21GRD04 - isoMET

D1: Report on the use of synthetic reference materials in the characterisation and comparison of at least four IRMS and OIRS analysers across a range of amount fractions (1.9-10.0 µmol mol^{-1}) and isotope ratios

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Deliverable Cover Sheet

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1 Summary

The aim of task 1.1 is to establish a more robust link between the isotopic methane (CH_4) gas reference materials (RMs) developed in the EMPIR JRP 19ENV05 STELLAR (VPDB and VSMOW/SLAP scale assigned) and isotope CH_4 measurements across different laboratories in Europe. This will allow an analytical advancement in understanding errors and biases introduced by different procedures by different laboratories, quantification of the current offsets between different laboratories, and creation of a harmonised protocol for continued monitoring of this offset. The midterm perspective is to support a central calibration laboratory infrastructure developed with the resources to disseminate a central metrological gas standard.

For A1.1.1 of isoMET, the National Physical Laboratory (NPL) prepared 35 CH_4 isotopic RMs with CH_4 mole fractions between 1.8 and 10.0 µmol mol^{-1}, $\delta^{13}C(CH_4)$ values ranging from -46.22 ‰ to -39.15 ‰, and $\delta^{2}H(CH_4)$ values ranging from -195.10 ‰ to -175.30 ‰ (as measured by the University of Utrecht's laboratory isotope ratio mass spectrometry (IRMS) system and will be taken as the reference values for this activity). These RMs were distributed to seven participants (intended for characterisation/calibration purposes). Additionally, four RMs were prepared for a round-robin intercomparison involving the seven laboratories using optical isotope ratio spectroscopy (OIRS) or IRMS measurement techniques. It is these four intercomparison RMs that are the focus of this report.

Between May 2024 and August 2025, the four round robin high pressure cylinders were measured by NPL, Royal Holloway University London (RHUL), Laboratory for Climate and Environmental Sciences (LSCE), the University of Utrecht (UU), the Swiss Federal Laboratories for Materials Science and Technology (EMPA), the University of Heidelberg (UHEI) and the Physikalisch-Technische Bundesanstalt (PTB). Each participating laboratory followed its standard procedures for sample handling from compressed gas cylinders, data treatment and for calibration against internal standards. Two partners used the IRMS technique, with one reporting on both laboratory-based IRMS (whose results will serve as the reference values for this report) and travelling system measurements. As IRMS remains the most precise method for CH_4 isotope ratio analysis, values from UU's Institute for Marine and Atmospheric Utrecht (IMAU) research laboratory serve as the reference (designated Lab 1). All other labs are anonymized and numbered 2 to 8, with Labs 1–3 using IRMS and Labs 4–8 using OIRS.

$\delta^{13}C(CH_4)$: Inter-laboratory differences often exceeded the internal reproducibility of individual systems. Averaged over the four intercomparison cylinders, the IRMS laboratories (Lab2 and Lab3) demonstrated good precision, with consistent offsets of –0.07 ± 0.03 ‰ and +0.23 ± 0.07 ‰, respectively.

The OIRS laboratories showed a wider range of deviations from the reference lab, with mean $\delta^{13}C(CH_4)$ differences between –0.26 ‰ and +0.39 ‰, and standard deviations ranging from 0.09 ‰ to 0.87 ‰. Lab7 showed a systematic offset of +0.24 ‰ with low variability (±0.09 ‰), while Lab8 showed a minimal mean difference (–0.01 ‰) but higher variability (±0.19 ‰). Lab5 displayed significant non-linearity, leading to a large mean offset of +0.39 ± 0.87 ‰. These results highlight the ongoing challenge for OIRS instruments to meet the extended $\delta^{13}C(CH_4)$ WMO compatibility goal of ±0.2 ‰.

$\delta^{2}H(CH_4)$: Data were provided only by two IRMS laboratories (Lab1 and Lab2) and two OIRS laboratories (Lab4 and Lab6). Mean differences to the reference lab of –2.6 ± 0.6 ‰, –2.5 ± 1.0 ‰, and –1.8 ± 0.4 ‰, respectively, indicate that all laboratories performed within the extended compatibility goal (±5‰) for regional studies, with values approaching the stricter threshold required for background atmospheric studies of ±1‰.

2 Intercomparison of the IRMS and OIRS analysers using isotopic CH_4 reference materials (round robin)

2.1 Objective

The aim of this task is to develop a harmonised in situ CH_4 isotope dataset of ambient air in Europe to resolve compatibility issues of measurements of $\delta^{13}C(CH_4)$ or $\delta^{2}H(CH_4)$ across multiple laboratories. This harmonisation includes an improved validation of IRMS and OIRS measurement techniques across Europe through interlaboratory comparisons (round robin).

Within the 21GRD04 isoMET project NPL prepared a suite of static CH_4 isotopic gas reference materials across an amount fraction range of 1.9 and 10.0 µmol mol^{-1}, $\delta^{13}C(CH_4)$ range of -46.22 to -39.15 ‰, and $\delta^{2}H(CH_4)$ range of -195.10 to -175.30 ‰. Thirty-five RMs in total were prepared and distributed to seven participants. In addition, four RMs were prepared for a for a round-robin intercomparison between seven participants using OIRS and IRMS measurement techniques.

2.2 Intercomparison Protocol (NPL)

This protocol describes the intercomparison exercise for the measurement of $\delta^{13}C(CH_4)$ and $\delta^{2}H(CH_4)$ isotope ratios in CH_4 by IRMS and OIRS.

A set of four primary reference materials (PRMs) were prepared in activity A1.1.1 by NPL from a set of high-purity CH_4 sources, with a range of isotopic signatures, diluted to a near-ambient amount fractions of 1.8 µmol mol^{-1}. The gas mixtures are prepared by gravimetric dilution of high-purity CH_4 into a synthetic air matrix in 10 L cylinders filled to 100 bar. The gas matrix contains components known to be important for OIRS measurements: carbon dioxide (CO_2), nitrous oxide (N_2O) and argon (Ar) in addition to oxygen (O_2) and nitrogen (N_2). The pure CH_4 was sourced from a commercial gas supplier and from sources from the STELLAR project. This was done by screening samples for $\delta^{13}C(CH_4)$ and $\delta^{2}H(CH_4)$ by OIRS and selecting four cylinders with the most widely separated isotope ratios.

Table 1 provides an overview of the filled cylinders provided by NPL for this intercomparison. The table shows values as measured by the reference laboratory (UU-IMAU lab instrument). The selected pure CH_4 sources have $\delta^{13}C(CH_4)$ isotope ratios that span a range of 7.07‰, which are slightly more enriched than the atmosphere. The $\delta^{2}H(CH_4)$ ratios are all well below the atmospheric values but span a range of 19.8 ‰. The stability of CH_4 in synthetic air mixtures with respect to fractionation of isotope ratio has been determined in the STELLAR project. The set will be measured by NPL and UU at the start and end of the exercise to identify any fractionation.

