Intercomparisons of $\delta^{13}$C and $\delta$D measurements of atmospheric CH$_4$ for combined use of datasets from different laboratories

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Abstract. We report results from intercomparison exercises between laboratories that conduct measurements of stable carbon and hydrogen isotope ratios of atmospheric CH$_4$ ($\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$). The offsets between the laboratories are larger than the measurement reproducibility of individual
laboratories. To disentangle plausible offsets between worldwide laboratories, we evaluated and critically assessed a large number of intercomparison results documented previously in the literature. The results indicate significant offsets of $\delta^{13}$C-CH$_4$ and $\delta^D$-CH$_4$ measurements among datasets reported from different laboratories; the data spread over ranges of 0.5 ‰ for $\delta^{13}$C-CH$_4$ and 13 ‰ for $\delta^D$-CH$_4$.

The intercomparison results summarized in this study may be of help when combining isotope datasets from different laboratories in future studies.

1 Introduction

Methane (CH$_4$) is an important anthropogenic and natural greenhouse gas and moreover participates in atmospheric chemistry through its reaction with the hydroxyl radical. Since individual CH$_4$ source types have characteristic isotope signatures and loss processes are associated with specific kinetic isotope effects, carbon and hydrogen isotope ratios of CH$_4$ ($\delta^{13}$C-CH$_4$ and $\delta^D$-CH$_4$) have been useful to constrain the global CH$_4$ budget (e.g. Quay et al., 1991, 1999; Miller et al., 2002; Turner et al., 2017; Rigby et al., 2017). It has been pointed out that assignment of representative isotopic signatures of various CH$_4$ sources remains uncertain due to their large spatial and temporal variability across the globe (e.g. Sherwood et al., 2017), which could result in large uncertainties of isotope-based estimates of the global CH$_4$ budget (Schwietzke et al., 2016). Nonetheless, the value of isotope measurements was amply demonstrated by recent studies which suggested shifts in the global CH$_4$ source over the last decades (Schaefer et al., 2016; Rice et al., 2016; Nisbet et al., 2016; Schwietzke et al., 2016); without isotopic analyses such conclusions would have been difficult to achieve. The isotopic ratios are commonly reported using the delta notation:

$$\delta = \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1$$  \hspace{1cm} (1)

where $R$ represents the atomic ratio of the heavy over the light isotope in the sample and the standard, respectively. Conventionally, measured values are reported relative to the international isotope scales VPDB for $\delta^{13}$C-CH$_4$ and VSMOW for $\delta^D$-CH$_4$ in per mil.

In early years, atmospheric $\delta^{13}$C-CH$_4$ and $\delta^D$-CH$_4$ were analyzed using an offline technique in which CH$_4$ was separated from sample air and converted to CO$_2$ (H$_2$) for subsequent offline $\delta^{13}$C-CH$_4$ ($\delta^D$-
CH₄ analyses by dual-inlet isotope ratio mass spectrometry (DI-IRMS) (e.g. Stevens and Rust, 1982; Lowe et al., 1991; Quay et al., 1991, 1999; Sugawara et al., 1996; Poß, 2003). The original methodology was based on the combustion of CH₄ in sample air from which all CO₂ and other condensable organic gases had been removed first. The number of measurements was limited not only because of laborious and time-consuming laboratory procedures but also because large-volumes of air sample were required (> 100 L STP for δD-CH₄). Later, a method based on continuous-flow gas chromatography isotope ratio mass spectrometry (GC-IRMS) technique combined with combustion and pyrolysis furnaces became available (Meritt et al. 1995), which dramatically reduced time and efforts in the laboratory and likewise the amount of sample air required (now typically 100 mL STP). Such systems are now used in most laboratories worldwide for acquiring δ¹³C-CH₄ and δD-CH₄ data in the current and past atmosphere (e.g. Rice et al., 2001; Miller et al., 2002; Sowers et al., 2005; Ferretti et al., 2005; Fisher et al., 2006; Umezawa et al., 2009; Brass and Röckmann, 2010; Schmitt et al., 2014; Bock et al., 2014; Brand et al., 2016).

Given the atmospheric lifetime of CH₄ to be about a decade, its atmospheric variations are relatively small and for that matter, its concentration and isotopic analyses have to be done with high precision and accuracy. For δ¹³C-CH₄ and δD-CH₄, researchers have achieved measurement reproducibility of < 0.1 ‰ for δ¹³C-CH₄ and < 2 ‰ for δD-CH₄. Incorporating δ¹³C-CH₄ and δD-CH₄ datasets in chemistry transport models is useful to quantitatively separate different types of CH₄ sources (e.g. Fung et al., 1991; Hein et al., 1997; Mikaloff Fletcher et al., 2004a, 2004b; Monteil et al., 2011; Ghosh et al., 2015; Rice et al., 2016; Röckmann et al., 2016; Turner et al., 2017; Rigby et al., 2017). Increasingly, δ¹³C-CH₄ and δD-CH₄ measurements can contribute to reduction of uncertainties in the global CH₄ budget (e.g. Rigby et al., 2012; Kirschke et al., 2013; Schaefer et al., 2016; Schwietzke et al., 2016). One critical issue is that until recently, no widely accepted standards and calibration methods for atmospheric δ¹³C-CH₄ and δD-CH₄ measurements were available (Sperlich et al., 2012, 2016). Individual groups have thus developed calibration strategies and reported observation datasets according to their own laboratory standards, although in principle measurements are ultimately anchored to unique isotope reference materials provided by the International Atomic Energy Agency (IAEA) (Coplen et al., 2006; Brand et al., 2014). Consequently, although an increasing number of δ¹³C-CH₄ and δD-CH₄ data has
been reported over the last decades, significant calibration offsets of $\delta^{13}$C-CH$_4$ between laboratories have been found (e.g. Levin et al., 2012). Clear is that both reliable calibrations and inter-laboratory comparisons are indispensable for combined use of $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ data from different laboratories. Many such laboratory intercomparisons, ad hoc, or on a broader scale have already been made. However, a systematic evaluation of the underlying primary calibrations and calibration offsets has been lacking. Here we unravel most of the intercomparison results to help optimal use of $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ data. This study opens possibility for merging historic CH$_4$ isotope data reported from multiple laboratories (i.e. synthesis analysis of the existing datasets) for better understanding of the global CH$_4$ budget.

The switch from DI-IRMS to GC-IRMS analyses was not without surprises. It was recently found that the atmospheric krypton (Kr) in sample air can interfere with the $\delta^{13}$C-CH$_4$ measurements on a GC-IRMS system, unless Kr is sufficiently separated from the CH$_4$-derived peak (Schmitt et al., 2013). This effect had not been recognized for more than a decade since the early years of GC-IRMS measurements (Merrit et al., 1995), and thus has not been taken into account in many datasets of atmospheric $\delta^{13}$C-CH$_4$ reported in the meantime (e.g. Miller et al., 2002; Morimoto et al., 2006; Fisher et al., 2011; Umezawa et al., 2012a, 2012b). In addition, because the Kr effect is system-dependent and variable with time (Schmitt et al., 2013), applying plausible corrections for all datasets analyzed in the past may not be feasible. Likewise, several gas species including Kr could influence $\delta$D-CH$_4$ measurements, and the effect is also system-dependent (Bock et al., 2014). This tricky aspect again highlights importance of intercomparison between laboratories as a robust and reasonable solution. It is also noted that some measurement programs for $\delta^{13}$C-CH$_4$ and/or $\delta$D-CH$_4$ have discontinued, and keeping access to such datasets with inter-laboratory offsets is important research. Recently, Sperlich et al. (2016) prepared calibrated sets of reference gases to accurately anchor $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ measurements to internationally recognized reference materials. Sharing these reference gases in the research community, as planned by Sperlich et al. (2016), will be of fundamental help for harmonizing $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ datasets from different laboratories with identical anchoring points.

In this study, we review laboratories that have contributed to atmospheric and ice core $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ measurements (section 2). Research groups involved in this study are tabulated in Table 1,
together with list of references for past and present intercomparison programs as well as for isotope measurement systems. Then we report new intercomparison exercises between these groups (section 3). After that, we link the intercomparison results through survey of previous intercomparison programs in the literature and provide plausible calibration offsets between laboratories (section 4). Finally, we discuss possible causes of the calibration offsets and remaining issues that should be kept in mind for combined use of CH$_4$ isotope datasets from different laboratories (section 5). The uncertainties presented in the following sections are ordinarily standard errors of the mean, but numbers in the literature are cited as is. It should be therefore noted that the uncertainties, in particular those calculated by error propagation, are not rigorously consistent at all places in the manuscript.

2 Measurement systems

In this section, we briefly document measurement systems of individual laboratories for ease of reference for the intercomparison. For details, we refer to more dedicated publications listed in Table 1.

2.1 NIWA

National Institute for Water and Atmospheric Research (NIWA, known as DSIR prior to 1992) successfully initiated systematic measurements of atmospheric $\delta^{13}$C-CH$_4$ by means of offline CH$_4$ separation and conversion followed by a DI-IRMS measurement from the early years (Lowe et al., 1988, 1991). A suite of CO$_2$ working gases with $\delta^{13}$C-CH$_4$ values around $-47 \, \%$ referenced to IAEA materials are regularly utilized to calibrate the measurements. An overall precision of the $\delta^{13}$C-CH$_4$ measurement was evaluated to be 0.02 ‰ (Lowe et al., 1991). The long-term $\delta^{13}$C-CH$_4$ records have been presented since then (Lowe et al., 1994, 1997, 2004; Schaefer et al., 2016). Bromley et al. (2012) reported that repeated measurements of the two working reference gases and archived air indicated no detectable drift over 16 years since 1992. NIWA also operates a GC-IRMS system since 2004 (Ferretti et al., 2005) with precision of 0.1 ‰. The Kr interference on the GC-IRMS $\delta^{13}$C-CH$_4$ measurement has been identified, which is corrected by an offset relative to the conventional DI-IRMS measurement (see section 4.1).
2.2 IMAU

The GC-IRMS system at Institute for Marine and Atmospheric research Utrecht (IMAU) has been described by Brass and Röckmann (2010). The measurement reproducibility is estimated to be 0.07 ‰ and 2.3 ‰ for δ\textsuperscript{13}C-CH\textsubscript{4} and δD-CH\textsubscript{4}, respectively. Sample air is measured against reference air that is processed in the GC-IRMS system in the same manner. The δ\textsuperscript{13}C-CH\textsubscript{4} calibration is based on a set of assigned values for 13 firn air samples measured at Max Planck Institute for Chemistry (MPIC) (Bräunlich et al., 2001) and they are ultimately referenced to a CO\textsubscript{2} gas produced from NBS-19 provided by IAEA (Röckmann, 1998; Bergamaschi et al., 2000). The δD-CH\textsubscript{4} calibration is based on a set of reference gases originally produced at MPIC (see section 2.3). These calibration details have been documented also by Sperlich et al. (2016). The IMAU system was originally affected by Kr but later modified to remove it. A correction was applied for data obtained before the system modification to account for the Kr effect (Schmitt et al., 2013).

