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# Comparisons of continuous atmospheric $CH_4$, $CO_2$ and $N_2O$ measurements – results of InGOS travelling instrument campaign at Mace Head

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## Abstract

A two-month measurement campaign with a Fourier Transform InfraRed (FTIR) analyser as a Travelling Comparison Instrument (TCI) was performed at the AGAGE and WMO GAW station Mace Head, Ireland. The aim was to evaluate the compatibility of atmospheric $CH_4$, $CO_2$ and $N_2O$ measurements of the routine station instrumentation, consisting of a gas chromatograph (GC-MD) 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 to the Heidelberg GC (GC-HEI) before and after the measurement campaign at Mace Head. Median differences between the GC-HEI and the TCI were well within the WMO Inter Laboratory Compatibility (ILC) target for all three greenhouse gases. At Mace Head, the median difference between the GC-MD and the TCI were $-0.04\,\mathrm{nmol\,mol^{-1}}$ for $CH_4$ and $-0.37\,\mathrm{nmol\,mol^{-1}}$ for $N_2O$. For $N_2O$ a similar difference ($-0.40\,\mathrm{nmol\,mol^{-1}}$) 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 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 $0.12\,\mathrm{nmol\,mol^{-1}}$ for $CH_4$ and $0.14\,\mathrm{\mu mol\,mol^{-1}}$ 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-MD and the CRDS G1301 at Mace Head are smaller than the WMO Inter Laboratory compatibility (ILC) target (WMO, 2009), while this is not the case for $CO_2$ and $N_2O$. During the campaign it was also demonstrated that the new optical instrumentation allows detection of very small vertical $CO_2$ and $CH_4$ gradients, here between

10 m a.g.l. and 25 m a.g.l. This provides a new opportunity of evaluating greenhouse gases gradients in terms of regional fluxes.

## 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 WMO experts have set ILC targets for each individual GHG 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 been indeed 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). 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 WMO-GAW and AGAGE station Mace Head in the Republic of Ireland. A Fourier Transform Infrared

Spectrometer (FTIR) was used as the travelling instrument, which 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 to the station instrumentation. $N_2O$ and $CH_4$ concentrations measured with the locally installed gas chromatographic 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 to the Heidelberg gas chromatographic system (GC-HEI) (Hammer, 2008) in order to check its performance and stability.

## 2 Methods, site descriptions and instrumentation

### 2.1 The travelling comparison instrument (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), since it is 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 FTIR measurements is generally better than $\pm 0.05\,\mu\text{mol}\,\text{mol}^{-1}$ for $CO_2$, $\pm 0.25\,\text{nmol}\,\text{mol}^{-1}$ for $CH_4$ and $\pm 0.05\,\text{nmol}\,\text{mol}^{-1}$ for $N_2O$. Within the InGOS project the three working standards of the FTIR system were calibrated relative to WMO Central Calibration Laboratory (NOAA in Boulder) 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 at Heidelberg

Heidelberg is a medium-size city located in the densely populated Rhine-Neckar region (49°25′ N, 8°43′ E). Routine ambient air measurements are made on the University campus at the Institut für Umweltphysik located to the north-west of the Heidelberg city center. 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 gaschromatographic system (GC-HEI), which measures $CO_2$, $CH_4$, $N_2O$, $SF_6$, CO and $H_2$ simultaneously at a maximum temporal resolution of 5 min. 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 CCL at NOAA in Boulder. The reproducibility of the GC-HEI measurements is ±0.05 $\mu mol\,mol^{-1}$ for $CO_2$, ±2.4 $nmol\,mol^{-1}$ for $CH_4$ and ±0.1 $nmol\,mol^{-1}$ for $N_2O$. A detailed description of the entire GC-HEI system can be found in Hammer (2008). To allow for better comparability between the continuous TCI measurements and the discrete GC-HEI measurements, a buffer volume was installed in the GC-HEI sample intake line. The buffer volume allows capturing and integrating the short-term concentration variations between the discontinuous GC-HEI measurements. Details of the integration scheme of the buffer can be found in Hammer et al. (2013a) while the standard operating conditions of the TCI are described in Hammer et al. (2013b).

Normally the FTIR uses the same main air intake line as the GC-HEI (with a separate by-pass, pump and drying system, Hammer et al., 2013b), but for the performance test before the intercomparison campaign at Mace Head, a separate intake line was installed in Heidelberg for the TCI.

