

Reply to reviewer #1

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10 The authors would like to thank the reviewer for their helpful comments. We have endeavoured to incorporate the suggestions that they have made. The locations of changes to the paper are given as Page Number, Line number of the new paper while the reviewers comments contain the locations in the original paper. Our responses are shown here in blue text and the reviewers' comments in black.

15 **Overall framing:**

There are several other papers already describing CRDS installations at field sites. The novel aspect of this paper is that two different drying methods were deployed -- each for a significant amount of time, and laboratory tests have been performed to quantify their errors. Currently the manuscript does not adequately describe the extent to which systematic errors introduced by the CRDS water correction are mitigated by calibrating through the nafion. This is a crucial question and should be
20 relatively easily addressed with existing data. Specific suggestions for figures to address this question are given below. If it is the case that passing calibration gases through the nafion substantially mitigates the systematic errors, then the initial configuration would seem to be clearly superior in terms of ease of implementation/maintenance and remaining systematic errors. It would be especially useful for the discussion to consider implications of complex and frequent instrument specific annual water correction strategy versus ease of operations for the original configuration.

25 If it is the case that dried air samples versus humidified calibration gases have nearly the same water content, then any bias associated with the picarro water correction should be nearly or entirely calibrated out (see specific comments below). To what extent does the daily measurement of the ambient standard remove bias introduced by the CRDS water correction? I think the systematic errors should be estimated based on the difference between the humidity of humidified drift-tracking standard versus the humidity of the dried ambient sample. It would be useful to provide some details in section 2.3.8 about

the extent to which standards are humidified and how much variability in ambient humidity is observed between daily (drift) calibration episodes.

It would be interesting to include a figure in the paper or in the supplement showing the complete h₂O time series prior to removal of the nafion, i.e. showing the CRDS measurements of post-nafion humidity with enough detail to show how it varied over different timescales, including seasonally and diurnally (some variability in drying performance is expected given that the effectiveness of nafion drying is strongly dependent on the temperature of the membrane).

Also consider including a panel(s) showing typical humidity difference between ambient sample air and during a daily drift calibrations (i.e. how much water does the calibration gas pick up and does it dry out perceptibly during the course of a 20 minute calibration interval?).

10 It is critically important to understand the extent to which calibrating through the nafion once per day mitigates errors associated with the crds water correction. If the amount of water stored in the nafion membrane is sufficient to (1) humidify the standard to the same humidity as the ambient sample is dried and (2) to largely mitigate within-day variability of sample h₂O, then errors related to h₂O are likely negligible. It seems that the original nafion strategy may have had only very small systematic errors and that these could likely be further reduced if necessary by increasing the frequency of the daily CRDS
15 analyzer drift calibrations through the nafion.

For the second phase, where the nafion dryers were removed, the authors have gone to great trouble to track the instrument specific water corrections, and the findings are very interesting. In the end, I wonder if perhaps the errors associated with using a single pre-deployment water correction are actually tolerable for the application of estimating UK scale fluxes (at least in the case where some drying is used to keep h₂O < ~2%). Looking at Figure 8 a and b, and given the large differences
20 among the h₂O corrections for humidity > ~2%, it seems that the errors are unacceptably large, and unlikely to be improved even with weekly testing.

It would be useful to discuss the significance of systematic errors with respect to the current model errors and goals of the UK network (i.e. for national-scale evaluation of reported emissions by atmospheric monitoring to be useful). Based on all of tests and analysis, what are the recommendations about how to simplify the operations and reduce the systematic errors
25 going forward? My reading is that the systematic errors would be greatly reduced if nafion dryers were to be reinstalled, so long as the calibration gases are also routed through the nafion dryer and so long as the membrane provides an adequate reservoir of h₂O such that the humidity of cal gases and ambient samples is the same. It is worth reemphasizing the need to calibrate through the nafion for any system that has a large partial pressure gradient of CO₂ and/or CH₄ across the membrane.
The authors would like to thank the reviewer for their detailed response to the paper. The reviewer outlines four key
30 improvements to the paper and provides some suggests as to how these may be addressed.

1. *A better description of the extent to which systematic errors introduced by the CRDS water correction are mitigated by calibrating through the Nafion®. Specifically, including information on the humidification of the daily standards, their ability to track changes in ambient humidity and how this would reduce systematic errors.*
2. *A more detailed discussion of the advantages and disadvantages of the two drying techniques namely the advantage to the Nafion® based drying system in terms of minimising systematic error and practicality and the use of an annually determined water correction for samples with $H_2O < 2\%$.*
3. *A discussion of the significance of the systematic errors in terms of the goals of the UK tall tower network and a conclusion in terms of the optimum drying process for the network.*
4. *A reemphasis of the importance when using Nafion® drying systems of drying the calibration and standards gases in an identical manner to the sample to account for any loss of CO_2 across the membrane.*

We thank the reviewer for the suggestions and discuss them each in turn.

1. *A better description of the extent to which systematic errors introduced by the CRDS water correction are mitigated by calibrating through the Nafion®. Specifically, including information on the humidification of the daily standards, their ability to track changes in ambient humidity and how this would reduce systematic errors.*

As the reviewer notes passing the calibration and the standard gases through the Nafion® does substantially mitigate systematic errors in the CRDS water correction. These systematic errors, as demonstrated in Figure S8, tend to peak at low (0.05 to 0.5% H_2O) moisture contents - the typical moisture content of samples dried using a Nafion® based drying system. However, as the moisture content of the standard closely follows that of the sample (see Figure S4) these systematic errors should be substantially mitigated. Following the suggestion of the reviewer Section 2.3.9 (previously Section 2.3.8) now includes a description of the moisture content of the standard, its variability over time and relationship to the moisture content of the ambient air samples. We have also included three new plots, Figure S1, S2 and S3. Additions to the text and references to the new figures are listed below.

Page 7, lines 3 – 7: “When functioning correctly this drying method 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 and temperature. However, at Bilsdale, due to problems with the TOC and the tubing initially installed at the site, the Nafion® was not drying optimally and significant periods of 2014 had far higher moisture contents (Figure S1).”

Page 7, lines 13 – 15: “Plots of the water content of all air samples along with the comparisons of the diurnal and seasonal cycles in sample moisture content can be found in the supplement (Figures S1 and S2).”

Page 15, line 23 – Page 16, line 13: “During the period that the Nafion® drying system was used these standards were partially humidified as they passed through the wet Nafion® dryer. The level of humidification is dependent on that of the air samples measured prior to the standard. The moisture content of the standard closely tracks that of the air samples with variations in

the humidity of the samples clearly reproduced in the standard (Figure S1). However, the moisture content of the standard is generally slightly lower. On average the standard has a mean moisture content 88 % that of the average of the 30 mins of air sample either side of the standard (on average 0.02 % H₂O lower). The moisture content of the standard also decreases slightly during the 20-minute measurement period as the dry standard air dries out the Nafion® membrane. The size of this decrease is dependent on the moisture content of the prior air samples with larger decreases during the more humid times of the year. As a worst-case example, the change in the water content of the Heathfield standard during each run of August 2014 is shown in Figure S6. This shows a maximum drift of 0.07 % H₂O equating to 30 % of the mean moisture content of air observations collected 30 minutes either side of the standard.

In contrast, due to the time taken to take replicate measurements of the calibration cylinders (at least 240 mins) only the first 20-minute measurement block of each calibration cylinder is significantly humidified. with the water content of the calibration measurement dropping rapidly to < 0.02 % H₂O (10 to 20 % of the typical ambient air measurements). However, the exact level of humidification varies with ambient humidity and temperature. As such, in an effort to maintain consistency between calibration runs all runs with > 0.02 % H₂O were excluded from analysis.”

Page 25, line 13 – Page 26, line 2: “The poor performance of the CRDS pressure sensor at low H₂O mole fractions, 0.02 to 0.5 % H₂O, is not expected to be a large source of error for undried samples as the majority of these, 92 % of the BSD and HFD data, contain > 0.5 % H₂O. But this could be a source of error for Nafion® dried samples where low moisture contents are typically obtained. However, for this study, where 95 % of HFD and 92 % of BSD Nafion® dried samples contain < 0.5 % H₂O, this effect is expected to be substantially mitigated by the humidification of the daily standard. As described earlier (Section 2.3.9 and Figure S1) the moisture content of the daily standard closely tracks that of the ambient air with the standard mean moisture content almost 90% that of the ambient air. Hence the bulk of the error in the H₂O correction at lower water contents should be accounted for during the drift correction process.

In contrast, without the humidification of the standard the error when Nafion® drying may well be significant. It is difficult to quantify this error, as it will vary with sample water content and the sensitivity of the individual instrument’s pressure sensor to low H₂O mole fractions. However, assuming that the residuals of the droplet water tests are an accurate reflection of the likely error (Figure S8), we expect there to be a systematic offset of the order of -0.05 to -0.1 $\mu\text{mol mol}^{-1}$ CO₂ and -1 to -2 nmol mol⁻¹ CH₄. Assuming that a 90 % match in sample and standard moisture content equates to a 90% reduction in offset then we can estimate the offset in the BDS and HFD data as between 0.005 and 0.01 $\mu\text{mol mol}^{-1}$ CO₂ and -0.1 to -0.2 nmol mol⁻¹ CH₄, negligible in comparison to the WMO reproducibility guidelines.”

2. *A more detailed discussion of the advantages and disadvantages of the two drying techniques namely the advantage to the Nafion® based drying system in terms of minimising systematic error and practicality and the use of an annually determined water correction for samples with H₂O < 2%.*

While we have incorporated the reviewer's suggestion of additional discussion of the pros and cons of the two drying systems and the use of an annually determined water correction for samples with $\text{H}_2\text{O} < 2\%$ we politely disagree with their conclusion that the Nafion® based drying system is superior. Instead, we would contend that both approaches have advantages and the choice of method should be based primarily on the humidity and accessibility of the site in question. We have broadened the discussion in the conclusions section to make this apparent.

Page 30, line 10 – Page 31, line 26: “The two drying methods implemented at Bilsdale and Heathfield - Nafion® drying with an empirical water correction and an annual empirical water correction without drying - have a number of practical and scientific advantages and disadvantages. The Nafion® drying method, once installed and running correctly can provide reliable drying to between 0.05 and 0.2 % H_2O . While this method requires little on-going maintenance if the TOC fails, as has occurred at a number of UoB run tall tower sites, then the replacement of the entire TOC system or removal and repair off site is required. Due to the expense of the TOC instrumentation having spares available for immediate installation is often not practicable. The sporadic and unpredictable nature of these failures also makes it impossible to incorporate this into routine scheduled site visits. As such, a failure of this nature typically leads to multiple unscheduled trips to site and periods of poor drying. In contrast, using an annual empirical requires a single trip to site which can be easily scheduled as part of routine site maintenance. Allowing time for leak checking and at least three replicate droplet tests such a trip would generally take 2-3 days. As such, for remote or difficult to access sites the annual empirical water correction is preferred.

As shown in Table 5, the systematic errors associated with the Nafion® drying method, as applied at these two sites, was small, $< 0.01 \mu\text{mol mol}^{-1}$ of CO_2 and $< 0.2 \text{ nmol mol}^{-1}$ of CH_4 , and did not vary with sample water content. However, care must be taken with the implementation of the method as, for samples with water content $> 0.7\%$, an additional $0.02 \mu\text{mol mol}^{-1}$ of CO_2 was lost from the sample across the membrane. Even samples as dry as the calibration gases were affected by this loss, although to a smaller degree ($\sim 0.015 \mu\text{mol mol}^{-1}$ for $\text{H}_2\text{O} < 0.0001\%$) as residual moisture remained in the membrane. However, as in this application of the method the calibration gases are dried in an identical manner to the samples, this loss is mostly calibrated out with only a very small ($\leq 0.005 \mu\text{mol mol}^{-1}$) constant residual bias of the order of the instrumental precision. As such, when using a Nafion® based drying method it is essential that the calibration and standard gases are dried in an identical manner to the samples.

By comparison the annual CRDS empirical water correction has a narrower optimum range with minimal systematic errors only at water contents very near 0% and between 0.5 and 2.5% H_2O (Figures 8, 9, S8 and S9). As such, the choice to use an annual empirical water correction method alone must be strongly influenced by the ambient humidity of the site of interest. Estimates of these systematic errors (Table 5), determined for different water content ranges, were based on the water correction residuals (Figure S8) and the temporal variability in the annual H_2O corrections at each site (Figures 8a and b). The maximum error associated with the empirical water correction alone ranged between 0.05 and 0.2 $\mu\text{mol mol}^{-1}$ CO_2 and 1 and 3 nmol mol^{-1} CH_4 with the majority of observations at the lower end of the range. It is important to note that these estimates

were calculated for the Picarro CRDS and may vary significantly to those of other CRDS instrumentation or optical techniques that use alternative cell pressure sensors (Reum et al., 2018).

This weakness in the CRDS water correction also has notable implications for sample drying. Namely, while sample drying may not be an inherent source of bias, the partial drying of the sample puts it within the range of peak error in the CRDS water correction (0.05 to 0.5 % H₂O). This source of error, as demonstrated in the implementation of the Nafion® based drying system outlined here, can be mitigated by matching the water content of the daily standard to the sample. Again this re-emphasises the importance of treating the sample, standards and calibration gases in an identical manner.

Considering the relatively narrow humidity range observed at Bilsdale and Heathfield, with no observations > 2.4 % H₂O and > 95 % of observations > 0.5 % H₂O (> 99 % > 0.35 % H₂O) and the relative remoteness of the locations the decision to remove the Nafion® based drying systems and rely on the annual empirical water correction appears justified. In contrast, at other more easily accessible or more humid sites the use of a Nafion® based drying system may be more advantageous.”

3. *A discussion of the significance of the systematic errors in terms of the goals of the UK tall tower network and a conclusion in terms of the optimum drying process for the network.*

Page 32, lines 1 - 8: “While these errors are significant relative to the WMO internal reproducibility goals they are for the majority of observations smaller than the extended WMO measurement compatibility goals ($\pm 0.2 \mu\text{mol mol}^{-1} \text{CO}_2$ and $\pm 5 \text{nmol mol}^{-1} \text{CH}_4$). It is also important to note that they are orders of magnitude smaller than baseline excursions observed at the sites (see Figures 4 & 5). They are also a factor of 10 smaller than the CH₄ model-data mismatch within the UK DECC network as estimated by Ganesan et al. (2015) at $\sim 20 \text{nmol mol}^{-1}$. Considering this difference, it is highly unlikely that, without significant improvement in modelled atmospheric transport, the systematic errors reported here would significantly alter estimates of UK-scale GHG fluxes or impede national emissions verification efforts.”

Page 31, lines 22 - 26: “Considering the relatively narrow humidity range observed at Bilsdale and Heathfield, with no observations > 2.4 % H₂O and > 95 % of observations > 0.5 % H₂O (> 99 % > 0.35 % H₂O) and the relative remoteness of the locations the decision to remove the Nafion® based drying systems and rely on the annual empirical water correction appears justified. In contrast, at other more easily accessible or more humid sites the use of a Nafion® based drying system may be more advantageous.”

4. *A reemphasis of the importance when using Nafion® drying systems of drying the calibration and standards gases in an identical manner to the sample to account for any loss of CO₂ across the membrane.*

This has been highlighted on:

Page 31, lines 3-4: “As such, when using a Nafion® based drying method it is essential that the calibration and standard gases are dried in an identical manner to the samples.”

Page 31, lines 20-21: “Again this re-emphasises the importance of treating the sample, standards and calibration gases in an identical manner.”

Specific comments:

5 page 4, line 19: uncertainties related to other components (such as?) sample collection

Page 4, line 19: The text “such as” has been inserted in to the sentence

page 7, line 2: Nafion drying performance is a strong function of temperature (see product literature). How much did nafion membrane temperature vary seasonally and/or diurnally. Might nafion temperature be the driver of output sample humidity variability rather than input sample humidity? In order to understand the extent to which water correction systematic errors are calibrated out, it would be useful to include a figure showing the extent to which humidified calibration gas air typically resembles dried sample air (and/or worst case difference between sample and standard humidity as measured by the CRDS). To what extent do daily drift correction calibrations capture variations in humidity at the CRDS? (see Figure 7 of Andrews et al., <https://www.atmos-meas-tech.net/7/647/2014/amt-7-647-2014.pdf>) If nafion output humidity is very smooth in time, then the daily drift corrections may entirely mitigate errors due to the CRDS water correction. If this is the case, then the original configuration with the nafion would seem to be the superior method, since instrument-specific and time-dependent h₂o corrections would be unnecessary. What can you say about the extent to which variations in the dried sample air humidity drive day-to-day drift in the CRDS signal during the period when the nafion was installed? See the response to point 1 of “Overall framing” (above) and alterations/additions to the text found on Page 7, lines 3 – 7, Page 7, lines 13 – 15, Page 15, line 23 – Page 16, line 13 and Page 25, line 13 – Page 26, line 2 as given above.

page 8, line 10: wet/mean(dry)?

Page 8, line 20: This has been corrected to mean “wet”/“dry”

25 page 9 line 12: Here, dry air from four cylinders with varying CO₂... was humidified.

Page 9, line 22: Corrected

page 9, line 22: An experiment was designed *to* observe

Page 11, line 20: Corrected

page 9, line 24: Not sure why it is necessary to mention the series of inconclusive experiments

Page 11, line 18: Sentence removed.

5 page 11, line 15, "all components of the cylinder air path between the DPG and the multiport valve, excluding the water trap, and the pump"

--> does the water trap refer to the cryotrap? This is confusing because according to the text and the drawing neither the cryotrap nor the pump are located between the DPG and the multiport valve.

Page 10, line 24: We thank the reviewer for noting this. It has been corrected.

10

Page 12, equation (1), it seems unnecessary/trivial to define $\text{TrueCP} = \text{CPin}$. I can't think of a reason to suspect that it would be otherwise.

Page 13, equation (1), we can understand the perspective of the reviewer however for completeness and to maintain

15 consistency in the notation we would prefer to leave the equation as it stands.

Page 13, line 12, "These experiments assume that any changes in the CO₂ or CH₄ mole fraction are driven solely by the Nafion drying process..."

20 --> Is it not the case that the experiment was designed to isolate the impact of the other possible sources of error or bias that are identified, i.e. I think the setup aims to measure differences that are solely due to the Nafion. Maybe I do not understand how the data are analyzed.

Yes, experiment 2.3.7 was designed to isolate the differences due solely to the Nafion®. However, as with all experiments there is the possibility that small biases or errors may occur. This section explores these. The opening paragraph has been rewritten to clarify this.

25 Page 14, lines 4-8: "While experiments 2.3.5, 2.3.6 and 2.3.7 were designed to isolate key processes, for example experiment 2.3.7 examined changes in the CO₂ or CH₄ mole fraction driven by the Nafion® drying processes other possible sources of error or bias may exist. These include, adsorption and desorption effects within the regulator and walls of the tubing, gas solubility within the condenser of the dew point generator and instrumental drift."

30 page 14, line 4: dependent, not depended

Page 14, line 25: Corrected

page 14, line 25: according to Stanley et al 2018, the daily standard is measured for 20 minutes. Please state that here also. Is the standard always measured at the same time of day? Or does it run on e.g. a 21 or 23 hour cycle so that it rotates throughout the day in order to check for sensitivity to room temperature variations or similar.

5 Page 15, line 20: Yes, the daily standard is measured for 20 minutes. This information has now been included in the text. This is conducted at a fixed time of the day. However, that time of day is manually adjusted sometimes to allow for instrument servicing or when specific events (e.g. flight over passes) are taking place. The suggestion of adjusting it to a 21- or 23-hour cycle is interesting and something to consider.

10 page 15, line 16: Can you rule out the worst case scenario of -0.155 ppm bias (i.e. based on the likely fraction of added industrial air in your standards)? Possible bias of -0.155 is obviously quite large compared to other systematic errors related to water that are the focus of this paper. Why has there not been more effort to quantify this possible source of bias for these installations? It could be easily addressed by having the cylinders measured for $^{13}\text{CO}_2$. Perhaps the labs that supplied the calibration gases could provide information about the isotopic abundance of their spiking/dilution cylinders so that you could
15 make a specific estimate of the errors (and correct them) for each set of unique calibration gases used at the sites. Given the amount of verbiage devoted to the 0.02 ppm nafion error above, the authors seem remarkably unconcerned about the possible impacts of isotopic composition of the standards on the reported ambient CO_2 values.

Due to the, already considerable, length of the paper and its focus on the drying strategies a more detailed discussion of the impact of the isotopic composition of the calibration gases will be included in a future paper.

20 Page 32, Lines 12-14: “The development of a full uncertainty analysis incorporating such target tank measurements, along with an assessment of the calibration strategy, instrumental, water correction and sampling errors and errors induced by the isotopic composition of the calibration gases is also planned.”

page 26, line 20, is the average standard deviation of the 15 min block means really 0.002 ppm, or is that the standard error
25 (Where the std dev has been divided by \sqrt{N}).

It's the average standard deviation of the 15-minute block means not the standard error.

page 26: A nafion membrane can store quite a lot of water. I think the results of this test may depend on how the membrane was conditioned. A membrane that has been conditioned with ambient air at e.g. 2.5% humidity for several days may be
30 more permeable than a membrane that has been conditioned with dry air from a cylinder. The permeability of the membrane might also depend on its temperature. How might these tendencies map onto the dataset (i.e. how was the membrane conditioned prior to the experiment and how does the level of water stored in the membrane compare to what is expected in

the field in the summer during a high-humidity event)? Might the membrane be more permeable if it were equilibrated with high-humidity air). Perhaps the day-to-day variations of the ambient standard for the period when the nafion membrane was installed at the field sites might reflect changes in nafion permeability. It would be useful to repeat this experiment to explore whether permeability is impacted by the amount of water stored in the membrane (i.e. flow air with >2% h₂o through the nafion for several days prior to starting the test). Andrews et al. also reported permeability of nafion for co₂ (page 652,653), but with a somewhat different configuration. They found cross-membrane transport of 0.1 ppm CO₂ for a partial pressure gradient of ~1700 hPa - 265 hPa = 1435, which is approximately proportional to your finding of 0.02 ppm co₂ difference for a ~400 hPa gradient.

Indeed, as reported in other papers the permeability of the Nafion® is can be influenced by temperature and moisture content along with membrane age and other factors (e.g. Naudy et al. (2014); Collette et al. (2009); Ma and Skou (2007)). However, as shown by Ma and Skou (2007), who compared the permeability of a water soaked and water equilibrated membrane, the moisture content dependence is small, typically of the order of the variability of the permeability measurement (see Figure 4, Ma and Skou (2007)). While comparisons between the wet membranes and a completely dry Nafion® showed significant differences in CO₂ permeability (c.f. Figure 4 and Figure 5, Ma and Skou (2007)) this dry membrane was prepared for 48 hours in a vacuum oven at 40°C and is, therefore, not representative of the laboratory or field conditions described in this paper. Similarly, considering the expected range of temperatures (20 – 40°C) experienced by the Nafion® membranes deployed in our experiments the temperature driven shifts in permeability observed by Ma and Skou (2007) were far smaller than the measurement precision. As such, while future experiments looking into the effects of these parameters may be of interest we consider them outside the scope of the current article.

Page 28, line 3: I don't agree with the current wording. So long as calibration gases are passed through the nafion then no significant bias is introduced by this implementation of the nafion drying method. The rest of the paragraph is fine, but I think the opening sentence is confusing.

Page 30, line 25 – Page 31, line 3: The paragraph has been reworded, now reading “However, care must be taken with the implementation of the method as, for samples with water content > 0.7 %, an additional 0.02 μmol mol⁻¹ of CO₂ was lost from the sample across the membrane. Even samples as dry as the calibration gases were affected by this loss, although to a smaller degree (~ 0.015 μmol mol⁻¹ for H₂O < 0.0001 %) as residual moisture remained in the membrane. However, as in this application of the method the calibration gases are dried in an identical manner to the samples, this loss is mostly calibrated out with only a very small (≤ 0.005 μmol mol⁻¹) constant residual bias of the order of the instrumental precision.”

Page 28, line 15: I am confused about how these data are being post-processed to apply the calibration data from the field analyzer. The text says: "Altering the drying method to better match the moisture content of the calibration gases to the sample may minimise this error." For the early period where the nafion was deployed, is it not the case that the nafion humidified standards and the nafion-dried ambient air samples have the same humidity by the time they enter the CRDS? Or does the

nafion membrane dry out significantly during the 20-minute calibration interval. The Nafion® membrane dries out only slightly during the 20-minute measurement of the standards, with the standard and the ambient air samples having very similar moisture contents.

5 Page 15, line 28 – Page 16, line 1: “On average the standard has a mean moisture content 88 % that of the average of the 30 mins of air sample either side of the standard (on average 0.02 % H₂O lower).”

