



HAL
open science

Comparisons of continuous atmospheric CH₄, CO₂ and N₂O measurements – results from a travelling instrument campaign at Mace Head

S. Vardag, S. Hammer, S. O'Doherty, T. Spain, B. Wastine, A. Jordan, I. Levin

► **To cite this version:**

S. Vardag, S. Hammer, S. O'Doherty, T. Spain, B. Wastine, et al.. Comparisons of continuous atmospheric CH₄, CO₂ and N₂O measurements – results from a travelling instrument campaign at Mace Head. *Atmospheric Chemistry and Physics*, 2014, 14 (16), pp.8403-8418. 10.5194/acp-14-8403-2014 . hal-03213228

HAL Id: hal-03213228

<https://hal.science/hal-03213228v1>

Submitted on 30 Apr 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Comparisons of continuous atmospheric CH₄, CO₂ and N₂O measurements – results from a travelling instrument campaign at Mace Head

S. N. Vardag¹, S. Hammer¹, S. O'Doherty², T. G. Spain³, B. Wastine⁴, A. Jordan⁵, and I. Levin¹

¹Institut für Umweltphysik, Heidelberg University, Germany

²School of Chemistry, University of Bristol, Bristol, UK

³National University of Ireland, Galway, Ireland

⁴Laboratoire des Sciences du Climat et de l'Environnement (LSCE), CEA/CNRS/UVSQ, Gif sur Yvette, France

⁵Max Planck Institute for Biogeochemistry, Jena, Germany

Correspondence to: S. N. Vardag (svardag@iup.uni-heidelberg.de)

Received: 18 February 2014 – Published in Atmos. Chem. Phys. Discuss.: 25 April 2014

Revised: 8 July 2014 – Accepted: 12 July 2014 – Published: 21 August 2014

Abstract. A 2-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 at Mace Head, Ireland. The aim was to evaluate the compatibility of atmospheric methane (CH₄), carbon dioxide (CO₂) and nitrous oxide (N₂O) measurements of the routine station instrumentation, consisting of a gas chromatograph (GC) for CH₄ and N₂O as well as a cavity ring-down spectroscopy (CRDS) system for CH₄ and CO₂. 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 $-0.04 \text{ nmol mol}^{-1}$ for CH₄ and $-0.37 \text{ nmol mol}^{-1}$ for N₂O (GC-TCI). For N₂O, a similar difference ($-0.40 \text{ nmol mol}^{-1}$) 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 N₂O X2006a reference scale used for the TCI and the Scripps Institu-

tion 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 $0.12 \text{ nmol mol}^{-1}$ for CH₄ and $0.14 \text{ } \mu\text{mol mol}^{-1}$ for CO₂ (CRDS G1301 – TCI). The difference between both instruments for CO₂ could not be explained, as direct measurements of calibration gases show no such difference. The CH₄ 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 CO₂ and N₂O.

1 Introduction

Since the industrial revolution, the global abundances of the long-lived greenhouse gases carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) 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), which need to be reached in order 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 Umweltp Physik 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). N₂O and CH₄ mole fractions measured with the locally installed GC-MD system as well as CH₄ and CO₂ measurements performed by a cavity ring-down spectroscopy (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 10 m level to obtain sufficient data for the GC-MD comparison, while the CRDS systems have their air intake at the 25 m level, we used the opportunity of this comparison campaign to investigate the corresponding vertical gradients of CO₂ and CH₄ 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. These results nicely illustrate how capable current optical instrumentation is in terms of precision. As our com-

parison 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 we extended it beyond CO₂ and CH₄ to include N₂O. We used the FTIR since it turned out to be robust and compact and since it measures CO₂, CH₄ and N₂O 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 3-minute data recorded by the FTIR is generally better than $\pm 0.05 \mu\text{mol mol}^{-1}$ for CO₂, $\pm 0.25 \text{ nmol mol}^{-1}$ for CH₄ and $\pm 0.05 \text{ nmol mol}^{-1}$ for N₂O. Within the Integrated non-CO₂ 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, Germany, using CRDS for CH₄ and CO₂ and gas chromatography with electron-capture detection (GC-ECD) for N₂O. The scales in use were the WMO CO₂ X2007 scale (Tans et al., 2011), the WMO CH₄ X2004 scale (Dlugokencky et al., 2005) and the WMO N₂O X2006a scale (Hall et al., 2007).

2.2 Site description and routine instrumentation in Heidelberg

Heidelberg is a medium-sized 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 Umweltp Physik, 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 bypass to the GC-HEI system, which measures CO₂, CH₄, N₂O, SF₆, CO and H₂ 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 counterflow mode followed by Mg(ClO₄)₂) and sample pumps. The working gases for the GC-HEI system are calibrated on the WMO X2007 scale for CO₂, the WMO X2004 scale for CH₄ and the WMO X2006a scale for N₂O, based on Heidelberg tertiary standards calibrated at the WMO GAW CCL at National Oceanic and Atmospheric Administration (NOAA) in Boulder, USA. These standards, with a N₂O 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 measurements is

$\pm 0.05 \mu\text{mol mol}^{-1}$ for CO₂, $\pm 2.4 \text{ nmol mol}^{-1}$ for CH₄ and $\pm 0.1 \text{ nmol mol}^{-1}$ for N₂O. 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 mole fraction 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 bypass, 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 (France) as part of the AGAGE (CH₄ and N₂O) (Prinn et al., 2000) and Integrated Carbon Observation System (ICOS) demonstration (CO₂ and CH₄) (<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 ECD and a flame-ionization detector (FID) is used to measure N₂O and CH₄, while a reduction gas analyser (RGA) measures CO and H₂ within the AGAGE network. One working standard, which is measured alternately with ambient air or other samples, is used for on-site calibration. These whole air standards last for approximately 8 months and are analysed at Scripps Institute of Oceanography (SIO) before and after use at Mace Head, for details see Prinn et al. (2000). New working standards are always compared on-site with the old working standards and agree well with the values assigned at the SIO on a different instrument but applying the same non-linearity correction. For more than 15 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 vari-