## 2.3 Site description and routine instrumentation at Mace Head

The Mace Head station is located on the west coast of Ireland (53°20′ N, 9°45′ W) about 100 m from the Atlantic shore. The station is operated by the National University of Ireland, Galway, and is classed as a global background station within the WMO-GAW network. At the station trace gas measurements are carried out by the University of Bristol (UK) and by the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) Gif sur Yvette (F) as part of the AGAGE ($CH_4$ and $N_2O$) (Prinn et al., 2000) and ICOS Demonstration ($CO_2$ and $CH_4$) (http://www.icos-infrastructure.eu/) networks. A description of the station can be found in Jennings et al. (2003). A gas chromatography system with multiple detectors (GC-MD), including an electron-capture detector (ECD) and a flame-ionization detector (FID) is used to measure $N_2O$ and $CH_4$, while a reduction gas analyser (RGA) measures CO and $H_2$ within the AGAGE network. One working standard, which is measured alternately with ambient air or other samples, is used for calibration. The precision of the measurements is approximately 0.1 $\mathrm{nmol\,mol^{-1}}$ for $N_2O$ and 1.5 $\mathrm{nmol\,mol^{-1}}$ 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 dewpoint 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). A water vapor correction according to Chen et al. (2010) is applied to both instruments. 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 min. The CRDS analysers measure $CO_2$ and $CH_4$ with a precision of about 0.02 $\mu mol\,mol^{-1}$ 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 h. The (1$\sigma$)-reproducibility of the target cylinder measurement is about 0.02 $\mu mol\,mol^{-1}$ for $CO_2$ and 0.21 $nmol\,mol^{-1}$ for $CH_4$ for the G1301 from March to June 2013 and 0.03 $\mu mol\,mol^{-1}$ 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. However, the ambient air measurements of both CRDS instruments agreed within $0.02 \pm 0.05\,\mu mol\,mol^{-1}$ for $CO_2$ and $0.38 \pm 0.49\,nmol\,mol^{-1}$ 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 (15th WMO/IAEA Meeting GAW Report No. 194, 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 Integrated non-$CO_2$ Greenhouse Gas Observation System (InGOS) project by the MPI-BGC GasLab Jena) and the nominal WMO CCL values of these cylinders are smaller than the WMO compatibility targets for all $CH_4$, $CO_2$ and $N_2O$ measurements (see Fig. 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 concentration 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 compatibility targets.

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

In order to check the calibration compatibility between different instruments, target and working standards were measured on all instruments directly. In Fig. 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 ($-0.02 \pm 0.04\,\mu mol\,mol^{-1}$, mean ± standard error) for $CO_2$. The G1301 CRDS instrument shows very good agreement with the TCI in $CO_2$ results ($-0.01 \pm 0.02\,\mu mol\,mol^{-1}$), while the G2301 results are consistently higher ($0.05 \pm 0.03\,\mu mol\,mol^{-1}$) than the $CO_2$ concentrations 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 $0.06\,\mu mol\,mol^{-1}$, while it is usually only $0.02\,\mu mol\,mol^{-1}$ during target measurements and only $0.01\,\mu mol\,mol^{-1}$ during the ambient air measurements (from 1 March 2013–31 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 ($0.11 \pm 0.05\,nmol\,mol^{-1}$). The reason for the difference between the GC-HEI and the TCI is not clear. The $N_2O$ cylinder measurements with the GC-MD show significantly lower values than the TCI by $-0.40 \pm 0.06\,nmol\,mol^{-1}$. This is a rather large and unexpected offset between the two instruments, since current known scale differences between SIO-1998 and WMO X2006a are on the order of 0.03 to $0.05\,nmol\,mol^{-1}$ (Hall et al., 2007; B. Hall, personal communication, 2013) and thus cannot explain the difference in the cylinder measurements found here. We will discuss this point in Sect. 4 after having presented ambient air measurements of both instruments.

### 3.3 Sample intake system (SIS) tests

Since the ambient air sample intake systems of the different instruments can possibly introduce a bias into ambient air concentration measurements (Hammer et al., 2013a), a sample intake system (SIS) test was performed in Heidelberg as well as at Mace Head. For this purpose a gas cylinder was connected via the respective intake line to the individual instruments. The pressure on the low pressure side of the regulator was chosen such that the pressure in the intake line was always very close to (but slightly higher than) ambient air pressure. Then the cylinder gas was flushed through the entire intake system and the measured results were compared to the direct measurements of the same cylinder. Figure 3 shows all results of these tests in Heidelberg and at Mace Head.

### 3.3.1 Sample intake system test in Heidelberg

A SIS test was performed in Heidelberg (Fig. 3a, c and e) on the independent intake lines of the GC-HEI (green symbols) and the TCI (black symbols). The measurements of the SIS cylinder on the TCI and the GC-HEI show similar differences as the direct cylinder measurements (see Fig. 2). For both instruments the measurements via the SIS agree with the direct cylinder measurements within their measurement uncertainties. The differences between the direct measurement and the measurement via the SIS of the TCI in Heidelberg (±convolution of their reproducibility and their standard deviations during the SIS tests) was SIS – direct = $0.1 \pm 0.35\,\mathrm{nmol\,mol^{-1}}$ for $CH_4$, $0.03 \pm 0.07\,\mu\mathrm{mol\,mol^{-1}}$ for $CO_2$ and $0.02 \pm 0.07\,\mathrm{nmol\,mol^{-1}}$ for $N_2O$ and for the GC-HEI it was SIS – direct = $-0.65 \pm 3.5\,\mathrm{nmol\,mol^{-1}}$ for $CH_4$, $0.03 \pm 0.11\,\mu\mathrm{mol\,mol^{-1}}$ for $CO_2$ and $0.04 \pm 0.11\,\mathrm{nmol\,mol^{-1}}$ for $N_2O$. These differences are 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 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 Fig. 3b, d and f. The comparison between the direct measurements before and after the campaign indicate a concentration change in the cylinder for $CO_2$ in the order of $0.1\,\mu mol\,mol^{-1}$. This change is observed by all instruments which measured the gas before and after the test. A significant concentration jump is seen between the SIS tests at 25 m and 10 m. Significant increases of $CO_2$ concentration 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 concentration change in the SIS cylinder was not unexpected.

