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Atmospheric Chemistry and Physics Discussions

ACPD

Interactive comment

Interactive comment on "In situ observation of atmospheric oxygen and carbon dioxide in the North Pacific using a cargo ship" *by* Yu Hoshina et al.

Anonymous Referee #2

Received and published: 23 April 2018

In this manuscript, Hoshina et al. describe the construction, installation and performance of a fuel-cell/NDIR-based instrument for measuring O2 and CO2 aboard ships of opportunity. They also present a year of data collected while underway across the North Pacific. Overall, this is a very straightforward presentation of careful work. Nothing about this project is revolutionary or ground-breaking, but the continued development of O2-CO2 systems is important for the advancement of atmospheric potential oxygen (APO) as a useful oceanographic tool, and the data they have collected fill an significant gap in the APO community's records. This is valuable work and definitely deserves to be published. I have very few scientific questions or concerns about the content. With many years of excellent work in this field, the Tohjima lab knows what it

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Discussion paper

is doing, and this paper reflects that expertise. It is also quite well written.

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Questions/comments on substance

P3 line 3: Change to “The mole fraction is not used as a measure of O2 abundance because, for example, a change” Furthermore, it would be helpful if the authors gave an explanation of why mole fraction changes when per meg doesn’t. This is alluded to on page 7 (around eq. 4), but it should be stated more explicitly at the outset.

P5 line 5-6: I believe you are trying to say that the outlet pressures (and by extension, the pressures in the analysis cells), are kept at the same absolute value at all times by actively matching them to a reference volume. If this is what you do in fact mean to say, you should probably make it a bit more explicit.

P5 line 11: Is the “mechanical mass flow controller” the same as the one mentioned on P4 line 25? If so please make it clearer. If not, specify this one more completely.

P5 line 23: Is there more than one SUS tube? If so, explain how many and why.

P6 line 10: To what do you attribute the improved performance of the 2nd trap design? Is it simply larger glass volume, more complete chilling of the glass due to the insulation, the coaxial design of the glass trap…? Please give a few words of explanation.

P6 line 17: At what interval did you operate your changeover valve? “1-5 minutes” is not specific enough, as the frequency of these switches can have a significant impact on the precision of your results (see, for example, Keeling et al, 2004). How did you settle on this interval?

P6 line 20-21: It’s not at all clear from the plot that the CO2 ever reaches a plateau before the changeover valve changes state again. My concern is that the CO2 values you infer will be consistently biased toward the value of whatever gas was previously in the analysis chamber. Perhaps a better approach is to fit each transition with function like (1 – exponential), with 2 free parameters (rise time and asymptote) and use the asymptote as the true mixing ratio, even this value is never measured in the instrument.

P6 lines 26: What happens when i=1? I recognize that this formula represents the difference between a block and the average of the blocks before and after, but the formula doesn't work for the first block after a calibration run.

P7 line 24-25: I'm a bit confused by your calibration procedure. I think you're saying that you used two span tanks for O_2 and calculated a linear response function for the Oxzilla every 25 hours. How did you interpolate the response of the instrument for the many observations that were made during the intervening 23.5 hours? Similarly, it seems like you had a 3-point calibration for CO_2 made just once at the beginning of the week of observations. If you have a 3-point calibration, did you assume a linear response function, or did you allow a 3-parameter form with some curvature? Am I correct that you did not repeat the CO_2 calibration at any time during or after the 7-day period of observations? Please clarify these points.

P8 line 19: I think you mean "During every 24hr period, these three reference gases were measured for 32min each." If that's right, please reword. If not, clarify.

P8 line 28: There is no way for us to tell (from Fig. 6b) that there are 20s cycles. It would be very helpful if there were an inset figure that zoomed in on a subset of the data with a much-expanded time-scale.

P9 line 15-16: Are the "hourly averages" mentioned on line 16 tank values, or atmospheric data? If the latter, wouldn't natural variability in the atmosphere lead you to expect more scatter? See also my comments on Fig. 7 below.

P10 lines 10-14: I am puzzled about why the authors didn't just deconvolve the flask errors to get a separate value for the uncertainty in the shipboard data. If the (shipboard data – flask values) have a scatter of XX per meg and the flasks themselves have an uncertainty of YY, then isn't the uncertainty in shipboard data alone just given by ZZ =

sqrt(XXˆ2 – YYˆ2)? This way one can report a meaningful error for the system, rather than an upper limit.

P10 line 20: I cannot see the “noticeable decrease” in Figure 9. Perhaps a zoomed-in inset would show it. In fact, when I look at Figure 8, I think I seen an _increase_ in APO during the eastbound leg of NC2-125.

