

Interactive comment on “A high-frequency atmospheric and seawater $p\text{CO}_2$ data set from 14 open ocean sites using a moored autonomous system” by A. J. Sutton et al.

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Received and published: 29 August 2014

We thank all referees for their thoughtful and constructive comments and suggestions on our manuscript “A high-frequency atmospheric and seawater $p\text{CO}_2$ data set from 14 open ocean sites using a moored autonomous system.” The revised manuscript will be much improved as a result of the careful critiques. Below we discuss the comments from Referee #1 point by point including original referee comments and our responses bulleted underneath.

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This paper describes new mooring technology and data sets. It is a significant contribution in a few ways. First, it provides a description and comprehensive assessment of MAPCO₂ sensors, which have been developed over the past decade and allow high frequency CO₂ measurements on moorings for extended periods. The only other published assessment of sensors capable of long deployments on moorings, including this sensor type, has been made through the Alliance of Coastal Technologies. However these were focused on short-term field measurements (days-week). The text does mention another comparison in Japan that indicates the sensors are capable of high accuracy and precision measurements on short time scales, but the results of the Japan intercomparison are not easy to find. Second, the paper describes a major new data set of high frequency measurements made at fourteen ocean sites, particularly in the equatorial Pacific and will be a significant contribution to improving estimates of air-sea CO₂ exchange. Third, the paper shows clearly the MAPCO₂ sensors provide data of similar quality to underway observations and are of acceptable standard for constraining air-sea fluxes.

– We agree that the results of the Japan comparison are not easy to find. We’ve added a link to the referenced IOC report: http://www.ioccp.org/images/D3meetingReports/WR229_eo.pdf

The data described will have widespread use for determining air-sea CO₂ exchange, testing of models, and for assessing controls on ocean-atmosphere CO₂ exchange and ocean acidification. I believe the paper should be published with some revisions suggested below.

The data are only reported to 2011, and this is related to submission of data to the Carbon Dioxide Information Analysis Center. It is a pity more recent data is not included.

– This data publication addresses the methods and data quality control for the mooring CO₂ data that appear in the most recent version of the Surface Ocean CO₂ Atlas (SOCAT), which includes data through 2011 (Version 2, Bakker et al. 2014). We plan to

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submit updated mooring data publications every 3-5 years as methods are updated or additional parameters are added to the data sets (e.g., pH). Regardless of a formal data publication, our mooring data are typically available at the Carbon Dioxide Information Analysis Center (CDIAC) two years after recovery of the instrumentation from the field. This time is often dictated by collection of comparison data sets to inform the data QC process.

The text mentions that two of the moorings have been removed. A statement in the table 1 caption on what sites are no longer operating would be useful.

– Good point. At the request of another reviewer, we've added a new table listing all sites and the coordinates, so we've added information on what sites are no longer operating to that new table as well.

Introduction: pg 388, A reference to the accuracy of CO₂ measurements required to constrain regional air-sea CO₂ fluxes to 0.2PgC/yr should be included. Why 0.2 PgC/yr?

– That was an oversight that all of the reviewers pointed out. We've added references and explanation to that statement. This level of resolution was identified by Bender et al. 2002 as necessary to use the observations to test process-based models, which is critical to predicting the future behavior of the carbon cycle. Ref: Bender, M., Doney, S., Feely, R. A., Fung, I. Y., Gruber, N., Harrison, D. E., Keeling, R., Moore, J., Sarmiento, J., Sarachik, E., Stephens, B., Takahashi, T., Tans, P. P., and Wanninkhof, R.: A Large Scale Carbon Observing Plan: In Situ Oceans and Atmosphere (LSCOP). Nat. Tech. Info. Service, Springfield, p.201, 2002.

Methods:

Page 390: Has the linearity of the Licor 820 sensor response over the range of CO₂ (e.g. 0-500 ppm) been determined? This will have an impact on the precision and accuracy and is not considered.