No significant concentration 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 Fig. 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 $3.7 \pm 1.7\,nmol\,mol^{-1}$ (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 Fig. 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 h). 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 $N_2O$ ($0.07 \pm 0.10\,nmol\,mol^{-1}$), which could, however, be also due to a small $N_2O$ drift in the cylinder concentration. For $CO_2$ the TCI and CRDS measurements show only a small SIS influence within their measurement uncertainties: TCI at 25 m: $-0.01 \pm 0.08\,\mu mol\,mol^{-1}$, TCI at 10 m: $0.03 \pm 0.08\,\mu mol\,mol^{-1}$, CRDS G1301: $-0.07 \pm 0.12\,\mu mol\,mol^{-1}$ (SIS effect was determined relative to the TCI measurements at 25 m and after the SIS test), CRDS G2301:

$-0.02 \pm 0.03\,\mu\text{mol}\,\text{mol}^{-1}$ when taking into account the concentration jump after the SIS test at the 25 m intake of about $0.1\,\mu\text{mol}\,\text{mol}^{-1}$.

## 3.4 Comparison of ambient air measurements

### 3.4.1 Comparison of ambient air measurements in Heidelberg

Ambient air comparisons were performed in Heidelberg before and after the measurement campaign. For this purpose the TCI data was smoothed exponentially ($\tau = 20\,\text{min}$) to make them comparable to the GC-HEI measurements where an integration volume is installed. Details of this so-called buffer system can be found in Hammer et al. (2013a).

The $CH_4$ measurements of the TCI and the GC-HEI (Fig. 4a and b) show a difference GC-HEI – TCI of $-0.25 \pm 3.61\,\text{nmol}\,\text{mol}^{-1}$ (median and interquartile range, see Fig. 5) before the campaign and a difference of $-0.24 \pm 2.43\,\text{nmol}\,\text{mol}^{-1}$ after the campaign. In each intercomparison period this difference was constant over time (see Fig. 4b). The TCI target measurements were stable during both comparison periods and showed a reproducibility of $0.16\,\text{nmol}\,\text{mol}^{-1}$ (see Fig. 4c).

All $CO_2$ measurements of the TCI in Heidelberg and the GC-HEI agree very well (see Fig. 4d and e). The difference (GC-HEI – TCI) between the instruments was nearly the same in both intercomparison phases.

The $N_2O$ measurements show a median difference of $0.03 \pm 0.15\,\text{nmol}\,\text{mol}^{-1}$ (GC-HEI – TCI) during the first comparison period in February and a median difference of $-0.02 \pm 0.14\,\text{nmol}\,\text{mol}^{-1}$ in the second period in June 2013. The particular structure of the difference in ambient air measurements between the TCI and the GC-HEI (decrease after 15 June, see Fig. 4h) is partly due to a respective structure of the TCI and GC-HEI measurement, which can be detected in the $N_2O$ target gas measurement of both instruments (see Fig. 4i). The reproducibility of the TCI in this last period was not worse than usual, showing that 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 a high degree of 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 the 6 March 2013 until the 1 May 2013. Differences between the TCI and the GC-MD are shown in Fig. 6b and j and in Fig. 7 (left panels). From the 1 May 2013 until the 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 Fig. 6c and g and Fig. 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 min, whereas the TCI measurements are continuous and smoothed due to the TCI cell volume of 3 L 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 minutely CRDS data with the three-minutely 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 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 $\pm 0.12\,\mathrm{nmol\,mol^{-1}}$. 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 $0.14 \pm 0.04\,\mathrm{\mu mol\,mol^{-1}}$ (median and IQR, see Fig. 7 right panel). No concentration 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 $-0.37 \pm 0.22\,\mathrm{nmol\,mol^{-1}}$ (median and IQR). A difference of $-0.40 \pm 0.06\,\mathrm{nmol\,mol^{-1}}$ (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 $CH_4$ 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 $\text{nmol mol}^{-1}$ (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.

## 4.3 $CO_2$ comparison at Mace Head

For $CO_2$ the difference in ambient air measurements at Mace Head between the TCI and the CRDS G1301 was $0.14 \pm 0.04\,\mu\text{mol mol}^{-1}$. 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 Fig. 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.

However, it seems worth noting that the difference between the two CRDS instruments was rather large during the direct measurements (0.06 ± 0.13 µmol mol$^{-1}$, see Fig. 2 and Table 1). This is surprising since the same working standards were used for calibration of both instruments and since the CRDS instruments normally agree very well (target and ambient air differences usually agree within ca. 0.02 µmol mol$^{-1}$). Therefore the large difference could possibly point towards instrumental problems of one (or both) of the CRDS systems during the direct cylinder measurement. Still the differences between the CRDS G1301 and the TCI during ambient air measurements remain unexplained. Note that principally the calibration of the CRDS systems using synthetic working standards may introduce a bias into the $CO_2$ measurements (Nara et al., 2012), but should effect ambient air measurements to the same degree as direct cylinder measurements.

