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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

Anonymous Referee #2

Received and published: 28 August 2013

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 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. 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 the

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hemispheric gradient of the atmospheric N₂O. As this manuscript discloses incomplete experiments in the laboratory and field, I cannot recommend publication as it is. Please consider the following comments in mind when revising the manuscript.

Major points

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.

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.

Specific points and technical comments

1. P. 1034 L. 22: Becker et al. (2012) is not found in the section of References.
2. P.1035 L.11: Was the instrument calibrated for x(H₂O)? If so, describe how to do it.
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?
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?

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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.
6. P.1038 L.19: Right side of Eq.5 include water vapor correction, e.g. $P \times (1 - PH_2O)$
7. P.1038 L.21: Insert the unit of height. . . . Wind speed at 10 m (Eq. 6).
8. P.1038 L.23: It is recommended to apply Sweeney et al. (2007)'s parameterization to estimate the flux, too.
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.
10. P.1039 L.5: Typo in Eq. 6. “. . . + 0.333U²]. . .”. Remove superscript 2 of wind speed U.
11. P. 1039 L.6: Explain why to compare in-situ and 30 day weighted average of wind speeds for N₂O flux and gas exchange coefficient.
12. P. 1041 L.18-19: I do not understand the sentence “ The gas volume of Corresponds to 40 mL ..”. In view of context, the pressure should be 10 kPa NOT 100 kPa.
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 during AMT20? This is not clearly written in the text.
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?
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.

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.

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

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.

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.

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

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?

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

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than that from GC-MS.

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.

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

25. P. 1058 Fig. 3: In case of air and reference gas measurement, the exhaust from the analyzer goes into equilibrator and then vents to outside. I wonder if this won't influence the measurement of dissolved 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.

Reference Johnson, Evaluation of a seawater equilibrator for shipboard analysis of dissolved oceanic trace gases, *Anal. Chim. Acta*, 395:119-132, 1999

Please also note the supplement to this comment:

<http://www.ocean-sci-discuss.net/10/C432/2013/osd-10-C432-2013-supplement.pdf>

Interactive comment on *Ocean Sci. Discuss.*, 10, 1031, 2013.

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