Comparisons of continuous atmospheric CH_4, CO_2 and N_2O measurements – results from a travelling instrument campaign at Mace Head

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Abstract

A two-month measurement campaign with a Fourier Transform InfraRed analyser as a Travelling Comparison Instrument (TCI) was performed at the Advanced Global Atmospheric Gases Experiment (AGAGE) and World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) station Mace Head, Ireland. The aim was to evaluate the compatibility of atmospheric methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O) measurements of the routine station instrumentation, consisting of a gas chromatograph (GC) for CH_4 and N_2O as well as a Cavity Ring-Down Spectroscopy (CRDS) system for CH_4 and CO_2. The advantage of a TCI approach for quality control is that the comparison covers the entire ambient air measurement system, including the sample intake system and the data evaluation process. For initial quality and performance control the TCI was run in parallel with the Heidelberg GC before and after the measurement campaign at Mace Head. Median differences between the Heidelberg GC and the TCI were well within the WMO Inter

Laboratory Compatibility target for all three greenhouse gases. At Mace Head, the median difference between the station GC and the TCI were -0.04 nmol mol^{-1} for CH_4 and -0.37 nmol mol^{-1} for N_2O (GC-TCI). For N_2O a similar difference (-0.40 nmol mol^{-1}) was found when measuring surveillance or working gas cylinders with both instruments. This suggests that the difference observed in ambient air originates from a calibration offset that could partly be due to a difference between the WMO N_2O X2006a scale used for the TCI and the Scripps Institution of Oceanography (SIO-1998) scale used at Mace Head and in the whole AGAGE network. Median differences between the CRDS G1301 and the TCI at Mace Head were 0.12 nmol mol^{-1} for CH_4 and 0.14 µmol mol^{-1} for CO_2 (CRDS G1301 – TCI). The difference between both instruments for CO_2 could not be explained, as direct measurements of calibration gases show no such difference. The CH_4 differences between the TCI, the GC and the CRDS G1301 at Mace Head are much smaller than the WMO Inter Laboratory Compatibility target, while this is not the case for CO_2 and N_2O.

1   Introduction

Since the industrial revolution the global abundances of the long-lived greenhouse gases carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) have been rising in the atmosphere, causing an anthropogenic greenhouse effect. However, estimates of their global and regional sources and sinks are still associated with large uncertainties (Schulze *et al.,* 2009). In order to monitor the temporal and spatial changes of the greenhouse gases and gain from this quantitative information about the fluxes and their variability using inverse modelling approaches, precise and compatible measurements in the atmosphere are required. Based on the size of atmospheric gradients and variability of the different greenhouse gases, the World Meteorological Organization (WMO) experts have set Inter Laboratory Compatibility (ILC) targets for each individual greenhouse gas species (WMO, 2009), required to allow merging data from different stations and networks for global and regional budget estimates.

In order to assure the quality and consistency of previous and future measurements it is, therefore, important to compare different measurement techniques and their results and check whether the ILC targets have indeed been reached. This has been done through a number of different international comparison exercises, such as analysis of round-robin cylinders (Zhou *et al.,* 2011), co-located flask sampling (Masarie *et al*., 2001) and recently also via in situ

comparison of co-located instruments (Zellweger *et al*., 2012; Hammer *et al.,* 2013a, Rella *et al.,* 2013). For a fully comprehensive quality control of continuous atmospheric measurements a Travelling Comparison Instrument (TCI) approach has proven to be most appropriate (Hammer *et al*., 2013a); this was also recognized at the 16th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT-2011).

Here we present the results of a measurement campaign at the World Meteorological Organization - Global Atmosphere Watch (GAW) and Advanced Global Atmospheric Gases Experiment (AGAGE) station Mace Head in the Republic of Ireland. A Fourier Transform Infrared Spectrometer (FTIR) was used as the travelling instrument, which was manufactured by the University of Wollongong, Australia, (Griffith et al., 2012) and is normally run at the Institut für Umweltphysik at Heidelberg University for routine ambient air measurements (Hammer *et al.,* 2013b). At Mace Head, it performed independent continuous ambient air measurements from March to May 2013, in parallel with the station gas chromatograph (GC-MD). N_2O and CH_4 mole fractions measured with the locally installed GC-MD system as well as CH_4 and CO_2 measurements performed by a Cavity Ring-Down Spectrometer (CRDS) were compared with those made with the travelling FTIR instrument. Before and after the campaign the TCI was run in parallel with the Heidelberg GC (GC-HEI) (Hammer, 2008) in order to check its performance and stability.

As most of the time the TCI was sampling air from the 10m level to obtain sufficient data for the GC-MD comparison, while the CRDS systems have their air intake at the 25m level, we used the opportunity of this comparison campaign to investigate the corresponding vertical gradients of CO_2 and CH_4 at Mace Head from March to April 2013. Co-located measurements of the TCI and the CRDS at the same height performed in May 2013 allowed us to correct the earlier data for any systematic offsets between both instruments. Very small but still significant vertical gradients could indeed be resolved; these data are presented here as an Appendix as they do not really fit into the context of the paper. Nevertheless, these results nicely illustrate how capable - in terms of precision - current optical instrumentation is. As our comparison study shows, the biggest challenge in fully exploiting this precision capability is now, making sure that these instruments also measure highly accurate and compatible.

2   Methods, site descriptions and instrumentation

2.1 The TCI and its calibration

For the comparison campaign at Mace Head we used the same in situ multi-species FTIR analyser as Hammer *et al.* (2013a), however extended it besides CO_2 and CH_4 also to N_2O. The FTIR is used since it turned out to be robust and compact and measures CO_2, CH_4, and N_2O continuously and simultaneously with a precision that allows it to meet all ILC targets for these species (Hammer *et al.,* 2013b). The reproducibility of the three minutely data recorded by the FTIR is generally better than $\pm$ 0.05 µmol mol^{-1} for CO_2, $\pm$ 0.25 nmol mol^{-1} for CH_4 and $\pm$ 0.05 nmol mol^{-1} for N_2O. Within the Integrated non-CO_2 Greenhouse Gas Observation System (InGOS) project the three working standards of the FTIR system were calibrated relative to WMO Central Calibration Laboratory (CCL) tertiary standards by the Max-Planck Institute for Biogeochemistry (MPI-BGC GasLab) in Jena, using CRDS for CH_4 and CO_2 and gas chromatography with electron-capture detection (GC-ECD) for N_2O. The scales in use were the WMO CO_2 X2007 scale (Tans *et al*., 2011), the WMO CH_4 X2004 scale (Dlugokencky *et al.,* 2005) and the WMO N_2O X2006a scale (Hall *et al.,* 2007).

2.2   Site description and routine instrumentation in Heidelberg

Heidelberg is a medium-size city (ca. 150,000 inhabitants) located in the densely populated Rhine-Neckar region (49°25'N, 8°43'E) in Germany. Routine ambient air measurements are made on the University campus at the Institut für Umweltphysik, located to the north-west of the Heidelberg city centre. On the roof of the institute's building (at ca. 30 m a.g.l.) air is drawn through a permanently flushed intake line (1/2" stainless steel) with a by-pass to the GC-HEI system, which measures CO_2, CH_4, N_2O, SF_6, CO and H_2 simultaneously at a maximum temporal resolution of 5 minutes. The GC-HEI and the TCI have independent drying systems (GC-HEI: cryogenic cooler at -45°C, TCI: Nafion dryer in counter-flow mode followed by $Mg(ClO_4)_2$) and sample pumps. The working gases for the GC-HEI system are calibrated on the WMO X2007 scale for CO_2, the WMO X2004 scale for CH_4 and the WMO X2006a scale for N_2O, based on Heidelberg tertiary standards calibrated at the WMO GAW CCL at National Oceanic and Atmospheric Administration (NOAA) in Boulder, U.S.A. These standards, with a N_2O range of 306 to 343 nmol mol^{-1}, are also used to check the non-linearity of the electron-capture detector (ECD) regularly. The reproducibility of the GC-HEI

1 measurements is ± 0.05 μmol mol^{-1} for CO_2, ± 2.4 nmol mol^{-1} for CH_4 and ± 0.1 nmol mol^{-1}

2 for N_2O. A detailed description of the entire GC-HEI system can be found in Hammer (2008).

