Inter-laboratory comparison~~s~~ of δ^{13}C and δD measurements of atmospheric CH_4 for combined use of datasets from different laboratories

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Abstract. We report results from a worldwide inter-laboratory comparison ~~exercises~~ of samples ~~between~~ among laboratories that ~~conduct~~ measure~~ments of~~ (or measured in the past) stable carbon and hydrogen isotope ratios of atmospheric CH_4 (δ^{13}C-CH_4 and δD-CH_4). The offsets ~~between~~ among the laboratories are larger than the measurement reproducibility of individual laboratories. To disentangle plausible measurement offsets ~~between worldwide laboratories~~, we evaluated and critically assessed a large number of intercomparison results, some of which have been documented previously in the literature. The results indicate significant offsets of δ^{13}C-CH_4 and δD-CH_4 measurements among datasets reported from different laboratories; the ~~data~~ differences among laboratories at modern atmospheric CH_4 level spread over ranges of 0.5 ‰ for δ^{13}C-CH_4 and 13 ‰ for δD-CH_4. The intercomparison results summarized in this study may be of help for future attempts to harmonize ~~when combining isotope~~ δ^{13}C-CH_4 and δD-CH_4 datasets from different laboratories in order to jointly incorporate them into modelling studies ~~in future studies~~. However, establishing such a merged dataset, which includes δ^{13}C-CH_4 and δD-CH_4 data from multiple laboratories with desirable compatibility, is still challenging due to differences among laboratories in instrument settings, correction methods, traceability to reference materials and long-term data management. Further efforts are needed to identify causes of the inter-laboratory measurement offsets and to decrease those towards the best use of available δ^{13}C-CH_4 and δD-CH_4 datasets.

1 Introduction

Methane (CH_4) is an important anthropogenic and natural greenhouse gas, and ~~moreover~~ it also has a large role ~~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 (δ^{13}C-CH_4 and δD-CH_4) have been useful to constrain the global CH_4 budget. Dictated by global mass balance, the average isotopic composition of CH_4 in the atmosphere (δ^{13}C-CH_4 or δD-CH_4) equals the flux-weighted isotopic composition of the sources, corrected for the total kinetic isotope effects of removal processes (e.g. Stevens and Rust, 1982; Cicerone and Oremland, 1988; 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:

$$\delta = \frac{R_{sample}}{R_{standard}} - 1 \tag{1}$$

where R represents the atomic ratio of the ~~heavy~~ less abundant over the ~~light~~ most abundant isotope in the sample and the standard, respectively. Conventionally, measured values are reported relative to the international isotope scales VPDB for δ^{13}C-CH_4 and VSMOW for δD-CH_4 in per mil.

~~In early years, atmospheric δ^{13}C-CH_4 and δD-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 δ^{13}C-CH_4 (δD-CH_4) 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 CH_4 in sample air from which all CO_2 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-CH_4). 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 δ^{13}C-CH_4 and δD-CH_4 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 that the atmospheric lifetime of CH_4 ~~to be~~ is about a decade, its ~~atmospheric~~ variation~~s~~ in background air ~~are~~ is relatively small. ~~and f~~For that ~~matter~~reason, its ~~concentration~~ mole fraction and isotopic ~~analyses~~ measurements have to be ~~done~~ made with high precision and accuracy. For δ^{13}C-CH_4

and δD-CH_4, researchers have achieved measurement reproducibility of < 0.1 ‰ for δ^{13}C-CH_4 and < 2 ‰ for δD-CH_4. Incorporating δ^{13}C-CH_4 and δD-CH_4 datasets in chemistry transport models is useful to quantitatively separate different types of CH_4 source categories and such attempts have been contributed to reduction of uncertainties in the global CH_4 budget (e.g. Fung et al., 1991; Hein et al., 1997; Mikaloff Fletcher et al., 2004a, 2004b; Monteil et al., 2011; Kirschke et al., 2013; Ghosh et al., 2015; Rice et al., 2016; Schaefer et al., 2016; Schwietzke et al., 2016; Röckmann et al., 2016; Turner et al., 2017; Rigby et al., 2017). Increasingly, δ^{13}C-CH_4 and δD-CH_4 measurements can contribute to reduction of uncertainties in the global CH_4 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 δ^{13}C-CH_4 and δD-CH_4 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). ConsequentlyHowever, although an increasing number of δ^{13}C-CH_4 and δD-CH_4 data has been reported over the last decades, significant calibration measurement offsets of δ^{13}C-CH_4 between among laboratories have been found for both δ^{13}C-CH_4 (e.g. Levin et al., 2012) and δD-CH_4 (Bock et al., 2014). It is Clear clear is that both reliable calibrations traceability to the standard scales and inter-laboratory comparisons (intercomparisons) are indispensable for combined use of δ^{13}C-CH_4 and δD-CH_4 data from different laboratories. Many such interlaboratory intercomparisons have already been made, either on an ad hoc basis, or on a broader more organized scale have already been made. However, a systematic evaluation of the underlying primary calibrations and calibration related measurement offsets among laboratories has been lacking. It is also noted that some measurement programs for δ^{13}C-CH_4 and/or δD-CH_4 have been discontinued, and maintaining access to such datasets including well-established inter-laboratory offsets is important. Here we unravel combine and evaluate most of the interexisting comparison results to quantify inter-laboratory measurement differences in order to facilitate help the optimal use of δ^{13}C-CH_4 and δD-CH_4 data. This study therefore opens the 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 δ^{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 δ^{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 δD-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 δ^{13}C-CH_4 and/or δD-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 δ^{13}C-CH_4 and δD-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 δ^{13}C-CH_4 and δD-CH_4 datasets from different laboratories with identical anchoring points.

In this study, wWe first present a technical overview of atmospheric δ^{13}C-CH_4 and δD-CH_4 measurements and potential causes of measurement offsets among currently available datasets (section 2), and then we review summarize measurement methods by the laboratories that have contributed conducted to- atmospheric and ice core δ^{13}C-CH_4 and δD-CH_4 measurements for air and ice core samples (section 23). 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 In section 4, we report new intercomparison exercises between these some groups (section 3). After that, wWe then link the inter-laboratory comparison results through survey of previous published intercomparisons programs in the literature and provide the current best estimates of measurement plausible calibration offsets between among datasets from different laboratories (section 45). Finally, we discuss summarize the current status and briefly discuss possible causes of the calibration measurement offsets and as well as remaining issues that should be kept in mind for combined use of currently existing CH_4 isotope datasets of isotopic composition of CH_4 from different laboratories (section 56). 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 Overview systemsof Atmospheric δ^{13}C-CH_4 and δD-CH_4 Measurement Techniques

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 IRMS Measurements for δ^{13}C-CH_4 and δD-CH_4

In the 1990s, atmospheric δ^{13}C-CH_4 (δD-CH_4) was analyzed using an offline technique in which CH_4 was separated from sample air and converted to CO_2 (H_2) for subsequent offline δ^{13}C-CH_4 (δD-CH_4) 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 CH_4 in sample air, with interfering compounds such as CO_2, H_2O, N_2O, CO and non-methane hydrocarbons being removed cryogenically, chemically or by gas chromatography before the CH_4 combustion. 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-CH_4). Later, a method based on continuous-flow gas chromatography isotope ratio mass spectrometry (GC-IRMS) technique combined with combustion and pyrolysis furnaces became available (Merritt et al., 1995; Burgoyne and Hayes, 1998; Hilkert et al., 1999), 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 δ^{13}C-CH_4 and δD-CH_4 data in the current and past atmosphere (Rice et al., 2001; Miller et al., 2002; Sowers et al., 2005; Ferretti et al., 2005; Morimoto et al., 2006; Fisher et al., 2006; Behrens et al., 2008; Umezawa et al., 2009; Brass and Röckmann, 2010; Sperlich et al., 2013; Schmitt et al., 2014; Bock et al., 2014; Brand et al., 2016; Röckmann et al., 2016). Although these systems use a similar measurement principle, they vary in the use of pre-concentration of CH_4 in sample air, GC separation, and combustion/pyrolysis, data corrections and in the specific IRMS instrument among laboratories (see Schmitt et al., 2013, section 3 and Table 1). Besides analysis by IRMS, laser-based spectroscopy has also been developed for atmospheric δ^{13}C-CH_4 and δD-CH_4 measurements (Bergamaschi et al., 2000; Eyer et al., 2016), but detailed discussion on the technique is beyond the scope of this study.

2.2 Standard Scales

VPDB and VSMOW are the standard scales for δ^{13}C-CH_4 and δD-CH_4, respectively. To make measurements traceable to these standard scales, each laboratory needs to calibrate its laboratory reference gases against reference materials (RMs) with known values on the standard scales. In this study, the term “calibration” means to measure a laboratory gas (for instance a laboratory working standard gas that is routinely compared with samples) against a standard at higher hierarchy level and to assign to that working standard a δ^{13}C-CH_4 or δD-CH_4 value traceable to the standard scale. In principle, all measurements at individual laboratories intended to ultimately anchor their working standards and sample gases to the VPDB or VSMOW scale using the RMs provided by the International Atomic Energy Agency (IAEA) or National Institute of Standards and Technology (NIST) (Coplen et al., 2006; Brand et al., 2014). However, since RMs and recommended calibration methods for measurements of δ^{13}C-CH_4 and δD-CH_4 in air have not yet been provided (Sperlich et al., 2012, 2016), individual groups have developed their own calibration strategies.

Since δ^{13}C-CH_4 measurement by IRMS is made by δ^{13}C analysis in CO_2 oxidized from CH_4 in air, some laboratories use pure CO_2 gases as a working standard. In many laboratories, these internal CO_2 standard gases were calibrated against pure CO_2 produced from the primary anchor of the VPDB scale NBS-19 or other RMs by using DI-IRMS (Table 1). Since the typical atmospheric δ^{13}C-CH_4 value (about −47 ‰) differs considerably from the δ^{13}C value of NBS-19 (+1.95 ‰), some laboratories have used other RMs with VPDB values close to the atmospheric δ^{13}C-CH_4 such as LSVEC, IAEA-CO-9 and RM 8563 as a second anchoring point of the VPDB scale (see Table 1) in order to minimize the risk for significant errors in realization of the standard scale (due to scale contraction or ^{17}O correction, described in the following sections). A standard scale established this way at an individual laboratory was often propagated to laboratory-internal CO_2 standard gases at lower hierarchy levels, and they were used as the reference in DI-IRMS or GC-IRMS measurement of CO_2 processed from CH_4 in sample air. Ideally, this accurately links δ^{13}C-CH_4 of the sample to the international isotope scale. In contrast, it has been recommended that a measured value of a sample is determined against a reference gas that undergoes the all preparation steps in the sample measurement line in order to cancel out possible isotopic fractionations due to different treatment between the sample and reference gases (principle of identical treatment; Werner and Brand, 2001). This concept has been taken into account in some laboratories; a working standard is calibrated for δ^{13}C-CH_4 and sample measurements are referenced by comparison with measurements of that working standard processed in the same manner (e.g. Brand et al., 2016). Despite intensions for best traceability to RMs, the variety of calibrations has resulted in diverse realizations of the VPDB scale across δ^{13}C-CH_4 measurement programs. As in Table 1, the different RMs that have been applied for δ^{13}C-CH_4 calibration include NBS-19 (limestone), IAEA-CO-9 (barium carbonate), LSVEC (lithium carbonate), and RM 8562–8564 (CO_2); see Coplen et al. (2006), Brand et al. (2014) and Sperlich et al. (2016). It is also noted that uncertainty of assigned values for these RMs ranges up to a few tenths ‰ and the assigned values have been revised over time (Brand et al., 2014), which might have complicated the realization of the standard scale at each laboratory. Furthermore, most of these RMs are in different chemical forms, and different isotopic fractionations may have occurred during acid digestion to CO_2, which could have biased calibrations at each laboratory. Lastly, WMO (2016) has reported exhaustion of NBS-19 and instability of LSVEC, both of which are critical RMs for the VPDB scale. Associated possible revision of δ^{13}C values of RMs in the future will affect consistency of the datasets from different laboratories.

