Reply to the comments of reviewer #2 of "UK greenhouse gas measurements at two new tall towers for aiding emissions verification"

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General Comments

The paper reports on the installations of GHG measurement systems at two new tall tower sites, describes their setups and their contribution to uncertainty reduction for UK CH4 emission estimates. In addition, the paper describes extensive tests and evaluates the impact of two different sample air drying strategies applied for CRDS instruments in the lab and installed at these two sites. From these subjects, I consider the latter the most relevant and best described in the paper. The text's length, the writing style and the text structure make it often difficult to follow the work and reasoning of the authors. This regarding, substantial improvements are necessary (i.e. shorten and restructure the text). Also, two of the three instruments measure carbon monoxide (CO) – why was this opportunity not used to evaluate the effects of drying / water corrections on the measurements of CO as well? The experiments and findings related to air drying strategies represent an important contribution to this field of research and should thus be accepted for publication after major corrections and only if the comments within this review are adequately and fully addressed.

The authors would like to thank Reviewer 2 for their helpful comments. We have endeavoured to reply to and incorporate all the suggestions that they have made. As requested by the reviewer we have removed and simplified large sections of the text. As such some technical corrections are no longer applicable, these have been noted as such. Reviewer 2 commented on the lack of discussion of the impact of Nafion® drying and the CRDS water correction on CO mole fractions. As the Nafion® drying experiments were conducted using a Picarro CRDS G2301, which does not measure CO, the effect of Nafion® drying on CO mole fractions was not investigated. While instrument specific CO water corrections were calculated, the large minute-mean variability inherent in the G2401 CO measurements (> 4 nmol mol^{-1}) meant that the difference between the instrument specific and in-built correction was not statistically significant (Page 22, Lines 10-14). As such, these corrections were not presented in the body of the paper, however, further information can be found in Figure S5 of the supplementary. Even with the inclusion of the extra information requested by the reviewers these changes have reduced the length main body of the paper by 6 pages and removed 4 figures.

Specific comments and technical corrections

Page 1, Line 15 (1/15): ". . .were located. . .": I would rather go for "are located"

Removed.

1/20: “by between” -> “by up to 20 %”
Section removed

1/29: “..default factory..” it is well established that the default factory water correction is not to be used for the purposes described – this fact should be stated more clearly here.
Reference to default factory corrections has been removed from the abstract. Details of the issues associated with this correction are given in the introduction. Page 3, Lines 15-20, “Initially, it was hoped that the inbuilt water correction would remove the need for sample drying, inherent in most other methods (e.g. FTIR or NDIR) but subsequent studies questioned its stability over time and between instruments (Yver Kwok et al., 2015;Chen et al., 2010;Winderlich et al., 2010). In response to this, researchers have typically developed their own water corrections or have returned to sample drying in order to minimise the effect (Welp et al., 2013;Winderlich et al., 2010;Schibig et al., 2015).”

2/17: write out the names of the gas molecules at first use.
Completed as requested Page 25, Line 15.

3/3: need “While,”?
Section removed.

3/10: delete “recognised”
Deleted.

3/16: A dramatic reduction in the cost of these instruments could be debated. I suggest you keep only the next sentence, starting in line 17.
Sentence deleted.

4/4: Please explain why dry zero air was chosen for the counter flow purge gas (instead of using the reflux method with sample air from the instrument’s outlet). This is relevant because it is on one side true that the drying with dry (zero) air is more effective, but on the other side trace gas species gradients can influence the transition dynamics of these trace species across the Nafion membrane and thus the composition of the dried sample air as well.
Page 3, Line 22 – 25, “For ease of servicing, the CRDS instrumentation at GAUGE and UK DECC Network sites was initially deployed using an identical drying method to that of the co-located GC instrumentation. This method relied on drying the sample with a Nafion® water permeable membrane in combination with dry zero air as a counter purge gas.”

If I am not much mistaken, Nafion must be written as Nafion®.
We have replaced all references to “Nafion” with “Nafion®”.

5/18: correct to: “m a.g.l.”
Corrected throughout text.

6/2: it would be advantageous, if you stated at least once the serial numbers of the Picarro instruments used in your setups.
This information has been added to the text.
Page 5, Line 20, "Both sites are equipped with a CRDS (G2401 Picarro Inc., USA, CFKADS2094 and CFKADS2075 deployed at Bilsdale and Heathfield, respectively) making high frequency (0.4 Hz) CO_2, CH_4, CO and H_2O measurements."