Cylinder	**$\delta^{13}C(CH_4)$ [‰]**	**$\delta^{2}H(CH_4)$ [‰]**	**CH_4 [ppb]**
D180452	-43.26	-195.10	1799.84
D180454	-46.22	-175.30	1799.60
D180466	-44.81	-186.80	1806.11
D180467	-39.15	-187.20	1799.23

Table 1: Isotopic signatures of high purity CH_4 intercomparison cylinders (round robin). Values as reported by UU-IMAU lab instrument.

The set of four 10 L cylinders were shipped to each partner following the order shown in Figure 1. The cylinders were shipped with dedicated pressure regulators with 1/16” Swagelok tubing outlets. The cylinders have been given arbitrary numbers, and all measurements should be made without reference to the nominal isotope ratios. Each participating laboratory should measure the isotope ratios $\delta^{13}C(CH_4)$ and $\delta^{2}H(CH_4)$ following standard procedures for sample handling from a compressed gas cylinder, and data treatment for calibration to in-house standards. The intercomparison cylinders were first measured at NPL in May/June 2024 and then shipped to RHUL. The latest analysis was carried out by PTB in July/August 2025. Table 2 summarizes the measurement date and the analyser type of all participating laboratories.

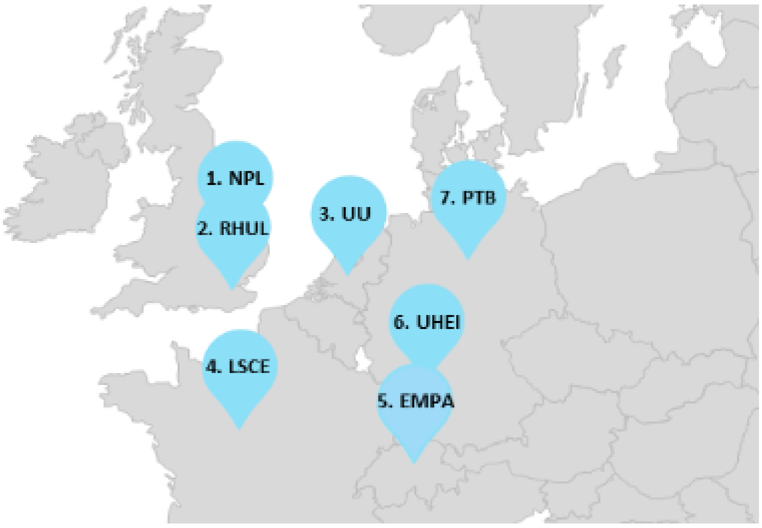

Figure 1: Measurement order for the for a round-robin intercomparison conducted within the isoMET project.

Project Partner	**Time of Measurement**	**Instrument(s)**	**Measured Species**
NPL	May/June 2024	OIRS-precon	$\delta^{13}C(CH_4)$, $\delta^{2}H(CH_4)$
RHUL	July 2024	IRMS, (OIRS)	$\delta^{13}C(CH_4)$
UU (IMAU)	Aug 2024	IRMS (Lab), IRMS (Travel)	$\delta^{13}C(CH_4)$, $\delta^{2}H(CH_4)$
LSCE	Sep 2024	OIRS	$\delta^{13}C(CH_4)$
EMPA	Jan 2025	OIRS-precon	$\delta^{13}C(CH_4)$, $\delta^{2}H(CH_4)$
UHEI	April/May 2025	OIRS	$\delta^{13}C(CH_4)$
PTB	July/Aug 2025	OIRS	$\delta^{13}C(CH_4)$

Table 2: Overview of isotope measurements by project partners, including time of measurement, instruments used, and isotopic species analysed. OIRS = Optical Isotope Ratio Spectrometer; IRMS = Isotope Ratio Mass Spectrometer.

All laboratories reported $\delta^{13}C(CH_4)$ isotope ratios and uncertainties to the Vienna Pee Dee Belemnite (VPDB) and Vienna Standard Mean Ocean Water/ Standard Light Antarctic Precipitation (VSMOW/SLAP) scales and four laboratories measured and reported $\delta^{2}H(CH_4)$ as well, whereby UU used two setups based on IRMS for measurements which are therefore listed as two separate labs. More details on the experimental set-up were written by each laboratory including the measurement protocol and any issues with these samples (see 2.3). New PRMs have been prepared in A1.1.1, but it is not essential to use these for calibration and traceability of travelling PRM measurements, and laboratories can use the in-house reference materials.

2.3 Laboratory setup and calibration strategy of individual partners

IRMS Laboratories

University of Utrecht Institute of Marine and Atmospheric Utrecht (UU-IMAU): Two IRMS setup (Lab system and travelling system) were used by UU (IMAU) to analyser the round robin cylinders. Both data sets were analysed and reported separately.

The Lab system consists of a Thermo Fisher Delta plus XP IRMS, equipped with a home-built Gas Bench and a home built CH_4-extraction system (IVAN, 2015). The following reference cylinder was used: "WILLI", CH_4: 2044.9 ppb; $\delta^2H(CH_4)$: -90.66 ‰ (VSMOW); $\delta^{13}C(CH_4)$: -48.28 ‰ (VPDB).

The travelling system consists of a Thermo Fisher Delta V IRMS, equipped with a ConFlo IV and a home built CH_4-extraction system (CELIA, 2020). Reference cylinder "MJB2021", CH_4: 2032.0 ppb; $\delta^2H(CH_4)$: -92.07 ‰ (VSMOW); $\delta^{13}C(CH_4)$: -48.303 ‰ (VPDB).

For both systems the principle of the extraction is based on the Max-Plank Institutes for biogeochemistry's (MPI-BGC's) ISAAC, and (described in Röckmann et al., 2016). Methane is combusted to CO_2 to measure $\delta^{13}C(CH_4)$, or pyrolyzed to Hydrogen (H_2) to measure $\delta^2H(CH_4)$. The gas configuration of the IRMS alternates between CO_2 and H_2.

Methane from 40 mL air for $\delta^{13}C(CH_4)$ or 50 ml air for $\delta^2H(CH_4)$ is collected on HayeSep D at ~-135˚C. After the air matrix is flushed out by Helium (He), the trap is warmed and the CH_4 is directed to a smaller HayeSepD focusing trap. By heating the focus, the CH_4 is either injected into the CarbonPLOT gaschromatographer (GC) or the combustion oven (Ni wire in Al2O3 at 1150˚C) or the nafion dryer or the PoraPLOT Q GC to measure CO_2 for $\delta^{13}C(CH_4)$, or into the pyrolysis oven (Al_2O_3 at 1350˚C) or the CarbonPLOT GC to measure H_2 for δ^2H (CH_4).