able amount of air being injected. The precision of the measurements is approximately $0.1 \text{ nmol mol}^{-1}$ for N₂O and $1.5 \text{ nmol mol}^{-1}$ for CH₄. The working gases for the GC-MD system are calibrated on the Tohoku University scale for CH₄ (Cunnold et al., 2002) and the SIO-1998 scale for N₂O (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 CO₂ and CH₄ in un-dried 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 $-45 \text{ }^\circ\text{C}$ before measuring CO₂ and CH₄. 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 vapour 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 of the difference of both CRDS instruments (G1301–G2301) and the absolute humidity, of $0.13 \mu\text{mol mol}^{-1} \text{ CO}_2 \%^{-1} \text{ H}_2\text{O}$ for the period from March 2013 until July 2013. The H₂O-dependency 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 CO₂ values of the G1301 instrument of $0.01\text{--}0.04 \mu\text{mol mol}^{-1}$ 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 min (the first 10 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 CO₂ and CH₄ with a precision of about $0.02 \mu\text{mol mol}^{-1}$ for CO₂ and $0.1 \text{ nmol mol}^{-1}$ for CH₄ (Crosson, 2008). A common target cylinder is used for quality control purposes and is measured on both instruments every 11 h. The (1σ) reproducibility of the target

cylinder measurement is about $0.02 \mu\text{mol mol}^{-1}$ for CO₂ and $0.21 \text{ nmol mol}^{-1}$ for CH₄ for the G1301 from March to June 2013 and $0.03 \mu\text{mol mol}^{-1}$ for CO₂ and $0.33 \text{ nmol mol}^{-1}$ for CH₄ 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 $0.02 \pm 0.10 \mu\text{mol mol}^{-1}$ for CO₂ and $-0.20 \pm 0.70 \text{ nmol mol}^{-1}$ for CH₄ during the comparison campaign (from 1 March 2013 to 31 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 $0.03 \mu\text{mol mol}^{-1}$ for CO₂, $0.16 \text{ nmol mol}^{-1}$ for CH₄ and $0.05 \text{ nmol mol}^{-1}$ for N₂O (see also Sects. 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 CH₄, CO₂ and N₂O measurements (see Fig. 1). For CH₄, the mean difference (measured TCI value – WMO CCL value and standard error) of $0.04 \pm 0.01 \text{ nmol mol}^{-1}$ is negligible. For CO₂ in the ambient mole fraction range (380–480 $\mu\text{mol mol}^{-1}$), a difference of $-0.03 \pm 0.04 \mu\text{mol mol}^{-1}$ was observed, while the N₂O difference in the ambient range (325–338 nmol mol^{-1}) was $-0.00 \pm 0.03 \text{ nmol mol}^{-1}$. It can thus be confirmed that the accuracy of the TCI measurements meets the WMO ILC targets.

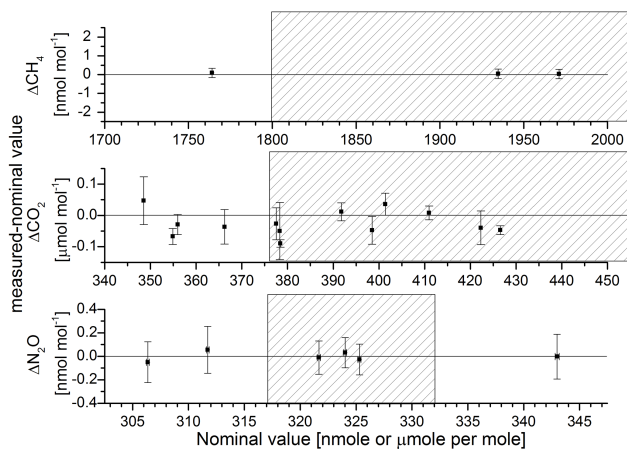


Figure 1. Difference between TCI-measured Heidelberg WMO CCL tertiary standards and their respective nominal value given by WMO CCL (TCI-measured – WMO CCL nominal value). The measurements were performed on 30 May 2013, 24 June 2013, 3 July 2013, 2 September 2013 and 3 September 2013. The standard deviation plotted combines 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.

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 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 CH₄ and CO₂, all instruments compare well within the WMO ILC target. The GC-HEI and the TCI instruments agree very well with each other ($-0.02 \pm 0.04 \mu\text{mol mol}^{-1}$, mean \pm standard error) for CO₂. The G1301 CRDS instrument shows very good agreement with the TCI in CO₂ results ($-0.01 \pm 0.02 \mu\text{mol mol}^{-1}$), while the G2301 results are consistently higher ($0.05 \pm 0.03 \mu\text{mol mol}^{-1}$) than the CO₂ 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 $0.06 \mu\text{mol mol}^{-1}$, while it was $0.02 \mu\text{mol mol}^{-1}$ 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 N₂O, the values obtained with the GC-HEI were higher than those obtained with the TCI

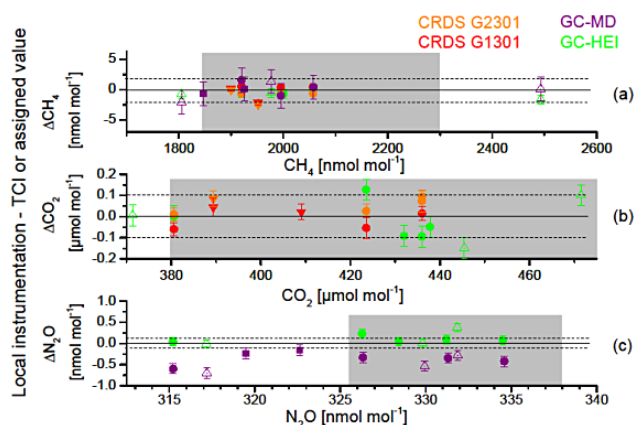


Figure 2. Differences (local instrument – TCI or assigned value in the case of the TCI standards shown as open symbols) of the measured mole fractions of (a) CH₄, (b) CO₂ and (c) N₂O of different cylinders: Mace Head AGAGE target cylinders (squares), Heidelberg target cylinders (circles), TCI working 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 (24–26 February 2013) and partly at the end of the campaign (21 May 2013).