2.3 MPIC

MPIC has reported δ\textsuperscript{13}C-CH\textsubscript{4} and δD-CH\textsubscript{4} measurements at a baseline station (Bergamaschi et al., 2000) and for firn air samples (Bräunlich et al., 2001) based on an offline DI-IRMS measurement for δ\textsuperscript{13}C-CH\textsubscript{4} (Bergamaschi et al., 2000) and a tunable diode laser based absorption spectrometer (TDLAS) for δD-CH\textsubscript{4} (Bergamaschi et al., 1994). Part of firn air measurements by Bräunlich et al. (2001) was performed by using a GC-IRMS system at Laboratory of Glaciology and Geophysics of the Environment. As described in section 2.2, the MPIC δ\textsuperscript{13}C-CH\textsubscript{4} and δD-CH\textsubscript{4} calibrations are basis of that of IMAU. For the δ\textsuperscript{13}C-CH\textsubscript{4} DI-IRMS measurement, the CH\textsubscript{4}-derived CO\textsubscript{2} was measured against a working standard (pure CO\textsubscript{2}) that was calibrated against VPDB on a DI-IRMS system (Röckmann, 1998; Bergamaschi et al., 2000). The MPIC δD-CH\textsubscript{4} scale is based on measurements of standard gases at the Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany; CH\textsubscript{4} was combusted to CO\textsubscript{2} and H\textsubscript{2}O, followed by reduction of H\textsubscript{2}O to H\textsubscript{2} for subsequent DI-IRMS analysis on H\textsubscript{2}; the calibration was made against VSMOW and SLAP (Bergamaschi et al., 2000). The measurements of atmospheric δ\textsuperscript{13}C-CH\textsubscript{4} and δD-CH\textsubscript{4} at MPIC were discontinued.
2.4 MPI-BGC

Max Planck Institute for Biogeochemistry (MPI-BGC) set up a GC-IRMS system for $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ measurements and it has been operated for air samples collected at a baseline stations (Brand et al., 2016). The long-term (3 years) precisions were assessed to be 0.12 ‰ for $\delta^{13}$C-CH$_4$ and 1.0 ‰ for $\delta$D-CH$_4$. Initially, the GC-IRMS measurements had been anchored to a working standard air calibrated by IMAU. The Kr effect was eliminated by the post-combustion separation column and the initial calibration has in the meantime been replaced by a new primary calibration (Sperlich et al., 2016). This calibration, termed JRAS-M16, is the basis for the $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ values from MPI-BGC reported in this manuscript.

2.5 UCI

University of California Irvine (UCI) measured atmospheric $\delta^{13}$C-CH$_4$ by offline DI-IRMS and $\delta$D-CH$_4$ by GC-IRMS (Tyler et al., 1999, 2007; Kai et al., 2011). The UCI GC-IRMS system for both $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ has been described in detail by Rice et al. (2001). The measurement reproducibility of the GC-IRMS system was estimated to be 0.05 ‰ and 1.5 ‰ for $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$, respectively, while that of the offline DI-IRMS $\delta^{13}$C-CH$_4$ measurement was 0.05 ‰. For the GC-IRMS measurements, samples were measured against laboratory working standard gases of pure CO$_2$ for $\delta^{13}$C-CH$_4$ and pure H$_2$ for $\delta$D-CH$_4$. The $\delta^{13}$C-CH$_4$ calibration is based on a CO$_2$ reference gas provided by NIWA, which was compared with CO$_2$ produced from NBS-19 and IAEA-CO$_2$-9 (Lowe et al., 1999). The $\delta$D-CH$_4$ calibration is referenced to three H$_2$ gas cylinders purchased from Oztech Gas Company (Rice et al., 2001). The possible Kr interference on the GC-IRMS system is unclear (the laboratory closed), but it appears that the Kr effect had been avoided because of using liquid nitrogen cooling of the GC column as surmised by Schmitt et al. (2013).

2.6 TU

The GC-IRMS system at Tohoku University (TU) has been described by Umezawa et al. (2009). The measurement reproducibility is estimated to be 0.08 ‰ for $\delta^{13}$C-CH$_4$ and 2.2 ‰ for $\delta$D-CH$_4$. Sample measurements are made against pure CO$_2$ and H$_2$ working standard gases for $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$,
respectively. The $\delta^{13}$C-CH$_4$ calibration is based on a CO$_2$ primary gas produced from NBS-18 provided by IAEA, while laboratory standards (pure CO$_2$) were also well compared with NBS-19. The H$_2$ working standard for $\delta$D-CH$_4$ measurement is referenced to water laboratory standards that are calibrated against VSMOW and SLAP provided by IAEA. Measured $\delta$D-CH$_4$ values are corrected so that the value of a laboratory test gas is kept constant over time because measured value could fluctuate depending on condition of the pyrolysis furnace (Umezawa et al., 2009, 2012a). The Kr interference on the $\delta^{13}$C-CH$_4$ measurement was identified, but modification or correction has not been implemented. It has been documented that $\delta^{13}$C-CH$_4$ measurement at TU shifted by +0.27 ‰ after July 2008 (the cause of this sudden shift has yet to be identified) and measurements afterwards were corrected for this value to keep the data consistency (Umezawa et al., 2012a, 2012b). Note that TU made rigorous re-evaluation of the long-term measurements of their working standard gas recently, and the TU $\delta^{13}$C-CH$_4$ datasets will be revised accordingly. Therefore, the comparison numbers presented here are not comparable to those for earlier publications (Umezawa et al., 2009, 2011, 2012a, 2012b).

2.7 NIPR

National Institute of Polar Research (NIPR) reported $\delta^{13}$C-CH$_4$ measurements at an Arctic site using a GC-IRMS system (Morimoto et al., 2006). The measurement reproducibility was evaluated to be 0.06 ‰. The $\delta^{13}$C-CH$_4$ calibration follows same procedure as TU. By injecting different quantities of Kr, it was confirmed that ambient Kr does not significantly interfere with the $\delta^{13}$C-CH$_4$ measurements at NIPR.

2.8 UW

University of Washington (UW) reported extensive $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ measurements using an offline DI-IRMS system (Quay et al., 1991, 1999). The precisions were estimated to be 0.1 ‰ for $\delta^{13}$C-CH$_4$ and 3–4 ‰ for $\delta$D-CH$_4$. The $\delta^{13}$C-CH$_4$ calibration is based on measurements against NBS-19. The $\delta$D-CH$_4$ was anchored to calibration by VSMOW and SLAP. Systematic measurements of air standards showed that no significant time shift (+0.001±0.002 ‰ yr$^{-1}$) affected their $\delta^{13}$C-CH$_4$ dataset for 1988–1995 (Quay et al., 1999).
2.9 UHEI

University of Heidelberg (UHEI) carried out δ\textsuperscript{13}C-CH\textsubscript{4} measurements by DI-IRMS (Levin et al., 1999, 2012). The typical measurement reproducibility was evaluated to be 0.05 ‰ (Levin et al., 1999). The UHEI δ\textsuperscript{13}C-CH\textsubscript{4} measurements are calibrated against CO\textsubscript{2} reference materials (RM 8562, RM 8563 and RM 8564) (Behrens et al., 2008). Although reported previously only for signatures of source CH\textsubscript{4} (Levin et al., 1993), UHEI also has made offline δD-CH\textsubscript{4} measurements on atmospheric samples by DI-IRMS and TDLAS (Poß, 2003). The δD-CH\textsubscript{4} measurements by DI-IRMS have been made on pure H\textsubscript{2} (H\textsubscript{2}O from CH\textsubscript{4} oxidation converted to H\textsubscript{2} with zinc as catalyst) and were calibrated against VSMOW and SLAP. Note that UHEI recently re-evaluated all their atmospheric δ\textsuperscript{13}C-CH\textsubscript{4} and δD-CH\textsubscript{4} measurements rigorously, based on the history of laboratory standards used; therefore, comparison numbers published in earlier works are not comparable to the revised values presented here.

2.10 INSTAAR

Institute of Arctic and Alpine Research (INSTAAR) of University of Colorado Boulder has measured δ\textsuperscript{13}C-CH\textsubscript{4} and, intermittently, δD-CH\textsubscript{4} using a GC-IRMS system for flask air samples from the cooperative sampling network of National Oceanic and Atmospheric Administration (NOAA) (Miller et al., 2002). Precisions of the δ\textsuperscript{13}C-CH\textsubscript{4} and δD-CH\textsubscript{4} measurements are evaluated to be 0.08 ‰ and 2 ‰, respectively (Miller et al., 2002; White et al., 2016). The INSTAAR δ\textsuperscript{13}C-CH\textsubscript{4} measurement currently follows the UCI calibration, while the δD-CH\textsubscript{4} measurement is not explicitly anchored to the VSMOW scale (White et al., 2016). The Kr interference on the δ\textsuperscript{13}C-CH\textsubscript{4} measurement was recently identified to be significant, and the post-combustion separation column was therefore implemented into the system in May 2017. Correction for the dataset interfered by Kr (1998–present) is under evaluation. Of the data presented here, only the ice core intercomparison round robin (section 3.4) and the INSTAAR-MPI-BGC comparison (section 3.5) have had Kr removal.