Each cylinder used in the round robin exercise was measured in three sets of four repetitions, with each set bracketed by three measurements of the working standard (WS) reference air. A one-point calibration was applied using the assigned values of the WS reference cylinder. From each set of 12 isotopic values the most enriched and the most depleted measurement were removed, and the reported values are the average and standard deviation of the remaining 10 values.

UU-IMAU did not use primary reference materials to establish their scale. Sperlich et al., 2016 linked CH_4 isotope measurements to the international standards, and our system showed only minor deviations from the MPI-BGC system. Details on the origin of the scale are published in Umezawa et al., 2018, Brass and Röckmann, 2010, Bräunlich et al., 2001 and Bergamaschi et al., 2000. The scale is maintained by keeping and regularly measuring a series of Dome Concordia firn air samples.

Royal Holloway University of London (RHUL): Isotopic analysis of $\delta^{13}C$ in methane at RHUL is carried out using two methods. When using the IRMS method cylinders containing air samples are connected to the inlet of a Trace Gas instrument which is connected in continuous flow to an IsoPrime 100 mass spectrometer, as described in Fisher et al. (2006). For ambient air concentrations a 75 mL sample volume is evacuated and then filled with air from the cylinder. A flow of He directs the sample through chemical traps: magnesium perchlorate to remove water (H_2O), Carbosorb to remove CO_2, and Sofnocat to oxidise carbon monoxide (CO) to CO_2. A liquid nitrogen cryotrap is used to remove remaining CO_2 from the sample. The sample then passes through a combustion furnace at 790°C containing a palladium powder on quartz wool catalyst where CH_4 is oxidised to CO_2 and H_2O, using O_2 from within the air sample. The water is H_2O with a nafion membrane. The CO_2 from the CH_4 oxidation is trapped and focussed on a liquid nitrogen cryotrap, which is then heated to release the CO_2 to a GC column and then into the mass spectrometer. Within the mass spectrometer the sample peaks are bracketed with reference gas CO_2 pulses. Each sample is measured at least three times, and the mean and standard deviation are calculated, to assess the repeatability. The analyses are corrected using an internal WS which is analysed at least 4 times at the start of the day, and then between every two samples throughout the day, and at the end of the day. The WS is a 60L stainless steel tank of dry ambient air, initially filled to 8 bar, which has had a $\delta^{13}C(CH_4)$ value internally assigned at RHUL by measurement against a cylinder of air filled by the National Oceanic and Atmospheric Administration (NOAA) which has been analysed at the Institute of Arctic and Alpine Research (INSTAAR) laboratory, University of Colorado. The WS typically lasts for more than two years of measurements. A target gas cylinder is regularly measured on the IRMS system to identify the longer-term precision of the instrument. The following corrections are applied to the raw measurement data: blank correction (considering the peak height and $\delta^{13}C(CH_4)$ values of measurements when no CH_4 is present in a sample), offset from the working standard $\delta^{13}C(CH_4)$ value, and scale contraction (0.02 ‰ correction per 1 ‰ difference from the working standard).

During the 2017-2021 MEMO[2] project the $\delta^{13}C(CH_4)$ scale from -60 to -40‰ was compared against UU-IMAU by exchange of cylinders containing diluted landfill and natural gas samples with 10 and 2 ppm CH_4 and showed very good agreement. Each travelling cylinder was measured four times on two different days. The results are in very good agreement with a set prepared for RHUL by NPL (A.1.1.2) to 9 ppm CH_4 from the same source mixtures by NPL and measured over the same period in July 2024, showing that the IRMS response is linear over the range 2 to 9 ppm CH_4 (4 to 15 nA instrument peak height).

For the OIRS measurements, cylinders containing air samples are connected directly to the inlet of a Picarro 2210-i, a cavity-ring down spectrometer (CRDS) measuring CH_4 concentrations and $\delta^{13}C(CH_4)$ isotope ratios. The instrument is used mostly for source measurements during mobile surveys for comparison with bag samples collected for IRMS analysis, but when between surveys it is used for continuous measurement from the RHUL rooftop inlet. The calibration approach is still being developed for this instrument, but intercomparisons have been made with the IRMS for many standards including the travelling set and the set prepared to 9 ppm CH_4 which are used to check for changes in calibration of the OIRS over time for the –46.4 to –39.2‰ range.

OIRS Laboratories:

The National Physical Laboratory (NPL): The OIRS coupled to a preconcentrator system uses a commercial direct absorption spectrometer (TILDAS dual laser trace gas analyser, Aerodyne Research Inc.) coupled with a custom-built preconcentrator (named Boreas) system that cryogenically separates CH_4 from the air matrix. The preconcentration step increases the amount fraction of CH_4 to above 500 µmol mol^{-1} increasing the signal to noise ratio in the spectrum, improving the precision of the $\delta^{13}C(CH_4)$ and $\delta^{2}H(CH_4)$ measurements.

The system has been described in (Rennick et al., 2021 and Safi et al., 2024). The travelling standard gases and WS gases were connected to the inlet of the preconcentrator through a multiselector valve (Vici Valco valve with universal actuator). The regulator pressure for each tank is set to 3.8 bar, which is adjusted to achieve a trapping flow rate of 540 sccm for all gases. The sample flows through a trap packed with Hayesep-D adsorbent (Thames Restek) that is maintained at around −165°C by a cryogen-free cryocooler (CryoTel GT, Sunpower Inc.). After the 540 s trapping duration multiposition valves (Vici Valco) switch from the sample gas to high-purity nitrogen (Air Products BIP) that flows at a much lower flow rate of 8 sccm while the trap temperature is increased. The multiposition valves first direct the flow to vent, then the spectrometer is loaded with the CH_4 at the known elution time. The valve timings for trapping and elution have been optimised to quantitatively transfer all trapped CH_4 to the spectrometer and minimise fractionation (Safi et al., 2024). The trapping and analysis cycle takes 1.5 hours.

Two calibration steps are applied to the measurement. First, the spectrometer is calibrated using two CH_4 in N_2 mixtures that bracket the amount fraction of CH_4 that is eluted from the preconcentrator and match the matrix. These are 500 µmol mol^{-1} and 625 µmol mol^{-1} mixtures prepared using the CH_4 that has been isotopically characterised by IRMS in a previous project (19ENV05 STELLAR) as $\delta^{13}C(CH_4)$ −39.19 ‰ and $\delta^{2}H(CH_4)$ −194.52 ‰. The spectrometer response is calibrated for the $^{12}CH_4$, $^{13}CH_4$ and $^{12}CH_3D$ amount fraction by calculating the amount fraction of these in the standards by adapting the method described in (Griffith, 2018) to CH_4. This high amount fraction calibration is performed while the sample is collected on the trap.

