

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 #2 for his detailed comments. Our replies to the comments are indicated as AC. A number of comments refer to errors introduced during copy-editing, which were unfortunately overlooked in the PDF proofs.

RC: This manuscript describes a dissolved N₂O analysis system based on an off-axis cavity ring-down spectroscopy and its application in the Atlantic by attending Atlantic Meridional Transect expedition. Although the authors argued excellence of the

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system compared to the conventional system based on gas chromatograph equipped with electron capture detector, they did not provide enough material to prove in the manuscript.

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 conventional GC method for dissolved N₂O analysis is about an order of magnitude worse than the one presented here (2 % rather than 0.2 %), 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, differences between CTD samples and underway lines (Juraneck et al., 2010), etc. 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. We would like to emphasize that the existence of a previous alternative method to measure dissolved nitrous oxide concentrations does not establish the prior method as a benchmark for subsequent developments. Of course, it is important to compare both methods (which we have started with a GC-MS comparison and strongly recommended further comparisons with GC-ECD), but a detailed comparison between them is beyond the scope of the present work.

RC: Although the new system shows 0.2 ppb precision for short-term period, its unexpected long-term drift weakens such an argument. Because of this horrible drift of the instrument during the expedition, the results from the expedition are not able to show

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the hemispheric gradient of the atmospheric N₂O.

AC: We have highlighted potential problems with the laser analyser, which users need to be aware of in the future. While we agree that the drift encountered during the first deployment of the laser spectrometer during AMT20, we would not go as far as calling it "horrible". In fact, using the 8 hourly-reference gas analyses, it was entirely and satisfactorily correctible to within 0.7 nmol mol⁻¹. This exceeds the 10 second-precision of 0.2 nmol mol⁻¹ (and the 1 second-precision of better than 0.2 nmol mol⁻¹ stated by the manufacturer), but is much better than the precision achieved for dissolved N₂O measurements by previous reports. The interhemispheric gradient is of the order of 0.8 nmol mol⁻¹ (Forster et al., 2007; Prinn et al., 2000). The calibrated atmospheric mole fractions agree well with independent measurements by the AGAGE network so we can be confident about the accuracy of the results. It is presumably due to the small number of atmospheric measurements (n = 26 in the Northern Hemisphere and n = 29 in the Southern Hemisphere) coupled with the residual error due to the drift correction that the interhemispheric gradient could not be detected. However, we note that is within 2σ of the measurement error (including the additional error caused by the drift correction) so we would not (falsely) conclude based on this that it is absence. The atmospheric N₂O measurement community requires an N₂O measurement precision of the order of 0.1 nmol mol⁻¹, which is likely to be achievable with the same type of instrument, but we would recommend deploying a dedicated instrument for this purpose rather than combining air and dissolved phase measurements. Subsequent deployments including the JR255 cruise discussed in the paper have not shown the same laser drift, which was caused by a faulty electronic component powering the laser, as explained in the paper.

RC: As this manuscript discloses incomplete experiments in the laboratory and field, I cannot recommend publication as it is.

AC: We disagree with the reviewer that manuscript disclosed incomplete experiments. There are many papers in the literature that present data of similar quality and quantity,

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e.g. (Forster et al., 2009; Gülzow et al., 2011; Rhee et al., 2009; Walter et al., 2006)

1.) It needs to describe clearly objective of the manuscript. It looks like describing an instrumental system developed in the laboratory without showing any progress compared to the conventional system. The author used the same equilibration system that Cooper et al. (1998) have already developed. The CRDS is commercially available without any further modification. Regarding the equilibration time experiment, this has already tested by Gulzow et al. (2011) but for CO₂ and CH₄. That the equilibration time depends on seawater flow rate has been tested thoroughly by Johnson (1999). Therefore, the laboratory experiments provide little information on the performance of the system. This manuscript would have been better if the laboratory test have had carried out rigorously with various flow rates, different dissolved N₂O concentrations, etc. with changing parameter which may affect N₂O solubility and equilibration time.