3 To allow for better comparability between the continuous TCI measurements and the discrete

4 GC-HEI measurements, a buffer volume was installed in the GC-HEI sample intake line. The

5 buffer volume allows capturing and integrating the short-term mole fraction variations

6 between the discontinuous GC-HEI measurements. Details of the integration scheme of the

7 buffer can be found in Hammer *et al.* (2013a) while the standard operating conditions of the

8 TCI are described in Hammer *et al.* (2013b).

9 Normally the FTIR uses the same main air intake line as the GC-HEI (with a separate by-

10 pass, pump and drying system (Hammer *et al.,* 2013b)), but for the performance test before

11 the intercomparison campaign at Mace Head, a separate intake line was installed in

12 Heidelberg for the TCI.

13

2.3   Site description and routine instrumentation at Mace Head

15 The Mace Head station is located on the west coast of Ireland (53°20'N, 9°45'W) about 100 m

16 from the Atlantic shore. The station is operated by the National University of Ireland,

17 Galway, and is classed as a global background station within the WMO-GAW network. At

18 the station trace gas measurements are carried out by the University of Bristol (UK) and by

19 the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) Gif sur Yvette (F) as

20 part of the AGAGE (CH_4 and N_2O) (Prinn *et al*., 2000) and Integrated Carbon Observation

21 System (ICOS) Demonstration (CO_2 and CH_4) (http://www.icos-infrastructure.eu/) networks.

22 A description of the station can be found in Jennings *et al.* (2003). A gas chromatography

23 system with multiple detectors (GC-MD), including an ECD and a flame-ionization detector

24 (FID) is used to measure N_2O and CH_4, while a reduction gas analyser (RGA) measures CO

25 and H_2 within the AGAGE network. One working standard, which is measured alternately

26 with ambient air or other samples, is used for on-site calibration. These whole air standards

27 last for approximately eight months and are analysed at Scripps Institute of Oceanography

28 (SIO) before and after use at Mace Head, for details see Prinn et al. (2000). New working

29 standards are always compared on-site with the old working standards and agree well with the

30 values assigned at the SIO on a different instrument, but applying the same non-linearity

correction. For more than fifteen years weekly pressure-programmed injections of the standard were used to determine the non-linearity of the ECD response. It was also compared to non-linearities measured using primary gases spanning a range of concentrations. From May 2009 onwards, the non-linearity tests were discontinued, as it was found that the non-linearity between AGAGE instruments was remarkably consistent and stable, and because the pressure-programmed non-linearity tests also introduced occasional artifacts due to the variable amount of air being injected. The precision of the measurements is approximately 0.1 nmol mol^{-1} for N_2O and 1.5 nmol mol^{-1} for CH_4. The working gases for the GC-MD system are calibrated on the Tohoku University scale for CH_4 (Cunnold *et al.,* 2002) and the SIO-1998 scale for N_2O (Prinn *et al.,* 2000). The GC-MD intake line allows sampling of ambient air from a height of 10 m a.g.l. The ambient air is dried using a Nafion drier. A separate intake line (1/2" O.D. Synflex) was installed at the same height for ambient air intake of the TCI. This 10 m intake line of the TCI was used from March until the end of April 2013.

Further, two CRDS instruments are running at the Mace Head station which draw air from a height of 25 m a.g.l. One instrument is a Picarro G1301, which belongs to the Irish Environmental Protection Agency (EPA) and measures CO_2 and CH_4 in undried ambient air since May 2009. The second instrument, a Picarro G2301, belongs to the LSCE and dries the ambient air with a cryogenic water trap to a dew point of about -45°C before measuring CO_2 and CH_4. Each of the two instruments is equipped with a designated ambient air intake line (1/2" O.D. Synflex). Both instruments share the same calibration and target cylinders, connected via a multi-position valve, as well as the same measurement sequence (i.e. ambient measurements and calibration are performed at the same time interval). A water vapor correction according to Chen *et al.* (2010) is applied to both instruments. Even though the water vapour correction of the (wet) G1301 instrument was tested at LSCE before installation at Mace Head, we found a weak correlation between the difference of both CRDS instruments (G1301-G2301) and absolute humidity of 0.13 μmol mol^{-1} CO_2 /% H_2O for the period from March 2013 until July 2013. The H_2O-dependancy is most likely due to an incomplete water vapour correction of the G1301 instrument. During the comparison period, the absolute humidity varied between 0.55 and 0.8%, which could result in slightly increased CO_2 values of the G1301 instrument of 0.01-0.04 μmol mol^{-1} compared to the dry G2301 instrument. The calibration suite of the CRDS systems consists of four cylinders filled with synthetic gas mixture by Deuste Steininger (Mühlhausen, Germany). They were calibrated by the MPI-

BGC GasLab in Jena using CRDS. The two CRDS instruments are routinely calibrated once per month, according to a calibration sequence where each standard is measured four times for 20 minutes (the first ten minutes are not used to calculate the response function since they still incorporate a settling-in effect). The measurement interval is 5 s. The sample flow rate is about 0.3 slpm at about 1 bar absolute pressure. In this study we will use hourly aggregates for the intercomparison, since the data is computed and stored like this in the common database.

The CRDS analysers measure CO_2 and CH_4 with a precision of about 0.02 µmol mol^{-1} for CO_2 and 0.1 nmol mol^{-1} for CH_4 (Crosson, 2008). A common target cylinder is used for quality control purpose and is measured on both instruments every 11 hours. The (1σ)-reproducibility of the target cylinder measurement is about 0.02 µmol mol^{-1} for CO_2 and 0.21 nmol mol^{-1} for CH_4 for the G1301 from March to June 2013 and 0.03 µmol mol^{-1} for CO_2 and 0.33 nmol mol^{-1} for CH_4 for the G2301. For the last week of the measurement campaign the TCI intake was moved to a height of 25 m a.g.l. in order to compare TCI measurements directly with the measurements performed with the CRDS instruments. Due to a malfunctioning pump the G2301 was not measuring during this period. Therefore we present here only ambient air comparisons between the non-dried CRDS G1301 and the TCI. The ambient air measurements of both CRDS instruments agreed within 0.02 ± 0.10 µmol mol^{-1} for CO_2 and -0.20 ± 0.70 nmol mol^{-1} for CH_4 during the comparison campaign (from 1 March 2013 to 30 May 2013 with two interruptions).

3   Experimental results

3.1 Quality check of the travelling instrument in Heidelberg

To assure that the TCI meets the WMO compatibility requirements we studied precision, accuracy and compatibility (as defined in http://gaw.empa.ch/glossary/glossary.html) relative to the GC-HEI in Heidelberg before and after the measurement campaign. The reproducibility can be estimated by measuring a so-called target or surveillance gas every day under reproducible conditions, and the standard deviations of the target gas measurements are a good measure of the precision. It was 0.03 µmol mol^{-1} for CO_2, 0.16 nmol mol^{-1} for CH_4 and 0.05 nmol mol^{-1} for N_2O (see also Sect. 3.4.1 and 3.4.2) before as well as after the Mace Head campaign for the TCI. The accuracy of the measurements is determined by the closeness of agreement between the measured value and the accepted reference value (WMO, 2009). In

order to determine the accuracy of the TCI we measured the Heidelberg WMO CCL tertiary standards, which were calibrated by the WMO CCL at NOAA, Boulder (http://www.esrl.noaa.gov/gmd/ccl/). The differences between the TCI measured value (working standards calibrated in the framework of InGOS project by the MPI-BGC GasLab Jena) and the nominal WMO CCL values of these cylinders are smaller than the WMO ILC targets for all CH_4, CO_2 and N_2O measurements (see Figure 1). For CH_4 the mean difference (measured TCI value - WMO CCL value and standard error) of 0.04 ± 0.01 nmol mol^{-1} is negligible. For CO_2 in the ambient mole fraction range (380 - 480 µmol mol^{-1}) a difference of -0.03 ± 0.04 µmol mol^{-1} was observed, while the N_2O difference in the ambient range (325 – 338 nmol mol^{-1}) was -0.00 ± 0.03 nmol mol^{-1}. It can thus be confirmed that the accuracy of the TCI measurements meets the WMO ILC targets.

3.2 Comparison of direct target/standard gas measurements on different instruments

In order to check the calibration compatibility between different instruments in Heidelberg and at Mace Head, target and working standards were measured on all instruments directly. In Figure 2 the differences between the cylinder measurements with the local instrumentation and with the TCI are plotted. For the TCI working standards we plot the difference between the cylinder measurements with the local instrumentation and the assigned value (open symbols). For CH_4 and CO_2 all instruments compare well within the WMO ILC target. The GC-HEI and the TCI instruments agree very well with each other (-0.02 ± 0.04 µmol mol^{-1}, mean ± standard error) for CO_2. The G1301 CRDS instrument shows very good agreement with the TCI in CO_2 results (-0.01 ± 0.02 µmol mol^{-1}), while the G2301 results are consistently higher (0.05 ± 0.03 µmol mol^{-1}) than the CO_2 mole fraction determined using the TCI. Since both CRDS instruments are calibrated with the same cylinders, the difference between the CRDS instruments is remarkable. It is questionable if both CRDS instruments were functioning correctly during the direct measurements since the difference between the CRDS instruments was 0.06 µmol mol^{-1}, while it is was 0.02 µmol mol^{-1} during target and ambient air measurements (from 1 March 2013 until 31 May 2013). Nevertheless all differences of direct analyses lie within the WMO ILC target for the Northern hemisphere.