### 4.4 $N_2O$ comparisons at Mace Head

For $N_2O$, the difference of ambient air measurements at Mace Head between the TCI and the GC-MD was found to be −0.37 ± 0.22 nmol mol$^{-1}$ (GC-MD – TCI). Since a similar difference of −0.40 ± 0.06 nmol mol$^{-1}$ was found for the direct cylinder gas measurements between both instruments, it is unlikely that the difference originates from the sample intake system. The difference in $N_2O$ is significantly larger than the WMO ILC targets. Note, however, that the TCI is calibrated on the WMO $N_2O$ X2006a scale whereas the GC-MD measured on the SIO-1998 scale. Hall et al. (2007) found a difference between the SIO-1998 and the WMO X2006 scale of 0.01 %, which corresponds to a difference of only +0.03 $\text{nmol}\,\text{mol}^{-1}$ (SIO-1998 – WMO X2006). Scale update from WMO X2006 to WMO X2006a shows a *mean* difference for all calibrations in the ambient range of zero. But calibrations performed between 2007 and 2010 were still affected with the mean difference in the ambient range over this period being 2006A – 2006 = –0.05 $\text{nmol}\,\text{mol}^{-1}$ (B. Hall, personal communication, 2013). Altogether currently known scale differences between WMO X2006a and SIO-1998 are all smaller than 0.1 $\text{nmol}\,\text{mol}^{-1}$ and thus would not explain the observed differences in ambient air and direct cylinder gas measurements found during the Mace Head campaign.

Possibly, scale transfer errors from primary standards to working standards could explain this difference partly. For the WMO CCL tertiary standards the reproducibility of $N_2O$ assignments is about 0.08 $\text{nmol}\,\text{mol}^{-1}$ (for the ambient range: 310–330 $\text{nmol}\,\text{mol}^{-1}$) (Hall et al., 2007). The scale transfer error of a set of tertiary cylinders will decrease with the number of 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 cylinder by the TCI, no systematic difference in the ambient range was found (see Fig. 1). Therefore we estimate the total scale transfer uncertainty from WMO CCL primary standards to working standards to be rather small.

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 ±0.03 % ($1\sigma$ of the difference), which corresponds to about $0.1\,\text{nmol mol}^{-1}$ in the ambient concentration range (R. Weiss, personal communication, 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 $0.15\,\text{nmol mol}^{-1}$. 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 $0.3\,\text{nmol mol}^{-1}$ ($1\sigma$-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 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 $-0.11 \pm 0.14\,\text{nmol mol}^{-1}$ (SIO-1998 – WMO $N_2O$ X2006a). The comparison between AGAGE GC-MD in-situ measurements and NOAA HATS flasks at four common sites (Cape Grim, American Samoa, Trinidad Head and Mace Head) show a difference during the same time period of $-0.14 \pm 0.23\,\text{nmol mol}^{-1}$ (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 flaks the trend is on the order of ca. 0.04 nmol mol$^{-1}$ year$^{-1}$ and for NOAA HATS flaks the trend is about 0.08 nmol mol$^{-1}$ year$^{-1}$ (P. Krummel, personal communication, 2013).

## 5 Vertical concentration gradients of $CH_4$ and $CO_2$ at Mace Head

From 6 March 2013 to 1 May 2013 the TCI was measuring at 10 m height and the CRDS G1301 at 25 m height. Comparing the measurements at different heights along with measurements at the same height allows us to analyse the vertical concentration gradients between 10 and 25 m. These may principally be used to estimate net greenhouse gases fluxes in the catchment area of the site. Since Mace Head station is located at the Atlantic coast, it samples two principally different regimes of air masses: a marine sector and a continental sector. As a criterion to distinguish between continental and marine air masses we use the $^{222}$Rn activity concentrations measured with a Heidelberg $^{222}$Radon monitor (Levin et al., 2002) at Mace Head station, that was installed there during the intercomparison campaign at about 5 m height. When the prevailing wind direction is from the west, the air masses have a marine footprint and the $^{222}$Rn concentration is low ($< 0.5$ Bq m$^{-3}$), whereas wind from other directions brings air masses with higher $^{222}$Rn concentrations (0.5–5 Bq m$^{-3}$) (see Fig. 8d). During the measurement campaign at Mace Head from the 6 March 2013 until 11 March 2013 and from the 18 March 2013 until 13 April 2013 the prevailing wind direction was from the east while from the 12 March 2013 until 18 March 2013 and from the 14 April 2013 until 30 April 2013 the main wind direction was from the west.

For the continental regime the median $^{222}$Rn concentration was 0.8 Bq m$^{-3}$and showed a diurnal cycle (green line in Fig. 8c). This variation is mainly caused by diurnal changes in the planetary boundary layer height because the $^{222}$Rn flux from continental soils does not show a diurnal cycle. The data from the marine regime showed no significant diurnal cycle and a mean concentration of 0.2 Bq m$^{-3}$.

As a first step to determine vertical gradients the differences between both instruments when measuring at the same height (i.e. from 1–7 May 2013) must be compared. This comparison serves as a reference for determining the instrumental concentration differences. As described before, we found a difference between the CRDS G1301 and TCI measurements of 0.12 nmol mol$^{-1}$ for $CH_4$ and 0.14 µmol mol$^{-1}$ for $CO_2$. The difference when measuring at the same height (black curves in Fig. 8a and b) has no diurnal cycle, but shows this systematic offset. Other than the unresolved discrepancy between both instruments we therefore see no diurnal variation of concentration difference.

In a next step we compare the difference between instruments when measuring at different heights (25 m – 10 m). For continental air masses we then see a weak diurnal cycle in $CH_4$. The concentration gradient increases from ca. −1 nmol mol$^{-1}$ during night time to −0.5 nmol mol$^{-1}$ during day time (the TCI measurement at 10 m height being always higher than the CRDS measurement at 25 m height). This finding suggests that there is a positive $CH_4$ flux from the ground throughout the day. For the marine air masses (low Rn activity concentration) there are only marginal differences in measured $CH_4$ compared to the measurements at the same height, which suggests only a very small $CH_4$ flux from the ocean (if at all significant).

