

Comment on os-2020-120

Anonymous Referee #2

Referee comment on "Technical note: Stability of tris pH buffer in artificial seawater stored in bags" by Wiley H. Wolfe et al., Ocean Sci. Discuss.,
<https://doi.org/10.5194/os-2020-120-RC2>, 2021

Oceanic pH is affected globally by climate change and on smaller scales by a range of physical, chemical and biological processes. Quantifying and understanding these changes is dependent on an effective quality assurance system for oceanic pH measurements. This manuscript contributes to this development by assessing the stability of bagged pH buffers deployed in seawater: use of these bagged buffers provides the ability to include reference standards in pH measurement campaigns in situ. I recommend that the authors address the following points before publication:

- Line 33: the "climate" and "weather" uncertainty levels are the wrong way round.
- Lines 104-120: set the definitions of Tests 1, 2 and 3 in separate subparagraphs
- Line 139: state the sources of the impure and pure dyes
- Line 216: reference to an "ad hoc speciation model" is unacceptably vague: if a speciation model is to be used then full details should be given. In this case I advise strongly against using a model since even at the standard physical chemistry temperature of 25°C we lack an adequate model of Tris chemistry in seawater. The correlation shown in Figure 3 is good evidence that CO₂ is the culprit: modelling Tris buffer chemistry does not provide additional evidence given the uncertainties in the available models.
- The authors conclude that bag storage has been shown to be adequate, and do not propose any further development. I consider this conclusion to be premature for two reasons. First, the commercial bag that was tested delaminated when stored in seawater, so that the only bag shown to perform adequately in seawater was Bag 1, which appears to have been made in the authors' laboratory. If the use of bagged buffers is to become routine for in situ pH measurements, then bags that meet the drift specifications need to be commercially available: I consider that this point should be made in the conclusions. Second, the authors conclude that two factors may contribute to the observed decline in buffer pH: leakage of CO₂ into the bag; and production of CO₂ by respiration. In order to optimise bag design and the cleaning and filling procedure, experiments should be undertaken to identify the major cause of CO₂. This should also be stated in the conclusions.