

Interactive comment on “Equilibrator-based measurements of dissolved nitrous oxide in the surface ocean using an integrated cavity output laser absorption spectrometer” by I. Grefe and J. Kaiser

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We thank reviewer #1 for their detailed comments. Our replies to the comments are indicated by AC. A number of comments refer to errors introduced during copy-editing, which were unfortunately overlooked in the PDF proofs.

1) P.1036 L. 1 “The equilibrator. . .” sentence unclear. Please rephrase.

AC: Rephrased as “The equilibrator itself was bypassed during this test because it communicates with the atmosphere at three points: the water inlet, the water outlet

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and the pressure vent.”

2) P.1037 L. 17-19 Referring to the temperature dependent solubility of N₂O in seawater temperature probes with a precision of 0.01 °C are recommended.

AC: The stated precision of “better than 0.1 °C” for the temperature in the equilibrator actually refers to a precision of 0.03 °C (based on the standard deviation of measurements over 2 minute intervals). However, for the calculation of accurate N₂O concentrations, the accuracy of temperature measurements is key. The accuracy of our temperature probes inside the equilibrator was 0.06 °C, based on calibration against a mercury reference thermometer. An uncertainty of 0.06 °C leads to a 0.17 % (at 30 °C) to 0.25 % (at 0 °C) uncertainty in the derived surface seawater concentration just due to temperature. Gas chromatographic (GC) dissolved N₂O measurements have uncertainties of about 2 % (McIlvin and Casciotti, 2010; Walter et al., 2006). Our 10 s-average measurement precision of N₂O mole fractions was about 0.06 % (0.2 nmol mol⁻¹), so as far as we know this is the first time in the history of oceanic dissolved N₂O measurements that the accuracy of the temperature measurement in the equilibrator has become crucial for the accuracy of the derived N₂O concentration and we agree that a temperature calibration to better than 0.01 °C should be recommended for future studies. However, overall the accuracy of the N₂O measurement is still an order of magnitude better than traditional GC measurements. Furthermore, for the calculation of N₂O air-sea exchange fluxes, the N₂O saturation concentration is required in addition to the actual dissolved concentration. This requires accurate measurements of sea surface temperature at the same level of precision. Even though we measured sea surface temperature with an accuracy of 0.003 °C at the scientific seawater intake at about 6 m depth below the surface, this temperature does not necessarily correspond to the temperature of the boundary layer (skin layer) in the top few millimetres of the water column, which determines rate of air-sea exchange (Robertson and Watson, 1992).

3) P.1037 L. 27 “Dried air with 323.7 nmol/mol. . .” Please specify gas phase by adding

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N₂O?

AC: Yes, this mole fraction refers to N₂O.

4) P.1038 L. 21 “where u is wind speed at 10. . .” Please add m.

AC: Thank you for pointing out this error, which was unfortunately introduced during copy-editing.

5) P.1038 L. 23 Did you consider Wanninkhof 2010?

AC: We are not familiar with this paper. The only 2010 paper with Wanninkhof as first author we could find is the following: Wanninkhof R, Doney SC, Bullister JL, Levine NM, Warner M, Gruber N (2010) Detecting anthropogenic CO₂ changes in the interior Atlantic Ocean between 1989 and 2005 *Journal of Geophysical Research: Oceans* 115:C11028 However, Wanninkhof et al. (2010) use a budget approach to detect anthropogenic CO₂ changes in the Atlantic and make no reference to wind speed-gas exchange parameterisations. Perhaps the referee meant the review paper by Wanninkhof et al. (2009)? The latter paper notes that the Nightingale (2000) parameterisation we used agrees well with several subsequent studies, e.g. Ho et al. (2006) and Sweeney et al. (2007).

6) P 1039 2.3 You introduce a new method for N₂O measurements in surface waters. The comparison to conventional methods like GC-MS measurements remains very short with only 3 CTD samples and no data shown and should be extended.

AC: We agree that a more detailed method comparison is highly desirable and explicitly recommend this in Section 4 (“Summary and conclusions”). However, since the precision of the traditional GC method for dissolved N₂O analysis is about an order of magnitude worse than the one presented here, it would be difficult to accept a validation of the new technique based on the traditional one. In any case, such an effort would require a large number of variables to be tested, including different equilibrator designs, extraction procedures, N₂O detection methods, offsets between

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CTD samples and underway lines (Juranek et al., 2010), etc. and is beyond the scope of the present work. As the importance of non-CO₂ greenhouse gases rises up the agenda, there are now a number of international efforts underway to compare methods and results across different laboratories, e.g. the European FP7 InGOS project (<http://www.ingos-infrastructure.eu>), a SCOR Working Group initiative on dissolved N₂O and CH₄ measurements and the SOLAS and COST-sponsored CH₄-N₂O database MEMENTO (<http://memento.geomar.de>). The new method presented here should be included in these international efforts because it greatly reduces the measurement effort, has improved precision and allows automation, higher measurement resolution as well as precise measurement of atmospheric mole fractions.

