Response to interactive comment of anonymous Referee #3 on "Comparison of continuous atmospheric CH_4, CO_2 and N_2O 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 CH_4, CO_2 and N_2O 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 N_2O 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 regulary 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 CO$_2$ differences of the wet (G1301) and dry (G2301) CRDS systems from March 2013 until July 2013. Both CRDS instruments showed a mean CO$_2$ difference of about 0.02 ± 0.10 μmol mol^{-1}. The difference is weakly correlated to absolute humidity (slope: 0.13 μmol mol^{-1} CO$_2$ /% absolute humidity). This can be seen in Fig. D1 for CO$_2$ (D1a) and CH$_4$ (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 0.01-0.04 μmol mol^{-1} higher CO$_2$ values of the G1301. However, this explains only less than 30% of the difference of 0.14 μmol mol^{-1}, which was found during the comparison period between the TCI and the CRDC G1301.

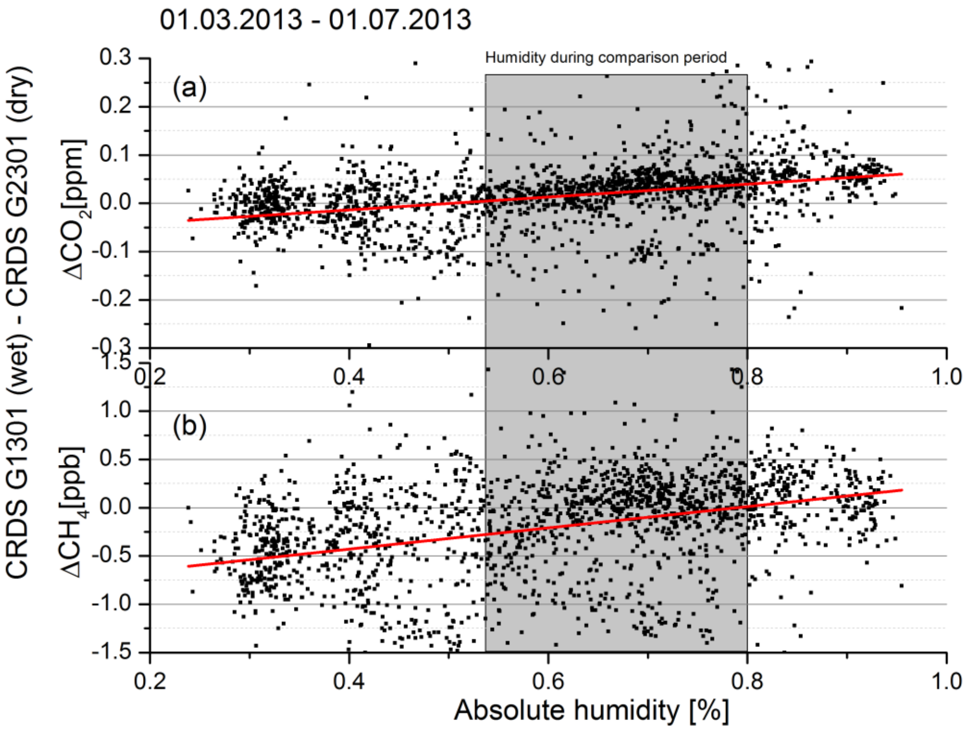

Fig. D1: Difference between the CRDS G1301 and CRDS G2301 instrument versus absolute humidity measured with the G1301 instrument.

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 nmol mol^{-1} CH_4 during night time to −0.5 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 CO2 would be observed from the ocean, considering that the change in pCO2 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 µatm in the North Atlantic (Takahaschi 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 CH4 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., Hoefer, 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 (CO_2 and CH_4) 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 radiatevely 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*.*

Response to interactive comment of anonymous Referee #2 on "Comparison of continuous atmospheric CH_4, CO_2 and N_2O measurements – results of InGOS travelling instrument campaign at Mace Head"

We wish to thank this referee for his/her effort to review our manuscript and give our reply below.

This paper describes results from a measurement campaign to evaluate the compatibility of station measurements of CH4, CO2, and N2O. The transfer standard instrument used was a FTIR that was also compared with standard samples and GC measurements comparable to those used in the station network. The work is high quality and the paper is well written and organized. The paper is a technical paper and it is borderline whether the paper is appropriate for publication in ACP. A better journal choice would probably have been AMT (many of the previous papers from this group and on this subject have been published in AMT). I recommend that the paper be accepted in ACP, but that for further articles on this subject that the authors submit to another more appropriate journal.