Page 28: In this conclusions section, it would be helpful to make a clear distinction between the early period where the nafion was installed versus the later period with no nafion. It seems that the systematic errors associated with the h₂o correction are likely substantially larger during the later period. Also, it would be appropriate to include a brief
10 discussion/summary of the pros and cons of each method, including complexity of implementation for the latter period when annual water calibrations for each crds analyzer were used but evidently with little reduction in uncertainty (given the relatively large variability seen in the daily and weekly lab water corrections.)

See the response to point 2 of “Overall framing” (above) and additions/alterations to the text found on Page 30, Line 10 – Page 31, Line 26.

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page 28, line 20: How are you computing the max errors reported in Table 5? It looks like they are perhaps based on the residuals plots shown in Fig S5. But how are you accounting for uncertainty in the annual h₂o correction itself? For cases such as BSD 2016 vs 2017 in Fig 8a, there are large differences between subsequent H₂O corrections. Given that and the weekly variability for UoB in the weekly tests, how do you estimate the errors associated with assuming that a single
20 realization of the H₂O correction equation is valid on a particular day?

The maximum errors reported in Table 5 are an estimate based on both the residuals plotted in Fig S5, which represent an estimate of the error at a specific point in time, while the temporal uncertainty in the annual H₂O correction for each site is estimated from the absolute difference between consecutive annual water tests. Specifically, we combine the maximum residual-based error with the drift in the H₂O correction in quadrature for the given water content range. This is a worst-case
25 scenario estimate. The temporal uncertainty in the H₂O correction could also be approximated by examining the variability in the weekly UoB H₂O tests as suggested by the reviewer. Estimating this uncertainty using the standard deviation of the weekly runs gives, to a single significant figure, the same uncertainty estimates as those in Table 5. A summary of this method is now included in the text (Page 31, lines 8-10).

30 page 28, line 27: "While drift in the instrumental water correction typically small it is important that it is identified and accounted for through regular water tests." This could be clarified and elaborated upon. My reading is that the annual h₂o tests don't seem to provide much reduction in uncertainty, given the results in Fig 8e and f versus Fig 8a and b. Weekly tests would

apparently provide little benefit given that the week to week scatter is comparable to the differences among the annual tests. I do think it's a good idea to check the h₂o correction at least annually if possible, but the droplet test has documented problems and returning an instrument to the lab for a more rigorous test could lead to lengthy data gaps. Given that the nafion errors are quite small based on tests done to date, it would be useful to include a few sentences about whether they should be reinstalled in the future.

Due to the restructure of the conclusion the line referred to here has been removed, however, we completely agree with the reviewer that an increase in the frequency of the water correction tests above that of an annual check is unlikely to significantly reduce the uncertainty, particularly for moisture contents between 0.5 and 2.5% H₂O. As discussed in the text rather than attempting to capture the temporal variability of the water correction we suggest that:

10 Page 26, Lines 23-25: “In light of the temporal variability of the water correction over time at higher water contents for sites with high humidity (> 2 % H₂O) using a Nafion® dryer or alternative drying method to obtain a relatively low and stable sample water content would be an advantage.”

We also note that:

15 Page 27, Lines 2-8: “...within the bounds of the data typically observed at the BSD and HFD sites, the use of annually derived instrument specific water corrections are sufficient. This may not be the case at sites with higher levels of humidity and CO₂ and CH₄ mole fractions where water corrections may need to be determined more frequently, perhaps even weekly. The impracticality of such a frequent testing regime along with the apparent unreliability of the droplet test at H₂O > 2.5 % (for example Figure S8g) mean that an alternative method, possibly partial drying, or a higher level of uncertainty may need to be applied to measurements made at higher water contents.”

20 Finally, while the systematic errors of the Nafion® drying approach appear small there are no plans to reinstate these drying systems. As:

25 Page 31, Lines 22-25: “Considering the relatively narrow humidity range observed at Bilsdale and Heathfield, with no observations > 2.4 % H₂O and > 95 % of observations > 0.5 % H₂O (> 99 % > 0.35 % H₂O) and the relative remoteness of the locations the decision to remove the Nafion® based drying systems and rely on the annual empirical water correction appears justified.”

page 29: line 6: Perhaps reprocessing of the data to implement a post-hoc water correction to remove/mitigate the systematic and humidity dependent errors that are evident in Fig S5 should be considered. Such a correction would be different for the nafion and no-nafion periods. Perhaps no correction would be required for the initial period with the nafion driers.

30 This is indeed an interesting option for future work. We have added the following text to the conclusions in an effort to incorporate this suggestion.

Page 32, Line 15 – 17: –“ Further work to fully characterise the humidity dependent error in the water correction of each instrument, like that of (Reum et al., 2018), possibly using a piecewise post hoc correction, would also be beneficial in an effort to reduce the estimated error associated with the observations.”

5 Figure 3: define DPG in the legend or caption.

Figure 3: Done

Fig 4: Have these been filtered? It is surprising that 42m CO₂ is not significantly higher than upper levels during summer night time.

10 Fig 4: These have not been filtered. As can be seen in the diurnal cycle shown in Figure 6 the 42m intake (blue) is often 1-2 ppm higher than the higher intakes during summer night time periods.

Fig 5: caption refers to mean diurnal cycle, but that seems to appear in Fig 6.

Fig 5: Corrected

15

Fig 6, 7. Figures are hard to read due to small size and overlapping symbols/bars. Maybe it is not practical to show figures for all molecules in the body of the paper.

We completely agree with the reviewer that the figures are difficult to read. However, as we feel that all gases are of interest rather than removing some from the figures we have instead adopted a simpler plotting strategy. This new strategy, based on that of Satar et al. (2016), presents diurnal and seasonal cycles based on the means of trimmed linearly detrended data. These plots are far easier to read and have the advantage of retaining all the gases of interest.

Page 19, line 18 - 23: - Updated to describe the new plotting strategy.

25 “The long-term trend in mole fraction at each site was estimated as the mean linear trend in the minute mean data over the period 2014-2017, inclusive. Seasonal and diurnal trends in the data were assessed using monthly and hour-of-day means of trimmed detrended minute-mean data developed using the Python numpy package. Here the long-term trend was removed by using a least-squares fit between a quadratic and the minute mean data. The data for each hour (or month for the seasonal plots) were trimmed following the approach of Satar et al. (2016) who removed the highest and lowest 5% of all data points.”

New Figures 6 & 7

Figure 8: references to the individual panels in the caption are awkward and confusing. Also, (c & d) look to be daily and (e & f) look to be weekly, which seems to be opposite from the caption

5 Figure 8: The caption has been clarified now reading “The change with water in the difference in CO₂ and CH₄ dry mole fraction between: the first annual mean instrument specific water correction and subsequent annual corrections (a & b); the first individual water correction and subsequent daily corrections (c & d) and the first individual water correction and subsequent weekly tests (e & f). The daily and weekly tests were conducted using only the UoB instrument while the annual tests were conducted using all three instruments.”

10 Figure 10: I don't understand the point of Figure 10 b & d, which seem to show only that the cryogenic drier was working. Figure 10 b and d and references to these figures have been removed. Figure 10 c has been relabelled as Figure 10 b.

Supplement page 1, line 16: error in stated range for F3 0.5 - 0.5 L per min

Corrected to 0.1 – 0.5 L min⁻¹.

15

Figure S1 caption: instead of writing "TOC" in the caption, consider "writing gas generator used to supply the counterpurge flow"

20 Caption changed. It now reads “Figure S1: (a) CO₂, (b) CH₄, (c) CO and (d) H₂O mole fractions of the gas generator used to supply the Nafion® counter purge flow. Note the HFD gas generator was powered up just before to analysis in contrast to the other sites where the TOCs had been running for at least 12 hours prior to analysis.”

Figure S5g and Figure S6: What is the explanation for the negative values at high water in the CO₂ water correction residuals at U of Bristol but not seen at the field sites?

25 While much less common at sites other than the University of Bristol (UoB) negative residual values are evident at high water contents for both the Heathfield and Bilsdale sites (see Figure S8 a, c and e). We expect they appear more common at UoB as the data shown in Figure S9 g for UoB is from 13 droplet tests compared to a maximum of three for the other sites.

30 Figure S5: Given that the residuals show similar structure for most sites/years (i.e. CO₂ and CH₄ residuals are negative at low H₂O), could the water correction be improved by using a piecewise correction or a post-hoc correction to remove the systematic residuals that are typical with the current approach?

This is indeed an interesting option for future work. We have added the following text to the conclusions in an effort to incorporate this suggestion.

Page 32, Line 15 – 17: –“ Further work to fully characterise the humidity dependent error in the water correction of each instrument, like that of (Reum et al., 2018), possibly using a piecewise post hoc correction, would also be beneficial in an effort to reduce the estimated error associated with the observations.”

- 5 Collette, F. M., Lorentz, C., Gebel, G., and ThomINETTE, F.: Hygrothermal aging of Nafion®, *Journal of Membrane Science*, 330, 21-29, <http://dx.doi.org/10.1016/j.memsci.2008.11.048>, 2009.
- Ganesan, A. L., Manning, A. J., Grant, A., Young, D., Oram, D. E., Sturges, W. T., Moncrieff, J. B., and O'Doherty, S.: Quantifying methane and nitrous oxide emissions from the UK and Ireland using a national-scale monitoring network, *Atmos. Chem. Phys.*, 15, 6393-6406, [10.5194/acp-15-6393-2015](https://doi.org/10.5194/acp-15-6393-2015), 2015.
- 10 Ma, S., and Skou, E.: CO₂ permeability in Nafion® EW1100 at elevated temperature, *Solid State Ionics*, 178, 615-619, [dx.doi.org/10.1016/j.ssi.2007.01.030](https://doi.org/10.1016/j.ssi.2007.01.030), 2007.
- Naudy, S., Collette, F., ThomINETTE, F., Gebel, G., and Espuche, E.: Influence of hygrothermal aging on the gas and water transport properties of Nafion® membranes, *Journal of Membrane Science*, 451, 293-304, [dx.doi.org/10.1016/j.memsci.2013.10.013](https://doi.org/10.1016/j.memsci.2013.10.013), 2014.
- 15 Reum, F., Gerbig, C., Lavric, J. V., Rella, C. W., and Göckede, M.: Correcting atmospheric CO₂ and CH₄ mole fractions obtained with Picarro analyzers for sensitivity of cavity pressure to water vapor, *Atmos. Meas. Tech. Discuss.*, 2018, 1-29, [10.5194/amt-2018-242](https://doi.org/10.5194/amt-2018-242), 2018.
- Satar, E., Berhanu, T. A., Brunner, D., Henne, S., and Leuenberger, M.: Continuous CO₂/CH₄/CO measurements (2012–2014) at Beromünster tall tower station in Switzerland, *Biogeosciences*, 13, 2623-2635, [10.5194/bg-13-2623-2016](https://doi.org/10.5194/bg-13-2623-2016), 2016.

20

Reply to editors' comments

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The authors would like to thank the editor, Dominik Brunner, for his helpful comments. We have endeavoured to incorporate all the suggestions that he has made. The locations of changes to the paper are given as Page Number, Line number of the new paper while his comments contain the locations in the original paper. Our responses are shown here in blue text and the editors' comments in black.

15

Associate Editor Decision: Publish subject to minor revisions (review by editor) (04 Apr 2019) by Dominik Brunner
Comments to the Author:

Dear authors,

20

Thank you very much for the amendments to the manuscript and detailed responses to the reviewers. By dropping the inverse modelling part the publication has clearly gained in focus and conciseness.

25

Reviewer #1 reassessed your revised manuscript and, overall, was satisfied with the changes. However, the reviewer has a number of further comments I would like you to consider.

In particular, the reviewer would like to see more discussion of the advantages and disadvantages of active drying (original configuration) versus no drying but compensating for errors through frequent droplet tests (current configuration).

Following the suggestion of Reviewer #1 we have incorporated a fuller discussion of the advantages of an active drying configuration in the "Conclusions and future work" section of the paper. Specifically, we have added

30

Page 30, line 10 – Page 31, line 27: "The two drying methods implemented at Bilsdale and Heathfield - Nafion® drying with an empirical water correction and an annual empirical water correction without drying - have a number of practical and scientific advantages and disadvantages. The Nafion® drying method, once installed and running correctly can provide reliable drying to between 0.05 and 0.2 % H₂O. While this method requires little on-going maintenance if the TOC fails, as has occurred at a number of UoB run tall tower sites, then the replacement of the entire TOC system or removal and repair off site is required.

Due to the expense of the TOC instrumentation having spares available for immediate installation is often not practicable. The sporadic and unpredictable nature of these failures also makes it impossible to incorporate this into routine scheduled site visits. As such, a failure of this nature typically leads to multiple unscheduled trips to site and periods of poor drying. In contrast, using an annual empirical requires a single trip to site which can be easily scheduled as part of routine site maintenance. Allowing time for leak checking and at least three replicate droplet tests such a trip would generally take 2-3 days. As such, for remote or difficult to access sites the annual empirical water correction is preferred.

As shown in Table 5, the systematic errors associated with the Nafion® drying method, as applied at these two sites, was small, $< 0.01 \mu\text{mol mol}^{-1}$ of CO_2 and $< 0.2 \text{ nmol mol}^{-1}$ of CH_4 , and did not vary with sample water content. However, care must be taken with the implementation of the method as, for samples with water content $> 0.7 \%$, an additional $0.02 \mu\text{mol mol}^{-1}$ of CO_2 was lost from the sample across the membrane. Even samples as dry as the calibration gases were affected by this loss, although to a smaller degree ($\sim 0.015 \mu\text{mol mol}^{-1}$ for $\text{H}_2\text{O} < 0.0001 \%$) as residual moisture remained in the membrane. However, as in this application of the method the calibration gases are dried in an identical manner to the samples, this loss is mostly calibrated out with only a very small ($\leq 0.005 \mu\text{mol mol}^{-1}$) constant residual bias of the order of the instrumental precision. As such, when using a Nafion® based drying method it is essential that the calibration and standard gases are dried in an identical manner to the samples.

By comparison the annual CRDS empirical water correction has a narrower optimum range with minimal systematic errors only at water contents very near 0% and between 0.5 and 2.5% H_2O (Figures 8, 9, S8 and S9). As such, the choice to use an annual empirical water correction method alone must be strongly influenced by the ambient humidity of the site of interest. Estimates of these systematic errors (Table 5), determined for different water content ranges, were based on the water correction residuals (Figure S8) and the temporal variability in the annual H_2O corrections at each site (Figures 8a and b). The maximum error associated with the empirical water correction alone ranged between 0.05 and $0.2 \mu\text{mol mol}^{-1}$ CO_2 and 1 and 3 nmol mol^{-1} CH_4 with the majority of observations at the lower end of the range. It is important to note that these estimates were calculated for the Picarro CRDS and may vary significantly to those of other CRDS instrumentation or optical techniques that use alternative cell pressure sensors (Reum et al., 2018).

This weakness in the CRDS water correction also has notable implications for sample drying. Namely, while sample drying may not be an inherent source of bias, the partial drying of the sample puts it within the range of peak error in the CRDS water correction (0.05 to 0.5% H_2O). This source of error, as demonstrated in the implementation of the Nafion® based drying system outlined here, can be mitigated by matching the water content of the daily standard to the sample. Again this re-emphasises the importance of treating the sample, standards and calibration gases in an identical manner.

Considering the relatively narrow humidity range observed at Bilsdale and Heathfield, with no observations $> 2.4 \%$ H_2O and $> 95 \%$ of observations $> 0.5 \%$ H_2O ($> 99 \%$ $> 0.35 \%$ H_2O) and the relative remoteness of the locations the decision to remove the Nafion® based drying systems and rely on the annual empirical water correction appears justified. In contrast, at other more easily accessible or more humid sites the use of a Nafion® based drying system may be more advantageous.”

In addition, I read your manuscript carefully myself and have a few additional comments as detailed in the following:

Main points:

5 A new section 2.3.6 an "Assessing the CRDS water correction" has been added. Details of this experiment are reported in the supplement section S1 and Figure S3. Actually, the text in this supplement is partly identical to the text presented later in the main body of the manuscript in Section 2.3.7. I actually think, it would make more sense to present that text here in the new Section 2.3.6 and to shorten Section 2.3.7 accordingly. I thus propose the following changes:

1. Move most of the text currently in Supplement S1 to Section 2.3.6 "Assessing the CRDS water correction." Furthermore, I
10 don't see a reason for placing Figure S3 in the supplement but Figure 3 in the main body of the text. Why not combining the two into a single Figure 3 with panels a) and b). Like this one would immediately see the differences in the setups.

Page 9, line 20 to Page 11, 12 - As suggested by the editor the text in Section S1 has been moved to Section 2.3.6 and Figures 3 and S3 have been combined into a new Figure 3 in the main body of the paper. Figure S3 has been removed from the supplement.

15

2. Remove all parts of the text in Section 2.3.7, that would now be described under "Assessing the CRDS water correction". Actually, in Section 2.3.7 you could simply state that the experimental setup is very similar to 2.3.6, but with modifications XYZ.

As far as I can see, those parts in Section 2.3.7 that could be dropped to avoid repetition include P10, Lines 10-17, P11,

20 Lines13-19, P12, Lines 7-11.

As suggested by the editor we have removed the lines listed above.

3. Please also make clear that the same CRDS G2301 at UoB was used in all experiments. Currently, you state in 2.3.6 that "a Picarro G2301" was used, but it remains unclear whether this is the same as in 2.3.5.

25 This has now been made clear.

Page 9, lines 24: "...using the same Picarro G2301 CRDS used in Sections 2.3.5 and 2.3.7."

Page 11, lines 19-20: "... UoB laboratory Picarro CRDS as used in Sections 2.3.5 and 2.3.6"

30 Another concern I have is that the loss of CO₂ across the Nafion membrane may not be quantified from the experiment as it is done currently. The loss is currently quantified as 0.02 $\mu\text{mol mol}^{-1}$ (e.g. page 27, Line 7), based on the differences between CP_{in} and CP_{out} measurements in the experiment described in 2.3.7. However, if the flow rate (and pressure?) of the counter purge air is not the same as the flow rate of the sample, the change in mole fraction in the counter purge air is not identical to the corresponding change in the sample.

We thank the editor for this note, however we feel it is important to note that CRDS used in these experiments does not

sample the whole counter purge gas stream. Instead it takes a highly pressure-controlled subsample of the counter purge gas (See Figure 3). As such, while the native flow rates and pressures of the counter purge gas and air samples may differ the pressure of the gas within the CRDS sample cell is held at 140 ± 0.05 Torr. Hence, the pressures of the sample and counter purge are matched during measurement and therefore a change in the mole fraction of the counter purge air should be
5 identical to the change in the sample.

Small points:

- Page 7, line 1: Here it is stated that the Nafion drying results in air samples with water mole fractions between 0.05 and 0.2%. At the end of Section 2.3.1 (P6, L23), however, a value of $<0.0002\%$ H₂O is mentioned for the samples with Nafion
10 drying. I have difficulties bringing these numbers together. In addition, how can the samples become dryer than the counter-purge air (which has humidity of $<0.005\%$ H₂O)?

The figure of 0.0002% H₂O is taken directly from Young, 2007. This measurement was made of the GC-ECD Nafion using a Xentuar portable dewpoint meter. In comparison the reference on Page 7, line 1 (now Page 8, lines 4-5) is to the counter
15 purge of the CRDS Nafion® and was made using the CRDS. Similarly, measurements of the counter purge air given in the text were made using the CRDS. As such differences between these numbers may be due to calibration and sensitivity differences between the CRDS and the Xentuar portable dewpoint meter. It is also important to note that the counter purge flow rates differ significantly between the two, with the GC-ECD counter purge flow rate typically 5 times higher than the CRDS counter purge. The large difference in relative flow rates between the sample and counter purge of the GC-ECD Nafion® greatly increases the drying capacity of the counter purge air stream. The text has been altered to provide more
20 details.

Page 6, Lines 24 – 26: “Previous examinations of this drying method using a Xentuar portable dewpoint meter have found that samples are dried to dew points of around -40°C when using a counter purge at approximately -70°C (Young, 2007).”

- P7, L4: Change "membrane this drying" to "membrane, this drying"
25 Page 7, Line 10: Done

- P7, L3-5: Long sentence that is difficult to understand. Should be reformulated.

Page 7, lines 10-13: Reformulated to:

“The CRDS Nafion® drying systems were removed on the 30th of September 2015 & 17th of June 2015 at BSD and HFD,
30 respectively. Following this undried air was analysed and the data post corrected with an instrument specific water correction.”

- P7, L14-15: Sentence "While the CO mole ..." is incomplete.

Page 7, lines 23-14: Rewritten. Now reads:

“Similarly, the zero air CO mole fraction is significantly lower than the minimum CO mole fractions typically observed at the HFD and BSD sites (~ 60 nmol mol⁻¹).”

- P8, L5: Change "effected" to "affected"

5 Page 8, line 15: Corrected

- P8, L7: Change "(Rella et al. 2013)" to "Rella et al. (2013)"

Page 8, line 17: Corrected

10 - P8, L16: Change "for CO however this used" to "for CO. However, this used"

Page 8, line 26: Corrected

- P8, L23: Add comma in "measuring dry air, they often"

Page 9, line 5: Corrected

15

- P9, L7-8: Make clear that the "sub- and above ambient air mole fraction cylinders" refer to CO₂ below or above ambient, not to H₂O.

Page 9, lines 15-17: Now reads “A set of instrument specific water corrections was also determined in triplicate, using dried sub- and above ambient CO₂ and CH₄ mole fraction cylinders.”

20

- P10, L2: Change to "cylinders, one of dry air near"

Page 10, line 20 – Corrected

- P10, L10: Why do you say "but"?

25 Sentence removed

- P10, L13 and later lines: The figure does not show any labels for the T-pieces. There is just no use in calling them T1, T2, etc. in the text.

These have been removed.

30

- P10, L20: delete "valve" after "(Switzerland)"

Page 10, Line 11 - Corrected

- P12, L3: Is this where the third stage starts? Thus, wouldn't it make sense to state "As third stage, the multiport valve was

used to switch .."?

The role of the cryogenic trap in this third stage should probably also be described, or not?

Page 12, line 28 – Page 13, line 2: Corrected to read:

5 “At the start of the third stage, the multiport valve was used to switch between the CP_{in} or CP_{out} flows, measuring each for repeated 20-minute blocks ($n > 3$) at each dew point (see Figure S3 red and blue). The H₂O trap remained inserted in the silicone oil throughout the third stage.”

- P13, L2: You mention that the difference between CP_in and CP_out is also affected by the water correction. Shouldn't you add ".. and the effect of the water correction AT LOW HUMIDITIES."?

10 Page 13, Line 22: Corrected.

- P13, L12-L28: To what extent are these factors specific for experiment 2.3.7 only? The question of regulator and tubing adsorption/desorption effects, for example, seems to be applicable to other experiments as well. Thus why discussing all this here?

15 We thank the editor for this note and have now broadened this section to encompass experimental assumptions relating to experiments 2.3.5, 2.3.6 and 2.3.7. The section is now a stand-alone section (2.3.8 Key experimental assumptions) rather than a subsection of section 2.3.7.

Page 14, lines 4-8: “While experiments 2.3.5, 2.3.6 and 2.3.7 were designed to isolate key processes, for example experiment 2.3.7 examined changes in the CO₂ or CH₄ mole fraction driven by the Nafion® drying processes other possible sources of error or bias may exist. These include, adsorption and desorption effects within the regulator and walls of the tubing, gas solubility within the condenser of the dew point generator and instrumental drift.”

20

- P15, L18: It is unclear how you came up with the number of "<0.04%".

This number was determined based on the typical ambient sample mole fraction of 400 $\mu\text{mol mol}^{-1}$ CO₂ and 2000 nmol mol^{-1} CH₄ and error range of 0.001 – 0.155 $\mu\text{mol mol}^{-1}$ CO₂ and 0.1 – 0.7 nmol mol^{-1} CH₄ as discussed in Griffith (2018). We have edited the text to make this more apparent.

25

Page 17, lines 2-4: “Based on this we expect a worst-case scenario estimate of the error associated with our typical ambient measurements to be < 0.04 % for both CO₂ and CH₄.”

30 - P17, L4: I am somewhat confused about the frequency of calibrations. Here you talk about "daily measurements of 4 standard cylinders at each site", but I thought, that full calibrations were only done once a month.

Yes, full calibrations are completed only monthly. However, a single 20-minute measurement of a standard cylinder is made each day. As these standard cylinders are consumed over time 4 of these types of cylinders have been used at the HFD and

BSD sites, respectively, during the time period examined in this paper (i.e. 8 cylinders in total). We have rewritten the text to clarify this.

Page 18, lines 17-20: “The long-term reproducibility of a 20-minute mean was estimated as the mean standard deviation of the daily 20-minute measurements of the standard cylinders used at each site. A total of 8 standard cylinders have been used
5 in succession at the two sites with the usage periods and CO₂, CH₄ and CO mole fractions listed in Table 3.”