7/7: Please summarize here briefly the reason for discontinuing the Nafion drying. State the main arguments/problems that are thus avoided or minimized. If the reader jumps to Section 3.3.3 to find out about it s/he will have a hard time finding the explanation. Sentence in 7/12 is similarly ambiguous.
These have been clarified.
Page 6, Line 25 to Page 7, Line 6. "In an attempt to minimise the water correction required for dry mole fraction CRDS measurements, CRDS samples were initially dried using a Nafion® in an identical manner to those of the GC-ECD. This resulted in air samples with water mole fractions between 0.05 and 0.2 % H_2O depending on the original moisture content of the air. However, due to concerns that the mole fraction gradient between the sample and the Nafion® counter purge might lead to CO_2 transport across the Nafion® membrane this drying approach was discontinued. The CRDS Nafion® drying systems were removed on the 17th of June 2015 & 30th of September 2015 at BSD and HFD, respectively and undried air analysed and the data post corrected with an instrument specific water correction."
And
Page 7, Lines 18 – 19, "Motivated by the possibility of CO_2 transport across the Nafion® membrane, the decision was made to measure wet samples and correct using an instrument specific water correction."

7/26: Note: Picarro analyzers are not calibrated for H2O measurements and often show different positive or negative values close to zero at third place behind the comma. For the sake of completeness of information, it would be informative to know what the zero was for water on all three Picarro instruments.
The below information has been added to the text.
Page 8, Lines 23-27, "As Picarro analysers are not calibrated for H_2O measurements when measuring dry air they often show different positive or negative values close to zero. For the instruments studied in this paper these "zero-water" values were 0.00001, -0.0003 and -0.002 for the Bilsdale, Heathfield and University of Bristol laboratory instruments respectively. These values were determined using measurements of cylinders of dry air where the first 120 minutes were ignored and the "zero-water" value calculated as the mean H_2O of the subsequent data (> 60 min)."

8/2: please add a short justification/explanation on how the criteria were decided on (particularly the thresholds for 1 min mean standard deviations).
The below information has been added to the text.
Page 7, Lines 4-9, "Data collected in the first five minutes immediately following the injection, the typical line equilibration period, were excluded from the fit. This avoids using data adversely effected by the effect of rapid changes in H_2O content on the cell pressure sensor, as identified by Reum et al. (2018) and the erroneous post-injection CO_2

enhancement identified by (Rella et al., 2013). Again, due to cell pressure sensor concerns, data points with minute-mean H_2O standard deviations > 0.5 % H_2O were excluded. This 5-minute cut-off reduced the maximum H_2O value included in the fit to 4 % H_2O."

8/11: I am not convinced by the nomenclature for gases; what do you mean with "close- to-ambient standard"? From the continuation of the text, I guess this is a "working tank" that helps you to account/correct for short-term drift? You should then use "standard gas" for what you now call "calibration gas".
As the reviewer has noted the standard cylinder is used to account for short-term drift and as such could also be called a "working tank" (Page 14, Line 7). The text has been updated to include a reference to this term. However, we would prefer to leave the labelling of the calibration cylinders unchanged. These cylinders are calibrated to WMO calibration scales and used to propagate these scales to the atmospheric observations (i.e. calibrate) as such we feel "calibration cylinders" is the most appropriate terminology. The use of the nomenclature "standard cylinder" and "calibration cylinders" in this way is also consistent with other related publications (e.g. Stanley et al. (2018)) and as such we feel it is important to maintain it.

8/17: "greatly increases the error" – what does this explicitly mean? How much? Better reformulate, drop "greatly" and, if possible, add facts-based estimates.
Added to the text.
Page 14, Lines 13 – 23, "Assigning mole fractions to values outside the range of the calibration suite will increase the error. The magnitude of this error will depend on the magnitude of the mole fraction difference between the lowest calibration cylinder and the sample. This error has been estimated using measurements made at the Heathfield site of cylinders of known CO mole fractions, 6 and 57 nmol mol^{-1} CO below the lowest calibration cylinder. These show a percentage error of 2.41 and 3.09 %, respectively. A similar assessment of the error associated with samples above the highest calibration standard were made using cylinders 87 and 686 nmol mol^{-1} CO above the highest calibration standard. These correspond to percentage errors of 2.98 and 2.56%, respectively. As all the minute-mean CO measurements below of the calibration range are within 57 nmol mol^{-1} of the lowest calibration cylinder and the vast majority of minute-mean CO measurements above the calibration range are within 686 nmol mol^{-1} of the highest calibration cylinder (99%) we expect that this error would typically be < 3%."

