

Interactive comment on “Intercomparison of carbonate chemistry measurements on a cruise in northwestern European shelf seas” by M. Ribas-Ribas et al.

Anonymous Referee #2

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General comments:

The authors present an extensive carbonate chemistry dataset acquired during a cruise in the northwestern European shelf seas, during which the carbonate system was over-determined by measurements of $p\text{CO}_2$, pH, AT and CT. Overall, measurements compare surprisingly well with each other and the authors are to be congratulated for the high quality of the dataset. While I greatly appreciate the efforts to unravel systematic discrepancies between different methods to characterise marine carbonate chemistry and the explanations provided for the remaining discrepancies, the manuscript currently still has some major deficits that should be fixed before final publication in BG.

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(1) My biggest criticism concerns the insufficient discussion (and citation) of previous work. Generally, rather few citations can be found in the discussion even though a lot of work has been done in this field. With respect to the intercomparison of different methods, several studies have provided similar levels of agreement between estimated carbonate chemistry parameters (e.g. McElligott et al. 1998, Luecker et al. 2000), so the conclusion that the “results show that it is possible to obtain good consistency between measurements” (P2810, L22-24) is neither surprising nor new. This impression can be avoided by referring to previous findings. Similarly, it remains unclear how much of the ‘best practise suggestions’ are novel. Please clarify which suggestions have been made before (and by whom).

(2) The authors seem to be undecided if they consider the dataset to prove high consistency between the different datasets (e.g. P2794, L12 and P2808, L2-6) or to contain systematic discrepancies (e.g. P2794, L15 or P2808 L9-11). Some of my confusion between these two conclusions seems to arise from the differences between “raw” and corrected pCO₂ values. Please distinguish between these two levels more clearly. Also, isn't it common practise to correct measured pCO₂ levels for the differences between SST and temperature in the equilibrator? If so, why is the non-temperature corrected data discussed?

(3) In the abstract (P2794, L12-14) as well as the discussion, the authors state that the present dataset is “suitable to be used as a basis for evaluations of the impact of OA on ocean biogeochemistry” (P2828, L5-6). It remains unclear how the authors come to this conclusion. How does the dataset provide information on Ocean Acidification and its effects on marine biogeochemistry? On which timescales do you expect in-situ OA to be measurable, also in view of measurement uncertainties as well as temporal and spatial variability of carbonate chemistry? Is this study thought to serve as a baseline for future investigations? Please clarify.

Specific comments:

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P2794- P2796: The introduction reads as a list of various related studies rather than an introduction to or a rationale for the presented manuscript. Please restructure/rewrite and put the different studies (more) in context with each other.

P2794, L11-18: If diurnal cycles with differences as high as 41 μatm were observed, can you really state that the datasets “were all of really high quality”? What would be your definition of “really high quality”?

P2794, L12-14 & P2796, L10-11: How can this study be used to the evaluation of OA impacts?

P2797, L17-19: Sentence sound a bit clumsy, maybe change to “The pCO₂-1 and pCO₂-2 systems undertook 6187 and 26671 measurements of surface water pCO₂ during the cruise, respectively.”

P2798 L29-P2799, L3: This is a very long sentence, please consider rewording.

P2801, L13-14: Please state the number of (CRM?) measurements used to gain these values.

P2801, L24: Please state that this is the Matlab version.

P2801, L24-29: Why were different borate constants, but not carbonate equilibria constants compared?

P2803, L6-9: Please reword this sentence in order to improve grammar.

P2803, L24 – P2806, L7: It is not clearly stated which paragraph of this section refers to which level of correction of raw pCO₂ measurements. Maybe it would help to change the order of the paragraphs, starting with raw data followed by corrected data.

P2804, L-12-16: In addition to the average difference, the RMSE should be discussed here, as the average difference alone does not provide enough information on the performance in relation to “strong gradients of temperature, salinity and pCO₂”.

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P2804, L15-16: Why do you judge this results to be only “reasonable” (I would say it is pretty good!)? If the average difference in your study is comparable to the one described by Körtzinger et al. (2000), wouldn’t that mean that the “less ideal” settings of your intercomparison do not seem to negatively affect overall consistency?

P2804, L22-25: Please state average and maximum differences.

P2805, L14ff: Is this temperature corrected data or not? Did you check for auto-correlations between PAR and temperature differences (I would expect that temperature offsets could be influenced by exposure of the equilibrator to bright sunlight)?

P2805, L27 – P2806, L1: But pCO₂-2 was the one being closer to the values calculated from AT and CT (cf. P2804, L18). Please comment on this in the manuscript.

P2806, L1-L7: Are these novel suggestions? If not, please reference the statements appropriately.

P2807, L8-15: There are much more differences between both studies (e.g. measurement quality/overall uncertainty, number of samples, sample volume, scientific background of conductors, etc.) which could be discussed here. From my perspective, the presented dataset should compare well with other field-based intercomparisons (e.g. Luecker et al. 2000) rather than the OA-related lab-based datasets presented by Hoppe et al. (2012).

P2808, L6: How can this study be used to the evaluation of OA impacts?

P2808, L9 – P2809, L27: Are these novel suggestions? Otherwise please refer to other publications.

P2809, L21: Does “We estimated. . .” refer to Rérolle et al. 2013? Then please state “They estimated. . .”.

P2811, L6: This will prevent phototrophic growth but not microbial growth in general.

P2811, L8-10: Please provide references for the statement.

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Table 1: How can the calculated uncertainty be identical for the two pCO₂-measurements if you know that there are systematic differences between the two systems (light exposure, length of inlet system etc.)?

Figure 2: Caption should read "... here defined as the residual of pCO₂-1 (a) or pCO₂-2 (b) and another measured or calculated..."

Figure 3: Is this corrected data? If so, how do you end up with a RMSE of only 10 μatm ? Caption should read "Comparison between the pCO₂ between instruments 1 and 2 (μatm ; white circles) and the photosynthetically active radiance (PAR (W m^{-2}), in black circles) measured over five days".

Figure 5: Given that you identify more problems with equilibrator 2, you should also show these plots for pCO₂-2. Please add panel identifications (a-d). Caption should read "Box-and-whisker plots of the residuals between measured pCO₂ (a), pH (b), CT (c), AT (d) and the respective estimates calculated from different pairs of measured variables (denoted on the x axis) for the two sets of borate constants. ..."

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