- P17, L5: Should "repeatability" be changed to "reproducibility" also here?

Page 18, line 20: Corrected

10 - P18, L17-19: Strange sentence. Should probably be reformulated (and split in 2 or more sentences).

Page 20, Lines 11-13: Reformulated to read: “In contrast, events that do not show corresponding high CO and CH₄ mole fractions tend to occur in the higher two intakes. As such, they are likely to be driven by more remote CO₂ sources, for example power plants.”

15 - P18, L13: Delete "suggesting a change in the background mole fraction" as this basically repeats what was said in the same sentence before.

Deleted.

- P19: Discussion of the vertical gradients and diurnal profiles at the towers: You could/should discuss your results also in
20 the context of other tall tower studies, notably Winderlich et al. (2010; <https://www.atmos-meas-tech.net/3/1113/2010/amt-3-1113-2010.pdf>) and Satar et al. (2016; <https://www.biogeosciences.net/13/2623/2016/>), especially their Figure 3, which also shows the seasonal evolution of diurnal profiles of CO₂, CH₄ and CO at different vertical levels similar to your Figure 6.

References to these papers have now been incorporated:

Page 20, line 20 to Page 21, line 10: “Both sites show a clear relationship between CO₂ mole fraction and intake height with
25 the lowest height generally having the most elevated mole fractions, followed by the higher heights (Figures 4a & 5a). This trend, also apparent for CH₄ and CO (Figures 4b & c and Figure 5b & c), is typical of tall tower measurements and is driven by proximity to surface sources (Bakwin et al., 1998; Winderlich et al., 2010; Satar et al., 2016). This gradient in CO₂ and CH₄ mole fraction is most apparent in the warmer seasons and during the early hours of the morning (Figure 6a, b, c & d) when the boundary layer is the lowest, a trend observed previously by Winderlich et al. (2010). While a reversal of this gradient, lower
30 heights having lower CO₂ mole fractions, occurs in the middle of the day (Figure 6 a and b). As described in Satar et al. (2016) this decrease in near surface CO₂ is most likely driven by local photosynthetic activity. Interestingly, this trend is also apparent in spring, summer and autumn CH₄ mole fractions at BSD (Figure c) but not HFD (Figure 6d). This suggests a midday sink of CH₄ local to BSD but not HFD. Considering that BSD is located high in the Yorkshire moors (379.1 m a.s.l) while HFD is

located in a lower agricultural region (157.3 m a.s.l) a large difference in soil moisture, and therefore methanotrophic activity (Topp and Pattey, 1997), between the two sites is possible.”

- P19, L13: change ". Suggesting" to ", suggesting"

5 Page 21, lines 15-16: Corrected

- P20, L7: Saying that this comparison is "meaningless" is a bit far stretched. I wouldn't expect the effect of using different calibration scales to be so large to make a comparison meaningless.

Page 22, line 9: Changed to “difficult to interpret”.

10

- P20, L17: I guess that agriculture is the main source of N₂O. I wouldn't call this a "point source".

Page 22, line 19: Changed from “local point sources” to “local sources”.

- P21, L2: Change to "In contrast, in a UK focused inversion study Ganesan et al. (2015) found that .."

15 Page 22, line 4: Corrected

- P22, L2: I think it would be useful to say again how the instrument specific water correction was made. E.g. with "The annual instrument-specific water corrections, determined through regular droplet tests, are typically very similar ... "

Page 23, line 4: Corrected

20

- P24, L26: Change to "may need to be applied"

Page 25, line 7: Corrected

- P25, L24: Change to "The full range of H₂O".

25 Page 28, line 5: Corrected

- P28, L17: The role of the "cell pressure sensors" will not be clear to a reader reading only the conclusions. Probably you should add a reference to Reum et al. here.

Page 31, lines 14-15: Corrected

30

- P28, 27: Change to "While the drift in the instrumental water correction is typically small, it is .."

Sentence removed

- Caption of Figure 8: I think weekly and daily are mixed up here in the last line of the caption.

UK greenhouse gas measurements at two new tall towers for aiding emissions verification

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Abstract. Under the UK focused Greenhouse gAs and Uk and Global Emissions (GAUGE) project, two new tall tower greenhouse gas (GHG) observation sites were established in the 2013/2014 Northern
15 Hemispheric winter. These sites, located at existing telecommunications towers, utilised a combination of cavity ring-down spectroscopy (CRDS) and gas chromatography (GC) to measure key GHGs (CO₂, CH₄, CO, N₂O and SF₆). Measurements were made at multiple intake heights on each tower. CO₂ and CH₄ dry mole fractions were calculated from either CRDS measurements of wet air which were post corrected with an instrument specific empirical correction or samples dried to between 0.05 and 0.3 %
20 H₂O using a Nafion® dryer, with a smaller correction applied for the residual H₂O. The impact of these two drying strategies was examined. Drying with a Nafion® drier was not found to have a significant effect on the observed CH₄ mole fraction; however, Nafion® drying did cause a 0.02 μmol mol⁻¹ CO₂ bias. This bias was stable for sample CO₂ mole fractions between 373 and 514 μmol mol⁻¹ and for sample H₂O up to 3.5 %. As the calibration and standard gases are treated in the same manner, the 0.02 μmol
25 mol⁻¹ CO₂ bias is mostly calibrated out with the residual error (≪ 0.01 μmol mol⁻¹ CO₂) well below the World Meteorological Organization's (WMO) reproducibility requirements. Of more concern was the error associated with the empirical instrument specific water correction algorithms. These corrections are relatively stable and reproducible for samples with H₂O between 0.2 and 2.5 %, CO₂ between 345 and

449 $\mu\text{mol mol}^{-1}$ and CH_4 between 1743 and 2145 nmol mol^{-1} . However, the residual errors in these corrections increase to $> 0.05 \mu\text{mol mol}^{-1}$ for CO_2 and $> 1 \text{ nmol mol}^{-1}$ for CH_4 (greater than the WMO internal reproducibility guidelines) at higher humidities and for samples with very low ($< 0.5 \%$) water content. These errors also scale with the absolute magnitude of the CO_2 and CH_4 mole fraction. As such, water corrections calculated in this manner are not suitable for samples with low ($< 0.5 \%$) or high ($> 2.5 \%$) water contents and either alternative correction methods should be used or partial drying or humidification considered prior to sample analysis.

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1 Introduction

The adverse effects of anthropogenically driven increases of greenhouse gas concentrations on global temperatures and climate have been well established (IPCC, 2013). Governmental efforts to curb these emissions include the UK 2008 Climate Change Act, which will soon be amended to require the UK to produce net-zero emissions by 2050 (Parliament of the United Kingdom, 2008 Chapter 27). This in turn motivated the Greenhouse gAs Uk and Global Emissions (GAUGE) project, which aimed to better quantify the UK carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) emissions. These new emission estimates would then be used to assess the impact of emission abatement and reduction strategies. Key to the GAUGE project was combining new and existing GHG data streams, including high-density regional observation studies, tall tower sites, moving platforms (ferry and aircraft) and satellite observations, with innovative modelling approaches.

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This paper describes the establishment of two new UK GHG tall tower (TT) sites funded under the GAUGE project. Here we provide an analysis of the observations made at the sites and investigate the error associated with empirical instrument specific water correction algorithms and the Nafion®-based sample drying approach used at these TT sites. A further paper, currently in preparation, will discuss the integration of these new sites with the existing UK Deriving Emissions linked to Climate Change (DECC) network (Stanley et al., 2018) funded by the UK Department of Business, Energy and Industrial Strategy (BEIS) and provide a full uncertainty analysis for data collected at all the DECC/GAUGE sites. A second companion paper, also in preparation, will discuss the integration and inter-calibration of all the CO_2 ,

CH₄, CO, N₂O and SF₆ data streams including near surface, tall tower, ferry and aircraft measurements along with an analysis of the impact of identified site biases on UK GHG emission estimates.

Like the UK DECC network, the new sites, Bilsdale (BSD) and Heathfield (HFD), are equipped with a combination of cavity ring-down spectrometer (CRDS) and gas chromatograph (GC) instrumentation
5 (Stanley et al., 2018). These instruments, along with the associated calibration gases (linked to WMO calibration scales) and automated sampling systems are located at the base of telecommunication towers within the UK. Further details of the sites and instruments used along with a description of the data collected to date are provided in the subsequent sections.

The precision, stability, relative autonomy and robustness of CRDS instrumentation has led to a rapid
10 increase in their deployment in global, continental and regional GHG monitoring networks including the GAUGE network, the European Integrated Carbon Observing System (ICOS) (Yver Kwok et al., 2015) and the Indianapolis Flux Experiment (INFLUX) (Turnbull et al., 2015). These instruments also claim the advantage of being able to measure un-dried (“wet”) air samples which are then post corrected to “dry” values using an inbuilt algorithm (Rella, 2010).

15 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;Rella et al.,
20 2013). As such the examination of any errors or biases induced by drying and water correction methods is essential for fully quantifying the uncertainty of CRDS measurements.

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
25 as a counter purge gas. Here, due to the moisture gradient between the sample and the counter purge, the water passed from the wet sample through the membrane to the dry counter purge. Drying in this manner has a history of successful application for the measurements of halocarbons (Foulger and Simmonds, 1979), N₂O (Prinn et al., 1990) and SF₆ (Fraser et al., 2004). However, studies have found that CO₂ and

CH₄ can also pass across a dry Nafion® membrane (Chiou and Paul, 1988) and that this transport increases with the water saturation of the membrane (Naudy et al., 2014). As the transport process is driven by a partial pressure difference between the sample and counter purge gas it is possible that changes in the sample CO₂ and CH₄ mole fraction relative to the counter purge gas, along with the water (H₂O) content of the sample, may alter the magnitude of any cross-membrane leakage.

A study by Welp et al. (2013) examined this issue and concluded that the leakage was small and well within the WMO compatibility guidelines. However, the drying approach used by Welp et al. (2013) is not directly comparable to that of the GAUGE sites as they used dry sample gas as the counter purge rather than zero air. That study also only examined two water contents (0 % or 2 % H₂O) and conducted only dry (0 % H₂O) experiments on samples with CO₂ and CH₄ mole fractions above ambient concentrations. Considering the importance of water in gas transport across the membrane (Chiou and Paul, 1988) and the range of water contents observed in undried air samples measured within the DECC/GAUGE network (up to 3.5 % H₂O) further investigation of this issue was required.

As such, this paper also aims to quantify the magnitude of Nafion® CO₂ and CH₄ transport using the drying method used at the DECC/GAUGE TT sites along with errors associated with instrument specific water corrections. It also examines how these might change within the range of H₂O, CO₂ and CH₄ mole fractions typically observed at these sites. The importance of these errors are assessed in comparison to the WMO internal reproducibility guidelines (WMO, 2018) which incorporate not only the instrumental precision but uncertainties related to other components such as 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.

2 Experimental

2.1 Site descriptions

Two new tall tower sites, Heathfield (HFD; 50.977 °N, 0.231 °E) and Bilsdale (BSD; 54.359 °N, -1.150 °E) were established at existing telecommunication towers in December 2013 and January 2014,

respectively. The general set up of these sites is similar to that described for the DECC sites in Stanley et al. (2018) and the locations of these two new sites relative to these sites described in Stanley et al. (2018) are shown in Figure 1.

The Heathfield tower is located in rural East Sussex, 20 km from the coast and 157.3 m above sea level.

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5 The closest large conurbation (Royal Tunbridge Wells) is located 17 km NNE from the tower. The area surrounding the tower is > 90 % woodland and agricultural areas with some residential (0.7 %) and light industrial areas (0.3 %) (East Sussex in figures, 2006). Notable local industry includes a large horticultural nursery located only 200 m north of the tower.

10 Bilsdale is a remote moorland plateau site within the North York Moors National Park. The base of the tower is located 379.1 m above sea level. It is 25 km NNW of Middlesbrough (the closest large urban area) and 30 km from the coast. The tower is situated in a predominantly rural area, including moorland, woodland, forest and farmland (North York Moors National Park Authority, 2012; Chris Blandford Associates, 2011).

15 Inverted stainless steel intake cups were mounted at 42, 108 and 248 m a.g.l. (metres above ground level) on the BSD tower and 50 and 100 m a.g.l. at HFD. Air was pulled through the intake cups via ½ ” Synflex Dekabon metal/plastic composite tubing (EATON, USA) and a 40 µm filter (SS-8TF-40, Swagelok, UK) using a line pump (DBM20-801 linear pump, GAST Manufacturing, USA) operating at > 15 L min⁻¹. The instruments located at the sites sub-sampled from the tower intakes via a T-piece prior to the line pump. Further details can be found in Stanley et al. (2018).

20 2.2 Instrumentation

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) CO₂, CH₄, CO and H₂O measurements. A GC coupled to a micro-electron capture detector (GC-ECD, Agilent GC-7890) is used to measure N₂O and SF₆ every 10 mins. For further instrumental details, including flow diagrams

25 and column details, see Stanley et al. (2018).

The sample lines, calibration and standard gas cylinders are linked to two multipoint valves (EUTA-CSD10MWEPH, VICI Valco AG International, Switzerland), one for the CRDS and a second for the GC-ECD, the output of each valve is connected to the intakes of the instruments. Filters (7µm, SS-4F-7, Swagelok, UK) are located on the intake lines prior to the valve while a 2µm filter (SS-4F-2, Swagelok, UK) is located between the valve and the CRDS. The GC-ECD flow path, instrumentation and part numbers are described in detail in Stanley et al. (2018). However, in brief, air entering the GC-ECD system is first dried (Section 2.3.1) before flushing an 8 mL sample loop. The contents of the loop are transferred onto a combination of pre-, main and post chromatographic columns using P-5 carrier gas (a mixture of 5 % CH₄ in 95 % Ar; Air Products, UK).

The automated switching of valves and control of GC-ECD temperatures and flows, as well as logging the data and a range of other key parameters (flows, pressures, temperatures) is achieved using custom Linux based software (GCWerks, www.gcwerks.com). The CRDS instrument makes measurements at each intake height, switching between heights every 20 mins at BSD and 30 mins at HFD. While the GC-ECD measures only a single intake, initially the 108 m a.g.l. intake at BSD (switched to the 248 m a.g.l. intake on 17th March 2017) and the 100 m a.g.l. intake at HFD. Other than the tower sample lines, all tubing within the system is 1/16 ", 1/8 " or 1/4 " (O.D.) stainless steel (Supelco, Sigma-Aldrich, UK). A generalised diagram of the original sampling scheme for the two sites is shown in Figure 2.

2.3 Sample Drying and CRDS water correction

2.3.1 GC-ECD

All samples measured on the GC-ECD (air, standards and calibration) are dried using a Nafion® permeation drier (MD-050-72S-1, Permapure, USA) prior to analysis. The counter purge gas for the drier is generated from compressed room air. The counter purge is dried to < 0.005 % H₂O by the compressor (50 PLUS M, EKOM, Slovak Republic) and a gas generator designed for total organic carbon instruments (TOC-1250, Parker Balston, USA). Previous examinations of this drying method using a Xentuar portable dewpoint meter have found that samples are dried to dew points of around -40°C when using a counter purge at approximately -70°C (Young, 2007).

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2.3.2 CRDS

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. When functioning correctly this drying method resulted in air samples with water mole fractions between 0.05 and 0.2 % H₂O depending on the original moisture content of the air and temperature. However, at Bilsdale, due to problems with the TOC and the tubing initially installed at the site, the Nafion® was not drying optimally and significant periods of 2014 had far higher moisture contents (Figure S1). Due to concerns that the mole fraction gradient between the sample and the Nafion® counter purge might lead to CO₂ transport across the Nafion® membrane and difficulties associated with maintaining a complex drying system at remote locations, this drying approach was discontinued. The CRDS Nafion® drying systems were removed on the 30th of September 2015 & 17th of June 2015 at BSD and HFD, respectively. Following this undried air was analysed and the data post corrected with an instrument specific water correction. Plots of the water content of all air samples along with the comparisons of the diurnal and seasonal cycles in sample moisture content can be found in the supplement (Figures S1 and S2).

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2.3.3 Composition of the counter purge dry air stream

As the drying technique implemented in this study uses a Nafion® drier which relies on a dry counter purge air stream measurements of the HFD, BSD and University of Bristol (UoB) laboratory counter purge were made using the HFD, BSD and UoB CRDS instruments, respectively. All counter purge streams showed mole fractions of CO₂ < 0.3 μmol mol⁻¹, CH₄ < 2 nmol mol⁻¹, CO < 12 nmol mol⁻¹ and H₂O < 0.01 % (Figure S3). All these zero air streams have CO₂ and CH₄ mole fractions far lower than the 2015 mean global concentrations, 400.99 μmol mol⁻¹ CO₂ and 1840 nmol mol⁻¹ CH₄ (Dlugokencky and Tans, 2015; Dlugokencky, 2015). Similarly, the zero air CO mole fraction is significantly lower than the minimum CO mole fractions typically observed at the HFD and BSD sites (~ 60 nmol mol⁻¹). As such there is a clear and sizable partial pressure difference across the Nafion® membrane for all three species.

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2.3.4 Calculating instrument specific water corrections

Motivated by the possibility of CO₂ transport across the Nafion® membrane, the decision was made to measure wet samples and correct using an instrument specific water correction. These corrections were determined in the field by conducting a droplet test, similar to those described in Rella et al. (2013). In this test, air from a cylinder of dry (< 0.002 % H₂O) natural air was humidified and the change in CO₂ and CH₄ mole fraction with water content examined. In brief, a 1.5 m length of 3/8 " Synflex Dekabon metal/plastic composite tubing (EATON, USA) was introduced between the standard cylinder outlet and the CRDS intake. Distilled water (0.7 mL) was injected through a septum located on a T-piece fixed on the "cylinder end" of the Dekabon tubing (See Figure S4 for flow diagram). This water evaporated into the sample stream, with the H₂O mole fraction typically peaking at up to 4.5 % (dependent on room temperature) before decreasing to pre-injection concentrations. The effect of this changing H₂O concentration on the raw (without the inbuilt H₂O correction) CO₂ and CH₄ concentrations was then observed. The experiment was repeated in at least triplicate annually.

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 affected by the effect of rapid changes in H₂O content on the cell pressure sensor, as identified by Reum et al. (2018) and the erroneous post-injection CO₂ enhancement identified by Rella et al. (2013). Again, due to cell pressure sensor concerns, data points with minute-mean H₂O standard deviations > 0.5 % H₂O were excluded. This 5-minute cut-off reduced the maximum H₂O value included in the fit to 4 % H₂O.

A water correction was then determined from a fit between the mean "wet"/"dry" ratio and the H₂O of the droplet test data and the equation given by Rella (2010). Here we defined "dry" data as any data with H₂O < 0.003 %, as measured by the CRDS, and the remaining data as "wet". We use minute mean uncorrected CRDS CO₂ and CH₄ data for this analysis, that is, minute averaged data from the "co2_wet" and "ch4_wet" columns of the raw Picarro data files along with data from the "h2o" column. This H₂O data, unlike the "h2o_reported" data has been corrected for spectral self-broadening as detailed in Rella (2010). A similar analysis was conducted for CO. However, this used the "co" data, which has water vapour and line interference corrections applied to it. The raw co values (i.e. "co_wet") are not provided in the CRDS output files.

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The fit was conducted using orthogonal distance regression weighted by both the minute mean standard deviation of the H₂O and gas of interest (CO₂ or CH₄). The resulting correction parameters are shown in Table 1. These corrections were then applied to minute mean observational data through the GCWerks software completely bypassing the built-in CO₂ and CH₄ water corrections.

5 As Picarro analysers are not calibrated for H₂O measurements when measuring dry air, they often show different positive or negative values close to zero. 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 H₂O of the subsequent data (> 60 min).

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10 2.3.5 Temporal stability and mole fraction dependence of instrument specific water corrections

The typical temporal stability and mole fraction dependence of the CRDS water correction was examined using a laboratory based CRDS (G2301, Picarro Inc., USA; CO₂, CH₄ and H₂O series). Here the water correction was determined using the droplet experiment, as described in Section 2.3.4. The mid-term and short-term stabilities were examined by repeating the experiment approximately weekly over a three-month period and daily for a 5-day period using a cylinder of dried ambient mole fraction air. A set of instrument specific water corrections was also determined in triplicate, using dried sub- and above ambient CO₂ and CH₄ mole fraction cylinders. As this instrument was not able to measure CO the effect of CO mole fraction on the CRDS instrument specific water correction is not addressed in this paper.

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2.3.6 Assessing the CRDS water correction

20 The CRDS water correction was assessed through a series of simple Dew Point Generator (DPG; Licor LI-610 Portable Dew Point Generator, USA) experiments. Here, dry air from four cylinders with varying CO₂ and CH₄ mole fractions (Table 2) were humidified to a range of set dew points between 2.5 and 30 °C (0.6 to 3.5 % H₂O) and measured, with and without cryogenic drying, at the University of Bristol (UoB) laboratory using the same Picarro G2301 CRDS used in Sections 2.3.5 and 2.3.7. Cylinder delivery pressure was controlled using single stage high purity stainless steel Parker Veriflow regulators (95930S4PV3304, Parker Balston, USA) or TESCOM regulators (64-2640KA411, Tescom Europe).

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In brief, the output of the cylinder regulator was plumbed to the input of the DPG. A T-piece connected prior to the DPG input vented any excess gas via a flow meter (F1, Figure 3a) ensuring that the DPG input remained at close to ambient atmospheric pressure throughout the experiment. The output of the DPG passed through a second T-piece with the over flow outlet also connected to a flow meter (F2) to ensure that the CRDS input pressure remained near ambient. A third flowmeter (F3) was placed on the outflow of the Nafion counter purge. Flow meters F1 and F2 had a range of 0.1–1 L min⁻¹ (VAF-G1-05M-1, Swagelok, UK) while F3 had a smaller flow range 0.1–0.5 L min⁻¹ (FR2A12BVBN-CP, Cole-Palmer, USA). Typical output flows were 0.1, 0.3 and 0.3 L min⁻¹ for F1, F2 and F3 respectively. After F2 the sample flow was further split using a T-piece, with half the flow passing through a cryogenic water trap before reaching a 4-port 2-position valve, V1 (EUDA-2C6UWEPH, VICI Valco AG International, Switzerland, actually a 6-port valve configured as a 4-port valve). The other half bypassed the water trap and connected directly to V1. One of the outputs of V1 went via the Nafion to a second identical valve, V2, while the second output went directly to V2. The first output of V2 connected directly to the input of the CRDS while the second connected to a pump (PICARRO Vacuum pump S/N PB2K966-A) set to a flow rate matching that of the CRDS (0.3 L/min) to ensure uniform flow through both branches of the system. These valves were controlled manually using a VALCO electronic controller and universal actuator.

The cryogenic water trap consisted of a coil of ¼” diameter (I.D. 3.36mm) stainless steel tubing immersed in a Dewar of silicone oil (Thermo Haake SIL 100, Thermo Fisher Scientific, USA). The silicone oil was cooled using an immersion probe (CC-65, NESLAB) to less than -50 °C. Other than the water trap and two short sections (< 10 cm) of ¼” (O.D.) 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.

The experiment was conducted in a temperature-controlled laboratory at 19 °C, and thus, at temperatures lower than a number of the dew points used within the experiment. Hence, in order to avoid condensation forming on the walls of the tubing all components of the system between the cylinder, excluding the water trap, and the outputs of V2 were contained within a chamber heated to > 32 °C. Tubing between the

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heated chamber and the input of the CRDS was also heated with heating tape to $> 32\text{ }^{\circ}\text{C}$ while the internal temperature of the CRDS was $> 32\text{ }^{\circ}\text{C}$ throughout the experiment.

Multiple measurement blocks of each sample treatment were conducted after a lengthy initial stabilisation period. This period allowed for the establishment of equilibrium between the water in the condenser block of the DPG and the sample gas and lasted at least 2 hours (sometimes up to 5 hours). The treatment blocks varied in length depending on the time required for the concentration to stabilise. At least 15 minutes of data was collected after the concentration stabilised.

It is important to note that the DPG was not calibrated but the H_2O concentration was measured directly by the CRDS during the undried experiments. These values were used as the reference H_2O concentration in all calculations and plots.

Flow rates, cylinder pressure, chamber temperature and H_2O trap temperature were manually logged after each valve position change and when the water trap was inserted into the silicone oil bath.

2.3.7 Quantifying CO_2 and CH_4 cross membrane transport using measurements of the counter purge gas

15 Experimental details

An experiment was designed to observe gas exchange across the Nafion[®] membrane by measuring the counter purge gas before (CP_{in}) and after (CP_{out}) the Nafion[®] while varying the water and CO_2 and CH_4 content of the sample gas stream.

