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Interactive comment on "Technical Note: Maximising accuracy and minimising cost of a potentiometrically regulated ocean acidification simulation system" *by* C. D. MacLeod et al.

C. D. MacLeod et al.

colin.macleod@postgrad.otago.ac.nz

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For all changes to this manuscript, please refer to the supplemental document

Comments:

1) This is a useful manuscript which I would recommend publishing after some further editing. It shows that it is practical to maintain an ocean acidification simulation system within ±0.05 pH units of a target value, even when using relatively economical pH measuring and control systems, provided that the pH electrodes used are tested to ensure that they exhibit an approximately Nernstian response, and as long as care is taken to adjust for electrode calibration drift on a regular basis. Nevertheless, I feel

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that the current version is not as carefully written as it could be; it seemed somewhat disorganized and repetitive to me.

Authors' response: we agree that the structure of the article should be reviewed.

Authors' proposed change: the order of sections 2.2.2 and 2.2.3 have been reversed to improve the logical flow of the description of the system. Two redundant descriptions of the TUNZE apparatus have been removed. Small changes have been made throughout the manuscript to improve its readability.

2) The key initial point is to explicitly recognize that adequate control of CO2 chemistry in seawater media requires that one control as many variables as would be needed to fully describe the CO2 chemistry.

Authors' response: we agree that this point should be made more clearly.

Authors' proposed change: this point has been added to the section that reviews OA simulation systems on page 5, lines 1-10.

3) In the case of the system described here, pH and T are actively controlled, while S and AT are more passively controlled by the choice of water replacement rate. This is never stated clearly, and indeed it is not until the discussion that the importance of water replacement rate is clearly acknowledged.

Authors' response: we agree that the passive control of salinity and alkalinity should be discussed earlier in the article.

Authors' proposed change: passive control of salinity and alkalinity are now described on page 7, lines 4-6.

See also page 7, lines 29-32 for details of seawater replacement rate.

4) Indeed, there are real advantages in controlling pH rather than p(CO2) as there is less sensitivity to temperature fluctuations.

Authors' response: we believe that this point was made on page 7, lines 1-4.

Authors' proposed change: The section describing the benefits of pH control has been rewritten to more clearly state the advantages of this approach. See page 6, lines 28-31 and page 7, lines 1-4.

5) I also feel that the authors should explicitly discuss what they feel would be adequate tolerances for these parameters, given the goal of achieving an ocean acidification simulation system. The only tolerance that is even explicitly mentioned is ±0.05 in pH, and – as far as I can – the justification for this seems to be that it can be met. I feel it would be useful to look at the sensitivity to changes in the other parameters and point out that they are indeed adequately controlled in this system. (For this too, the discussion of AT control comes too late, I believe.)

Authors' response: we agree with the reviewer that the reasons for choosing 0.05 pH should be expanded upon, and that we should look at sensitivity of pH to changes in other parameters.

Authors' proposed change: we have inserted some discussion of these points, both in the context of what tolerance is realistically achievable for the majority of OA researchers, and with a view to standardising tolerances of potentiometric systems. See page 3, lines 19-26.

A section discussing the regulation and reporting of temperature, salinity and AT, has been added to the manuscript. See page 6, lines 3-21 and page 12, lines 18-21.

A table has also been added to the manuscript that illustrates the sensitivity of calculated carbonate parameters to offsets in temperature, salinity, and AT (Table 3, page 23).

6) Finally, I feel uneasy with the use of the word "accuracy"; pH measurements are seldom "accurate", insofar as they accurately provide values for the parameter that is specified – –log a(H+) – or even a hydrogen ion concentration.

Authors' response: we agree that the term 'accuracy' should be used more carefully.

Authors' proposed change: the term 'accuracy' has been replaced throughout the manuscript with 'tolerance' (with a definition given on page 3, line 22) or other, more appropriate, terms.