Further, for continental air masses we find a rather strong diurnal cycle in the $CO_2$ gradient. The difference between both levels (25 m – 10 m) increases during night from −0.16 to 0.06 µmol mol$^{-1}$ relative to the offset between both instruments when measuring at the same height. The $CO_2$ level at 10 m height is higher than at 25 m height during the night time, but it is lower during the day time. This behavior is expected since ecosystem respiration during the night time leads to a positive $CO_2$ flux and plant photosynthesis during the day time leads to a net $CO_2$ uptake. During the marine air mass regime the diurnal cycle is decreased, but still a slight positive $CO_2$ flux from below is found during the nighttime and a negative flux during the daytime. This may either be due to surface ocean $CO_2$ respiration or uptake or it might be due to some continental air mass influence also in the periods which we marked as marine situations. The latter would also explain the small $CH_4$ gradient. Such small gradients of $CO_2$ (and $CH_4$) have, to our knowledge, not been resolved before. This shows that the modern instrumentation used here opens a new dimension in precision and interpretation of greenhouse gas measurements.

## 6 Conclusions

New optical instrumentation allows measuring $CH_4$, $CO_2$ and also $N_2O$ with very high precision, which principally opens the door to 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 within 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 asses 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 concentration measurements differ by ca. $0.4\,\mathrm{nmol\,mol^{-1}}$ 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.

The TCI campaign also showed differences between $CO_2$ measurements of the CRDS G1301 and the TCI as large as $0.14\,\mathrm{\mu mol\,mol^{-1}}$, 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, including the sample intake system and the entire evaluation process. But even though the origin of the discrepancy we found at Mace Head could not be resolved so far, the TCI campaign revealed that there are possible problems with the $CO_2$ measurements 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 $0.21 \pm 0.09\,\mu\text{mol mol}^{-1}$ and $0.13 \pm 0.10\,\mu\text{mol mol}^{-1}$ (TCI larger than local instrumentation in 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 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 $0.10\,\mu\text{mol mol}^{-1}$ remained between ambient air measurements that did not show up in direct calibration gas comparisons.

We can 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. 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. Further bureaucratic regulations needed to be managed in advance (which could be more difficult when campaigns take place outside of Europe) and the instrument had to be transported to and from the station by car, since the FTIR is rather heavy and large, should not be tilted or shaken and can only be moved by two people.

As a proposal for improvement, calibrated data should be available within 24 h. This had already been pointed out by Hammer et al. (2013a), but has not yet been successfully transposed. 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.

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**Table 1.** Median differences and interquartile ranges between the ambient air measurements, mean difference and standard deviation of direct cylinder gas measurements and SIS effect (SIS – direct measurement) of the GC-HEI and the TCI in Heidelberg (before and after the measurement campaign) and of the GC-MD, the CRDS 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 |
|---|---|---|---|---|---|---|
| $\Delta CH_4$ [nmol mol$^{-1}$] | Ambient air | −0.25 ± 3.61 | −0.04 ± 3.38 | 0.12 ± 0.25 | – | −0.24 ± 2.43 |
| | 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 | – |
| $\Delta CO_2$ [µmol mol$^{-1}$] | Ambient air | 0.04 ± 0.22 | – | 0.14 ± 0.04 | – | 0.03 ± 0.31 |
| | 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 | – |
| $\Delta N_2O$ [nmol mol$^{-1}$] | Ambient air | 0.03 ± 0.15 | −0.37 ± 0.22 | – | – | −0.02 ± 0.15 |
| | 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 | – | – | – | – |

[1] Same sampling height, independent intake lines.
[2] Same sampling height, same intake line as TCI.

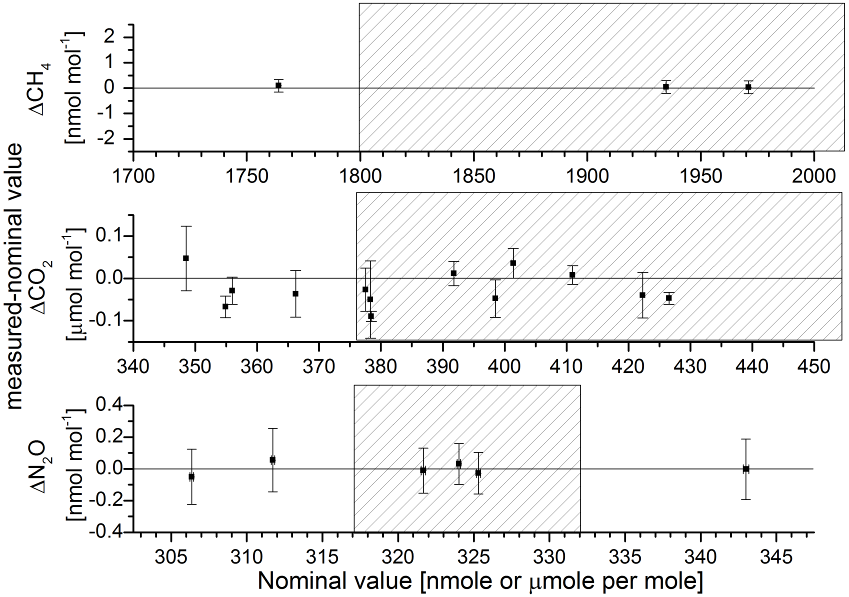

**Fig. 1.** Difference between TCI measured Heidelberg WMO CCL tertiary standards and their respective nominal value given by WMO CCL (TCI measured – WMO CCL nominal value). The measurements were performed on the 30 May 2013, 24 June 2013, 3 July 2013, 2 September 2013 and 3 September 2013. The standard deviation plotted is the convolution of the standard error of the repeated cylinder measurements and the error of the nominal WMO CCL tertiary cylinder value. Shaded areas indicate the calibrated TCI mole fraction ranges.