For N_2O the values obtained with the GC-HEI were higher than those obtained with the TCI (0.11 ± 0.05 nmol mol^{-1}). The reason for the difference between the GC-HEI and the TCI is

1 not clear. The N_2O cylinder measurements with the GC-MD show significantly lower values

2 than the TCI by -0.40 ± 0.06 nmol mol^{-1}. This is a rather large and unexpected offset between

3 the two instruments, since current known scale differences between SIO-1998 and WMO

4 X2006a are on the order of 0.03 to 0.05 nmol mol^{-1} (Hall *et al.*, 2007; pers. communication B.

5 Hall, 2013) and thus cannot explain the difference in the cylinder measurements found here.

6 We will discuss this point in Sect. 4 after having presented ambient air measurements of both

7 instruments.

8

3.3 Sample intake system (SIS) tests

10 Since the ambient air sample intake systems of the different instruments can possibly

11 introduce a bias into ambient air mole fraction measurements (Hammer *et al.,* 2013a), a

12 sample intake system (SIS) test was performed in Heidelberg as well as at Mace Head. For

13 this purpose a gas cylinder was connected via the respective intake line to the individual

14 instruments. The pressure on the low pressure side of the regulator was chosen such that the

15 pressure in the intake line was always very close to (but slightly higher than) ambient air

16 pressure. Then the cylinder gas was flushed through the entire intake system and the

17 measured results were compared to the direct measurements of the same cylinder. Figure 3

18 shows all results of these tests in Heidelberg and at Mace Head.

19

3.3.1 Sample intake system test in Heidelberg

21 A SIS test was performed in Heidelberg (Figure 3 a, c, e) on the independent intake lines of

22 the GC-HEI (green symbols) and the TCI (black symbols). The measurements of the SIS

23 cylinder on the TCI and the GC-HEI show similar differences as the direct cylinder

24 measurements (see Figure 2). For both instruments the measurements via the SIS agree with

25 the direct cylinder measurements within their measurement uncertainties. The differences

26 between the direct measurement and the measurement via the SIS of the TCI in Heidelberg (±

27 convolution of their reproducibility and their standard deviations during the SIS tests) was

28 SIS – direct = 0.1 ± 0.35 nmol mol^{-1} for CH_4, 0.03 ± 0.07 µmol mol^{-1} for CO_2 and 0.02 ± 0.07

29 nmol mol^{-1} for N_2O and for the GC-HEI it was SIS – direct = -0.65 ± 3.5 nmol mol^{-1} for CH_4,

30 0.03 ± 0.11 µmol mol^{-1} for CO_2 and 0.04 ± 0.11 nmol mol^{-1} for N_2O. These differences are

31 not significant.

3.3.2 Sample intake system test at Mace Head

For Mace Head one dedicated cylinder for the different SIS tests was available. This cylinder was different to the one used for the Heidelberg SIS test, but was first measured directly on the GC-HEI and the TCI in Heidelberg. At Mace Head a SIS test via the GC-MD 10 m sample intake line was performed first. Next, the cylinder was measured in parallel by the CRDS G1301, the CRDS G2301 and the TCI via their 25 m height intake lines followed by a TCI measurement through the 10 m height intake system. Prior to the SIS tests at 25 m and prior to the SIS test of the TCI at 10 m, the intake line was evacuated to a pressure of about 80 mbar. The cylinder was also measured directly on the TCI, the GC-MD, the CRDS G1301 and the CRDS G2301 at Mace Head and after return to Heidelberg (in March 2013) it was measured again on the GC-HEI system. All results are displayed in Figure 3 b, d, f. The comparison between the direct measurements before and after the campaign indicate a mole fraction change in the cylinder for CO_2 in the order of 0.1 μmol mol^{-1}. This change is observed by all instruments which measured the gas before and after the test. A significant mole fraction jump is seen between the SIS tests at 25 m and 10 m. Significant increases of CO_2 mole fraction in cylinders have often been observed in the laboratory, in particular when cylinders are emptied at high flow rates and below a pressure of 500 psi (Chen *et al.,* 2013). Since the SIS cylinder was emptied to a pressure of 300 psi, a mole fraction change in the SIS cylinder was not unexpected.

No significant mole fraction change was observed for CH_4, but for N_2O also a slight but not significant change of 0.1 nmol mol^{-1} is indicated by the GC-HEI (see Figure 3f). For CH_4 we found that the TCI and the CRDS systems showed no significant difference between direct measurements and measurements via the SIS. The GC-MD showed a large difference on the order of 3.7 ± 1.7 nmol mol^{-1} (difference ± convolution of the standard deviation during the SIS test and the reproducibility during the direct measurement), but no stable value could be reached during the SIS test for the GC-MD and the data points for the GC-MD SIS test for CH_4 and N_2O must be discarded (bracketed symbols in Figure 3). This is surprising since the residence time of the sample air in the intake line is less than a minute and an equilibrium should have been reached within the SIS test (duration of the 10 m SIS test was 2 hours). Therefore no SIS effect could be verified nor proven false for the GC-MD intake system during the SIS test. The TCI SIS test at 10 m showed a small, yet insignificant, SIS effect for

1   N_2O (0.07 ± 0.10 nmol mol^{-1}), which could, however, be also due to a small N_2O drift in the

2   cylinder mole fraction. For CO_2 the TCI and CRDS measurements show only small SIS

3   influence within their measurement uncertainties: TCI at 25 m: -0.01 ± 0.08 µmol mol^{-1}, TCI

4   at 10 m: 0.03 ± 0.08 µmol mol^{-1}, CRDS G1301: -0.07 ± 0.12 µmol mol^{-1} (SIS effect was

5   determined relative to the TCI measurements at 25 m and after the SIS test), CRDS G2301:

6   -0.02 ± 0.03 µmol mol^{-1} when taking into account the mole fraction jump after the SIS test at

7   the 25 m intake of about 0.1 µmol mol^{-1}.

8

9   3.4 Comparison of ambient air measurements

10   3.4.1 Comparison of ambient air measurements in Heidelberg

11   Ambient air comparisons were performed in Heidelberg before and after the measurement

12   campaign. For this purpose the TCI data was smoothed exponentially (τ=20 minutes) to make

13   them comparable to the GC-HEI measurements where an integration volume is installed.

14   Details of this so-called buffer system can be found in Hammer *et al.* (2013a).

15   The CH_4 measurements of the TCI and the GC-HEI (Figure 4 a,b) show a difference GC-HEI

16   – TCI of -0.25 ± 3.61 nmol mol^{-1} (median and interquartile range, see Figure 5) before the

17   campaign and a difference of -0.24 ± 2.43 nmol mol^{-1} after the campaign. In each

18   intercomparison period this difference was constant over time (see Figure 4b). The TCI target

19   measurements were stable during both comparison periods and showed a reproducibility of

20   0.16 nmol mol^{-1} (see Figure 4c).

21   All CO_2 measurements of the TCI in Heidelberg and the GC-HEI agree very well (see Figure

22   4 d, e). The difference (GC-HEI – TCI) between the instruments was nearly the same in both

23   intercomparison phases.

24   The N_2O measurements show a median difference of 0.03 ± 0.15 nmol mol^{-1} (GC-HEI – TCI)

25   during the first comparison period in February and a median difference of -0.02 ± 0.14 nmol

26   mol^{-1} in the second period in June 2013. The particular structure of the difference in ambient

27   air measurements between the TCI and the GC-HEI (decrease after 15 June, see Figure 4h) is

28   partly due to a respective structure of the TCI and GC-HEI measurement, which can be

29   detected in the N_2O target gas measurement of both instruments (see Figure 4i). The

30   reproducibility of the TCI in this last period was not worse than usual, showing that

31   unexplained drifts and long term variability occur and can be detected by the target cylinder

measurement. In addition, this example highlights that systematic variations, which are observed in the target gas measurements, are present at the same time in the ambient air measurement. Thus regular target gas measurements are essential as quality control measures and for a comprehensive uncertainty estimate of ambient air measurements.

Altogether the measurement results of the FTIR in Heidelberg (TCI) and the GC-HEI have shown very good agreement, meeting the WMO ILC targets. Due to its high precision the FTIR instrument is able to detect even small drifts in all components and is thus very well suited as travelling comparison instrument. This has been shown earlier for CO_2 and CH_4 by Hammer *et al.* (2013a), but is confirmed here, for the first time, also for N_2O.

