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Dr Andreas Zahn, Editor
Atmospheric Measurement Techniques

Dear Dr Zahn,

Please find below our response to the comments from the anonymous referee #1 on our paper: “Assessing site-to-site greenhouse gas measurement consistency in the UK and Ireland atmospheric monitoring network using whole and synthetic air reference materials”.

We would like to thank the reviewer for taking the time to look over our manuscript and provide us with comprehensive and constructive feedback.

Best regards,

Emmal Safi

(on behalf of all co-authors)

General comments:

This study evaluates the consistency of greenhouse gas measurements (CO₂, CH₄, and N₂O) by comparing traditional whole air reference materials traceable to the WMO-NOAA calibration scales with synthetic SI-traceable reference materials. The study demonstrates that whole air standards are generally better suited for high-precision atmospheric monitoring, while synthetic standards still face challenges related to uncertainty, matrix effects, and long-term stability that need to be addressed before they can fully replace whole air standards in atmospheric monitoring networks.

The manuscript makes a valuable contribution to ongoing discussions regarding future calibration and reference material requirements as atmospheric greenhouse gas monitoring networks continue to expand.

The article is clearly structured, well written, and falls well within the scope of Atmospheric Measurement Techniques. In my opinion, only minor revisions are required before the manuscript can be accepted for publication. My specific comments and suggestions are provided below.

Thank you for your positive feedback on our manuscript. We have carefully addressed your comments below. We appreciate your time to review the manuscript and the feedback you have provided.

Specific comments:

Title

Consider adding "CO₂, CH₄, and N₂O" to the title. Currently, the trace gases investigated are not mentioned until line 30 of the abstract.

Thank you for the suggestion. We considered adding CO₂, CH₄ and N₂O to the title, however, we felt listing the gases would make it overly lengthy and reduce its readability. We agree the gases investigated should be made clear earlier and have revised the first sentence of the abstract to explicitly introduce CO₂, CH₄ and N₂O.

Abstract and Introduction

Lines 34–35:

It is difficult to understand why small atmospheric variability would make it more difficult to meet the compatibility goals. Please clarify.

Thank you for this comment. We agree the original wording was unclear. Small atmospheric variability does not itself make it more difficult to achieve measurement compatibility. Rather, it means the smaller measurement differences can become significant relative to the atmospheric signals we are trying to resolve. For N₂O, the relatively small spatial and temporal variations means that more stringent compatibility goals are needed to distinguish genuine atmospheric differences from measurement biases. The difficulty in achieving those goals comes from the limitations of measurement precision, instrument stability and calibration, rather than the small atmospheric variability itself. We have revised the text to clarify this distinction.

Line 41:

Please clarify whether "matrix effects" refer to effects within the cylinder itself or during instrument analysis. I assume the latter is more relevant. If so, this issue may largely depend on instrument-specific responses and therefore extend beyond the control of the reference material producer.

Thank you for this comment. We agree that this distinction was not sufficiently clear. In this manuscript, "matrix effects" refers to changes in instrument response caused by differences between composition of the synthetic air RM and that of whole air RMs. The magnitude of these effects is dependent on the measurement technique and analyser response. Although the instrument specific response is beyond the control of the RM producer, the composition of the synthetic air matrix can be controlled during preparation and designed to minimise potential differences from whole air. The major components of the synthetic air RMs used in this study were therefore chosen to closely match atmospheric levels. We have revised the text to reflect this distinction.

Line 41:

"...mole fraction dependent instrument responses." Instrument responses are, of course, expected to be mole-fraction dependent. Please rephrase to clarify the intended meaning.

Thank you for the comment. We agree that the original wording was unclear, as instrument response is inherently dependent on mole fraction. Here, we intended to refer specifically to non-linearity in the instrument response across the relevant mole fraction range. We have revised the wording accordingly.

Line 60:

Consider adding a reference to the WMO/IG3IS report #319, Integrated Global Greenhouse Gas Information System Good Practice Guidance for Estimating National-scale Greenhouse Gas Emissions using Atmospheric Observations, <https://library.wmo.int/idurl/4/69714>

Added.