AC: We are grateful for the comments of the referee, which allow us to clarify a few points in the manuscript. The objective of the paper is to present a novel analytical setup for dissolved oceanic N₂O measurements, which allows measurements with unprecedented analytical precision and has great potential for automation due to its similarity to existing dissolved CO₂ analysers. We also present first data from the North and South Atlantic and compare them to existing measurements as well as a limited number of discrete samples. Conventional GC-ECD analyses suffer from a number of problems, e.g. low temporal resolution (unless coupled with an equilibrator) (Butler et al., 1989; Walter et al., 2004) and detector non-linearity (Butler and Elkins, 1991). The commercially available N₂O analyser for atmospheric measurements was successfully coupled for the first time to a periphery for gas injection and an equilibrator-system for seawater measurements. High-resolution measurements were acquired with a short-time precision of 0.2 nmol mol⁻¹ (0.1% for reference gas measurements). Long-time precision was found to be 0.4 % (24 h experiment) before laser replacement and 0.3 % after (research cruise JR255A, reference gas measurements). The equilibrator-based N₂O measurement method using laser spectroscopy is inherently more precise (better

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than 0.7 nmol mol⁻¹ or 0.2 % compared to e.g. 1.8 % for GC-ECD (Walter et al., 2006). Equilibration times for N₂O were determined for conditions experienced during field deployment. The work by Gülzow et al. (2011) provides equilibration times for CO₂ and CH₄, under slightly different conditions (e.g. different flow rate), but not for N₂O. Measurements of equilibration times for different seawater flow rates are not expected to yield different equilibration times because of the high solubility of N₂O (Cooper et al., 1998; Rafelski et al., 2013) and we have found no evidence of such variations.

2. The results from the field experiment can be flawed due to malfunction of the laser that the authors mentioned. In addition, irregular fluctuation of seawater flow may influence equilibration time and thus dissolved concentration. The authors should thoroughly examine that the data shown in the manuscript are reliable.

AC: Please see our reply above regarding the laser malfunction. Regarding the seawater flow, 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 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

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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.

Specific points and technical comments 1) P. 1034 L. 22: Becker et al. (2012) is not found in the section of References.

AC: The reference indeed seems to have been lost during copy-editing and will be added again.

2) P.1035 L.11: Was the instrument calibrated for x(H₂O)? If so, describe how to do it.

AC: The instrument is factory calibrated for H₂O using a dewpoint generator. Good agreement between wet and dry N₂O mole fractions was demonstrated on p. 1041 l. 1-12. Also, the good agreement between our measurements and AGAGE data shows that water vapour correction works well.

3) P.1036 L.3: Was Cell pressure 100 kPa (1 bar) NOT 10 kPa? And was the pressure constant at 100 kPa without any drift?

AC: Thank you for pointing this out this error, which appears to have been introduced during copy-editing; the cell pressure should be 10 kPa throughout the manuscript.

4) P.1036 L. 26: When the gas flow rate reduced at 100 mL/min, what was the cell pressure? Did this change in the mole fraction of N₂O?

AC: The cell pressure is held constant at 10 kPa by the instrument's software, independent of the gas flow rate.

5) P. 1037 L.28: Why was the N₂O analysis system calibrated every 8 hour? If it is due to instrumental stability, please show experimental results.

AC: The 8-hourly calibration interval was initially not deemed necessary, as stability

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over 24 hours during laboratory tests was satisfactory (p. 1041 l. 13 to 16). It was nevertheless done to monitor instrument behaviour during the first ever field deployment, and then continued throughout AMT20 as the laser drift was discovered. In retrospect, we were extremely glad to have followed this frequent calibration regime without which it would have been very difficult to correct for the laser drift. In any case, the 8-hourly calibration interval is a significant improvement over the hourly calibrations required for Li-Cor CO₂ analysers, e.g. Cooper et al. (1998). Subsequent deployments including during the JR255 cruise discussed in the paper have shown that daily calibration intervals are sufficient when there is no laser drift. The effects of the drift are shown in Figures 6 and 7 of the paper.

6) P.1038 L.19: Right side of Eq.5 include water vapor correction, e.g. $P \times (1 - PH_2O)$

AC: A water vapour correction is not required because it is already included in the parameterisation of F (Weiss and Price, 1980). F requires the equilibrator pressure to be close to $p^\circ = 1 \text{ atm} = 1013.25 \text{ hPa}$. Perhaps the reviewer referred to the small residual error due to this assumption? The correction term for deviations of the equilibrator pressure p_{eq} from p° is given in the equation below (last term) and is between 0.9998 at $p_{eq} = 970 \text{ hPa}$ and 1.0002 at $p_{eq} = 1050 \text{ hPa}$ for temperatures between -2 and 30 °C. We consider this correction of less than $\pm 0.02 \%$ to be negligible. Equation given in figure 1.