3.4.2 Comparison of ambient air measurements at Mace Head

At Mace Head the TCI was connected to the intake line mounted at 10 m height from 6 March 2013 until 1 May 2013. Differences between the TCI and the GC-MD are shown in Figure 6 b & j and in Figure 7 (left panels). From 1 May 2013 until 7 May 2013 the intake line of the TCI was mounted at a height of 25 m. During the measurements in May at 25 m height the CRDS G2301 was not working and therefore only CRDS G1301 data are shown and compared here to the TCI (see Figure 6 c & g and Figure 7 right panels). The flushing flow of the TCI intake line was adjusted to the flow of the GC-MD (ca. 5.5 slpm), so that the same ambient air was analysed simultaneously in both instruments. But ambient air measurements of the GC-MD are always discrete with a temporal resolution of about 20 minutes and without a buffer volume, whereas the TCI measurements are continuous and smoothed due to the TCI cell volume of 3 liters flushed at 1 slpm. This should not introduce a bias into the averaged difference between both instruments, but the standard deviation of the distribution will be augmented slightly. The flushing flow of the TCI intake line was not adjusted to the flow of the CRDS G1301 (3.3 slpm) during the comparison period with the CRDS G1301. Further, the cavity volume of the CRDS is much smaller than that of the TCI. Therefore principally a slight temporal asynchrony can be introduced influencing the standard deviation of differences. But comparison of the 1-minute CRDS data with the 3-minute TCI data (not shown here) revealed that both instruments measured temporally synchronously throughout the comparison.

The CH_4 measurements of the TCI, the GC-MD and the CRDS G1301 compare very well with each other. All differences lie within the WMO ILC targets. It is obvious that the

scattering of the GC-MD is much larger than that of the CRDS (see Figure 7) which is due to the higher reproducibility uncertainty of the GC-MD. The TCI target measurements were stable during the entire measurement period and showed a reproducibility of $\pm$ 0.12 nmol mol^{-1}. No target gas was measured with the GC-MD.

The CO_2 measurements of the CRDS G1301 and the TCI show an offset (CRDS G1301 – TCI) of 0.14 $\pm$ 0.04 µmol mol^{-1} (median and IQR, see Figure 7 right panel). No CO_2 mole fraction dependence in the difference of both instruments was observed. The results of the ambient air measurements and the direct cylinder measurements do not agree with each other. This finding will be further discussed in Sect. 4.

For N_2O the ambient air measurements of the GC-MD and the TCI show a difference (GC-MD – TCI) of -0.37 $\pm$ 0.22 nmol mol^{-1} (median and IQR). A difference of -0.40 $\pm$ 0.06 nmol mol^{-1} (mean and standard error) was found for the direct cylinder gas comparison which is in very good agreement with the ambient air differences. The possible origin of the difference will also be discussed in Sect. 4.

4.   Discussion of differences in ambient air measurements

The differences of the ambient air and calibration gas measurements as well as the sample intake effects of all instruments are summarized in Table 1.

4.1 Comparisons in Heidelberg

For CH_4, CO_2 and N_2O the TCI and the GC-HEI ambient air measurements agreed within the WMO ILC targets before and after the measurement campaign. The compatibility between the GC-HEI and the TCI before and after the campaign at Mace Head, together with the stable TCI target gas record of CH_4, CO_2 and N_2O confirms the excellent performance of the TCI during the entire measurement campaign. Differences in CH_4, CO_2 and N_2O in direct cylinder measurements agreed within their uncertainties to differences in ambient air measurements. For N_2O, measurements with the GC-HEI were higher than with the TCI for direct cylinder analysis. This indicates that a TCI approach may potentially give more insight into differences between laboratories than direct cylinder measurement comparisons.

4.2 CH₄ comparison at Mace Head

At Mace Head we found that the CH_4 measurements of the three different instruments, the FTIR (TCI), CRDS and GC-MD, agree very well with each other to better than the WMO ILC target value of ± 2 nmol mol^{-1} (WMO, 2009). The GC-MD obtained nearly the same values in the ambient air comparisons as the TCI (Table 1). The CRDS showed slightly higher CH_4 mole fractions, whereas the GC-HEI showed slightly lower CH_4 mole fractions. The good agreement between the CH_4 measurements of the two different networks NOAA and AGAGE also confirms that the measurements on the WMO CH_4 X2004 and the Tohoku University scale are very well compatible (see also Dlugokencky et al., 2005).

4.3 CO₂ comparison at Mace Head

For CO_2 the difference in ambient air measurements at Mace Head between the TCI and the CRDS G1301 was 0.14 ± 0.04 µmol mol^{-1}. The working standards of the TCI as well as those of the CRDS G1301 have both been calibrated at the MPI-BGC GasLab in Jena (on the WMO X2007 scale). Therefore possible scale propagation errors from WMO CCL primary standards to tertiary standards are not relevant for the ambient CO_2 mole fraction differences. Only scale propagation errors from tertiary to working standards at the MPI-BGC GasLab may principally contribute to this difference. However, large scale transfer errors in the calibration of the TCI working standards seem unlikely since the difference between the assigned values of the Heidelberg WMO CCL tertiary cylinder gases and the TCI measured values were only -0.03 ± 0.04 µmol mol^{-1} (see Figure 1). Scale transfer errors in the calibration of the CRDS G1301 working standards have not been examined so far, but direct analysis of cylinder gases by the CRDS G1301 yielded almost the same value as with the TCI (see Table 1), indicating excellent agreement of calibration. The discrepancy between the ambient air comparison and the direct cylinder gas comparison could possibly be due to a SIS effect of the CRDS G1301 or the TCI. However, the small and insignificant biases found (-0.07 ± 0.12 µmol mol^{-1} for the CRDS G1301 and 0.01 ± 0.08 µmol mol^{-1} for the TCI) would only explain slightly *smaller* CRDS G1301 values. The insignificant bias found during the SIS test can therefore not explain the CO_2 differences in ambient air measurements. Another reason for the difference between ambient air and cylinder measurements could be an incorrect water correction of the (not dried) G1301 instrument, which influences the wet ambient air measurement differently than the measurement of dry cylinder gas. However, it was found that an incomplete water

1   correction could explain only 0.01 - 0.04 μmol mol^{-1} CO_2 of the difference. On the other hand,

2   it seems worth noting that the difference between the two CRDS instruments was rather large

3   during the direct cylinder measurements (0.06 ± 0.13 μmol mol^{-1}, see Figure 2 and Table 1).

4   This is surprising, since the same working standards were used for calibration of both

5   instruments and since the CRDS instruments normally agree very well (target and ambient air

6   differences usually agree within ca. 0.02 μmol mol^{-1}). Still the differences between the CRDS

7   G1301 and the TCI during ambient air measurements remain unexplained. Note that

8   principally the calibration of the CRDS systems using synthetic working standards may

9   introduce a bias into the CO_2 measurements (Nara et al., 2012), but should effect ambient air

10   measurements to the same degree as direct real air cylinder measurements.

11

12   **4.4 N_2O comparisons at Mace Head**

13   For N_2O, the difference of ambient air measurements at Mace Head between the TCI and the

14   GC-MD was found to be -0.37 ± 0.22 nmol mol^{-1} (GC-MD - TCI). Since a similar difference

15   of -0.40 ± 0.06 nmol mol^{-1} was found for the direct cylinder gas measurements between both

16   instruments, it is unlikely that the difference originates from the sample intake system. The

17   difference in N_2O is significantly larger than the WMO ILC targets. Note, however, that the

18   TCI is calibrated on the WMO N_2O X2006a scale whereas the GC-MD measured on the SIO-

19   1998 scale. Hall *et al.* (2007) found a difference between the SIO-1998 and the WMO X2006

20   scale of 0.01%, which corresponds to a difference of only $+0.03$ nmol mol^{-1} (SIO-1998 -

21   WMO X2006). Scale update from WMO X2006 to WMO X2006a shows a *mean* difference

22   for all calibrations in the ambient range of zero. But calibrations performed between 2007

23   and 2010 were still affected with the mean difference in the ambient range over this period

24   being WMO2006A - WMO2006 = -0.05 nmol mol^{-1} (pers. communication B. Hall, 2013).

25   Altogether currently reported scale differences between WMO X2006a and SIO-1998 are all

26   smaller than 0.1 nmol mol^{-1} and thus would not explain the observed differences in ambient

27   air and direct cylinder gas measurements found during the Mace Head campaign.

28   Possibly, scale transfer errors from primary standards to working standards could explain this

29   difference partly. For the WMO CCL tertiary standards the reproducibility of N_2O

30   assignments is about 0.08 nmol mol^{-1} (for the ambient range: 310-330 nmol mol^{-1}) (Hall *et al.*,

31   2007). The scale transfer error of a set of tertiary cylinders will decrease with the number of

32   tertiary cylinders; however the calibration errors are not always independent from each other,

especially when tertiary standards were calibrated shortly after each other. The calibration of working standards from WMO CCL tertiary standards introduces a further uncertainty. In our case, TCI working standards have been calibrated relative to a set of WMO CCL tertiary cylinder gases at the MPI-BGC GasLab in Jena. When analysing the Heidelberg WMO CCL tertiary cylinders by the TCI, no systematic difference in the ambient range was found (see Figure 1). Therefore we estimate the total scale transfer uncertainty from WMO CCL primary standards to working standards to be less than 0.1 nmol mol^{-1}.

