

Response to interactive comment of anonymous Referee #3 on “Comparison of continuous atmospheric CH₄, CO₂ and N₂O measurements – results of InGOS travelling instrument campaign at Mace Head”

We wish to thank this reviewer for his/her helpful comments and suggestions for changes of our manuscript; our replies and respective changes in the revised manuscript are described below.

General comments

This study examines the differences in measurements of atmospheric CO₂, CH₄ and N₂O between two stations, Mace Head and Heidelberg, relative to a Travelling Comparison Instrument (TCI). High precision measurements of atmospheric constituents, specifically greenhouse gases, are essential for monitoring emissions from human activities as well as changes in biogenic sources and sinks. Achieving the required levels of repeatability and inter-comparability between measurements, stations and networks is a challenge and the TCI is an important tool to meet this challenge. The manuscript is scientifically sound and well written. However, it is a very technical paper and does not present a lot of original research. In any case, I think it provides useful information for data-users and, therefore, I recommend the paper for publication after minor revisions.

Response

We agree that our paper is essentially a technical one, but we nevertheless felt that submitting it to ACPD would help to increase its visibility to data users and modellers, making them aware of the potential problems in compatibility of CH₄, CO₂ and N₂O records from different stations and networks (such as AGAGE and NOAA).

Specific comments

P10431, L2: A gradient between 10 and 25 m asl would rather reflect local emissions rather than regional ones, therefore, suggest changing “regional” to “local”.

Response

Agreed, will be changed to “local”.

P10434, L11-14: The authors state that one working standard is used for calibration. A one-point measurement can only correct for instrumental drift. So, I presume that the GC was calibrated using a suite of working standards and that this was repeated at regular intervals to account for any changes in the detectors etc. This should be mentioned. Also, for N₂O, the FID response is not linear so at least 3-points are needed for the calibration. In general, I suggest the authors mention how the instruments were calibrated and how often this calibration was repeated. The instrument calibration may be a source of error for e.g. in N₂O at MHD, which was found to differ from the TCI by about -0.4 ppb for both working standard and ambient measurements.

Response

One working standard, which is measured alternately with ambient air or other samples, is used for the on-site calibration at Mace Head (and Heidelberg).

At Mace Head, the whole air standard lasts for approximately eight months and is analysed at Scripps Institute of Oceanography before and after use at Mace Head. For details, see Prinn et al. (2000). Using whole air standards in which the N₂O concentration is close to the ambient concentration minimises the error due to changes of the nonlinearity of the ECD response. New calibration gases are always compared on-site with the old calibration gases. This comparison agrees well with the values assigned to both tanks at the calibration lab at Scripps Institution of Oceanography on a different instrument, but applying the same nonlinearity correction. For more than ten years, weekly pressure-programmed injections of the standard were used at Mace Head to determine the nonlinearity of the ECD response. It was also compared to nonlinearities measured using primary gases spanning a range of concentrations. The only compounds that had any significant non-linearity were CFC-11 and N₂O, with a very small non-linearity for CH₃CCl₃. For these compounds it was found that the non-linearity between instruments were remarkably consistent and stable, especially over the small range of concentrations measured. This is plausible because all the instruments are identical (same generation) and operated under virtually identical conditions. In addition, the pressure-programmed non-linearity, while measuring the true non-linearity, also introduced occasional artifacts due to the variable amount of air being injected. These artifacts needed to be corrected for, and it was realized that applying the pressure-programmed non-linearity directly was not a benefit compared with applying a fixed nonlinearity for these three compounds. From May 2009 onwards, the nonlinearity tests were discontinued at Mace Head, as it was found the shape of the nonlinearity curve did not change significantly over time.

In Heidelberg we check the non-linearity of the ECD regularly with our primary standards calibrated at the WMO CCL (NOAA) and spanning a range of 306 to 343 nmole mole⁻¹.

We will add additional information about the calibration, as well as about the non-linearity correction of the ECDs in the manuscript.

