**Response to Referee #1**

We provide below our point-by-point responses (in blue) to the comments from Dr. Griffith, and the corresponding changes implemented in the revised manuscript.

This paper provides a thorough analysis of water vapour correction and calibration strategies for measurements of delta-$^{13}C$ in $CH_4$ using a Picarro G2201-i CRDS analyser in humid- and dried-air field measurements. The paper is very clearly written and well structured, and comprehensive in its treatment. There are few typos or cases of unclear language. The biases between the two calibration methods (isotopologue- vs delta-based) are clearly documented and assessed. It is clearly suitable for publication in AMT and I recommend publication with only minor technical corrections and clarifications listed below.

AR: We sincerely thank you for the encouraging comments on our manuscript. We are pleased that the referee finds the paper clearly written, well structured, and suitable for publication in AMT. We have addressed all minor technical corrections and clarifications listed below and revised the manuscript accordingly.

**General comments:**

L118 et seq. It isn't clear at this point if the Picarro water corrections on $d^{13}CH_4$ are applied automatically, or replaced by new ones from this work. Are the water-corrected and un-corrected raw data available from the Picarro logs, and if so, which have you used to define your own water vapor correction coefficients?

AR: The Picarro G2201-i data logs provide raw outputs of $^{12}CH_4$, $^{13}CH_4$, and $\delta^{13}CH_4$, but water-corrected outputs only for $^{12}CH_4$, i.e., $^{12}CH_{4,\,dry}$. In this study, we used the raw (uncorrected) outputs of $^{12}CH_4$, $^{13}CH_4$ and $\delta^{13}CH_4$ to derive our empirical water-vapor correction functions, and we applied these correction functions offline to obtain the final water-corrected $\delta^{13}CH_4$ results. We have clarified these in the revised manuscript. The added paragraph in the revised version reads as follows:

"In this study, we used the raw (uncorrected) outputs from the G2201-i logs, so the reported $^{12}CH_4$, $^{13}CH_4$, and $\delta^{13}CH_4$ values represent humid-air conditions prior to applying our offline water correction. Manufacturer-corrected outputs were not used in the calibration workflow to avoid double correction."

Sections 3.2-3.4 compare calibration strategies and identify systematic $CH_4$-dependent inter-method bias, and discuss the linear and inverse $CH_4$ dependence. As a comment here, perhaps useful for future work, if the analyser can be calibrated for the delta method with a set of at least 3 reference gases covering a reasonable $CH_4$ range, and the simple linear delta-based calibration equation (6) is replaced with a 3-parameter equation of the form of Eq 15 in Griffith 2018,
Del13CH4(cal) = alpha*del13CCH4(meas) + (alpha-1) + beta/CH4 + gamma*CH4
(alpha ~ 1, gamma ~ 0, see also section 3.4) the concentration dependence is automatically taken into account in the delta calibration. No spread in $del^{13}C$ values across the reference gases is required.

AR: Thank you for this valuable suggestion. We agree that extending the delta-based calibration to include explicit $CH_4$-dependent terms (e.g., inverse and linear $CH_4$ terms,

as in Griffith, 2018) is an elegant and physically well-motivated way to account for the systematic $CH_4$-dependent behavior discussed in Sects. 3.2–3.4. We have added this point to the revised manuscript as a clear future improvement. The added paragraph in the revised version reads as follows:

"The concentration dependence diagnosed here suggests that, in future deployments, $CH_4$ concentration dependence could be incorporated directly into the delta-based calibration. With a set of at least 3 reference gases covering a reasonable $CH_4$ concentration range, the linear delta-based calibration (Eq. 8) could be replaced with a 3-parameter equation presented in Eq. 15 of Griffith (2018), without requiring a spread in $\delta^{13}CH_4$ values across the reference gases."

**Technical comments:**

L 21 introduce not introduces

AR: This has been corrected.

L28 Site not stie

AR: To ensure consistent usage, we have standardized the capitalization throughout the manuscript and revised all instances of "Site" to "site" when referring to the proper names of the field sites (e.g., "SORPES site" and "Jurong site").