8/21: no "target gas" seems to be used – for the appropriate QC, this is required. There is a comment on this in Chapter 4. – but it would be helpful if the authors comment on how the absence of a target gas is influencing the current performance of the system (i.e. what is the impact on the uncertainties, etc.).
Target tanks, as defined by the World Meteorological Organisation (WMO, 2016), are an extremely useful quality control tool and "function as a warning that there might be a problem" but they are "not to be used to define a second, optional, path of traceability". As such, although they can be used to assess the uncertainty of the measurements, their use (or not) does not contribute to the uncertainty of any measurements. With this in mind, the authors believe that, although the use of a target tank would be a useful addition to the system, the lack thereof does not negatively impact the uncertainties of the measurements it merely impacts our ability to characterise these uncertainties.

This has been clarified in the text.
Page 29, Lines 3 – 8, "Future improvements to the Bilsdale and Heathfield records include the addition of target tanks at the sites. Although the use of target tanks do not directly influence measurement uncertainty they allow independent long-term monitoring of instrument performance and are a useful tool for assessing measurement uncertainty. The development of a full uncertainty analysis incorporating such target tank measurements, along with an assessment of the calibration strategy and any instrumental, water correction and sampling errors is also planned."

9/8: In Table 3, the pre- and post-site calibration values should be given (where applicable).
Where available the pre- and post-site calibration values have been added to Table 3.

10/2: The statement ". . .with the mean absolute precision increasing (i.e. becoming less precise)" seems wrong to me.
We can understand why this sounds odd to the reviewer and have clarified the text. Page 16, Lines 23 – 24, "Both sites showed a small trend with the mean absolute precision worsening with increasing CO_2 and CH_4 mole fraction."

10/22: the numbers for pressure and temperature are switched – correct.
Page 17, Line 17, Corrected.

12/15: 2.3 Results and discussion; 3.3 has the same name, which is confusing. A paper should have one Results/Discussion section.
The paper has been restructured to remove the second Results/Discussion section.

13/19: What does ". . .green space. . ." refer to?
Green space refers to protected areas of undeveloped landscape this can include areas of native vegetation along with parks and reserves, however, for clarity the term has been replaced with "native vegetation" (Page 19, Lines 9-10).

14/8-19: I can only second the comments by Anonymous Referee #1 on this subject.
As detailed in our reply to reviewer #1 the FFT based curve fitting method has been removed from the paper and diurnal and seasonal trends are now examined using box plots.

14/23: I am reserved about calling a 3.5 years long data set as sufficient for calculating long-term trend curves.
Section removed

15/2: put spaces between number and unit (e.g., 108 m).
Corrected throughout the text.

17/25: you can safely drop "extremely low" without losing any information. What were the values for CO?
Removed "extremely low". Carbon monoxide was <12 nmol mol^{-1}, this information has been added to the text (Page 7, Line 11).

18:21: this would be an excellent place to state the maximum humidity of air in the cylinders.
This section has been removed and instead the typical humidity of the dried cylinders has been included in an earlier part of the paper.
Page 7, Line 21, "…air from a cylinder of dry (<0.002 % H_2O) natural air…"

19/3: typo in the flow range
Corrected
Page 11, Line 6, "…had a flow range of 0.1–0.5 L min^{-1}…"

19/14: analogously to I.D.; 1 " O.D.
Corrected
Page 10, Line 25, "…coil of ¼ " diameter (I.D. 0.12 ")…"

19/17: please specify "polymeric plastic tubing" better and explain why it was necessary to include it (particularly as this introduces further possible "active" surfaces that can influence the performance of the system).
We understand that this does introduce possible active surfaces, however, due to the fittings of the DPG this was unavoidable. The text has been updated to address this and to specify the exact tubing type.
Page 11, Lines 9-12, "Other than the cryogenic water trap and two short sections (< 10 cm) of ¼" (O.D.) "Bev-a-line" plastic tubing immediately prior to and post the DPG, 1/16 " stainless steel tubing was used throughout the system. Due to the air output and input connections of the DPG the use of the plastic tubing was unavoidable."

19/27: typo "2-5"
Section removed.

20/7: please be more explicit than "were monitored closely and regularly logged."
The text has been updated to Page 12, lines 9-11, "Flow rates, cylinder pressure, chamber temperature and H2O trap temperature were manually logged after each valve position change and when the water trap was inserted into the silicone oil bath."

20/27: a flowmeter rather "monitors' than "ensures"
Section removed.

21/2: it would be helpful for the reader, if you added how this value translates to % H2O
This equates to approximately 2.9% H_2O. This value has been added to the text Page 11, Line 19.

21/7: please specify "stabilise".
Page 11, Lines 18- 19, "A stable water content was defined as one where the standard deviation of the minute mean values was < 0.003 % H_2O for a 15-min period."