Response

As noted in our reply to referee 3, 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 modelers, i.e. making them aware of the potential problems in compatibility of CH_4, CO_2 and N_2O records from different stations or networks (such as AGAGE and NOAA).

Response to interactive comment of anonymous Referee #1 on “Comparison of continuous atmospheric CH_4, CO_2 and N_2O 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 are described below.

The submitted manuscript presents results from a two-month parallel on-site comparison of greenhouse gases observations with gas chromatography, cavity ringdown spectroscopy and Fourier Transform Infrared Spectrometry at Mace Head, Ireland. In particular, it reveals that novel spectrometric measurement techniques (such as the fourier transform infrared spectrometer used here) are suitable for quality control of continuous observations through short (in the order of a few weeks) side-by-side measurement campaigns in the field as the novel techniques are transportable, easily deployable, robust and are sufficiently precise to also detect small systematic differences in the range of the WMO/GAW compatibility goals.
The paper is scientifically sound, well written, and clearly structured and deserves to be published in ACP even if I agree with reviewer #2 that it is a conceptual paper that would have also fit (maybe even better there) in AMT. Moreover, I have a few comments that should be addressed prior to publication in ACP.

It should be clearly stated that the present approach, analysis and structure of the manuscript is very similar to the work of Hammer et al., 2013 (Atmos. Meas. Tech., 6, 1201–1216, 2013), but that it is applied to another measurement site, longer time series and also to N2O in addition to CO2 and CH4.

Response
This is correct and we will make a respective statement now explicitly at the beginning of chapter 2.

The authors should carefully check the manuscript with respect to the use of acronyms. Some are most likely unnecessary, some are introduced several times (e.g. ILC twice in the abstract), some aren’t at all (e.g. AGAGE, ICOS, HATS, CCGG) or at least not at first use (e.g. GC-MD). InGOS is introduced first in chapter 3.1 even if this acronym is even part of the title. I suggest to reduce the use of acronyms in particular in the abstract to a minimum and to introduce all acronyms at first use in the main text body even if it was already introduced in the abstract (e.g. ILC, page 10431, line 17).

Response
We will remove unhelpful acronyms in the abstract and introduce all acronyms at first use (and if occurring in the abstract, again in the main text body).

Is it of importance in the title that it is an InGOS travelling analyser? I suggest removing InGOS in the title.

Response
Yes, indeed this is not important and we will remove InGOS in the title (and abstract).

Page 10430, line 25: Remove citation (WMO, 2009) since it isn't common to use references in the abstract. The same statement with the same reference is once more made in the introduction.

Response
We will remove this reference in the abstract.

Page 10431, lines 20-21: add Rella et al. (Atmos. Meas. Tech., 6, 837–860, 2013) that also shows side-by-side results of a travelling instrument.

Response
We will add this reference.

Chapter 2.1: why don't you mention the manufacturer of the FTIR? what is the sample and recording rate of the FTIR?

Response
We will include the manufacturer (i.e. University Wollongong) in the Introduction and add the recording rate of the FTIR in Sec. 2.1.

Page 10433, line 2: "medium-size city", be more precise.

Response
We will add the number of inhabitants (about 150,000).

Page 10443, line 16: add Dlugokencky et al. (JGR, VOL. 110, D18306, doi:10.1029/2005JD006035, 2005) as reference.

Response
All scales are cited explicitly in Sec 2.1 of the manuscript, such as the above mentioned. Nevertheless, Dlugogencky et al., (2005) have also found small differences between both scales. So we agree that we should cite this paper also here.

Page 10435, line 3: The water correction parameters from Chen et al. (2010) were used for both Picarro analysers. It was shown that the parameters can slightly vary from instrument to instrument (see e.g. Rella et al. (Atmos. Meas. Tech., 6, 837– 860, 2013)). Have the parameters used been experimentally verified? See also the comment to paragraph 4.3 below.

