Ocean Sci. Discuss., 10, C490–C494, 2013
www.ocean-sci-discuss.net/10/C490/2013/

Ocean Science
Discussions

Interactive comment on "A new method for continuous measurements of oceanic and atmospheric N_2O, CO and CO_2: performance of off-axis integrated cavity output spectroscopy (OA-ICOS) coupled to non-dispersive infrared detection (NDIR)" *by* D. L. Arévalo-Martínez et al.

Anonymous Referee #1

Received and published: 20 September 2013

The paper by Arévalo-Martínez et al. presents a new analytical set-up for the simultaneous measurement of fCO2, N2O and CO in surface waters. Though the combination of an open equilibrator with an oa-ICOS instrument is not new, the system design in this configuration has not been described before, and performance of both optical instrument and integrated system has been thoughtfully tested in the lab and in the field. At the end of the paper, some nice data from the Atlantic upwelling system are shown, and this is at the moment hidden both with respect to the title as well as with respect

to the structure of the paper. The paper is well written and a nice read, and should be published in Ocean Sci. with some modifications.

That said, I have two main issues with the paper which should be addressed before the paper should be published in its final form, which I state before the line by line suggestions and remarks following behind.

1.) I cannot understand the mere statement of a good agreement between the N2O measurements from discrete sampling and the equilibration system, despite a reasonable linear correlation, given discrepancies of more than 1 nmol/L in quite a No of cases. The authors quote these differences to be a result of large gradients, but I have difficulties to follow this interpretation. So despite the nice linear correlation, this needs an in depth discussion. Also, for the discrete sampling method, the use of 3 replicates should allow to put an error bar on the data (in one direction).

2.) Based on the data shown, it is not really possible to judge the accuracy of the CO measurement, and this should not be hidden. As pointed out at some place in the text, the by far lower solubility of CO compared to N2O and CO2 does not only affect the response time, but also makes the measurement way more sensitive to contamination (i.e. Johnson, 1999). Given that the equilibrator design is an open system with permanent water vapor withdrawal and even without the use of a help equilibrator, a demonstration of the accuracy of the system for CO has to be performed before these data are interpreted (in terms of absolute values, see also Fig. 11). However, this should not impede the publication in Ocean Sciences, but rather encourage the authors to state remaining problems.

Line by line

Intro:

- a little redundancy between functional description of oa-ICOS in the introduction and in the first paragraphs of 2.1, which could be avoided.

- Referencing in 1284-line 28; should also cite Gülzow et al 2013 showing the potential of long term VOS-based measurements using the technique, as well as the Paper by Grefe and Kaiser, currently also under discussion in Ocean Sci., about one month ahead (this might even better be handled in a paragraph in the discussion (Grefe and Kaiser, Ocean Sci. Discuss., 10, 1031-1065, 2013, www.ocean-sci-discuss.net/10/1031/2013/, doi:10.5194/osd- 10-1031-2013).

2.1 Instrumentation: - 1287 line 1 and 1289, line 17 Gas flow. In these lines, a gas flow of 235 ml/min and "ca. 200 ml/min" is quoted. As the gas flow in the set up appears to be completely maintained by the DLT 100 internal pump, they should match, and only one can be correct.

- 1289 line 27: the authors should state the remaining water pressure, at the end of the drying procedure

- 1293 the mathematical background linking response time so solubility is explicitly given in Schneider et al. 2007 or Gülzow et al, 2011, and it would be worth to cite one of them in the context.

4. At sea tests 1298 – line 9: state year and duration of the expeditions Paragraph 1299 17ff: I think the method has been described by members of the group before (Walter et al., 2006???, also stated later). If so, the ref. is missing here, and the description of N20 discrete sample analysis could be shortened. If the method deviates from earlier descriptions, this should be explicitly stated.

1301 Equation 9 – there is (at least) a parenthesis missing. The way it is formulated now, the term is negative (as long as xCO x Pa < Pw); also, I think the description of alpha and the formulation in line 18 are incorrect (oswald solubility equals Bunsen solubilty x a T-ratio???). Please check.

1302 despite a nice linear regression, I think at least for the N2O measurements, the mere statement of a good agreement needs some further discussion of the data shown

in Fig 8a. Surface concentrations do not vary that rapidly for N2O (as seen in Fig 10), yet the data scatter considerably, with more than a nmol/L differences. Also, the use of triplicates should allow putting an error estimate o the discrete samples – please do so. Given the claimed accuracy and precision of both methods, they do not match in a way expected. Please discuss.

1304, Line11 ff The paper should have a new chapter here, with a header describing the content (e.g. surface water trace gas measurements in the equatorial upwelling system (or so), as the following text is not addressing "At-sea-tests" issues any more, but rather a short discussion on the findings in terms of marine sciences.

1304 lines 26 ff. There is a flaw in the argumentation. The fact that the drop in T goes ahead with an increase in the N2O concentration does not necessarily lead to the conclusion of upwelling-induced oversaturation, as the solubility also increases. I do not doubt the statement, but the argumentation is not precise. I suggest adding a line with the equilibrium concentrations relative to the atmospheric partial pressure in plots 10ab, as this would allow seeing the concentrations and the excess concentration (i.e. the difference between measured concentration and equilibrium concentration), which is directly related to oversaturation.

1305 lines 19ff I have to admit that I have strong problems to assess the quality of the CO data. As quoted in the text before, CO measurements by the technique are VERY sensitive to leakage because of the low solubility. The system design constantly removes water from the air stream due to the drying procedure. This might be partly compensated by warming between intake and equilibration system, but the average Delta T is not handled. So the authors should be frank enough to quote that at the moment, they cannot judge the accuracy of the CO-line of the instrument.

5.) Summary and conclusions

1306 lines 23-25 I suggest to remove the second part of the sentence .., although the speed . . ." . The time resolution is clearly stated, and yes, this might be sufficient for some processes, but not for others.

1306 Line 22 Again, please extend discussion on the match – or mismatch, of the discrete vs continuous N2O and then – if needed – rephrase. I cannot fully understand the large – individual – differences reflected in the scatter in Fig. 8a.

1307 line 26 and 1308 line 11 and 12: again, please reconsider what you know about accuracy and precision of the CO-measurement, given the finding by Johnson 1999 and your own statement at the end of chapter 2.3. You cannot judge from the performance of the two other gases with a solubility that is larger by more than an order of magnitude. Be frank about it.

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