2.11 RHUL

Royal Holloway University of London (RHUL) conducted atmospheric δ\textsuperscript{13}C-CH\textsubscript{4} measurements by using an offline DI-IRMS technique (Lowry et al., 2001) and a GC-IRMS system (Fisher et al., 2006,
2011; Nisbet et al., 2016). Reproducibility of the DI-IRMS measurement was evaluated to be 0.04 ‰ (Lowry et al., 2001) and that by the GC-IRMS is 0.05 ‰ (Fisher et al., 2006). They made $\delta^{13}$C-CH$_4$ calibrations ultimately to IAEA carbonate materials NBS-19 and IAEA-CO-9 (Lowry et al., 2001; Fisher et al., 2006).

5 2.12 PDX

Portland State University (PDX) reported $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ measurements for archive air samples (Rice et al., 2016). The PDX measurement system has been described in Teama (2013) with some updates since Rice et al. (2001). The $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ precisions are 0.07 ‰ and 2.0 ‰, respectively, and PDX shares calibrations with UCI for both $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ (Rice et al., 2016).

10 2.13 PSU

Pennsylvania State University (PSU) reported $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ data from ice cores and firm air using a GC-IRMS system (e.g. Sowers et al., 2005; Sowers, 2010). The overall measurement uncertainties including every step for ice core measurements were evaluated to be 0.3 ‰ for $\delta^{13}$C-CH$_4$ and 3 ‰ for $\delta$D-CH$_4$ (Sowers, 2010). The PSU $\delta^{13}$C-CH$_4$ measurements are calibrated against CO$_2$ reference materials (RM 8563 and RM 8564). The $\delta$D-CH$_4$ calibration is made against gas bottles from Oztech Gas Company (Sowers, 2006).

2.14 UB

University of Bern (UB) makes $\delta^{13}$C-CH$_4$ measurements from ice cores using a GC-IRMS system with an overall reproducibility of 0.15 ‰ (Schmitt et al., 2014). The UB measurements are referenced to a whole-air working standard with CH$_4$ concentration of 1508.2 ppb and an assigned $\delta^{13}$C-CH$_4$ value of −47.34±0.02 ‰ (named “Boulder, CA08289” in Schmitt et al., 2014). This standard is anchored to the INSTAAR calibration (section 2.10). UB also measures $\delta$D-CH$_4$ for ice core samples (Bock et al., 2010, 2014). The overall measurement precision for ice core sample was evaluated to be 2.3 ‰. The UB $\delta$D-CH$_4$ measurement is referenced by using an ambient air cylinder (named “Air Controlé”) with a $\delta$D-CH$_4$ value of −93.6±2.8 ‰, which was cross-referenced to an Antarctic bottled air (“Alert 2002/11” with $\delta$D-CH$_4$ of −82.2±1.0 ‰) analyzed on the scale maintained at UHEI (Bock et al., 2014). However,
this value has to be corrected to \(-85.2\pm1.0\ \%\) to account for the recent re-evaluation at UHEI (section 2.9). All UB data published after 2011 are free of Kr interference.

2.15 AWI

Alfred Wegener Institute Helmholtz Center for Polar and Marine Research (AWI) reported $\delta^{13}$C-CH$_4$ measurements from ice cores using a GC-IRMS system (Behrens et al., 2008; Fischer et al., 2008; Möller et al., 2013). The measurement reproducibility was estimated to be 0.2 \%. The $\delta^{13}$C-CH$_4$ measurements follow the UHEI calibration via comparison of measurements of an Antarctic air sample (Möller et al., 2013).

2.16 CIC

Centre for Ice and Climate (CIC) has reported $\delta^{13}$C-CH$_4$ measurements from ice cores (Sperlich et al., 2015) using a GC-IRMS system with measurement reproducibility of 0.09 \%. CIC also set up an offline combustion system for large CH$_4$ samples, which is combined with DI-IRMS for $\delta^{13}$C-CH$_4$ and with either a high Temperature Conversion/Elemental Analyser (TC/EA) coupled to IRMS or laser spectroscopy for $\delta$D-CH$_4$ (Sperlich et al., 2012); the measurement reproducibility is 0.04 \% for $\delta^{13}$C-CH$_4$ and 0.7 \% for $\delta$D-CH$_4$. The combined uncertainty of this analytical system including the uncertainty of the entire traceability chain was estimated as 0.07 \% for $\delta^{13}$C-CH$_4$ and 0.7 \% for $\delta$D-CH$_4$ (Sperlich et al., 2016).

3 Present Intercomparison Exercises

3.1 Intercomparison between UCI and IMAU

An intercomparison between UCI and IMAU was made by analyzing 6 air samples at both laboratories; the air samples were collected along a flight track of commercial aircraft in the upper troposphere in the early phase of the CARIBIC (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container) project (Brenninkmeijer et al., 1999). The original samples were collected into large stainless steel cylinders (21 L in volume) and aliquots of them were transferred into smaller stainless steel canisters (~2.3 L) for storage after delivery to the MPIC laboratory. Different sub samples...
from identical original samples were sent to UCI and IMAU for analyses, and they were measured at UCI in 2008 and at IMAU in 2012 to 2013. The measurement results at both laboratories are summarized in Table 2. The result indicated significant offsets of $+0.42\pm0.04\‰$ for $\delta^{13}C$-CH$_4$ (UCI value is higher than IMAU) and of $-10.7\pm0.7\‰$ for $\delta^{D}$-CH$_4$ (UCI value is lower than IMAU).

5.2 Intercomparison between TU/NIPR and IMAU

Intercomparison between TU/NIPR and IMAU was carried out during 2013–2015. The TU laboratory prepared four stainless steel canisters (~1 L in volume) filled with dried ambient air (canisters MD1 and MD2) and synthetic standard air (canisters MD3 and MD4) with CH$_4$ concentrations ranging from 899 to 2117 ppb on the TU CH$_4$ scale (Aoki et al., 1992; Umezawa et al., 2014) (Table 3). The canisters were analyzed at TU and then sent to IMAU, after which they were sent back to TU and analyzed again to confirm the stability of the air samples in the canisters during the intercomparison exercise. The measurements at TU before (April 2013) and after (July 2015) the transportation to IMAU indicated that possible drifts during canister storage and transportation are small (< 0.1 ‰ for $\delta^{13}C$-CH$_4$ and < 3.5 ‰ for $\delta^{D}$-CH$_4$). NIPR also measured the canisters for $\delta^{13}C$-CH$_4$. The intercomparison results indicate significant calibration offsets of $+0.51\pm0.07\‰$ for $\delta^{13}C$-CH$_4$ (TU value is higher than IMAU) and of $-13.9\pm0.9\‰$ for $\delta^{D}$-CH$_4$ (TU value is lower than IMAU) (Table 3). The measurements of the four canisters at NIPR were $+0.48\pm0.11\‰$ higher than IMAU. However, the differences of $\delta^{13}C$-CH$_4$ measurements are smaller for ambient air samples (MD1 and MD2) than synthetic standard air samples (MD3 and MD4). It is also noted that the $\delta^{13}C$-CH$_4$ difference between the laboratories is largest for the low CH$_4$ concentration (~900 ppb) sample (MD3). The cause is unclear, but might be related to (1) deviation in $\delta^{13}C$-CH$_4$ of the latter samples from the typical atmospheric value i.e. scale compression effect, (2) difference in air matrix i.e. natural versus synthetic air and (3) difference in linearity with CH$_4$ concentration. This result therefore indicates that the offset is not constant for wide range of $\delta^{13}C$-CH$_4$ values and CH$_4$ concentrations as well as difference in air matrix. Since we focus in this study on comparison for atmospheric samples, the intercomparison results for the ambient air samples are considered as inter-laboratory offsets. The average differences for ambient air are $+0.41\pm0.04\‰$ for TU
and +0.31±0.03 ‰ for NIPR relative to IMAU. Likewise, the δD-CH₄ offset of TU versus IMAU is considered to be −13.1±0.6 ‰.

### 3.3 Intercomparison between UHEI and MPI-BGC

An intercomparison between UHEI and MPI-BGC was conducted in 2013 on six archived air samples from Neumayer station, Antarctica. These samples, collected in the time period from 1988 to 2008 had been analyzed by UHEI for δ¹³C-CH₄ and δD-CH₄ by DI-IRMS (two samples were analyzed for δD-CH₄ additionally by TDLAS) during 2003–2010 and were stored in high-pressure cylinders. In 2013, duplicate aliquots were sampled in 1-L glass flasks and analyzed at MPI-BGC. The measurement results at both laboratories are summarized in Table 4. The results show insignificant offsets of +0.02±0.05 ‰ for δ¹³C-CH₄ and of +0.4±0.6 ‰ for δD-CH₄ (with the MPI-BGC values being more negative than those from UHEI in both cases).

### 3.4 Ice Core Intercomparison Round Robin

A round robin cylinder intercomparison exercise was initiated to facilitate intercomparison of those laboratories who measure δ¹³C-CH₄ and δD-CH₄ in ice core and firn air samples. Part of this intercomparison exercise has been presented previously (Table 2 in Schmitt et al., 2013). Three high-pressure Al cylinders were filled with varying trace gas composition to mimic present day, pre-industrial and last glacial air concentrations. The CH₄ concentrations of these cylinders were 1830.6 ppb (CA 03560), 904.0 ppb (CC 71560) and 372.2 ppb (CA 01179) on the NOAA-2004 CH₄ scale (Dlugokencky et al., 2005), respectively. The cylinders were shipped to the laboratories listed in Table 5 for analyses of the elemental and isotopic composition of all constituents that each lab was capable of measuring at that time. In Table 5, we list the δ¹³C-CH₄ and δD-CH₄ results from each laboratory. The Kr interfering artifact associated with GC-IRMS δ¹³C-CH₄ analyses has been removed in many of the analyses (Schmitt et al., 2013). In some cases, aliquots from the tanks were measured using offline combustion to CO₂ followed by δ¹³C-CH₄ analyses via conventional DI-IRMS. The cylinders were remeasured at PSU at the end of the round robin to verify that the isotopic composition had not shifted over the 9 years during the transportation of the cylinders. The difference between the 2007 and 2016
δ¹³C-CH₄ measured at PSU were less than 0.14 ‰ for two of the three cylinders signifying the isotopic composition of air remained intact throughout the intercomparison exercise. The third cylinder (CA 01179) was 0.58 ‰ off from the original measurement which is just outside the analytical uncertainty associated with PSU measurements and may indicate slight drift over the 9 years between measurements. The results of the δ¹³C-CH₄ intercomparison showed general agreement with the average standard deviation amongst all six participating laboratories better than 0.37 ‰ for the high and middle cylinders. δD-CH₄ results show more scatter due to the difficult nature of the measurements and the offset between the calibration scales.