Scale transfer uncertainties from SIO primary standards to tertiary standards used in the AGAGE network are generally small as well, as all working gases are calibrated at Scripps Institution of Oceanography (Prinn *et al.*, 2000). Differences between high pressure tertiary SIO standards going to the stations and standards at low pressure when they are returned for recalibration at the Scripps laboratory are usually on the order of $\pm$ 0.03% (1σ of the difference), which corresponds to about 0.1 nmol mol^{-1} in the ambient mole fraction range (pers. communication R. Weiss, 2013). This difference is thus a good upper estimate of scale transfer error in the AGAGE network. Merging the different scale propagation uncertainties, the observed difference of N_2O in ambient air between the GC-MD and the TCI includes a total uncertainty due to scale transfer which is on the order of 0.15 nmol mol^{-1}. Since the scale transfer uncertainty is smaller than the difference observed during the TCI campaign this may point towards instrumental errors or to a potential difference between the two absolute scales. The absolute accuracy of the N_2O scales is due to uncertainties in the preparation of N_2O primary standards and is typically on the order of 0.3 nmol mol^{-1} (1σ-standard deviation, Prinn *et al.,* 2000; Hall *et al.,* 2007). A scale difference of this order may therefore be possible, although it is not consistent with previous comparisons of the WMO X2006a and the SIO-1998 scales by Hall *et al.* (2007).

Intercomparison activities between the AGAGE network (on the SIO-1998 scale) and the NOAA flask network (WMO N_2O X2006a scale) are performed regularly and should capture a possible scale difference between both networks as well. The comparisons between AGAGE GC-MD in-situ measurements and NOAA CCGG (Carbon Cycle Greenhouse Gases) flasks at five globally distributed observatories (Cape Grim, American Samoa, Trinidad Head, Mace Head and Ragged Point Barbados) show a mean difference between the two networks from August 2011 to August 2013 of -0.11 $\pm$ 0.14 nmol mol^{-1} (SIO-1998 - WMO N_2O X2006a). The comparison between AGAGE GC-MD in-situ measurements and

NOAA HATS (Halocarbons and other Atmospheric Trace Species) flasks at four common sites (Cape Grim, American Samoa, Trinidad Head and Mace Head) show a difference during the same time period of -0.14 ± 0.23 nmol mol^{-1} (both from pers. communication P. Krummel, 2013). Within their uncertainties the difference between AGAGE and NOAA networks has been steadily increasing since the beginning of the intercomparison activity in 1994. The differences between the two networks found for the last two years during flask comparisons are within their uncertainties consistent with the difference found during the TCI comparison campaign at Mace Head (March-May 2013), however, they are only about one third. This may reinforce the possibility of a current small scale difference between the WMO X2006a scale and the SIO-1998 scale, which could be on the order of -0.1 to -0.4 nmol mol^{-1} (SIO-1998 - WMO X2006a). Note, however, that Thompson *et al.* (2014) estimated scale differences between SIO-1998 and WMO X2006a to have the opposite sign in the years from 1999 to 2009. This finding, along with our results during the TCI campaign is in accordance with the intercomparison results at AGAGE sites showing a long-term trend of the flask – in situ difference. For the NOAA CCGG flasks the trend is about 0.04 nmol mol^{-1} per year and for NOAA HATS flasks the trend is about 0.08 nmol mol^{-1} per year (P. Krummel pers. communication 2013).

5. Conclusions

New optical instrumentation allows measuring CH_4, CO_2 and also N_2O with very high precision, which principally opens the door for merging data from different observation networks and estimating fluxes with great confidence. But even though a high compatibility between different instruments can be achieved (as shown for CH_4 and for the comparison period in Heidelberg), the compatibility between different networks still suffers from insufficient comparability of calibration scales, potential errors in scale transfer and also potential instrumental problems. It is, thus, of utmost importance to check, control and update the scale propagation for these greenhouse gases and assess in-situ instrumentation and its calibration, in order to be able to use the globally distributed data sets from different measurement programs for source, sink and flux estimation.

The comparison between the GC-MD and the TCI at Mace Head showed that the mole fraction measurements differ by ca. 0.4 nmol mol^{-1} in N_2O. This difference could partly be due to a general small scale difference between the WMO X2006a and the SIO-1998 scales

and partly due to scale transfer and instrumental errors, such as remaining non-linearity effects.

The TCI campaign also showed differences between CO_2 measurements of the CRDS G1301 and the TCI as large as 0.14 µmol mol^{-1}, which were not seen when comparing the direct cylinder measurements. This difference between the direct measurement of target/standard gases and the ambient air measurements emphasizes the importance of the travelling instrument approach, which is a comprehensive comparison and quality control, and should include a sample intake system test and the entire evaluation process. But even though the origin of the discrepancy we found at Mace Head could not be fully resolved so far, the TCI campaign revealed that there are possible problems with the CO_2 measurements and the water-correction of the CRDS G1301, which need to be investigated in more detail. Earlier TCI campaigns at Cabauw, Netherlands, and OPE, France, revealed differences in CO_2 between the TCI and the local instrumentation of 0.21 ± 0.09 µmol mol^{-1} and 0.13 ± 0.10 µmol mol^{-1} (TCI larger than local instrumentation contrary to the results from the TCI campaign at Mace Head) (Hammer *et al.*, 2013a). Only between the GC-HEI and the TCI in Heidelberg differences between both systems were within the WMO ILC targets. This clearly shows the difficulty of performing compatible CO_2 measurements in the field, reaching the WMO ILC targets. Although in all three experiments working standards for the instruments had been calibrated in the same laboratory (MPI-BGC GasLab), CO_2 differences larger than 0.10 µmol mol^{-1} remained between ambient air measurements that did not show up in direct calibration gas comparisons.

We can, thus, conclude that the TCI approach is well suited as a comprehensive comparison measure. Due to the high precision of the TCI measurements in all three components, it was possible to detect even small differences and offsets between the greenhouse gas measurements of the local instruments and the TCI. Principally, the higher the precision and stability of the local instrument is, the shorter the time period for parallel measurement of ambient air can be, but a comparison period of about one week still seems necessary to obtain satisfactory statistics and cover the typical range of ambient mole fractions. The preparation and follow-up processing of the campaign included a preparatory line test in Heidelberg, a preparatory and subsequent parallel measurement with the GC-HEI as well as direct measurements of working standards and/or target gases on every instrument.

As a proposal for improvement, calibrated data should be available within 24 hours. This had already been pointed out by Hammer *et al.* (2013a), but has not yet transpired. Since the data evaluation is often time-consuming, it was not performed in near-real time, but only a month later for the CRDS and the GC-MD. Therefore, some problems were encountered only after the measurement campaign when additional tests could no longer be performed.

Finally, we could also demonstrate during the campaign at Mace Head, that small gradients of CO_2 and CH_4 can be resolved. This starts a new era of highly precise atmospheric greenhouse gas observations and gradients, provided that calibration and systematic instrumental biases can be overcome.

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5

1   Table 1. Median differences and interquartile ranges between the ambient air measurements
2   (local instrumentation – TCI), mean difference and standard deviation of direct cylinder gas
3   measurements and SIS effects (SIS - direct measurement) of the GC-HEI and the TCI in
4   Heidelberg (before and after the measurement campaign) and of the GC-MD, the CRDS
5   systems and the TCI at Mace Head.

Component		GC-HEI difference[1] before campaign	GC-MD difference[1]	CRDS G1301 difference[1]	CRDS G2301 difference	GC-HEI difference[2] after campaign
ΔCH_4	Ambient air	-0.25 ± 3.61	-0.04 ± 3.38	0.12 ± 0.25	-	-0.24 ± 2.43
[nmol mol^{-1}]	Cylinder gases	-0.76 ± 0.22	-0.01 ± 1.58	-0.92 ± 0.46	-0.05 ± 0.42	-
	SIS effect of TCI	0.10 ± 0.35	-0.19 ± 0.15	-0.11 ± 0.13	-0.11 ± 0.13	-
	SIS effect of local instrument	-0.65 ± 3.50	-	0.13 ± 0.13	0.09 ± 0.10	-
ΔCO_2	Ambient air	0.04 ± 0.22	-	0.14 ± 0.04	-	0.03 ± 0.31
[µmol mol^{-1}]	Cylinder gases	-0.02 ± 0.04	-	-0.00 ± 0.02	0.05 ± 0.03	-
	SIS effect of TCI	0.03 ± 0.07	0.03± 0.08	0.01 ± 0.08	0.01 ± 0.08	-
	SIS effect of local instrument	0.03 ± 0.11	-	-0.07 ± 0.12	-0.02 ± 0.03	-
ΔN_2O	Ambient air	0.03 ± 0.15	-0.37 ± 0.22	-	-	-0.02 ± 0.15
[nmol mol^{-1}]	Cylinder gases	0.11 ± 0.05	-0.40 ± 0.06	-	-	-
	SIS effect of TCI	0.02 ± 0.07	0.08 ± 0.10	-	-	-
	SIS effect of local instrument	-0.04 ± 0.11	-	-	-	-