($0.11 \pm 0.05 \text{ nmol mol}^{-1}$). The reason for the difference between the GC-HEI and the TCI is not clear. The N₂O cylinder measurements with the GC-MD show significantly lower values than the TCI, by $-0.40 \pm 0.06 \text{ nmol mol}^{-1}$. This is a rather large and unexpected offset between the two instruments, since current known scale differences between SIO-1998 and WMO X2006a are of 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 mole fraction 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.

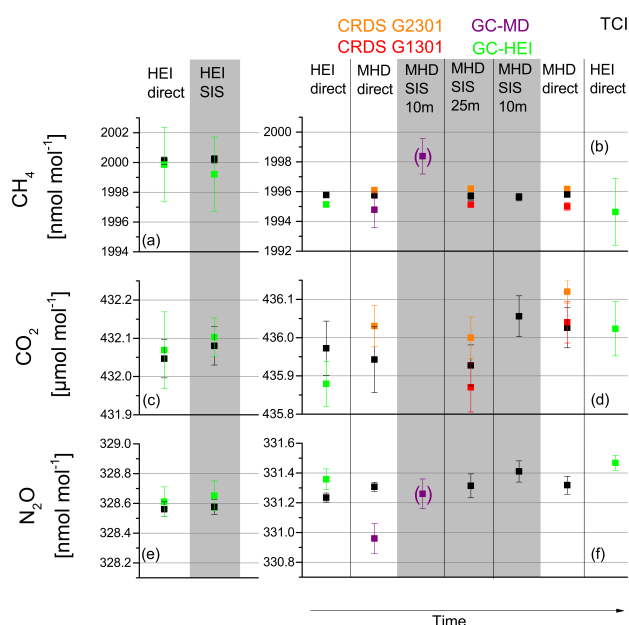


Figure 3. Direct cylinder gas measurement (direct) and SIS test on the 12 January 2013 for (a) CH₄, (c) CO₂ and (e) N₂O in Heidelberg (HEI) and on the 26/27 February 2013 for (b) CH₄, (d) CO₂ and (f) N₂O at Mace Head (MHD). Different cylinders were used for the SIS test in Heidelberg and Mace Head. Grey 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.

3.3.1 Sample intake system test in Heidelberg

A SIS test was performed in Heidelberg (Fig. 3a, c, 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 (\pm combined errors of their reproducibility and their standard deviations during the SIS tests) was SIS – direct = $0.1 \pm 0.35 \text{ nmol mol}^{-1}$ for CH₄, $0.03 \pm 0.07 \mu\text{mol mol}^{-1}$ for CO₂ and $0.02 \pm 0.07 \text{ nmol mol}^{-1}$ for N₂O; for the GC-HEI it was SIS – direct = $-0.65 \pm 3.5 \text{ nmol mol}^{-1}$ for CH₄, $0.03 \pm 0.11 \mu\text{mol mol}^{-1}$ for CO₂ and $0.04 \pm 0.11 \text{ nmol mol}^{-1}$ for N₂O. 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 different than 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 Fig. 3b, d, f. The comparison between the direct measurements before and after the campaign indicate a mole fraction change in the cylinder for CO₂ in the order of 0.1 $\mu\text{mol mol}^{-1}$. 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 and 10 m. Significant increases of CO₂ 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 35 bar (Chen et al., 2013). Since the SIS cylinder was emptied to a pressure of 20 bar, a mole fraction change in the SIS cylinder was not unexpected.

No significant mole fraction change was observed for CH₄, but for N₂O also a slight but not significant change of 0.1 nmol mol^{-1} was indicated by the GC-HEI (see Fig. 3f). For CH₄, 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 of the order of $3.7 \pm 1.7 \text{ nmol mol}^{-1}$ (difference \pm combined error 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 CH₄ and N₂O 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 N₂O ($0.07 \pm 0.10 \text{ nmol mol}^{-1}$), which could, however, be also due to a small N₂O drift in the cylinder mole fraction. For CO₂, the TCI and CRDS measurements show only small SIS influence within their measurement uncertainties: TCI at 25 m: $-0.01 \pm 0.08 \mu\text{mol mol}^{-1}$, TCI at 10 m: $0.03 \pm 0.08 \mu\text{mol mol}^{-1}$, CRDS G1301: $-0.07 \pm 0.12 \mu\text{mol mol}^{-1}$ (SIS effect was determined relative to the TCI measurements at 25 m and after the SIS test), CRDS G2301: $-0.02 \pm 0.03 \mu\text{mol mol}^{-1}$ when taking into account the mole fraction jump after the SIS test at the 25 m intake of about 0.1 $\mu\text{mol mol}^{-1}$.

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 CH₄ measurements of the TCI and the GC-HEI (Fig. 4a, b) show a difference of $-0.25 \pm 3.61 \text{ nmol mol}^{-1}$ (median and interquartile range, see Fig. 5) before the campaign and a difference of $-0.24 \pm 2.43 \text{ nmol mol}^{-1}$ 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 nmol mol^{-1} (see Fig. 4c).

All CO₂ measurements of the TCI in Heidelberg and the GC-HEI agree very well (see Fig. 4d, e). The difference (GC-HEI – TCI) between the instruments was nearly the same in both intercomparison phases ($0.04 \pm 0.22 \mu\text{mol mol}^{-1}$ before the campaign and $0.03 \pm 0.31 \mu\text{mol mol}^{-1}$ after the campaign).

The N₂O measurements show a median difference of $0.03 \pm 0.15 \text{ nmol mol}^{-1}$ (GC-HEI – TCI) during the first comparison period in February and a median difference of $-0.02 \pm 0.14 \text{ nmol mol}^{-1}$ 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 measurements, which can be detected in the N₂O 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 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 a travelling comparison instrument. This has been shown earlier for CO₂ and CH₄ by Hammer et al. (2013a) and it is confirmed here. Further we show this for the first time for N₂O.