### 3.5 Intercomparison between INSTAAR and MPI-BGC

An intercomparison between INSTAAR and MPI-BGC was recently made by analyzing three air cylinders at both laboratories. They were measured at MPI-BGC between April and July of 2016 and at INSTAAR between May and June of 2017. Two of the cylinders have ambient CH₄ concentration (~1900 ppb; HUEY-001 and DEWY-001) and the other has a lower value (~1500 ppb; LOUI-001) (Table 6). In addition, air from another suite of cylinder was sampled into flasks at INSTAAR and sent to MPI-BGC. Measurements at MPI-BGC and INSTAAR were made in January–February of 2017 and May–June of 2017, respectively. The four cylinders (CART-001, STAN-001, KENN-001 and KYLE-001) have different CH₄ concentrations and δ¹³C-CH₄ values. The measurement results are summarized in Table 6. The INSTAAR data presented here were not interfered by Kr by installing a post-combustion separation column into the system. The results show significant but consistent offsets of +0.28±0.01 ‰ for the five cylinders with different CH₄ concentrations and ambient δ¹³C-CH₄ values (with the INSTAAR values being more positive than those from MPI-BGC). The measurements for the cylinder with low δ¹³C-CH₄ value were 0.60 ‰ off between both laboratories presumably due to the scale compression effect. It is noted that the INSTAAR measurements without the Kr removal had yielded a higher δ¹³C-CH₄ value (+0.44±0.02 ‰ relative to the MPI-BGC measurement) for one cylinder (LOUI-001), which presumably reflects the Kr interference pronounced at lower CH₄ concentration.
3.6 Intercomparison based on co-located samples through the NOAA cooperative sampling network

The Cooperative Flask Sampling Network, operated by the NOAA Global Monitoring Division, collects air samples from numerous sites around the world, and INSTAAR has analyzed those air samples for $\delta^{13}$C-CH$_4$ since 1998. There are several sites where air sample collections by other laboratories have been made concurrently. RHUL has analyzed air samples at Alert (ALT), Canada and Ascension Island (ASC), and NIWA has done at Baring Head (BHD), New Zealand. Although the individual laboratories do not measure the same sample air in these cases, these co-located air samples provide an opportunity for assessment of possible calibration offsets as examined previously (Levin et al., 2012). (1) For the RHUL-INSTAAR offset, the $\delta^{13}$C-CH$_4$ data at ALT during 2009–2014 and at ASC during 2010–2015 were compared to each other if both air samples were collected within a 10 hour interval. The ALT and ASC comparisons indicated that the INSTAAR measurement is $+0.05\pm0.01$‰ ($N=350$) and $+0.00\pm0.02$‰ ($N=80$) higher than RHUL, respectively. Note that, for this comparison, the RHUL GC-IRMS data was corrected by $-0.20$‰; the offset value was estimated from measurements of flasks filled from two different cylinders (CH$_4$ in air, both at ambient concentration level, one at ambient $\delta^{13}$C-CH$_4$ and the other at about $-56$‰ by spiking $^{13}$C-depleted CH$_4$). (2) For the NIWA-INSTAAR comparison, the $\delta^{13}$C-CH$_4$ data at BHD during 2009–2014 from both laboratories were compared if both air samples were collected within a 15 hour interval. The result indicates that the INSTAAR measurement is $+0.08\pm0.02$‰ ($N=45$) higher than NIWA.

4 Calibration offsets between laboratories

Here we revisit intercomparisons published previously. It has also happened that some laboratories employed a calibration scale from another laboratory. Such intercomparisons and scale transfers reported in the literature are organized in Fig. 1. In this section we review the previous and present intercomparison measurements and accordingly suggest plausible calibration offsets between different laboratories (Fig. 2). Relevant information is summarized in Table 1 and the subsections below correspond to those in section 2. Since some laboratories focus on $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ measurements from ice core and firn air samples to elucidate changes of atmospheric CH$_4$ in the past, Fig. 2 also gives
an opportunity for combining \( \delta^{13} \text{C-CH}_4 \) and \( \delta \text{D-CH}_4 \) data both for the modern and past atmosphere. It is however noted that Fig. 2 suggests the calibration offsets at the modern CH\(_4\) concentration and isotopic ratios and that such values could be different for the past atmosphere (see sections 3.2, 3.4 and 3.5).

In this study, we report \( \delta^{13} \text{C-CH}_4 \) offsets with respect to the conventional DI-IRMS measurement at NIWA (Lowe et al., 1991) because NIWA’s \( \delta^{13} \text{C-CH}_4 \) measurements have been compared with those from most laboratories to date (Table 1 and Fig. 1). In contrast, \( \delta \text{D-CH}_4 \) measurements from different laboratories have been limited. We report \( \delta \text{D-CH}_4 \) offsets of different laboratories with respect to the IMAU measurement.

4.1 NIWA

\( \delta^{13} \text{C-CH}_4 \): As listed in Table 1, the DI-IRMS measurement at NIWA has been repeatedly intercompared with other laboratories. Importantly for this comparison, Bromley et al. (2012) reported that the long-term stability of the measurement over the years 1992–2007, and it is likewise confirmed until 2011. The NIWA GC-IRMS system, based on the methodology of Miller et al. (2002), has an offset relative to the DI-IRMS of \( -0.19\pm0.26 \) ‰. Measurements on the GC-IRMS informing this instrument comparison are subject to the Kr interference. A Kr-correction has since been derived in an empirical equation from the ice core intercomparison results (Schmitt et al., 2013 and section 3.4), accounting for differences in CH\(_4\) concentration and an exponential fit to the GC-IRMS versus DI-IRMS results. The GC-IRMS system has since been equipped with a post-combustion separation column.

4.2 IMAU

\( \delta^{13} \text{C-CH}_4 \): According to Schmitt et al. (2013), the IMAU measurement at the present CH\(_4\) concentration level is in agreement to NIWA with the offset value of \( -0.04\pm0.07 \) ‰ (No. 2 in Fig. 2a). This corresponds to the high CH\(_4\) cylinder comparison in Table 5 (section 3.4). The difference is \( -0.03\pm0.05 \) ‰ for data analyzed before the modification to remove the Kr effect (see Table 2 in Schmitt et al. (2013)). The intercomparison in this study (section 3.4) also shows that the IMAU offset is \( -0.08\pm0.11 \) ‰ for the middle CH\(_4\) cylinder.
\( \delta \text{D-CH}_4 \): As listed in Table 1, IMAU has made most intercomparisons with other laboratories so far. It is noted that the calibration at IMAU was propagated from MPIC (Bergamaschi et al., 2000; section 2.2), and that it recently showed a reasonable agreement with the primary calibration at MPI-BGC (Sperlich et al., 2016).

5 4.3 MPIC

\( \delta \text{^{13}C-CH}_4 \): As written in section 2.3, the calibration scale at MPIC was transferred to IMAU (Brass and Röckmann, 2010; Sperlich et al., 2016). Since no direct comparison with NIWA is available, the MPIC offset relative to NIWA is estimated to be \(-0.04\pm0.07 \, \text{%}\), identical to the IMAU offset (No. 3 in Fig. 2a).

\( \delta \text{D-CH}_4 \): Bock et al. (2010) reported an intercomparison using firn air samples between UB and MPIC, which indicated that, combined with the UB \( \delta \text{D-CH}_4 \) offset (section 4.14), the MPIC \( \delta \text{D-CH}_4 \) offset is \(+0.3\pm1.1 \, \text{%}\) with respect to IMAU (No. 3 in Fig. 2b).

4.4 MPI-BGC

\( \delta \text{^{13}C-CH}_4 \): Sperlich et al. (2016) quantified the offset of the IMAU calibration relative to their primary calibration scale. They indicated that the MPI-BGC measurement differs by \(-0.03\pm0.10 \, \text{%}\) from the IMAU scale. Combined with the IMAU offset relative to NIWA (section 4.2), the MPI-BGC offset is estimated to be \(-0.07\pm0.12 \, \text{%}\) (No. 4 in Fig. 2a).

\( \delta \text{D-CH}_4 \): According to Sperlich et al. (2016), the MPI-BGC measurement is \(-4.2\pm1.2 \, \text{%}\) from IMAU (No. 4 in Fig. 2b).

4.5 UCI

\( \delta \text{^{13}C-CH}_4 \): Intercomparison exercises of UCI with external laboratories have been made several times. The oldest intercomparison (Lowe et al., 1991) has reported good agreement (< 0.02 \%\) between the former UCI laboratory (S. Tyler at NCAR) and NIWA (DSIR at that time). Among the later measurements, there are two direct intercomparisons with NIWA. (1) Tyler et al. (2007) reported an intercomparison result of UCI to be \(-0.01\pm0.09 \, \text{%}\) with respect to NIWA (No. 5 left in Fig. 2a). For
this comparison, 16 air samples collected at Niwot Ridge, Colorado or Baring Head, New Zealand were exchanged between UCI and NIWA in 1998–1999. (2) This study (section 3.4 and Table 5) shows that the UCI measurement is $+0.14\pm0.12$ $\%$ (No. 5 middle in Fig. 2a) and $+0.04\pm0.08$ $\%$ higher than NIWA for the high and middle CH$_4$ cylinders, respectively. (3) In contrast, the intercomparison in this study (section 3.1 and Table 2) combined with the IMAU offset (section 4.2) yields $+0.42\pm0.04$ $\%$ relative to NIWA (not shown in Fig. 2a), inconsistent with the above intercomparison results made earlier. The determinate error has yet to be resolved, but might be related to the instrument circumstance under which the samples were analyzed on the GC-IRMS system.

$\delta^D$-CH$_4$: According to the intercomparison in this study (section 3.1), the UCI has a $\delta^D$-CH$_4$ offset of $-10.7\pm0.7$ $\%$ with respect to IMAU (No. 5 in Fig. 2b).