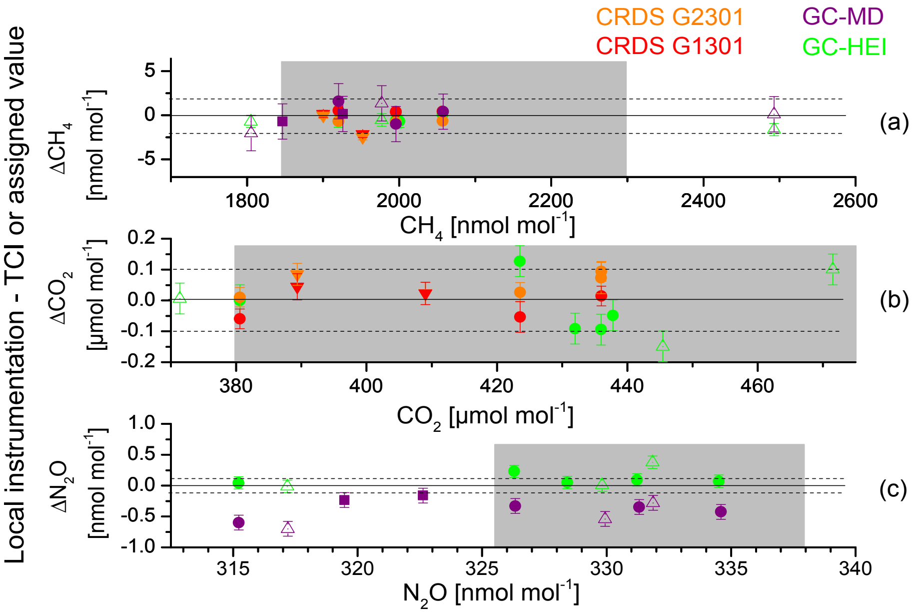

**Fig. 2.** Differences (local instrument – TCI or assigned value in the case of the TCI standards shown as open symbols) of the measured concentrations of **(a)** $CH_4$, **(b)** $CO_2$ and **(c)** $N_2O$ of different cylinders: Mace Head AGAGE target cylinders (squares), Heidelberg target cylinders (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 concentration range during the measurement campaign at Mace Head. The direct cylinder measurements at Mace Head were performed partly at the beginning of the campaign (24–26 February 2013) and partly at the end of the campaign (21 May 2013).

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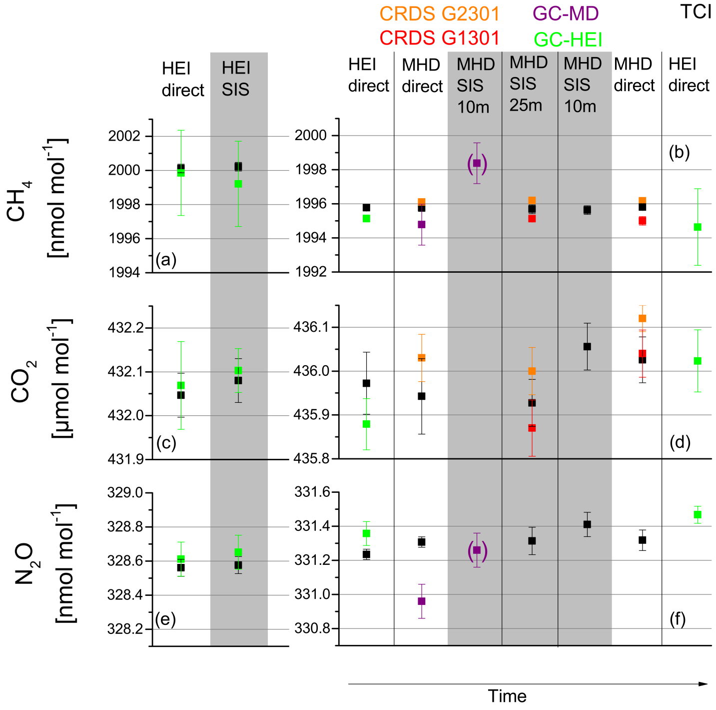

**Fig. 3.** Direct cylinder gas measurement (direct) and SIS test on the 12 January 2013 for **(a)** $CH_4$, **(c)** $CO_2$ and **(e)** $N_2O$ in Heidelberg (HEI) and on the 26/27 February 2013 for **(b)** $CH_4$, **(d)** $CO_2$ and **(f)** $N_2O$ at Mace Head. Grey shaded areas show results when the 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.