For δD-CH_4, in the conventional offline measurements, CH_4 in sample air needs to be processed to H_2O followed by reduction to H_2 for a subsequent DI-IRMS measurement. GC-IRMS requires pyrolysis of CH_4 to H_2. Therefore, individual laboratories have prepared internal standards of H_2O (liquid) or H_2

(gas), which were calibrated against primary RMs (water) or H_2 reference gases certified for δD (Table 1). Although the situation is less complicated compared to δ^{13}C-CH_4 in terms of variety in chemical properties of RMs, the lack of RMs for δD-CH_4 forced laboratories to develop their calibration method standard scale individually. It is also noted that, similar to δ^{13}C-CH_4, principle of identical treatment has not been followed strictly at the all laboratories. If not followed, sample measurements are subject to subtle changes in conditions of the all preparation steps (e.g. conversion of CH_4), while such changes do not affect the measured value of a reference gas injected directly to the IRMS.

2.3 Scale Contraction

It has been found that cross contamination between sample and reference CO_2 gases shrinks the δ^{13}C distance measured on DI-IRMS (Meijer et al., 2000; Verkouteren et al., 2003a, 2003b). This effect is known as scale contraction or η effect, and the magnitude is specific to the IRMS instrument and its settings. Since the VPDB scale for δ^{13}C-CH_4 has been realized and propagated via CO_2 calibrations by DI-IRMS at individual laboratories, the instrument-dependent scale contraction effect could have caused a significant difference in measurement values, especially at the low δ^{13}C values of atmospheric CH_4 of about −47 ‰ (Wendeberg et al., 2013).

2.4 ^{17}O Correction

For measurement of δ^{13}C-CH_4 by IRMS, CH_4 is first oxidized to CO_2 and the different isotopic variants of the produced CO_2 are then registered on Faraday cups with mass to charge ratios *m/z* of 44, 45 and 46. Since the raw ion beam intensity for m/z = 45 is the sum of $^{13}C^{16}O_2$ and $^{12}C^{17}O^{16}O$, the final δ^{13}C value is obtained by correcting for the contribution of the ^{17}O containing isotopologue, known as ^{17}O correction (e.g. Assonov and Brenninkmeijer, 2003). Several algorithms such as Craig (1957) and Santrock et al. (1985) have been suggested (see Assonov and Brenninkmeijer (2003) and references therein) and implemented into software/programs of the IRMS companies and individual laboratories. Assonov and Brenninkmeier (2003) showed that the bias caused by different ^{17}O-correction algorithms could exceed general repeatability achieved by IRMS measurements. The ^{17}O correction method of each laboratory is listed in Table 1.

2.5 Krypton Interference in GC-IRMS

The transition from DI-IRMS to GC-IRMS analyses reduced the analytical effort, but also introduced complications that were initially not recognized and taken into account. It was recently found that atmospheric krypton (Kr) interferes with the δ^{13}C-CH_4 GC-IRMS analysis if Kr is present in the ion source during the data acquisition of the CO_2 peak generated from CH_4 oxidation (hereafter CH_4-derived CO_2 peak) (Schmitt et al., 2013). Thus the δ^{13}C-CH_4 measurements on a GC-IRMS system can be biased if Kr is not separated sufficiently from either CH_4 or from the CH_4-derived CO_2 peak after the CH_4 combustion. Schmitt et al. (2013) demonstrated that the doubly charged krypton isotope $^{86}Kr^{2+}$, produced in the ion source of an IRMS, can cause lateral tailing extending into the Faraday cups used for δ^{13}C analysis (i.e. *m/z* of 44, 45 and 46), which compromises the measured signal of the CH_4-derived CO_2 peak. This effect had not been recognized for more than a decade since the early years of GC-IRMS measurements (Merritt et al., 1995), and thus has not been taken into account in many datasets of atmospheric δ^{13}C-CH_4 reported in the meantime (e.g. Miller et al., 2002; Morimoto et al., 2006; Fisher et al., 2011; Röckmann et al., 2011; Umezawa et al., 2012a, 2012b). Furthermore, because the Kr effect is system-dependent and variable with time (Schmitt et al., 2013), applying plausible corrections to past data may not be feasible. Likewise, several gas species including Kr can affect δD-CH_4 measurements, and this effect is also system-dependent (Bock et al., 2014).

Several solutions have been suggested to eliminate or account for the Kr interference (Schmitt et al., 2013). Among them, three methods have been implemented at different laboratories (Table 1). Briefly, (1) After the CH_4 oxidation to CO_2, Kr is separated from the CH_4-derived CO_2 by using a post combustion separation column (PCS) or cryogenically. (2) An offset due to the Kr interference is estimated by comparison with a DI-IRMS measurement (DI-offset). (3) The Kr interference peak is subtracted from the raw ion current time series of the IRMS acquisition (raw ion current correction). More detailed description has been presented in Schmitt et al. (2013).

3. Measurements of Participating Laboratories

In this section, we briefly document measurement systems of individual laboratories for ease of reference in ~~for~~ the following intercomparisons (sections 4 and 5). For details, we refer to more dedicated publications listed in Table 1. The table also visualizes differences among laboratories in terms of possible causes of the measurement offsets described in section 2.

~~2~~3.1 NIWA

National Institute for Water and Atmospheric Research (NIWA, ~~known as~~ originally INS (Institute of Nuclear Sciences, later INGS (Institute of Nuclear and Geological Sciences) ~~DSIR prior to~~ until 1992) successfully initiated systematic measurements of atmospheric δ^{13}C-CH_4 by means of offline CH_4 separation and conversion followed by a DI-IRMS measurement ~~from the early years~~ in 1988 (Lowe et al., 1988, 1991). A suite of CO_2 working gases with δ^{13}C-CH_4 values around −47 ‰ referenced to IAEA materials ~~are~~ were ~~regularly~~ utilized to calibrate the measurements. An overall ~~precision~~ reproducibility of the δ^{13}C-CH_4 measurement was evaluated to be 0.02 ‰ (Lowe et al., 1991). The δ^{13}C-CH_4 measurements at NIWA are ultimately calibrated against CO_2 produced from NBS-19, IAEA-CO-9 and LSVEC. The long-term δ^{13}C-CH_4 records have been presented since then (Lowe et al., 1994, 1997, 2004; Bergamaschi et al., 2001; 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~~ reproducibility of 0.1 ‰. The Kr interference on the GC-IRMS δ^{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~~3.2 IMAU

The GC-IRMS system at the 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^{13}C-CH_4 and δD-CH_4, respectively. Sample air is measured against reference air that is processed in the GC-IRMS system in the same manner as a sample. The IMAU δ^{13}C-CH_4 ~~calibration~~ standard scale 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_2 gas produced from NBS-19 ~~provided by IAEA~~ (Röckmann, 1998; Bergamaschi et al., 2000). The δD-CH_4 ~~calibration~~ standard scale 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~~this interference. A correction was applied for data obtained before the system modification ~~to account for the Kr effect~~ (Schmitt et al., 2013).

~~2~~3.3 MPIC

MPIC has reported δ^{13}C-CH_4 and δD-CH_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^{13}C-CH_4 (Bergamaschi et al., 2000) and a tunable diode laser based absorption spectrometer (TDLAS) for δD-CH_4 (Bergamaschi et al., 1994). ~~Part of~~ Some firn air measurements by Bräunlich et al. (2001) ~~was~~ were performed by using a GC-IRMS system at Laboratory of Glaciology and Geophysics of the Environment. As described in section ~~2~~3.2, the MPIC δ^{13}C-CH_4 and δD-CH_4 calibrations are basis of that of IMAU. For the δ^{13}C-CH_4 DI-IRMS measurement, the CH_4-derived CO_2 was measured against a working standard (pure CO_2) that was calibrated against ~~VPDB~~ NBS-19 on a DI-IRMS system (Röckmann, 1998; Bergamaschi et al., 2000). The MPIC δD-CH_4 scale is based on measurements of standard gases at the Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany; CH_4 was combusted to CO_2 and H_2O, followed by reduction of H_2O to H_2 for subsequent DI-IRMS analysis on H_2; the calibration was made against VSMOW and SLAP (Bergamaschi et al., 2000). The measurements of atmospheric δ^{13}C-CH_4 and δD-CH_4 at MPIC were discontinued.

~~2~~3.4 MPI-BGC

Max Planck Institute for Biogeochemistry (MPI-BGC) set up a GC-IRMS system for δ^{13}C-CH_4 and δD-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~~ reproducibility ~~were~~ was assessed to be 0.12 ‰ for δ^{13}C-CH_4

and 1.0 ‰ for δD-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~~ ~~a post-combustion separation~~ PCS column, and the initial calibration has in the meantime been replaced by a new primary calibration, where measurements are ultimately anchored to NBS-19 and LSVEC for δ^{13}C-CH_4 and VSMOW-2 and SLAP-2 for δD-CH_4 (Sperlich et al., 2016). This calibration, termed JRAS-M16, is the basis for the δ^{13}C-CH_4 and δD-CH_4 values from MPI-BGC reported in this manuscript.