### 4.6 TU

$\delta^{13}$C-CH$_4$: The intercomparison in this study (section 3.2) and the IMAU offset (section 4.2) give an offset of the TU measurements relative to NIWA to be $+0.37\pm0.08$ $\%$ (No. 6 in Fig. 2b). Measurements at TU have been regularly compared with those at NIPR and they are in agreement within reproducibility of both systems (Umezawa et al., 2009 and additional measurements since then). This is consistent with the previous intercomparison between NIPR and NIWA (section 4.7) and indicates long-term intra-laboratory consistency of TU and NIPR measurements. It is reasonable that TU shares the offset level with NIPR, because both institutions follow the same calibration. As described in section 2.6, it should be noted that the above offset value is not for the datasets currently available to the research community (Umezawa et al., 2011, 2012a, 2012b), for which $+0.32\pm0.08$ $\%$ (not shown in Fig. 2) is recommended. Correction of the datasets from the earlier publications is under evaluation.

$\delta^D$-CH$_4$: The intercomparison in this study (section 3.2) gives an offset of $-13.1\pm0.6$ $\%$ for the TU atmospheric $\delta^D$-CH$_4$ measurement (No. 6 in Fig. 2b).

### 4.7 NIPR

$\delta^{13}$C-CH$_4$: An intercomparison between NIPR and NIWA was conducted in 2004 (Morimoto et al., 2006). After the recent update of the NIPR calibration, the NIPR offset is evaluated to be $+0.33\pm0.04$ $\%$. 


higher than NIWA (No. 7 left in Fig. 2a). The intercomparison in this study (section 3.2) combined with the IMAU offset (section 4.2) indicates the NIPR measurement is $+0.27\pm0.08$ ‰ with respect to NIWA (No. 7 right in Fig. 2a), consistent with the above value.

4.8 UW

$\delta^{13}$C-$CH_4$: Quay et al. (1999) exchanged 30 air samples with NIWA; the average offset was evaluated to be $+0.02\pm0.14$ ‰ (No. 8 left in Fig. 2a), although some individual samples disagreed by up to 0.5 ‰ (Lowe et al., 1994; Quay et al., 1999). Later, Levin et al. (2012) estimated that the UW offset is $+0.058\pm0.004$ ‰ with respect to NIWA based on co-located sampling at BHD (No. 8 right in Fig. 2a).

$\delta^D$-$CH_4$: To our knowledge, no intercomparison exercises with UW have been reported.

4.9 UHEI

$\delta^{13}$C-$CH_4$: Levin et al. (2012) estimated the UHEI $\delta^{13}$C-$CH_4$ offset to be $-0.169\pm0.031$ ‰ relative to NIWA (No. 9 left in Fig. 2a). The intercomparison in this study (section 3.3) together with the MPI-BGC offset (section 4.4) also infers the UHEI offset to be $-0.05\pm0.13$ ‰ (No. 9 right in Fig. 2a), consistent with the above value. Earlier measurements of three air samples at both UHEI and NIWA indicated that the UHEI offset is $-0.04\pm0.04$ ‰ relative to NIWA (Poß, 2003; Behrens et al., 2008). It is also noted that, in an intercomparison exercise by Nisbet (2005), the UHEI measurement was $-0.07\pm0.04$ ‰ lower than NIWA. As these earlier comparison results have been published before the rigorous corrections of the UHEI measurements, these values are not included in Fig. 2a.

$\delta^D$-$CH_4$: The intercomparison in this study (section 3.3), combined with the MPI-BGC offset (section 4.4), indicates that UHEI has an offset of $-3.8\pm1.3$ ‰ relative to IMAU.

4.10 INSTAAR

$\delta^{13}$C-$CH_4$: Levin et al. (2012) estimated that the INSTAAR measurements have an offset of $+0.132\pm0.022$ ‰ with respect to NIWA (No. 10 left in Fig. 2a). In an intercomparison exercise reported by Nisbet (2005), the INSTAAR measurement was $+0.14\pm0.06$ ‰ higher than NIWA (not shown in Fig. 2a), consistent with the above value. This study (section 3.4) indicates that the INSTAAR measurement
is +0.15±0.05 ‰ higher than NIWA for the high (ambient) CH\textsubscript{4} cylinder (No. 10 middle in Fig. 2a). The intercomparison between INSTAAR and MPI-BGC (section 3.5) indicates that, combined with the MPI-BGC offset (section 4.4), the INSTAAR offset is +0.21±0.12 ‰ relative to NIWA (No. 10 right in Fig. 2a). Lastly, the co-located sample intercomparison (section 3.6) indicates the INSTAAR offset to be +0.08±0.02 ‰ (not shown in Fig. 2a). This value is smaller than those in the above from different pathways and the cause has yet to be identified. It is important to note again that only the ice core intercomparison round robin measurements (section 3.4 and No. 10 middle in Fig. 2a) and the intercomparison with MPI-BGC (section 3.5) were made with the post-combustion column to remove the Kr effect, and that the dataset currently available to the public from INSTAAR will be evaluated for the Kr interference for future correction.

As described in section 2.10, INSTAAR follows the calibration scale of UCI. Tyler et al. (2007) reported that measurements of 10 air cylinders filled at Niwot Ridge, Colorado in 2000–2001 were analyzed at both laboratories and that the result indicated an offset of INSTAAR to be +0.04±0.12 ‰ relative to UCI. The collection of air samples at Niwot Ridge for the UCI-INSTAAR comparison had been continued until 2003. A revisit to the measurement record showed that the INSTAAR offset relative to UCI had shifted over the years; the average differences are +0.02±0.08 ‰ for 2000 (N=7), +0.12±0.07 ‰ for 2001 (N=2) and +0.26±0.03 ‰ for 2002 (N=12). This fact may infer excursions of the internal calibration of either laboratory for these years, but the cause has yet to be resolved; this problem will be addressed in a subsequent paper from either group. It is noted that the offsets relative to NIWA for both laboratories inferred from the different intercomparison pathways are consistent with each other within the uncertainties (Figure 2a).

4.11 RHUL

\( \delta ^{13} \text{C-CH}_4 \): Nisbet (2005) reported results of an intercomparison exercise; the RHUL DI-IRMS measurements agree well with NIWA with an offset of 0.00±0.02 ‰ (No. 11 left in Fig. 2a). At the same time, they indicated that the RHUL GC-IRMS measurement has an offset of +0.11±0.13 ‰ with
respect to NIWA, and later Nisbet et al. (2016) reported that the GC-IRMS system has an offset of about +0.3 ‰ relative to NIWA (not shown in Fig. 2a). Based on cylinder exchange measurements between RHUL and NIWA in 2011 and 2014, RHUL applied to an offset correction (−0.20 ‰) to the all data (see section 3.6), by which the RHUL offset has now been evaluated to be +0.12±0.03 ‰ (No.11 middle in Fig. 2a). The intercomparisons based on the co-located air samples via INSTAAR (section 3.6), combined with the INSTAAR offset (section 4.10), infer that the RHUL offset is +0.10±0.03 ‰ relative to NIWA (No. 11 right in Fig. 2a).

4.12 PDX

δ¹³C-CH₄: Rice et al. (2016) presented an offset of +0.024±0.088 ‰ of the PDX measurements relative to UW by comparing coinciding measurements of archive air samples at PDX and δ¹³C-CH₄ records from Quay et al. (1999) from stations Mauna Loa, Hawaii and Tutuila, American Samoa (1995–1996). With the UW offset with respect to NIWA (section 4.8), it is indicated that the PDX measurement is +0.08±0.09 ‰ higher than NIWA (No. 12 in Fig. 2a). This offset is consistent with the UCI offset with respect to NIWA within the uncertainties (note that PDX follows the UCI calibration).

δD-CH₄: Since PDX follows the UCI calibration (Teama, 2013; Rice et al., 2016), the likely offset is same as that of UCI (No. 12 in Fig. 2b).

4.13 PSU

δ¹³C-CH₄: According to Schmitt et al. (2013), the PSU measurement has an offset of +0.03±0.16 ‰ relative to NIWA after being corrected for the Kr effect. As described earlier, the above value is part of the intercomparison in this study (section 3.4). The high-CH₄ cylinder measurements at PSU are +0.03±0.16 ‰, +0.27±0.16 ‰ and +0.13±0.05 ‰ (No. 13 left, middle and right, respectively in Fig. 2a) higher than NIWA for different Kr corrections at different measurement times, these values being consistent with each other within the uncertainties.

δD-CH₄: An intercomparison result using three firm air samples gives the PSU offset of −12.1±1.5 ‰ relative to the IMAU measurement (Sapart et al., 2011; No. 13 left in Fig. 2b). The intercomparison in
this study (section 3.4) shows the offset to be $-13.6\pm1.5\,\text{%}$ relative to IMAU for the high CH$_4$ cylinder (No. 13 right in Fig. 2b).

4.14 UB

$\delta^{13}$C-CH$_4$: The UB measurement has an offset of $-0.18\pm0.09\,\text{%}$ relative to NIWA (Schmitt et al., 2013; No. 14 in Fig. 2a). This is part of measurements tabulated as the ice core intercomparison (section 3.4 and Table 5).

$\delta^D$-CH$_4$: Sapart et al. (2011) gives an intercomparison result between UB and IMAU, indicating the UB offset of $0.0\pm1.6\,\text{%}$ relative to IMAU (No. 14 left in Fig. 2b). This value is consistent with the intercomparisons between UB and IMAU reported by Bock et al. (2010). Later UB modified the measurement set up, but the measurements of same air samples before and after were in good agreement as presented by Bock et al. (2014). The intercomparison in this study (section 3.4) shows that the UB measurement differs insignificantly by $-0.8\pm2.5\,\text{%}$ for the high CH$_4$ cylinder (No. 14 right in Fig. 2b).

4.15 AWI

$\delta^{13}$C-CH$_4$: The AWI offset is reported to be $-0.09\pm0.06\,\text{%}$ with respect to NIWA (Schmitt et al., 2013; No. 15 in Fig. 2a).