In this experiment, a system (Figure 3b) was constructed allowing the controlled humidification, using a DPG, of two high-pressure cylinders, one of dry near ambient and one above ambient CO_2 and CH_4 mole fraction (Table 2; UoB-15 and UoB-16). These humidified air samples were measured using the UoB laboratory Picarro CRDS as used in Sections 2.3.5 and 2.3.6. This experimental setup is very similar to that described in Section 2.3.6. However, the range of dew points examined was slightly smaller (between 5 and $25\text{ }^{\circ}\text{C}$), equating to water contents of between 0.786 ± 0.001 and $2.883 \pm 0.003\text{ }\%$ H_2O . This limitation was introduced as multiport valve was heated to only $> 25\text{ }^{\circ}\text{C}$.

Other differences include the placement of the Nafion[®], water trap and the addition of a multiport valve. In this experiment the humidified cylinder air exiting the third T-piece is split with half passing through the Nafion[®] before reaching a 4-port 2-position valve, V1 (EUDA-2C6UWEPH, VICI Valco AG

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International, Switzerland, actually a 6-port valve configured as a 4-port valve). The other half bypassed the Nafion® and connected directly to V1. The first output of V1 connected to a multiport valve (EUTA-CSD10MWEPH, VICI Valco AG International, Switzerland) while the second connected to a pump (PICARRO Vacuum pump S/N PB2K966-A) set to a flow rate matching that of the CRDS (0.3 L/min) to ensure uniform flow through both branches of the system. The V1 valve was controlled manually using a VALCO electronic controller and universal actuator while the multiport valve was controlled by the GCWerks software. The output of the multiport valve was connected to the CRDS via the cryogenic water trap (See section 2.3.6).

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Counter purge air, both before (CP_{in}) and after (CP_{out}) the Nafion® were also sampled using the multiport valve. To do this a T-piece was placed on the counter purge tubing prior to the Nafion® connecting to the multiport valve while a second T-piece located after the Nafion® was again connected to the multiport valve. Two flowmeters, F3 and F4, were used to monitor the counter purge flow. Flowmeter F3 was placed on the outflow of the Nafion® counter purge prior to the T-piece while a second F4 was connected to one output branch of the T-piece. These flowmeters had a flow range of 0.1–0.5 L min⁻¹ (FR2A12BVBN-CP, Cole-Palmer, USA). When not sampling the counter purge F3 and F4 had flow rates of 0.4 L min⁻¹, when sampling CP_{out} the F4 flowrate dropped to 0.2 L min⁻¹.

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As the reliability of CRDS water correction was also under investigation it was important to isolate the effect of the Nafion® from that of the CRDS water correction. To do this the experiment was conducted in three stages (see Figure S5). Firstly, the H₂O content of the DPG humidified sample stream was allowed to stabilise (Figure S5 purple). A stable water content was defined as one where the standard deviation of the minute mean values was < 0.003 % H₂O for a 15-min period. During this period the H₂O trap remained out of the Dewar of silicone oil and the CRDS measured an undried, Nafion® bypassed sample, while the secondary pump maintained the flow of DPG sample through the Nafion®. After this criterion was reached the second stage was commenced. Here the H₂O trap was inserted into the silicone oil and the water content monitored until 10 minutes of dry air (defined as < 0.002 % H₂O) was obtained (Figure S5 grey). Together these two stages took typically 2 to 3 hours to complete — allowing the Nafion® time to equilibrate while ensuring that the H₂O trap was drying the sample and the DPG had reached the required set point. At the start of the third stage, the multiport valve was used to switch between the CP_{in} or CP_{out}

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Deleted: 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. The experiment was conducted in a temperature-controlled laboratory at 19 °C, and thus, at temperatures lower than a number of the dew points used within the experiment. Hence, in order to avoid condensation forming on the walls of the tubing, all components of the cylinder air flow path between the DPG and the multiport valve, excluding the water trap, and the pump were contained within a chamber heated to > 32 °C. Tubing between the heated chamber and the input of the CRDS was also heated with heating tape to > 32 °C while the internal temperature of the CRDS was > 32 °C throughout the experiment. The multiport valve was heated to > 25 °C hence only dew points below 25 °C (2.9 % H₂O) were used in this experiment.

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Moved up [3]: The multiport valve was heated to > 25 °C hence only dew points below 25 °C (2.9 % H₂O) were used in this experiment.

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flows, measuring each for repeated 20-minute blocks ($n > 3$) at each dew point (see Figure [S5](#) red and blue). [The H₂O trap remained inserted in the silicone oil throughout the third stage.](#) The experiment was also repeated with the DPG excluded and the cylinder of dried air measured directly, a water content of $< 0.0001\%$ equating to a dew point of $< -70\text{ }^{\circ}\text{C}$.

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5 Data processing

All CO₂ and CH₄ data were corrected using the instrument specific water correction (Section 2.3.4). Minute mean values of all data were calculated from the raw 0.4 Hz data and exported from the GCWerks software. Data processing was completed using code written using the Anaconda distribution of the Python programming language (Python Software Foundation, 2017; van Rossum, 1995) and a variety of standard packages including NumPy1.11.1 (Walt et al., 2011), SciPy 0.18.1 (Jones et al., 2001) and Matplotlib 2.0.2 (Hunter, 2007).

Deleted: It is important to note that the DPG was not independently calibrated but the H₂O concentration was measured directly by the CRDS during the initial part of the experiment. These values were used as the reference H₂O concentration in all calculations and plots. 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.

The counter purge measurements made during the humidification experiments represent a combination of effects.

$$CP_{in} = True_{CP} \quad (1)$$

$$CP_{out} = True_{CP} - N_{X\%} \quad (2)$$

Where,

$True_{cp}$ the true mole fraction of the counter purge gas

$N_{X\%}$ is the effect of the Nafion® at $X\%$ H₂O in the sample stream

$X\%$ is the water content of the sample gas before the Nafion®

Hence the difference between the mean of CP_{in} and the mean of CP_{out} represents both any transport of CO₂ (or CH₄) through the Nafion® membrane and the effect of the water correction [at low humidities](#).

In order to remove any valve switching or line equilibration effects the first 5 mins of data of each sample period was discarded and the mean of the final 15-minute period of each sample type at each dew point was calculated. The uncertainty of this mean was determined as the 95 % confidence interval based on the larger of either the standard deviation of the minute means or average of the standard deviations of the minute means. Examples of the raw data collected during the experiment are given in Figure [S5](#). As the experiment was subject to a small temporal drift the mean CP_{in} values were linearly interpolated and

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the $CP_{out} - CP_{in}$ difference calculated as the difference between the CP_{out} and time adjusted CP_{in} values and the uncertainty estimated as the combined uncertainty of the CP_{in} and CP_{out} values.

2.3.8 Key experimental assumptions

While experiments 2.3.5, 2.3.6 and 2.3.7 were designed to isolate key processes, for example experiment 2.3.7 examined changes in the CO_2 or CH_4 mole fraction driven by the Nafion® drying processes, other possible sources of error or bias may exist. These include, adsorption and desorption effects within the regulator and walls of the tubing, gas solubility within the condenser of the dew point generator and instrumental drift.

Regulator and tubing adsorption and desorption effects has been previously examined by Zellweger and Steinbacher (2017, personal communication). They found that for Parker Veriflo type regulators, as used in this experiment, the effects can be quite large, up to $0.5 \mu\text{mol mol}^{-1} CO_2$ or $2 \text{ nmol mol}^{-1} CH_4$. But that these effects were only evident at flow rates $< 250 \text{ ml min}^{-1}$ and after significant periods of stagnation (15 hours). Considering the high flow rates ($> 1 \text{ L min}^{-1}$) and long flushing times (2 to 3 hours) used in our experiment it is highly unlikely that regulator effects would make a significant impact on the results.

As discussed earlier, a lengthy equilibration period was used at the start of each DPG run and following any change in DPG set point. This was to account for the dissolution of sample gas, in particular CO_2 , in the DPG water chamber. After this initial equilibrium period there were no rapid changes in the CO_2 mole fraction with only a slow drift, apparent in the data. CRDS instrumental drift is also typically very small and slow. For the UoB CRDS instrument, long-term measurements of target style standard cylinders have shown the drift to be $< 0.001 \mu\text{mol mol}^{-1} \text{ day}^{-1} CO_2$ and $< 0.03 \text{ nmol mol}^{-1} \text{ day}^{-1} CH_4$. These drift rates are at least an order of magnitude smaller than the mole fraction differences observed in this study.

Although small, any time dependent drifts were accounted for by temporally interpolating between each block of data. Also key to the design of this experiment is the examination of differences between two very similar mole fractions rather than absolute mole fractions. As such, any systematic errors that might drive a systematic offset cancel out and any mole fraction dependent biases are minimised.

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2.3.9 Calibration and traceability

Calibration procedures for both the CRDS and GC-ECD are as described in detail in Stanley et al. (2018). In brief, CRDS measurements are calibrated using a close-to-ambient standard (“working tank”) and a set of three calibration cylinders, which span the typical ambient range (Table 3). Only a small number of elevated observations, < 0.4 % of the CO₂ and < 1.5 % of the CH₄ minute mean observations, were outside the range of the calibration cylinders. However, a much higher proportion of the CO observations were outside the range of the calibration suites used at site, 28 % at BSD and 43 % at HFD, with the majority of these data points (> 98 %) below the lowest calibration cylinder.

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 closest 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 %.

Daily 20-minute-long measurements of the ambient standard are used to account for any linear drift, while monthly measurements of the calibration suite are used to characterise the nonlinear instrumental response. This calibration procedure is controlled by the GCWerks software and allows near real-time examination of calibrated data. During the period that the Nafion® drying system was used these standards were partially humidified as they passed through the wet Nafion® dryer. The level of humidification is dependent on that of the air samples measured prior to the standard. The moisture content of the standard closely tracks that of the air samples with variations in the humidity of the samples clearly reproduced in the standard (Figure S1). However, the moisture content of the standard is generally slightly lower. On average the standard has a mean moisture content 88 % that of the average of the 30

mins of air sample either side of the standard (on average 0.02 % H₂O lower). The moisture content of the standard also decreases slightly during the 20-minute measurement period as the dry standard air dries out the Nafion® membrane. The size of this decrease is dependent on the moisture content of the prior air samples with larger decreases during the more humid times of the year. As a worst-case example, the change in the water content of the Heathfield standard during each run of August 2014 is shown in Figure S6. This shows a maximum drift of 0.07 % H₂O equating to 30 % of the mean moisture content of air observations collected 30 minutes either side of the standard

In contrast, due to the time taken to take replicate measurements of the calibration cylinders (at least 240 mins) only the first 20-minute measurement block of each calibration cylinder is significantly humidified, with the water content of the calibration measurement dropping rapidly to < 0.02 % H₂O (10 to 20 % of the typical ambient air measurements). However, the exact level of humidification varies with ambient humidity and temperature. As such, in an effort to maintain consistency between calibration runs all runs with > 0.02 % H₂O were excluded from analysis.

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All CRDS standards and calibration gases are composed of natural air, some spiked or diluted with scrubbed natural air (TOC gas generator, Model No. 78-40-220, Parker Balston, USA) to achieve the required concentrations of CO₂, CH₄ and CO. All standard cylinders were filled at Mace Head with well-mixed Northern Hemisphere air. The cylinder spiking and filling techniques of the calibration cylinders varied. The Heathfield calibration suite and the second Bilsdale calibration suite were filled at GasLab MPI-BGC Jena and consisted of natural air spiked using a combination of pure CO₂ and a commercial mixture of 2.5 % CH₄ and 0.5 % CO in synthetic air. The “high” calibration cylinder of the first calibration suite used at the Bilsdale site was filled with peak-hour ambient air at EMPA, Dübendorf, Switzerland while the “low” and “mid” cylinders were based on Mace Head air, in the case of the “low” this was diluted with scrubbed natural air. Using natural air based calibration and standard gases removes any pressure broadening effects inherent in the use of non-matrix matched artificial standards (Nara et al., 2012). As the CRDS is an isotopologue-specific method filling the cylinders in such a manner ensures that the isotopic composition was as close to those of the sampled air as possible. The effect of an isotopic mismatch between the calibration standards and the sample has been examined in detail by Flores et al. (2017), Griffith (2018) and Tans et al. (2017). With Griffith (2018) showing that, for a sample of 400

$\mu\text{mol mol}^{-1}$ CO_2 and $2000 \text{ nmol mol}^{-1}$ CH_4 , the error will range between $0.001 - 0.155 \mu\text{mol mol}^{-1}$ CO_2 and $0.1 - 0.7 \text{ nmol mol}^{-1}$ CH_4 depending on the magnitude of the sample to standard mismatch. Based on this, we expect a worst-case scenario estimate of the error associated with our typical ambient measurements to be $< 0.04 \%$ for both CO_2 and CH_4 .

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5 GC-ECD measurements are made relative to a natural air standard of known N_2O and SF_6 concentration. This standard is measured hourly and used to linearly correct the samples (Table 4). The instrumental nonlinearity response was characterised prior to deployment by dynamically diluting a high concentration standard with zero air and was repeated in the field at the BSD site on 30th September 2015. This approach, dynamic dilution, has a history of use in similar field locations (Hammer et al., 2008) and is able to
10 generate multiple calibration points using just two cylinders. This greatly reduces the number of cylinders needed, a key concern for space-limited locations like BSD and HFD. An assessment of the uncertainty associated with this non-linearity approach will be included in a future paper currently in preparation. However, previous studies (Hall et al., 2011; van der Laan et al., 2009; Hammer et al., 2008) have found the ECD detector response to be extremely stable over time and very linear for both SF_6 and N_2O in the
15 mole fraction range typical of the HFD and BSD stations. As such, we expect the uncertainty of the nonlinearity correction to be very small.

GC-ECD and CRDS standards and calibration cylinders were, where possible, calibrated both before and after deployment at the sites. If these two measurements agreed then a mean mole fraction was used, otherwise a linearly drift corrected mole fraction was used. The CRDS cylinders were calibrated through

20 WMO linked calibration centres (either WCC-EMPA, Dübendorf, Switzerland or GasLab MPI-BGC, MPI, Jena, Germany). This ties the ambient measurements to the WMO CO_2 x2007 (Zhao and Tans, 2006), CH_4 x2004A (Dlugokencky et al., 2005) and CO x2014A (Novelli et al., 1991) scales. The calibration of the GC-ECD standards was conducted at either the AGAGE Mace Head laboratory or the University of Bristol laboratory and are reported here on the recently released SIO-16 N_2O scale and the
25 SIO SF_6 scale. Most cylinders were or will be calibrated before and after deployment and the mean of the two values used. Some cylinders, due to logistical constraints were only calibrated once (Table 4).

2.3.10 Instrument short-term precision and long-term repeatability

The short-term (1-minute) precision of the CRDS data was determined as the mean of the standard deviations of the 1-minute mean data. This was calculated from measurements of the standard cylinder and the calibration suite allowing the relationship between CO₂, CH₄ and CO mole fraction and short-term precision to be examined. This analysis included 18 cylinders covering a wide range of mole fractions (Table 3).

The mean absolute short-term precision for all cylinders was consistent between the two sites across all three gases. At BSD the short-term precision was 0.024 μmol mol⁻¹ CO₂, 0.18 nmol mol⁻¹ CH₄ and 4.2 nmol mol⁻¹ CO while at HFD it was 0.021 μmol mol⁻¹ CO₂, 0.22 nmol mol⁻¹ CH₄ and 6 nmol mol⁻¹ CO.

Both sites showed a small trend with the mean absolute precision worsening with increasing CO₂ and CH₄ mole fraction. However, this was not observed in the relative precision which remained unchanged at ~ 0.005 % for CO₂ and ~ 0.01 % for CH₄. This was not the case for CO where the relative precision improved with increasing mole fraction from ~ 4 % at CO < 100 nmol mol⁻¹ to < 1.5 % at CO > 250 nmol mol⁻¹. We suspect that this tendency is inherent in the spectroscopic approach as the CO peak measured by the Picarro CRDS is much smaller than those of the CO₂ and CH₄ (Chen et al., 2013) and hence more susceptible to noise in the baseline particularly at low mole fractions.

The long-term reproducibility of a 20-minute mean was estimated as the mean standard deviation of the daily 20-minute measurements of ~~the~~ standard cylinders used at each site. ~~A total of 8 standard cylinders have been used in succession at the two sites with the usage periods and CO₂, CH₄ and CO mole fractions listed in Table 3.~~ Like short-term precision, mean long-term ~~r~~reproducibility (calculated over a period of approximately a year) is consistent between the two sites, 0.018 and 0.013 μmol mol⁻¹ CO₂, 0.20 and 0.20 nmol mol⁻¹ CH₄, and 1.1 and 1.7 nmol mol⁻¹ CO at BSD and HFD respectively.

Repeatability of individual injections on the GC instruments were calculated as the standard deviation of the hourly standard injection. These were found to be < 0.3 nmol mol⁻¹ and < 0.05 pmol mol⁻¹, for N₂O and SF₆ respectively, and did not differ between the two sites.

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2.4 Data analysis

2.4.1 Data quality control

A three-stage data flagging and quality control system was used for the HFD and BSD data. Initially, automated flags based on the stability of key parameters including cell temperature & pressure and instrument cycle time (the time taken to collect and process each measurement) were applied. Here, data with a cycle time > 8 seconds were filtered out along with any data with cell temperature outside the range 45 ± 0.02 °C or cell pressure outside 140 ± 0.1 Torr. Secondly, a daily manual examination of the GC chromatograms and key GC/CRDS parameter values of each site were made. Data points were flagged if instrument parameters varied beyond thresholds determined to reduce their accuracy and a reason for the removal was logged. Finally, all sites were reviewed simultaneously and the mixing ratio of the same gas from each site are overlaid to look for differences between sites. Any significant differences between the background values at each site were investigated by examining key instrumental parameters, calibration pathways and 4-hourly air mass history maps to ensure that these differences represent true signals rather than instrumental or calibration driven artefacts. The hourly air mass history maps were produced using the Numerical Atmospheric dispersion Modelling Environment (NAME) Lagrangian dispersion model (Manning et al., 2011).

2.4.2 Statistical processing, baseline fitting and seasonal cycles

The long-term trend in mole fraction at each site was estimated as the mean linear trend in the minute mean data over the period 2014-2017, inclusive. Seasonal and diurnal trends in the data were assessed using monthly and hour-of-day means of trimmed detrended minute-mean data developed using the Python pumpy package. Here the long-term trend was removed by using a least-squares fit between a quadratic and the minute mean data. The data for each hour (or month for the seasonal plots) were trimmed following the approach of Satar et al. (2016) who removed the highest and lowest 5% of all data points.

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3 Results and discussion

3.1 CO₂, CH₄ and CO key features

The minute mean CO₂ observations range between a low of 379.50 to a high of 497.48 μmol mol⁻¹ CO₂ at Heathfield and 379.77 to 587.17 μmol mol⁻¹ CO₂ at Bilsdale. High CO₂ mole fractions observed at BSD are generally higher than those of the HFD site (Figures 4a & 5a). The high mole fraction events observed at BSD are generally sporadic — lasting only a couple of hours — and appear as a brief pulse relative to the normal diurnal cycle; a pattern indicative of a nearby point source. Considering BSD is remote from large conurbations, measured signals are expected to be dominated by biogenic sources. In this instance, we suspect high mole fraction events at BSD are due to local heather (*Calluna vulgaris*) burning. These CO₂ events also typically coincide with periods of elevated CH₄ and CO, again suggesting a biomass burning source. In contrast, events that do not show corresponding high CO and CH₄ mole fractions tend to occur in the higher two intakes. As such, they are likely to be driven by more remote CO₂ sources, for example power plants.

HFD is located in southern England, just south of London (Figure 1). Here, high CO₂ events are typically longer — 2 to 3 days — and coincide with elevated CH₄, CO, N₂O and SF₆. Rather than appearing as peaks superimposed on a background value these periods have a positive shift in the entire diurnal cycle. Air histories, based on the output of the Numerical Atmospheric dispersion Modelling Environment (NAME) Lagrangian dispersion model, outlined in Manning et al. (2011), for these periods of elevated CO₂ typically show the source of the air to be from over London or Europe.

Both sites show a clear relationship between CO₂ mole fraction and intake height with the lowest height generally having the most elevated mole fractions, followed by the higher heights (Figures 4a & 5a). This trend, also apparent for CH₄ and CO (Figures 4b & c and Figure 5b & c), is typical of tall tower measurements and is driven by proximity to surface sources (Bakwin et al., 1998; Winderlich et al., 2010; Satar et al., 2016). This gradient in CO₂ and CH₄ mole fraction is most apparent in the warmer seasons and during the early hours of the morning (Figure 6a, b, c & d) when the boundary layer is the lowest. a trend observed previously by Winderlich et al. (2010). While a reversal of this gradient, lower heights having lower CO₂ mole fractions, occurs in the middle of the day (Figure 6 a and b). As described in Satar et al. (2016) this decrease in near surface CO₂ is most likely driven by local photosynthetic

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activity. Interestingly, this trend is also apparent in spring, summer and autumn CH₄ mole fractions at BSD (Figure c) but not HFD (Figure 6d). This suggests a midday sink of CH₄ local to BSD but not HFD. Considering that BSD is located high in the Yorkshire moors (379.1 m a.s.l) while HFD is located in a lower agricultural region (157.3 m a.s.l) a large difference in soil moisture, and therefore methanotrophic activity (Topp and Pattey, 1997), between the two sites is possible.

Interestingly, Winderlich et al. (2010) suggest that their ability to observe gradients on an hourly timeframe is only revealed due to their use of buffer volumes and fast switching (every 3 minutes). In contrast, the measurements presented here, made without buffer volumes and at a much lower switching rate, were also able to identify gradients between the heights (Figure S7). Suggesting that the use of buffer volumes and fast switching is not necessary required in order to observe these trends.

The timings and magnitude of the HFD and BSD seasonal cycles are similar, with CO₂ mole fractions highest in the colder months and lowest during the Northern Hemisphere summer (Figure 7a & b). Although both sites are located in areas consisting of predominantly agricultural space or native vegetation the HFD site is more urbanised. This appears to be reflected in more elevated CO₂ and CO events in October, November and December relative to the BSD site (Figure 6a & b and e & f), suggesting that the HFD site is more sensitive to fossil fuel emissions.

As with the seasonal cycle, the shape of the CO₂ diurnal cycle is similar at both sites, with mole fractions peaking near sunrise and the lowest CO₂ mole fractions observed in the late afternoon (Figure 6a & b). Again, the amplitude of these cycles varies between the sites with HFD, the more anthropogenically influenced site, typically showing a higher maximum in the early morning than BSD.

Although there is a very large range in the minute mean CH₄ observations, 1841 to 3065 nmol mol⁻¹ at BSD and 1843 to 3877 nmol mol⁻¹ at HFD, > 99.99 % of measurements, are less than 2400 nmol mol⁻¹ CH₄, with only 6 events in the combined record exceeding this threshold. These events have been clipped from the data shown in Figures 4b and 5b for ease of viewing. Like CO₂, the CH₄ observations show seasonal cycles with the mole fractions the highest in the winter months and the lowest in midsummer (Figure 7c & d). A small CH₄ diurnal cycle peaks in the morning usually 1 to 2 hours after sunrise (this is after the CO₂ maximum) and then dips in the mid-afternoon (Figures 6c & d). The CH₄ diurnal cycle is also more pronounced and smoother in the HFD data and evident throughout the year, whereas the BSD

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cycle is only strongly apparent in the summer months. This could be linked to differences in the relative magnitude of key local sources/sinks of CH₄ between the two sites.

Of the 5 gases measured at HFD and BSD, CO is the only gas to show a decrease in mole fraction between 2013 and 2017, roughly -7 nmol mol⁻¹ yr⁻¹. In contrast, the CO₂ and CH₄ data increase by 2-3 μmol mol⁻¹ yr⁻¹ and 5-9 nmol mol⁻¹ yr⁻¹ respectively, varying with the intake height. These agree well with the ~2 μmol CO₂ mol⁻¹ yr⁻¹ and ~8 nmol CH₄ mol⁻¹ yr⁻¹ trends observed at Mace Head (MHD, 53.327 °N, -9.904 °E, Figure 1), a remote site within the UK DECC network located on the west coast of Ireland. However, the CO data collected at MHD is not on the NOAA x2014 CO calibration scale making direct comparisons between growth rates difficult to interpret.

While the range of minute mean CO mole fractions was significantly larger at BSD, 63 to 9500 nmol mol⁻¹ than HFD, 60 to 4850 nmol mol⁻¹, the high CO values observed at BSD were relatively rare. This is reflected in the smaller spread of the BSD data compared with the HFD data (Figure 7e & f).