The second calibration step uses a whole air working standard that is also preconcentrated, following the principle of identical treatment. This is used to account for drift in the preconcentrator and offsets due to variable matrix components – small amounts of oxygen co-trapped with the CH_4. This standard gas is air filled into a 50 L Luxfer cylinder at Mace Head atmospheric observatory under conditions that are representative of the Northern-Hemisphere well-mixed background. The working standard has been measured against an in-house standard as $\delta^{13}C(CH_4)$ = −48.03 ‰ and $\delta^{2}H(CH_4)$ = −84.95 ‰. The NPL in-house standard has been assigned $\delta^{13}C(CH_4)$ and $\delta^{2}H(CH_4)$ at UU-IMAU, using standards that are traceable to VPDB and VSMOW.

The offset between the assigned isotope ratio and that measured on Boreas is used to scale the $^{13}CH_4/^{12}CH_4$ and $^{12}CH_3D/^{12}CH_4$ ratios of the traveling standard measurements.

The travelling standards were measured over two separate days using Boreas, at the Heathfield atmospheric observatory, using the instrument sequence normally employed for atmospheric air measurements. The sequence runs a working standard, followed by two (three on the second day) travelling standards, then the working standard, which was repeated and the first run discarded to purge the gas cylinder regulators and tubing. All measurements were analysed with the routines and quality control procedures that are standard for air measurements.

University of Heidelberg (UHEI): A G2201-i CRDS analyser (Picarro, Inc., Santa Clara, CA) is used to continuously measure the dry-air mole fraction of CH_4 and its carbon isotope ratio $\delta^{13}C(CH_4)$ in ambient air, with a temporal resolution of a few seconds (0.27 Hz). The analytical set-up is described in more detail by Hoheisel and Schmidt, 2024. Ambient air, calibration gases and samples in flasks are selected and directed to the analyser using a 16-port rotary valve (model EMT2CSD16UWE, VICI Valco, Switzerland). Before entering the analyser, the ambient air and gas samples are dried using a nafion tube operated in counter-flow, following the setup described by Welp et al., 2012. The gas flow through the analyser is typically around 80 mL min^{-1}. For routine measurements, the ambient air measurement is interrupted every 5 hours to analyse one set of calibration and quality control gases for 30 min each. The raw data are averaged to 1 min values and calibrated using a one-point calibration as described by Hoheisel and Schmidt, 2024.

The measurements of the isotopic compositions of CH_4 are traced to the VPDB isotopic scale (Sperlich et al., 2016). The $\delta^{13}C(CH_4)$ values of the calibration gases were measured by the Stable Isotope Laboratory at MPI-BGC in Jena. Additionally, as part of the isoMET project, we received four reference cylinders from NPL, containing different isotopic signatures and CH_4 concentration levels (A1.1.2). Co-measurement of two of these cylinders, with the lower CH_4 concentrations (around 2.2 ppm), enabled us to calibrate the intercomparison gases in addition to our regular calibration standards.

The four traveling intercomparison cylinders have been measured on two separate days for 120 min, bracketed by 30 min measurements of both our calibration and target cylinder. Since the intercomparison cylinders are more enriched (-46.22 ‰ to -39.15 ‰) compared to our calibration cylinder (-48.1 ‰), we decided to add the reference cylinder from NPL(A1.1.2), which is closest to the $\delta^{13}C(CH_4)$ value of the respective intercomparison cylinder, to the measurements. Therefore, each intercomparison cylinder was measured again using the following sequence:

30 min calibration cylinder – 30 min target cylinder – 60 min reference cylinder from NPL – 60 min intercomparison cylinder – 30 min calibration cylinder – 60 min intercomparison cylinder – 60 min reference cylinder from NPL – 30 min calibration cylinder – 30 min target cylinder

All measurements were evaluated using our routine protocol as described above, while the later measurements were additionally evaluated by using the reference cylinders from NPL as the calibration cylinder.

The Swiss Federal Laboratories for Materials Science and Technology (EMPA): A Quantum cascade laser absorption spectroscopy (QCLAS, QCL-76-D, Aerodyne Research Inc., USA) coupled to a trace gas extractor (TREX-III, Prokhorov et al., 2022) was applied for $\delta^{13}C(CH_4)$ and $\delta^{2}H(CH_4)$ analysis (Eyer et al., 2016). The spectrometer is equipped with a multi-pass cell of 76m optical path length and a volume of 0.5L and operates at 1295.6 cm^{-1} ($\delta^{13}C(CH_4)$) and 1307.0 cm^{-1} ($\delta^{2}H(CH_4)$).

Reference materials were provided within the EURAMET project STELLAR project (19ENV05): Cal1: cyl. 12990 (prod. VSL), CH_4 in N_2 (6.0), $[CH_4]$ = 2040 ppm (VSL), $\delta^{13}C(CH_4)$ = -47.128 ± 0.22 ‰ (MPI-BGC), $\delta^{2}H(CH_4)$ = -192.321 ± 1.29 ‰ (MPI-BGC); Cal2: cyl. 12985 (prod. VSL), CH_4 in N_2, $[CH_4]$ = 587 ppm (Picarro), $\delta^{13}C(CH_4)$ = -57.124 ± 0.08- ‰ (MPI-BGC, provisionary), $\delta^{2}H(CH_4)$ = -319.186 ± 6.97‰ (MPI-BGC, provisionary); Cal3: cyl. A1U0681 (Carbagas), pressurized air, $[CH_4]$ = 2.12 ppm (Picarro), $\delta^{13}C(CH_4)$ = -48.780 ± 0.06 -48.99 ‰ (MPI-BGC, provisionary), $\delta^{2}H(CH_4)$ = -106.684 ± 1.77 ‰ (MPI-BGC, provisionary). Empa results are provisionary as calibration standards will be re-assigned by MPI-BGC.

A CH_4 concentration correction and a two-point calibration of isotope ratios were applied to calculated delta values.

Laboratory for Climate and Environmental Sciences (LSCE): A G2201-i CRDS analyser (Picarro, Inc., Santa Clara, CA) is used to measure the dry-air mole fraction of CH_4 and its carbon isotope ratio $\delta(^{13}CH_4)$ in the cylinders, with a temporal resolution of a few seconds (0.27 Hz). Cylinder gases are selected and directed to the analyser using a 16-port rotary valve (model: EMT2CSD16UWE, VICI Valco, Switzerland).

The measurements of the isotopic compositions of CH_4 are traced to the VPDB isotopic scale (Sperlich et al., 2016). The $\delta^{13}C(CH_4)$ values of the three calibration gases LSCE used were measured by Royal Holloway from flask samples taken from the calibration gases. Additionally, as part of the isoMET project, LSCE received four reference cylinders from NPL, containing different isotopic signatures and methane concentration levels (A1.1.2).