Response
As noted in our reply to referee 3, we indeed 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 described properly by the water correction provided by Chen et al. (2010). To confirm the correctness of the water correction we have now again compared the CO_2 differences of the wet (G1301) and dry (G2301) CRDS systems from March 2013 until July 2013. Both CRDS instruments showed a mean CO_2 difference of about 0.02 ± 0.10 µmol mol^{-1}. The difference is weakly correlated to absolute humidity (slope: 0.13 µmol mol^{-1} CO_2 /% absolute humidity). This can be seen in Fig. D1 for CO_2 (D1a) and CH_4 (D1b) in the reply to referee 3. Since the CRDS G2301 was always measuring dried air, 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 0.01-0.04 µmol mol^{-1} higher CO_2 values of the G1301. However, this explains only less than 30% of the difference of 0.14 µmol mol^{-1}, which was found during the comparison period between the TCI and the CRDC G1301.

Chapter 2.3: what are the sample and recording rates of the Picarro analysers? Which aggregates were used for the intercomparisons?

Response

The measurement frequency of the Picarro CRDSs is 0.2Hz (concentration updated every 5s in the data files) and the sample flow rate is about 0.3 slpm at about 1 bar absolute pressure. For the comparison we used hourly aggregates since the data is computed and stored like this in the common database. This information will be added in the manuscript.

Page 10437, lines 8 ff: is there any idea what could have happened?

Response

Unfortunately we don’t have any idea. It cannot be due to a calibration issue since both cylinders use the same working standards for calibration and stable values have been reached during the standard gas measurements for both instruments.

Paragraph 3.3, Fig. 3: mention explicitly that different cylinders with different mole

Response

We will mention this in a revised manuscript.

Paragraph 3.4.2: no buffer volumes were used at Mace Head?

Response

This is correct and will be mentioned in a revised manuscript.

Page 10442, line 1: do I understand it correctly that the FTIR records 3-min averages and CRDS data are stored as 1-min means?

Response

This is correct, but we compare here hourly averages of both instruments.

Paragraph 4.3: As mentioned above, the water correction parameters published by Chen et al. are based on tests with one single G1301 analyser. Is it possible that the observed differences of the CO2 (dry air) mole fractions determined with the two Picarro analysers can be caused by some improper humidity corrections? Standard and target gases are dry, thus, this could also explain why no systematic difference was observed for the measurements of the cylinders.

Response

With the information about the water correction given above, we would argue that the effect of the incomplete water correction does not exceed 0.04 µmol mol^{-1} CO_2 during the comparison period. It definetly does not explain the majority of the difference between the G1301 and the TCI instrument. We will make a comment on the effect of a possibly incomplete humidity correction in the revised manuscript.

Page 10447, first paragraph: the authors could also consult the paper by Corazza et al. (Atmos. Chem. Phys., 11, 2381–2398, 2011) that retrieved bias corrections (in comparison to NOAA flasks) from different European stations based on inverse modelling.

Response

Ambient air differences in 2006 (as given in the paper by Corazza et al., 2011) have been significantly different to those we observed in 2013. Nevertheless, Corazza et al., 2011 indicate how important the assessment of biases between stations/networks is.

Page 10447, lines 9 and 10: correct the typo “flaks” (twice).

Response

Will be done in a revised manuscript.

Chapter 5: To my mind, this chapter doesn’t really fit into this paper. Either skip it or elaborate.

Response

Principally, the referee is correct with this statement. However, in this section we wanted to emphasise that the precision of our measurements is excellent with this new instrumentation, but as long as we are not able to overcome biases in calibration and achieve a high compatibility between instruments, we will not be able to fully use this excellent instrumentation. We agree that Sec. 5 seemingly does not fit to the rest of the paper, which is more technical. In order not to disturb the clear structure of the paper, but nevertheless emphasize our statement, we will move this section into an Appendix.

E.g. Page 10448, line 24: add reference for CH4 emissions from the ocean.

Response

Supersaturation of CH_4 in the ocean mixed layer potentially leading to a CH_4 flux from the ocean to the atmosphere has been observed, but the mechanisms are not fully understood yet (Bakker et al., 2014). We will also include this reference in the manuscript.

Add references to flux observations at Mace Head (if available). If flux strengths are available, do the observed gradients correspond to what is expected? Can you calculate fluxes out of the gradients?

Response

Principally,yes, however, it is not within the scope of this paper to present a flux estimate. For ^{222}Radon-based flux estimates we would need to make assumptions about the temporal and spatial homogeneity of ^{222}Rn fluxes and secondly we have not measured ^{222}Rn at both heights. Nevertheless, we want to show that it principally is feasible to detect very small CO_2 or CH_4 gradients with the new optical instruments.