~~2~~3.5 UCI

University of California Irvine (UCI) measured atmospheric δ^{13}C-CH_4 by offline DI-IRMS and δD-CH_4 by GC-IRMS (Tyler et al., 1999, 2007; Kai et al., 2011). The UCI GC-IRMS system for both δ^{13}C-CH_4 and δD-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 δ^{13}C-CH_4 and δD-CH_4, respectively, while that of the offline DI-IRMS δ^{13}C-CH_4 measurement was 0.05 ‰. ~~For the GC-IRMS measurements, s~~Samples were measured against laboratory working standard gases of pure CO_2 for δ^{13}C-CH_4 and pure H_2 for δD-CH_4. The δ^{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-9 (Lowe et al., 1999). The δD-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 is now 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~~3.6 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 δ^{13}C-CH_4 and 2.2 ‰ for δD-CH_4. Sample measurements are made against pure CO_2 and H_2 working standard gases for δ^{13}C-CH_4 and δD-CH_4, respectively. The δ^{13}C-CH_4 calibration is based on a CO_2 primary gas produced from NBS-~~18~~19~~provided by IAEA, while laboratory standards (pure CO_2) were also well compared with NBS-19~~. The H_2 working standard for δD-CH_4 measurement is referenced to water laboratory standards that are calibrated against VSMOW and SLAP~~ provided by IAEA~~. Measured δD-CH_4 values are corrected so that the value of a laboratory test gas is kept constant over time ~~because measured value could~~ to account for ~~fluctuate~~ fluctuations in the measured value ~~depending on~~ due to the condition of the pyrolysis furnace (Umezawa et al., 2009, 2012a). The Kr interference on the δ^{13}C-CH_4 measurement was identified, but modification or correction has not been implemented. It has been documented that δ^{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 δ^{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~~3.7 NIPR

National Institute of Polar Research (NIPR) reported δ^{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 δ^{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 δ^{13}C-CH_4 measurements at NIPR.

~~2~~3.8 UW

University of Washington (UW) reported extensive δ^{13}C-CH_4 and δD-CH_4 measurements using an offline DI-IRMS system (Quay et al., 1991, 1999). The ~~precisions~~ reproducibility ~~were~~ was estimated to be 0.1 ‰ for δ^{13}C-CH_4 and 3–4 ‰ for δD-CH_4. The δ^{13}C-CH_4 calibration is based on measurements against NBS-19 (Quay et al., 1999), while the earlier measurements were calibrated against NBS-20 and NBS-16 (Quay et al., 1991). The δD-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 δ^{13}C-CH_4 dataset for 1988–1995 (Quay et al., 1999).

~~2~~3.9 UHEI

University of Heidelberg (UHEI) carried out $\delta^{13}C\text{-}CH_4$ 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 $\delta^{13}C\text{-}CH_4$ measurements are calibrated against CO_2 reference materials (RM 8562, RM 8563 and RM 8564) (Behrens et al., 2008). Although reported previously only for signatures of source CH_4 (Levin et al., 1993), UHEI also ~~has~~ made offline $\delta D\text{-}CH_4$ measurements on atmospheric samples by DI-IRMS and TDLAS (Poß, 2003). The $\delta D\text{-}CH_4$ measurements by DI-IRMS ~~have been~~ were made on pure H_2 (H_2O from CH_4 oxidation converted to H_2 with zinc as catalyst) and were calibrated against VSMOW and SLAP. Note that UHEI recently re-evaluated all their atmospheric $\delta^{13}C\text{-}CH_4$ and $\delta D\text{-}CH_4$ 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~~3.10 INSTAAR

Institute of Arctic and Alpine Research (INSTAAR) of the University of Colorado Boulder has measured $\delta^{13}C\text{-}CH_4$ and, intermittently, $\delta D\text{-}CH_4$ 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~~ Reproducibilities of the $\delta^{13}C\text{-}CH_4$ and $\delta D\text{-}CH_4$ measurements are evaluated to be 0.08 ‰ and 2 ‰, respectively (Miller et al., 2002; White et al., 2016). The INSTAAR $\delta^{13}C\text{-}CH_4$ measurement currently follows the UCI calibration, while the $\delta D\text{-}CH_4$ measurement is not explicitly anchored to the VSMOW scale (White et al., 2016). The Kr interference on the $\delta^{13}C\text{-}CH_4$ measurement ~~was recently identified to~~ is ~~be~~ significant, and ~~the post-combustion separation~~ a PCS column was therefore implemented into the system in May 2017. Correction of ~~for~~ the data~~set~~ for the ~~interfered by~~ Kr interference (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~~ not been interfered by Kr ~~removal~~.

23.11 RHUL

Royal Holloway University of London (RHUL) conducted measured atmospheric δ^{13}C-CH_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 δ^{13}C-CH_4 calibrations ultimately to IAEA carbonate materials NBS-19 and IAEA-CO-9 (Lowry et al., 2001; Fisher et al., 2006). Note that RHUL applies an offset correction of −0.20 ‰ for the measured value by GC-IRMS (sections 4.6 and 5.11).

23.12 PDX

Portland State University (PDX) reported δ^{13}C-CH_4 and δD-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 δ^{13}C-CH_4 and δD-CH_4 precisions reproducibilities are 0.07 ‰ and 2.0 ‰, respectively, and PDX shares calibrations the standard scales with UCI for both δ^{13}C-CH_4 and δD-CH_4 (Rice et al., 2016).

23.13 PSU

Pennsylvania State University (PSU) reported δ^{13}C-CH_4 and δD-CH_4 data from ice cores and firn air using a GC-IRMS system (e.g. Sowers et al., 2005; Sowers, 2010). The overall measurement uncertainties reproducibility including every step for ice core measurements were was evaluated to be 0.3 ‰ for δ^{13}C-CH_4 and 3 ‰ for δD-CH_4 (Sowers, 2010). The PSU δ^{13}C-CH_4 measurements are calibrated against CO_2 reference materialRMs (RM 8563 and RM 8564). The δD-CH_4 calibration is made against H_2 gas bottles from Oztech Gas Company (Sowers, 2006).

23.14 UB

University of Bern (UB) makes δ^{13}C-CH_4 measurements from ice cores using a GC-IRMS system with an overall reproducibility of 0.15 ‰ (Schmitt et al., 2014; Bock et al., 2017). The UB measurements are referenced to a whole-air working standard with CH_4 concentration mole fraction of 1508.2 ppb and an assigned δ^{13}C-CH_4 value of −47.34±0.02 ‰ (named "Boulder, CA08289" in Schmitt et al., 2014). This ~~standard~~ value is anchored to the standard scale used at INSTAAR ~~calibration~~ (section ~~2~~3.10). UB also measures δD-CH_4 for ice core samples (Bock et al., 2010, 2014, 2017). The overall measurement precision for ice core sample (including extraction of air from an ice sample) was evaluated to be 2.3 ‰. The UB δD-CH_4 measurement is referenced by using an ambient air cylinder (named "Air Controlé") with a δD-CH_4 value of −93.6±2.8 ‰, which was cross-referenced to a~~n~~ ~~Antarctic bottled air~~ high pressure cylinder filled at the Alert Station ("Alert 2002/11" with δD-CH_4 of −82.2±1.0 ‰) analyzed on the scale maintained at UHEI (Bock et al., 2010, 2014). However, this value has to be corrected to −85.2±1.0 ‰ to account for the recent re-evaluation at UHEI (section ~~2~~3.9). All UB data published after 2011 are free of Kr interference.

~~2~~3.15 AWI

Alfred Wegener Institute Helmholtz Cent~~e~~re for Polar and Marine Research (AWI) reported δ^{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 δ^{13}C-CH_4 measurements ~~follow~~ employed the UHEI ~~calibration~~ standard scale via comparison of measurements of an ~~Antarctic~~ air sample collected at Neumayer Station, Antarctica (Möller et al., 2013).

~~2~~3.16 CIC

Centre for Ice and Climate (CIC) of the Niels Bohr Institute has reported δ^{13}C-CH_4 measurements from ice cores (Sperlich et al., 2015) using a GC-IRMS system with measurement reproducibility of 0.09 ‰ (Sperlich et al., 2013). CIC also set up an offline combustion system for ~~large CH_4~~ samples with large amount of CH_4, which is combined with DI-IRMS for δ^{13}C-CH_4 and with either a high Temperature Conversion/Elemental Analyser (TC/EA) coupled to IRMS or laser spectroscopy for δD-CH_4 (Sperlich et al., 2012); the measurement reproducibility is 0.04 ‰ for δ^{13}C-CH_4 and 0.7 ‰ for δD-CH_4. The CIC measurements are referenced to RM 8563 for δ^{13}C-CH_4 and VSMOW-2 and SLAP-2 for δD-CH_4. The combined uncertainty of this analytical system including the uncertainty of the entire traceability chain was estimated as 0.07 ‰ for δ^{13}C-CH_4 and 0.7 ‰ for δD-CH_4 (Sperlich et al., 2016).

~~3~~ 4 ~~Present~~ Intercomparison Exercises

~~3~~4.1 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~~ differences of +0.42±0.04‰ for δ^{13}C-CH_4 (UCI value is higher than IMAU) and of −10.7±0.7‰ for δD-CH_4 (UCI value is lower than IMAU).

~~3~~4.2 Intercomparison between TU/NIPR and IMAU

An ~~Intercomparison~~ 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 CH_4-in-air ~~standard~~ gas ~~air~~ (canisters MD3 and MD4) with CH_4 ~~concentrations~~ mole fractions 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 reanalyzed ~~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 transport~~ation~~ to IMAU throughout April 2013 to July 2015 indicated that possible drifts during canister storage and transportation are small (< 0.1 ‰ for δ^{13}C-CH_4 and < 3.5 ‰ for δD-CH_4). NIPR also measured the canisters for δ^{13}C-CH_4. The ~~intercomparison~~ results indicate significant ~~calibration offsets~~ differences of +0.~~51~~50±0.07 ‰ for δ^{13}C-CH_4 (TU value is higher than IMAU) and of −13.9±0.9 ‰ for δD-CH_4 (TU value is lower than IMAU) (Table 3). The measurements of the four canisters at NIPR were +0.48±0.11 ‰ higher than IMAU. However, the differences of δ^{13}C-CH_4

measurements are smaller for the ambient air samples (MD1 and MD2) than the ~~synthetic standard~~ CH_4-in-synthetic air ~~air~~ samples (MD3 and MD4). It is also noted that the δ^{13}C-CH_4 difference between the laboratories is largest for the low CH_4 ~~concentration~~ mole fraction (~900 ppb) sample (MD3). The cause is unclear, but might be related to (1) deviation in δ^{13}C-CH_4 of the latter samples from the typical atmospheric value, i.e., scale ~~compression~~ contraction effect, (2) difference in air matrix, i.e., natural versus synthetic air and (3) difference in linearity with respect to CH_4 ~~concentration~~mole fraction. This result therefore indicates that the measurement offset is not constant for a wide range of δ^{13}C-CH_4 values and CH_4 ~~concentrations~~ mole fractions as well as differences 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 measurement offsets. The average differences for ambient air are +0.~~41~~40±0.04 ‰ for TU and +0.31±0.03 ‰ for NIPR relative to IMAU. Likewise, the δD-CH_4 offset of TU versus IMAU is considered to be −13.1±0.6 ‰.