4.16 CIC

$\delta^{13}$C-CH$_4$: Sperlich et al. (2012) has reported measurements of an air cylinder at CIC, IMAU and UB. The CIC measurement insignificantly different by $+0.01\pm0.09\,\text{%}$ from IMAU, by which the CIC offset with respect to NIWA is estimated to be $-0.03\pm0.11$ (No. 16 left in Fig. 2a). They have also reported that the CIC measurement is in agreement with UB with difference of $+0.00\pm0.14\,\text{%}$. It is noted that, although the UB offset relative to NIWA is estimated to be significant (section 4.14), the difference is still within uncertainties of the intercomparison exercises. Two pure CH$_4$ gases prepared by Sperlich et al. (2012) constitute crucial components of the reference gas series developed at MPI-BGC (Sperlich et al., 2016). This has provided a direct intercomparison between CIC and MPI-BGC. The CIC
measurement is +0.09±0.14 ‰ higher than MPI-BGC. Combined with the MPI-BGC offset (section 4.4), the CIC offset with respect to NIWA is estimated to be +0.02±0.18 ‰ (No. 16 right in Fig. 2a), consistent with the aforementioned value.

δD-CH₄: Sperlich et al. (2016) reported δD-CH₄ measurement results of the two reference gases prepared by Sperlich et al. (2012) at CIC and MPI-BGC. The results indicated that the CIC measurement differs by +2.1±1.8 ‰ from MPI-BGC. Combined with the MPI-BGC offset (section 4.4), the CIC offset relative to IMAU is estimated to be −2.1±2.1 ‰ (No. 16 in Fig. 2b).

5 Summary and Discussion

We carried out intercomparison exercises for atmospheric δ¹³C-CH₄ and δD-CH₄ covering many laboratories around the world. In addition, we reviewed previous intercomparison programs in the literature. The results indicated calibration offsets between laboratories, which range from −0.2 to +0.3 ‰ with respect to the NIWA DI-IRMS measurement for δ¹³C-CH₄ and up to −13 ‰ with respect to the IMAU measurement for δD-CH₄. These offset values are larger than measurement uncertainties of individual laboratories.

The significant δ¹³C-CH₄ offsets between laboratories are obvious even though all laboratories ultimately reference to materials certified by IAEA on the identical VPDB scale (Coplen et al., 2006; Brand et al., 2014). Possible causes are hidden in all preparation and measurement steps of standard materials. First, the scale compression effect for DI-IRMS CO₂ analysis (Meijer et al., 2000; Wendeberg et al., 2013), which is instrument-dependent, could be responsible for considerable part of the observed offsets, given the fact that the atmospheric δ¹³C-CH₄ value (about −47 ‰) differs considerably from the primary anchor of the VPDB scale (NBS 19). Second, individual laboratories have made calibrations against different certified materials (e.g. from IAEA and NIST) with different uncertainties of assigned values (see Sperlich et al., 2016 and reference therein); such diverse calibration trajectories have also definitely contributed to the inter-laboratory offsets. Third, such certified reference materials have different chemical properties and are processed to CO₂ at individual laboratories, in which different fractionation is possible. Fourth, the Kr interference on a GC-IRMS
system is in several cases a probable cause of the offsets and unfortunately this effect is system-dependent and can vary with time depending on the instrument settings (Schmitt et al., 2013). Lastly, it is important to note that we summarized $\delta^{13}$C-CH$_4$ offsets at the atmospheric CH$_4$ concentration level, but the offset may vary with the amount of CH$_4$ analyzed (e.g. lower concentrations in ice core analyses), see Table 3, 5 and 6), because of non-linear response of IRMS (Umezawa et al., 2009) and of the Kr interference varying with relative changes in Kr to CH$_4$ ratio (Schmitt et al., 2013). Furthermore, the intercomparisons summarized here focus on modern atmospheric CH$_4$ of typically ~47‰ and such comparisons for high and low $\delta^{13}$C-CH$_4$ values (e.g. CH$_4$ from ice cores or enriched/depleted source signatures) are to date very limited (Tables 3 and 6 in this study).

Concerning $\delta$D-CH$_4$ offsets between laboratories, it is interesting that the listed laboratories can be roughly split into two groups whose $\delta$D-CH$_4$ measurements differ by ~10‰. Some laboratories with higher $\delta$D-CH$_4$ values reference to an identical set of standards produced at MPIC (MPIC and IMAU) or to the UHEI calibration (UHEI and UB), and measurements of these groups have been cross-referenced (see sections 2 and 4), thereby showing the reasonable agreements. The original calibrations were made by an offline CH$_4$ processing technique (cryogenic separation and conversion of CH$_4$ to CO$_2$ and H$_2$O followed by H$_2$O reduction to H$_2$) with subsequent DI-IRMS. The other laboratories with higher $\delta$D-CH$_4$ values recently developed their own primary calibrations independently (CIC and MPI-BGC). CIC used an offline CH$_4$ processing combined with DI-IRMS, whereas MPI-BGC adopted TC/EA coupled to continuous-flow IRMS. For the lower $\delta$D-CH$_4$ group, some laboratories made calibrations against Oztech gases (UCI, PDX and PSU) or have other calibration pathways (TU and INSTAAR) (see section 2). These laboratories used local H$_2$ working gas standards for GC-IRMS, which were calibrated by a separate DI-IRMS procedure. As is the case for $\delta^{13}$C-CH$_4$, possible causes of the observed $\delta$D-CH$_4$ discrepancies could have arisen in all preparation and measurement steps. First, the classical technique for DI-IRMS involves processing of H$_2$O, and the associated steps in experimental lines are prone to surface adhesion and contamination of H$_2$O, thereby considerable memory effect is possible (Bergmaschi et al., 2000). Second, similarly to $\delta^{13}$C-CH$_4$, calibration for $\delta$D-CH$_4$ involves measurements of standards with different chemical properties (H$_2$O and H$_2$), and such calibrations at different laboratories could contribute to the offset. Third, difficulties in maintaining
stable pyrolysis conditions for GC-IRMS (Bock et al. 2010) might have affected measurements against local H2 working standards. Lastly, it is noted that non-linearity of the IRMS in δD-CH4 measurements (Brass and Röckmann, 2010) may also play a role for samples with low concentrations such as ice core analyses.

The calibration offsets indicated in this study should be thoroughly taken into account when data from different laboratories are combined, and this study will be of help for instance incorporating merged δ13C-CH4 and δD-CH4 datasets into a state-of-the-art chemistry transport model. It is however advisable that data users should contact the data providers directly for the latest information whenever possible. The Kr effect is under evaluation at some laboratories and it will possibly involve an update of the dataset currently available. More importantly, it is imperative to have common reference gases with transparent and reproducible traceability (for instance, Sperlich et al. 2016) and to carry out a systematic intercomparison program (flask or cylinder round robin) in the research community for attaining the necessary but ambitious high compatibility goals of 0.02 ‰ for δ13C-CH4 and 1 ‰ for δD-CH4 (WMO, 2016). Such thorough efforts will facilitate optimized use of δ13C-CH4 and δD-CH4 datasets in a combined way and maximize number of isotope datasets (and thus their spatial and temporal coverage) usable for enhancing our understanding of the global CH4 cycle.

List of Institution/Project Acronyms

AWI: Alfred-Wegener-Institut Helmholtz-Zentrum für Polar-und-Meeresforschung, Bremerhaven, Germany

CARIBIC: Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container

CIC: Center for Ice and Climate, University of Copenhagen, Copenhagen, Denmark

DSIR: Department of Scientific and Industrial Research, Division of Physical Sciences, Nuclear Science Group, Lower Hutt, New Zealand

IMAU: Institute for Marine and Atmospheric research Utrecht, Utrecht University, Utrecht, the Netherlands
IAEA: International Atomic Energy Agency
INSTAAR: Institute of Arctic and Alpine Research University of Colorado Boulder, Boulder, USA
MPI-BGC: Max Planck Institute for Biogeochemistry, Jena, Germany
MPIC: Max Planck Institute for Chemistry, Mainz, Germany
NCAR: National Center for Atmospheric Research, Boulder, USA
NIPR: National Institute of Polar Research, Tsukuba, Japan
NIWA: National Institute for Water and Atmospheric Research, Wellington, New Zealand
NOAA: National Oceanic and Atmospheric Administration, USA
PDX: Portland State University, Portland, USA
PSU: Pennsylvania State University, Pennsylvania, USA
RHUL: Royall Holloway, University of London, Egham, UK
TU: Tohoku University, Sendai, Japan
UB: University of Bern, Bern, Switzerland
UCI: University of California Irvine, Irvine, USA
UHEI: University of Heidelberg, Heidelberg, Germany
UW: University of Washington, Seattle, USA

Acknowledgement

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References


Brand, W., Rothe, M., Sperlich, P., Strube, M., and Wendeberg M.: Automated simultaneous measurement of the $\delta^{13}C$ and $\delta^2H$ values of methane and the $\delta^{13}C$ and $\delta^{18}O$ values of carbon dioxide in


Sperlich, P., Guillevic, M., Buizert, C., Jenk, T. M., Sapart, C. J., Schaefer, H., Popp, T. J., and Blunier, T.: A combustion setup to precisely reference $\delta^{13}$C and $\delta^{2}$H isotope ratios of pure CH$_4$ to produce

Sperlich, P., Buizert, C., Jenk, T. M., Sapart, C. J., Prokopiou, M., Röckmann, T., and Blunier, T.: An automated GC-C-GC-IRMS setup to measure palaeoatmospheric $\delta^{13}$C-CH$_4$, $\delta^{15}$N-N$_2$O and $\delta^{18}$O-N$_2$O in one ice core sample, Atmos. Meas. Tech., 6, 2027-2041, doi:10.5194/amt-6-2027-2013, 2013.


Table 1. List of laboratories that conduct measurements of $\delta^{13}$C-CH$_4$ and $\delta^D$-CH$_4$ and references for intercomparison programs.

See Figure 1 for overview of the past intercomparison exercises, Figure 2 for intercomparison summary and the list of institution/project acronyms in the text for the laboratory names.