7) P.1038 L.21: Insert the unit of height. Wind speed at 10 m (Eq. 6).

AC: Thank you for pointing this out. The unit m appears to have been lost during copy-editing

8) P.1038 L.23: It is recommended to apply Sweeney et al. (2007)'s parameterization to estimate λ the flux, too.

AC: The agreement of wind speed parameterisations after Nightingale et al. (2000) and Sweeney et al. (2007) is very good, see figure 2. The parameterisation of Sweeney et

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al. (2007) is ill-constrained because it assumes a gas exchange rate coefficient of the form $k = aU^2 + bU + c$, with $b = c = 0$, and we therefore prefer using the one by Nightingale et al. (2000).

9) P.1039 L.3: Does the wind speed in ECMWF represent at 10 m high? If not, describe how to estimate the wind speed at 10 m high.

AC: The ECMWF wind speed is for a height of 10 m.

10) P.1039 L.5: Typo in Eq. 6. "... + 0.333U²...". Remove superscript 2 of wind speed U.

AC: Thank you for pointing this out, an error appears to have happened during copy-editing. The correct equation is shown in figure 3.

11) P. 1039 L.6: Explain why to compare in-situ and 30 day weighted average of wind speeds for λ N₂O flux and gas exchange coefficient.

AC: The calculation of weighted gas exchange described in Reuer et al. (2007) was used to give a more robust estimate of gas exchange in light of variable wind speed over time. The calculation is an improvement over using instantaneous in-situ fluxes because it takes into account that wind speed varies over time at any given location and weighs it appropriately according to mixed layer depth, assuming a constant N₂O production/influx rate. A simple arithmetic average of gas exchange coefficients leads to biased results. In this case, the differences between both fluxes are small.

12) P. 1041 L.18-19: I do not understand the sentence " The gas volume of Corresponds to 40 μmL ..". In view of context, the pressure should be 10 kPa NOT 100 kPa.

AC: This observation is correct, the pressure was 10 kPa (see point 3).

13) P. 1042 L. 18-20: It would be better to make a figure showing the instrumental precision and accuracy for 3 calibration gases. Did these 3 gases use for calibration

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during AMT20? This is not clearly written in the text.

AC: The three calibration gases were only used for JR255A, not during AMT20. A figure showing the measurements is given in figure 4.

We have followed the suggestion of the reviewer and applied a calibration using all three gases. This has led to a lower standard deviation of the marine air measurements during JR255A, which now give (324.0 ± 0.7) nmol mol⁻¹ instead of (323.9 ± 1.3) nmol mol⁻¹. Thank you for this suggestion.

14) P. 1042 L. 25 and P. 1043 L.1: The atmospheric mole fraction during the campaign was either 323.2 ± 0.5 or 325.2 ± 0.5 . Which one is correct?

AC: Thank you for pointing this out, an error appears to have happened during copy-editing. The correct value is (323.2 ± 0.5) nmol mol⁻¹.

15) P. 1043 L. 1-4: The atmospheric value 325.2 ± 0.5 is fairly high end of the values from Mace Head (324.1 ± 0.7), and beyond the range of the value in Cape Grim (322.9 ± 0.3). Therefore, the measured atmospheric concentrations for AMT20 appear to be larger than the representative values at AGAGE stations and it is quite hard to agree with the authors' argument that their measurements are correct.

AC: Thank you for pointing this out, an error appears to have happened during copy-editing. The correct value is (323.2 ± 0.5) nmol mol⁻¹ (see point 14).

16) P. 1043 L. 9-14: Please show that ship's exhaust would not influence the measurement of atmospheric N₂O even though the intake was mounted at the bow of the ship.

AC: Neither during AMT20 nor during JR255A, N₂O mole fractions were influenced by wind direction relative to the ship (see figures 5 and 6).

17) P. 1043 L. 26: The authors suspect inverse flow of the lab air into the equilibrator which might lead to lower dissolved N₂O by the equilibrator than by discrete analysis.

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It can be proven by testing the system in the lab with connecting a flow meter at the end of the vent.