3.2 N₂O and SF₆ key features

The range of N₂O mole fractions observed from the two intakes of comparable height, 108 m at BSD and 100 m at HFD, were very similar, 326.6 to 340.0 and 326.4 to 338.5 nmol mol⁻¹ for BSD and HFD, respectively (Figures 4d and 5d). The N₂O data from the higher (248 m) intake at BSD, has narrower range, especially in the cooler months of the year than the lower 108m data (Figure 6g). As described earlier the smaller range in the 248 m data is typical of tall tower measurements and driven by increased mixing with increasing altitude, which reduces the influence of local sources.

The N₂O mole fraction seasonal cycle of both sites shows an unusual pattern with two maxima per year, one in early spring and a second in autumn (Figure 7g & h). Both the timings and amplitudes of these cycles are similar at both sites. The long-term trend, ~0.8 nmol N₂O mol⁻¹ yr⁻¹ (calculated using data from the 108 m and 100 m intakes at BSD and HFD over the period of coincident data collection, 2014 to mid 2016) also agrees well between the two sites and with MHD, also ~0.8 nmol N₂O mol⁻¹ yr⁻¹.

A previous study, Nevison et al. (2011) examined the monthly mean N₂O seasonality of baseline mole fraction data at Mace Head (MHD, 53.327 °N, -9.904 °E, Figure 1), a remote site within the UK DECC network located on the west coast of Ireland. They found that although biogeochemical cycles predict a

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single thermally driven summer time maximum in N₂O flux (and hence mole fraction) (Bouwman and Taylor, 1996), they actually observed a late summer minimum, with a single N₂O concentration peak in spring. This was attributed to the winter intrusion of N₂O depleted stratospheric air and its delayed mixing into the lower troposphere. In contrast, [in](#) a UK focused inversion study Ganesan et al. (2015), found that N₂O flux seasonality is driven not just by seasonal changes in temperature but by agricultural fertilizer application and post-rainfall emissions. They predict the largest net N₂O fluxes will occur between May and August while agricultural fluxes will peak during spring for eastern England and summer time for central England. However, the exact timings of these fluxes can vary year-to-year as they depend not only on the scheduling of agricultural fertilizer application but on rainfall and temperature. Like MHD, BSD and HFD are expected to experience a decrease in N₂O driven by stratospheric intrusion, which would account for the springtime maximum and summer minimum. However, both BSD and HFD are located much closer to significant agricultural sources of N₂O than MHD. Hence, it is likely that they are much more influenced by agricultural N₂O fluxes. As such, it is possible that although a summer time maximum in N₂O flux is completely offset by stratospheric intrusion, this summer time maximum may be so large that the residual autumn tail of this event appears as a second maximum at BSD and HFD.

Clear diurnal cycles in N₂O were observed at the HFD for the spring, summer and autumn months with the maximum N₂O mole fraction occurring 2 hours after sunrise and the minimum in the mid-afternoon (Figure 6h). These cycles were not as apparent at BSD (Figure 6g).

The long-term trend in the SF₆ mole fraction at BSD and HFD shows a gradual increase of 0.3 pmol mol⁻¹ yr⁻¹ again agreeing well with MHD which showed an identical growth rate. Although the predominant sources of SF₆ are electrical switchgear, which is not expected to have significant seasonality, there was a small seasonal cycle observed (Figure 7i & j). This cycle is more apparent in the 108 m BSD data and appears as a slight (0.1 to 0.15 pmol mol⁻¹) enhancement in SF₆ in the winter months. This seasonal shift occurs across the wider DECC-GAUGE network and air history maps suggest that it is not associated with an obvious UK or continental region. As such, instead of an atmospheric transport driven shift we believe this to be a true change in emissions and hypothesise that this may be due to increased load on, and hence increased failure of, the electrical switchgear during the colder months. SF₆ mole fractions averaged 8.9 pmol mol⁻¹ at both BSD and HFD. While HFD, located closer to large conurbations than

BSD, typically saw higher SF₆ pollution events. This was reflected in its larger range of 8.1 to 34.2 pmol mol⁻¹ compared with 8.1 to 22.9 pmol mol⁻¹ at BSD (Figures 4e and 5e).

3.3 Site specific water corrections

The annual instrument-specific water corrections, determined through regular droplet tests, are typically very similar at each site, often within the 95 % confidence interval of the triplicate runs (Table 1), suggesting that the corrections are fairly stable between years and instruments. The residuals of the instrument specific water corrections are generally quite small, with 25th and 75th quartiles of -0.03 and 0.05 μmol mol⁻¹ CO₂ and -0.4 and 0.3 nmol mol⁻¹ CH₄ (Table 1). The mean absolute residuals are, on average, smaller than those of the inbuilt correction and are notably smaller at higher H₂O content (see Figure S8). For example, the mean absolute residuals for 2015 data from HFD with H₂O > 2 % are 0.04 and 0.09 μmol mol⁻¹ CO₂ and 0.4 and 1.2 nmol mol⁻¹ CH₄ for the new and inbuilt correction, respectively. 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 data corrected using the instrument specific and in-built correction was not statistically significant. As such, these corrections were not presented in the body of the paper, however, further information can be found in Figure S8 of the supplementary.

Plots of the residuals typically show a common pattern, with the residual of zero at 0 % H₂O, before dipping below zero and then returning to zero at H₂O between 0.2 and 0.5 % (Figure S8). Unlike other tests, the depth and width of this dip is more pronounced for BSD 2017. However, the BSD 2017 data both spans a wider range of H₂O contents than the earlier BSD tests (0 to 3.5 % vs. 0 to 2.2 %) and has far fewer data points in the 0.1 to 1 % H₂O range (0.9 % of all data points vs. 34 % and 27 % for BSD 2015 and 2016, respectively). The BSD 2017 0.1 to 1.0 % minute-mean data also have an average standard deviation an order of magnitude larger than those of 2015 and 2016 (Figure S8a, b & c). Refitting the BSD 2017 correction using only data H₂O < 2.2 % decreases the depth of the deviation by 0.05 μmol mol⁻¹ CO₂ and 0.3 nmol mol⁻¹ CH₄ as well as decreasing its width slightly but the deviation remains. This suggests that the presence of the dip is robust but the change in its shape between 2017 and 2016 may well be a fitting artefact.

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Reum et al. (2018) previously identified this pattern in water correction residuals and linked it to a pressure sensitivity at low water vapour mole fractions. They proposed an alternative fitting function incorporating the “pressure bend” although they do not recommend using this fit for data collected during the droplet test due to the paucity of stable data typically obtained between 0.02 and 0.5 % H₂O and the effect of rapidly changing H₂O on the cell pressure sensor. Implementing a more controlled water test at the sites would allow the use of the new fitting function. But due to the complexity of such a test this would be logistically difficult at remote field sites.

It is also important to note that the magnitude of the dip observed by Reum et al. (2018) in their controlled water tests, ~ 0.04 μmol mol⁻¹ CO₂ and 1 nmol mol⁻¹ CH₄, are roughly half those observed for the HFD, BDS and UoB droplet tests. As such the increased residuals observed for our water corrections between 0.02 and 0.5 % H₂O are likely to be primarily driven by the rapidly changing H₂O content inherent in the droplet test rather than represent a true error in the water correction.

The poor performance of the CRDS pressure sensor at low H₂O mole fractions, 0.02 to 0.5 % H₂O, is not expected to be a large source of error for undried samples as the majority of these, 92 % of the BSD and

HFD data, contain > 0.5 % H₂O. But this could be a source of error for Nafion® dried samples where low moisture contents are typically obtained. However, for this study, where 95 % of HFD and 92 % of BSD Nafion® dried samples contain < 0.5 % H₂O, this effect is expected to be substantially mitigated by the humidification of the daily standard. As described earlier (Section 2.3.9 and Figure S1) the moisture content of the daily standard closely tracks that of the ambient air with the standard mean moisture content almost 90% that of the ambient air. Hence the bulk of the error in the H₂O correction at lower water contents should be accounted for during the drift correction process.

In contrast, without the humidification of the standard the error when Nafion® drying may well be significant. It is difficult to quantify this error, as it will vary with sample water content and the sensitivity of the individual instrument’s pressure sensor to low H₂O mole fractions. However, assuming that the residuals of the droplet water tests are an accurate reflection of the likely error (Figure S8), we expect there to be a systematic offset of the order of -0.05 to -0.1 μmol mol⁻¹ CO₂ and -1 to -2 nmol mol⁻¹ CH₄. Assuming that a 90 % match in sample and standard moisture content equates to a 90% reduction in offset

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then we can estimate the offset in the BDS and HFD data as between 0.005 and 0.01 $\mu\text{mol mol}^{-1} \text{CO}_2$ and -0.1 to -0.2 $\text{nmol mol}^{-1} \text{CH}_4$, negligible in comparison to the WMO reproducibility guidelines.

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The sample mole fraction dependence of the CRDS water correction was examined by conducting water droplet tests using dry cylinders of above and below ambient mole fractions (Section 2.3.5). Specific above and below ambient water corrections were calculated based on these data sets (Table 1 and Figure S9). If the water correction was independent of sample mole fraction then the residuals should be identical for both correction types. Although the above and below ambient residual plots are similar they do differ slightly with the residual of the above mole fraction sample becoming more positive at higher H_2O mole fractions while the below ambient mole fraction residuals become more negative. This is reflected in the difference in mean residuals and the shift in the interquartile ranges as seen for both CO_2 and CH_4 in Table 1.

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The change in the difference between dry mole fractions calculated using the earliest instrument specific water correction and subsequent water corrections for each instrument with water concentration is shown in Figure 8a & b. For a typical air sample (1.5 % H_2O , 400 $\mu\text{mol mol}^{-1} \text{CO}_2$ and 2000 $\text{nmol mol}^{-1} \text{CH}_4$) shifting between the annual water corrections drives CO_2 and CH_4 changes of < 0.05 $\mu\text{mol mol}^{-1}$ and < 1 nmol mol^{-1} . However, this difference does change with water content and can increase outside the WMO reproducibility bounds at higher (> 2.5 %) H_2O contents. For example, the difference between CO_2 dry mole fractions calculated using the Bilsdale 2015 and 2017 H_2O correction increases to 0.12 $\mu\text{mol mol}^{-1}$ at 2.5 % H_2O . It's also important to note that these differences will scale with CO_2 and CH_4 mole fraction.

Nevertheless, at the range of ambient water contents observed at BSD and HFD (0.1 to 2.5 %) these differences remain below the WMO comparability guidelines (WMO, 2018), for CO_2 and CH_4 mole fractions < 750 $\mu\text{mol mol}^{-1}$ and < 4000 nmol mol^{-1} , respectively, as observed in BSD and HFD air samples. In light of the temporal variability of the water correction over time, at higher water contents, for sites with high humidity (> 2 % H_2O) using a Nafion® dryer or alternative drying method to obtain a

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relatively low and stable sample water content would be an advantage.

A comparison of the individual daily and weekly tests, Figures 8c & d and 10e & f, conducted using the UoB instrument, show the daily tests to be far more similar than the weekly tests. That is, the variability over the 3-month period of the weekly test is much larger than that of the 5-day period of the daily test.

However, the variability of the weekly tests is similar to those of the annual tests, Figure 8a and b, suggesting that, within the bounds of the data typically observed at the BSD and HFD sites, the use of annually derived instrument specific water corrections are sufficient. This may not be the case at sites with higher levels of humidity and CO₂ and CH₄ mole fractions where water corrections may need to be determined more frequently, perhaps even weekly. The impracticality of such a frequent testing regime along with the apparent unreliability of the droplet test at H₂O > 2.5 % (for example Figure [S8g](#)) mean that an alternative method, possibly partial drying, or a higher level of uncertainty may need to be applied to measurements made at higher water contents.

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3.4 Quantifying the CRDS water correction error using the dew point generator

The change in the CRDS water correction with sample H₂O content was characterised using the difference between the *Wet* and *Dry* DPG runs. This error typically had a shallow negative parabolic trend for both CO₂ and CH₄ (Figure 9) and was similar to the shape seen in the residual of the CRDS water corrections (Figure [S8](#) and [S9](#)) with the error negative at H₂O mole fractions near 0.5 %, becoming more positive between 1 and 2 % H₂O before dropping at higher H₂O contents.

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Although the UoB CRDS was not deployed in the field we expect the results of the DPG tests to be typical of most Picarro G2401 CO₂/CH₄ CRDS instrumentation. The DPG tests show that for ambient and below ambient mole fraction samples the CH₄ error remained within the WMO internal reproducibility guidelines (WMO, 2018), at all water contents examined, that is 0.6 to 3.5 % H₂O, while the CO₂ error increased outside the guidelines for H₂O > 2.5 %. CO₂ errors increased rapidly outside this range reaching 0.3 μmol mol⁻¹ at 3.5 % H₂O. These results are broadly consistent with those of the droplet test residuals. Unlike the ambient and below ambient samples, the CRDS water correction error of the above ambient sample, UoB-04, exceeded the WMO internal reproducibility guidelines for both CO₂ and CH₄ at most H₂O mole fractions. For the H₂O range of the BSD and HFD sites the error peaked at 0.1 μmol mol⁻¹ for CO₂ near 1.75 % H₂O and at 2 nmol mol⁻¹ CH₄ near 2.25 % H₂O. As discussed earlier in Section 3.3, the absolute error in the CRDS water correction will scale with the absolute mole fraction of the sample due to the structure of the correction. The UoB CRDS correction was also optimised using a cylinder of significantly lower mole fraction (397.38 μmol mol⁻¹ CO₂ and 1918.73 nmol mol⁻¹ CH₄ compared with

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515.4 $\mu\text{mol mol}^{-1}$ and 2579.5 nmol mol^{-1}). This shift in error/residual was also observed in the H_2O droplet tests using higher mole fraction cylinders although it appears larger for the DPG tests, most likely due to the higher mole fractions used within these tests (515.4 and 2579.5 compared with 449.55 $\mu\text{mol mol}^{-1}$ CO_2 and 2148 nmol mol^{-1} CH_4 , respectively).

5 The full range of H_2O mole fractions observed at the HFD and BSD sites, 0.05 to 2.5 % H_2O , were not examined in these tests which due to limitations inherent in the experimental set up were restricted to a H_2O range of 0.6 – 3.5 %. However, it is possible to conclude that for observations of ambient and below ambient CO_2 and CH_4 mole fractions with $\text{H}_2\text{O} > 0.6$ % the water driven error in the CRDS water correction is not likely to be a major source of uncertainty. Even at other DECC sites that are subject to
10 higher humidity, for example the Angus site (Stanley et al., 2018) periods of high (> 2.5 % H_2O) water content are rare, < 0.03 % of the data record. In contrast, as elevated CO_2 and CH_4 mole fractions are regularly observed at both the HFD and BSD sites, the increase in CRDS error with mole fraction is a source of concern and must be quantified as part of a full uncertainty analysis.

3.5 Quantifying Nafion® cross membrane transport

15 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
20 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. During these experiments all measurement of the Nafion® counter
purge (CP_{in} and CP_{out}) were cryogenically dried to < 0.002 % H_2O prior to CRDS analysis. Hence the need to use an empirical CRDS water correction and any error associated with the correction was removed and differences between the CP_{in} and CP_{out} samples can be solely attributed to transport across the
Nafion® membrane ($N_{X\%}$). The results of these experiments are shown in Figure 10.
25 The counter purge experiments conducted with both the ambient (UoB-15) and above ambient (UoB-16) mole fraction cylinders show identical changes in CO_2 and CH_4 mole fractions, respectively. The wet sample $N_{X\%}$ difference is consistently positive for CO_2 with the CP_{out} mole fraction an average of 0.021

± 0.002 μmol mol⁻¹ ($\bar{x} \pm 95\%$ conf. int., $n > 19$) higher than CP_{in} , reflecting a loss from the sample to the counter purge across the Nafion® membrane (Figure 10a). Although small, this value is an order of magnitude larger than the average standard deviation of the 15 min block means (0.002 μmol mol⁻¹ CO₂) making it well within the typical measurement precision. This difference decreases slightly with
5 decreasing sample water content but it is never zero. Even with a dry sample, the $CP_{out} - CP_{in}$ difference ($N_{X\%}$), 0.015 ± 0.003 μmol mol⁻¹ CO₂, is still positive. This is in line with previous studies, which have found that, although water substantially increases membrane permeability, even dry membranes are permeable to CO₂ (Ma and Skou, 2007; Chiou and Paul, 1988). As earlier studies have found that membranes can take more than a week to fully dry out (Chiou and Paul, 1988), it is also highly likely that
10 the relatively brief length of this study (4 to 5 hours) was too short to remove all H₂O from the membrane. The CH₄ CP_{in} and CP_{out} mole fraction difference for both dry and wet samples is also slightly positive, 0.03 ± 0.01 and 0.04 ± 0.02 nmol mol⁻¹ CH₄, respectively (Figure 10b). This value is very close to the measurement precision, with the average CH₄ standard deviation of the 15-min block means of the order of 0.02 nmol mol⁻¹ CH₄.

15 The ~ 0.02 μmol mol⁻¹ loss of CO₂ across the Nafion® membrane from the sample stream to the counter purge observed here, although small, is of the order of the WMO internal reproducibility guidelines, 0.05 μmol mol⁻¹ in the northern hemisphere and 0.025 μmol mol⁻¹ in the southern hemisphere (WMO, 2018), and must be acknowledged. However, the calibration gases are also passed through the Nafion®. These cylinders are very dry, H₂O < 0.0001 %, equivalent to the driest conditions studied in the DPG
20 experiments (Figure 10a) and as such would be expected to show similar CO₂ loss across the Nafion® membrane, ~ 0.015 μmol mol⁻¹. Hence, as the bias is constant with sample CO₂ and H₂O mole fractions and as a bias would be present in both the calibration gases (~ 0.015 μmol mol⁻¹) and samples (~ 0.02 μmol mol⁻¹) the majority of the bias will be calibrated out, with only a very small (≤ 0.005 μmol mol⁻¹) constant bias, of the order of the instrumental precision, remaining. In contrast, the mean CH₄ Nafion®
25 bias, 0.04 ± 0.02 nmol mol⁻¹, is at least an order of magnitude smaller than the WMO internal reproducibility guidelines (WMO, 2018), and is extremely close to the typical measurement precision suggesting that it is not a bias of concern.

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4 Conclusions and future work

The newly established Bilsdale and Heathfield tall tower measurement stations provide important new data sets of GHG observations. These high-precision continuous in situ measurements show clear long term increases in baseline CO₂, CH₄, N₂O and SF₆ mole fraction and capture the seasonal and diurnal cycles of these key gases. It is expected that these observations, when combined with regional inversion modelling, will significantly improve our ability to quantify UK greenhouse gas emissions — both reducing the uncertainty and improving the spatial and temporal resolution. Future work using this data is focusing on better estimates of UK GHG emissions with a particular emphasis on the UK carbon budget.

10 The two drying methods implemented at Bilsdale and Heathfield - Nafion® drying with an empirical water correction and an annual empirical water correction without drying - have a number of practical and scientific advantages and disadvantages. The Nafion® drying method, once installed and running correctly can provide reliable drying to between 0.05 and 0.2 % H₂O. While this method requires little on-going maintenance if the TOC fails, as has occurred at a number of UoB run tall tower sites, then the replacement of the entire TOC system or removal and repair off site is required. Due to the expense of the TOC instrumentation having spares available for immediate installation is often not practicable. The sporadic and unpredictable nature of these failures also makes it impossible to incorporate this into routine scheduled site visits. As such, a failure of this nature typically leads to multiple unscheduled trips to site and periods of poor drying. In contrast, using an annual empirical requires a single trip to site which can be easily scheduled as part of routine site maintenance. Allowing time for leak checking and at least three replicate droplet tests such a trip would generally take 2-3 days. As such, for remote or difficult to access sites the annual empirical water correction is preferred.

15 As shown in Table 5, the systematic errors associated with the Nafion® drying method, as applied at these two sites, was small, < 0.01 μmol mol⁻¹ of CO₂ and < 0.2 nmol mol⁻¹ of CH₄, and did not vary with sample

20 water content. However, care must be taken with the implementation of the method as, for samples with water content > 0.7 %, an additional 0.02 μmol mol⁻¹ of CO₂ was lost from the sample across the membrane. Even samples as dry as the calibration gases were affected by this loss, although to a smaller degree (~ 0.015 μmol mol⁻¹ for H₂O < 0.0001 %) as residual moisture remained in the membrane.

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However, as in this application of the method the calibration gases are dried in an identical manner to the samples, this loss is mostly calibrated out with only a very small ($\leq 0.005 \mu\text{mol mol}^{-1}$) constant residual bias of the order of the instrumental precision. As such, when using a Nafion® based drying method it is essential that the calibration and standard gases are dried in an identical manner to the samples.

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5 By comparison the annual CRDS empirical water correction has a narrower optimum range with minimal systematic errors only at water contents very near 0% and between 0.5 and 2.5% H₂O (Figures 8, 9, S8 and S9). As such, the choice to use an annual empirical water correction method alone must be strongly influenced by the ambient humidity of the site of interest. Estimates of these systematic errors (Table 5), determined for different water content ranges, were based on the water correction residuals (Figure S8) and the temporal variability in the annual H₂O corrections at each site (Figures 8a and b). The maximum error associated with the empirical water correction alone ranged between 0.05 and 0.2 $\mu\text{mol mol}^{-1}$ CO₂ and 1 and 3 nmol mol^{-1} CH₄ with the majority of observations at the lower end of the range. It is important to note that these estimates were calculated for the Picarro CRDS and may vary significantly to those of other CRDS instrumentation or optical techniques that use alternative cell pressure sensors (Reum et al., 15 2018).

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This weakness in the CRDS water correction also has notable implications for sample drying. Namely, while sample drying may not be an inherent source of bias, the partial drying of the sample puts it within the range of peak error in the CRDS water correction (0.05 to 0.5 % H₂O). This source of error, as demonstrated in the implementation of the Nafion® based drying system outlined here, can be mitigated by matching the water content of the daily standard to the sample. Again this re-emphasises the importance of treating the sample, standards and calibration gases in an identical manner.

20 Considering the relatively narrow humidity range observed at Bilsdale and Heathfield, with no observations > 2.4 % H₂O and > 95 % of observations > 0.5 % H₂O (> 99 % > 0.35 % H₂O) and the relative remoteness of the locations the decision to remove the Nafion® based drying systems and rely on the annual empirical water correction appears justified. In contrast, at other more easily accessible or more humid sites the use of a Nafion® based drying system may be more advantageous.

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While these errors are significant relative to the WMO internal reproducibility goals they are for the majority of observations smaller than the extended WMO measurement compatibility goals ($\pm 0.2 \mu\text{mol mol}^{-1} \text{CO}_2$ and $\pm 5 \text{ nmol mol}^{-1} \text{CH}_4$). It is also important to note that they are orders of magnitude smaller than baseline excursions observed at the sites (see Figures 4 & 5). They are also a factor of 10 smaller than the CH_4 model-data mismatch within the UK DECC network as estimated by Ganesan et al. (2015) at $\sim 20 \text{ nmol mol}^{-1}$. Considering this difference, it is highly unlikely that, without significant improvement in modelled atmospheric transport, the systematic errors reported here would significantly alter estimates of UK-scale GHG fluxes or impede national emissions verification efforts.

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, instrumental, water correction and sampling errors and errors induced by the isotopic composition of the calibration gases is also planned.

Further work to fully characterise the humidity dependent error in the water correction of each instrument, like that of (Reum et al., 2018), possibly using a piecewise post hoc correction, would also be beneficial in an effort to reduce the estimated error associated with the observations.

5 Acknowledgements

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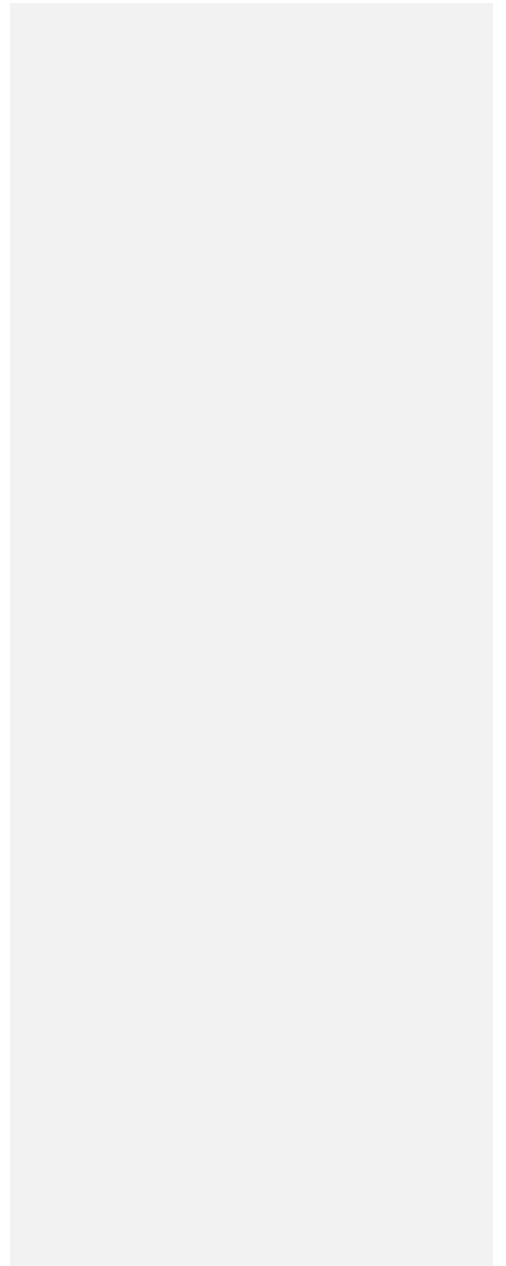
The authors would also like to acknowledge the support of Dr Carole Helfter and Dr Neil Mullinger from the NERC Centre for Ecology and Hydrology (CEH), Edinburgh, Scotland who helped to maintain and run the Bilsdale site. Lastly the authors would like to thank Dr Joseph Pitt from the University of Manchester for the use of the dew point generator used during a series of preliminary studies.