The four traveling intercomparison cylinders and the reference cylinders from NPL have been measured over four days for 6 times 30 min each, bracketed by 30 min measurements of both our calibration and target cylinders. All measurements were evaluated using two LSCE cylinders as calibration and one as target.

Physikalisch-Technische Bundesanstalt (PTB): A Picarro G2201-i CRDS spectrometer was used to measure the $\delta^{13}C$ in CH_4 from the four unknown samples. The precision of the CRDS instrument for $\delta^{13}C(CH_4)$ measurements is better than 0.8 ‰ as specified by the manufacturer. The instrument was calibrated with two reference gases provided by NPL as part of the isoMET project (A.1.1.2). The $\delta^{13}C(CH_4)$ results are traceable to the VPDB scale. For each sample four measurements were performed on different days a 30 min and an average value taken as the final result. A two-point calibration was applied to determine the $\delta^{13}C(CH_4)$ of the unknown sample and the uncertainties were additionally calculated using GUM principles.

2.4 Results

All partners reported their results on the isotopic composition of the four intercomparison cylinders, using their respective measurement setups and calibration strategies as described in Section 2.3. While all laboratories report δ^{13}(CH_4) values, not all laboratories are equipped to determine the δ^2H(CH_4) isotopic ratio. Two project partners used the IRMS technique. UU-IMAU reported both the results obtained using their laboratory-based IRMS system and those measured with the travelling IRMS. Since IRMS still represents the most precise technique for the measurement of stable isotopes in CH_4, the laboratory instrument (Lab system) at the University of Utrecht was selected to measure the reference values for each of the CH_4 sources by IRMS and provide traceability to VPDB for δ^{13}C(CH_4) and VSMOW for δ^2H(CH_4). Only the reference laboratory UU-IMAU is specified in this report and is further referred to as Lab 1, while the other laboratories/measurement systems have been anonymized and numbered from 2 to 8. A distinction is made with respect to the measurement technique: numbers 1–3 refer to IRMS technology, while 4–8 refer to OIRS.

The intercomparison of δ^{13}C(CH_4): measurements among the participating laboratories highlights varying levels of agreement with the reference values reported by Lab1 (red) as shown in Fig. 2. The World Meteorological Organization (WMO) compatibility goal for the carbon isotope δ^{13}C(CH_4) of atmospheric methane is ±0.02‰, with an extended target for regional-scale gradients of ±0.2‰. For OIRS measurements, which have lower precision, we aim to meet the extended intercomparison goal of ±0.2‰. In contrast, for IRMS measurements, we target the stricter ±0.02‰ goal.

Across the four cylinders, Lab2 (blue) consistently reports slightly lower δ^{13}C(CH_4) values than Lab1, with deviations from -0.04 ‰ up to -0.1 ‰ and a mean difference of -0.07 ± 0.03 ‰. The small standard deviation indicates a slight systematic offset. Nevertheless, the results confirm the high stability of the Lab2 IRMS system and prove its reliability.

Lab3 (green) shows stable positive deviations ranging from +0.14 ‰ to +0.32 ‰ with a mean difference of 0.23 ± 0.07 ‰, exceeding the strict compatibility goal of ±0.02 ‰, but approaching the extended goal of ±0.2 ‰. The high measurement precision and internal consistency of this IRMS setup suggest an offset that could be corrected.

Lab4 (violet) shows relatively small negative deviations, ranging from -0.03 ‰ to -0.48 ‰, with an average deviation of -0.26 ± 0.19 ‰. These values are close to the extended intercompatibility goal. The moderate but consistent underestimation indicates a possible minor scale compression or calibration mismatch

Lab5 (orange) shows significant deviations between -0.77 ‰ and +1.13 ‰ and a mean deviation of 0.39 ± 0.87 ‰ compared to the reference lab. Particularly large deviations are visible for D180452 and D180467, where the differences exceed 1.0 ‰. The difference clearly indicates a non-linear relationship with the isotope value. A review of standards, analytical procedures or potential instrument drift/ non-linearity is recommended.

Lab6 (yellow) shows a consistent negative bias, with deviations from Lab1 between -0.05 ‰ and –0.37 ‰ with an average value of -0.20 ± 0.12 ‰. The values are close to the extended compatibility goal, still suggesting a potential calibration or scale issue. However, the internal repeatability of Lab6 remains constant. This issue may be resolved in the near future, as the values of the calibration cylinder are scheduled to be remeasured at MPI Jena and the reporting of the results were only provisionary.

Lab7 (brown) shows deviations between +0.18 ‰ and +0.42 ‰ with a mean deviation of +0.24 ± 0.09 ‰ using their standardized calibration strategy. While these values are close to the extended compatibility threshold of ±0.2 ‰, the consistency of the deviation direction suggests a potential minor bias through calibration standards, which could be corrected for through targeted recalibration. To address this issue, the same measurements were re-evaluated using the NPL cylinders from A1.1.2. Here, the deviations remain positive but are smaller, ranging from +0.04 ‰ to +0.24 ‰ and averaging 0.16 ± 0.10 ‰. Therefore, using more specific calibration gases that are isotopically closer to the sample gases results in higher compatibility. The effect is especially pronounced at cylinder number D180467 which has the most different isotope ratio compared to the commonly used standard.

Deviations of Lab8 (pink) range from −0.41 ‰ to +0.14 ‰, with a mean of −0.01 ± 0.19 ‰, indicating no clear systematic bias. Except for sample D180466, all deviations lie within the ± 0.2 ‰ compatibility goal. The relatively large standard deviation of the mean further supports the absence of a systematic offset. In addition, PTB reported the GUM uncertainties (ISO guide, 2008) which are considerably larger, reaching up to 1.0 ‰.

It is notable that the largest average deviations across laboratories occur for the cylinder D180467. This mixture is isotopically the most enriched in ^{13}C, with a $\delta^{13}C(CH_4)$ value of approximately -39.15 ‰, and thus lies furthest from the calibration ranges typically covered by standard reference materials used for ambient air measurements. The increased spread in reported values may reflect reduced linearity or extrapolation errors in the calibration curves, especially for laboratories whose calibration gases are centered around more depleted values (e.g., -47 ‰ to -50 ‰) like Lab2, Lab5 and Lab7. This highlights the importance of including calibration standards that span the full range of expected sample isotopic compositions in order to ensure accuracy across the scale.

The intercomparison of $\delta^2H(CH_4)$: measurements among the four measurement setups from three different laboratories highlights varying levels of agreement with the reference values reported by Lab1 (Fig. 3). The compatibility goal for $\delta^2H(CH_4)$ for global background studies is ± 1 ‰ and the extended goal for regional studies is ± 5 ‰.