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– The NDIR has a non-linear response to CO₂, but that response is very well characterized by the manufacturer. Licor has a function built into their firmware that accounts for the non-linear response and linearizes the output data. The linear function is calibrated prior to each atmospheric and seawater measurement with the zero (intercept) and high CO₂ standard reference gas (slope). The accuracy of the linearized, calibrated output is confirmed prior to deployment by analyzing a range of intermediate CO₂ standards in our laboratory.

Page 391: The methods description mentions the drying of the gas before a measurement. No detail is given. Is this a chemical dryer and what substance? Data reduction:

– Thank you for pointing that out. We use a silica gel as the drying agent to prevent condensation in the Licor sensor and have added that detail to the methods section.

Page 393: Give the range of the four standard reference gases used on the 8050 underway system.

– We've added that the range is typically 0-1000 $\mu\text{mol mol}^{-1}$. Has the comparison between the General Oceanics 8050 and the MAPCO₂ system pre-deployment been done at a variety of pCO₂ values and temperatures, or at one value - ie the value in the seawater tank at room temperature? Are checks also made when the system is returned to the laboratory after recovery from the moorings?

– Prior to deployment we compare the MAPCO₂ system to the underway system in the lab at the value of the lab tank at room temperature. We only run a post deployment comparison with standard gases, not the underway system. We've modified the explanation in the methods to clarify these points.

Page 393, line 23: The description of data quality control mentions a post calibration curve is used for the final calculation. Is this a curve or a straight-line fit (only zero and span are measured for calibration)? How is it possible to generate a curve from two points?

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– Thank you for bringing the post calibration curve to our attention. We did not adequately cover how we generate the post calibration curve and have modified the text to clarify. In short, we use the temperature of the Licor and the Licor coefficient during the standard gas cycle to develop a linear relationship based on all measurements during an annual deployment. We then recalculate the raw Licor air and seawater values based on that relationship. The reality of only using two standards in the moored method (as opposed to four in the underway method) means that we rely more on the Licor than the standards to post calibrate the data. However, through the lab and in situ comparisons described in this manuscript, we've found comparable estimated levels of uncertainty of CO₂ measurements between these methods.

Equations 2 and 3 should be described more thoroughly. Equation 2 needs a reference, including where the coefficients are taken from, as only the 1.004 value appears to be referenced. The text describing equation 3 states RH_{sample} is "the RH of air sample (%)", with line 26 on page 394 stating "P_{Licor} is the pressure of the air and seawater samples" implying "air sample" means atmospheric air (and possibly span gas?). Does air mean atmospheric air or the gas in the Licor820 (ie atmospheric air, equilibrator headspace gas/air and span and zero gases)? This could be made clearer if "RH of air sample (%)" is changes to mean the RH of the gas stream measured by the Licor 820, or something like this. Also, is RH_{span} in equation 3 taken to be a background residual value for the system? These parameters and equations should be made clearer.

– These equations are from the Licor and humidity sensor manuals, so we've added those references to the manuscript. We agree with your suggestion of changing the text to "RH of the gas stream measured by the Licor" and we've made that modification as well. You are correct that the RH_{span} in equation 3 is considered the background RH level for the system and have clarified that in the text.

Page 397 "Further work to smooth and deseasonalize the data, as in most growth rate analyses, could provide further insight into the source of the larger differences between the MAPCO₂ and MBL observed at the KEO and MOSEAN/WHOTS sites."

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This sentence seems to be stating this approach should give a better data product and that the authors will not be doing this. More detailed trend analyses may also have the opposite effect of pointing to larger discrepancies between the MapCO₂ atmospheric data and MBL data. Either a more complete trend analysis should be performed, or the sentence removed.

– Performing a trend analysis is out of the scope of this data publication, so we have removed that statement as suggested.