~~3~~4.3 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 δ^{13}C-CH_4 and δD-CH_4 by DI-IRMS (two samples were analyzed for δD-CH_4 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 measurement offsets of +0.02±0.05 ‰ for δ^{13}C-CH_4 and of +0.4±0.6 ‰ for δD-CH_4 (with the MPI-BGC values being more negative than those from UHEI in both cases).

~~3~~4.4 ~~Ice Core Intercomparison~~ Round Robin Comparison among Ice Core Analysis Laboratories

A round robin cylinder ~~intercomparison~~ exercise was initiated to facilitate intercomparison of those laboratories who measure δ^{13}C-CH_4 and δD-CH_4 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, preindustrial and ~~last~~ last-glacial air ~~concentrations~~mole fractions. The CH_4 ~~concentrations~~ mole fractions of these cylinders were 1830.6 ppb (CA 03560), 904.0 ppb (CC 71560) and 372.2 ppb (CA 01179) on the NOAA-2004 CH_4 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 $\delta^{13}C\text{-}CH_4$ and $\delta D\text{-}CH_4$ results from each laboratory. The Kr interfering ~~artifact~~ artefact associated with GC-IRMS $\delta^{13}C\text{-}CH_4$ analyses ~~has been~~ was taken into ~~removed~~ account in many of the analyses (Schmitt et al., 2013). In some cases, aliquots from the tanks were measured using offline combustion to CO_2 followed by $\delta^{13}C\text{-}CH_4$ 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 $\delta^{13}C\text{-}CH_4$ measured at PSU were less than 0.14 ‰ for two of the three cylinders, ~~signifying~~ indicating that the isotopic composition of the cylinder air ~~remained intact~~ was stable 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~~ There may have been ~~indicate~~ slight drift over the 9 years between measurements, although the cause has yet to be resolved. The results of the $\delta^{13}C\text{-}CH_4$ intercomparison showed ~~general~~ agreement with the average standard deviation amongst all six participating laboratories better than 0.37 ‰ for the ~~high and middle~~ cylinders with high (CA 03560) and middle (CC 71560) mole fractions. $\delta D\text{-}CH_4$ results show more scatter due to the difficult nature of the measurements and the offset ~~between~~ among the ~~calibration~~ standard scales.

~~3~~4.5 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 CH_4 ~~concentration~~ mole fraction (~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 cylinders 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 CH_4 ~~concentrations~~ mole fractions and $\delta^{13}C$-CH_4 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~~ PCS column into the system. The results show significant but consistent measurement offsets of +0.28±0.01 ‰ for the five cylinders with different CH_4 ~~concentrations~~ mole fractions and ambient $\delta^{13}C$-CH_4 values (with the INSTAAR values being more positive than those from MPI-BGC). The measurements for the cylinder with low $\delta^{13}C$-CH_4 value were 0.60 ‰ off between both laboratories presumably due to the scale ~~compression~~ contraction effect. It is noted that the INSTAAR measurements without the Kr removal had yielded a higher $\delta^{13}C$-CH_4 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 CH_4 ~~concentration~~mole fraction.

~~3~~4.6 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~~ measurement offsets as examined previously (Levin et al., 2012). (1) For the RHUL-INSTAAR ~~offset~~difference, 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±0.~~01~~ 16 ‰ (N=350) and 0.00±0.~~02~~ 17 ‰ (N=80) higher than RHUL, respectively. Note that, for this comparison, the RHUL GC-IRMS data ~~was~~ were 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~~ mole fraction 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±0.02 11 ‰ (*N*=45) higher than NIWA.

4 5 Calibration Measurement offsets between among laboratories

Here we revisit intercomparisons published previously. It has also happened that sSome laboratories employed a calibration standard scale from another laboratory. Such intercomparisons and inter-laboratory scale transfers propagations reported in the literature are organized displayed in Fig. 1. In this section we review the previous and present intercomparison measurements and accordingly suggest plausible calibration measurement offsets between different laboratories (Fig. 2). Relevant information is summarized in Table 1 and the subsections below correspond to those in section 23. Since some laboratories focus on δ^{13}C-CH_4 and δD-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 combininges δ^{13}C-CH_4 and δD-CH_4 data both for the modern and past atmosphere. It is however noted that Fig. 2 suggests the calibration measurement offsets at the modern CH_4 concentration mole fraction and isotopic ratios and that such values could be different for the past atmosphere (see sections 34.2, 34.4 and 34.5).

In this study, we report δ^{13}C-CH_4 offsets with respect to the conventional DI-IRMS measurement at NIWA (Lowe et al., 1991) because NIWA's δ^{13}C-CH_4 measurements have been compared with those from most laboratories to date (Table 1 and Fig. 1). In contrast, δD-CH_4 measurements from different laboratories have been limited. We report δD-CH_4 offsets of different laboratories with respect to the IMAU measurement. The uncertainties presented in the following sections in this study are ordinarily generally 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.

45.1 NIWA

δ^{13}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±0.26 ‰. 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~~ round robin intercomparison results (Schmitt et al., 2013 and section ~~3~~4.4), accounting for differences in CH_4 ~~concentration~~ mole fraction and an exponential fit to the GC-IRMS versus DI-IRMS results. The GC-IRMS system ~~has since been~~ is currently equipped with a ~~post-combustion separation~~ PCS column to eliminate the Kr interference.

~~4~~5.2 IMAU

δ^{13}C-CH_4: According to Schmitt et al. (2013), the IMAU measurement at the present CH_4 ~~concentration~~ mole fraction level is in agreement to NIWA with ~~the~~ an offset value of −0.04±0.07 ‰ (No. 2 in Fig. 2a). This corresponds to the ~~high CH_4 cylinder~~ round robin comparison for the cylinder with CH_4 mole fraction of 1830.6 ppb (CA 03560) in Table 5 (section ~~3~~4.4). The difference is −0.03±0.05 ‰ for data analyzed before the modification to remove the Kr ~~effect~~ interference (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±0.11 ‰ for the ~~middle CH_4~~ cylinder with the CH_4 mole fraction of 904.0 ppb (CA 71560).

δD-CH_4: As listed in Table 1, IMAU has made most intercomparisons with other laboratories so far. It is noted that the ~~calibration~~ standard scale 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).

~~4~~5.3 MPIC

δ^{13}C-CH_4: As written in section ~~2~~3.3, the ~~calibration~~ standard 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±0.07 ‰, identical to the IMAU offset (No. 3 in Fig. 2a).

δD-CH_4: Bock et al. (2010) reported an intercomparison using firn air samples between UB and MPIC, which indicated that, combined with the UB δD-CH_4 offset (section ~~4~~5.14), the MPIC δD-CH_4 offset is +0.3±1.1 ‰ with respect to IMAU (No. 3 in Fig. 2b).

~~4~~5.4 MPI-BGC

δ^{13}C-CH_4: Sperlich et al. (2016) quantified the offset of the IMAU ~~calibration~~ standard scale relative to the ~~ir~~ primary ~~calibration~~ standard scale at MPI-BGC. ~~They~~ It was indicated that the MPI-BGC measurement differs by −0.03±0.10 ‰ from the IMAU standard scale. Combined with the IMAU offset relative to NIWA (section ~~4~~5.2), the MPI-BGC offset is estimated to be −0.07±0.12 ‰ (No. 4 in Fig. 2a).

δD-CH_4: According to Sperlich et al. (2016), the MPI-BGC measurement is −4.2±1.2 ‰ from IMAU (No. 4 in Fig. 2b).

~~4~~5.5 UCI

δ^{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~~ INS, IGNS 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±0.09 ‰ 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~~4.4 and Table 5) shows that the UCI measurement is +0.14±0.12 ‰ (No. 5 middle in Fig. 2a) and +0.04±0.08 ‰ higher than NIWA for the ~~high and middle CH_4~~ cylinders with high (CA 03560) and middle (CC 71560) CH_4 mole fractions, respectively. (3) In contrast, the intercomparison in this study (section ~~3~~4.1 and Table 2) combined with the IMAU offset (section ~~4~~5.2) yields +0.42±0.04 ‰ 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~~.

δD-CH_4: According to the intercomparison in this study (section ~~3~~4.1), the UCI has a δD-CH_4 offset of −10.7±0.7 ‰ with respect to IMAU (No. 5 in Fig. 2b).

~~4~~5.6 TU

δ^{13}C-CH_4: The intercomparison in this study (section 3.2) and the IMAU offset (section ~~4~~5.2) give an offset of the TU measurements relative to NIWA to be +0.~~37~~36±0.08 ‰ (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~~5.7) 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~~ use the same ~~calibration~~standard scale. 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±0.08 ‰ (not shown in Fig. 2) is recommended. Correction of the datasets from the earlier publications is under evaluation.

δD-CH_4: The intercomparison in this study (section ~~3~~4.2) gives an offset of −13.1±0.6 ‰ for the TU atmospheric δD-CH_4 measurement (No. 6 in Fig. 2b).

~~4~~5.7 NIPR

δ^{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~~standard scale, the NIPR offset is evaluated to be +0.33±0.04 ‰ higher than NIWA (No. 7 left in Fig. 2a). The intercomparison in this study (section ~~3~~4.2) combined with the IMAU offset (section ~~4~~5.2) indicates the NIPR measurement is +0.27±0.08 ‰ with respect to NIWA (No. 7 right in Fig. 2a), consistent with the above value.

~~4~~5.8 UW

δ^{13}C-CH_4: Quay et al. (1999) exchanged 30 air samples with NIWA; the average measurement offset was evaluated to be +0.02±0.14 ‰ (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±0.004 ‰ with respect to NIWA based on co-located sampling at BHD (No. 8 right in Fig. 2a).

δD-CH_4: To our knowledge, no intercomparison exercises with UW have been reported.

45.9 UHEI

δ^{13}C-CH_4: Levin et al. (2012) estimated the UHEI δ^{13}C-CH_4 offset to be −0.169±0.031 ‰ relative to NIWA (No. 9 left in Fig. 2a). The intercomparison between UHEI and MPI-BGC in this study (section 3.3)), together with the MPI-BGC offset (section 45.4), also infers the UHEI offset to be −0.05±0.13 ‰ (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±0.04 ‰ relative to NIWA (Poß, 2003; Behrens et al., 2008). It is also noted that, in an intercomparison exercise presented by Nisbet (2005), the UHEI measurement was −0.07±0.04 ‰ 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.

δD-CH_4: The intercomparison in this study (section 34.3), combined with the MPI-BGC offset (section 45.4), indicates that UHEI has an offset of −3.8±1.3 ‰ relative to IMAU.