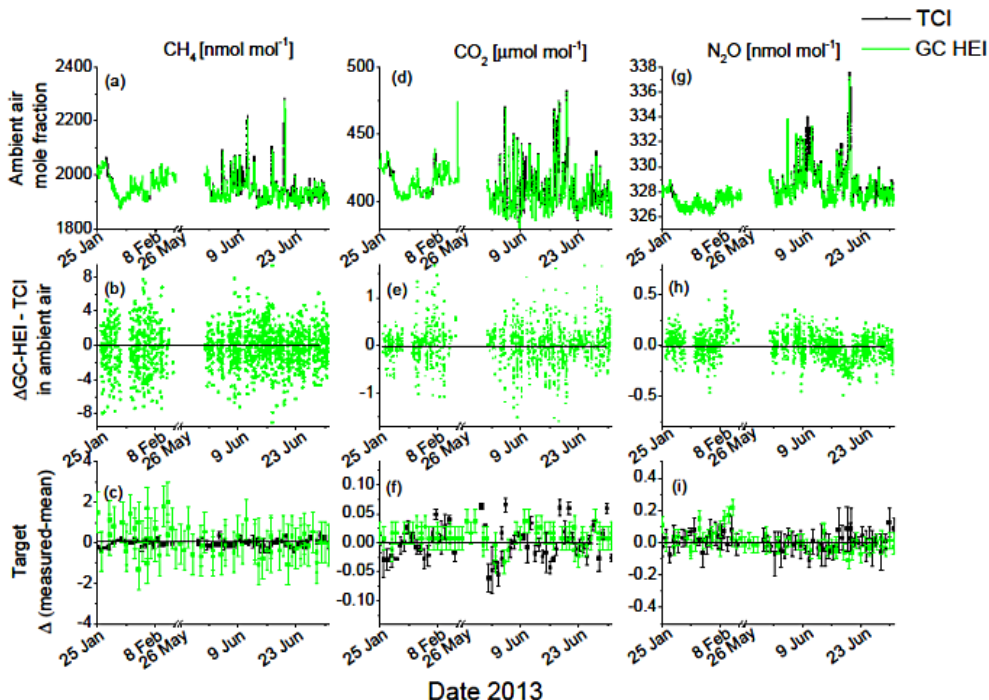


Figure 4. Upper panels: mole fraction of ambient air (a) CH₄, (d) CO₂ and (g) N₂O during the preparing and finalizing comparison periods in Heidelberg. From 25 January 2013 until 13 February 2013, both instruments were run in parallel, but with independent intake lines. From 1 June 2013 until 1 July 2013, both instruments used the same intake line. Middle panels: differences between the GC-HEI and the TCI for (b) CH₄, (e) CO₂ and (h) N₂O. Lower panels: TCI and GC-HEI daily target deviation from mean for (c) CH₄, (f) CO₂ and (i) N₂O. Notice the interruption in the x axis from February to May 2013 where the Mace Head measurement campaign took place.

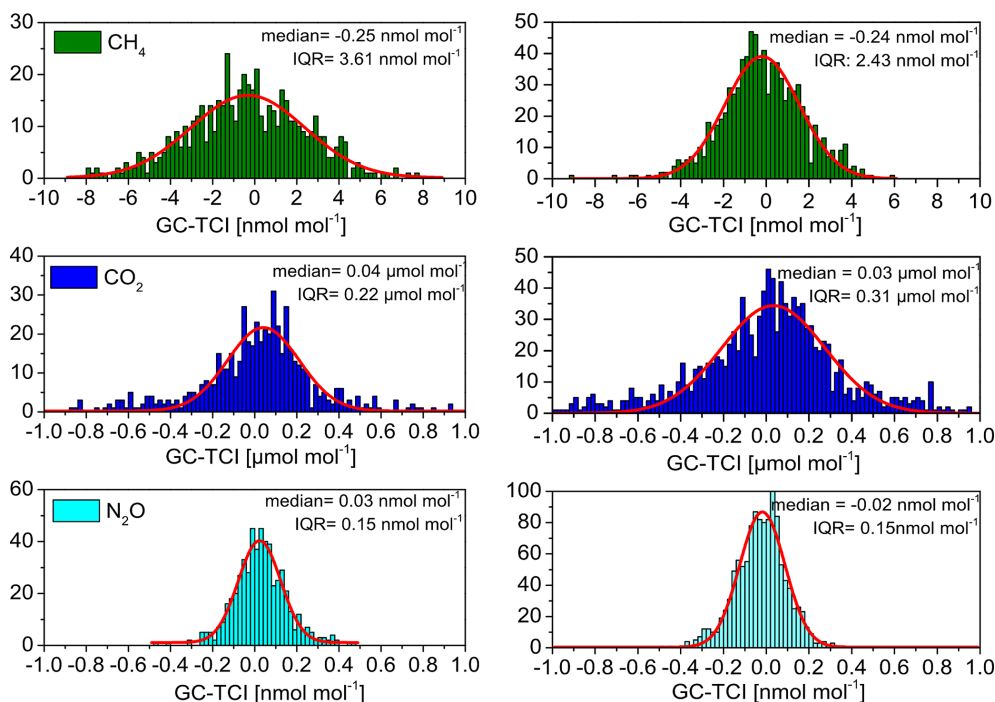


Figure 5. Distributions of the mole fraction differences measured with the GC-HEI and the TCI in Heidelberg (both with separate intake lines) from 25 January 2013 until 13 February 2013 (left panels) and from the 1 June 2013 to the 1 July 2013 with the same intake line (right panels). The red lines are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