Page 397 & 398: Line 19 on page 397 says the high-frequency MAPCO₂ varies from smoothed MBL data by <5 umol/mol. Page 398, lines 14-17 state, "Since atmospheric CO₂ is well mixed in the open ocean MBL, environmental variability introduces little error to the MAPCO₂ and MBL air comparison. The resulting mean differences in the atmospheric data are likely due primarily to uncertainty in the measurements, which in this case, we associate with the MAPCO₂ system". While this is a good check on the MAPCO₂ data, it only applies to a check near the atmospheric CO₂ value (about 395 umol/mol), and it is necessary to assume the zero is good throughout the whole deployment, or there could be offsets for values different from the atmospheric measurement. As far as I know, the MBL product is smoothed and is not particularly well constrained by data in all areas that measurement are likely to be made with the MAPCO₂ systems. My understanding is the MBL values are estimated from measurements made weeks apart in most cases and using data that can be large distances from the MAPCO₂ system locations. Given the seasonality and spatial changes in atmospheric CO₂, particularly in the Northern Hemisphere, I am concerned how reliable the MBL estimates are at the mooring sites and the use of this comparison to determine offsets for the MAPCO₂ data could bias the results, although probably at a level of less than 1-2 umol/mol. A brief discussion of the reliability of using the MBL estimates for atmospheric CO₂ would be useful. It may also be useful to show a frequency distribution plot of the offsets for one of the moorings and show if it is a normal distribution.

– This issue was raised by another reviewer as well and we agree on the limitations

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of the GLOBALVIEWCO2-MBL data product. We did not stress enough in the initial manuscript that adjustments to the MAPCO2 data are not made based solely on MBL comparisons. When a MAPCO2 system is recovered and a new system deployed, there is typically some overlap in measurements at each location. Only in cases when there is an offset between systems at the same location, which is often corroborated by an offset to the MBL data set as well, do we make any corrections to the MAPCO2 data. The MBL data set serves as a useful and unifying comparison data set, especially since other in situ comparison data are often lacking. As we build CO2 time series at each of these locations, we start to build an understanding of how our measurements typically compare to the MBL data set, which is an added piece of information to troubleshoot occasional offsets between deployed MAPCO2 systems. For example, winter air values measured by our MAPCO2 systems at Papa are consistently lower than MBL (Fig. 4a). We have modified the description of the MBL-MAPCO2 analysis to clarify these points.

Page 399, why were the Leucker constants used for the CO2SYS calculation? A 5% error is large (about 15-20 ppm).

– The Lueker et al. (2000) constants are recommended by the Dickson et al. (2007) and Riebesell et al. (2010) best practices for carbon system measurements. A 5% error is large and, therefore, a major challenge to comparing pCO2 measurements to pCO2 calculated from TA and DIC. We have modified this to < 5% in the manuscript, as at typical surface water conditions, this error is lower than 5%. Refs: Dickson, A. G., C.L. Sabine, and J.R. Christian (Editors) (2007). Guide to Best Practices for Ocean CO2 Measurements, North Pacific Marine Science Organization: 176. Riebesell, U., et al. (2010). Guide to best practices for ocean acidification research and data reporting. Luxembourg, Publications Office of the European Union: 260.

Page 401: The deployments over a year or longer are described. It would be useful to include a description of what happens to the RH values over this time and if the drying agent continues to work well over the period. This might not be relevant if the seasonal

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temperature change masks any drift in the RH values.

– To clarify, the sample gas stream is not completely dried as in the underway pCO2 method, due to lack of drying methods available for extended autonomous operation and discussed in more detail on pages 394-396. The silica gel is used to prevent condensation in the Licor and is still effective at preventing condensation when the systems return from each deployment. The drying agent is replaced after each deployment. We've included these details in the revised manuscript.

Figures: Figure 3. The interannual and seasonal rings in the plot are too difficult to see. A second panel with a pie chart for seasonal and interannual variability may provide better information or the size of the outer rings could be increased. The use of the circle diameters and the color to indicate the variability and mean $\Delta p\text{CO}_2$ is clear.

– We have increased the size of the outer rings in this figure.

Interactive comment on Earth Syst. Sci. Data Discuss., 7, 385, 2014.

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