21/16: I am not sure what you mean here – if we are talking about H2O < 0.0001 %, we go far below a dew point of 0 deg.C – please explain.
Sentence removed.

21/19: please clarify the frequency 1.5 Hz/data recording strategy here (as the Picarros record with 0.4 Hz).
Picarro's operate by taking an individual measurement of each gas of interest, in the case of a G2401 instrument CO2, CH4, H2O and CO, in series. For our instruments, these measurements are typically 0.7 sec (approx. 1.5 Hz) apart. Instead one, perhaps more correctly, could consider the time it takes to complete a full cycle through all the gases of interest. For our instruments, this typically takes 2.5 sec (approx. 0.4 Hz). We have updated the text to reflect this.

22/7: you should number the equations
Equations numbered

24/21: use "target gas"
The authors would prefer not to use the phrase "target gas" as this is a specific term reserved for a long term surveillance tank which is completely independent of the calibration and drift correction of the instrument (WMO, 2016). The tank referred to here is used to drift correct the measurements and cannot be classed as a target tank. Instead, as these cylinders are measured periodically over multiple years the raw uncorrected measurements can be used to estimate typical instrumental drift. This has been clarified in the text.
Page 13, Line 26 - "For the UoB CRDS, raw long-term measurements of standard cylinders have shown the typical instrumental drift to be < 0.001 µmol mol^{-1} day^{-1} CO_2 and < 0.03 nmol mol^{-1} day^{-1} CH_4."

25/14: wrong use of c.f. (cf) – use vs.
Corrected Page 22, Line 18.

27/6: "WMO internal reproducibility"; also, decide what you want to use: internal reproducibility guidelines/requirements/bounds and use throughout the text consistently. Please also explain somewhere (best at first use) why you (correctly) aim for Internal reproducibility and not for the Recommended compatibility.
Corrected throughout to the text to "WMO internal reproducibility guidelines".
Text added to clarify the choice of internal reproducibility guidelines.
Page 4, Lines 17 – 22, "The importance of these errors are assessed in comparison to the WMO internal reproducibility guidelines (WMO, 2016) which incorporate not only the instrumental precision but uncertainties related to other components sample collection and measurement including drying. These internal reproducibility guidelines are typically half the WMO recommended compatibility goals which, unlike the reproducibility guidelines, are driven by the need for compatibility between datasets."

30/8: can you please explain in a bit more detail how you did this – and how you were able to estimate Nafion-related errors, since, to my knowledge, Reum et al. (2017) did not use one?
Section removed

31/23: would you be able to discuss the role/importance of the trace gas species gradients between sample and counter flow gas? (see 4/4)
Added to the text.
Page 26, Lines 6 – 11, "Nafion® membranes, when combined with a dry counter purge gas stream, can be used to effectively dry air samples. This drying process is driven by the moisture gradient between the "wet" sample and the dry counter purge. In a similar manner, as long as the membrane is permeable to the gas, a sample to counter purge gradient in any other trace gas species will also drive exchange. In an effort to quantify the magnitude of CO_2 and CH_4 exchange a series of experiments measuring the composition of the Nafion® counter purge gas were conducted."

32/3: see 21/16
Clarified
Page 27, Lines 11 - 12 "These cylinders are very dry, $H_2O < 0.0001$ %, equivalent to the driest conditions studied in the DPG experiments"

37: North and scale are missing.
North and scale have been added. Figure 1.

38: all abbreviations used should be explained in the figure's caption
Caption now reads "Figure 2: A generalised schematic showing the initial Bilsdale and Heathfield site setup of the cavity ringdown spectrometer (CRDS) and the Gas Chromatograph – Electron Capture Dectector (GC-ECD) including the gas generator (TOC) and back pressure regulator (BP). Note that Bilsdale has three inlets, while Heathfield has only two as shown here. The Nafion® drying system located downstream of the CRDS multiport valve was removed at both sites in 2015. Black arrows and lines show the direction of sample, standard and calibration gas flow. Grey dashed lines and arrows show the flow path of the Nafion® counter purge gas."

39: I presume "Hour of day" means local time? Better replace with "Hour (LT)". Was summer / winter time used as well?
Data were not adjusted for summer/winter time daylight savings. All data were recorded and plotted on UTC as such, "Hour of day" has been replaced with "Hour (UTC)". Figure 6.

41: see 14/8-19 comment regarding spikes
This figure has been replaced with two using box plots (Figures 6 and 7) rather than a FFT based curve fitting method to examine diurnal and seasonal trends. This has removed the spikes.

Figure S3: equations not legible
Equation text font size has been increased on Figures S5 and S6.

References

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