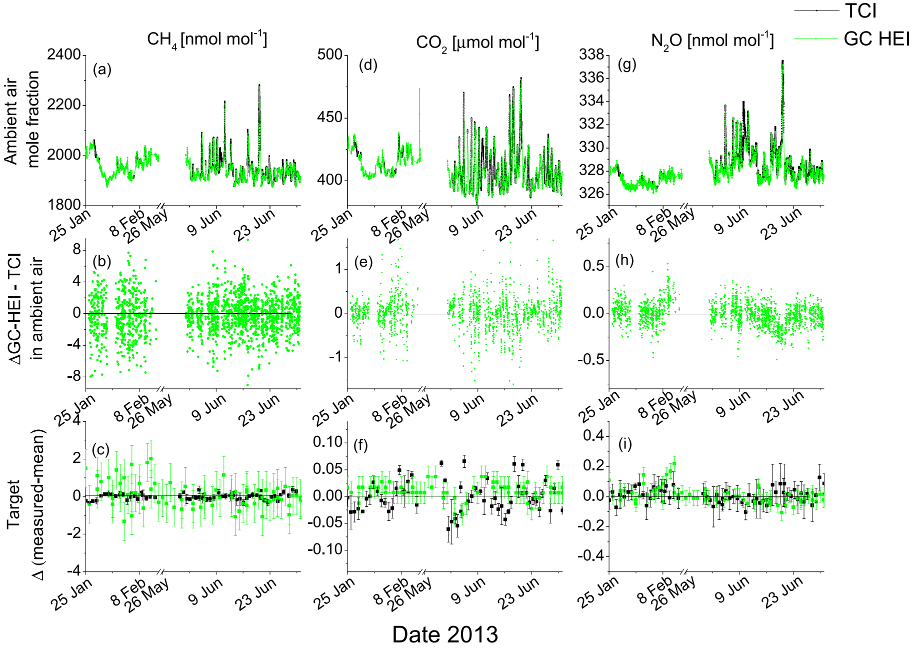

**Fig. 4.** Upper panels: concentration of ambient air **(a)** CH$_4$, **(d)** CO$_2$, and **(g)** N$_2$O during the preparing and finalizing comparison periods in Heidelberg. From 25 January 2013 until 13 February 2013 both instruments were run in parallel, but with independent intake lines. From 1 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$_2$O. Lower panels: TCI and GC-HEI daily target deviation from mean for **(c)** CH$_4$, **(f)** CO$_2$ and **(i)** N$_2$O. Notice the interruption in the x-axis from February to May 2013 where the Mace Head measurement campaign took place.

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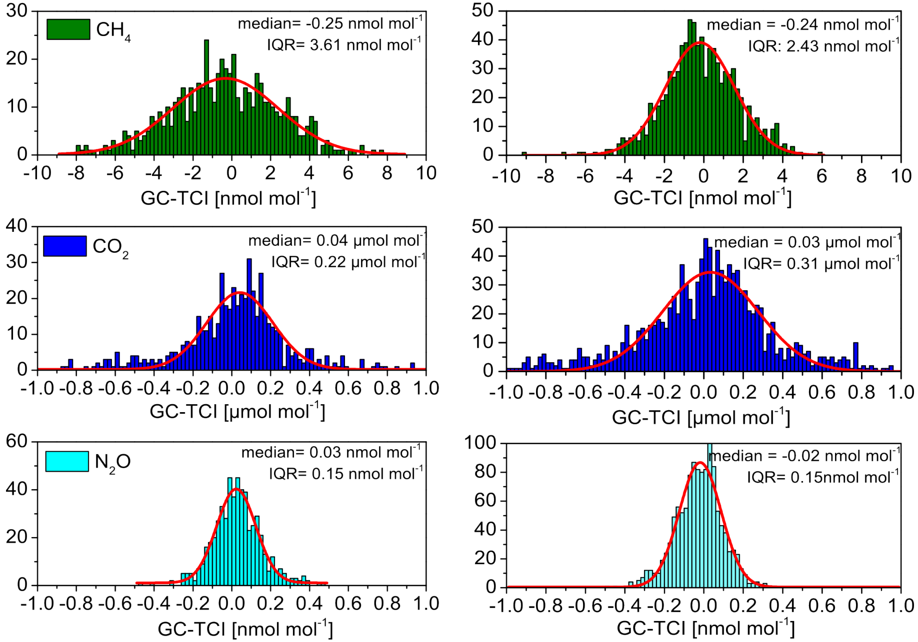

**Fig. 5.** Distributions of the concentration differences measured with the GC-HEI and the TCI in Heidelberg (both with seperate intake lines) from 25 January 2013 until 13 February 2013 (left panels) and from the 1 June 2013 to the 1 July 2013 with the same intake line (right panels). The red lines are Gauss fits to the distributions, IQR = interquartile range.