When evaluated against the Lab1 as reference, the results from Lab6 (yellow) show deviations ranging from –1.17 ‰ to –2.29 ‰ and with an average absolute deviation of -1.8 ± 0.4 ‰ across the four cylinders. This moderate but consistent underestimation indicates a possible minor scale compression or calibration mismatch. The measurements of Lab2 (blue) show systematically larger deviations from the reference lab values, ranging from -1.97 ‰ to -2.85 ‰, with an average deviation of -2.6 ± 0.6 ‰. Similarly, measurements from Lab4 (violet) also show deviations with differences ranging from -1.04 ‰ to -3.30 ‰ and an average deviation of -2.5 ± 1.0 ‰. Therefore, all labs are within the extended WMO compatibility goal of ± 5 ‰.

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		D180454	D180466	D180452	D180467
$\delta^{13}C(CH_4)$ [‰]	**Lab1 (IRMS)**	-46.22 ± 0.04	-44.81 ± 0.09	-43.26 ± 0.06	-39.15 ± 0.08
	Lab2 (IRMS)	-46.26 ± 0.06	-44.86 ± 0.05	-43.35 ± 0.08	-39.25 ± 0.06
	Lab3 (IRMS)	-46.00 ± 0.09	-44.49 ± 0.02	-43.02 ± 0.04	-39.01 ± 0.03
	Lab4 (OIRS)	-46.70 ± 0.15	-44.84 ± 0.11	-43.59 ± 0.22	-39.35 ± 0.16
	Lab5 (OIRS)	-46.99 ± 0.44	-44.59 ± 0.24	-42.26 ± 0.15	-38.02 ± 0.06
	Lab6* (OIRS)	-46.33 ± 0.21	-45.06 ± 0.07	-43.31 ± 0.07	-39.52 ± 0.22
	Lab7 (OIRS)	-46.04 ± 0.15	-44.63 ± 0.09	-43.03 ± 0.09	-38.78 ± 0.11
	Lab8 (OIRS)	-46.4 ± 0.5 (± 1.0 GUM)	-44.4 ± 0.3 (± 1.0 GUM)	-43.4 ± 0.2 (± 0.8 GUM)	-39.3 ± 0.1 (± 0.8 GUM)
$\delta^{2}H(CH_4)$ [‰]		**D180454**	**D180466**	**D180452**	**D180467**
	Lab1 (IRMS)	-175.26 ± 0.54	-186.77 ± 1.28	-195.11 ± 0.85	-187.22 ± 1.06
	Lab2 (IRMS)	-177.23 ± 0.83	-190.02 ± 0.49	-197.96 ± 0.68	-189.41 ± 0.70
	Lab3 (IRMS)				
	Lab4 (OIRS)	-177.76 ± 2.59	-189.91 ± 2.56	-196.15 ± 0.85	-190.52 ± 0.25
	Lab5 (OIRS)				
	Lab6* (OIRS)	-177.18 ± 0.29	-188.62 ± 0.65	-196.28 ± 0.71	-189.51 ± 0.27
	Lab7 (OIRS)				
	Lab8 (OIRS)				

Table 3: Reported $\delta^{13}C(CH_4)$ and $\delta^{2}H(CH_4)$ values and standard deviations from all project partners from the measurements of the four intercomparison cylinders given in ‰.* provisionary results

		D180454	D180466	D180452	D180467	Mean Diff
$\Delta\delta^{13}C(CH_4)$ [‰]	**Lab2 (IRMS)**	-0.04	-0.05	-0.09	-0.10	-0.07 ± 0.03
	Lab3 (IRMS)	+0.22	+0.32	+0.24	+0.14	+0.23 ± 0.07
	Lab4 (OIRS)	-0.48	-0.03	-0.33	-0.20	-0.26 ± 0.19
	Lab5 (OIRS)	-0.77	0.22	+1.00	+1.13	+0.39 ± 0.87
	Lab6* (OIRS)	-0.11	-0.25	-0.05	-0.37	-0.20 ± 0.12
	Lab7 (OIRS)	+0.18	+0.18	+0.23	+0.37	+0.24 ± 0.09
	Lab8 (OIRS)	-0.18	0.44	-0.14	-0.15	-0.01 ± 0.19
$\Delta\delta^{2}H(CH_4)$ [‰]		**D180454**	**D180466**	**D180452**	**D180467**	
	Lab2 (IRMS)	-1.97	-3.25	-2.85	-2.19	-2.6 ± 0.6
	Lab3 (IRMS)					
	Lab4 (OIRS)	-2.50	-3.14	-1.04	-3.30	-2.5 ± 1.0
	Lab5 (OIRS)					
	Lab6* (OIRS)	-1.92	-1.85	-1.17	-2.29	-1.8 ± 0.4
	Lab7 (OIRS)					
	Lab8 (OIRS)					

Table 4: Differences of reported $\delta^{13}C(CH_4)$ and $\delta^{2}H(CH_4)$ values to reference lab (Lab1) given in ‰.
* provisionary results

