

Ocean Sci. Discuss., author comment AC2
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Reply on RC2

Wiley H. Wolfe et al.

Author comment on "Technical note: Stability of tris pH buffer in artificial seawater stored in bags" by Wiley H. Wolfe et al., Ocean Sci. Discuss.,
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We thank the reviewer for their helpful comments and suggestions. We reply to each specific comment (reviewer comments in plain text) below (our response in italics). We also attach the response document as a PDF.

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.
Fixed.

Lines 104-120: set the definitions of Tests 1, 2 and 3 in separate subparagraphs
The information in these paragraphs was cut down as per the suggestion by another reviewer to avoid duplication between the text in Table 1.

Line 139: state the sources of the impure and pure dyes
The source or purified dy as been added to Line 138:

"impure dye (pHimpure; from Aldrich, lot MKBH6858V) and purified dye (pHpure; from Robert Byrne's Lab, University of South Florida)"

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 acid-base model description has been expanded to provide more information.

"To assess if the change in pH was driven by the addition of CO₂, the final pH and available CT measurements were compared with a model described here. The theoretical change in tris-artificial seawater (ASW) pH due to an increase in CT is straightforward to

calculate, since both tris and CO₂ acid-base equilibria are well-characterized in seawater and ASW media. The pH is calculated for tris-ASW + CT using an equilibrium model following the approach described in Chapter 2 of Dickson et al. (2007) for the case of known alkalinity and CT. In the case of ASW, the seawater equilibrium constants for CO₂ are appropriate because minor ions present in seawater and not ASW do not appreciably affect the CO₂ equilibrium constants (particularly when the goal is to compute relative changes in pH) as the ionic background of ASW is closely matched to that of seawater at salinity = 35. In our model, minor acid-base species important to seawater alkalinity but not present in ASW (borate, phosphate, silicate, fluoride) are set to zero. The definition of total alkalinity is modified to include the tris acid-base system following the definition of acid-base donor/acceptor criteria given by Dickson (1981): tris is assigned as a level-1 proton acceptor and tris-H⁺ is at the zero level. Thus, in our model, tristot = 0.08 molal and alkalinity = 0.04 molal and CT is a variable. An algorithm (see Annexe 1 in Dickson et al. (2007)) is then used to find the root of the alkalinity equation in its residual form by solving for pH."

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.

To address the reviewer's comment, the following sentences have been added to the conclusions.

"While valuable at the current stage of development (as demonstrated by, e.g., Lai et al. (2018) and Bresnahan et al. (2021)), further development would ideally result in a commercially available bag and filling procedure that can yield a rate of pH change less than the climate threshold of 0.003 per year. This will require further tests to identify the source of CO₂, gas exchange or microbial respiration, as well as steps to reduce or eliminate these sources."

Please also note the supplement to this comment:

<https://os.copernicus.org/preprints/os-2020-120/os-2020-120-AC2-supplement.pdf>