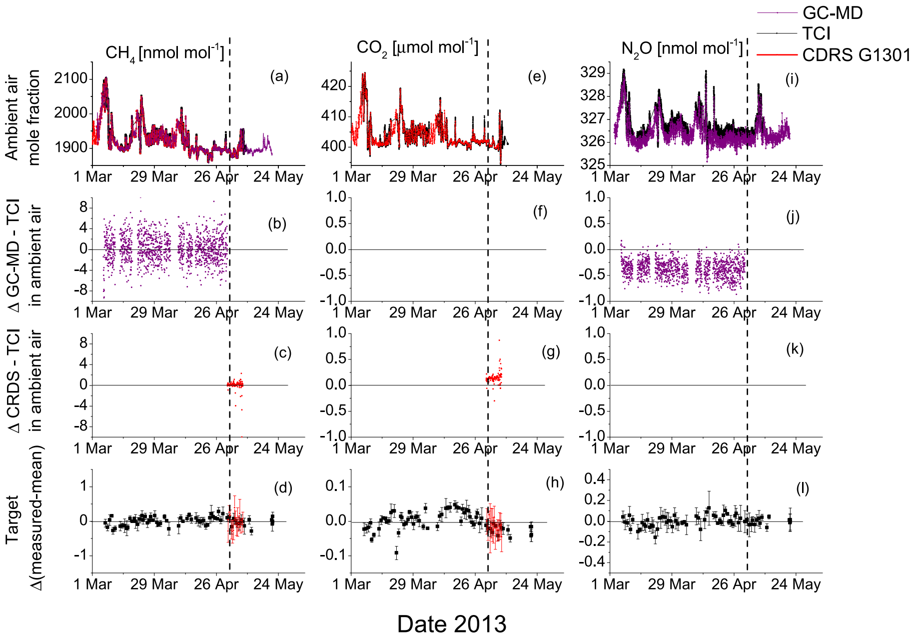

**Fig. 6.** Upper panels: concentration of **(a)** $CH_4$, **(e)** $CO_2$, and **(i)** $N_2O$ during the measurement campaign at Mace Head. All instruments were running in parallel to the TCI with independent intake lines to the same height. The GC-MD measured at a height of 10 m and the CRDS at a height 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 presented 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 2013–1 May 2013 Third row panels: difference between the CRDS G1301 and the TCI for **(c)** $CH_4$ and **(g)** $CO_2$ from 1–7 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.

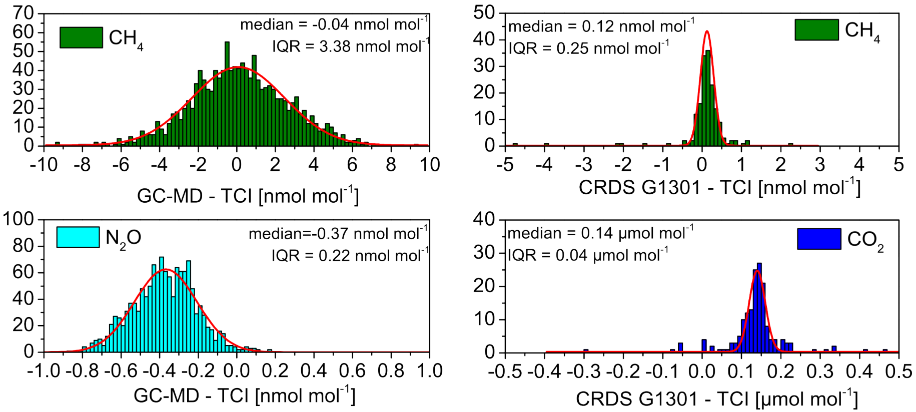

**Fig. 7.** Left panels: distribution of the differences in $CH_4$ and $N_2O$ between the discrete GC-MD measurements and the corresponding 3 minutely integrated values of the TCI at Mace Head from 6 March 2013 until 1 May 2013 (both instruments with separate intake lines at a height of 10 m). The red 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.

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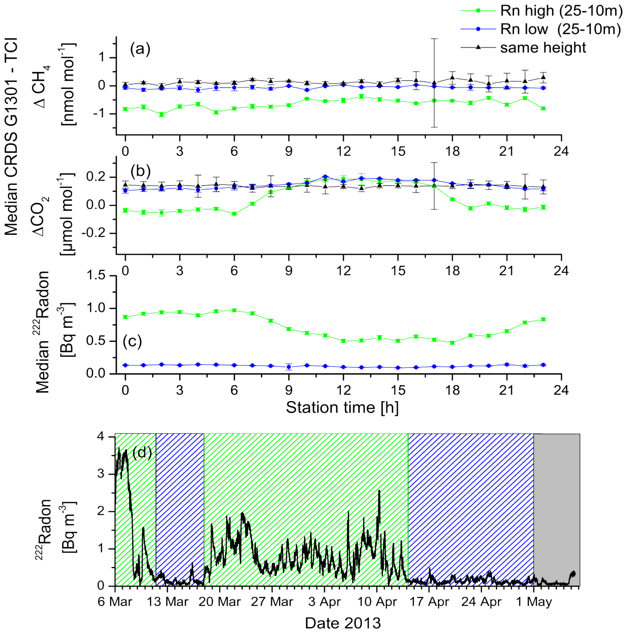

**Fig. 8. (a)** Median diurnal $CH_4$ differences (CRDS G1301 – TCI) and **(b)** median diurnal $CO_2$ differences (CRDS G1301 – TCI) between the CRDS G1301 at 25 m and the TCI at 10 m during periods of high (green) and low (blue) $^{222}$Radon activity concentration and **(c)** median diurnal Radon activity concentration at about 5 m height a.g.l. during periods of high (green) and low (blue) $^{222}$Radon activity concentration (see Fig. 8d). Black symbols in **(a)** and **(b)** show the difference between instruments when measuring at the same height (25 m). Phases of continental (green) and marine (blue) air mass regimes during measurement at different heights are shown in **(d)**. The grey background at the end of the period denotes the time period when both instruments measured at the same height.