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Discussions

Interactive comment on “On CO_2 pertubation experiments: over-determination of carbonate chemistry reveals inconsistencies” *by* C. J. M. Hoppe et al.

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Hoppe and co-authors describe a laboratory study where they “over-determine” the inorganic carbon system in nutrient and vitamin enriched North Sea water. They conclude that calculating pCO2 of seawater using TA and TCO2 significantly underestimates the pCO2 compared to the measured values while using pH yields much better agreement. They therefore recommend using pH and either TCO2 or TA in manipulation experiments done to study the impacts of ocean acidification. The authors point out that their effort is geared to providing information for groups performing perturbation studies that often are not fully conversant in the details of inorganic carbon speciation in seawater. However, this study confuses the issues at hand and their discrepancies are an order of magnitude greater then observed in previous studies suggesting issues with measurements or interpretation.

Prof. Dickson describes several of the shortcomings in the experimental approach in his review. The magnitude of the deviation is inconsistent with many of the studies performed before raising questions of experimental execution. It is troubling that while the community accepted standard protocols are referenced, the “best practices guides” of Dickson et al. 2010; Dickson et al. 2007) the recommendations are not strictly followed in this work. Rather then duplicating the remarks of Prof. Dickson I’ll provide some general remarks on protocols and interpretation.

Protocols: 1. Reference materials should not be [exclusively] used as a means of calibration. On page 1711 it is mentioned that the CRM’s are used to correct inaccuracies of the measurements. Provide the magnitude of the corrections 2. As described in Dickson et al. 2010 the programs to determine carbon speciation (CO2SYS etc.) should be used with caution with manipulated seawater as is used here 3. I am suspicious of the accuracy of the pCO2 aqueous measurements by MIMS. The calibration with bicarbonate is very difficult to do right. The amounts of bicarbonate needed are minute to fall in the range of the CO2 and weighing or contamination of the (dry) bicarbonate is difficult. 4. pH and pCO2 measurements are dependent on temperature. Temperature should be listed in the tables and captions 5. At high pCO2 levels the CO2aq becomes a more significant part of the TCO2. Loss of CO2 during analysis can become an issue

Interpretation: The conclusion that pH (with either DIC and TA) is a better predictor of pCO2 follows from the fact that pH and pCO2 are not “orthogonal”. That is the parameters are very similar. Indeed several of the pCO2 sensors (CARIOCA, SAMI, MICA etc.) are based on pH measurement. The correlation of pH and pCO2 are not too sensitive to variations in TCO2 and TA such that the results, combining with possible inaccuracies of TCO2 and TA measurement are not surprising.

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While we loosely speak of 4 inorganic carbon system parameters, TA and pH are indicative of other acid/base species in addition to inorganic carbon. I suspect that manipulation of the seawater and/or biological productivity changed the speciation which is not properly captured with the computer programs. In particular, the authors should determine if the non-carbonate contributions to TA are different than natural seawater and how this impact the carbon alkalinity (CA), which is the actual carbon system parameter needed in the calculation.

As pointed out in Prof. Dickson's review, while the offset in calculated pCO2 (fig 2 & 3) increases with pCO2, the ratio [pCO2 meas/pCO2 calc, or pCO2(TA, DIC)/pCO2(TA, pH)] looks pretty constant. This could be caused by a constant bias in measurement of one of the parameters (likely TA or DIC) or the dissociation constant used.

The authors point out that errors as presented can have a significant impact on the estimates of saturation states and in the introduction they mention the importance of the carbonate ion (CO3-) as the key species for these calculations. The sensitivity of carbonate parameter to different parameter combinations is different then that for pCO2. In particular TA and TCO2 are good parameters to estimate CO3– in that CA-TCO2 $\approx$ CO3– (at low pCO2).

It is unclear why the authors do not recommend measuring the pCO2 as the key parameter along with DIC or TA rather then focusing only on pH.

Interactive comment on Biogeosciences Discuss., 7, 1707, 2010.

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