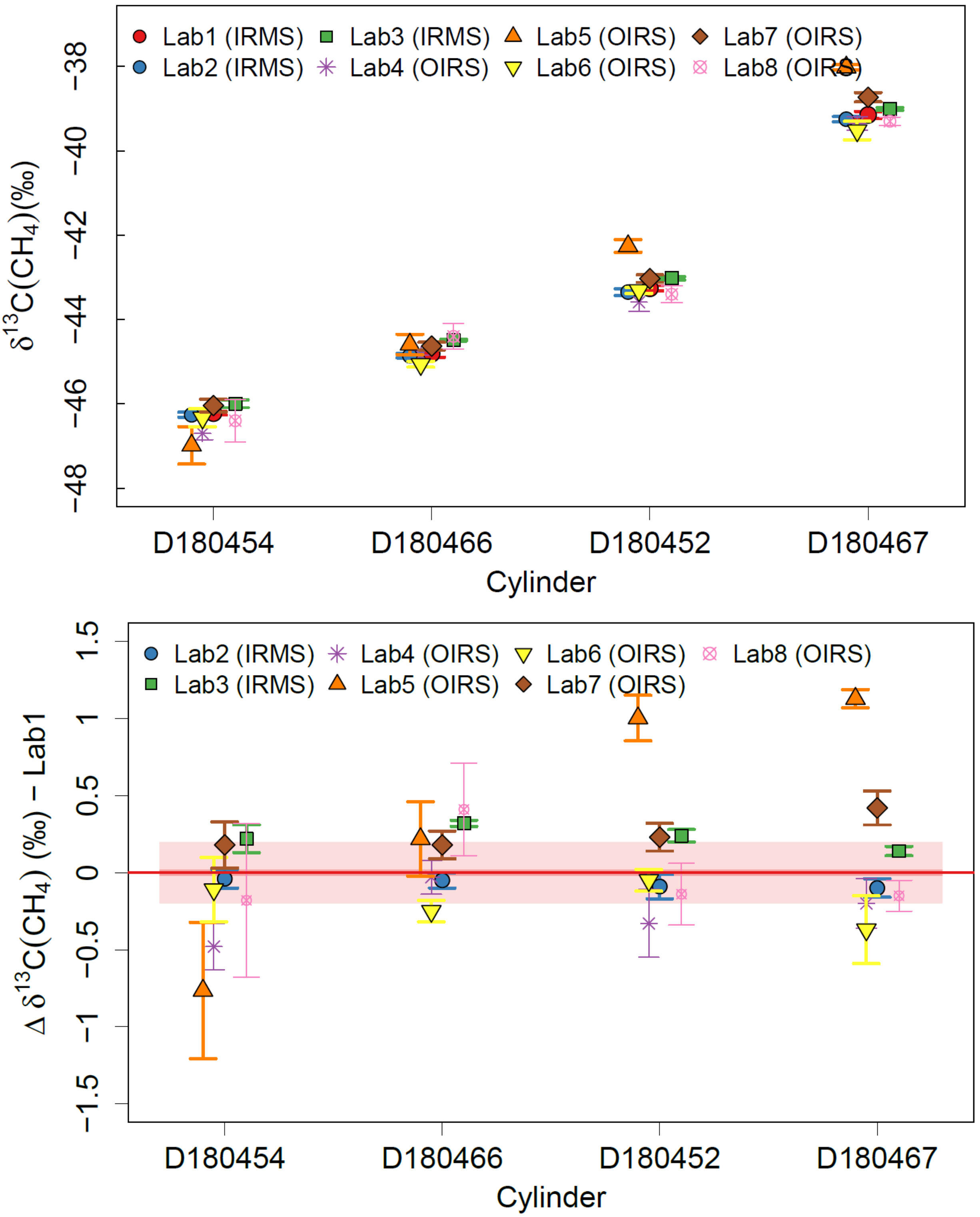

Figure 2: Overview on reported $\delta^{13}C(CH_4)$ values from all project partners from the measurements of the four intercomparison cylinders as (a) absolute values and (b) difference to the reported values from the lab instrument of UU-IMAU (Lab1) as reference. The red background indicates WMO compatibility goals.

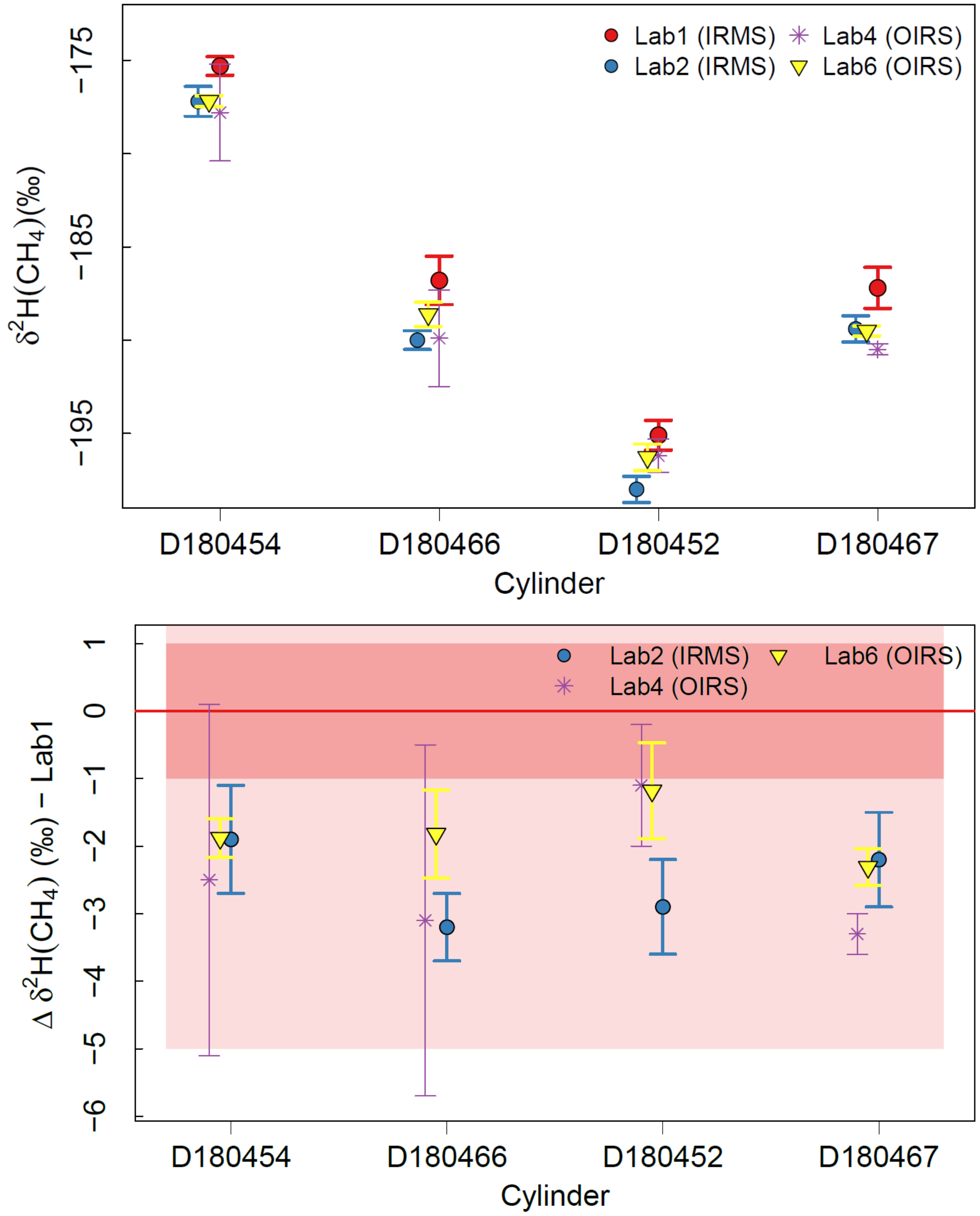

Figure 3: Overview on reported $\delta^2H(CH_4)$ values from all project partners from the measurements of the four intercomparison cylinders as (a) absolute values and (b) difference to the reported values from the lab instrument of UU-IMAU (Lab1) as reference. The red background indicates WMO compatibility goals.

2.5 Conclusion

This intercomparison of $\delta^{13}C(CH_4)$ and $\delta^{2}H(CH_4)$ measurements across multiple laboratories and measurement techniques provides a comprehensive overview of the current performance and compatibility in methane isotope analysis. The participating laboratories used either IRMS or OIRS. In this project, we aimed to meet with the OIRS analysers the extended network compatibility targets of ± 0.2 ‰ ($\delta^{13}C(CH_4)$) and ± 5 ‰ ($\delta^{2}H(CH_4)$) recommended by the World Meteorological Organisation Global Atmospheric Watch (WMO-GAW).