<table>
<thead>
<tr>
<th>No.</th>
<th>Laboratory</th>
<th>$\delta^{13}$C-CH$_4$ Intercomparison</th>
<th>$\delta^D$-CH$_4$ Intercomparison</th>
<th>Measurement System</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NIWA</td>
<td>Refs. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12</td>
<td>Not Measured</td>
<td>Ref. 13</td>
</tr>
<tr>
<td>2</td>
<td>IMAU</td>
<td>Refs. 9, 11, 14, 15, 16, 17, 18, 19</td>
<td>Refs. 11, 15, 16, 17, 18, 19, 20</td>
<td>Ref. 19</td>
</tr>
<tr>
<td>3</td>
<td>MPIC</td>
<td>Refs. 14, 19</td>
<td>Refs. 19, 20</td>
<td>Ref. 21</td>
</tr>
<tr>
<td>4</td>
<td>MPI-BGC</td>
<td>Ref. 16, 22</td>
<td>Ref. 16, 22</td>
<td>Ref. 23</td>
</tr>
<tr>
<td>5</td>
<td>UCI</td>
<td>Refs. 6, 11, 17, 24, 25, 26</td>
<td>Refs. 17, 26</td>
<td>Ref. 6, 27, 28</td>
</tr>
<tr>
<td>6</td>
<td>TU</td>
<td>Refs. 18, 29</td>
<td>Ref. 18</td>
<td>Ref. 29</td>
</tr>
<tr>
<td>7</td>
<td>NIPR</td>
<td>Refs. 7, 18, 29</td>
<td>Not Measured</td>
<td>Ref. 7</td>
</tr>
<tr>
<td>8</td>
<td>UW</td>
<td>Refs. 1, 2, 3, 24</td>
<td>No Ref. Available</td>
<td>Ref. 2</td>
</tr>
<tr>
<td>9</td>
<td>UHEI</td>
<td>Refs. 3, 4, 5, 8, 14, 22</td>
<td>Ref. 22</td>
<td>Ref. 4</td>
</tr>
<tr>
<td>10</td>
<td>INSTAAAR</td>
<td>Refs. 3, 6, 8, 10, 11, 12, 14, 25, 30</td>
<td>Ref. 20</td>
<td>Ref. 25</td>
</tr>
<tr>
<td>11</td>
<td>RHUL</td>
<td>Refs. 8, 10, 12</td>
<td>Not Measured</td>
<td>Refs. 31, 32</td>
</tr>
<tr>
<td>12</td>
<td>PDX</td>
<td>Refs. 24, 26</td>
<td>Ref. 24, 26</td>
<td>Refs. 26, 28</td>
</tr>
<tr>
<td>13</td>
<td>PSU</td>
<td>Refs. 9, 11, 14, 15</td>
<td>Refs. 11, 15, 20</td>
<td>Ref. 33</td>
</tr>
<tr>
<td>14</td>
<td>UB</td>
<td>Refs. 9, 11, 15, 30</td>
<td>Refs. 11, 15, 20, 34</td>
<td>Refs. 9, 20, 30, 34</td>
</tr>
<tr>
<td>15</td>
<td>AWI</td>
<td>Refs. 5, 9, 14, 15</td>
<td>Not Measured</td>
<td>Ref. 5</td>
</tr>
<tr>
<td>16</td>
<td>CIC</td>
<td>Refs. 16, 35</td>
<td>Refs. 16, 35</td>
<td>Refs. 35, 36</td>
</tr>
</tbody>
</table>

References—

1. Lowe et al. (1994); 2. Quay et al. (1999); 3. Levin et al. (2012); 4. Poß (2003); 5. Behrens et al. (2008); 6. Tyler et al. (2007); 7. Morimoto et al. (2006); 8. Nisbet (2005); 9. Schmitt et al. (2013); 10. Nisbet et al. (2016); 11. This study (section 3.4 Ice Core Intercomparison Round Robin); 12. This study (section 3.6 NOAA co-located sample intercomparison); 13. Lowe et al. (1991); 14. Möller (2013); 15. Sapart et al. (2011); 16. Sperlich et al. (2016); 17. This study (section 3.1 UCI-IMAU intercomparison); 18. This study (section 3.2 TU/NIPR-IMAU intercomparison); 19. Brass and Röckmann (2010); 20. Bock et al. (2010); 21. Bergamaschi et al. (1994); 22. This study (section 3.3 UHEI-MPI-BGC intercomparison); 23. Brand et al. (2016); 24. Rice et al. (2016); 25. Miller et al. (2002); 26. Teama (2013); 27. Tyler et al. (1999); 28. Rice et al. (2001); 29. Umezawa et al. (2009); 30. Schmitt et al. (2014); 31. Lowry et al. (2001); 32. Fisher et al. (2006); 33. Sowers et al. (2005); 34. Bock et al. (2014); 35. Sperlich et al. (2012); 36. Sperlich et al. (2013)
Table 2. Result of intercomparison of δ^{13}C-CH\textsubscript{4} and δD-CH\textsubscript{4} measurements between UCI and IMAU.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>CH\textsubscript{4} (ppb)</th>
<th>δ^{13}C-CH\textsubscript{4} (%)</th>
<th>Difference from IMAU</th>
<th>δD-CH\textsubscript{4} (%)</th>
<th>Difference from IMAU</th>
</tr>
</thead>
<tbody>
<tr>
<td>WAS-24-2</td>
<td>1784.7\textsuperscript{a}</td>
<td>-46.96±0.07 (N=3)</td>
<td>-47.33±0.05 (N=3)</td>
<td>-91.6±0.5 (N=2)</td>
<td>-78.9±0.1 (N=4)</td>
</tr>
<tr>
<td>WAS-24-5</td>
<td>1825.8\textsuperscript{a}</td>
<td>-47.16 (N=1)</td>
<td>-47.53±0.02 (N=6)</td>
<td>-93.8 (N=1)</td>
<td>-83.1±0.2 (N=4)</td>
</tr>
<tr>
<td>WAS-24-6</td>
<td>1827.5\textsuperscript{a}</td>
<td>-47.08±0.01 (N=2)</td>
<td>-47.55±0.04 (N=6)</td>
<td>-92.1±0.8 (N=2)</td>
<td>-83.6±0.1 (N=4)</td>
</tr>
<tr>
<td>WAS-24-9</td>
<td>1799.8\textsuperscript{a}</td>
<td>-47.05 (N=1)</td>
<td>-47.38±0.02 (N=6)</td>
<td>-92.3±1.8 (N=3)</td>
<td>-79.8±0.8 (N=4)</td>
</tr>
<tr>
<td>WAS-24-10</td>
<td>1789.8\textsuperscript{a}</td>
<td>-47.07 (N=1)</td>
<td>-47.42±0.02 (N=6)</td>
<td>-89.3 (N=1)</td>
<td>-79.7±0.8 (N=4)</td>
</tr>
<tr>
<td>WAS-24-11</td>
<td>1780.8\textsuperscript{a}</td>
<td>-46.77 (N=1)</td>
<td>-47.37±0.03 (N=6)</td>
<td>-89.0±0.9 (N=2)</td>
<td>-78.7±0.7 (N=4)</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td>+0.42±0.04</td>
<td></td>
<td>-10.7±0.7</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}NOAA-2004 CH\textsubscript{4} scale (Dlugokencky et al., 2005)
Table 3. Result of intercomparison of $\delta^{13}$C-CH$_4$ and $\delta^D$-CH$_4$ measurements between TU/NIPR and IMAU.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$\text{CH}_4$ (ppb)</th>
<th>TU</th>
<th>NIPR</th>
<th>IMAU</th>
<th>Difference from TU</th>
<th>TU</th>
<th>IMAU</th>
<th>Difference from IMAU</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD1</td>
<td>1901.1</td>
<td>$-47.03\pm0.02$</td>
<td>$-47.11\pm0.02$</td>
<td>$-47.40\pm0.04$</td>
<td>+0.37 (TU)</td>
<td>$-97.2\pm0.6$</td>
<td>$-85.0\pm0.1$</td>
<td>$-12.2$</td>
</tr>
<tr>
<td></td>
<td>(N=16)</td>
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<td>(N=5)</td>
<td>(N=9)</td>
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<td>(N=10)</td>
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</tr>
<tr>
<td>MD2</td>
<td>2116.6</td>
<td>$-46.80\pm0.02$</td>
<td>$-46.92\pm0.03$</td>
<td>$-47.26\pm0.03$</td>
<td>+0.46 (TU)</td>
<td>$-118.5\pm0.6$</td>
<td>$-104.5\pm0.3$</td>
<td>$-14.0$</td>
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<tr>
<td></td>
<td>(N=16)</td>
<td>(N=6)</td>
<td>(N=9)</td>
<td></td>
<td></td>
<td>(N=10)</td>
<td>(N=8)</td>
<td></td>
</tr>
<tr>
<td>MD3</td>
<td>899.1</td>
<td>$-41.13\pm0.04$</td>
<td>$-41.05\pm0.02$</td>
<td>$-41.81\pm0.03$</td>
<td>+0.68 (TU)</td>
<td>$-190.7\pm0.6$</td>
<td>$-175.8\pm0.6$</td>
<td>$-14.9$</td>
</tr>
<tr>
<td></td>
<td>(N=16)</td>
<td>(N=5)</td>
<td>(N=8)</td>
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<td>(N=8)</td>
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<tr>
<td>MD4</td>
<td>1700.5</td>
<td>$-42.46\pm0.03$</td>
<td>$-42.43\pm0.04$</td>
<td>$-42.98\pm0.02$</td>
<td>+0.52 (TU)</td>
<td>$-195.2\pm0.6$</td>
<td>$-180.6\pm0.2$</td>
<td>$-14.6$</td>
</tr>
<tr>
<td></td>
<td>(N=16)</td>
<td>(N=5)</td>
<td>(N=8)</td>
<td></td>
<td></td>
<td>(N=10)</td>
<td>(N=8)</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+0.41±0.04 (TU)</td>
<td></td>
<td></td>
<td>−13.1±0.6</td>
</tr>
<tr>
<td>(ambient</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+0.31±0.03 (NIPR)</td>
<td></td>
<td></td>
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<tr>
<td>air)</td>
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</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+0.51±0.07 (TU)</td>
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<td>−13.9±0.9</td>
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<tr>
<td>(all)</td>
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<td></td>
<td>+0.48±0.11 (NIPR)</td>
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</tbody>
</table>

