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## ***Interactive comment on “Implications of observed inconsistencies in carbonate chemistry measurements for ocean acidification studies” by C. J. M. Hoppe et al.***

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This paper raises an interesting question – whether a method that has been recommended and widely used up to now for characterising the carbonate chemistry of seawater in fact commonly leads to underestimation of the partial pressure of CO<sub>2</sub>. As explained clearly in the paper, this is especially important for ocean acidification (OA) research because many experiments estimate the impact of different CO<sub>2</sub> levels on various organisms and processes, and if the chemistry is not correctly determined then the nature of the sensitivity to OA is not properly characterised either. If an experiment actually carried out at 1000 ppm CO<sub>2</sub> is instead stated to have been carried out

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at 700 ppm, then this compromises the CO<sub>2</sub> sensitivity estimated by the research and will lead to incorrect advice being given to policy-makers.

This paper is a reworking of another manuscript previously submitted to Biogeosciences. The previous manuscript was criticised by reviewers (expert carbonate chemists) for some shortcomings in the techniques used to measure the carbonate chemistry. In a reply to the reviewers of the first MS (<http://www.biogeosciences-discuss.net/7/C2149/2010/bgd-7-C2149-2010.pdf>), Hoppe et al accepted some shortcomings, but with an exhaustive error analysis they argued that measurement error was unlikely to be the cause of the observed discrepancies. Also, Hoppe et al used techniques that are better than or equal in rigour to those employed most usually in OA research. Therefore, if such large (30%) discrepancies occurred in this study, then even worse discrepancies can be expected in other studies using less advanced methods and equipment. Regardless of the exact cause, it is important that the existence of such a problem is brought to general attention so that a solution can be found and so that the results of studies already published can be interpreted correctly. Assuming that this problem is widespread, as appears to be the case from the data shown, then the authors are to be thanked for bringing the issue to wider attention.

The revised MS is now written more appropriately. The target audience has been clarified: the paper is aimed more at ocean acidification researchers rather than carbonate chemists per se. The description of methods and errors is improved in the present MS, and the focus is shifted away from being solely on their own experimental results to being more on the general issue of pCO<sub>2</sub> discrepancies in OA experimental studies. Subject to some modifications listed below I am happy to recommend publication.

Specific comments:

Pg 1782, line 25: “a significant proportion”. This can be made more specific – e.g. 25% (Canadell et al., 2007).

Pg 1783, line 13: the carbonate chemistry is often not controlled at all (i.e. not pur-

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posefully kept quasi-constant) after the initial adjustment.

Pg 1783, line 18: another reason is that this combination of parameters had been thought by the community to lead to among the most accurate calculations of CO<sub>2</sub> and CO<sub>3</sub> (CaCO<sub>3</sub> saturation state) (e.g. table 1.6 of Dickson, A. 2010. The carbon dioxide system in seawater: equilibrium chemistry and measurements, In: Riebesell U., Fabry V. J., Hansson L. & Gattuso J.-P. (Eds.), 2010. Guide to best practices for ocean acidification research and data reporting, 260 p. Luxembourg: Publications Office of the European Union.)

Pg 1783, line 27: suggest to remove “and the quality of carbonate chemistry measurements at high pCO<sub>2</sub> levels is often unknown” - this is an implication drawn from the results in this MS rather than a description of the prior understanding.

Pg 1784, results section: it should be specified whether any studies were analysed but found not to show similar discrepancies.

Pg 1784, line 26: “If relevant data were not reported, values were estimated from other sources (e.g...”. The procedure for estimating missing data should be described for each case, in the supplementary information.

Pg 1785, lines 6-9: can outgassing of CO<sub>2</sub> be excluded as a cause of the discrepancy in the Iglesias-Rodriguez et al study? Either way, this should be stated.

Pg 1785, line 14: it would be more informative to reword as follows “Whereas all other pCO<sub>2</sub> data and calculations agreed with each other to within X%, in contrast...”

Pg 1785, lines 21-23: please state whether any of these earlier studies included comparisons at high pCO<sub>2</sub>.

Pg 1786, lines 4-5: it should be stated how the systematic errors in this data were ascertained, e.g. from measurements of CRMs.

Pg 1786, lines 17-18: for the AT adjustments, the authors may wish to compare  $\Delta T$

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from their measurements against the  $\Delta\text{AT}$  expected from the amount of HCl or NaOH added. Given that pCO<sub>2</sub> (as calculated from AT and CT) did not change as expected, either the  $\Delta\text{AT}$  was contrary to expectations, or else measured CT must have changed even though no carbon was added or removed. It sounds as if it should be possible to work out which, from the measurements made, which might help understand better the cause of the discrepancies.

Pg 1787, lines 18-19: or in reporting threshold CO<sub>2</sub> levels harmful to an organism, if derived from experiments in which pCO<sub>2</sub> was estimated from AT and CT measurements.

Pg 1788, line 5: the idea of error propagation in calculation programs is a worthwhile goal, although in practice the choice of method, instrument and operator affects the likely accuracy of measurement, and for a proper quantification of uncertainties then this would need to be input in some way to the program. The value of error propagation can also be questioned in the presence of systematic errors of unknown provenance, as here. Another obvious recommendation to follow from this study is the need for a wide intercomparison exercise. This should involve not just specialist carbonate chemists, but also laboratories in which OA experiments are carried out and the carbonate chemistry measurements made by non-specialists using less expensive instruments. I am aware that the authors are involved in trying to bring about such an exercise, but it would nevertheless be useful if the need for one can be stated explicitly in the paper.

Fig. 1: for consistency, replace TA and DIC with AT and CT in the axis labels. In the final sentence of the caption, does this refer to the Hoppe et al data or to all datasets?

SI, line 22: presumably a LIC-OR measures rather than controls.

SI, section 4: It is helpful that results of measurements of CRMs are reported. However, results for measurements of AT on CRMs should be reported in the same way as measurements of CT and pH on CRMs. They should all be reported in the same

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way, e.g. “<mean offset> ± <std.deviation of offset>, n=<number of measurements>”. Is something different meant by repeatability (pg 2, lines 9 and 34) as compared to reproducibility (pg 2, line 19 and pg 3, line 16)?

SI, pg 3, line 22: Dickson and Millero. This should be 1987. It is not listed in the references of either the MS or the SI.

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