$\delta^{13}C(CH_4)$: Inter-laboratory differences often exceeded the internal reproducibility of individual systems. Averaged over the four intercomparison cylinders, the IRMS laboratories (Lab2 and Lab3) demonstrated good precision, with consistent offsets of –0.07 ± 0.03 ‰ and +0.23 ± 0.07 ‰, respectively.

OIRS laboratories showed a wider range of deviations from the reference lab, with mean $\delta^{13}C(CH_4)$ differences between –0.78 ‰ and +0.24 ‰, and standard deviations ranging from 0.09 ‰ to 0.87 ‰. Lab7 showed a systematic offset of +0.24 ‰ with low variability (± 0.09 ‰), while Lab8 showed a minimal mean difference (–0.01 ‰) but higher variability (±0.19 ‰). Lab5 displayed significant non-linearity, leading to a large mean offset of +0.39 ± 0.87 ‰. These results highlight the ongoing challenge for OIRS instruments to meet the extended $\delta^{13}C(CH_4)$ compatibility goal of ± 0.2 ‰.

$\delta^{2}H(CH_4)$: Data were provided by IRMS laboratories (Lab1 and Lab2) and OIRS laboratories (Lab4 and Lab6). Mean differences to the reference lab (Lab1) of –2.6 ± 0.6 ‰, –2.5 ± 1.0 ‰, and –1.3 ± 0.4 ‰, respectively, indicate that all laboratories performed within the extended compatibility goal (± 5‰) for regional studies, with values approaching the stricter threshold required for background atmospheric studies of ± 1‰.

Overall, this intercomparison demonstrates that most laboratory systems maintain strong internal consistency confirming high stability and prove reliability. This consistent deviations in isotopic values could be corrected for through targeted recalibration. It also underscores the importance of using calibration gases that span the isotopic range of the samples being analysed, as mismatches can lead to non-linearities or systematic biases. Ongoing intercomparison exercises are essential for identifying and correcting such biases and for maintaining alignment across laboratories. While OIRS systems may not meet the stricter IRMS compatibility targets, well-calibrated OIRS instruments can still achieve reliable results within their designated tolerance levels.

Continued collaboration and transparent comparison efforts are necessary to ensure the global harmonization of isotopic methane datasets across techniques and laboratories. Regular repetition of such intercomparison exercises is strongly recommended to monitor long-term stability, identify methodological shifts, and maintain high-quality, comparable isotope data.

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4 Appendix: Additional Figures and Tables

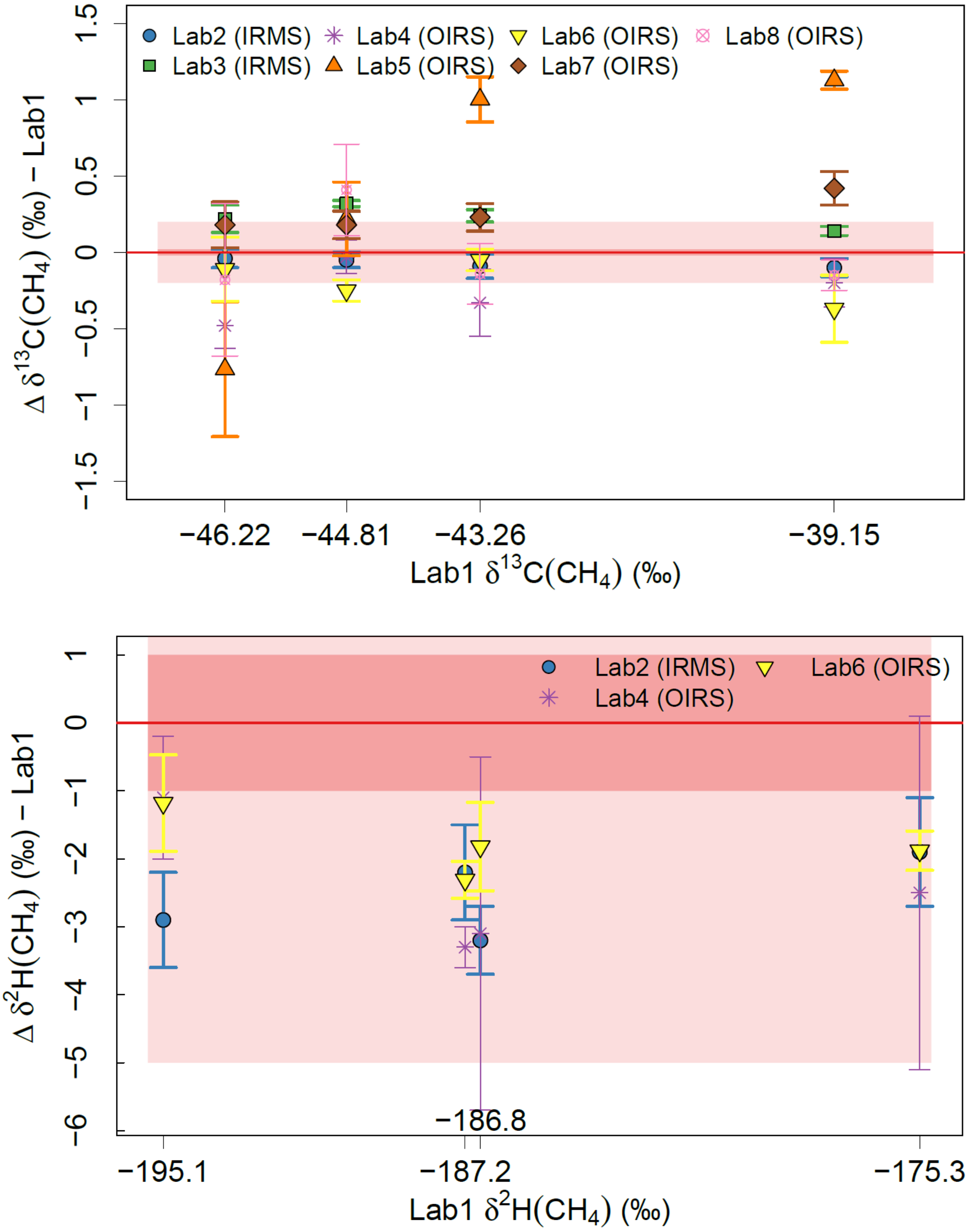

Figure A1: Overview on reported a) $\delta^{13}C(CH_4)$ and b) $\delta^{2}H(CH_4)$ values from all project partners from the measurements of the four intercomparison cylinders as difference to the reported values from the lab instrument of UU-IMAU (Lab1) as reference. The red background indicates WMO compatibility goals.