AC: The difference between discrete and equilibrator measurements is statistically not significant. We are only speculating about what might explain the observed small difference and attribute it to potential N₂O loss in the ship's pumped seawater system. Irrespective of this, we have tested this with a flow meter and the flow at the equilibrator vent is ± 0.3 ml/min. Given that about 100 times as much dissolved gas enters the equilibrator per time, this cannot explain the lower N₂O measured by the equilibrator. Moreover, the lab N₂O mole fraction is close or slightly above that of the dissolved air, so the minor vent flow cannot explain the small, statistically insignificant differences between equilibrator and discrete measurements.

18) P. 1044 L. 8: The instrument was calibrated every 8 hours with twice injection of calibration gas with 20 minutes apart. Thus, the authors assumed that the instrumental detector drifted in a linear manner for 8 hours. In this case, the dynamic range of the instrumental detector should be linear and pass through the origin. This can be done with 3 calibration gases and should show in the manuscript.

AC: We have tested this and there is a small deviation from the origin. The calibration function for 3 calibration gases with N₂O mole fractions of 297, 325 and 344 nmol mol⁻¹ gives a slope of 1.04 and a y-axis offset of about -15 nmol mol⁻¹ during JR255. As noted under point 13) above, this reduces the standard deviation of the air measurements. This would have a negligible influence for the range of N₂O mole fractions encountered during AMT20 due to their small variations of N₂O mole fractions of dissolved air around the nominal value of the reference gas. At the lower end (near 97 % saturation), it leads to positive bias of 0.5 nmol mol⁻¹ (or less than 0.2 %); at the upper end (near 103 % saturation), it leads to a negative bias of -0.4 nmol mol⁻¹. Clearly, to exploit the full precision of the instrument, the use of 3 calibration gas is recommend to improve the accuracy of the calibration and we have done just that during JR255A and subsequent cruises. It also important for the atmospheric measurement community to

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follow this approach if the full potential of the instrument is to be exploited.

19) P. 1047 L. 6-8: In general, dissolved N₂O concentrations reported in this manuscript are quite lower compared to the values published in literature, which leads to undersaturation of dissolved N₂O in large area, in particular in the northern hemisphere. Here the authors attributed microbial consumption of N₂O on the wall of the seawater supply line. In addition, on page 1044 line 6, the authors mentioned unregulated variation of seawater flow rate through the equilibrator. This can be another potential reason leading to lower concentration of dissolved N₂O due to lower. These factors should be written here clearly.

AC: We have no evidence to see that variations in seawater flow rate would lead N₂O undersaturations. This would require drawing in air with low N₂O mole fractions from the lab environment and the lab air actually has higher N₂O than the dissolved air. Also, as described for major point 2, occasions where a stop in seawater flow was observed were flagged and not considered for analysis.

20) P. 1047 L. 9: As the manuscript does not provide concrete conclusions I recommend the section title of Summary.

AC: We are unsure what the reviewer considers to be "concrete conclusions". We think that there are a number of conclusions and recommendations in this section on the use of laser cavity analysers for dissolved N₂O measurements in this section as well as more general observations about the use of equilibrators and underway seawater supplies on ships, as well as suggestions on what useful next steps would be in terms of method comparisons.

21) P. 1047 L. 17: What was the time resolution of measurements during AMT20? This should be described quantitatively. Was it every 140 (or 142) s or 203 s?

AC: The instrument recorded N₂O mole fractions every second, the data was then averaged over 10 s. The signal would then be "smeared out" due to the equilibration

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time constant τ of 203 s (p.1042 L. 5).

22) P. 1048 L.10: "... setup are comparable to previous ..." need to add "lower" as Table 1 shows the lower concentration of N₂O from the equilibrator-ICOS analyzer than that from GC-MS.

AC: "Previous studies" refer to published data of GC-ECD measurements, not our own GC-MS measurements. More measurements are needed to clarify whether the undersaturation in the gyres is due to natural variability or whether it can be attributed to microbial consumption in the ship's pipes. We note that consumption of O₂ has been documented during a number of cruises including AMT (Juraneck et al., 2010). Forster et al. (2009) also cite a personal communication by Hermann Bange who found loss of methane in underway sampling systems, but apparently no problems for N₂O, but this might be due to the lower precision of the conventional measurement system. There is actually further evidence for offsets between discrete and underway N₂O measurements during a previous AMT cruise (AMT7, 1998) in the paper by Rhee et al. (2009). On average, the difference of equilibrator to discrete CTD measurements is (2.2±5.7) %, but the range of deviations is from -8 to +13 %, with the lower values nearer the beginning of the cruise at 50 °N, see figure 7.