L31 In the abstract, better to avoid terms that you have not yet defined, here $Dd^{13}CH_4$. Better here to say "difference in $d^{13}CH_4$ between the calibration methods" and define $Dd^{13}CH_4$ at first use in the main text.

AR: We have revised the abstract to avoid using $\Delta\delta^{13}CH_4$ before it is defined, and now refer to it as "inter-method difference". We define $\Delta\delta^{13}CH_4$ at its first use in the main text:

"……significant inter-method difference ($\Delta\delta^{13}CH_4$) was observed, with which exhibiting a strong correlation with $1/CH_4$……"

L33 if there is a strong correlation with $1/CH_4$, do you mean non-linear effects at LOW concentrations, where the $1/CH_4$ term is largest?

AR: Yes. A strong correlation with $1/CH_4$ indicates that the non-linear effect is most pronounced at lower $CH_4$ mole fractions, where the $1/CH_4$ term is largest. This behavior is consistent with our results, which show larger deviations at the low- $CH_4$ end and progressively smaller deviations at higher $CH_4$ levels. We have clarified this point in the revised text:

"…… indicating non-linear spectral effects are most pronounced at lower $CH_4$ concentrations and compromise the performance of delta-based calibration."

L150 et seq – This section is unclear - there has been no reference to Ref1 and Ref 3 yet in the text and it is not clear if the calibrations referred to are for CH4 or for isotopic quantities. Firstly, please cross reference Table 1. Further, Ref1 and Ref 3 cover a wide CH4 span but only a narrow del13CH4 span. I assume that this "correction" refers to CH4 not del13CH4. At line 152-153 specify that that ref4 and ref5 have similar CH4 composition

AR: We have now revised the nomenclature of our standard gases to more clearly distinguish reference gases from working standard gases, and we updated the manuscript consistently to reflect this change. Specifically, we removed Ref0, which duplicated the assigned values of Ref2, and we now use Ref2 directly in its place. All related labels and references have been updated throughout the text, figures, tables, and processing description to avoid ambiguity and any impression of circular reasoning. We have revised Sect. 2.2.2 to (i) cross reference Table 1 when WS1/WS3 are first mentioned, (ii) clarify that the correction refers to $CH_4$ mole fractions. We also clarified the calibration procedure used at SORPES and removed the incorrect reference to Ref8. The revised text now reads:

"Calibration approaches also differed. Table 1 describes the compositions and assigned true values of the reference gases (Ref1–Ref3) and working standard gases (WS1–WS5). At Jurong, ambient measurements of $CH_4$ mole fractions were calibrated using a two-point linear correction based on WS1 and WS3. $\delta^{13}CH_4$ was calibrated using the same two reference gases via the linear delta-based calibration (Eq. 8). WS1 and WS3 span a wide $CH_4$ range, but exhibit a relatively narrow $\delta^{13}CH_4$ range (Table 1). At SORPES, WS4 and WS5 were used to determine the calibration slope applied throughout the observation period, whereas WS5 served as a single-point reference to correct instrument drift."

Fig 1 The multiport valve is labelled solenoid valve in one diagram and Valco in the other – is this correct? A solenoid would not normally be an 8-port valve.

AR: The field setups use two different valve types: a 6-way valve using a manifold of solenoid valves in the Jurong configuration and an 8-port Valco/VICI switching valve in the SORPES configuration. The solenoid valve manifold in the Jurong setup allows for multi-port switching, with each solenoid controlling individual ports. The circular symbol is used as a generic schematic representation, but the valve types differ between panels. We have revised Fig. 1 to label the valves explicitly and clarified the distinction in the figure caption.