7) The calibration buffers used here (Tris and AMP) are assigned pH values using spectrophotometry (using "pure" metacresol purple which is, as yet, not widely available together with the calibration of Liu et al.); however, no comment is made as to the possible uncertainties in this approach except to note that the buffers are not fully matched to the seawater being used. The discrepancy between the pH measured directly in the test seawater, and that calculated from measurements of AT and C T is about –0.04 at all 3 pH values, yet this is not discussed as a possible indication of overall uncertainty but rather as an indication that the estimate ±0.05 is correct. I recommend the authors rethink how they discuss this so as to make clear the primary sources of uncertainty and their implications, for other parameters such as saturation index, etc. (For example, the uncertainty in S, T, or AT.)

Authors' response: we agree that the issue of uncertainties inherent in all techniques should be appropriately discussed.

Authors' proposed change: we have added a section directly discussing sources of uncertainty in all measured parameters. See page 10, lines 12-25. See also Table 3, page 23.

Other comments:

8) The introduction seems poorly put together. As the level of CO 2 in the atmosphere continues to rise, the canonical values of 0.1 and 30% (a mismatched pair) get more and more outdated.

Authors' response: we agree that the general description of changes to atmospheric CO2 and oceanic pH should be updated based on the IPCC 2014 report.

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Authors' proposed change: the introductory section has been changed to incorporate more recent data. See page 2, lines 2-5.

9) The equations R2, R3 don't balance chemically (they don't need the H_2O); also, strictly, the process of acidification involves the excess hydrogen ion generated by carbonic acid dissociation going on to react with carbonate ion: it would be clearer for the reader if this was pointed out.

Authors' response: the authors agree with the suggestions regarding equations R2 and R3.

Authors' proposed change: H2O has been removed from equations R2 an R3, balancing them chemically. An additional equation (R4) has been added to show the reaction of carbonate ions and excess hydrogen ions. See page 2, lines 12-15.

10) Finally the discussions of future predictions are also somewhat dated (c.f. the recent AR5 reports), but my larger criticism is that it is not clear just what the postulated decreases in pH by 2100 (or 2300) are to be compared to: is it the current pH, or that at the start of the industrial revolution?

Authors' response: we agree with the reviewer's comments.

Authors' proposed change: this section has been replaced with references to the IPCC 2014 report and future changes to oceanic pH have been re-worded. See page 2, lines 2-4.

11) The discussion of carbonate chemistry too is not particularly rigorous: the statement that only 2 parameters need to be measured is an over-simplification. Of course one needs S, T, and (if alkalinity is used) information about other acid-base systems in addition to CO_2.

Authors' response: we agree with the reviewer's comments.

Authors' proposed change: the reviewer's comments have been incorporated into the description of carbonate chemistry on page 4, line 4 and page 5, lines1-5.

12) The AIRICA DIC analyzer is made by MARIANDA (not MIRIANDA)

Authors' response: we agree.

Authors' proposed change: The correction has been made on page 9, line 16.

13) Practical salinity does not have "units" (strictly it has unit 1) and "PSU" is meaningless.

Authors' response: we agree with the reviewer.

Authors' proposed change: the practical salinity scale has been described at the beginning of the manuscript, and no units for salinity have been used in the text.

14) I feel there should be some discussion as to why the salinity appears to have a significantly larger relative variability (~2%) than the alkalinity does (<0.5%). This seems odd.

Authors' response: we agree that this discrepancy should be discussed.

Authors' proposed change: this discrepancy is discussed on page 10, lines 5-8.

15) Despite these many criticisms, I do believe that this is potentially a valuable paper. But it needs significant editing to improve its readability and to address the points I note here. (I am not sure whether to refer to these as minor or major revisions; I feel the manuscript will benefit from substantial rewriting, but will not materially change its main points.)

Authors' response: we agree with the reviewer.

Authors' proposed change: we feel the manuscript has been improved by the editing suggested by the reviewer.

Please also note the supplement to this comment:

http://www.biogeosciences-discuss.net/11/C6070/2014/bgd-11-C6070-2014-supplement.pdf

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