45.10 INSTAAR

δ^{13}C-CH_4: Levin et al. (2012) estimated that the INSTAAR measurements have an offset of +0.132±0.022 ‰ with respect to NIWA (No. 10 left in Fig. 2a). In an intercomparison exercise reported by Nisbet (2005), the INSTAAR measurement was +0.14±0.06 ‰ higher than NIWA (not shown in Fig. 2a), consistent with the above value. This study (section 34.4) indicates that the INSTAAR measurement is +0.15±0.05 ‰ higher than NIWA for the high (ambient) CH_4 cylinder with high CH_4 mole fraction (CA 03560) (No. 10 middle in Fig. 2a). The intercomparison between INSTAAR and MPI-BGC (section 34.5) indicates that, combined with the MPI-BGC offset (section 45.4), the INSTAAR offset is +0.21±0.12 ‰ relative to NIWA (No. 10 second right in Fig. 2a). Lastly, the co-located sample intercomparison (section 34.6) indicates the INSTAAR offset to be +0.08±0.0211 ‰

(not shown No. 10 right 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 round robin intercomparison round robin measurements (section 34.4 and No. 10 middle in Fig. 2a) and the intercomparison with MPI-BGC (section 34.5) were made with the a post-combustion PCS column to remove the Kr effectinterference, 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 standard 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 suggest 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).

δD-CH_4: Bock et al. (2010) reported an intercomparison between UB and INSTAAR. This indicates that the INSTAAR measurement offset is −13.2±1.3 ‰ with respect to IMAU (No. 10 in Fig. 2b).

45.11 RHUL

δ^{13}C-CH_4: Nisbet (2005) reported results of an intercomparison exercise; the that RHUL DI-IRMS measurements agreed 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 of air in two cylinders exchanged between RHUL and NIWA in 2011 and 2014, RHUL applied to an offset correction (−0.20 ‰) to the all data (see section 34.6), 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~~4.6), combined with the INSTAAR offset (section ~~4~~5.10), infer that the RHUL offset is +0.10±0.03 ‰ relative to NIWA (No. 11 right in Fig. 2a).

~~4~~5.12 PDX

δ^{13}C-CH_4: 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 δ^{13}C-CH_4 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~~5.8), 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~~standard scale).

δD-CH_4: Since PDX follows the UCI ~~calibration~~ standard scale (Teama, 2013; Rice et al., 2016), the likely offset is same as that of UCI (No. 12 in Fig. 2b).

~~4~~5.13 PSU

δ^{13}C-CH_4: 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~~interference. ~~As described earlier, the above value is part of the intercomparison in this study (section 3.4).~~ The ~~high-CH_4 cylinder~~ measurements of the cylinder with high CH_4 mole fraction (CA 03560) 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-CH_4: An intercomparison result using three firn 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~~4.4) ~~shows the offset to be~~gives −13.6±1.5 ‰ relative to IMAU for the ~~high CH_4~~ cylinder with high CH_4 mole fraction (CA 03560) (No. 13 right in Fig. 2b).

~~4~~5.14 UB

δ^{13}C-CH_4: The UB measurement has an offset of −0.18±0.09‰ relative to NIWA (Schmitt et al., 2013; No. 14 in Fig. 2a). This ~~is part of measurements tabulated as the~~ was determined by the ~~ice core~~ round robin intercomparison (section ~~3~~4.4 and Table 5).

δD-CH_4: Sapart et al. (2011) gives an intercomparison result between UB and IMAU, indicating the UB offset of 0.0±1.6 ‰ 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 all modifications 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±2.5 ‰ with respect to IMAU for the ~~high CH_4~~ cylinder with high CH_4 mole fraction (CA 03560) (No. 14 right in Fig. 2b).

~~4~~5.15 AWI

δ^{13}C-CH_4: The AWI offset is reported to be −0.09±0.06‰ with respect to NIWA (Schmitt et al., 2013; No. 15 in Fig. 2a).

~~4~~5.16 CIC

δ^{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±0.09 ‰ from IMAU, ~~by which~~ and the CIC offset with respect to NIWA is estimated to be −0.03±0.11 (No. 16 left in Fig. 2a). They have also reported that the CIC measurement is in agreement with UB with difference of +0.00±0.14 ‰. It is noted that, although the UB offset relative to NIWA is estimated to be significant (section ~~4~~5.14), 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 45.4), 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-CH_4: Sperlich et al. (2016) reported δD-CH_4 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 6 Summary and Discussion

We carried out inter-laboratory comparison exercises for atmospheric δ^{13}C-CH_4 and δD-CH_4 covering many laboratories around the world. In addition, we reviewed previously published intercomparison programs resultsin the literature. The results indicated calibration measurement offsets between laboratories, which range from −0.2 to +0.3 ‰ with respect to the NIWA DI-IRMS measurement for δ^{13}C-CH_4 and up to −13 ‰ with respect to the IMAU measurement for δD-CH_4. These offset values are larger than measurement uncertainties of individual laboratories.

The significant δ^{13}C-CH_4 measurement offsets between among 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). We have presented potential causes of the measurement offsets in individual laboratories (section 2), with Possible possible further causes are being hidden in all preparation and measurement steps of standard materials. First, (1) the The scale compression contraction effect for DI-IRMS CO_2 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 δ^{13}C-CH_4 value (about −47 ‰) differs considerably from the primary anchor of the VPDB scale (NBS NBS-19). Second,(2) individual Individual laboratories have made calibrations against different certified materials RMs (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 measurement offsets. Third, sSuch certified reference materials RMs have different chemical properties and are processed to CO_2 at individual laboratories, in which different fractionation is possible. (3) Different algorithms for ^{17}O correction have been used for $\delta^{13}C$ measurements at different laboratories, which could have caused biases among available datasets. Fourth,(4) the 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 measurement offsets at the modern atmospheric CH_4 concentration mole fraction level, but the offset may vary with the amount of CH_4 analyzed (e.g. lower concentrations mole fractions in ice core analyses, see Table 3, 5 and 6), because of a non-linear response of IRMS (Umezawa et al., 2009) and because of the Kr interference is directly dependent on the varying with relative changes in Kr to CH_4 ratio (Schmitt et al., 2013). Furthermore, the intercomparisons summarized presented 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 δD-CH_4 measurement offsets between among laboratories, it is interesting that the listed laboratories can be roughly split into two groups whose δD-CH_4 measurements differ by ~10 ‰. Some laboratories with higher δD-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_2O followed by H_2O reduction to H_2) with subsequent analysis by DI-IRMS. The other laboratories with higher δD-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 δD-CH_4 group, some laboratories made calibrations against Oztech H_2 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 δD-CH_4 discrepancies could have arisen in all preparation and measurement steps. First,(1) the The classical technique for DI-IRMS involves processing of H_2O, and the associated steps in experimental lines are prone to surface adhesion and contamination of H_2O, thereby considerable memory effect is possible (Bergmaschi et al., 2000). Second, (2) sSimilarly to δ^{13}C-CH_4, calibration for δD-CH_4 involves measurements of standards with different chemical properties (H_2O and H_2), and such calibrations at different laboratories could contribute to the offset. Third,(3) difficulties Difficulties in maintaining stable pyrolysis conditions for GC-IRMS (Bock et al. 2010) might have affected measurements against local H_2 working standards where the principle of identical treatment principle (Werner and Brand, 2001) was not followed strictly. Lastly, it is noted that non-linearity of the IRMS in δD-CH_4 measurements (Brass and Röckmann, 2010) may also play a role for samples with low concentrations such as ice core analyses.

The calibration measurement offsets indicated summarized 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 when incorporating merged δ^{13}C-CH_4 and δD-CH_4 datasets into a state-of-the-art chemistry transport model. It is hHowever it is recommended that advisable that data users should contact the data providers directly for the latest information whenever possible. The Kr effect interference is under evaluation at some laboratories and it will possibly involve an update of the datasets 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 δ^{13}C-CH_4 and 1 ‰ for δD-CH_4 (WMO, 2016). Such thorough efforts will facilitate optimized use of δ^{13}C-CH_4 and δD-CH_4 datasets in a combined way and maximize the number of isotope datasets (and thus their spatial and temporal coverage) usable for enhancing our understanding of the global CH_4 cycle.

We welcome collaborative works to analyse the multiple datasets presented in this study (see data availability listed in Table 1). Data users can examine the offset numbers (Table 1 and Figure 2) to adjust the datasets at least for data points with values close to the modern atmosphere in δ^{13}C-CH_4 and δD-CH_4 as well as CH_4 mole fraction. For data with CH_4 mole fractions and isotopic ratios that are far from modern background values (e.g. sample air from ice core and stratosphere and those influenced by sources), more intercomparisons are needed to establish correction factors among datasets.

List of Participating Institution/Project Acronyms

AWI: Alfred- Wegener- Institute, Helmholtz- Zentrum Centre für for Polar- undand- MeeresforschungMarine Research, Bremerhaven, Germany

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

CIC: Centere for Ice and Climate, Niels Bohr Institute, 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, TsukubaTokyo, 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

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Table 1. List of laboratories that conduct measurements of δ^{13}C-CH_4 and δD-CH_4 and references for intercomparison programs. For each laboratory, measurement systems and relevant information that could have contributed the inter-laboratory measurement offsets are summarized. Brackets in the RM column indicate the laboratory from which the original standard scale was propagated. See Figure 1 for overview of the past intercomparison exercises, Figure 2 for intercomparison summary and the list of participating institution/project acronyms in the text for the laboratory names.

No.	Laboratory	δ^{13}C-CH_4 Intercomparison	δD-CH_4 Intercomparison	Measurement System
1	NIWA	Refs. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12	Not Measured	Ref. 13
2	IMAU	Refs. 9, 11, 14, 15, 16, 17, 18, 19	Refs. 11, 15, 16, 17, 18, 19, 20	Ref. 19
3	MPIC	Refs. 14, 19	Refs. 19, 20	Ref. 21
4	MPI-BGC	Ref. 16, 22	Ref. 16, 22	Ref. 23
5	UCI	Refs. 6, 11, 17, 24, 25, 26	Refs. 17, 26	Ref. 6, 27, 28
6	TU	Refs. 18, 29	Ref. 18	Ref. 29
7	NIPR	Refs. 7, 18, 29	Not Measured	Ref. 7
8	UW	Refs. 1, 2, 3, 24	No Ref. Available	Ref. 2
9	UHEI	Refs 3, 4, 5, 8, 14, 22	Ref. 22	Ref. 4
10	INSTAAR	Refs. 3, 6, 8, 10, 11, 12, 14, 25, 30	Ref. 20	Ref. 25
11	RHUL	Refs. 8, 10, 12	Not Measured	Refs. 31, 32
12	PDX	Refs. 24, 26	Ref. 24, 26	Refs. 26, 28
13	PSU	Refs. 9, 11, 14, 15	Refs. 11, 15, 20	Ref. 33
14	UB	Refs. 9, 11, 15, 30	Refs. 11, 15, 20, 34	Refs. 9, 20, 30, 34
15	AWI	Refs. 5, 9, 14, 15	Not Measured	Ref. 5
16	CIC	Refs. 16, 35	Refs. 16, 35	Refs. 35, 36