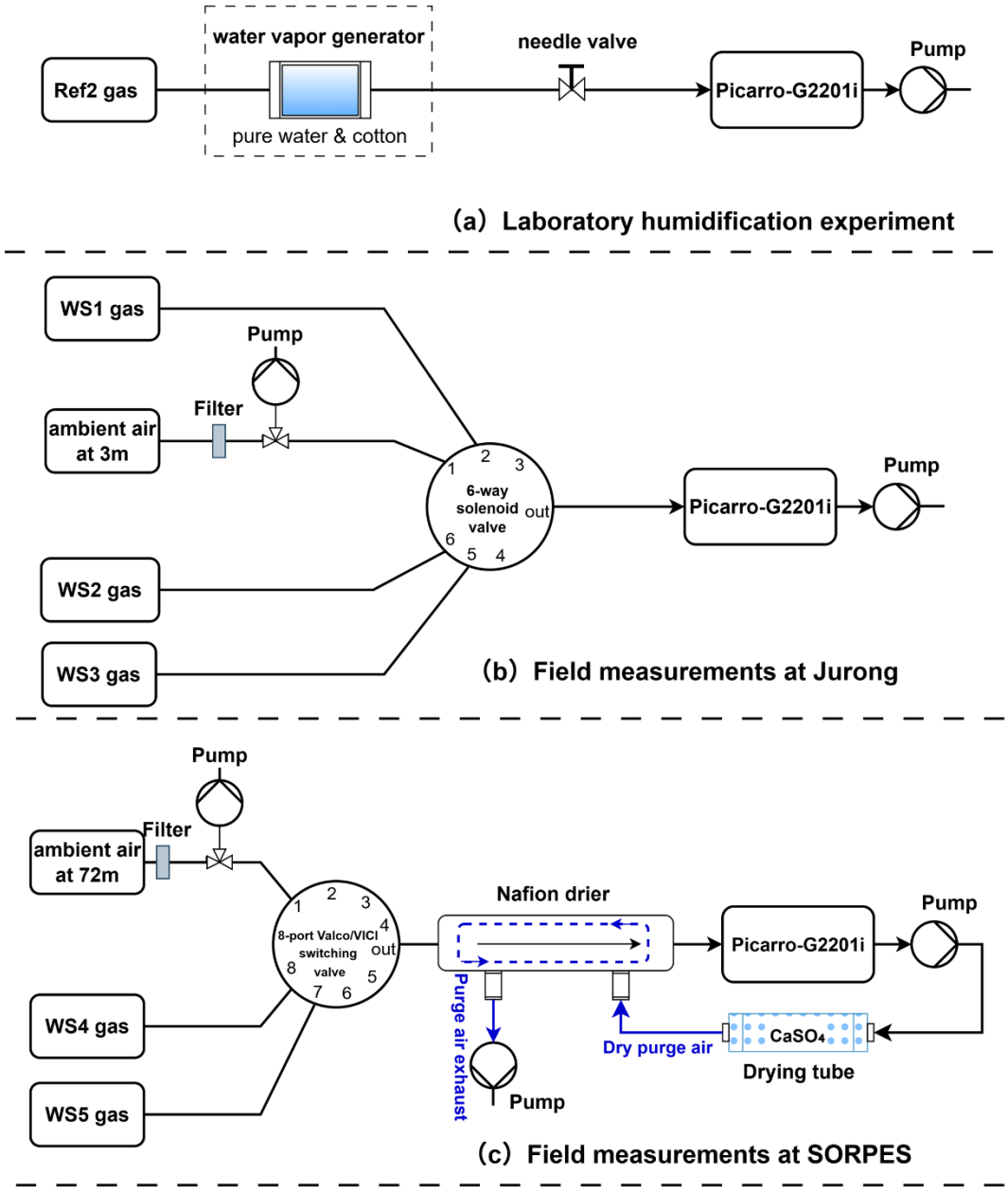


**Fig. 1 Laboratory and field setups for $CH_4$ and $\delta^{13}CH_4$ measurements using a Picarro G2201-i analyzer.** (a) Laboratory setup for deriving the water vapor correction function using humidified Ref2 gas. (b) Field setup at the Jurong site using WS1–WS3 and ambient air at 3m above the ground, streams selected via a solenoid valve. (c) Field setup at the SORPES site with WS4–WS5 and ambient air sampled at 72 m above the ground, equipped with a Nafion™ dryer. Note that a 6-way solenoid valve was used at Jurong, whereas an 8-port Valco or VICI switching valve was used at SORPES.

