

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

### **Anonymous Referee #1**

Received and published: 3 March 2014

P 2796 L 13 : “data collection effort was not planned in advance as an intercomparison exercise”. This statement contradicts to some extent statement of previous sentence. Also, I have a hard time believing that no one envisaged this prior to the cruise, and it was only after the cruise that suddenly someone realized that an internal consistency and intercomparison exercise was possible.

P 2797 L 20-21 : provide values of the NOAA standards.

P 2799 L 9 : provide manufacturer and model of the PT100 sensors

P 2799 L 17 : from a purely formal point of view, it's the precision of the Licor's pCO<sub>2</sub> measurements that's determined from the gas standards, not the actual seawater

C175

ter pCO<sub>2</sub> that will also depend on equilibrator performance, accuracy of temperature measurements, etc. . .

P2801 L 15 : data-sets were submitted to BODC but are not publicly available (or at least the link to the data are easily found). Please clarify.

P2802 : Replace “refitted by (Mehrbach et al., 1973); Dickson and Millero (1987)” by “refitted by Dickson and Millero (1987)”.

P2802 : There are several sets of constants. Please justify the choice of Mehrbach et al. (1973) as refitted by Dickson and Millero (1987).

P2802 : “borate constants” as stated stand in fact for the ratio of total boron to salinity.

P2802 : Specify which dissociation constants of boric acid were used.

P2802 : specify which KHSO<sub>4</sub> was used.

P2802 : The whole internal consistency exercise could have been also done using different sets of constants to determine which one would give the best fit.

P2804 : L1-6 : Please statistically test if the Y-intercept is significantly different from zero, and if the slope is significantly different from 1. Here and elsewhere.

P2804 L4 : The Y-intercept of the regression is given at 0.01  $\mu$ atm level which does not make sense given the uncertainty of the measurements.

P2804 : the authors used “different sets of calibration gases” as stated but they were re-calibrated in the lab. before and after the cruise against NOAA standards (P 2797). This should have significantly reduced the differences in calibration gases, and should correspond to situation virtually identical to using the same calibration gases, if the Licors were working properly.

P 2804 L13 : provide reference(s) to back statement “strong gradients in temperature, salinity and pCO<sub>2</sub>”

C176

P2804 L 17 : the residuals are given at 0.1  $\mu$ atm level which does not make sense given the uncertainty of the measurements.

P2804 L 19 : provide reference(s) to back statement "well within the expected accuracy of pCO<sub>2</sub> calculated from CT and AT"

P2805 L 1-13 : Please also include an additional panel to Figs. 2 and 3, with the plots of in-situ temperature, equilibrator temperature of equilibrator 1, and equilibrator temperature of equilibrator 2.

P2806 L 6-7 : this statement was already made by Koertzing et al. (2000).

P2807 : while I agree with the underlying idea, this needs to be worded differently because all the carbonate variables "are not fully independent". AT and CT are not fully independent either, both depend strongly on [CO<sub>3</sub><sup>2-</sup>] and [HCO<sub>3</sub><sup>-</sup>]. pCO<sub>2</sub> and pH do not make a good pair because [CO<sub>2</sub>] and [H<sup>+</sup>] are much smaller than the [CO<sub>3</sub><sup>2-</sup>] and [HCO<sub>3</sub><sup>-</sup>]. Hence, relatively small errors on CO<sub>2</sub> and H<sup>+</sup> will propagate into relatively large errors on [CO<sub>3</sub><sup>2-</sup>] and [HCO<sub>3</sub><sup>-</sup>] if the system is computed from CO<sub>2</sub> and H<sup>+</sup> (e.g. pCO<sub>2</sub> and pH).

P2808 L 25 : Continental shelf break regions are also characterized by strong gradients due to enhanced vertical mixing (internal tides or upwelling).

P2809 : "complete shielding from light" will not prevent bacterial growth

P2809 : Regarding measurements of pHindicator-dye techniques can the authors comment on the interference that could be expected from suspended matter and CDOM that are characteristically high in coastal waters ?

Some of the coastal areas sampled are characterized by blooms of coccolithophores. Can the authors comment on how the CaCO<sub>3</sub> could have affected the CT and AT measurements ?

Most of the discussion on the two pCO<sub>2</sub> equilibrator systems relies on the Koertzing

C177

et al. (2000) intercalibration. I'm surprised that the Koertzing et al. (1996) is not discussed and cited since it provided intercalibration of equilibrators in the North Sea (possibly the very first intercomparison in coastal waters).

Also there have been numerous intercalibration exercises of pCO<sub>2</sub> systems in pools (NIES, etc . . .). It could be useful to mention these in the discussion.

Seminal paper of Wanninkhof et al. (1999) could be useful in the discussion since it provides an extensive "overdetermination study" in open ocean conditions that could be useful versus the coastal study reported here.

Finally, there are several papers that have raised the issue of the impact of organic acids on computations of the CO<sub>2</sub> system in coastal waters. I'm surprised these aspects are not mentioned/discussed (Koeve & Oschlies 2012; Kim et al. 2006; Muller & Bleie 2008; Kim & Lee 2009; Hernández-Ayon et al. 2007).

Please clarify how the recommendations P 2808-2809 converge or differ from those already given by Koertzing et al. (2000) or by Dickson et al. (2007).

#### References

Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007. Guide to best practices for ocean CO<sub>2</sub> measurements. PICES Special Publication 3, 191 pp.

Hernández-Ayon et al. Estimating the contribution of organic bases from microalgae to the titration alkalinity in coastal seawaters, *Limnol. Oceanogr.: Methods* 5, 2007, 225–232

Kim & Lee, Significant contribution of dissolved organic matter to seawater alkalinity, *GEOPHYSICAL RESEARCH LETTERS*, VOL. 36, L20603, doi:10.1029/2009GL040271, 2009

Kim et al. 2006 Contribution of phytoplankton and bacterial cells to the measured alkalinity of seawater, *Limnol. Oceanogr.*, 51(1), 2006, 331–338

C178

Koertzinger, A., Thomas, H., Schneider, B., Gronau, N., Mintrop, Duinker, J.C., 1996. At-sea intercomparison of two newly designed underway pCO<sub>2</sub> systems: encouraging results. *Mar. Chem.* 52, 133–145.

Koeve W. and A. Oschlies, Potential impact of DOM accumulation on fCO<sub>2</sub> and carbonate ion computations in ocean acidification experiments, *Biogeosciences*, 9, 3787–3798, 2012

Muller & Bleie, Estimating the organic acid contribution to coastal seawater alkalinity by potentiometric titrations in a closed cell, *analytica chimica acta* 619 (2008) 183–191

Wanninkhof, R., Lewis, E., Feely, R.A., Millero, F.J., 1999. The optimal carbonate dissociation constants for determining surface water pCO<sub>2</sub> from alkalinity and total inorganic carbon. *Mar. Chem.* 65, 291–301.

---

Interactive comment on *Biogeosciences Discuss.*, 11, 2793, 2014.