23) P. 1048 L. 12: "... Measurement is excellent." As the authors admitted, no hemispheric gradient was detected and there is 2.3 ppb difference in the southern hemisphere (see 14 above). This does not appear to support the authors' argument of excellent performance of the analytical system.

AC: As mentioned under points 14) and 15) above, the apparent 2.3 nmol mol⁻¹ difference is due to a typo and the actual values agree well.

24) P. 1057 Fig. 2: What is the unit of x-axis?

AC: Thank you for pointing the missing x-axis label out. The unit is time in minutes.

25) P. 1058 Fig. 3: In case of air and reference gas measurement, the exhaust from

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the analyzer goes into equilibrator and then vents to outside. I wonder if this won't influence the measurement of dissolved gases.

AC: Yes, this affects the measurement and because of this, after each change of sample stream (i.e. marine air, reference gas, equilibrator headspace), the first 15 min of data were not used to allow for flushing of the cavity (p. 1038 l. 3 to 6). This allows for sufficient flushing of a 1.7 L equilibrator, given the equilibration time of 203 s. However, we have modified this design now and replaced the two 4-port valves with one 8-port valve with the CRDS outflow going to waste when running reference gases.

26) P. 1061 Fig. 6: It is recommended to plot the corrected values with different axis from the raw data, which will show any variation of atmospheric N₂O along the cruise track.

AC: The purpose of this figure was to show both, corrected and raw values on the same scale to compare the extent of the applied correction. The variability is characterized by the standard deviation reported in the text on p. 1042 l. 25.

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$$c(\text{N}_2\text{O}) = x(\text{N}_2\text{O})F(\text{N}_2\text{O}, T_{\text{eq}}, S)P_{\text{eq}} \frac{1 - \frac{P_{\text{vap}}(\text{H}_2\text{O}, T_{\text{eq}}, S)}{P_{\text{eq}}}}{1 - \frac{P_{\text{vap}}(\text{H}_2\text{O}, T_{\text{eq}}, S)}{P^{\circ}}}$$

Fig. 1. Equation water vapour correction.

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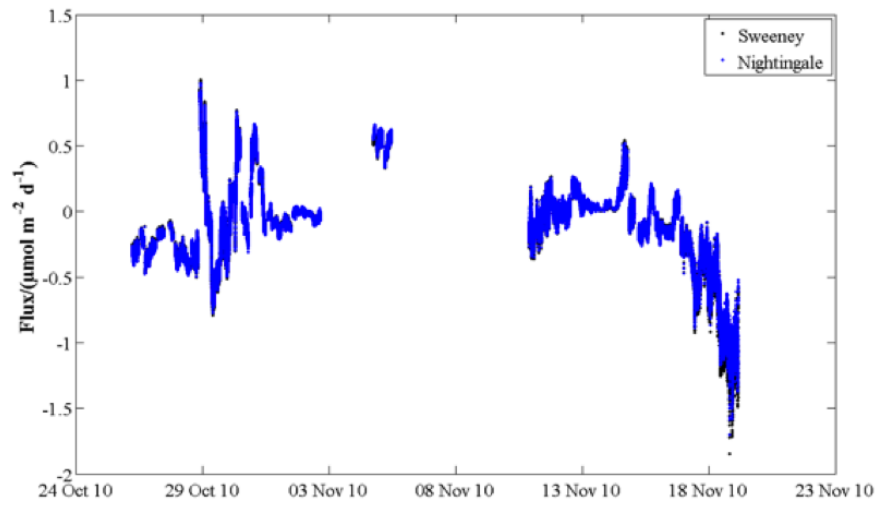


Fig. 2. Comparison Nightingale et al. (2000) and Sweeney et al. (2007).

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$$\frac{k_w}{\text{m d}^{-1}} = 0.24 \left[0.222 \left(\frac{u}{\text{m s}^{-1}} \right)^2 + 0.333 \frac{u}{\text{m s}^{-1}} \right] \left(\frac{Sc}{600} \right)^{-0.5}$$

Fig. 3. Equation for calculation of k_w .

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Fig. 4. Calibration gases used during JR255A.