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)

No	Lab	System	IRMS	^{17}O correction*	Kr interference	Additional Correction	RM	Reference‡		δ^{13}C-CH_4	δD-CH_4 offset	Data Availability§
								Measur	Intercomparison			

					Significance	**Measure**[†]		**δ^{13}C-CH$_4$**	**δD-CH$_4$**	**ement**	**δ^{13}C-CH$_4$**	**δD-CH$_4$**	**offset with respect to NIWA**	**with respect to IMAU**	
1	NIWA	DI	Nuclide (1988–1996) MAT 252 (1996–2013) MAT 253 (2013–)	C1/C2	N	—	N	NBS-19, IAEA-CO-9, LSVEC	Not measured	R1	R2, R3, R4, R5, R6, R7, R8, R9, R10, R11, R12, R13	Not measured	—	Not Measured	WDCGG & NIWA website (R1, R2, R14)
		CF	Isoprime	C3	Y	DI offset/PCS	Drift			R15, R16					On request to H. Schaefer (R17)
2	IMAU	CF	Delta plus XL	C2	Y	PCS	Non-linearity correction for small peaks	NBS-19 (MPIC)	VSMOW & SLAP (MPIC)	R18	R10, R12, R18, R19, R20, R21, R22, R23	R12, R18, R20, R21, R22, R23, R24	−0.04±0.07	—	Utrecht University website (R25, R26)
3	MPIC	DI & TDLAS	MAT 252	C2	N	—	N	NBS-19	VSMOW & SLAP	R27	R18, R19	R18, R24	−0.04±0.07	+0.3±1.1	On request to P. Bergamaschi (R28)
4	MPI-BGC	CF	Delta V Plus	C4	Y	PCS	Mole fraction dependent linearity correction	NBS-19 & LSVEC	VSMOW-2 & SLAP-2	R29	R21, R30	R21, R30	−0.07±0.12	−4.2±1.2	On request to H. Moossen (R21, R29)
5	UCI	DI	MAT 252	C2	N	—	N	NBS-19 & IAEA-CO-9	Oztech Gas	R7, R31	R7, R12, R15, R22, R32, R33	R22, R33	−0.01±0.09	−10.7±0.7	CDIAC (R31)
		CF	Delta Plus XL	C2	Y	DI offset/PCS	N			R7, R34					
6	TU	CF	Delta Plus XP	C3	Y	Not implemented	Daily correction with respect to a test gas; Constant offset for part of the dataset (R34, R35)	NBS-19	VSMOW & SLAP	R37	R23, R37	R23	+0.36±0.08	−13.1±0.6	WDCGG (R35) & On request to T. Umezawa (R36, R38)
7	NIPR	CF	MAT 252	C3	N	—	N	NBS-19	Not measured	R8	R8, R23,	Not	+0.33±0	Not	TU website (R8, R39)

								(TU)			R37	measured	.04	measured	
8	UW	DI	MAT 251	Information not available	N	—	Correction of N_2O produced during combustion & Drift correction	NBS-19	VSMOW & SLAP	R3	R2, R3, R4, R32	No comparison available	+0.02±0.14	No comparison	CDIAC (R3)
9	UHEI	DI	MAT 252	C2 with coefficients a=0.5 & K=0.008335	N	—	Drift correction of extraction and daily correction of IRMS	RM 8562, RM 8563 & RM 8564	VSMOW & SLAP	R5	R4, R5, R6, R19, R30	R30	−0.17±0.03	−3.8±1.3	UHEI website (R4)
10	INSTAAR	CF	Optima/Isoprime	C3	Y	PCS	Drift correction	NBS-19 & IAEA-CO-9 (UCI)	Not Anchored	R15	R4, R7, R9, R11, R12, R13, R15, R19, R41	R24	+0.13±0.02	−13.2±1.3	WDCGG & NOAA/ESRL/GMD website (R15)
11	RHUL	DI / CF	Prism / Isoprime	C3	N	—	Daily offset wrt working air std	NBS-19 & IAEA-CO-9	Not measured	R42 / R43	R9, R11, R13	Not measured	+0.12±0.03	Not measured	CEDA & On request to E. Nisbet (R11)
12	PDX	CF	Delta V	C2	Y	DI offset/PCS	N	NBS-19 & IAEA-CO-9 (UCI)	Oztech Gas (UCI)	R33, R34	R32, R33	R32, R33	+0.08±0.09	−10.7±1.5	PDX website (R32)
13	PSU	CF	MAT 252	C2	Y	Raw ion current correction/ DI offset/PCS	Daily offset with respect to primary air standard	RM 8563 & RM 8564	Oztech Gas	R20, R44	R10, R12, R19, R20	R12, R20, R24	+0.03±0.16	−12.1±1.5	NSIDC & On request to T. Sowers
14	UB	CF	Isoprime	C2	Y	PCS	Drift correction	NBS-19 & IAEA-CO-9 (UCI via INSTAAR)	VSMOW & SLAP (UHEI)	R10, R24, R41, R45	R10, R12, R20, R41	R12, R20, R24, R45	−0.18±0.09	0.0±1.6	PANGAEA (R46, R47)
15	AWI	CF	Isoprime	C3	Y	Not implemented	Drift correction	RM 8562, RM 8563 and RM 8564 (UHEI)	Not measured	R6	R6, R10, R19, R20	Not measured	−0.09±0.06	Not measured	PANGAEA (R19)
16	CIC	DI ($\delta^{13}C$-CH_4)	Delta V Plus, Delta V	C2	N	—	—	RM 8563	VSMOW-2 & SLAP-2	R48	R21, R48	R21, R48	−0.03±0.11	−2.1±2.1	All data in papers (R16, R21, R48)

		TC/EA-IRMS & Picarro (δD-CH_4)	Advantage and Picarro												
		CF	Delta V Plus	C2	Y	PCS	Daily offset vs working gas standard; CH_4 amount correction			R16	R16				

*C1: Allison et al. (1995), C2: Santrock et al. (1985), C3: Craig (1957), C4: Assonov and Brenninkmeijer (2003)

†Raw ion current correction: The Kr effect was corrected by subtracting the Kr-caused anomalies in the raw ion current data; DI offset: The Kr effect was corrected by an offset relative to a DI-IRMS measurement; PCS: Kr was separated by a post combustion separation column or cryogenically. See section 2.5.

‡R1: Lowe et al. (1991), R2: Lowe et al. (1994), R3: Quay et al. (1999), R4: Levin et al. (2012), R5: Poß (2003), R6: Behrens et al. (2008), R7: Tyler et al. (2007), R8: Morimoto et al. (2006), R9: Nisbet (2005), R10: Schmitt et al. (2013), R11: Nisbet et al. (2016), R12: This study (Section 4.4), R13: This study (Section 4.6), R14: Bergamaschi et al. (2001), R15: Miller et al. (2002), R16: Sperlich et al. (2013), R17: Ferretti et al. (2005), R18: Brass and Röckmann (2010), R19: Möller et al. (2013), R20: Sapart et al. (2011), R21: Sperlich et al. (2016), R22: This study (Section 4.1), R23: This study (Section 4.2), R24: Bock et al. (2010a), R25: Röckmann et al. (2010), R26: Röckmann et al. (2016), R27: Bergamaschi et al. (1994), R28: Bergamaschi et al. (2000); R29: Brand et al. (2016), R30: This study (Section 4.3), R31: Tyler et al. (1999), R32: Rice et al. (2016), R33: Teama (2013), R34: Rice et al. (2001), R35: Umezawa et al. (2012a), R36: Umezawa et al. (2012b), R37: Umezawa et al. (2009), R38: Umezawa et al. (2011), R39: Morimoto et al. (2017), R40: This study (Section 4.3), R41: Schmitt et al. (2014), R42: Lowry et al. (2001), R43: Fisher et al. (2006), R44: Sowers et al. (2005), R45: Bock et al. (2014); R46: Bock et al. (2010b), R47: Bock et al. (2017), R48: Sperlich et al. (2012)

§WDCGG (World Data Centre for Greenhouse Gases): http://ds.data.jma.go.jp/gmd/wdcgg/wdcgg.html
NIWA website: www.niwa.co.nz
Utrecht University website: http://www.projects.science.uu.nl/atmosphereclimate/Data.php
TU website (http://caos.sakura.ne.jp/tgr/data/en)
CDIAC (Carbon Dioxide Information Analysis Center): http://cdiac.ess-dive.lbl.gov/epubs/db/db1022/db1022.html (UCI), http://cdiac.ess-dive.lbl.gov/ndps/quay.html (UW)
UHEI website: www.iup.uni-heidelberg.de/institut/forschung/groups/kk/Data_html
NOAA/ESRL/GMD website: https://www.esrl.noaa.gov/gmd/dv/data/
PDX website: http://web.pdx.edu/~arice/atm_CH4.html
PANGAEA: https://doi.org/10.1594/PANGAEA.873918
CEDA (Centre for Environmental Data Analysis): http://www.ceda.ac.uk
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Table 2. Result of intercomparison of δ^{13}C-CH_4 and δD-CH_4 measurements between UCI and IMAU.

Sample ID	CH_4 (ppb)	δ^{13}C-CH_4 (‰) UCI	IMAU	Difference from IMAU	δD-CH_4 (‰) UCI	IMAU	Difference from IMAU
WAS-24-2	1784.7*	−46.96±0.07 (*N*=3)	−47.33±0.05 (*N*=3)	+0.37	−91.6±0.5 (*N*=2)	−78.9±0.1 (*N*=4)	−12.7
WAS-24-5	1825.8*	−47.16 (*N*=1)	−47.53±0.02 (*N*=6)	+0.37	−93.8 (*N*=1)	−83.1±0.2 (*N*=4)	−10.7
WAS-24-6	1827.5*	−47.08±0.01 (*N*=2)	−47.55±0.04 (*N*=6)	+0.47	−92.1±0.8 (*N*=2)	−83.6±0.1 (*N*=4)	−8.5
WAS-24-9	1799.8*	−47.05 (*N*=1)	−47.38±0.02 (*N*=6)	+0.33	−92.3±1.8 (*N*=3)	−79.8±0.8 (*N*=4)	−12.4
WAS-24-10	1789.8*	−47.07 (*N*=1)	−47.42±0.02 (*N*=6)	+0.35	−89.3 (*N*=1)	−79.7±0.8 (*N*=4))	−9.6
WAS-24-11	1780.8*	−46.77 (*N*=1)	−47.37±0.03 (*N*=6)	+0.60	−89.0±0.9 (*N*=2)	−78.7±0.7 (*N*=4)	−10.3
Average				+0.42±0.04			−10.7±0.7

*NOAA-2004 CH_4 scale (Dlugokencky et al., 2005)

Table 3. Result of intercomparison of δ^{13}C-CH_4 and δD-CH_4 measurements between TU/NIPR and IMAU.