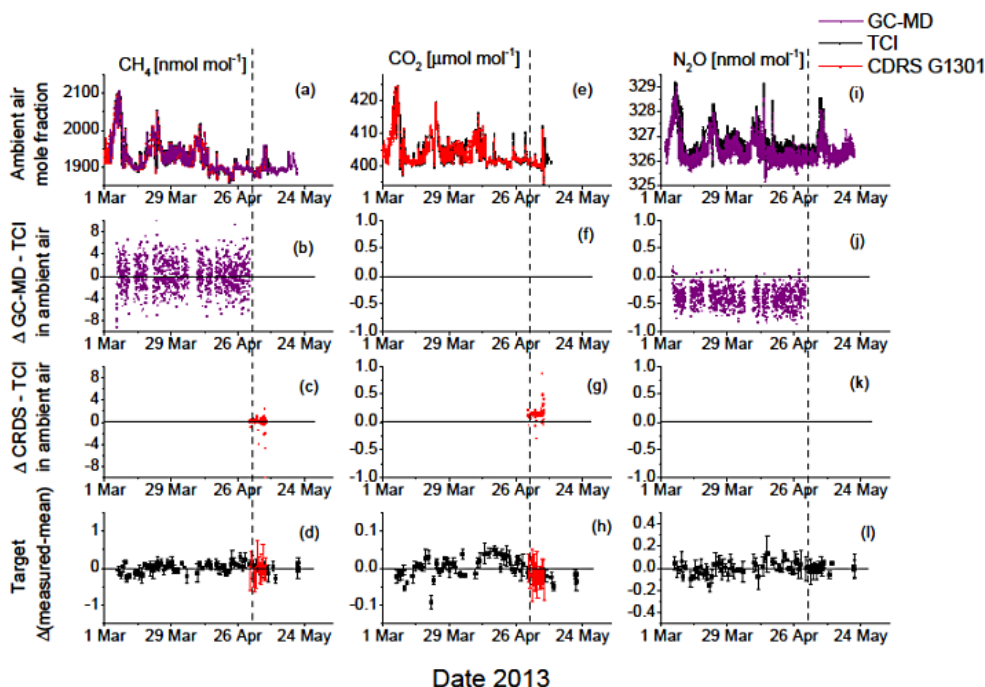


Figure 6. Upper panels: mole fraction of (a) CH₄, (e) CO₂ and (i) N₂O during the measurement campaign at Mace Head. All instruments were running in parallel with the TCI with independent intake lines to the same height. The GC-MD measured at a height of 10 m and the CRDS at a height of 25 m. On 1 May 2013, the TCI intake was switched on for 10 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) CH₄ and (j) N₂O from 6 March 2013 until 1 May 2013. Third row panels: difference between the CRDS G1301 and the TCI for (c) CH₄ and (g) CO₂ from 1 May 2013 until 7 May 2013. Lowest panels: TCI and CRDS daily target measurement deviation from mean for (d) CH₄, (h) CO₂ and (i) N₂O. No GC-MD target measurements are available.

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 Fig. 6b and j and in Fig. 7 (left panels). From 1 May 2013 until 6 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 and without a buffer volume, 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 pe-

riod with the CRDS G1301. Further, the cavity volume of the CRDS is much smaller than that of the TCI. Therefore, essentially a slight temporal asynchrony can be introduced influencing the standard deviation of the differences. But comparison of the 1 min CRDS data with the 3 min TCI data (not shown here) revealed that both instruments measured temporally synchronously throughout the comparison.

The CH₄ 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 Fig. 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 ± 0.12 nmol mol⁻¹. No target gas was measured with the GC-MD.

The CO₂ measurements of the CRDS G1301 and the TCI show an offset (CRDS G1301 – TCI) of 0.14 ± 0.04 μ mol mol⁻¹ (median and interquartile range (IQR), see Fig. 7 right panel). No CO₂ 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.

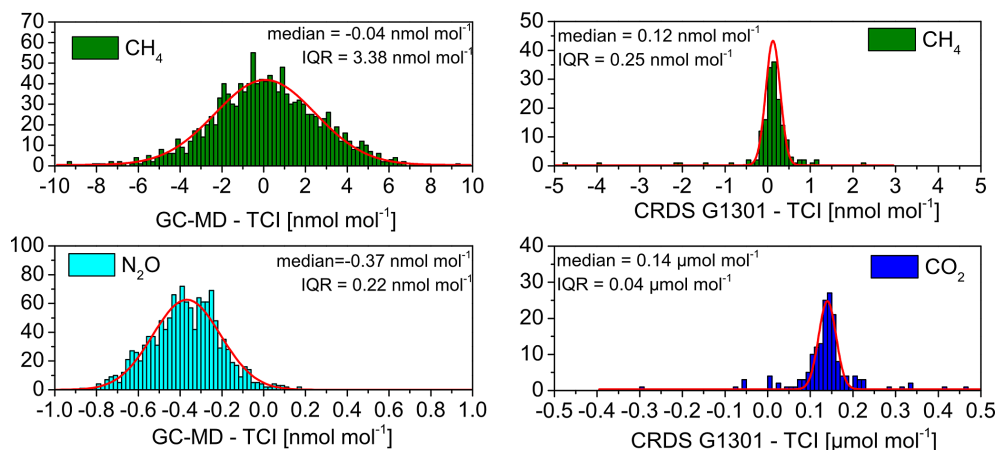


Figure 7. Left panels: distribution of the differences in CH₄ and N₂O between the discrete GC-MD measurements and the corresponding 3-minute averaged values of the TCI at Mace Head from 6 March 2013 until 1 May 2013 (both instruments with separate intake lines at a height of 10 m). Right panels: distribution of the differences between the hourly averaged CH₄ and CO₂ 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.

For N₂O, the ambient air measurements of the GC-MD and the TCI show a difference (GC-MD – TCI) of -0.37 ± 0.22 nmol mol⁻¹ (median and IQR). A difference of -0.40 ± 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 difference. 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 CH₄, CO₂ and N₂O, 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 CH₄, CO₂ and N₂O confirms the excellent performance of the TCI during the entire measurement campaign. Differences in CH₄, CO₂ and N₂O in direct cylinder measurements agreed within their uncertainties to differences in ambient air measurements. For N₂O, 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 CH₄ measurements of the three different instruments, the FTIR (TCI), CRDS and GC-MD agree very well with each other 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 CH₄ mole fractions, whereas the GC-HEI showed slightly lower CH₄ mole fractions. The good agreement between the CH₄ measurements of the two different networks NOAA and AGAGE also confirms that the measurements on the WMO CH₄ X2004 scale and the Tohoku University scale are very compatible (see also Dlugokencky et al., 2005).

4.3 CO₂ comparison at Mace Head

For CO₂, 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 CO₂ 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). Reference scale transfer errors in the calibration of the CRDS G1301 working standards have not been examined

Table 1. Median differences and interquartile ranges between the ambient air measurements (local instrumentation – TCI), mean difference and standard deviation of direct cylinder gas measurements and SIS effects (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 ¹ difference	CRDS G2301 difference	GC-HEI difference ² after campaign
ΔCH_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	–
ΔCO_2 ($\mu\text{mol mol}^{-1}$)	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	–
$\Delta\text{N}_2\text{O}$ (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.