Line 66:

The reference to "WMO, 2022" appears to be missing from the bibliography. It may need to read "WMO, 2024". More importantly, I suggest updating the citation to the most recent WMO GGM report (GAW Report No. 317; WMO, 2025) [I cannot provide the url since the WMO e-library (<https://library.wmo.int/>) is currently down].

In addition, it would be useful to elaborate on the GAW definition and rationale behind network compatibility goals. The footnote to Table 1 in WMO (2025) states: "Scientifically desirable level of network compatibility for measurements of well-mixed background air. These represent the maximum bias that can generally be tolerated in measurements of well-mixed background air used in global models to infer regional fluxes."

Thank you for this comment. The WMO (2022) reference was included in the submitted bibliography; however, we agree that the most recent WMO GGMT report should be cited. We have updated the relevant citations and bibliography to refer to GAW report No. 317 (WMO, 2026).

We agree that further explanation of the rationale behind the WMO/GAW network compatibility goals would provide useful context. We have expanded the text to clarify that the compatibility goals represent the scientifically desirable level of network compatibility for measurements of well-mixed background air and reflect the maximum measurement bias that can generally be tolerated when these observations are used in global models to infer regional fluxes. The relevant citation has been updated to WMO (2026).

Lines 68–69:

Consider citing Worthy et al. (2023) (<https://doi.org/10.5194/amt-16-5909-2023>), which provides an assessment of the level of agreement currently achievable among leading greenhouse gas measurement laboratories.

Added.

Line 83:

Consider revising to: "In addition, several independently maintained calibration scales ..."

Modified.

Line 83:

Consider revising to: "For example, the Scripps Institution of Oceanography ..."

Modified.

Lines 104–114:

This paragraph could better emphasize the importance of independent calibration scales for identifying flaws or inconsistencies in existing scales and for maintaining continuity when scales are revised. Relevant references include:

<https://doi.org/10.1029/2005JD006035>,

<https://doi.org/10.5194/amt-12-517-2019>,

<https://doi.org/10.5194/amt-14-3015-2021>

Thank you for this suggestion. We have revised the text to clarify that independent realisations provide an important means of evaluating established calibration scales, identifying potential biases or inconsistencies and maintaining continuity when scales are revised. We have also incorporated the suggested references.

Methods**Line 135:**

Consider citing: <https://doi.org/10.1175/BAMS-D-19-0364.1>

Added.

Line 137:

WAO and RGL are described both as ICOS sites and DECC sites (Lines 130–131). Are separate measurement and data-processing systems operating in parallel? Please clarify.

Thank you for highlighting this. WAO and RGL (and now also MHD) are associated with both the ICOS and DECC monitoring networks. The answer to this question is different for the three sites:

WAO – all CH₄/CO₂/N₂O measurements presented here are made using ICOS-labelled instruments and the data is processed solely using the ICOS data processing chain.

RGL - all CH₄/CO₂ measurements presented here are made using ICOS-labelled instruments. N₂O measurements using the GC-ECD are not ICOS compliant (this instrument has now been replaced by an ICOS-compliant CRDS system, but that is not relevant to the time period of this study). The CH₄/CO₂ measurements are processed using both ICOS and DECC (GCWerks) processing chains in parallel, while the GC-ECD N₂O measurements are only processed via the DECC processing chain. All RGL data presented here have been processed via the DECC processing chain.

MHD – all CRDS measurements presented here are made using ICOS-labelled instruments and the data is processed solely using the ICOS data processing chain. The GC-ECD measurements are not ICOS-compliant and are processed via the DECC processing chain.

There is ongoing work to compare the ICOS and DECC processing chains (starting with the same raw data) at multiple sites through the NUBICOS project. We have summarised this in the text. We have also corrected the first sentence of section 3.1.5 to clarify that the MHD CRDS systems are not calibrated using the DECC network approach and added additional information on the MHD CRDS calibration within the same section.

Line 138:

According to <https://meta.icos-cp.eu/labeling/> the Mace Head laboratory is listed as approved. Please update accordingly.