6   1= Same sampling height, independent intake lines

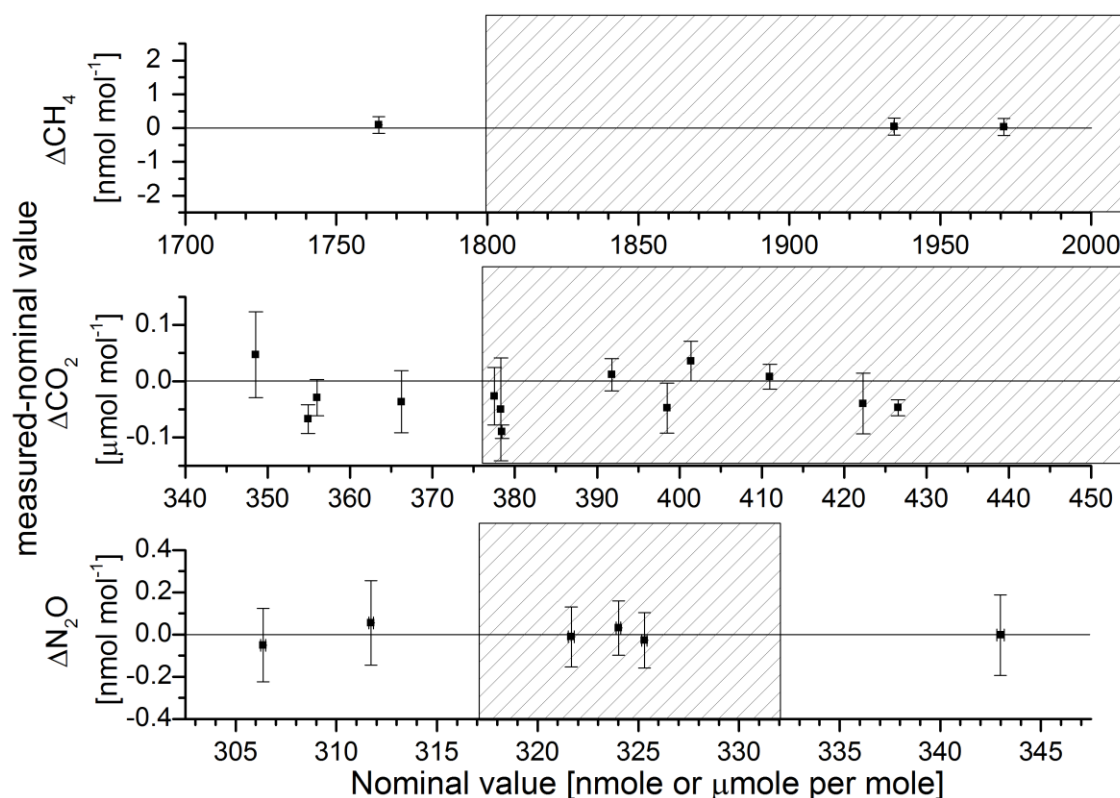7   2= Same sampling height, same intake line as TCI

8

1

2　Figure 1: Difference between TCI measured Heidelberg WMO CCL tertiary standards and

3　their respective nominal value given by WMO CCL (TCI measured - WMO CCL nominal

4　value). The measurements were performed on 30 May 2013, 24 June 2013, 3 July 2013, 2

5　September 2013 and 3 September 2013. The standard deviation plotted is the convolution of

6　the standard error of the repeated cylinder measurements and the error of the nominal WMO

