Bay. Such dynamics may apply more broadly in Delaware Bay and other systems around world.

Since this applications requires additional environmental data and work beyond the simple calculations outlined in equations 3 and 4 in the manuscript, it may lie beyond the scope and intended purpose of this manuscript. Two follow-up analyses/papers are currently in prep that - (1) Look at multiple years of proton flux data in the same systems to examine annual and interannual trends in the proton source-sink dynamics and (2) Linking trends in proton concentrations and fluxes to other marine carbonate system parameters and nutrients to examine interactions between acidification and eutrophication in the same system. Works remain in progress but the initial results are promising. I definitely think will turn into a useful application of proton concentrations for nearshore OA studies but may lie beyond the scope of this manuscript and detract from the main points this manuscript already makes.

Conclusions - Sufficient for the information/discussion provided in the first draft of the manuscript. Please modify accordingly if needed if any of the suggested additions/revisions are incorporated into the final version.

References (not already included in the manuscript) -

Carstensen, J., & Duarte, C. M. (2019). Drivers of pH variability in coastal ecosystems. Environmental science & technology, 53(8), 4020-4029.

Lowe, A. T., Bos, J., & Ruesink, J. (2019). Ecosystem metabolism drives pH variability and modulates long-term ocean acidification in the Northeast Pacific coastal ocean. Scientific reports, 9(1), 1-11.

Pettay, D. T., Gonski, S. F., Cai, W. J., Sommerfield, C. K., & Ullman, W. J. (2020). The ebb and flow of protons: A novel approach for the assessment of estuarine and coastal acidification. Estuarine, Coastal and Shelf Science, 236, 106627. (also attached)

Please also note the supplement to this comment:
https://bg.copernicus.org/preprints/bg-2020-348/bg-2020-348-SC1-supplement.pdf

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