

Technical Note: Maximizing accuracy and minimizing cost of a potentiometrically regulated ocean acidification simulation system

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Comments:

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

The key initial point is to explicitly recognize that adequate control of CO_2 chemistry in seawater media requires that one control as many variables as would be needed to fully describe the CO_2 chemistry. In the case of the system described here, pH and T are actively controlled, while S and A_T 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. Indeed, there are real advantages in controlling pH rather than $p(\text{CO}_2)$ as there is less sensitivity to temperature fluctuations.

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 A_T control comes too late, I believe.)

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 – $-\log a(\text{H}^+)$ – or even a hydrogen ion concentration. The calibration buffers used here (Tris and AMP) are assigned pH values using spectrophotometry (using “pure” *meta*-cresol 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 A_T 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 A_T .)

Other comments

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. 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. 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?

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 .

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

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

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

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.)