P10437: L4-8: The G1301 instrument samples “wet” air. Residual moisture in the gas-handling system for this instrument means that it may take longer for a stable value to be reached for CO₂ due to absorption/desorption effects. Did the authors check for this instrument whether or not stable values were reached for CO₂ when switching to the working standard?

Response

Stable values have been reached during the measurement after 10 minutes. Target and standard tanks were measured for 20 minutes, and the last 10 minutes of measurements were averaged to determine their mole fractions. We will add this information in a revised manuscript.

P10437: Related to the above comment, I think it would be helpful to state what the water correction used for the G1301 instrument and the precision of the water measurement. Could errors in the water correction explain the difference between the TCI and G1301?

Response

We used the correction described in detail by Chen et al. (2010) for both CRDS instruments. The water dependency of the wet CRDS system (G1301) was tested at LSCE prior to installation at Mace Head station and was found to be properly described by the water correction provided by Chen et al. (2010).

To ensure the correctness of the water correction we have now again compared the CO₂ differences of the wet (G1301) and dry (G2301) CRDS systems from March 2013 until July 2013. Both CRDS instruments showed a mean CO₂ difference of about $0.02 \pm 0.10 \mu\text{mol mol}^{-1}$. The difference is weakly correlated to absolute humidity (slope: $0.13 \mu\text{mol mol}^{-1} \text{CO}_2 / \% \text{ absolute humidity}$). This can be seen in Fig. D1 for CO₂ (D1a) and CH₄ (D1b). Since the CRDS G2301 was always dried, the absolute humidity dependency is most likely due to the incomplete water correction of the G1301 instrument. The absolute humidity during the comparison period varied between 0.55 and 0.8% (see gray shaded area in Fig. D1). Thus, the incomplete water correction would explain about $0.01\text{-}0.04 \mu\text{mol mol}^{-1}$ higher CO₂ values of the G1301. However, this explains only less than 30% of the difference of $0.14 \mu\text{mol mol}^{-1}$, which was found during the comparison period between the TCI and the CRDC G1301.

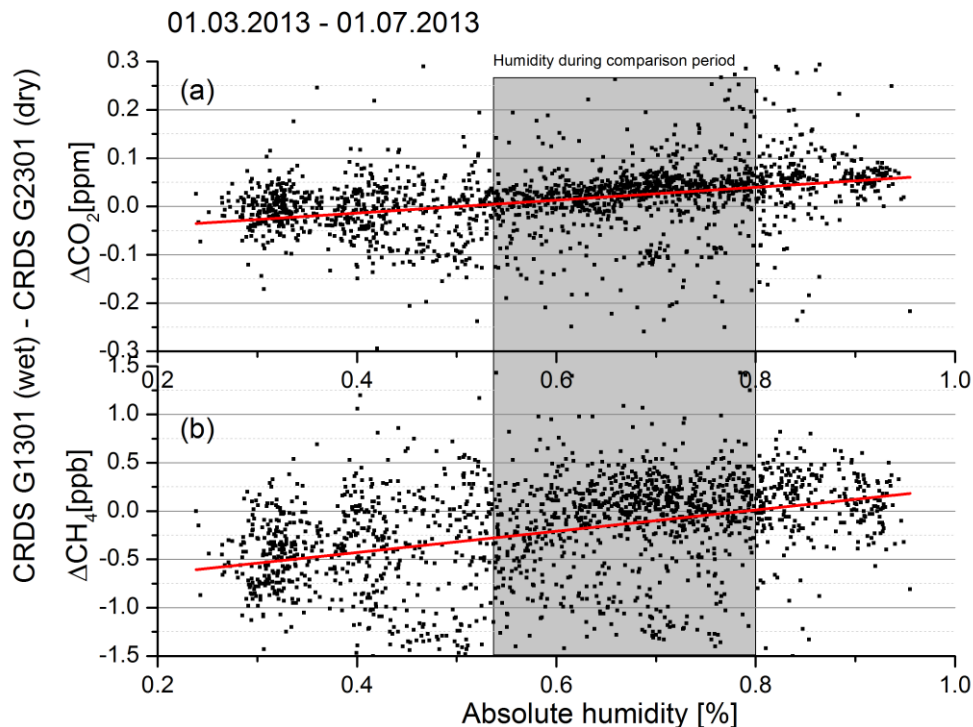


Fig. D1: Difference between the CRDS G1301 and CRDS G2301 instrument versus absolute humidity measured with the G1301 instrument.