7) P. 1042 L. 4 “relaxation time (=3t)...” $t = \tau$? 8) P. 1042 L. 5 “increased t to...” $t = \tau$?

9) P.1042 L. 6 “the value for t...” $t = \tau$?

AC: Thank you for pointing out these errors, which were unfortunately introduced during copy-editing of the final publication file.

10) P.1044 L.6 “It was difficult to keep the water flow through the equilibrator constant. . .” You mention the use of a seawater flow regulator in the summary. Why was the regulation of a stable water flow through the equilibrator still an issue? It significantly influences the N₂O measurements.

AC: In our strife for concise presentation of the results, we may have unfortunately caused some confusion here. During AMT20, the seawater flow was regulated via a valve. It generally remained constant, which was verified by regular (at least hourly) monitoring of the constancy of the water level in the equilibrator and manual measurements of the rate of water flow from the bottom of the equilibrator. However, on four occasions during the cruise, the water flow stopped completely; three of these cases happened while the ship was on station. There were a number of other users of the underway system during this cruise who required high volumes and flow rates of seawater and there appears to have been increased demand of pumped seawater in other

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laboratories on the ship during these times. We attributed the flow stagnations to pressure fluctuations in the underway system caused by these other users. By opening the seawater valve further, it was possible to restart the flow. Data, which may have been affected by the stagnant flow, have been removed from the results presented in this paper, as well as the first 15 minutes of data after re-adjustment of the water flow. Also, values were flagged back to the last observation of correct water flow. Increases in water flow were never observed. We therefore believe that data shown in this manuscript have been thoroughly quality-controlled. However, as a consequence of this experience during AMT20, we installed a separate flow restrictor on subsequent cruises (containing a small butyl rubber o-ring that reduces the size of an orifice under increasing pressure) that kept the water flow rate constant at 1.8 L/min, independent of the inlet pressure (over a range from 1 to 3 bar). This allowed us to keep the seawater valve fully open and maintain sufficient flow even during episodes of high demand from other users.

11) P.1044 L. 24 Why is the coherence of upwelling and N₂O values not shown via correlation with oxygen values or temperature for verification?

AC: Thank you for this suggestion. We checked for a correlation between N₂O saturation and sea surface temperature (see figure 1, attached) and N₂O saturation and O₂ saturation. In the 11° to 24° N region, where the three episodes of high N₂O saturation occurred, neither comparison shows an effect of upwelling of high-N₂O subsurface waters with correspondingly low temperature and low O₂ saturations, so we can exclude the hypothesis that these high-N₂O episodes are caused directly by entrainment of deep waters.

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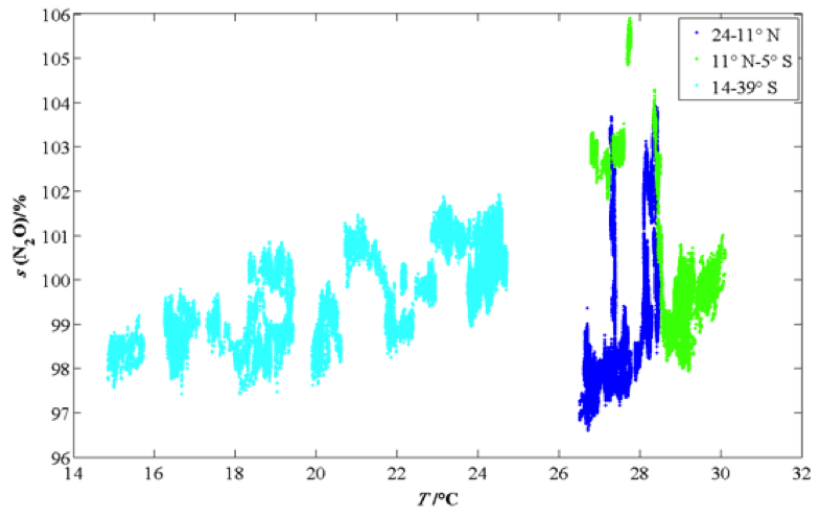


Fig. 1.

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