7　CCL tertiary cylinder value. Shaded areas indicate the calibrated TCI mole fraction ranges.
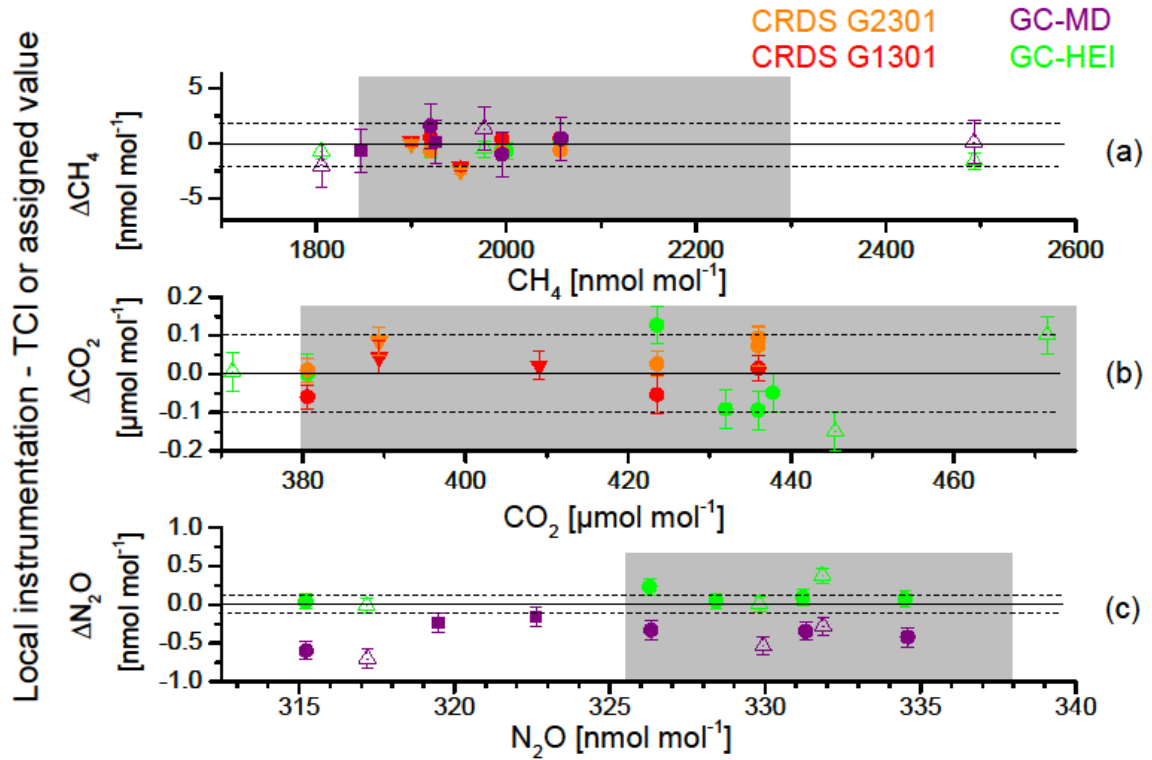
Figure 2: Differences (local instrument - TCI or assigned value in the case of the TCI standards shown as open symbols) of the measured mole fractions of a) CH_4, b) CO_2 and c) N_2O of different cylinders: Mace Head AGAGE target cylinders (squares), Heidelberg target cylinders (circles), TCI working standards calibrated by MPI-BGC GasLab (upward open triangles) and Mace Head CRDS target cylinders (downward triangles). The grey shaded area shows the ambient mole fraction range during the measurement campaign at Mace Head. The direct cylinder measurements at Mace Head were performed partly at the beginning of the campaign (24 February 2013 – 26 February 2013) and partly at the end of the campaign (21 May 2013).
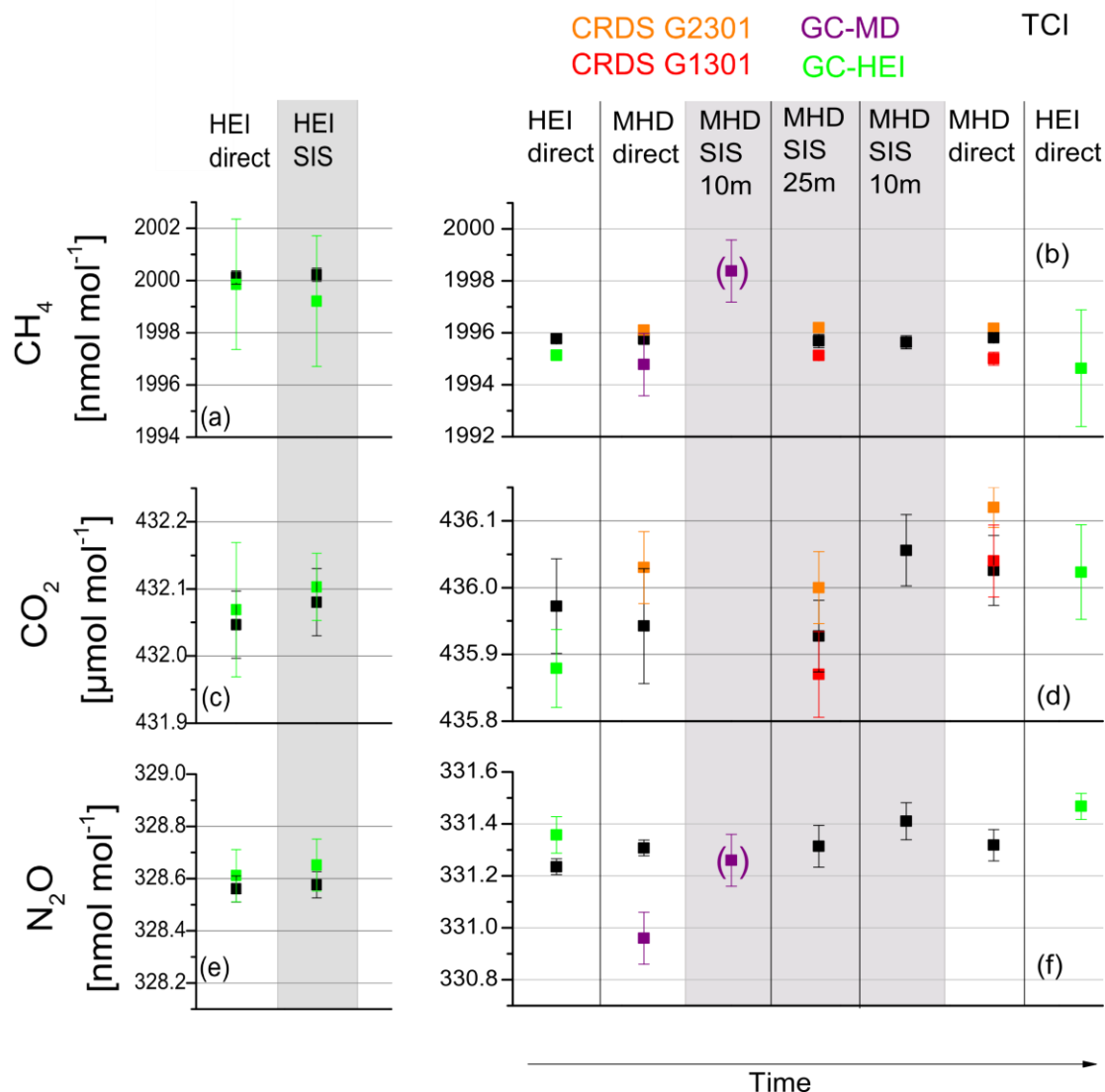
Figure 3: Direct cylinder gas measurement (direct) and SIS test on the 12 January 2013 for a) CH_4, c) CO_2 and e) N_2O in Heidelberg (HEI) and on the 26/27 February 2013 for b) CH_4, d) CO_2 and f) N_2O at Mace Head. Different cylinders were used for the SIS test in Heidelberg and Mace Head. Grey shaded areas show results when the cylinder was measured via the SIS. The SIS measurement of the GC-MD did not reach a stable value. The error bars given here are the reproducibility of direct measurements or the standard deviation during the SIS test, respectively.
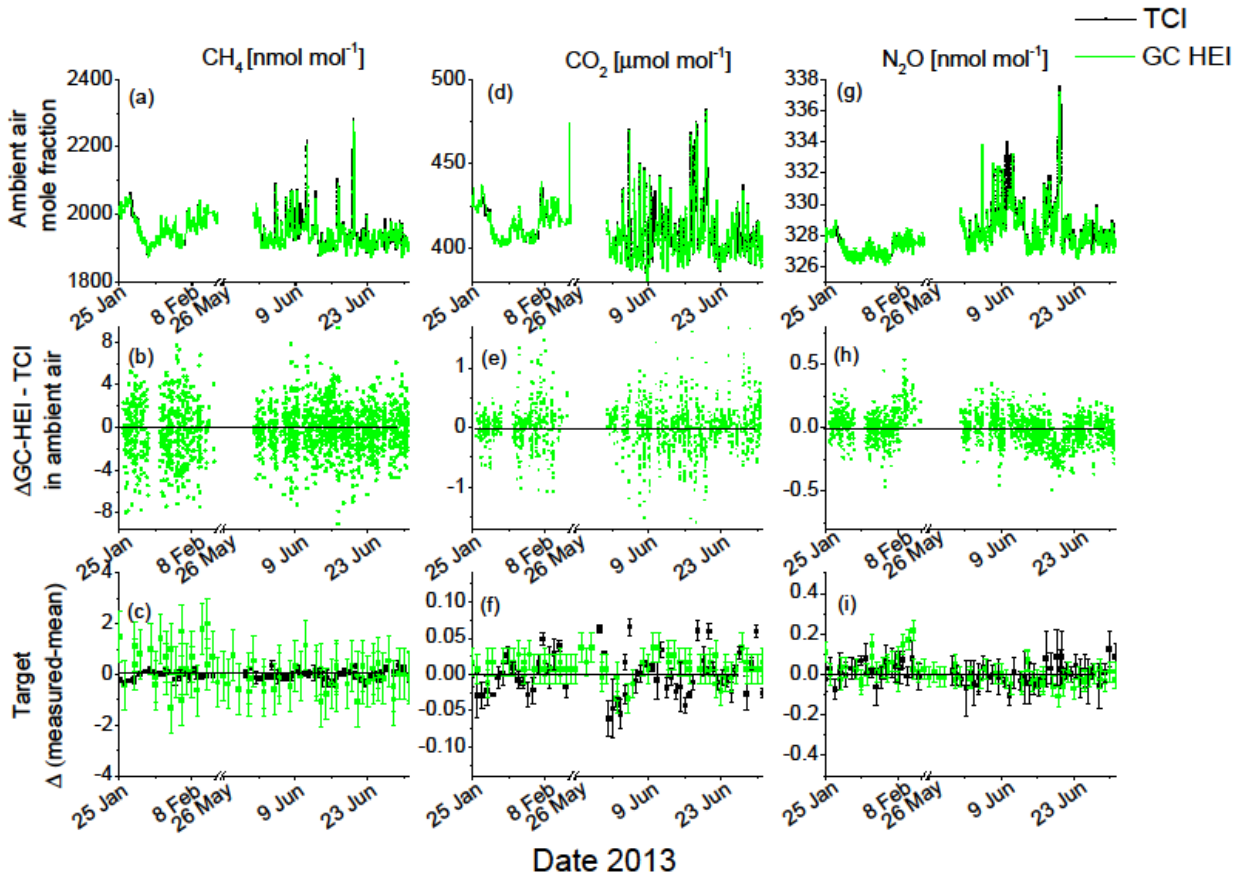
Figure 4: Upper panels: Mole fraction of ambient air a) CH_4, d) CO_2, and g) N_2O during the preparing and finalizing comparison periods in Heidelberg. From 25 January 2013 until 13 February 2013 both instruments were run in parallel, but with independent intake lines. From 1 June 2013 until 1 July 2013 both instruments used the same intake line. Middle panels: Differences between the GC-HEI and the TCI for b) CH_4, e) CO_2 and h) N_2O. Lower panels: TCI and GC-HEI daily target deviation from mean for c) CH_4, f) CO_2 and i) N_2O. Notice the interruption in the x-axis from February to May 2013 where the Mace Head measurement campaign took place.
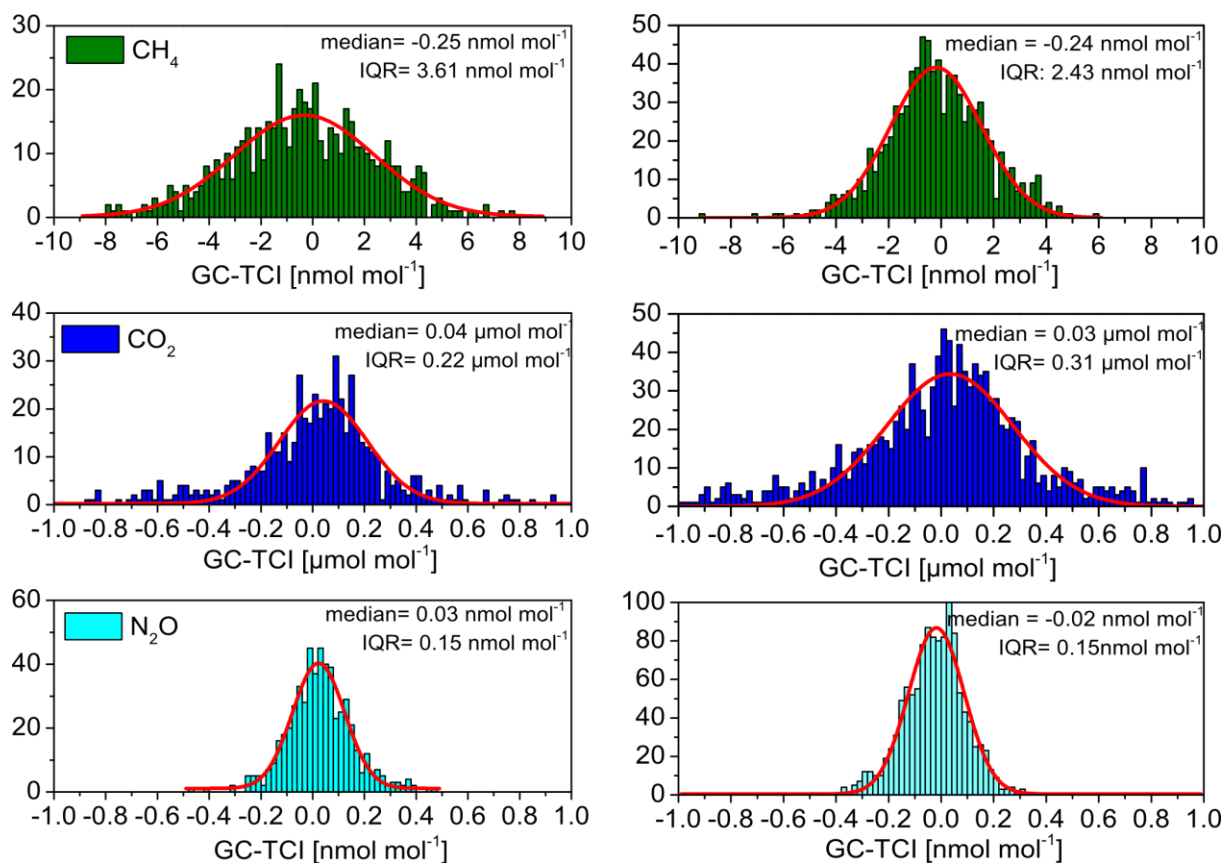
Figure 5: Distributions of the mole fraction differences measured with the GC-HEI and the TCI in Heidelberg (both with seperate intake lines) from 25 January 2013 until 13 February 2013 (left panels) and from the 1 June 2013 to the 1 July 2013 with the same intake line (right panels). The red lines are Gauss fits to the distributions, IQR = interquartile range.