P11 line 5: The period 2014-2016 is not 4 years in length. Please correct either the dates or the duration.

P11 line 7: Presumably the figure referenced here is the one labelled “A12”. It’s odd to me that this one figure would comprise an entire appendix. I would suggest simply making it a part of the normal figures (since it is a valuable one). At the very least, make sure it is correctly referenced in the text.

Figure 3: This would be much more valuable if there were fewer cycles shown with more detail. Perhaps an inset with one representative cycle (for each of plots “a” and “b”) would make the true stability of the measurements more apparent.

Figure 7: I am puzzled that the error bars on the black circles (when the ship is in port) are not apparently any smaller than the scatter in the blue points (taken at sea). I’m just going by eye, but it certainly looks like the error bars in port capture more than 68% of the blue points. Wouldn’t the rocking of the ship and the resulting response in the Oxzilla II make the scatter a bit larger when at sea? In lines 19-20 you say the scatter is actually bigger in the blue points, but I just can’t see that. Also, on lines 20-21, you say you are only using the in-port measurements for calibration of the Oxzilla. Really? What if the instrument response varies during the time between ports? Why not use the information from the tank runs taken at sea (the blue points in Figure 7) to address this possibility.

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Strictly editorial comments:

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Throughout the mansucript: Please italicize “in situ”

Throughout the manuscript: Please change “onboard” to “aboard”

P1 line 6: Change “observed” to “measured”

P1 line 19: Change to “compared the year of”

P2 line 11-12: Change to “the introduction of the tracer atmospheric”

P2 line 14: Remove “the” (the first word of the line)

P2 line 20-21: Change to “about 21%. Keeling (1988) was the first to develop an atmospheric O2 measurement technique with this precision, using an interferometer and showing the usefulness”

P3 line 2: Should read “Keeling and Shertz”

P3 line 17: Change to “trasects of the data in the western Pacific region revealed that variation in the magnitude of the bulge in annual mean APO”

P3 line 18-20: Change to “Tohjima et al., 2015). This analysis was made possible by the relatively high spatiotemporal sampling desnity in the western Pacific.”

P3 line 21: Change to “route made it”

P3 line 25: Change to “Therefore, in December 2015 we initiated a program of in situ measurements aboard”

P3 line 26: Remove “was also desired”

P3 line 28: For consistency, this should read “along the North American route in the Pacific.”

P4 line 1: Change to “since it is difficult to load and unload”

P4 line 2: Remove “are cumbersome”

P4 line 3: Change to “frequency. With these constraints the GC/TCD”

P4 line 5: Change to “and CO_2 measurements aboard NC2.”

P4 line 16: Change to “cm^3. The air”

P4 line 20: Change to “tubing. The technique of sampling from a spherical”

P4 line 22: Change to “The gas sampled from the spherical vessel”

P5 lines 3-4: Change to “controllers until the readings of the flow meters for the two air streams matched. The outflows of the”

P5 line 18: Change to “water vapor shows”

P6 lines 12-13: Change to “gas is reported as a relative”

P6 line 18 : Change to “analyzer during a test run in which a reference gas from a high-pressure cylinder was used as a sample gas.”

P6 line 19-20: Change to “min^{-1}) is more than four times slower than the flow rates used in previous studies, the”

P6 line 25: Change to “signal for the second minute of the i-th 2-minute interval”

P7 line 6: Change to “the average of the last 10s of data for the i-th 2-minute interval.”

P7 line 14: Change to “Eqs. (2), (3), and (4) for “sample” gas provided”

P7 lines 16-17: Change to “which likely represents the best possible precision, because the”

P8 line 1: Change to “O_2/N_2) shown in Figure 5, reveals a diurnal cycle”

P8 line 2: Change to “ratio. A scatter plot of CO_2 and”

P8 line 16: Change to “-579 mer peg (tank #CPD-00010)”

P8 line 19: Change to “During the shipboard measurements”

P9 line 2: Change to “fuel cells in an Oxzilla-II analyzer. However, in her instrument, the differential”

P9 line 8: Change to “succeeded in describing the”

P9 line 11: Change to “motions with a”

P10 line 7: Change to “because of significant contamination by anthropogenic”

P10 line 21: Change to “distributions of the 5-hr running”

P10 lines 23-24: Change to “APO distributions. Preliminary analysis of the cause of these anomalies points to atmospheric transport and the”

P10 line 25: Change to “will be presented in a future publication.”

P11 line 4: Change to “-7.9 per meg yr-1) determined from the APO values”

P12 line 5: Remove the unneeded “-“ before variation

P12 line 22: Change to “Grant-in-Aid”

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