Sample ID	CH_4 (ppb)*	δ^{13}C-CH_4 (‰) TU	NIPR	IMAU	Difference from IMAU	δD-CH_4 (‰) TU	IMAU	Difference from IMAU
MD1	1901.1	−47.~~03~~04±0.02 (N=16)	−47.11±0.02 (N=5)	−47.40±0.04 (N=9)	+0.~~37~~ 36 (TU) +0.28 (NIPR)	−97.2±0.6 (N=10)	−85.0±0.1 (N=8)	−12.2
MD2	2116.6	−46.~~80~~81±0.02 (N=16)	−46.92±0.03 (N=6)	−47.26±0.03 (N=9)	+0.~~46~~ 45 (TU) +0.34 (NIPR)	−118.5±0.6 (N=10)	−104.5±0.3 (N=8)	−14.0
MD3	899.1	−41.~~13~~14±0.04 (N=16)	−41.05±0.02 (N=5)	−41.81±0.03 (N=8)	+0.~~68~~ 67 (TU) +0.76 (NIPR)	−190.7±0.6 (N=10)	−175.8±0.6 (N=8)	−14.9
MD4	1700.5	−42.~~46~~47±0.03 (N=16)	−42.43±0.04 (N=5)	−42.98±0.02 (N=8)	+0.52 (TU) +0.56 (NIPR)	−195.2±0.6 (N=10)	−180.6±0.2 (N=8)	−14.6
Average (ambient air)					+0.~~41~~40±0.04 (TU) +0.31±0.03 (NIPR)			−13.1±0.6
Average (all)					+0.~~51~~50±0.07 (TU) +0.48±0.11 (NIPR)			−13.9±0.9

*Tohoku University CH_4 scale (Aoki et al., 1992; Umezawa et al., 2014)

Table 4. Result of intercomparison of δ^{13}C-CH_4 and δD-CH_4 measurements between UHEI and MPI-BGC.

Sample ID (Collection Date)	Preparation Date UHEI	Analysis Date MPI-BGC	δ^{13}C-CH_4 (‰)			δD-CH_4 (‰)		
			UHEI	MPI-BGC*	UHEI −MPI-BGC	UHEI	MPI-BGC*	UHEI −MPI-BGC
GvN 88/20 (24 Jul. 1988)	17 Dec. 2003	9 Jul. 2013	−47.54±0.02 (*N*=1)	−47.66 (0.07, *N*=2)	+0.13	−83.3±2.2 (*N*=1)	−82.1 (0.8, *N*=2)	−1.2
GvN 92/12 (11 May. 1992)	11 Dec. 2008	17 Jun. 2013	−47.43±0.02 (*N*=1)	−47.40 (0.04, *N*=2)	−0.03	−79.1±1.6 (*N*=1)	−81.2 (0.9, *N*=2)	+2.1
GvN 96/03 (13 Feb. 1996)	11 Nov. 2003	17 Jun. 2013	−47.27±0.02 (*N*=1)	−47.18 (0.26, *N*=2)	−0.08	−73.9±1.4 (*N*=2)	−74.6 (0.9, *N*=2)	+0.8
GvN 99/14 (29 Dec. 1999)	3 Apr. 2003	9 Jul. 2013	−47.30±0.02 (*N*=1)	−47.23 (0.16, *N*=2)	−0.07	−75.2±1.3 (*N*=2)	−74.6 (1.3, *N*=2)	−0.5
GvN 06/14 (23 Sep. 2006)	7 May. 2003	9 Jul. 2013	n.a.	−47.19 (0.09, *N*=2)	n.a.	−72.3±1.6 (*N*=1)	−73.1 (0.0, *N*=2)	+0.8
GvN 08/03 (6 Mar. 2008)	28 Jul. 2010	17 Jun. 2013	−47.18±0.05 (*N*=1)	−47.35 (0.05, *N*=2)	+0.17	n.a.	−67.4 (2.9, *N*=2)	n.a.
Average					+0.02±0.05			+0.4±0.6

*Difference of duplicate flask measurements is shown in parenthesis.

Table 5. Results from the Ice Core Intercomparison Round Robin conducted during 2007–2016.

Laboratory	CA 03560 (1830.6 ppb) $\delta^{13}C\text{-}CH_4$ (‰)	CA 03560 (1830.6 ppb) $\delta D\text{-}CH_4$ (‰)	CA 71560 (904.0 ppb) $\delta^{13}C\text{-}CH_4$ (‰)	CA 71560 (904.0 ppb) $\delta D\text{-}CH_4$ (‰)	CA 01179 (372.2 ppb) $\delta^{13}C\text{-}CH_4$ (‰)	CA 01179 (372.2 ppb) $\delta D\text{-}CH_4$ (‰)	Kr corr.	Analysis Date $\delta^{13}C\text{-}CH_4$	Analysis Date $\delta D\text{-}CH_4$
PSU	−47.20±0.16	−93.2±0.9	−47.41±0.10	−95.5±2.3	−47.52±0.06	−106.3±2.4	~~Trace[a]~~ Raw ion current correction[a]	Jul. 2007	Jul. 2007
	−46.96±0.16		−47.20±0.10		−47.41±0.12		DI ~~Corr.~~offset[b]	Jul. 2007	
	−47.10±0.05		−47.09±0.06		−46.83±0.12		~~PCP[c]~~PCS[c]	May 2016	
UCI (DI-IRMS)	−47.09±0.12		−47.40±0.08		−47.23±0.06		—	Dec. 2007*	
INSTAAR	−47.08±0.05		−47.20±0.06		−46.78±0.06		~~PCP[c]~~PCS[c]	Dec. 2008	
NIWA (DI-IRMS)	−47.23±0.02		−47.44±0.02		−47.43±0.02		—	Jun. 2009	
NIWA (GC-IRMS)	−47.44±0.21		−48.34±0.28		−47.62±0.11		DI ~~Corr.~~offset[b]	Jun. 2009	
UB	−47.41±0.09	−80.4±2.2	−47.37±0.07	−81.0±2.0	−47.31±0.11	−86.2±3.3	No[d]	Jan. 2011	Dec. 2010–Jan. 2011
IMAU	−47.27±0.07	−79.6±1.2	−47.52±0.11	−83.6±3.8	−47.20±0.20	−78.8±12.4	~~PCP[c]~~PCS[c]	May & Aug. 2012	May 2010

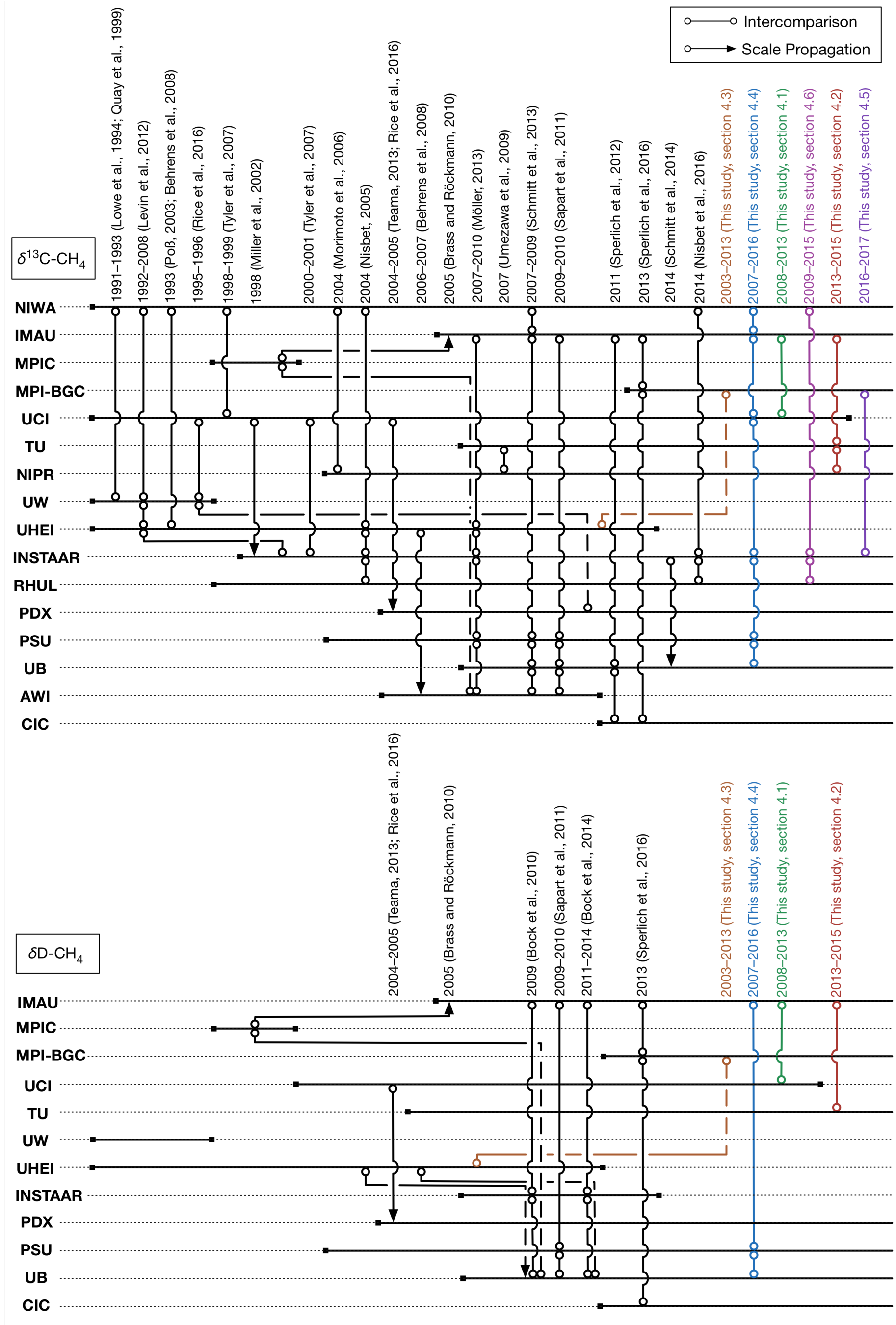
~~[a]Trace~~[a]Raw ion current correction: The Kr effect was corrected by ~~tracing~~ subtracting the Kr-caused anomalies in the raw ~~beam~~ ion current data (section 5.4 of Schmitt et al., 2013); [b]DI ~~Corr.~~offset: The Kr effect was corrected by an offset relative to a ~~dual-inlet~~ DI-IRMS measurement; [c]PCP: Kr was separated by a ~~Post~~ post ~~Combustion~~ combustion ~~Plot~~ separation column (section 5.2 of Schmitt et al. 2013); [d]No: No ~~correction because~~ Measurements are affected by the Kr ~~effect~~ interference (old system without PCS) and raw ion current correction was not ~~identified~~possible.

*Estimated because no exact record on the analysis date at UCI is unfortunately available.