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 ($-0.07 \pm 0.12 \mu\text{mol mol}^{-1}$ for the CRDS G1301 and $0.01 \pm 0.08 \mu\text{mol mol}^{-1}$ for the TCI) would only explain slightly smaller CRDS G1301 values. The insignificant bias found during the SIS test can therefore not explain the CO₂ 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 correction could explain only 0.01 – $0.04 \mu\text{mol mol}^{-1}$ CO₂ of the difference. On the other hand, it seems worth noting that the difference between the two CRDS instruments was rather large during the direct cylinder measurements ($0.06 \pm 0.13 \mu\text{mol mol}^{-1}$, 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. $0.02 \mu\text{mol mol}^{-1}$). 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 CO₂ measurements (Nara et al., 2012), but should affect ambient air measurements to the same degree as direct real air cylinder measurements.

4.4 N₂O comparisons at Mace Head

For N₂O, the difference of ambient air measurements at Mace Head between the TCI and the GC-MD was found to be $-0.37 \pm 0.22 \text{ nmol mol}^{-1}$ (GC-MD – TCI). Since a similar difference of $-0.40 \pm 0.06 \text{ nmol mol}^{-1}$ 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 N₂O is significantly larger than the WMO ILC targets. Note, however, that the TCI is calibrated on the WMO N₂O 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 $+0.03 \text{ nmol mol}^{-1}$ (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 WMO2006A – WMO2006 = $-0.05 \text{ nmol mol}^{-1}$ (B. Hall, personal communication, 2013). Altogether, currently reported scale differences between WMO X2006a and SIO-1998 are all smaller than $0.1 \text{ nmol mol}^{-1}$ 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 partly explain this difference. For the WMO CCL tertiary standards, the reproducibility of N₂O assignments is about $0.08 \text{ nmol mol}^{-1}$ (for the ambient range: 310 – $330 \text{ nmol mol}^{-1}$) (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 cylinders 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 less than $0.1 \text{ nmol mol}^{-1}$.

Reference 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 of the order of $\pm 0.03\%$ (1σ of the difference), which corresponds to about $0.1 \text{ nmol mol}^{-1}$ in the ambient mole fraction 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 N₂O in ambient air between the GC-MD and the TCI includes a total uncertainty due to scale transfer which is of 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 N₂O scales is due to uncertainties in the preparation of N₂O primary standards and is typically of the order of $0.3 \text{ nmol mol}^{-1}$ (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 N₂O 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 $-0.11 \pm 0.14 \text{ nmol mol}^{-1}$ (SIO-1998 – WMO N₂O 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 $-0.14 \pm 0.23 \text{ nmol mol}^{-1}$ (both from P. Krümmel, personal communication, 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, however only about one third of, the differences found during the TCI comparison campaign at Mace Head (March–May 2013). This may reinforce the possibility of a current small-scale difference between the WMO X2006a scale and the SIO-1998 scale, which could be of the order of -0.1 to $-0.4 \text{ nmol mol}^{-1}$ (SIO-1998 – WMO X2006a). Note, however, that Thompson et al. (2014) estimated scale differences between SIO-1998 and WMO X2006a as having 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 $0.04 \text{ nmol mol}^{-1}$ per year and for NOAA HATS flasks the trend is about $0.08 \text{ nmol mol}^{-1}$ per year (P. Krümmel, personal communication, 2013).

5 Conclusions

New optical instrumentation allows measuring CH₄, CO₂ and also N₂O with very high precision, which essentially 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 CH₄ 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. $0.4 \text{ nmol mol}^{-1}$ in N₂O. This difference could partly be due to a general small reference scale difference between the WMO X2006a and the SIO-1998 scales and partly due to reference scale transfer and instrumental errors, such as remaining non-linearity effects.

The TCI campaign also showed differences between CO₂ measurements of the CRDS G1301 and the TCI as large as $0.14 \mu\text{mol mol}^{-1}$, 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, 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 CO₂ measurements and the water correction of the CRDS G1301, which need to be investigated in more detail. Earlier TCI campaigns at Cabauw, Netherlands, and Houdelaincourt (Observatoire Pérenne de l'Environnement, OPE), France, revealed differences in CO₂ 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 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 were differences between both systems within the WMO ILC targets. This clearly shows the difficulty of performing compatible CO₂ measurements in the field and 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), CO₂ 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 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. Basically, the higher the precision and stability of the local instrument, the shorter the time period for parallel measurement of ambient air, but a comparison period of about 1 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 and 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 h. 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 ended when additional tests could no longer be performed.

Finally, we were also able to demonstrate during the campaign at Mace Head that small gradients of CO₂ and CH₄ 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.

Appendix A: Vertical mole fraction gradients of CH₄ and CO₂ 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 principally allows us to detect the vertical mole fraction 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 ²²²Rn daughter activity concentrations measured with a Heidelberg 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 ²¹⁴Po concentration is low (<0.5 Bq m⁻³), whereas wind from other directions brings air masses with higher ²¹⁴Po 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 ²¹⁴Po activity 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 ²²²Rn flux from continental soils does not show a diurnal cycle. The data from the marine regime showed no significant diurnal cycle and a mean activity concentration of 0.2 Bq m⁻³.

As a first step to determine vertical gradients, the differences between CRDS G1301 and TCI when measuring at the same height (i.e. from 1 May 2013–7 May 2013) must be compared. This comparison serves as a reference for determining the instrumental mole fraction differences. As described in Sect. 3, we found a difference between the CRDS G1301 and TCI measurements of 0.12 nmol mol⁻¹ for CH₄ and 0.14 μmol mol⁻¹ for CO₂. The difference when measuring at the same height (black curves in Fig. 8a, 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 mole fraction difference.

In a next step we compare the difference between instruments when measuring at different heights (25–10 m). For continental air masses we then see a weak diurnal cycle in CH₄. The mole fraction gradient decreases 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).