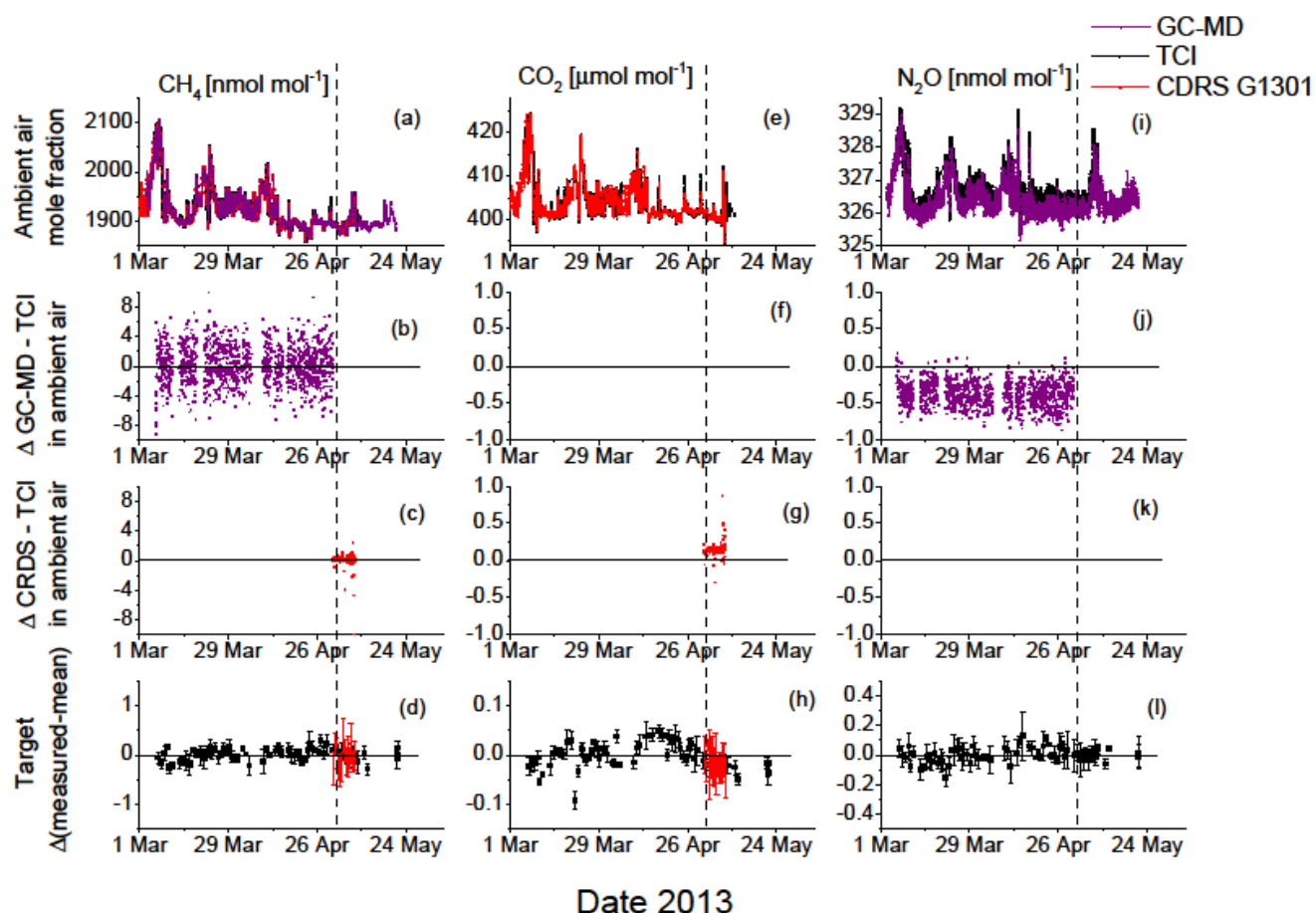Figure 6: Upper panels: Mole fraction of a) CH_4, e) CO_2, and i) N_2O during the measurement campaign at Mace Head. All instruments were running in parallel with the TCI with independent intake lines to the same height. The GC-MD measured at a height of 10 m and the CRDS at a height of 25 m. The TCI intake was switched on the 1 May 2013 from 10 m to 25 m (dashed vertical line). Here only comparisons of measurements made at the same height are shown and will be evaluated. Second row panels: Difference between the GC-MD and the TCI for b) CH_4 and j) N_2O from 6 March 2013 until 1 May 2013. Third row panels: Difference between the CRDS G1301 and the TCI for c) CH_4 and g) CO_2 from 1 May 2013 until 7 May 2013. Lowest panels: TCI and CRDS daily target measurement deviation from mean for d) CH_4, h) CO_2 and i) N_2O. No GC-MD target measurements are available.
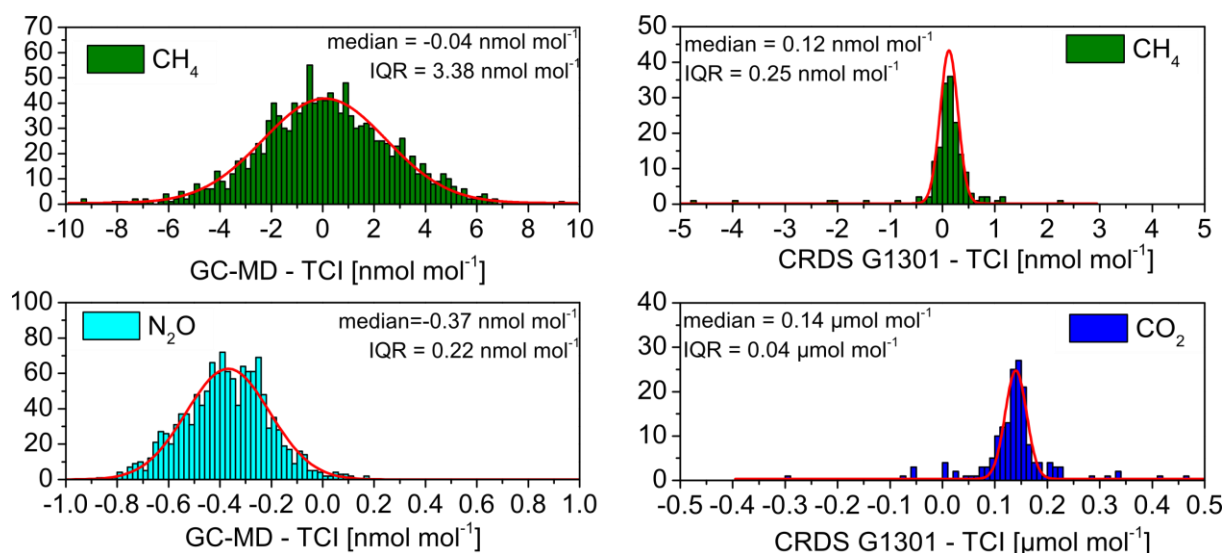
Figure 7: Left panels: Distribution of the differences in CH_4 and N_2O between the discrete GC-MD measurements and the corresponding 3-minutely averaged values of the TCI at Mace Head from 6 March 2013 until 1 May 2013 (both instruments with separate intake lines at a height of 10 m). The red curves are Gauss fits to the distributions. Right panels: Distribution of the differences between the hourly averaged CH_4 and CO_2 differences between the CRDS G1301 and the TCI from 1 May 2013 until 6 May 2013 (both instruments with separate intake lines at a height of 25 m). The red curves are Gauss fits to the distributions