Page 10450, line 24: one week seems to be definitely on the short side.

Response

The gradient was measured over the course of two months. During this time the FTIR was measuring at 10 m a.g.l. and the CRDS system at 25 m a.g.l. Both instruments were measuring at the same height for one week.

Page 10450, lines 27 ff.: skip the part with the bureaucratic regulations. Such issues shouldn't be a determining factor.

Response

We will skip this part.

One thing that wasn't mentioned at all and that I suppose that can be crucial for a best possible comparison result is the perfect match of the time series taking exactly into account the residence times in the individual inlet lines etc. This is only possible if you compare two high time resolution analysers that allow shifting the time series even only by a few seconds before calculating higher aggregates. Table 1 and Figs. 4 to 7: which aggregates were compared and shown?

Response

It was stated before (p.10442 line 1) that one minutely CRDS data was compared with three-minutely TCI data, but these were not shown here. No asynchrony was detected in this comparison. The results in Table 1 and Fig. 4-7 are the comparison of hourly data from the CRDS and the FTIR.

Figure captions Fig. 4 and 6: figure captions says “concentration” while the y-axis labels says “mole fraction”. Mole fraction is right. Please correct.

Response
This will be corrected in the revised manuscript.

Do you really need Fig. 5?

Response

We want to show how well both instruments agreed in Heidelberg and how the distribution of differences looked like. We think the Heidelberg comparison campaign is just as important as the Mace Head campaign, as this gives best confidence into the TCI setup as a whole.

References

Bakker, D.C.E., Bange, H.W., Gruber, N., Johannessen, T., Upstill-Goddard, R.C., Borges, A.V., Delille, B., Löscher, C.R., Naqvi, S.W.A.,Omar, A.M., Santana-Casiano, J. M.: Air-Sea Interactions of Natural Long-Lived Greenhouse Gases (CO_2, N_2O, CH_4) in a Changing Climate. In: Liss, P.S. and Johnson, M.T. (eds.) Ocean-atmnopsheric interactions of gases and particles. Springer Verlag. 315 pp. doi:10.1007/978-3-642-25643-1, 2014.

Chen, H., Winderlich, J., Gerbig, C., Hoefer, 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 (CO_2 and CH_4) using the cavity ring-down spectroscopy (CRDS) technique, Atmos. Meas. Tech., 3, 375-386, 2010.

Corazza, M., Bergamaschi, P., Vermeulen, A. T., Aalto, T., Haszpra, L., Meinhardt, F., O'Doherty, S., Thompson, R., Moncrieff, J., Popa, E., Steinbacher, M., Jordan, A., Dlugokencky, E., Brühl, C., Krol, M., and Dentener, F.: Inverse modelling of European N_2O emissions: assimilating observations from different networks, Atmos. Chem. Phys., 11, 2381-2398, doi:10.5194/acp-11-2381-2011, 2011.

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Hammer, S., Konrad, G., Vermeulen, A. T., Laurent, O., Delmotte, M., Jordan, A., Hazan, L., Conil, S., and Levin, I.: Feasibility study of using a "travelling" CO_2 and CH_4 instrument to validate continuous in-situ measurement stations, Atmos. Meas. Tech. 6, 1201-1216, doi:10.5194/amt-6-1201-2013, 2013a.

List of relevant changes made in the manuscript:

Title and Abstract:

- Removed acronym in title

1. Introduction

- Added manufacturer of FTIR in the Introduction
- Added explanation/motivation of appendix at the end of the Introduction

2. Methods, site description and instrumentation

- Emphasized the similarities and differences to Hammer et al. 2013a
- Added information about the GC-MD calibration and non-linearity correction of the ECD
- Added information on the water vapour correction and on the magnitude of an incomplete water vapour correction in the CO_2 difference between the G1301 and the TCI
- Added information concerning the measurement interval and flow rates of the CRDSs

3. Experimental results

- Only minor or technical corrections

4. Discussion of differences in ambient air measurements

- Added discussion of incomplete water vapour correction

5. Vertical mole fraction gradients of CH_4 and CO_2 at Mace Head

- This chapter was moved to the Appendix
- Supersaturation of CH_4 in the ocean mixed layer was mentioned as possible reason for a positive CH4 flux