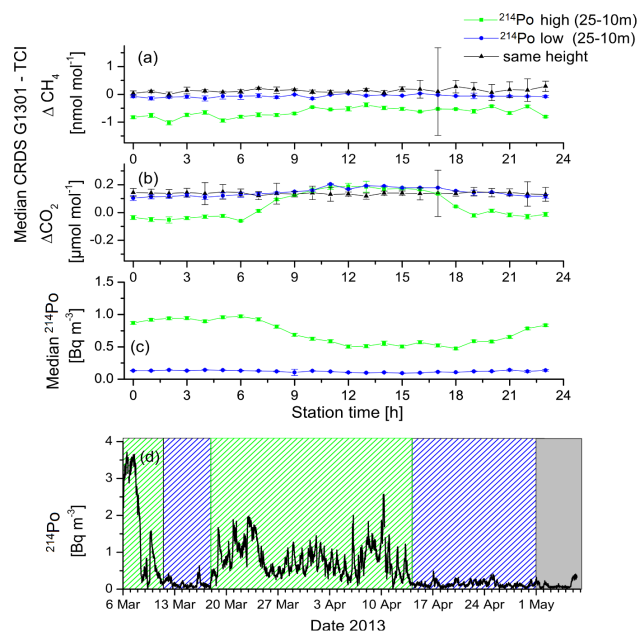


Figure A1. (a) Median diurnal CH₄ differences (CRDS G1301 – TCI) and (b) median diurnal CO₂ differences (CRDS G1301–TCI) between the CRDS G1301 at 25 m and the TCI at 10 m during periods of high (green) and low (blue) ²²²Radon daughter (i.e. ²¹⁴Po) activity concentration and (c) median diurnal ²¹⁴Po activity concentration at about 5 m height a.g.l. during periods of high (green) and low (blue) ²¹⁴Po 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.

This finding suggests that there is a positive CH₄ flux from the ground throughout the whole day (24 h). For the marine air masses (low ²¹⁴Po activity concentration) there are only marginal differences in measured CH₄ compared to the measurements at the same height, which suggests only a very small or negligible CH₄ flux from the ocean. Supersaturation of CH₄ in the ocean mixed layer potentially leading to a CH₄ flux from the ocean to the atmosphere, has often been reported, but direct fluxes to the atmosphere due to this supersaturation are difficult to observe (Bakker et al., 2014).

For continental air masses we find a rather strong diurnal cycle in the CO₂ gradient. The difference between both levels (25–10 m) decreases 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 CO₂ level at 10 m height is thus 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 CO₂ flux and plant photosynthesis during the day time leads to a CO₂ uptake. During marine air mass

regimes the diurnal cycle is decreased, but still a slight positive CO₂ flux from below is found during night time and a negative flux during the day time. This may either be due to surface ocean CO₂ respiration or uptake by phytoplankton 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 CH₄ gradient. All in all, such small gradients of CO₂ (and CH₄) have, to our knowledge, not been resolved before. This shows that the modern instrumentation used here opens a new dimension in precision and evaluation of greenhouse gas measurements.

Acknowledgements. We are very grateful for the feedback, suggestions and input from B. Hall, P. Krummel, M. Ramonet, R. Weiss and C. Zellweger. We further thank D. Dodd and the Environmental Protection Agency, Ireland for providing the CRDS G1301 instrument data. We wish to thank M. Sabasch and D. Schmithuesen (both Institut für Umweltphysik) for their support during the campaign. This work has been funded by the InGOS EU project (284274). Further, we acknowledge the financial support given by Deutsche Forschungsgemeinschaft and Ruprecht-Karls-Universität Heidelberg within the funding program Open Access Publishing.