Updated.

Line 155:

Is the reference to CO relevant here?

We have removed CO from this sentence.

Line 166:

Likewise, is a reference to CO required here?

We have removed CO from this sentence.

Line 170:

The statement:

"The same sensitivity to water vapour interference exists for OA-ICOS as for CRDS" is not entirely correct. While the dilution effect is similar for both techniques, spectroscopic water-vapour effects differ between OA-ICOS and CRDS.

Thank you for pointing this out. We have removed the sentence describing the same sensitivity of CRDS and OA-ICOS to water vapour.

Lines 170 ff.:

For TAC, where a Nafion dryer is used, is an additional H₂O correction applied to account for residual water vapour?

Droplet tests were performed to assess the water dependence of the TAC LGR and the internal factory correction was found to perform sufficiently well (in that errors associated with this water correction are much smaller than errors associated with instrument drift and nonlinearity). Hence the internal factory correction was used in this case. We have added this to the text.

Line 193:

Consider citing: <http://www.atmos-meas-tech.net/6/1153/2013/>

Added.

Lines 203 ff.:

When introducing whole air mixtures, please consider referring to Section 3.2.1 and providing there a short introductory description, similar to the approach used for synthetic mixtures in Lines 280–281.

Thank you for the suggestion. We have added a short introductory description of whole air at the beginning of section 3.2.1., consistent with the approach used to introduce synthetic air. We have also added a cross-reference to section 3.2.1 when whole air RMs are first introduced.

Lines 206–208:

Consider citing: <https://doi.org/10.18160/V2NS-9WXH> (also available via: https://www.icos-cal.eu/static/images/docs/FCL-QC_Report_2024_v_1.0.pdf)

Added.

Lines 211 ff.:

This section clarifies that RGL operates a single CRDS analyser, while the data are processed according to two different protocols. This interpretation should perhaps be clarified earlier (see comment on Line 137).

This has been clarified at the beginning of section 2.2 and the relevant sentence in this section removed.

Lines 225–226:

You may wish to cite: <https://doi.org/10.5194/acp-11-2381-2011> which quantified network N2O biases using inverse modelling.

Added.

Line 284:

The cited reference is missing a publication year and does not appear in the bibliography.

Thank you for pointing this out. We have added the reference to the bibliography.

Lines 290–293:

Please provide the mole fractions (and associated uncertainties) of N₂, O₂, and Ar.

We have added the mole fractions of N₂, O₂ and Ar, together with associated uncertainties, to table 2.

Line 309:

The statement:

"The GC-ECDs used within the network collected data at 10 min intervals..." could be misinterpreted. Please clarify that these measurements represent discrete sample injections (of xx mL) every 10 minutes rather than 10-minute averages.

Thank you for highlighting this. We have revised the text to clarify that the GC-ECD measurements represent discrete samples injected at 10 min intervals, rather than measurements averaged over 10 min periods (20 mind for MHD).

Line 312:

For the FTIR measurements at WAO, are the reported values one-minute averages?

The FTIR only produces a data point every minute, so it is not an average. We have modified the text to reflect this.

Results and Discussion

Figure 2:

Consider adding compatibility goals, similar to Figure 3. The same suggestion applies to Figure 4. A shaded grey band could be an effective way to illustrate the target range.

Thank you for the suggestion. We considered including the compatibility goals as shaded bands in Figures 2 and 4 and tested this. However, we found that this reduced the visibility of the individual differences, which are the primary focus of these figures. We therefore decided to retain the current presentation to preserve the detail needed to distinguish between individual sites and instruments.

Table 2:

Please consider whether this table is necessary. The values are difficult to interpret and receive limited discussion in the manuscript.

Thank you for this suggestion. We considered removing table 2; however, we have retained it for completeness and to provide equivalent information on the synthetic air RMs to that provided for the whole air RMs in table 1. To improve the usefulness and interpretation of the table, we have expanded it to include the mole fractions and associated uncertainties of the major matrix gases in the synthetic RMs.

