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Interactive
comment

Interactive comment on "An intercomparison of oceanic methane and nitrous oxide measurements" *by* Samuel T. Wilson et al.

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Referee #2 In their manuscript, Wilson et al. present data from a recent international intercomparison study which evaluated the analytical procedures used to measure the concentrations of methane and nitrous oxide dissolved in seawater. Specifically, seawater samples and gaseous standards were sent to several different laboratories for analysis. Since the measurement of methane and nitrous oxide concentrations are mainly done in the gas, not liquid, phase, the different laboratories had different protocols to first separate the dissolved gas prior to analysis as well as the final analysis; while the different labs had different protocols, they mainly involved either headspace equilibration or a purge and trap technique. The results of this intercomparison are striking, with different laboratories reporting concentrations that could be different by

several hundred percent. The highest percent differences were reported for the lowest concentration samples, and since low concentrations are typically reported in the near-surface waters, this inter-laboratory difference is particularly troubling for global extrapolation of sea-to-air fluxes for these two gases. The impact of this manuscript is that it identifies significant inconsistencies between laboratories, and while the data from any one laboratory is likely valid for testing hypotheses, combining data from multiple laboratories for global extrapolation or time series analysis will lead to significant unknowns. A the end of the manuscript, the reader is left hungry for more, wondering how these inconsistencies might be rectified with a hypothetical Standard Operating Procedure. But while the authors provide a few recommendations for how to lower uncertainties, they do not prove the major cause of these inconsistencies, and thus which procedure might be preferred. The authors appropriately did not attempt this recommendation as it was beyond what their data can illuminate. For example, a full analysis of the headspace equilibration procedure would require each laboratory to establish the accuracy and precision of each variable in Equation 1 (pressure, temperature, salinity, headspace volume, and water volume) using their procedures. The authors assess the calibration of the analytical instrument and the variability of the overall results, but not these specific variables. In addition, the authors recognize that storage time is a variable significantly influencing the results. Since these additional variables were not systematically investigated, the authors are correct in not recommending a preferred procedure, and instead choose to report overall inconsistencies. We thank Reviewer #2 for their comments. We are building on the results from this intercomparison exercise and in the future will have a Best Practice Guide for the measurements of dissolved methane and nitrous oxide.

Sample storage: I recommend that the authors expand section 3.4. I found this section too brief on experimental details and I was left assuming how storage time was assessed. Was the sample storage time variable controlled in any systemic way or is this simply the time it took different labs to actually conduct their analyses? Is there any way to normalize the data in Figures 1 and 4 to sample storage time or would that be ex-

tending this data too far? Can the authors assess how much variation in the dissolved concentrations is due to storage vs. procedure? The specific questions are answered separately below. In response to the general comment, we have re-structured Section 3.4 to improve its clarity. Lines 448-459 now read "Because prolonged samples storage can influence dissolved gas concentrations, including methane and nitrous oxide, the intercomparison dataset was analyzed for sample storage effects (Table S5 in the Supplement). It should, however, be noted that assessing the effect of storage time on sample integrity was not a formal goal of the intercomparison exercise and replicate samples were not analyzed at repeated intervals by independent laboratories, as would normally be required for a thorough analysis. Nonetheless our results did provide some insights into potential storage-related problems. Most notably, there were indications that an increase in storage time caused increased concentrations and increased variability for methane samples with low concentrations, i.e. PAC1 and PAC2 samples which had median methane concentrations of 0.9 and 2.3 nmol kg-1, respectively (Fig. 7). In comparison, for samples of nitrous oxide with low concentrations there was no trend of increasing values as observed for samples with low methane concentrations.'

Was the sample storage time variable controlled in any systemic way or is this simply the time it took different labs to actually conduct their analyses? The sample storage time represents the time taken for different laboratories to conduct the analysis. There was no control of the storage time.

Is there any way to normalize the data in Figures 1 and 4 to sample storage time or would that be extending this data too far? We would be uncomfortable doing this conversion because it would insinuate a higher influence of sample storage on concentrations than what we can currently prove. We refer the readers to Figure 7 which shows concentration and coefficient variation against storage time for the samples with the lowest concentration of methane.

Can the authors assess how much variation in the dissolved concentrations is due to storage vs. procedure? This would require a time-course set of measurements

which was not conducted as part of this exercise. This would be a very interesting experiment and could feature in future intercomparisons. What we have noted in our response to the overall comment, is that contamination is considered most likely for the samples of methane collected from the Pacific Ocean. These samples had methane concentrations of 0.9 and 2.3 nmol kg-1 and therefore were most sensitive to release of small quantities of hydrocarbons by the septa.

The authors suggest that leakage may be a source of uncertainty for longer storage times, but they don't raise the possibility of inadequate preservation. Most groups analyzing these dissolved gases assume that adding enough mercuric chloride to a sample will halt all biological activity, but that may not be the case. In addition, what is the chance that gases are outgassing or adsorbing to the stopper? Since these are both possible influences on the final results, I suggest that the authors also briefly raise these possibilities. In response to the comments made by Reviewer #2, we have restructured the relevant part of the Discussion to specifically address the issue of sample storage. Lines 589-598 now read 'This study also revealed that sample storage time can be an important factor. Specially, the results from this study corroborate the findings of Magen et al. (2014) who showed that samples with low concentrations of methane and more susceptible to increased values as a result of contamination. The contamination was most likely due to the release of methane and other hydrocarbons from the septa which interfere with the dissolved methane in the sample (Niemann et al., 2015). Since the release of hydrocarbons occurs over a period time, it is recommended to keep storage time to a minimum and to store samples in the dark. It should be noted that sample integrity can also be compromised due to other factors including inadequate preservation, outgassing, and adsorption of gases onto septa. Due to all of these reasons, it is recommended to conduct an evaluation of sample storage time for the environment that is being sampled.'

Please note that in response to comments by Reviewer #1 we addressed the issue about alternatives to mercuric chloride and Lines 188-193 now read 'The choice of mer-

curic chloride as the preservative for dissolved methane and nitrous oxide was due to its long history of usage. It is recognized that other preservatives have been proposed (e.g. Magen et al., 2014, Bussmann et al., 2015), however pending a community-wide evaluation of their effectiveness over a range of microbial assemblages and environmental conditions for both methane and nitrous oxide, we recommend continuing with a long-established method.'

Overall, this investigation appears robust and the manuscript is well written. The authors have uncovered a significant result which will benefit the community. Thank you for your comments

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