

Interactive comment on “Technical Note: How long can seawater oxygen samples be stored before titration?” by M. Lankhorst et al.

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Abstract

This response refers to comment osd-11-C1116-2014 received for the following paper in *Ocean Science Discussions*:
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1 Comments from referees/public

The key point of criticism in this comment is that the claims in the abstract of the manuscript are not supported by the data.

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Other points of criticism are that:

- the comparison with the oxygen electrodes and optodes is irrelevant,
- the different samples should be comparable to within the one-operator precision since they are treated and sampled at the same time,
- the water samples should have been drawn from the same Niskin water bottle to possibly reduce variability in the NH data sets,
- the number of samples is too small to produce statistically robust results to support the hypothesis.

The comment does make positive remarks about the usefulness of the study, and makes suggestions about how to repeat or expand the study, including a request for larger numbers of samples.

2 Authors' response

Regarding the main criticism by the reviewer, we maintain that the data presented in fact do support our claim that storage of the samples does not degrade the samples beyond a certain threshold, and that our data put a value on what that threshold might be. To our knowledge, this is the first ever attempt to determine this value. The data from the *Melville* expedition suggest that that number might indeed be the WOCE target for precision, as discussed in the manuscript (the Dickson reference therein). The numbers shown in table 3 of the original manuscript unambiguously support this. The data from the *New Horizon* expedition are scattered more widely and do not support such a claim, but at least they definitely show that the number is better than what WOCE would have accepted as an inter-laboratory bias (same reference, as discussed

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in the manuscript). Again, the statistical details are presented in table 3 of the original manuscript. To resolve the differences in opinion between the reviewer and ourselves, we will suggest a change in title of the manuscript and a few text passages, as outlined further below.

Regarding the other points of criticism: The comparison with the sensor accuracies of the electrodes and optodes is not only relevant for us, it is the one and only reason these measurements were made in the first place. Both expeditions (*New Horizon* and *Melville*) had the core mission to deploy moorings and gliders carrying these sensors, and the oxygen data that we reported on were collected as part of the calibration/validation effort for these deployments. We thought we made this perfectly clear in the original manuscript (page 3, lines 6 and onwards), but perhaps we need to make this even clearer. This in turn answers the question of what we would consider an acceptable bias: if the resulting discrepancies are smaller than the sensor accuracies, they will be acceptable. This is the case, and we conclude that they are acceptable in the first sentences of the “Interpretation and conclusions” on page 6. If other programs have tighter requirements, they will perhaps draw a different conclusion, but e.g. WOCE seems to accept an inter-operator bias that is even larger than our results (again, see our discussion of the Dickson reference). In our opinion, this is a result significant enough to justify publication.

The referee comment insists that we should test against the WOCE single-operator precision standard because the samples were sampled at the same time. However, the *Melville* data were titrated by different operators. To move away from the discussion what we would like to see in the data (discrepancies smaller than X), we propose to change the wording of the manuscript such that it reports what is found, and leave it open to the reader whether this is good enough.

Regarding the comment that the water should have been sampled from the same Niskin bottle, that would be the case if the purpose of the samples had been this comparison study alone. However, the purpose of the samples was to cal/val other

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instruments, and this study is a spin-off. The original reason to take duplicates from separate Niskins was to guard against failed/leaking Niskin bottles and still have water samples from a small number (3-4) of long stops, during which the whole rosette was stopped at constant depth. If we ever do a repeat study, we will take the samples from the same bottles.

Regarding the comment that the number of samples is too small to reach a meaningful conclusion, we disagree. Table 3 of the original manuscript presents mean values, standard deviations, and sample numbers. From these, one can also compute the standard errors of the means. While more data is always better, the statistics presented here are perfectly well-defined. The result is that we now know an upper bound of whatever damage this sample storage issue might cause (glancing over the RMS values of table 3, it is certainly no worse than 0.042 ml/l, and the more stable data from the *Melville* batch gives reason to hope that it is more like 0.007 ml/l). This is a novel result, and the samples deterioration is small enough for our particular purpose. That said, we can make an attempt to collect additional samples for a revised version of the manuscript, at the editors’ discretion.

Further comments: The review comments makes a statement about the “problems” identified in tables 1 and 2. We believe that at least the three occasions of bubbles in the samples were actually not corrupted samples, but rather gas bubbling out of solution as the samples warmed up to room temperature. This would presumably not be oxygen, which was fixated with the iodine product, but other dissolved gas. The number of “problem” samples is therefore likely smaller.

- The Langdon quote of “many days” is already in the original manuscript (page 4 line 5).
- The sample bottles used on board *Melville* had about 130 ml volume and were individually calibrated. For the ODF methodology and equipment, see their website: <http://odf.ucsd.edu/index.php?id=11>

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- We can add a picture of a water seal.
- We will not drop the aspect of the sensor cal/val, because this is the driving question for us. However, we are proposing some changes in title and text that should help clarify the purpose of the study.

3 Authors' changes in manuscript

To address the main points of criticism, the following changes to the manuscript are proposed:

Change in title: We acknowledge that the manuscript does not answer the question in the present title in that there is no number given to answer the question. Therefore, we propose this new title: "Effect of storing seawater oxygen samples before titration is no worse than 0.04 ml/l, possibly better", whereby the 0.04 number is a rounded version of the RMS numbers presented in table 3 of the original manuscript. Incidentally, this is the same as the mean plus the standard error of the mean.

Modify abstract: Mention that purpose of the study is to cal/val electronic sensors, and change the implication of the last sentence such that it is specific to that purpose.

Other text modifications: In the final paragraph of the conclusions, repeat that the target accuracies are those of the electronic sensors.

Figure: add picture of bottle with seal as additional figure.

Attempt to collect more data: We can make an attempt to collect more data during upcoming field work. This will, however, require permission by the editor to allow

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for additional time to collect and analyze these samples before submitting a revised manuscript. If this is desired, we will try to estimate together with the editor how many additional samples are needed, and how much extra time would be required.

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