*Tohoku University CH$_4$ scale (Aoki et al., 1992; Umezawa et al., 2014)
### Table 4. Result of intercomparison of $\delta^{13}$C-CH$_4$ and $\delta^D$-CH$_4$ measurements between UHEI and MPI-BGC.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Preparation Date</th>
<th>Analysis Date</th>
<th>$\delta^{13}$C-CH$_4$ (%)</th>
<th>$\delta^D$-CH$_4$ (%)</th>
<th>UHEI − MPI-BGC</th>
<th>UHEI − MPI-BGC</th>
</tr>
</thead>
<tbody>
<tr>
<td>GvN 88/20</td>
<td>17 Dec. 2003</td>
<td>9 Jul. 2013</td>
<td>$-47.54 \pm 0.02$</td>
<td>$-47.66$</td>
<td>+0.13</td>
<td>−83.3±2.2</td>
</tr>
<tr>
<td>(24 Jul. 1988)</td>
<td></td>
<td></td>
<td>(N=1)</td>
<td>(0.07, N=2)</td>
<td>(N=1)</td>
<td>(0.8, N=2)</td>
</tr>
<tr>
<td>GvN 92/12</td>
<td>11 Dec. 2008</td>
<td>17 Jun. 2013</td>
<td>$-47.43 \pm 0.02$</td>
<td>$-47.40$</td>
<td>−0.03</td>
<td>$-79.1 \pm 1.6$</td>
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<tr>
<td>(11 May. 1992)</td>
<td></td>
<td></td>
<td>(N=1)</td>
<td>(0.04, N=2)</td>
<td>(N=1)</td>
<td>(0.9, N=2)</td>
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<tr>
<td>GvN 96/03</td>
<td>11 Nov. 2003</td>
<td>17 Jun. 2013</td>
<td>$-47.27 \pm 0.02$</td>
<td>$-47.18$</td>
<td>−0.08</td>
<td>$-73.9 \pm 1.4$</td>
</tr>
<tr>
<td>(13 Feb. 1996)</td>
<td></td>
<td></td>
<td>(N=1)</td>
<td>(0.26, N=2)</td>
<td>(N=2)</td>
<td>(0.9, N=2)</td>
</tr>
<tr>
<td>GvN 99/14</td>
<td>3 Apr. 2003</td>
<td>9 Jul. 2013</td>
<td>$-47.30 \pm 0.02$</td>
<td>$-47.23$</td>
<td>−0.07</td>
<td>$-75.2 \pm 1.3$</td>
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<tr>
<td>(29 Dec. 1999)</td>
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<td></td>
<td>(N=1)</td>
<td>(0.16, N=2)</td>
<td>(N=2)</td>
<td>(1.3, N=2)</td>
</tr>
<tr>
<td>GvN 06/14</td>
<td>7 May. 2003</td>
<td>9 Jul. 2013</td>
<td>n.a.</td>
<td>$-47.19$</td>
<td>n.a.</td>
<td>$-72.3 \pm 1.6$</td>
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<tr>
<td>(23 Sep. 2006)</td>
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<td></td>
<td>(N=1)</td>
<td>(0.09, N=2)</td>
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<td>(0.0, N=2)</td>
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<tr>
<td>GvN 08/03</td>
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<td>17 Jun. 2013</td>
<td>$-47.18 \pm 0.05$</td>
<td>$-47.35$</td>
<td>+0.17</td>
<td>n.a.</td>
</tr>
<tr>
<td>(6 Mar. 2008)</td>
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<td></td>
<td>(N=1)</td>
<td>(0.05, N=2)</td>
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<td>(2.9, N=2)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>+0.02±0.05</td>
<td>+0.4±0.6</td>
</tr>
</tbody>
</table>

*Difference of duplicate flask measurements is shown in parenthesis.
Table 5. Results from the Ice Core Intercomparison Round Robin conducted during 2007–2016.

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>CA 03560 (1830.6 ppb)</th>
<th>CA 71560 (904.0 ppb)</th>
<th>CA 01179 (372.2 ppb)</th>
<th>Kr corr.</th>
<th>Analysis Date</th>
<th>Analysis Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSU</td>
<td>~47.20±0.16</td>
<td>~93.2±0.9</td>
<td>~47.41±0.10</td>
<td>~95.5±2.3</td>
<td>Trace(^{a})</td>
<td>Jul. 2007</td>
</tr>
<tr>
<td></td>
<td>~46.96±0.16</td>
<td>~47.20±0.10</td>
<td>~47.52±0.06</td>
<td>~106.3±2.4</td>
<td>DI</td>
<td>Jul. 2007</td>
</tr>
<tr>
<td></td>
<td>~47.10±0.05</td>
<td>~47.09±0.06</td>
<td>~47.41±0.12</td>
<td></td>
<td>DI Corr.(^{b})</td>
<td></td>
</tr>
<tr>
<td>UCI (DI-IRMS)</td>
<td>~47.09±0.12</td>
<td>~47.40±0.08</td>
<td>~47.23±0.06</td>
<td></td>
<td>—</td>
<td>Dec.</td>
</tr>
<tr>
<td></td>
<td>—</td>
<td>—</td>
<td>—</td>
<td></td>
<td></td>
<td>2007(^{7})</td>
</tr>
<tr>
<td>INSTAAR</td>
<td>~47.08±0.05</td>
<td>~47.20±0.06</td>
<td>~46.78±0.06</td>
<td></td>
<td>PCP(^{c})</td>
<td>Dec. 2008</td>
</tr>
<tr>
<td>NIWA (DI-IRMS)</td>
<td>~47.23±0.02</td>
<td>~47.44±0.02</td>
<td>~47.43±0.02</td>
<td></td>
<td>—</td>
<td>Jun. 2009</td>
</tr>
<tr>
<td>NIWA (GC-IRMS)</td>
<td>~47.44±0.21</td>
<td>~48.34±0.28</td>
<td>~47.62±0.11</td>
<td></td>
<td>DI Corr.(^{b})</td>
<td></td>
</tr>
<tr>
<td>UB</td>
<td>~47.41±0.09</td>
<td>~80.4±2.2</td>
<td>~47.37±0.07</td>
<td>~81.0±2.0</td>
<td>~47.31±0.11</td>
<td>~86.2±3.3</td>
</tr>
<tr>
<td></td>
<td>~79.6±1.2</td>
<td>~47.52±0.11</td>
<td>~83.6±3.8</td>
<td>~47.20±0.20</td>
<td>~78.8±12.4</td>
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</tr>
<tr>
<td>IMAU</td>
<td>~47.27±0.07</td>
<td>~79.6±1.2</td>
<td>~47.52±0.11</td>
<td>~83.6±3.8</td>
<td>~47.20±0.20</td>
<td>~78.8±12.4</td>
</tr>
</tbody>
</table>

\(^{a}\)Trace: The Kr effect was corrected by tracing the Kr-caused anomalies in the raw beam data (section 5.4 of Schmitt et al., 2013); \(^{b}\)DI Corr.: The Kr effect was corrected by an offset relative to a dual-inlet measurement; \(^{c}\)PCP: Kr was separated by Post Combustion Plot column (section 5.2 of Schmitt et al. 2013); \(^{d}\)No: No correction because the Kr effect was not identified.\(^{5}\)

\(^{5}\)Estimated because no exact record on the analysis date at UCI is unfortunately available.
Table 6. Results of $\delta^{13}$C-$\text{CH}_4$ intercomparison between INSTAAR and MPI-BGC.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$\text{CH}_4$ (ppb)$^*$</th>
<th>INSTAAR $\delta^{13}$C-$\text{CH}_4$ (‰)</th>
<th>MPI-BGC $\delta^{13}$C-$\text{CH}_4$ (‰)</th>
<th>INSTAAR–MPI-BGC</th>
</tr>
</thead>
<tbody>
<tr>
<td>HUEY-001</td>
<td>1905.5</td>
<td>−47.37±0.01 (N=22)</td>
<td>−47.67±0.01 (N=24)</td>
<td>+0.29</td>
</tr>
<tr>
<td>DEWY-001</td>
<td>1879.9</td>
<td>−47.38±0.01 (N=26)</td>
<td>−47.67±0.01 (N=22)</td>
<td>+0.28</td>
</tr>
<tr>
<td>LOUI-001</td>
<td>1496.0</td>
<td>−47.26±0.01 (N=17)</td>
<td>−47.55±0.02 (N=22)</td>
<td>+0.29</td>
</tr>
<tr>
<td>CART-001</td>
<td>1848.1</td>
<td>−42.98±0.01 (N=21)</td>
<td>−43.30±0.03 (N=7)</td>
<td>+0.32</td>
</tr>
<tr>
<td>STAN-001</td>
<td>1696.4</td>
<td>−56.60±0.01 (N=7)</td>
<td>−57.20±0.05 (N=8)</td>
<td>+0.60</td>
</tr>
<tr>
<td>KENN-001</td>
<td>1847.6</td>
<td>−47.65±0.01 (N=26)</td>
<td>−47.94±0.05 (N=7)</td>
<td>+0.28</td>
</tr>
<tr>
<td>KYLE-001</td>
<td>1847.6</td>
<td>−47.27±0.01 (N=29)</td>
<td>−47.51±0.07 (N=6)</td>
<td>+0.24</td>
</tr>
</tbody>
</table>

$^*$NOAA-2004 CH$_4$ scale (Dlugokencky et al., 2005)
Figure 1. A schematic overview of the previous and present intercomparisons between laboratories for δ\textsubscript{13}C-CH\textsubscript{4} (top) and δD-CH\textsubscript{4} (bottom). Intercomparisons are marked by lines with open circles at both ends, and scale transfers are by lines with an arrow at one end.
Figure 2. (a) δ¹³C-CH₄ offsets of the different laboratories with respect to the NIWA DI-IRMS measurement with gray shades for ease of viewing. (b) δD-CH₄ offsets of the different laboratories with respect to the IMAU GC-IRMS measurement. See Table 1 and text for corresponding subsections in sections 2 and 4. Numbers shown in each laboratory column are the plausible calibration offsets estimated in this study. Note that this result represents intercomparisons for CH₄ in ambient air.