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

Anonymous Referee #2

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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 per-

cent 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.

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 extending this data too far? Can the authors assess how much variation in the dissolved concentrations is due to storage vs. procedure?

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.

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

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