Lines 390–391:

Consider reordering the sentence:

"...it is composed of the propagation uncertainty and the uncertainty of the analytical instrumentation used to assign the values (see Tables 1 and 2)..." since propagation uncertainties are reported in Table 2, while assignment uncertainties are reported in Table 1.

Thank you for highlighting this. The original reference to tables 1 and 2 has caused confusion. The sentence refers specifically to the uncertainties associated with the assigned values of the whole air RMs reported in table 1, which include contributions from the propagation of the WMO-NOAA scales to the RMs and from the analytical measurements used for value assignment. We have therefore removed the reference of table 2 and revised the sentence for clarity. We have added further clarification to the caption of table 1 describing the reporting uncertainties.

Table 5:

Why is the CH₄ standard error largest for NPL-3064? Most other values appear to scale approximately with mole fraction, with lower mole fractions corresponding to lower standard errors in both the D66 and NPL subsets.

For NPL-3064, the CH₄ measurements were available from only five of the seven participating sites/instruments due to damage to the cylinder stem during the intercomparison. The smaller number contributing to the weighted mean may therefore partly account for the larger standard error observed for this RM. To check this, we recalculated the standard error of the weighted mean for the other synthetic air RMs using only measurements from five rather than seven sites for a direct comparison to NPL-3064. Doing this shows that the apparent relationship between standard error and the CH₄ mole fraction was no longer observed. We have modified the text to reflect this on line 466 of the original manuscript.

Line 402:

The WMO compatibility goal of 0.1 $\mu\text{mol mol}^{-1}$ for CO₂ applies only to the Northern Hemisphere.

We have modified the text to reflect this.

Line 426:

Consider adding: "...can obscure atmospheric signals and jeopardize their use in global models for inferring regional fluxes."

Added.

Line 455:

Do the authors have any hypothesis regarding the large observed offset? Could isotope effects associated with the preparation of synthetic reference materials contribute?

Thank you for the comment. Potential explanations for the observed offsets are discussed in section 4.4.1., particularly in relation to the differences between the synthetic and whole air matrices and their influence on instrument response. This is highlighted in line 456 of the original manuscript. The potential contribution of isotopic effects was not investigated in this study and therefore cannot be assessed from the available data. We have added this as an additional consideration in the discussion in section 4.4.1.

Line 471:

Please provide a cross-reference to Section 4.4.2.

Added.

Section 4.4.1:

A discussion of isotopic effects may be worthwhile, particularly given that such effects could differ among measurement techniques depending on their spectral sensitivity (e.g., instruments with sensitivity to ¹²CO₂ only).

Thank you for this suggestion. We agree that differences in the isotopic composition of synthetic and whole air RMs could potentially result in technique dependent measurement effects, particularly where instruments differ in their sensitivity to individual isotopologues. The isotopic composition of the synthetic air RMs was not characterised in this study, so its contribution to the observed differences cannot be assessed. We have added this as an additional consideration in the discussion in section 4.4.1.

Conclusions and References

Line 525:

Please define "CIPM.

It has now been defined.

Line 526:

Please clarify NOAA's role in CIPM-related activities. My understanding is that NOAA can participate despite not being a National Metrology Institute because it has been designated by

WMO as the Central Calibration Laboratory of the GAW programme. If correct, this could be stated explicitly.

Thank you for highlighting this. You are correct in that NOAA participates within the CIPM MRA framework as a designated institute of the WMO, reflecting its role as the WMO/GAW CCL for CO₂, CH₄, N₂O, CO and SF₆. We have added this clarification when introducing the CIPM key comparison on line 526 of the original manuscript.

Editorial comments

There are several in-text citations that should be reformatted to conform to journal style. For example:

"AUTHOR et al. (YEAR) provide details..."

We have checked the manuscript and reformatted any reference not adhering to the journal format.

Overall, I find this to be a valuable and timely contribution. The manuscript is scientifically sound, clearly written, and highly relevant to the atmospheric greenhouse gas measurement community. The revisions suggested above are primarily intended to improve clarity, provide additional context, and strengthen the discussion. I therefore recommend minor revisions.

Thank you again for your time and valuable comments.