Edited by: J. B. Burkholder

References

- Bakker, D. C. E., Bange, H. W., Gruber, N., Johannessen, T., Upstill-Goddard, R. C., Borges, A. V., Delille, B., Löscher, C. R., Naqvi, S. W. A., Omar, A. M., and Santana-Casiano, J. M.: Air-Sea Interactions of Natural Long-Lived Greenhouse Gases (CO₂, N₂O, CH₄) in a Changing Climate, in: Ocean-atmospheric interactions of gases and particles, edited by: Liss, P. S. and Johnson, M. T., Springer Verlag, 315 pp., doi:10.1007/978-3-642-25643-1, 2014.
- Chen, H., Winderlich, J., Gerbig, C., Hoefler, A., Rella, C. W., Crosson, E. R., Van Pelt, A. D., Steinbach, J., Kolle, O., Beck, V., Daube, B. C., Gottlieb, E. W., Chow, V. Y., Santoni, G. W., and Wofsy, S. C.: High-accuracy continuous airborne measurements of greenhouse gases (CO₂ and CH₄) using the cavity ring-down spectroscopy (CRDS) technique, *Atmos. Meas. Tech.*, 3, 375–386, doi:10.5194/amt-3-375-2010, 2010.
- Chen, H., Dlugokencky, E., Hall, B., Kitzis D., Novelli, P. C., and Tans, P. P.: presentation at the 17th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT-2013), Long-term stability of calibration gases in cylinders for CO₂, CH₄, CO, N₂O and SF₆, available at: <http://ggmt-2013.cma.gov.cn/dct/page/70029> (last access: 17 February 2014), Beijing, China, 2013.
- Crosson, E. R.: A cavity ring-down analyzer for measuring atmospheric levels of methane, carbon dioxide, and water vapor, *Appl. Phys. B-Lasers O.*, 92, 403–408, 2008.
- Cunnold, D. M., Steele, L. P., Fraser, P. J., Simmonds, P. G., Prinn, R. G., Weiss, R. F., Porter, L. W., Langenfelds, R. L., Wang, H. J., Emmons, L., Tie, X. X., and Dlugokencky, E. J.: In situ measurements of atmospheric methane at GAGE/AGAGE sites during 1985–2000 and resulting source inferences, *J. Geophys. Res.*, 107, 4225, doi:10.1029/2001JD001226, 2002.
- Dlugokencky, E. J., Myers, R. C., Lang, P. M., Masarie, K. A., Crotwell, A. M., Thoning, K. W., Hall, B. D., Elkins, J. W., and Steele, L. P.: Conversion of NOAA atmospheric dry air CH₄ mole fractions to a gravimetrically prepared standard scale, *J. Geophys. Res.*, 110, D18306, doi:10.1029/2005JD006035, 2005.
- Griffith, D. W. T., Deutscher, N. M., Caldow, C., Kettlewell, G., Riggenbach, M., and Hammer, S.: A Fourier transform infrared trace gas and isotope analyser for atmospheric applications, *Atmos. Meas. Tech.*, 5, 2481–2498, doi:10.5194/amt-5-2481-2012, 2012.
- Hall, B. D., Dutton, G. S., and Elkins, J. W.: The NOAA nitrous oxide standard scale for atmospheric observations, *J. Geophys. Res.*, 112, D09305, doi:10.1029/2006JD007954, 2007.
- Hammer, S.: Quantification of the regional H₂ sources and sinks inferred from atmospheric trace gas variability, Doctoral thesis, Heidelberg University, 2008.
- Hammer, S., Konrad, G., Vermeulen, A. T., Laurent, O., Delmotte, M., Jordan, A., Hazan, L., Conil, S., and Levin, I.: Feasibility study of using a “travelling” CO₂ and CH₄ instrument to validate continuous in situ measurement stations, *Atmos. Meas. Tech.*, 6, 1201–1216, doi:10.5194/amt-6-1201-2013, 2013a.
- Hammer, S., Griffith, D. W. T., Konrad, G., Vardag, S., Caldow, C., and Levin, I.: Assessment of a multi-species in situ FTIR for precise atmospheric greenhouse gas observations, *Atmos. Meas. Tech.*, 6, 1153–1170, doi:10.5194/amt-6-1153-2013, 2013b.
- Jennings, S. G., Kleefeld, C., O’Dowd, C. D., Junker, C., Spain, T. G., O’Brien, P., Roddy, A. F., and O’Connor, T. C.: Mace Head Atmospheric Research Station – characterization of aerosol radiative parameters, *Boreal Environ. Res.*, 8, 303–314, 2003.
- Levin, I., Born, M., Cuntz, M., Langendörfer, U., Mantsch, S., Naegler, T., Schmidt, M., Varlagin, A., Verclas, S., and Wagenbach, D.: Observations of atmospheric variability and soil exhalation rate of radon-222 at a Russian forest site, *Tellus B*, 54, 462–475, doi:10.1034/j.1600-0889.2002.01346.x, 2002.
- Masarie, K. A., Langenfelds, R. L., Allison, C. E., Conway, T. J., Dlugokencky, E. J., Francey, R. J., Novelli, P. C., Steele, L. P., Tans, P. P., Vaughn, B., and White, J. W. C.: NOAA/CSIRO Flask-Air Intercomparison Program: A strategy for directly assessing consistency among atmospheric measurements made by independent laboratories, *J. Geophys. Res.*, 106, 20445–20464, doi:10.1029/2000JD000023, 2001.
- Nara, H., Tanimoto, H., Tohjima, Y., Mukai, H., Nojiri, Y., Katsumata, K., and Rella, C. W.: Effect of air composition (N₂, O₂, Ar, and H₂O) on CO₂ and CH₄ measurement by wavelength-scanned cavity ring-down spectroscopy: calibration and measurement strategy, *Atmos. Meas. Tech.*, 5, 2689–2701, doi:10.5194/amt-5-2689-2012, 2012.
- Prinn, R. G., Weiss, R. F., Fraser, P. J., Simmonds, P. G., Cunnold, D. M., Alyea, F. N., O’Doherty, S., Salameh, P., Miller, B. R., Huang, J., Wang, R. H. J., Hartley, C., Steele, L. P., Sturrock, G., Midgley, P. M., and McCulloch, A.: A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE, *J. Geophys. Res.*, 105, 17751–17792, 2000.
- Rella, C. W., Chen, H., Andrews, A. E., Filges, A., Gerbig, C., Hatakka, J., Karion, A., Miles, N. L., Richardson, S. J., Steinbacher, M., Sweeney, C., Wastine, B., and Zellweger, C.: High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air, *Atmos. Meas. Tech.*, 6, 837–860, doi:10.5194/amt-6-837-2013, 2013.
- Schulze, E. D., Luysaert, S., Ciais, P., Freibauer, A., Janssens, I. A., Soussana, J. F., Smith, P., Grace, J., Levin, I., Thiruchittampalam, B., Heimann, M., Dolman, A. J., Valentini, R., Bousquet, P., Peylin, P., Peters, W., Rödenbeck, C., Etiope, G., Vuichard, N., Wattenbach, M., Nabuurs, G. J., Poussi, Z., Nieschulze, J., Gash, J. H., and the CarboEurope Team: Importance of methane and nitrous oxide for Europe’s terrestrial greenhouse-gas balance, *Nat. Geosci.*, 2842–2850, 2009.
- Tans, P., Zhao, C., and Kitzis, D.: The WMO Mole Fraction Scales for CO₂ and other greenhouse gases, and uncertainty of the atmospheric measurements, Report of the 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases, and

- Related Measurement Techniques, 7–10 September 2009, GAW Report No. 194, WMO TD No. 1553, 152–159, 2011.
- Thompson, R. L., Chevallier, F., Crotwell, A. M., Dutton, G., Langenfelds, R. L., Prinn, R. G., Weiss, R. F., Tohjima, Y., Nakazawa, T., Krummel, P. B., Steele, L. P., Fraser, P., O'Doherty, S., Ishijima, K., and Aoki, S.: Nitrous oxide emissions 1999 to 2009 from a global atmospheric inversion, *Atmos. Chem. Phys.*, 14, 1801–1817, doi:10.5194/acp-14-1801-2014, 2014.
- WMO: Report of the 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2009), Jena, Germany, 7–10 September 2009, GAW Report No. 194, available at: <http://www.wmo.int/pages/prog/arep/gaw/gaw-reports.html> (last access: 17 February 2014), Jena, Germany, 2009.
- Zellweger, C., Steinbacher, M., and Buchmann, B.: Evaluation of new laser spectrometer techniques for in-situ carbon monoxide measurements, *Atmos. Meas. Tech.*, 5, 2555–2567, doi:10.5194/amt-5-2555-2012, 2012.
- Zhou, L. X., Kitzis, D. R., Tans, P. P., Masarie, K., and Chao, D.: WMO round-robin inter-comparison: progress and a new website, Report of the 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases, and Related Tracers Measurement Techniques, 7–10 September 2009, GAW Report No. 194, WMO TD No. 1553, 212–217, 2011.