L 167 Perhaps, in context, move the sentence "A detailed description of all reference gases is given in Table 1." up before first reference to ref gases at line 150

AR: We have moved the cross reference to Table 1 to the first introduction of the reference gases. The added paragraph in the revised version reads as follows:

"Calibration approaches also differed. The compositions and assigned true values of the reference gases (Ref0–Ref8) are described in detail in Table 1. At Jurong, $CH_4$ mole fractions in ambient measurements were corrected using a two-point linear calibration

based on Ref1 and Ref3. $\delta^{13}CH_4$ was calibrated using the same two reference gases via the linear delta-based calibration (Eq. 8). Ref1 and Ref3 span a wide $CH_4$ range but a relatively narrow $\delta^{13}CH_4$ range (Table 1). At SORPES, Ref4 and Ref5 were used to determine the calibration slope applied throughout the observation period, whereas Ref5 was used as a single-point reference to correct instrument drift via the intercept."

Eq 1 and 2 – subscript on LHS should be true not ture

AR: The typo has been corrected in the revised version.

Eq 1-7 I believe the IUPAC preferred, safest and least ambiguous way to include delta values in equations is to NOT include the factor 1000‰ explicitly. Thus Eq 3 for example would be
del13CH4 = (13r/13rref-1).
If the delta value is say 0.001 it can be referred to in text as d = 0.001 or more commonly d = 1‰. This is the same way % is normally treated. 1000‰ simply says "multiply by 1000 then divide by 1000".

AR: We have removed the factor 1000‰ from Eq. (3).

L218 and/or caption to Table 1, the quantity Rsum (introduced in Griffith 2018) may not de widely recognised. Although Griffith 2018 is widely cited elsewhere (perhaps even repetitively so), it would be useful to cite it directly here for practitioners following the calculations.

AR: We have now cited Griffith (2018) directly at the first occurrence of $R_{sum}$ in the text, i.e., "following Griffith (2018)", to guide practitioners following the calculation.

L220 It would be helpful to calculate and quote the error in del13C caused by an error in the assumed value of delD and hence Rsum for atmospheric air, to confirm that this is a minor error over reasonable range of values of delD in air.

AR: We have added a quantitative sensitivity estimate in the manuscript to evaluate the impact of uncertainty in the assumed atmospheric $\delta D–CH_4$ on $R_{sum}$ and total $CH_4$ mole fraction, and confirmed that the impact of $\delta D–CH_4$ uncertainty on total $CH_4$ is negligible. The added text in the revised manuscript now reads:

"A sensitivity estimate was conducted to assess the impact of uncertainty in the assumed atmospheric $\delta D–CH_4$ on $R_{sum}$ and total $CH_4$ mole fraction. Taking $\delta D–CH_4 = -100‰$ as a representative value, a conservative ±50% variation (−50‰ to −150‰) changes $^2r$ by ±5.6%, but propagates to $R_{sum}$ in Eq. (6) at only ±0.0031%. This corresponds to <0.1 ppb uncertainty in total $CH_4$ for typical atmospheric mole fractions of 2000–3000 ppb, which is negligible relative to measurement uncertainty. Note that $R_{sum}$ is used only to convert $^{12}CH_4$ to total $CH_4$ and does not enter the calculation of $\delta^{13}CH_4$, which is determined from the ratio $^{13}CH_4/^{12}CH_4$."

L240 Just to clarify, please confirm that all measurements were made with the same Picarro G2201 analyser, but several years apart? The correction factors may vary slightly from one instrument to another. This could also be done in section 2.2.

AR: We confirm that all laboratory experiments and field measurements were performed using the same Picarro G2201-i analyzer, although they were conducted

several years apart. We have added this clarification in Sect. 2.2. We also note in the revised text that any long-term instrumental drift was routinely corrected using reference-gas calibrations during each field campaign.

The added textin the revised manuscript now reads:

“All laboratory experiments and field measurements reported here were performed using the same G2201-i analyzer, although the field measurements were collected during different campaigns in different years (2018, 2022, and 2025).”