5

7 References

- Bakwin, P. S., Tans, P. P., Hurst, D. F., and Zhao, C.: Measurements of carbon dioxide on very tall towers: results of the NOAA/CMDL program, *Tellus B*, 50, 401-415, doi:10.1034/j.1600-0889.1998.t014-00001.x, 1998.
- 5 Bouwman, A. F., and Taylor, J. A.: Testing high-resolution nitrous oxide emission estimates against observations using an atmospheric transport model, *Global Biogeochemical Cycles*, 10, 307-318, 10.1029/96gb00191, 1996.
- Chen, H., Winderlich, J., Gerbig, C., Hoefler, A., Rella, C. W., Crosson, E. R., Van Pelt, A. D., Steinbach, J., Kolle, O., Beck, V., Daube, B. C., Gottlieb, E. W., Chow, V. Y., Santoni, G. W., and Wofsy, S. C.: High-accuracy continuous airborne measurements of greenhouse gases (CO₂ and CH₄) using the cavity ring-down spectroscopy (CRDS) technique, *Atmos. Meas. Tech.*, 3, 375-386, 10.5194/amt-3-375-2010, 2010.
- 10 Chen, H., Karion, A., Rella, C. W., Winderlich, J., Gerbig, C., Filges, A., Newberger, T., Sweeney, C., and Tans, P. P.: Accurate measurements of carbon monoxide in humid air using the cavity ring-down spectroscopy (CRDS) technique, *Atmos. Meas. Tech.*, 6, 1031-1040, 10.5194/amt-6-1031-2013, 2013.
- 15 Chiou, J. S., and Paul, D. R.: Gas permeation in a dry Nafion membrane, *Industrial & Engineering Chemistry Research*, 27, 2161-2164, 10.1021/ic00083a034, 1988.
- Chris Blandford Associates: North Yorkshire and York Landscape Characterisation Project, London, 2011.
- Dlugokencky, E. J., Myers, R. C., Lang, P. M., Masarie, K. A., Crotwell, A. M., Thoning, K. W., Hall, B. D., Elkins, J. W., and Steele, L. P.: Conversion of NOAA atmospheric dry air CH₄ mole fractions to a gravimetrically prepared standard scale, *Journal of Geophysical Research: Atmospheres*, 110, n/a-n/a, 10.1029/2005JD006035, 2005.
- 20 Flores, E., Viallon, J., Moussay, P., Griffith, D. W. T., and Wielgosz, R. I.: Calibration Strategies for FT-IR and Other Isotope Ratio Infrared Spectrometer Instruments for Accurate δ¹³C and δ¹⁸O Measurements of CO₂ in Air, *Analytical Chemistry*, 89, 3648-3655, 10.1021/acs.analchem.6b05063, 2017.
- Foulger, B. E., and Simmonds, P. G.: Drier for field use in the determination of trace atmospheric gases, *Analytical Chemistry*, 51, 1089-1090, 10.1021/ac50043a074, 1979.
- 25 Fraser, P., Porter, L. W., Baly, S. B., Krummel, P. B., Dunse, B. L., Steele, L. P., Derek, N., Langenfelds, R. L., Levin, I., Oram, D. E., Elkins, J. W., Vollmer, M. K., and Weiss, R. F.: Sulfer hexafluoride at Cape Grim: Long term trends and regional emissions, 18-23, 2004.
- Ganesan, A. L., Manning, A. J., Grant, A., Young, D., Oram, D. E., Sturges, W. T., Moncrieff, J. B., and O'Doherty, S.: Quantifying methane and nitrous oxide emissions from the UK and Ireland using a national-scale monitoring network, *Atmos. Chem. Phys.*, 15, 6393-6406, 10.5194/acp-15-6393-2015, 2015.
- 30 Griffith, D. W. T.: Calibration of isotopologue-specific optical trace gas analysers: A practical guide, *Atmos. Meas. Tech. Discuss.*, 2018, 1-19, 10.5194/amt-2018-187, 2018.
- Hall, B. D., Dutton, G. S., Mondeel, D. J., Nance, J. D., Rigby, M., Butler, J. H., Moore, F. L., Hurst, D. F., and Elkins, J. W.: Improving measurements of SF₆ for the study of atmospheric transport and emissions, *Atmos. Meas. Tech.*, 4, 2441-2451, 10.5194/amt-4-2441-2011, 2011.
- 35 Hammer, S., Glatzel-Mattheier, H., Muller, L., Sabasch, M., Schmidt, M., Schmitt, S., Schonherr, C., Vogel, F., Worthy, D., and Levin, I.: A gas chromatographic system for high-precision quasi-continuous atmospheric measurements of CO₂, CH₄, N₂O, SF₆, CO and H₂: https://www.researchgate.net/publication/255704060_A_gas_chromatographic_system_for_high-precision_quasi-continuous_atmospheric_measurements_of_CO2_CH4_N2O_SF6_CO_and_H2, 2008.
- Hunter, J. D.: Matplotlib: A 2D Graphics Environment, *Computing in Science & Engineering*, 9, 90-95, 10.1109/MCSE.2007.55, 2007.
- 40 IPCC: Summary for Policymakers, in: *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by: Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V., and Midgley, P. M., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1-30, 2013.
- 45 Ma, S., and Skou, E.: CO₂ permeability in Nafion® EW1100 at elevated temperature, *Solid State Ionics*, 178, 615-619, dx.doi.org/10.1016/j.ssi.2007.01.030, 2007.
- Manning, A. J., O'Doherty, S., Jones, A. R., Simmonds, P. G., and Derwent, R. G.: Estimating UK methane and nitrous oxide emissions from 1990 to 2007 using an inversion modeling approach, *Journal of Geophysical Research: Atmospheres*, 116, n/a-n/a, 10.1029/2010JD014763, 2011.
- 50 Nara, H., Tanimoto, H., Tohjima, Y., Mukai, H., Nojiri, Y., Katsumata, K., and Rella, C. W.: Effect of air composition (N₂, O₂, Ar, and H₂O) on CO₂ and CH₄ measurement by wavelength-scanned cavity ring-down spectroscopy: calibration and measurement strategy, *Atmos. Meas. Tech.*, 5, 2689-2701, 10.5194/amt-5-2689-2012, 2012.

- Naudy, S., Collette, F., Thominet, F., Gebel, G., and Espuche, E.: Influence of hygrothermal aging on the gas and water transport properties of Nafion® membranes, *Journal of Membrane Science*, 451, 293-304, dx.doi.org/10.1016/j.memsci.2013.10.013, 2014.
- Nevison, C. D., Dlugokencky, E., Dutton, G., Elkins, J. W., Fraser, P., Hall, B., Krummel, P. B., Langenfelds, R. L., O'Doherty, S., Prinn, R. G., Steele, L. P., and Weiss, R. F.: Exploring causes of interannual variability in the seasonal cycles of tropospheric nitrous oxide, *Atmos. Chem. Phys.*, 11, 3713-3730, 10.5194/acp-11-3713-2011, 2011.
- 5 North York Moors National Park Authority: North York Moors National Park Management Plan: A wider view, Helmsley, 2012.
- Novelli, P. C., Elkins, J. W., and Steele, L. P.: The development and evaluation of a gravimetric reference scale for measurements of atmospheric carbon monoxide, *Journal of Geophysical Research: Atmospheres*, 96, 13109-13121, doi:10.1029/91JD01108, 1991.
- 10 Prinn, R., Cunbold, D., Rasmussen, R., Simmonds, P., Alyea, F., Crawford, A., Fraser, P., and Rosen, R.: Atmospheric emissions and trends of nitrous oxide deduced from 10 years of ALE-GAGE data, *Journal of Geophysical Research: Atmospheres*, 95, 18369-18385, 10.1029/JD095iD11p18369, 1990.
- Rella, C.: Accurate Greenhouse Gas Measurements in Humid Gas Streams Using the Picarro G1301 Carbon Dioxide / Methane / Water Vapor Gas Analyzer 2010.
- 15 Rella, C. W., Chen, H., Andrews, A. E., Filges, A., Gerbig, C., Hataka, J., Karion, A., Miles, N. L., Richardson, S. J., Steinbacher, M., Sweeney, C., Wastine, B., and Zellweger, C.: High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air, *Atmospheric Measurement Techniques*, 6, 837-860, 10.5194/amt-6-837-2013, 2013.
- Reum, F., Gerbig, C., Lavric, J. V., Rella, C. W., and Gockede, M.: Correcting atmospheric CO₂ and CH₄ mole fractions obtained with Picarro analyzers for sensitivity of cavity pressure to water vapor, *Atmos. Meas. Tech. Discuss.*, 2018, 1-29, 10.5194/amt-2018-242, 2018.
- 20 Satar, E., Berhanu, T. A., Brunner, D., Henne, S., and Leuenberger, M.: Continuous CO₂/CH₄/CO measurements (2012-2014) at Beromünster tall tower station in Switzerland, *Biogeosciences*, 13, 2623-2635, 10.5194/bg-13-2623-2016, 2016.
- Schibig, M. F., Steinbacher, M., Buchmann, B., van der Laan-Luijckx, I. T., van der Laan, S., Ranjan, S., and Leuenberger, M. C.: Comparison of continuous in situ CO₂ observations at Jungfraujoch using two different measurement techniques, *Atmos. Meas. Tech.*, 8, 57-68, 10.5194/amt-8-57-2015, 2015.
- 25 Stanley, K. M., Grant, A., O'Doherty, S., Young, D., Manning, A. J., Stavert, A. R., Spain, T. G., Salameh, P. K., Harth, C. M., Simmonds, P. G., Sturges, W. T., Oram, D. E., and Derwent, R. G.: Greenhouse gas measurements from a UK network of tall towers: technical description and first results, *Atmos. Meas. Tech.*, 11, 1437-1458, 10.5194/amt-11-1437-2018, 2018.
- Tans, P. P., Crotwell, A. M., and Thoning, K. W.: Abundances of isotopologues and calibration of CO₂ greenhouse gas measurements, *Atmos. Meas. Tech.*, 10, 2669-2685, 10.5194/amt-10-2669-2017, 2017.
- 30 Topp, E., and Pattey, E.: Soils as sources and sinks for atmospheric methane, *Canadian Journal of Soil Science*, 77, 167-177, 10.4141/S96-107, 1997.
- Turnbull, J. C., Sweeney, C., Karion, A., Newberger, T., Lehman, S. J., Tans, P. P., Davis, K. J., Lauvaux, T., Miles, N. L., Richardson, S. J., Cambaliza, M. O., Shepson, P. B., Gurney, K., Patarasuk, R., and Razlivanov, I.: Toward quantification and source sector identification of fossil fuel CO₂ emissions from an urban area: Results from the INFLUX experiment, *Journal of Geophysical Research: Atmospheres*, 120, 292-312, 10.1002/2014JD022555, 2015.
- 35 van der Laan, S., Neubert, R. E. M., and Meijer, H. A. J.: A single gas chromatograph for accurate atmospheric mixing ratio measurements of CO₂, CH₄, N₂O, SF₆ and CO, *Atmos. Meas. Tech.*, 2, 549-559, 10.5194/amt-2-549-2009, 2009.
- van Rossum, G.: Python tutorial, Technical Report CS-R9526, Centrum voor Wiskunde en Informatica (CWI), Amsterdam, 1995.
- Walt, S. v. d., Colbert, S. C., and Varoquaux, G.: The NumPy Array: A Structure for Efficient Numerical Computation, *Computing in Science & Engineering*, 13, 22-30, 10.1109/MCSE.2011.37, 2011.
- 40 Welp, L. R., Keeling, R. F., Weiss, R. F., Paplawsky, W., and Heckman, S.: Design and performance of a Nafion dryer for continuous operation at CO₂ and CH₄ air monitoring sites, *Atmos. Meas. Tech.*, 6, 1217-1226, 10.5194/amt-6-1217-2013, 2013.
- Wunderlich, J., Chen, H., Gerbig, C., Seifert, T., Kolle, O., Lavrič, J. V., Kaiser, C., Höfer, A., and Heimann, M.: Continuous low-maintenance CO₂/CH₄/H₂O measurements at the Zotino Tall Tower Observatory (ZOTTO) in Central Siberia, *Atmos. Meas. Tech.*, 3, 1113-1128, 10.5194/amt-3-1113-2010, 2010.
- 45 WMO: 19th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques (GGMT-2017) Geneva, Switzerland, 2018.
- Young, D.: Development of a Pre-Concentration System for the Determination of Atmospheric Oxygenated Volatile Organic Compounds, Doctor of Philosophy, School of Chemistry, Faculty of Science, University of Bristol, Bristol, 2007.
- 50 Yyer Kwok, C., Laurent, O., Guemri, A., Philippon, C., Wastine, B., Rella, C. W., Vuillemin, C., Truong, F., Delmotte, M., Kazan, V., Darding, M., Lebégue, B., Kaiser, C., Xueref-Rémy, I., and Ramonet, M.: Comprehensive laboratory and field testing of cavity ring-down spectroscopy analyzers measuring H₂O, CO₂, CH₄ and CO, *Atmos. Meas. Tech.*, 8, 3867-3892, 10.5194/amt-8-3867-2015, 2015.
- Zhao, C. L., and Tans, P. P.: Estimating uncertainty of the WMO mole fraction scale for carbon dioxide in air, *Journal of Geophysical Research-Atmospheres*, 111, D08s09 10.1029/2005jd006003, 2006.
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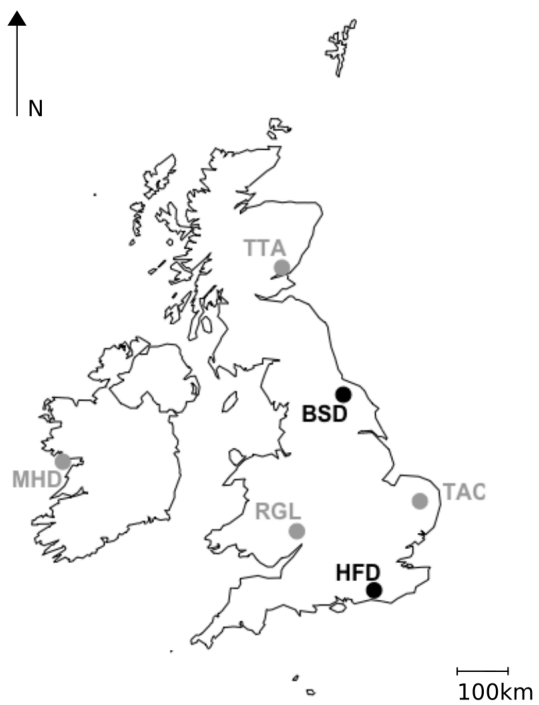
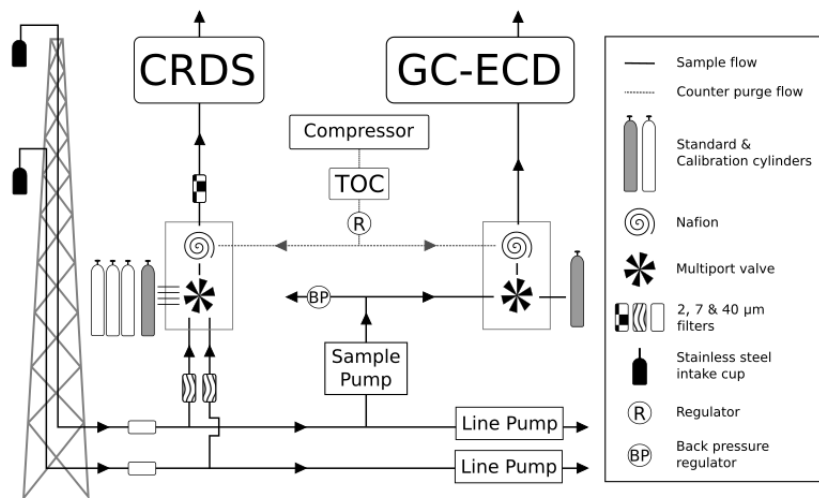
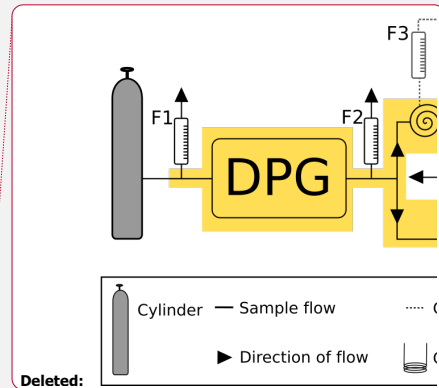
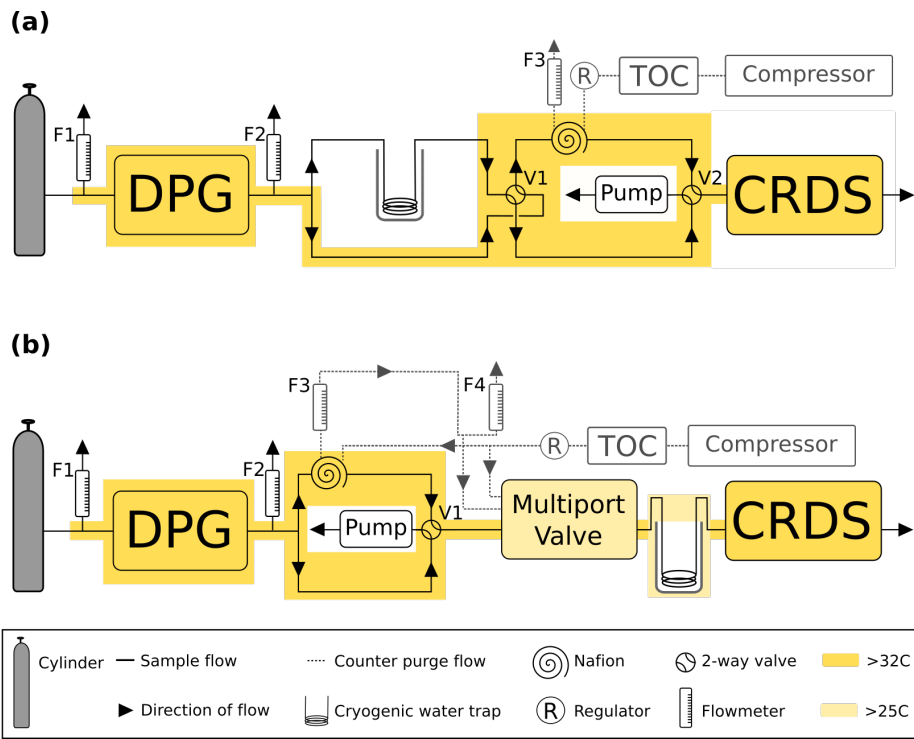


Figure 1: Locations of the GAUGE Bilsdale (BSD) and Heathfield (HFD) sites, shown in black and the UK DECC Mace Head (MHD), Ridge Hill (RGL), Tacolneston (TAC) and Angus (TTA) sites, shown in grey.



5 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 dry 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.



5 **Figure 3:** A schematic of the humidification system used in the **a) CRDS water correction assessment and b) Nafion® counter purge experiment including the dew point generator (DPG)**. Here the TOC is the dry gas generator. The Black arrows and lines show the direction of sample gas flow. Grey dashed lines and arrows show the flow path of the Nafion® counter purge gas. Heated zones are shown in yellow.



Figure 4: Minute mean (a) CO₂, (b) CH₄ and (c) CO and 10 minute discrete (d) N₂O and (e) SF₆ observations at the Bilsdale site for the 42 m (blue), 108 m (green) and 248 m (purple) intake heights.

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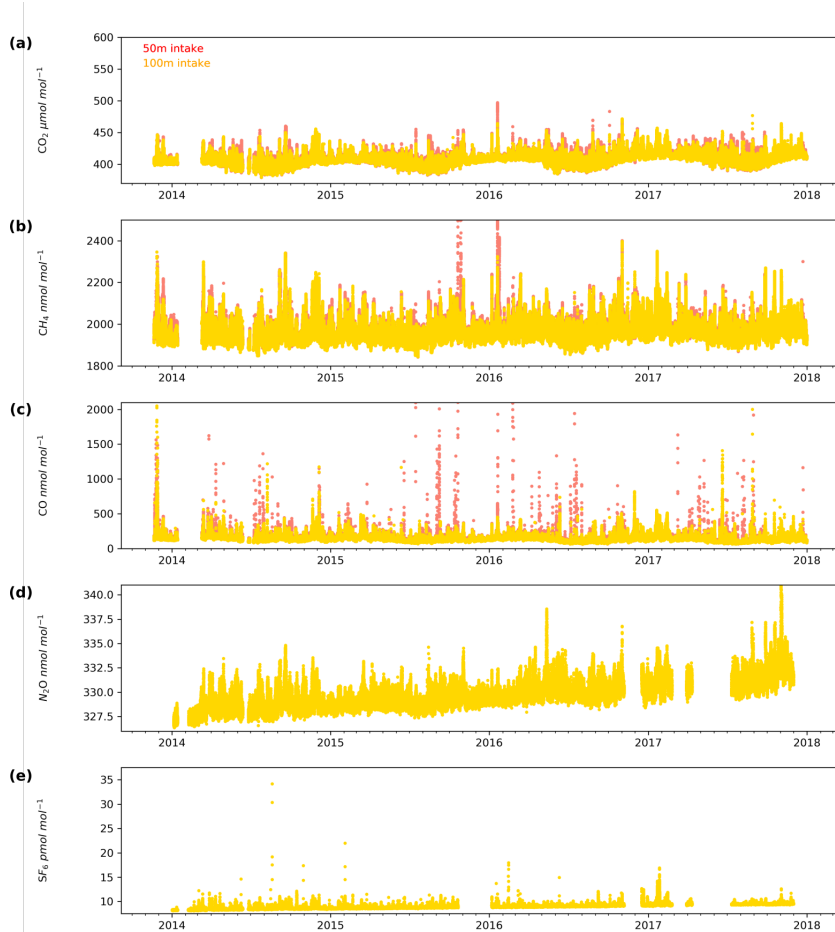
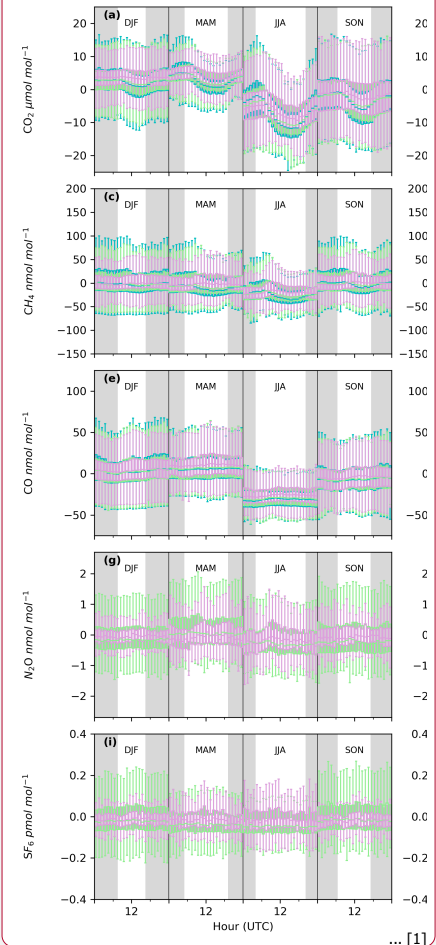
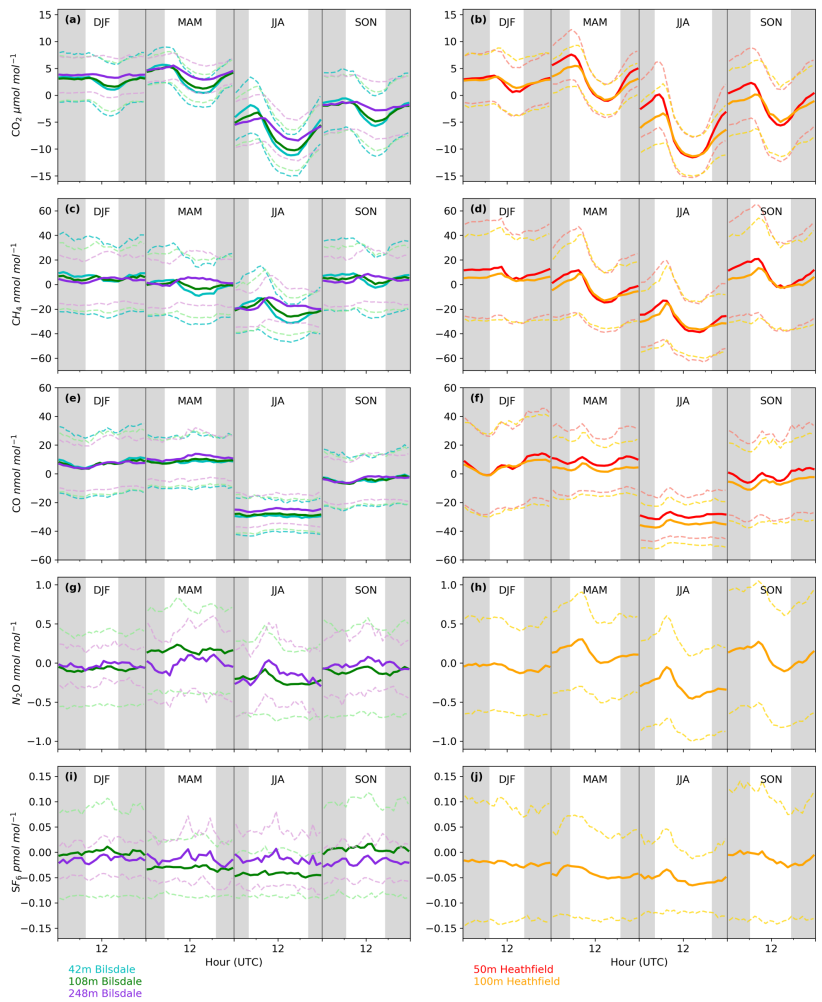


Figure 5: Minute mean (a) CO₂, (b) CH₄ and (c) CO and 10 minute discrete (d) N₂O and (e) SF₆ observations at the Heathfield site for the 50 m (red) and 100 m (yellow) intake heights.