We will add information on the uncertainty of the water correction to our revised manuscript.

P10448, L20: Do the authors mean only during the day or continuous i.e. over 24 h? Please clarify.

Response

The concentration gradient decreases from ca. $-1 \text{ nmol mol}^{-1} \text{ CH}_4$ during night time to $-0.5 \text{ nmol mol}^{-1}$ during day time (the TCI measurement at 10m height being always higher than the CRDS measurement at 25m height). This finding suggests that there is a positive CH_4 flux from the ground throughout the whole day (24hours). This point will also be clarified in the manuscript.

P10449, L4-7: I think it is extremely unlikely that an diurnal cycle in CO_2 would be observed from the ocean, considering that the change in pCO_2 in the surface layer is likely to be very small from marine photosynthesis/respiration and probably more dependent on ocean mixing. Much more likely, is that the air from the ocean sector also contains some continental signal.

Response

This is true, however, during this time of the year also surface ocean water may be largely undersaturated in CO_2 . Spring phytoplankton blooms are a large CO_2 sink in surface ocean water and lead to sea-air pCO_2 differences of up to $-160 \mu\text{atm}$ in the North Atlantic (Takahashi et al., 1993). Therefore, without additional information we will have to leave this point open.

Technical comments – we will correct all technical and typing errors in the revised manuscript.

P10431, L17: either remove “indeed” or change to “indeed been reached”

P10432, L8: “run in parallel with”

P10433, L5: I think ACP requests British spelling, thus “centre”

P10442: L1: Suggest “1-minute” and “3-minute”

P10447: L9-10: “flaks” -> “flasks”

P10448, L18: from -1 to -0.5 nmol/mol, the “gradient” decreases although the difference becomes more positive

P10448, L23-24: suggest changing this to “suggests only a very small or negligible CH_4 flux...” and removing “if at all significant”

P10448, L27: Again, the “gradient” has decreased (the absolute difference is smaller in the daytime) which is to be expected as the vertical mixing is stronger.

P10449, L19: “assess”

P10451, L5: “has not yet been successfully transposed” transposed is not the write word here, suggest changing to: “this has not yet transpired”

References:

Chen, H., Winderlich, J., Gerbig, C., Hofer, A., Rella, C. W., Crosson, E. R., Van Pelt, A. D., Steinbach, J., Kolle, O., Beck, V., Daube, B. C., Gottlieb, E. W., Chow, V. Y., Santoni, G. W., and Wofsy, S. C.: High-accuracy continuous airborne measurements of greenhouse gases (CO₂ and CH₄) using the cavity ring-down spectroscopy (CRDS) technique, *Atmos. Meas. Tech.*, 3, 375-386, 2010.

Prinn, R. G., Weiss, R.F., Fraser, P.J., Simmonds, P.G., Cunnold, D.M., Alyea, F.N., O'Doherty, S., Salameh, P., Miller, B.R., Huang, J., Wang, R.H.J., Hartley, C., Steele, L.P., Sturrock, G., Midgley, P.M. and McCulloch, A.: A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE. *J. Geophys. Res.*, Vol. 105, No. D14, p. 17,751-17,792, 2000.

Takahashi, T., J. Olafsson, J. G. Goddard, D. W. Chipman, *and* S. C. Sutherland (1993), Seasonal variation of CO₂ and nutrients in the high-latitude surface oceans: A comparative study, *Global Biogeochem. Cycles*, 7(4), 843–878, [doi:10.1029/93GB02263](https://doi.org/10.1029/93GB02263).