Table 6. Results of δ^{13}C-CH_4 intercomparison between INSTAAR and MPI-BGC.

		δ^{13}C-CH_4 (‰)		
Sample ID	**CH_4 (ppb)***	**INSTAAR**	**MPI-BGC**	**INSTAAR−MPI-BGC**
HUEY-001	1905.5	−47.37±0.01 (N=22)	−47.67±0.01 (N=24)	+0.29
DEWY-001	1879.9	−47.38±0.01 (N=26)	−47.67±0.01 (N=22)	+0.28
LOUI-001	1496.0	−47.26±0.01 (N=17)	−47.55±0.02 (N=22)	+0.29
CART-001	1848.1	−42.98±0.01 (N=21)	−43.30±0.03 (N=7)	+0.32
STAN-001	1696.4	−56.60±0.01 (N=7)	−57.20±0.05 (N=8)	+0.60
KENN-001	1847.6	−47.65±0.01 (N=26)	−47.94±0.05 (N=7)	+0.28
KYLE-001	1847.6	−47.27±0.01 (N=29)	−47.51±0.07 (N=6)	+0.24

*NOAA-2004 CH_4 scale (Dlugokencky et al., 2005)



Intercomparison
Scale Propagation
δ13C-CH4
1991–1993 (Lowe et al., 1994; Quay et al., 1999)
1992–2008 (Levin et al., 2012)
1993 (Poß, 2003; Behrens et al., 2008)
1995–1996 (Rice et al., 2016)
1998–1999 (Tyler et al., 2007)
1998 (Miller et al., 2002)
2000–2001 (Tyler et al., 2007)
2004 (Morimoto et al., 2006)
2004 (Nisbet, 2005)
2004–2005 (Teama, 2013; Rice et al., 2016)
2006–2007 (Behrens et al., 2008)
2005 (Brass and Röckmann, 2010)
2007–2010 (Möller, 2013)
2007 (Umezawa et al., 2009)
2007–2009 (Schmitt et al., 2013)
2009–2010 (Sapart et al., 2011)
2011 (Sperlich et al., 2012)
2013 (Sperlich et al., 2016)
2014 (Schmitt et al., 2014)
2014 (Nisbet et al., 2016)
2003–2013 (This study, section 4.3)
2007–2016 (This study, section 4.4)
2008–2013 (This study, section 4.1)
2009–2015 (This study, section 4.6)
2013–2015 (This study, section 4.2)
2016–2017 (This study, section 4.5)
NIWA
IMAU
MPIC
MPI-BGC
UCI
TU
NIPR
UW
UHEI
INSTAAR
RHUL
PDX
PSU
UB
AWI
CIC
δD-CH4
2004–2005 (Teama, 2013; Rice et al., 2016)
2005 (Brass and Röckmann, 2010)
2009 (Bock et al., 2010)
2009–2010 (Sapart et al., 2011)
2011–2014 (Bock et al., 2014)
2013 (Sperlich et al., 2016)
2003–2013 (This study, section 4.3)
2007–2016 (This study, section 4.4)
2008–2013 (This study, section 4.1)
2013–2015 (This study, section 4.2)
IMAU
MPIC
MPI-BGC
UCI
TU
UW
UHEI
INSTAAR
PDX
PSU
UB
CIC

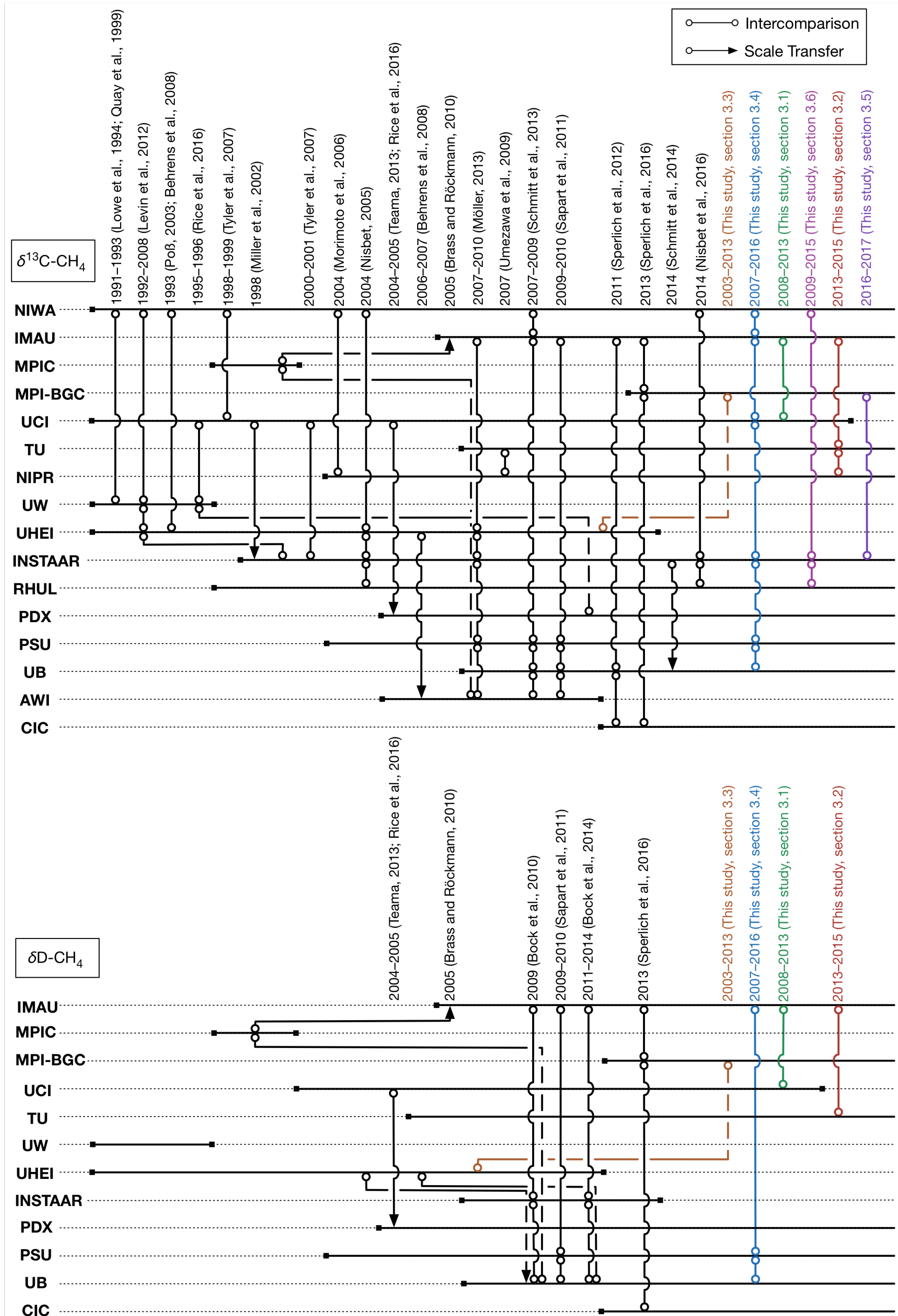


Figure 1. A schematic overview of the previous and present intercomparisons between laboratories for δ^{13}C-CH_4 (top) and δD-CH_4 (bottom). Intercomparisons are marked by lines with open circles at both ends, and scale ~~transfers~~ propagations are by lines with an arrow at one end.

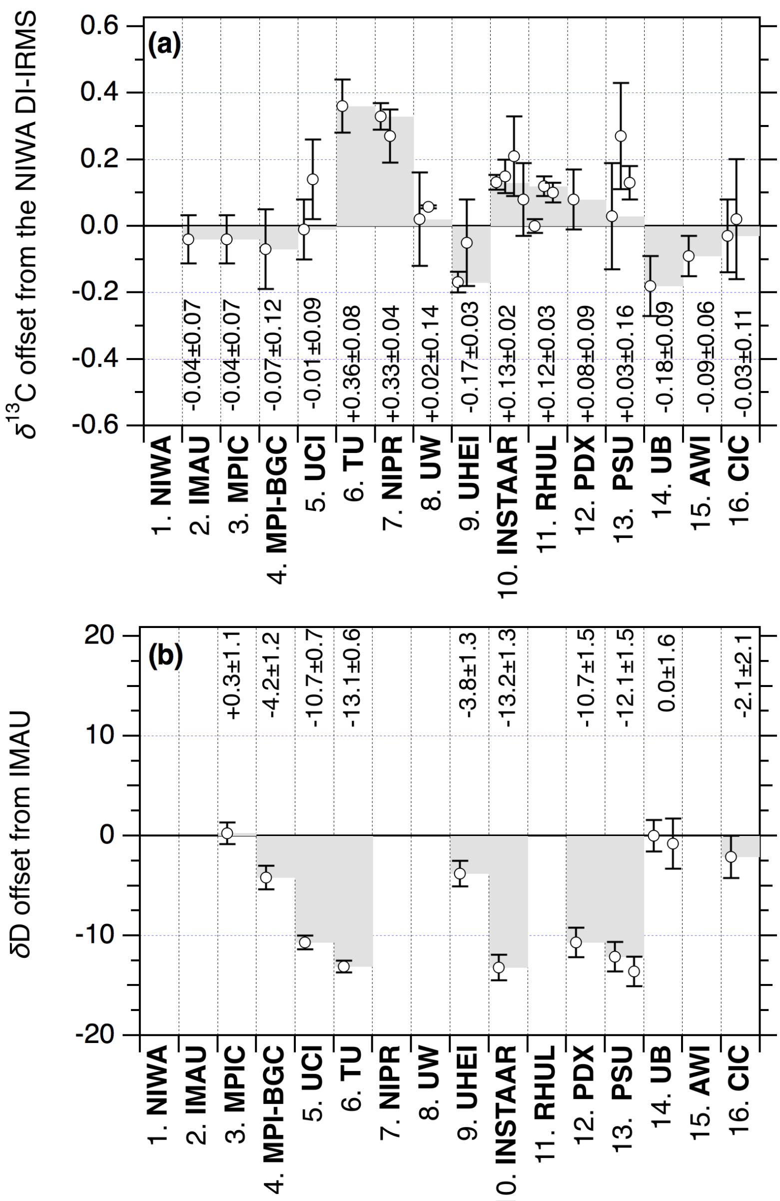


Figure 2. (a) $\delta^{13}C-CH_4$ offsets of the different laboratories with respect to the NIWA DI-IRMS measurement with gray shades for ease of viewing. (b) $\delta D-CH_4$ offsets of the different laboratories with respect to the IMAU GC-IRMS measurement. See Table 1 and text for corresponding subsections in sections ~~2~~ 3 and ~~4~~5. Numbers shown in each laboratory column are the plausible

~~calibration~~ measurement offsets estimated in this study. Note that this result represents intercomparisons for the modern atmospheric CH_4 ~~in ambient air.~~