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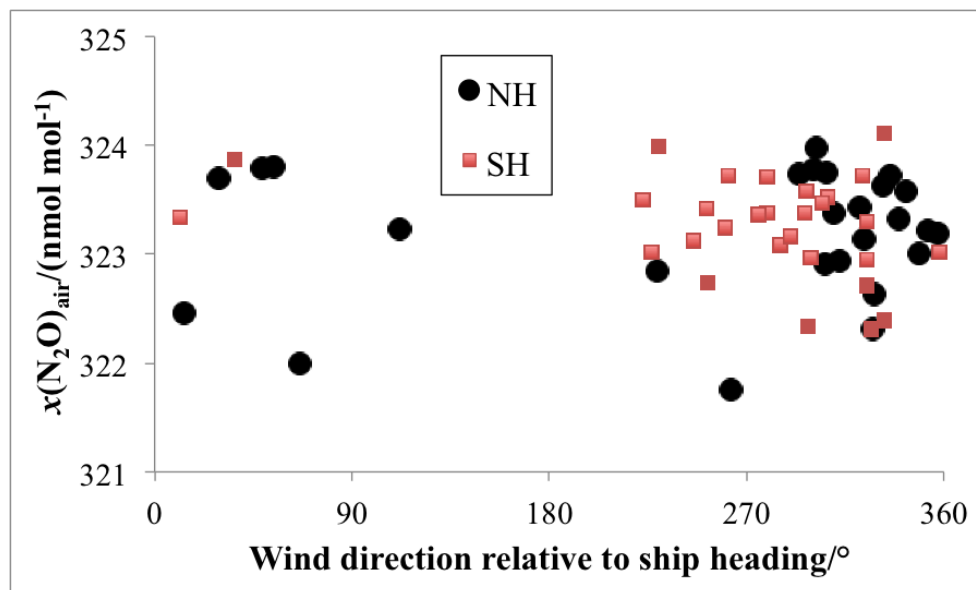


Fig. 5. N₂O mole fraction measurements relative to wind direction during AMT20.

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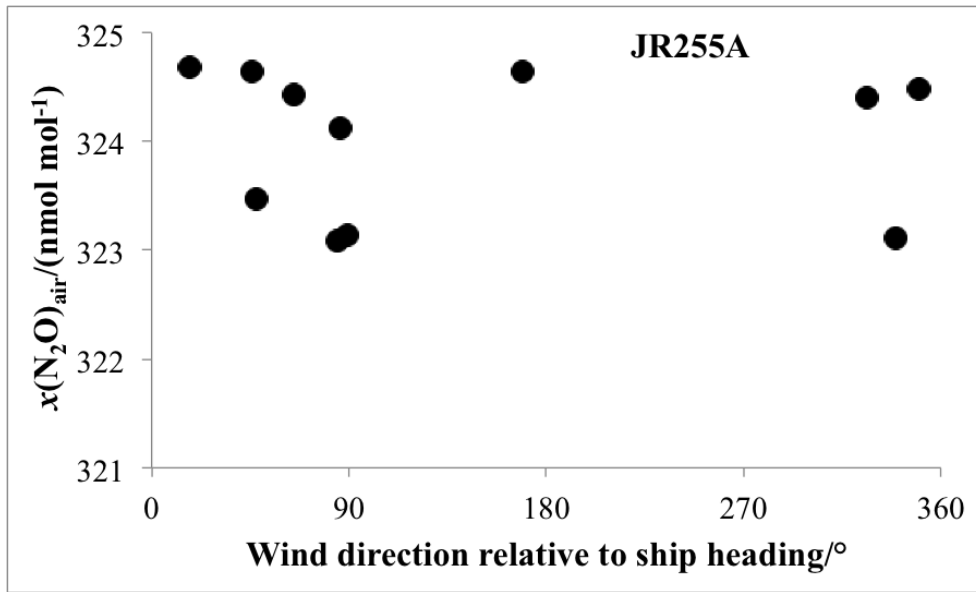


Fig. 6. N₂O mole fraction measurements relative to wind direction during JR255A.

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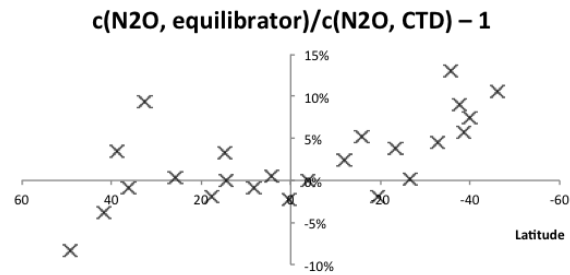


Fig. 7. Difference between equilibrator and discrete CTD measurements, Rhee et al. (2009).

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