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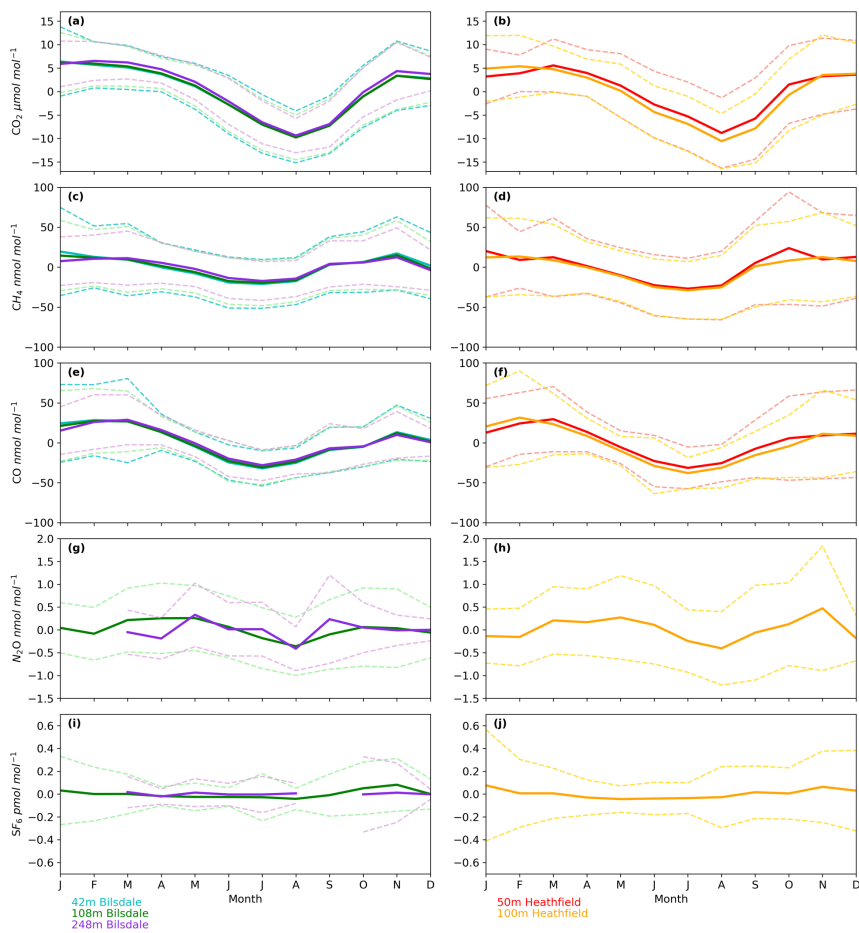




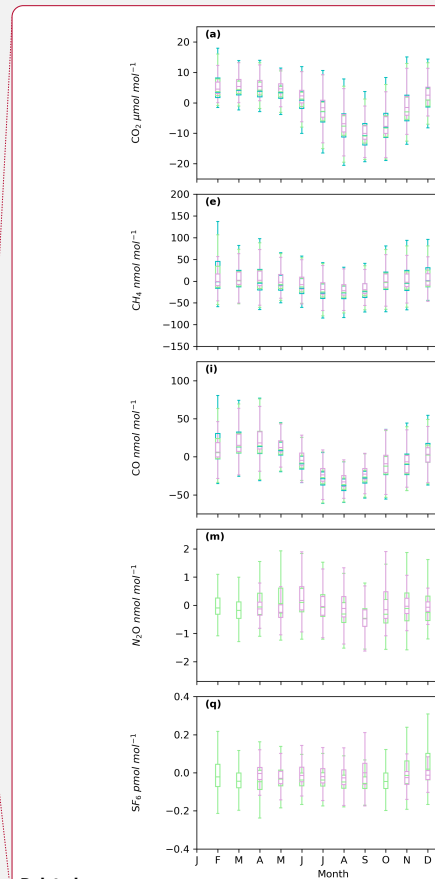
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Figure 6: Mean diurnal cycle by season of detrended hourly mean values for (a) & (b) CO₂, (c) & (d) CH₄, (e) & (f) CO, (g) & (h) N₂O and (i) & (j) SF₆ of the Bilsdale 42 m (blue), 108 m (green) & 248 m (purple) and Heathfield 50 m (red) & 100 m (yellow) intake heights. Dashed lines are the standard deviation.

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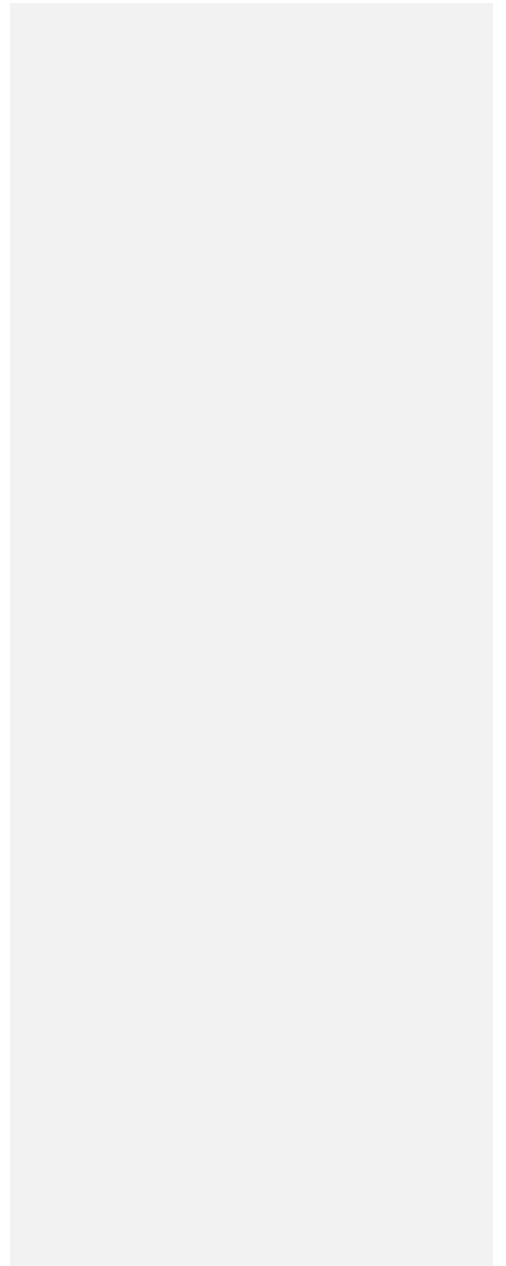
5 **Figure 7: Mean** seasonal cycle of detrended hourly mean values for (a) & (b) CO₂, (c) & (d) CH₄, (e) & (f) CO, (g) & (h) N₂O and (i) & (j) SF₆ of the Biltsdale 42 m (blue), 108 m (green) & 248 m (purple) and Heathfield 50 m (red) & 100 m (yellow) intake heights. Dashed lines are the standard deviation.

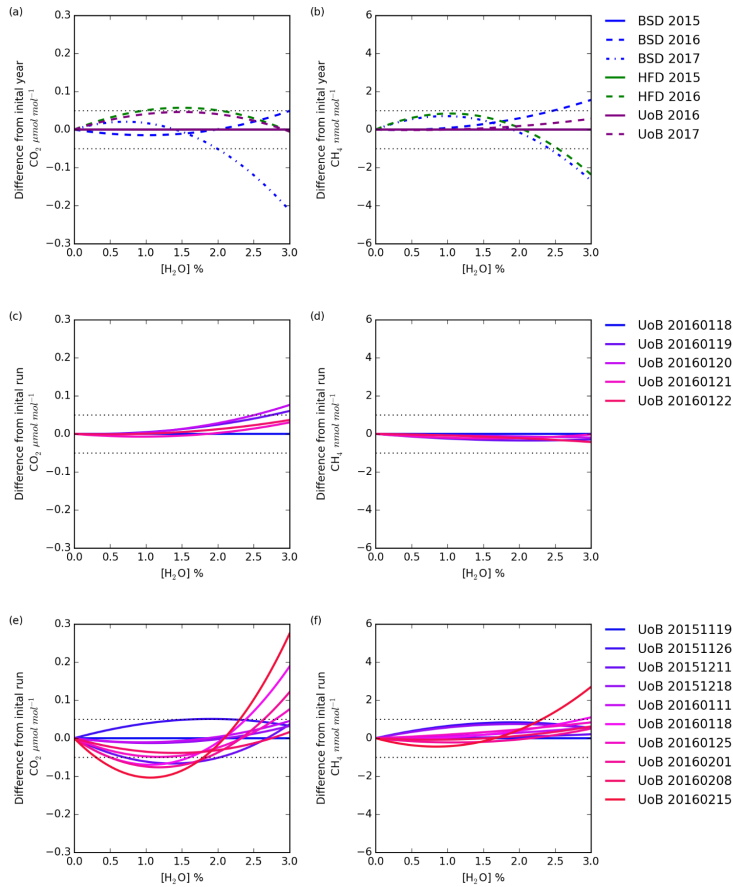


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5 **Figure 8: The change with water in the difference in CO_2 and CH_4 dry mole fraction between: the first annual mean instrument specific water correction and subsequent annual corrections (a & b); the first individual water correction and subsequent daily corrections (c & d) and the first individual water correction and subsequent weekly tests (e & f). The daily and weekly tests were conducted using only the UoB instrument while the annual tests were conducted using all three instruments.**

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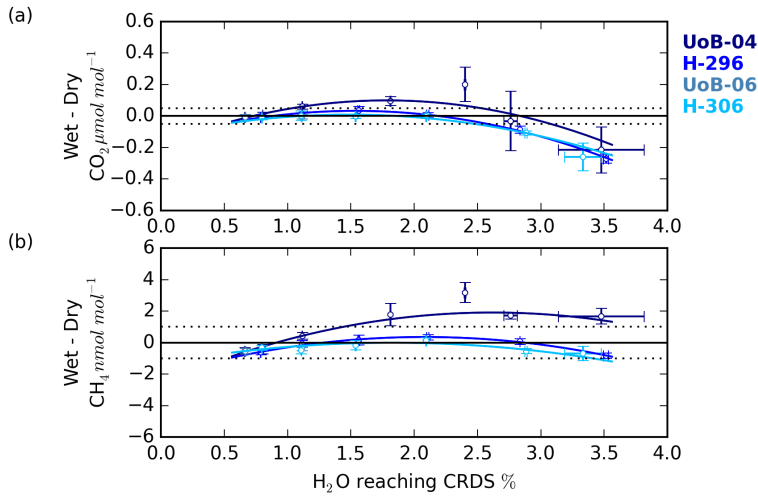


Figure 9: The (a) CO_2 and (b) CH_4 change in the Wet – Dry sample treatment difference with sample water content for cylinders UoB-04 ($515.3 \mu\text{mol mol}^{-1} \text{CO}_2$ and $2585 \text{ nmol mol}^{-1} \text{CH}_4$), H-296 ($406.6 \mu\text{mol mol}^{-1} \text{CO}_2$ and $1947 \text{ nmol mol}^{-1} \text{CH}_4$), UoB-06 ($384.8 \mu\text{mol mol}^{-1} \text{CO}_2$ and $1975 \text{ nmol mol}^{-1} \text{CH}_4$) and H-306 ($372.5 \mu\text{mol mol}^{-1} \text{CO}_2$ and $1776 \text{ nmol mol}^{-1} \text{CH}_4$). Error bars are the larger of either the standard deviation of the mean difference or the uncertainties of the two sample types added together in quadrature.

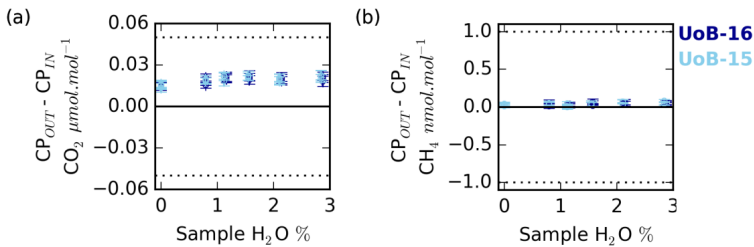
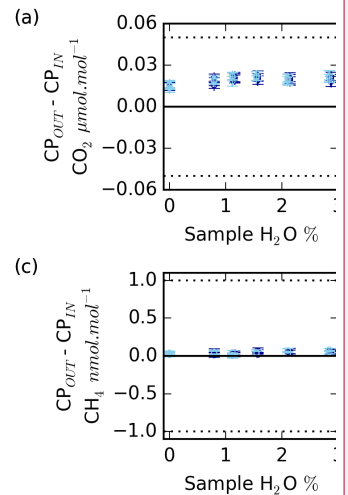


Figure 10: Change in the counter purge in (CP_{in}) and out (CP_{out}) (a) CO_2 and (b) CH_4 mole fraction with sample water content for ambient (UoB-15) and above ambient (UoB-16) mole fraction cylinders. Note that the gas stream was cryogenically dried before



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analysis. Error bars are larger of either the standard deviation of the mean difference or the uncertainties of the two sample types added together in quadrature. The dotted lines in (a) and (b) are the respective WMO internal reproducibility guidelines.

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Table 1 – Instrument specific water corrections for the Bilsdale (BSD), Heathfield (HFD) and University of Bristol (UoB) CRDS instruments. The parameters shown are the mean \pm the 95% confidence interval of tests repeated in triplicate. Water corrections labelled High and Low were determined using an above ambient and below ambient mole fraction cylinder, respectively, while the rest were determined using an ambient mole fraction cylinder. The mean residual along with the interquartile range of the residuals are included.

		A		B		Mean residual (25 th -75 th quartile) CO ₂ $\mu\text{mol mol}^{-1}$ CH ₄ nmol mol^{-1}	n
CO ₂	BSD	2015	-0.0157 \pm 0.0001	0.00018 \pm 0.00008	0.00008	0.0003 (-0.01 – 0.01)	4
		2016	-0.01578 \pm 0.00004	0.00022 \pm 0.00002	0.00002	-0.002 (-0.01 – 0.01)	3
		2017	-0.01556 \pm 0.00005	0.00008 \pm 0.00002	0.00002	-0.001 (-0.01 – 0.02)	5
	HFD	2015	-0.01558 \pm 0.00008	0.00010 \pm 0.00004	0.00004	-0.002 (-0.02 – 0.02)	3
		2016	-0.0154 \pm 0.0001	0.00004 \pm 0.00003	0.00003	0.004 (-0.003 – 0.02)	1*
	UoB	2015	-0.0156 \pm 0.0003	0.0001 \pm 0.0001	0.0001	-0.00002 (-0.03 – 0.03)	3
		2016	-0.01577 \pm 0.00007	0.00020 \pm 0.00004	0.00004	-0.02 (-0.03 – 0.02)	13
		2017	-0.01558 \pm 0.00008	0.00012 \pm 0.00004	0.00004	-0.006 (-0.02 – 0.007)	3
		2016 High	-0.0160 \pm 0.0003	0.0003 \pm 0.0001	0.0001	0.007 (0.007 – 0.05)	3
		2016 Low	-0.01606 \pm 0.00005	0.00030 \pm 0.00002	0.00002	-0.02 (-0.02 – 0.02)	3
CH ₄	BSD	2015	-0.0138 \pm 0.0002	0.0005 \pm 0.0001	0.0001	-0.02 (-0.2 – 0.1)	4
		2016	-0.0139 \pm 0.0002	0.0006 \pm 0.0001	0.0001	-0.04 (-0.2 – 0.1)	3
		2017	-0.01309 \pm 0.00009	0.00014 \pm 0.00002	0.00002	-0.04 (-0.2 – 0.1)	5
	HFD	2015	-0.01273 \pm 0.00004	0.00013 \pm 0.00004	0.00004	-0.03 (-0.2 – 0.2)	3
		2016	-0.0119 \pm 0.0005	-0.0002 \pm 0.0002	0.0002	-0.09 (-0.4 – 0.3)	1*
	UoB	2015	-0.0137 \pm 0.0003	0.0002 \pm 0.0001	0.0001	-0.06 (-0.2 – 0.1)	3
		2016	-0.0139 \pm 0.0001	0.00025 \pm 0.00005	0.00005	0.002 (-0.2 – 0.2)	13
		2017	-0.0139 \pm 0.0001	0.00027 \pm 0.00006	0.00006	-0.04 (-0.2 – 0.1)	3
		2016 High	-0.01393 \pm 0.00005	0.0004 \pm 0.0001	0.0001	0.1 (-0.02 – 0.3)	3
		2016 Low	-0.01402 \pm 0.00005	0.00028 \pm 0.00008	0.00008	-0.02 (-0.1 – 0.1)	3

*The fitted parameter and $1\sigma^2$ of a single test due to a leak in the septum

Table 2 – The cylinders used during the dew point generator CRDS water correction, Nafion® counter purge and UoB instrument specific water tests. Most measurements were made in-house and only corrected for linear drift against a standard calibrated at WCC-EMPA, Dübendorf, Switzerland and hence are simply indicative of the expected mole fractions. While those marked * were calibrated at GasLab MPI-BGC, Jena, Germany and linked to the WMO x2007 CO₂ and x2004A CH₄ scales.

Test type	Cylinder	CO ₂	CH ₄
		μmol mol ⁻¹	nmol mol ⁻¹
Dew point generator CRDS water correction	H-306	372.5	1776
	UoB-06	384.8	1975
	H-296	406.6	1947
	UoB-04	515.3	2585
Nafion® counter purge	UoB-15	399.3	1928
	UoB-16	430.7	2015
UoB instrument specific water correction	USN20104095*	346.91 ± 0.06	1742.9 ± 0.3
	H-283	379.1	1815
	USN20104068*	449.49 ± 0.05	2145.0 ± 0.4

Table 3 – CRDS calibration and standard cylinder mole fractions and usage start dates for the Heathfield (HFD) and Bilsdale (BDS) sites. Where available the mole fractions measured prior to and after deployment are given. Reported mole fractions from the WCC-EMPA, Dübendorf, Switzerland are given as mean \pm uncertainty. *Mole fraction measurement from GasLab MPI-BGC, Jena, Germany are given as mean \pm 1 σ .

Cylinder		CO ₂ WMO x2007 $\mu\text{mol mol}^{-1}$		CH ₄ WMO x2004A nmol mol^{-1}		CO WMO x2014 nmol mol^{-1}		Start date – End date		
		Prior	Post	Prior	Post	Prior	Post			
BDS	Calibration Suite #1	Low	-	379.2 \pm 0.2	-	1807 \pm 3	-	124 \pm 2	2014-30-1 – 2015-04-24	
		Ambient	-	394.7 \pm 0.2	-	1889 \pm 4	-	131 \pm 2	2014-02-20 – 2015-11-07	
		High	-	456.5 \pm 0.2	-	2074 \pm 4	-	583 \pm 6	2014-01-30 – 2015-04-24	
	Calibration Suite #2*	Low	379.51 \pm 0.06	-	1812.5 \pm 0.02	-	74.6 \pm 0.3	-	2016-01-20 – Current	
		Ambient	418.63 \pm 0.06	-	2090.0 \pm 0.03	-	246.1 \pm 0.4	-	2015-10-02 – Current	
		High	471.17 \pm 0.06	-	2404.8 \pm 0.04	-	469.2 \pm 0.5	-	2015-10-02 – Current	
	Standard	H-239	-	395.2 \pm 0.2	-	1900 \pm 4	-	118 \pm 3	2014-01-30 – 2014-09-23	
		H-252	402.3 \pm 0.2	402.3 \pm 0.2	1906 \pm 2	1906 \pm 4	138 \pm 2	144 \pm 3	2014-09-23 – 2015-07-22	
		H-251	402.2 \pm 0.2	402.3 \pm 0.2	1906 \pm 2	1906 \pm 4	138 \pm 2	145 \pm 3	2015-07-22 – 2016-05-06	
		USN-20141394*	399.31 \pm 0.05	-	1939.3 \pm 0.02	-	123.7 \pm 0.3	-	2016-05-06 – Current	
	HFD	Calibration Suite*	Low	369.24 \pm 0.06	-	1845.9 \pm 0.3	-	128.8 \pm 0.3	-	2013-12-16 – Current
			Ambient	420.24 \pm 0.06	-	1993.8 \pm 0.3	-	321.7 \pm 0.5	-	2013-12-16 – Current
High1			441.26 \pm 0.06	-	2211.0 \pm 0.4	-	224.23 \pm 0.4	-	2013-12-16 – 2017-01-27	
High2			477.59 \pm 0.06	-	2282.1 \pm 0.4	-	104.65 \pm 0.3	-	2017-02-24 – Current	
Standard		H-240	-	394.3 \pm 0.2	-	1882 \pm 4	-	121 \pm 3	2013-12-16 – 2014-12-17	
Standard	H-255	402.1 \pm 0.2	402.1 \pm 0.2	1908 \pm 2	1908 \pm 4	135 \pm 2	141 \pm 3	2014-12-17 – 2015-10-21		
	H-254	402.1 \pm 0.2	402.2 \pm 0.2	1908 \pm 2	1908 \pm 4	135 \pm 2	142 \pm 3	2015-10-21 – 2016-09-21		
	H-285	393.6 \pm 0.2	-	1928 \pm 4	-	105 \pm 2	-	2016-09-21 – Current		

Table 4 – GC-ECD standard cylinder mole fractions and usage start dates

Site	Cylinder	N ₂ O	SF ₆	Start date
		SIO-16 nmol mol ⁻¹	SIO-SF6 pmol mol ⁻¹	
HFD	H-234	326.67	8.20	14/11/2013
BDL	H-235	326.56	8.13	14/1/2014
	H-222	326.23	8.05	2/10/2015

Table 5 –Estimates of the maximum error associated with the measurement of ambient CO₂ and CH₄ mole fraction samples using the given drying and/or water correction method for the BSD and HFD sites

Site	Time period	Drying method	Water mole fraction at CRDS	Maximum CO ₂ error $\mu\text{mol mol}^{-1}$	Maximum CH ₄ error nmol mol^{-1}
Bilsdale (BSD)	2014-01-01 – 2015-06-17	Nafion drying with instrument specific water correction	0.05 – 0.2 %	0.1	2
	2015-06-18 – 2016-10-13	Instrument specific water correction	0 – 0.2 %	0.1	2
			0.2 – 2.1 %	0.05	1
	2016-10-14 - Current	Instrument specific water correction	0 – 1 %	0.2	2
1 – 2.2 %			0.05	1	
Heathfield (HFD)	2013-12-01 – 2015-09-30	Nafion drying with instrument specific water correction	0.05 – 0.2 %	0.1	2
	2015-10-01 – 2016-08-23	Instrument specific water correction	0 – 0.2 %	0.1	1
			0.2 – 2.4 %	0.07	1
	2016-08-23 – Current	Instrument specific water correction	0 – 1.7 %	0.1	3
1.7 – 2.4 %			0.05	1	

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8 Supplementary

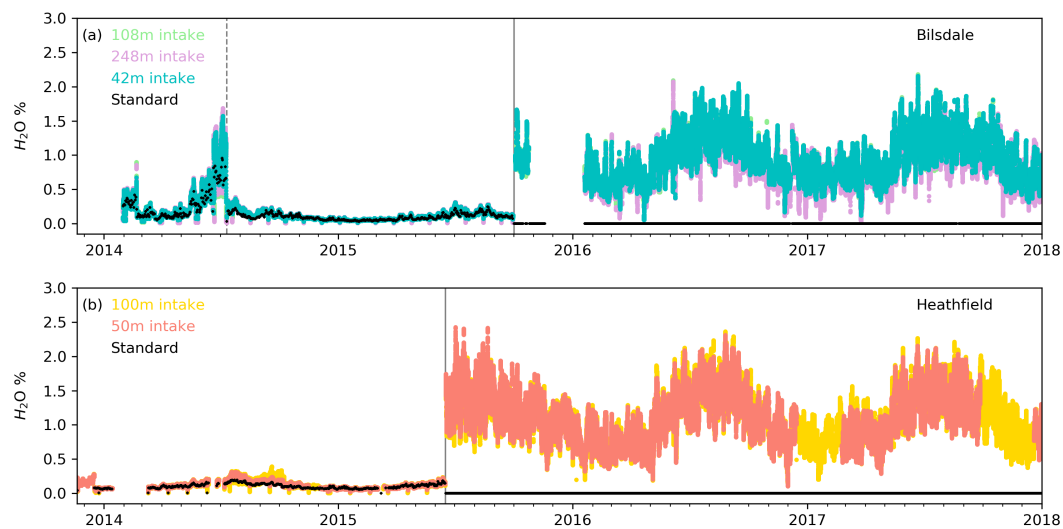


Figure S1: The minute mean water observations for (a) Bilsdale and (b) Heathfield. Blue, green and purple data points represent the Bilsdale 42m, 108m and 248m intakes and the red and yellow data points represent the Heathfield 50m and 100m intakes, respectively. The black data points are the 20min mean of the daily standards. The dashed grey line indicates when the TOC system at the Bilsdale site was repaired. The solid grey line indicates when the Nafion® driving systems were removed from the sites.

