Biogeosciences Discuss., 7, C1286–C1293, 2010
www.biogeosciences-discuss.net/7/C1286/2010/

Biogeosciences
Discussions

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

A. Dickson (Referee)

adickson@ucsd.edu

Received and published: 8 June 2010

CONCLUSION This manuscript should not be published in its present form, there are too many ways in which the quality of the experiment is unclear, particularly given the potential significance were the reported observations to be correct.

SO WHAT'S WRONG WITH THIS PAPER? First, this paper makes a very significant claim. It states that, for the seawater compositions they studied, the p(CO2) values calculated from measurements of total alkalinity and total dissolved inorganic carbon measurements are about 25% smaller than those calculated from measurements of pH used with either the measurement of total alkalinity or that of total dissolved inorganic carbon. Furthermore direct measurements of [CO2] are in broad agreement with the higher values.

This claim is not compatible with previous work in this area (see e.g., Lueker et al., 2000 and Millero et al., 2002), which also found an unexplained discrepancy of similar sign but of one fifth of the magnitude suggested here, and then only at high p(CO2) values. Which should we trust? Or are these sufficiently different experiments that it is reasonable to expect that compatibility with previous work should not be expected?

The authors make the statement: "As the experimental setup and data quality of these studies differ from those of the ocean acidification community, implications of the inconsistencies described above are currently unknown." This is – I feel – misleading. It is true that the data quality of the work described here is far worse than in the work reported by Lueker et al. and Millero et al. Nevertheless, at the very least the work of Lueker et al., based on addition of CO2, should be directly comparable with that given here. In addition, it there is no a priori reason to suggest that at different CO2 system compositions (as are obtained by the acid addition approach) that the CO2 chemistry should be drastically different (it doesn't seem to be in this manuscript).

Finally, if one is to have confidence in the conclusions drawn, one must have confidence in the measurements that are reported. I am afraid that I do not. My concerns fall into a number of areas. In many of these, it is not clear that the authors are necessarily in error, rather they do not provide a description of their methods that engenders confidence in their results.

(a) It is stated in the manuscript (Section 2.2) that the "Manipulations were conducted at 15 ± 0.2 °C", also in Section 2.6, this temperature is again mentioned when using a computer program to estimate partial derivatives. One is left to infer that the pH and [CO2] measurements reported in Table 1 were also performed at 15 °C – as indeed they would have to be for this interpretation to be valid. This important information is omitted.

(b) The samples for alkalinity and for total dissolved inorganic carbon were – as far as I can tell – not poisoned prior to storage and analysis. This is a problem. There is no way to tell how much (or if) they changed between sampling and analysis. Nor is there a statement about the time period that elapsed before pH and [CO2] were measured.

(c) The individual descriptions of the analytical methods employed do not provide a clearly justified statement of their overall uncertainties, however it is the propagated overall uncertainty that is central to any assertion of inconsistencies. The separation of error terms into precision and bias for the discussion is potentially misleading, particularly as there is little data in the paper about either. In modern discussions of analytical uncertainty the distinction is not usually made (see e.g. http://physics.nist.gov/cuu/Uncertainty/index.html).

(d) It is not clear what replications were done. I assume that the separate lines in Table 1 refer to separate experiments (individually adjusted 2 L seawater samples), though this is never explicitly stated. The text also suggests that on each of these: alkalinity was measured in duplicate; total dissolved inorganic carbon in triplicate; pH measurements and [CO2] have no degree of replication mentioned. However, there are terms for the "standard deviation of technical replicates" for colorimetric pH and [CO2], together with an unclear comment describing the approach in determining a standard deviation for the "NBS" pH measurement. (If n = 30, does this imply that this is a pooled standard deviation with 18 degrees of freedom – having evaluated 12 separate mean values?) Additional confusion arises when it is asserted in the text that "CO2 concentrations were measured with an average precision of 0.13 μmol kg–1 (n = 15)"; what relationship does this have to the information in Table 1? (e) Clearly an important aspect of the conclusions presented here is the assertion that it is the lower calculated p(CO2) that is necessarily the wrong one. This is based – it appears – on the measurement of [CO2] using membrane inlet mass spectrometry. As noted in (c), it is hard to judge how justified this assertion is.

One of the hardest things to assess in this paper is thus the likely overall uncertainty

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

of the various analysis techniques (not to mention the other parameters in the calculations such as total concentrations and equilibrium constants). This is difficult to assess. Although a brief statement is made in each description as to how the system is calibrated, there is too little information provided to engender confidence in the adequacy of the calibration.

As an example I can point out that for a seawater sample with a single salinity and temperature, where pH was measured both potentiometrically (using a single electrode, I assume) and colorimetrically (using a single source of dye), the difference between these two "pH" values would be expected to be (approximately) constant reflecting the combined effects of using different activity scales as well as the bias resulting from the residual liquid junction potential between the "NBS" buffers and the seawater. An examination of Table 1 shows that this difference ranges from 0.07 to 0.20, far more than would be expected from the assigned precisions, suggesting that an unrecognized source of uncertainty could be calibration uncertainties.

This lack of knowledge about the overall uncertainty is problematic. It is straightforward to imagine uncertainties of a magnitude that are certainly not out of the question and that would completely eliminate the proposed discrepancies. For example, for the data in the last line of the table it is possible to get p(CO2) results that are completely compatible with each other by decreasing the alkalinity by 12 μmol kg–1; increasing the total dissolved inorganic carbon by 15 μmol kg–1; and increasing the pH by 0.03. (The resulting p(CO2) is then about 1133 μatm, discrepant from that inferred from the MIMS measurement but again, I feel, not outrageously so (based on my examination of Tortell, 2005). This is not to say that these biases necessarily exist, simply that the work presented here does not rule them out.

