

Interactive
Comment

Interactive comment on “A new method for continuous measurements of oceanic and atmospheric N₂O, CO and CO₂: performance of off-axis integrated cavity output spectroscopy (OA-ICOS) coupled to non-dispersive infrared detection (NDIR)” by D. L. Arévalo-Martínez et al.

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On behalf of the authors I would like to thank both referees for the very constructive comments. On the following I will provide a summary of our replies to the issues mentioned by them during the interactive discussion, and which have been included/detailed in the revised manuscript.

Major points:

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1) Comparison between underway and discrete methods for N₂O measurements

Indeed the differences between the results obtained with both methods were not deeply explained in the text. First, the good correlation illustrated in figure 8a shows the consistency between discrete and underway N₂O measurements. On the other hand, despite of a large fluctuation on the differences between the measurements (deviations up to 7-20%) a mean offset of 0.43 ± 0.44 nmol L⁻¹ was found. Analysis of the regression residuals of discrete vs. underway CN₂O showed values within ± 1 nmol L⁻¹ and no systematic trends of increase or decrease, indicating that these results can't be only attributed to the accuracy differences between both analytical methods both rather to experimental errors associated to the nature of the discrete sampling scheme. In GC/ECD determinations, the sample collection and handling as well as the measuring procedures carried out add further uncertainty to the measurements, and thus larger errors are expected in comparison to those produced by using OA-ICOS. Furthermore, a reduction in the typical precision of the GC/ECD method is to expect since the N₂O samples were always collected while the ship was steaming, which suggests that the error among replicates of a given sampling period can be increased because of the spatial separation between them. This effect can, in turn, be more evident when sharp gradients are crossed (and this was quite often observed during these two cruises with meandering waters north of the Equator). This factors removed, a resulting mean offset of 0.22 nmol L⁻¹ between underway and GC/ECD measurements is achieved, which is rather low considering the different analytical setups.

2) Seawater CO measurements

Since no discrete method for CO measurements in seawater was available for the cruises, it was not possible to perform the same comparison exercise as for N₂O and CO₂. Also, no ancillary parameters which could help to explain the CO distribution in seawater were considered and therefore, the only way available to assess the quality of our data was to compare the results with previous estimates. In fact, the results obtained by means of the underway system fit reasonably well with data from different

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open ocean areas although they are always lying on the lower range of such estimates. It should be considered however, that all the surveys used as a reference employed the gas chromatography approach and this constrains our ability to directly compare them to the underway measurements. Possible contamination effects from ship plumes getting into the equilibrator were taken into account although the effect in this case was minimal. CO production on the equilibrator on the time scales of the equilibration process was not directly tested but based on the findings of Law (2002) this doesn't seem a very likely scenario. Thus, although the CO measurements are reasonable and fit to the expected trends (e.g diel cycle), a deep analysis of the obtained values requires further validation upon direct comparison with discrete methods in which the sampling program is carried out in parallel with the underway measurements like it was successfully done for N₂O and CO₂.

Line by line:

- 1) Introduction: cites regarding equilibrator measurements coupled to GC/ECD were preferentially included in the brief background paragraph given in the section 2.2 since they fit better to the context. Redundancies with section 2.1 have been corrected.
- 2) pp 1287 (L 6-9): Paragraph shortened and rephrased.
- 3) pp 1291: Accuracy of standards has been included.
- 4) pp 1299 (L 27): Synthetic air is N₂O-free, this is now explicitly stated on the text.
- 5) pp 1304 (L 11-24): Paragraph substantially abbreviated.
- 6) p 1284 (L 28): Additional references were added where needed.
- 7) 2.1 Instrumentation: The correct value for gas flow is 235 ml / min.
- 8) pp 1289 (L 27): Although not included in the text, the remaining H₂O molar fraction after drying is in the order of 4000-6000 ppb. This was accounted for during the final computations.

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9) pp 1293: The corresponding cite of the mathematical background for the estimation of the equilibrators time constant was added on the text.

10) pp 1298 (L 9): Additional cites added. Our method is a modification from the method by Bange et al. (2002)

11) pp 1301 (EQ. 9): Corrected formula was added. The definition of Oswald solubility coefficient is given by Battino (1984).

12) pp 1302: Vertical error bars added to figure 8a.

13) pp 1304 (L 11): A brief description of the data collected during the two expeditions has been separated on a new section: "5 Surface seawater N₂O/CO/CO₂ measurements in the equatorial Atlantic"

14) pp 1304 (L 26): Equilibrium concentration of N₂O was added to Fig. 10 in order to support the argument that the enhanced N₂O supersaturation conditions coincided with the onset of equatorial upwelling. In this case the good correlation between SST and N₂O concentration in surface water is taken as an indicator of upwelling since production processes on the area take place mostly at depth and therefore the only feasible process to explain such supersaturations is the physical displacement of sub-surface waters which are advected to the near surface during upwelling.

15) Summary and conclusions: The major points discussed earlier have been accordingly considered on this section.

Kind regards,

The authors

Interactive comment on Ocean Sci. Discuss., 10, 1281, 2013.

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