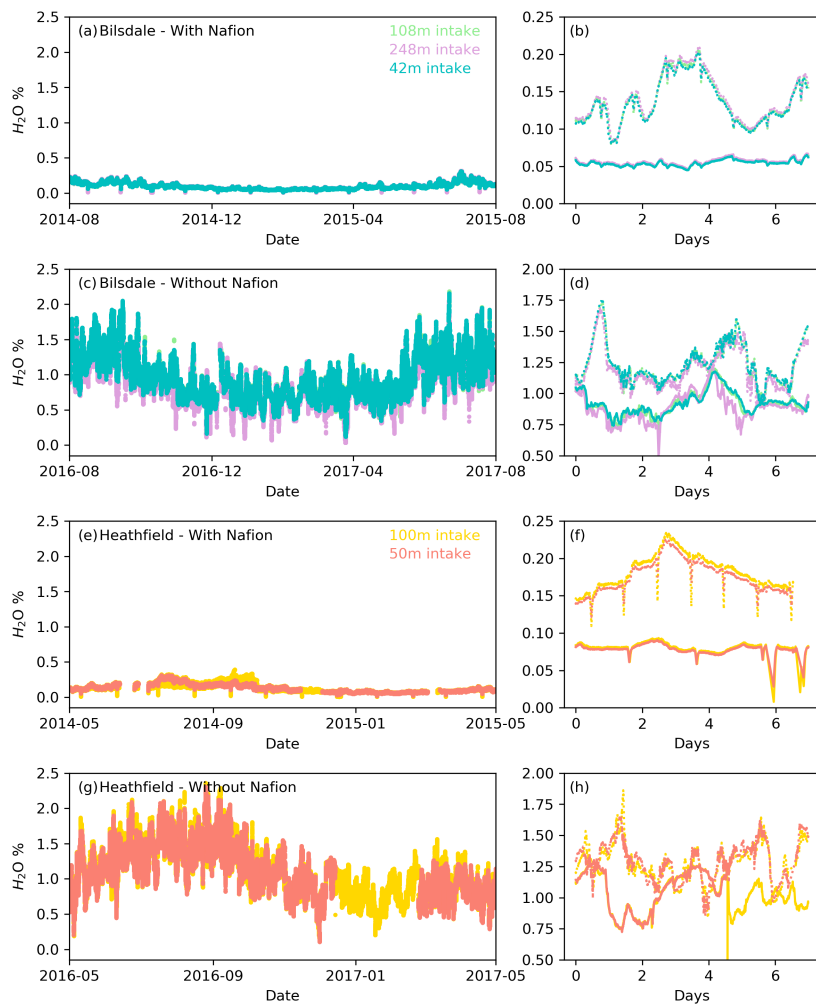


Figure S2: Seasonal and diurnal patterns in minute mean water observations. Blue, green and purple represent the Bilsdale 42m, 108m and 248m intakes and red and yellow represent the Heathfield 50m and 100m intakes, respectively. Figure (a) and (c) show a full year's worth of data at Bilsdale, with and without the Nafion® driving system, respectively. Similarly, Figures (e) and (g) show a full year's worth of data at Heathfield, with and without the Nafion® driving system. Figures (b) and (d) show week-long periods of data in summer (dashed lines) and winter (solid lines) at Bilsdale with and without the Nafion®, respectively. Similarly, Figures (f) and (h) show week-long periods of data in summer (dashed lines) and winter (solid lines) at Heathfield with and without the Nafion®, respectively.

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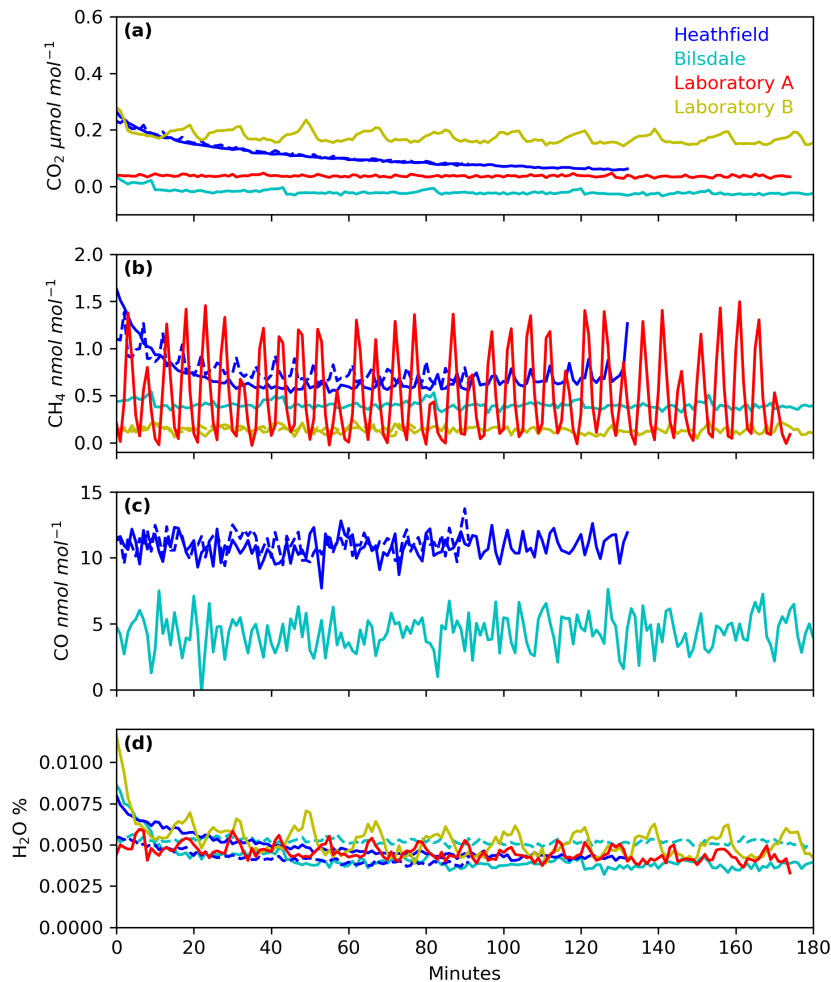


Figure S3: (a) CO₂, (b) CH₄, (c) CO and (d) H₂O mole fractions of the gas generator used to supply the Nafion® counter purge flow. Note the HFD gas generator was powered up just before to analysis in contrast to the other sites where the TOCs had been running for at least 12 hours prior to analysis.

Deleted: The CRDS water correction was assessed through a series of simple Dew Point Generator (DPG; Licor LI-610 Portable Dew Point Generator, USA) experiments. Here four cylinders of air with varying CO₂ and CH₄ mole fractions (Table 4) were humidified to a range of set dew points between 2.5 and 30 °C (0.6 to 3.5 % H₂O) and measured, with and without cryogenic drying, using a Picarro G2301 CRDS at the University of Bristol (UoB) laboratory. Cylinder delivery pressure was controlled using single stage high purity stainless steel Parker Veriflow regulators (95930S4PV3304, Parker Balston, USA) or TESCOM regulators (64-2640KA411, Tescom Europe). ¶

In brief, the output of the cylinder regulator was plumbed to the input of the DPG. A T-piece connected prior to the DPG input vented any excess gas via a flow meter (F1, Fig. S2) ensuring that the DPG input remained at close to ambient atmospheric pressure throughout the experiment. The output of the DPG passed through a second T-piece with the over flow outlet also connected to a flow meter (F2) to ensure that the CRDS input pressure remained near ambient. A third flowmeter (F3) was placed on the outflow of the Nafion counter purge. Flow meters F1 and F2 had a range of 0.1–1 L min⁻¹ (VAF-G1-05M-1, Swagelok, UK) while F3 had a smaller flow range 0.5–0.5 L min⁻¹ (FR2A12BVBN-CP, Cole-Palmer, USA). Typical output flows were 0.1, 0.3 and 0.3 L min⁻¹ for F1, F2 and F3 respectively. After F2 the sample flow was further split using a T-piece, with half the flow passing through a cryogenic water trap before reaching a 4-port 2-position valve, V1 (EUDA-2C6UWEPH, VICI Valco AG International, Switzerland, actually a 6-port valve configured as a 4-port valve). The other half bypassed the water trap and connected directly to V1. One of the outputs of V1 went via the Nafion to a second identical valve, V2, while the second output went directly to V2. The first output of V2 connected directly to the input of the CRDS while the second connected to a pump (PICARRO Vacuum pump S/N PB2K966-A) set to a flow rate matching that of the CRDS (0.3 L/min) to ensure uniform flow through both branches of the system. These valves were controlled manually using a VALCO electronic controller and universal actuator. ¶

The water trap consisted of a coil of ¼" diameter (I.D. 3.36mm) stainless steel tubing immersed in a Dewar of silicone oil (Thermo Haake SIL 100, Thermo Fisher Scientific, USA). The silicone oil was cooled using an immersion probe (CC-65, NESLAB) to less than -50 °C. Other than the water trap and two short sections (< 10 cm) of ¼" (O.D.) plastic tubing immediately prior to and post the DPG, 1/16" stainless steel tubing was used throughout the system. ¶

The experiment was conducted in a temperature-controlled laboratory at 19 °C, and thus, at temperatures lower than a number of the dew points used within the experiment. Hence, in order to avoid condensation forming on the walls of the tubing all components of the system between the cylinder, excluding the water trap, and the outputs of V2 were contained within a chamber heated to > 32 °C. Tubing between the heated chamber and the input of the CRDS was also heated with heating tape to > 32 °C while the internal temperature of the CRDS was > 32 °C throughout the experiment. ¶ Multiple measurement blocks of each sample treatment were conducted after a lengthy initial stabilisation period. This period allowed for the establishment of equilibrium between the water in the condenser block of the DPG and the sample gas and lasted at least 2 hours (sometimes up to 5 hours). The treatment blocks varied in... [2]

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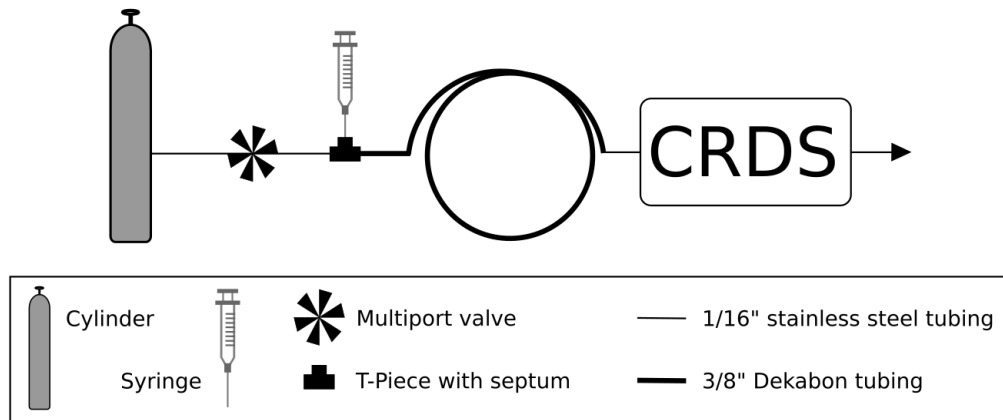
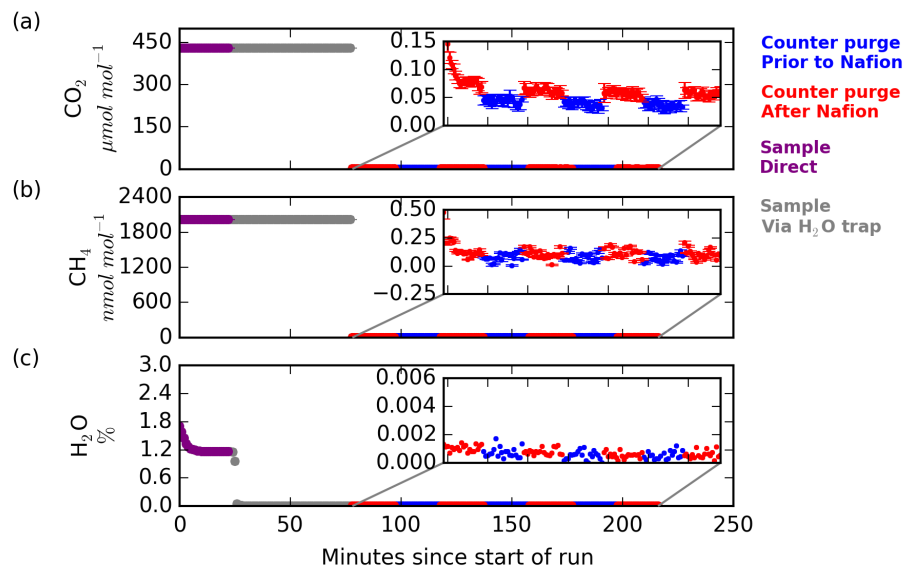


Figure S4: Droplet test instrument specific water correction flow path and procedure

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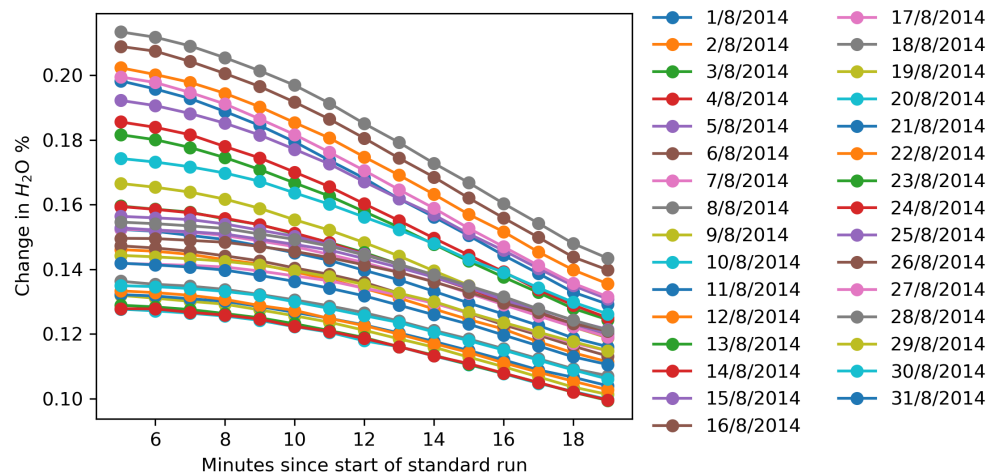
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Figure S5: The (a) CO₂, (b) CH₄ and (c) H₂O minute mean data obtained during the Nafion® counter purge experiments for cylinder UoB-16 at a dewpoint of 10C. Error bars are ± 1 standard deviation of each minute mean. Purple and grey data points are the sample without and with the H₂O trap, respectively, while blue and red data points are the Nafion® counter purge before and after the Nafion®, respectively.

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Figure S6: The change in the moisture content of standards measured at Heathfield during August 2014. Each colour represents a different standard run. The date of each run is given in the legend.

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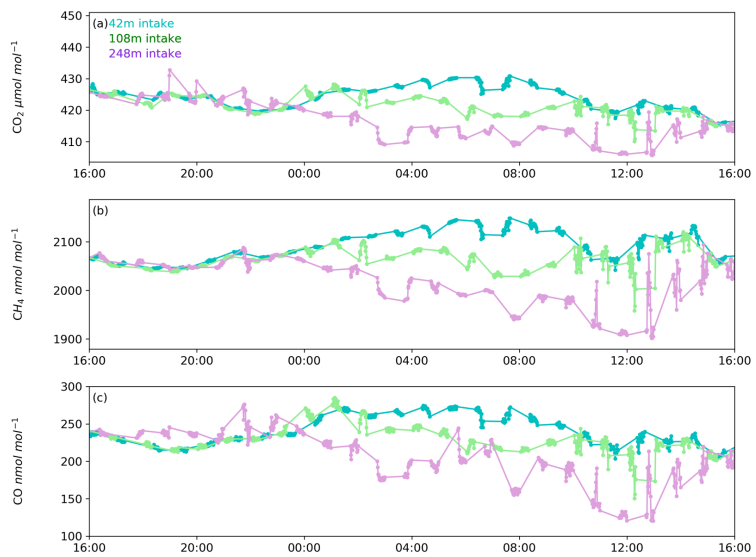
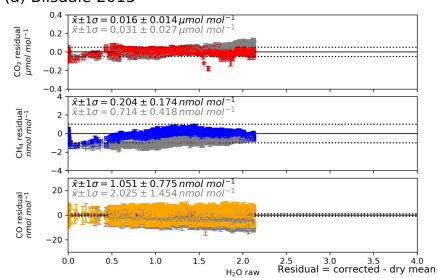
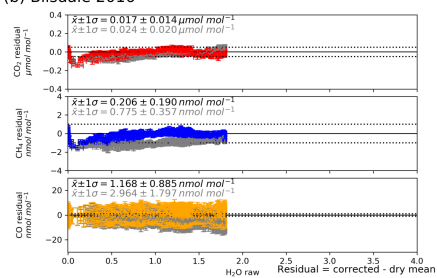


Figure S7: The (a) CO_2 , (b) CH_4 and (c) H_2O minute mean data for 24 hours starting 16:00 11/3/2016 at Bildsdaie. Blue, green and purple data points represent the 42m, 108m and 248m intakes, respectively.

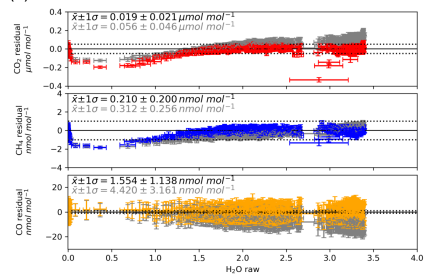
(a) Bilsdale 2015



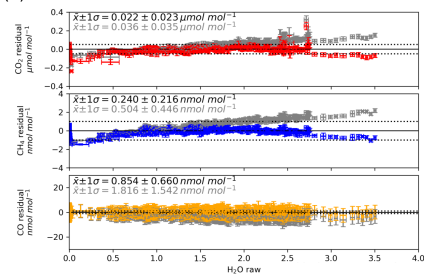
(b) Bilsdale 2016



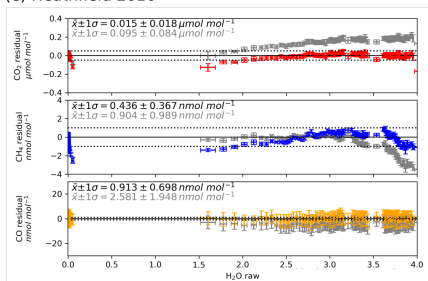
(c) Bilsdale 2017



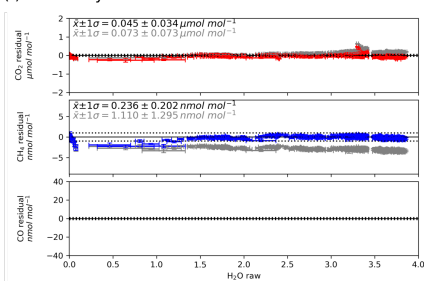
(d) Heathfield 2015



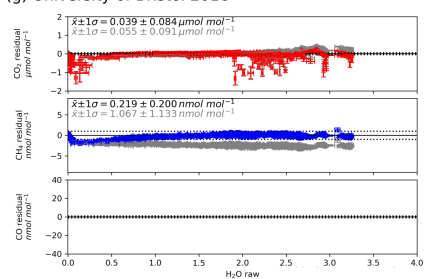
(e) Heathfield 2016



(f) University of Bristol 2015



(g) University of Bristol 2016



(h) University of Bristol 2017

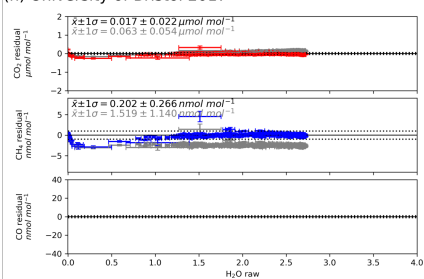


Figure S8: Droplet test residual, wet corrected data less dry mean, plots for Bilsdale (a) 2015, (b) 2016 and (c) 2017, Heathfield (d) 2015 and (e) 2016 and University of Bristol (f) 2015, (g) 2016 and (h) 2017. The instrument specific CO₂ residual values (red) are shown in the upper plots, CH₄ (blue) in the middle plots. And CO (orange) in the lower plots. The residuals of the factory determined water correction are also shown in grey. The mean $\pm 1\sigma^2$ of the residuals are given for each plot for both the instrument specific (black) and the factory (grey) corrections.

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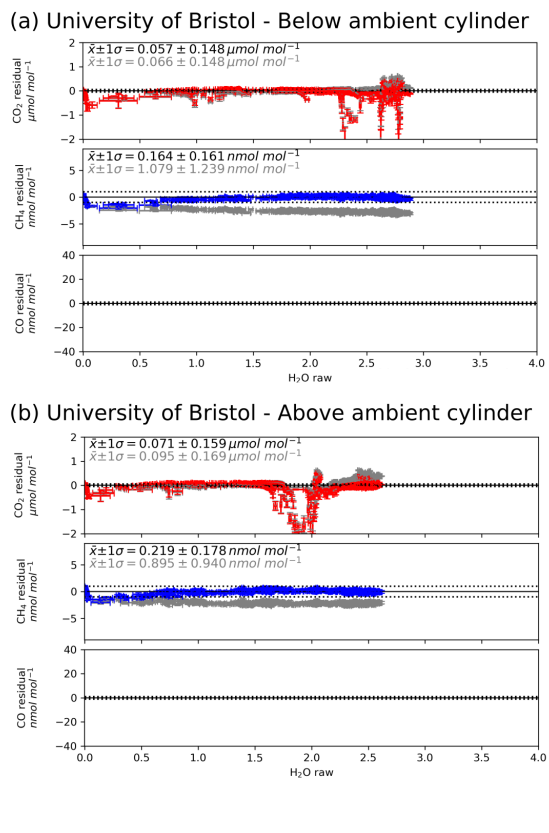


Figure S9: Droplet test residual, wet corrected data less dry mean, plots for (a) below ambient cylinder and (b) the above ambient cylinder at the University of Bristol. The instrument specific CO₂ residual values (red) are shown in the upper plots and CH₄ (blue) in the middle plots. The residuals of the factory determined water correction are also shown in grey. The mean $\pm 1\sigma^2$ of the residuals are given for each plot for both the instrument specific (black) and the factory (grey) corrections.

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