Figure 2 is intriguing; however, it is also difficult to feel completely confident in the data quality of the Schneider & Erez paper, where the methods are again not well characterized and the pH was measured electrometrically using "NBS" style buffers. (I confess I have not examined these results in detail.)

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

WHAT SHOULD THE AUTHORS HAVE DONE DIFFERENTLY? First, they should have taken the trouble to verify that their experimental methods – though clearly of poorer precision than those typically used to study the oceanic CO2 system – did not have any significant bias over the range of concentrations measured here. This would probably have required some collaboration with another laboratory.

Second they could have tested their methods on a sample of reference material. This water has been poisoned, and the alkalinity and total dissolved carbon dioxide levels are well known. It would then have been practical to compare the measured (colorimetrically determined) pH with that inferred from a calculation using the (usually preferred) Mehrbach constants. This difference is typically found to be within 0.01 – and can be smaller if the extinction coefficients of the dye were determined expressly for that batch of dye).

SUMMARY All in all, this paper does not provide sufficient confidence that it is necessarily correct in identifying the stated discrepancies. Furthermore, the observed discrepancies are sufficiently large to imply that there has to be a significant error in the model of CO2 chemistry in seawater, thus the assertion that measuring pH and either total alkalinity and total dissolved inorganic carbon will address this is disingenuous. The paper also fails to recognize that – at this time – significant uncertainties ($\sim$0.02 ?; Dickson, 2010) exist in the measurement of seawater pH, and thus these will, even if the model is correct, provide for meaningful uncertainty in the estimates of p(CO2).

APPENDIX

BACKGROUND This section is not – strictly – part of the review. It gives a little background to the "thermodynamic consistency" problem to help readers to see this review in context.

The hypotheses underlying the experiment described are: (1) The various acid-base systems in a sample of natural seawater are at equilibrium; (2) There is a known finite number of such systems in such a seawater sample; (3) These various acid-base

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

equilibria can be characterized by equilibrium constants defined with ionic medium standard states (i.e., unique to seawater of a given salinity); (4) These various ionic medium equilibrium constants can be closely approximated by concentration quotients that are thus a function of salinity, temperature, and pressure.

The laws of thermodynamics specify the number of independent pieces of information that will need to be measured to provide a complete description of a system at equilibrium. If more than this number have been measured, then the system is said to be over-determined.

In the manuscript reviewed here it is assumed (as is typical in marine chemistry) that the sample is at a known salinity, temperature, and pressure; that the corresponding concentration quotients are known for the ion product of water and for each of the various acid-base equilibria occurring in the sample; and that the total concentration of each of these acid-base systems is known, with the exception of that for the carbon dioxide system. There are then two remaining degrees of freedom and it is usual for these to be constrained by measuring a pair from the following analytical parameters for the seawater carbon dioxide system: total dissolved inorganic carbon, total alkalinity, pH, and [CO2] (typically estimated from a measurement of the partial pressure of CO2 in air in equilibrium with the seawater sample).

If the system is over-determined, that is more than two of these analytical parameters are measured, then it is possible (at least in principle) to test if all the various measurements: salinity, temperature, pressure, concentration quotients, and analytical information such as total concentrations, pH, etc.) are indeed consistent with assumptions (1) – (4) above. Of course, they never are: nor – given that all measurements will have an associated uncertainty – should they be expected to be.

A plethora of publications (more than 20 so far, I believe) have now been published, variously interpreting observed inconsistencies either as indicative of errors in measured values for the CO2 constants (typically couched as preferring one set of measurements to another), or in a few cases as indicating that either assumption (2) or (4) above is not true. Unfortunately, few of these papers unambiguously draw the same conclusions as each other, suggesting mostly – I fear – that their estimates of the uncertainties inherent in each of the various measurements and assumptions made are inadequate. (I am loath to distrust the laws of thermodynamics.)

The only accepted conclusion that has been drawn from such publications is that the equilibrium constants measured by Mehrbach et al. (1974) seem to be consistent with the various high-quality measurements and the assumptions noted above – at least at p(CO2) values typical of surface ocean water.

However, at least two papers (Lueker et al., 2000; Millero et al., 2002), based on seemingly high-quality analytical measurements, suggest that the measured values of p(CO2) – when the value of p(CO2) is greater than 500 μatm – are found to be higher than the calculated ones (as is suggested here). However, at a p(CO2) of 1200 μatm the deviation reported in these publications was about 60 μatm, abut one fifth of that reported in this manuscript ($\sim$300 μatm).

This apparent discrepancy at p(CO2) > 500 μatm has not yet been explained satisfactorily. Two hypotheses have been put forward to date: either that there is another acid-base system present that has been omitted from consideration – c.f. (2) above – or that one or more concentration quotients for acid-base equilibria are not “constants” over this range of conditions – c.f. (4) above. In my opinion, neither of these hypotheses is clearly adequate as a sole explanation.

The likely concentrations of additional inorganic acid-base system in seawater are reasonably known, and are too small to account for the observed discrepancy, yet it also seems unlikely that this effect is solely due to organic acids despite the suggestion by Millero et al. (2002), as typical seawater dissolved organic carbon values are too small to accommodate this together with the other information we believe we know about the molecular composition of dissolved organic carbon in seawater.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Furthermore, the suggestion that K2 changes (Millero et al., 2002) as the distribution of the acid-base species in seawater changes and as the total dissolved inorganic carbon levels increase also seems unlikely because the implied magnitude of the effect on activity coefficients is too large. In addition, I should point out that the K2 measurements of Mehrbach et al. (currently preferred) were made in seawater with a high p(CO2)!

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper