Response to “Interactive comment on “Correcting atmospheric CO2 and CH4 mole fractions obtained with Picarro analyzers for sensitivity of cavity pressure to water vapor” by Friedemann Reum et al.” by Anonymous Referee #2

We thank the referee for this thorough review, which uncovered a number of revisions needed to improve the manuscript.

General comments

Comment:
The paper is certainly relevant for users aiming at highest accuracy of their measurements. However, I miss a little bit the context to other potential sources of uncertainty. The effect seems to be small and less than the WMO compatibility goal.

Response:
The referee correctly points out that the cavity pressure dependence we address in this paper is only relevant for measurements aiming at the highest accuracy. Other measurement uncertainties are on the same order of magnitude as the biases we address, e.g. the accuracy of calibrations against the WMO scale (e.g. Andrews et al., 2014; Yver Kwok et al., 2015) or cylinder drift. Since the WMO inter-laboratory compatibility goals refer to compound errors from different sources of uncertainty, we regard any correction that is on the order of magnitude of the goals as a relevant contribution to the overall accuracy. Similarly, Yver Kwok et al. (2015) concluded that “to be able to reach the WMO comparison goals, we need biases as small as possible for every source of bias“.
We will add this information to the conclusions:
Sect. 5:
Before: “Accounting for cavity pressure-related biases of CO2 and CH4 readings contributes to keeping the overall measurement uncertainty of the widely used Picarro GHG analyzers operated in humid air below the WMO inter-laboratory compatibility goals.”
Revision: “The biases addressed here are on the order of magnitude of the WMO inter-laboratory compatibility goals, as are several other error sources that affect GHG measurements like tracing the calibration of the gas analyzer to a common primary scale (e.g. Andrews et al., 2014). Therefore, to reach the goals, biases from each individual source need to be as small as possible (Yver Kwok et al., 2015). Thus, accounting for cavity pressure-related biases of CO2 and CH4 readings contributes to keeping the overall measurement uncertainty of the widely used Picarro GHG analyzers operated in humid air below the WMO inter-laboratory compatibility goals”.

Comment:
The proposed alternative water vapor correction will too complicated to implement for most users, and therefore the authors are encouraged to give guidance on how the effect can be avoided.

Response:
We comment on the possibility to avoid the effect below. However, we would also like to follow the referee’s suggestion to provide an easier way to account for the pressure-related biases than our experiments. An alternative to our experiments could be to adjust the setup of water droplet experiments so that they can better maintain stable water vapor levels. This has been achieved with a so-called “water trap” by Winderlich et al.(2010), which we will reference in the conclusions:

Sect. 5:
Before: “The commonly used droplet method is not suitable for correcting biases of CO2 and CH4 readings related to cavity pressure without independent cavity pressure monitoring, because in these experiments, water vapor can vary faster than it takes cavity pressure to adjust to a new water vapor level.”
Addition: “Since the humidification via gas washing bottle is complicated to implement in the field and may have affected our CO2 results, alternative humidification methods may be more suitable. For example, Winderlich et al.(2010) achieved stable water vapor levels with much smaller amounts of liquid water in the air stream using a so-called “water trap”, which is akin to a droplet experiment with more controlled evaporation.”
See also the referee comment below on differences between droplet results for further modification of this section.

Comment:
This could be a recommendation that drying to very low humidity might be necessary if highest accuracy is required. I also think that a setup using Nafion dryers can be used if the calibration gases also pass over the dryer. The authors point out that the effect on the pressure sensor readings is also relevant for measurements made using a Nafion dryer. This certainly holds true if the calibration gas is not passing over the dryer. However, if the calibration gas is also passing over the Nafion dryer it will be humidified, which results in very small humidity changes between sample and calibration gas, and the effect might be neglected.

Response:
The pressure-related biases could be avoided by drying to very low humidities using a cryo trap. We will add this statement to the conclusions (see below).
We thank the referee for pointing out that, when employing Nafion, passing the calibration air through the membrane tube as well may resolve the humidity mismatch. However, even with this treatment, humidity differences can remain between sample and calibration air. Stavert et al. (2018) noted that their Nafion membrane humidified calibration air to less than 0.015 % H2O, while the sample air averaged 0.2 % H2O. This humidity difference would result in the maximum biases we observed. On the other hand, other studies reported smaller differences between the water levels of sample and calibration air after Nafion (Verhulst et al., 2017; Welp et al., 2013), which will considerably reduce the impact of the cavity-pressure related bias. Since we do not have much experience with the Nafion method, we will keep the conclusion that setups that employ Nafion may be affected, but will add that this will only be the case if sample and calibration air have different residual water vapor levels.
Abstract:
Before: “…and can therefore affect measurements obtained in humid air and in air dried with a Nafion membrane.”
Revision: “…and can therefore affect measurements obtained in humid air. Setups that dry sample air using Nafion membranes may be affected as well if there are differences in residual water vapor levels of sample and calibration air.”
Sect. 5:
Before: “As noted by Stavert et al. (2018), the biases may not only affect measurements without drying systems, but also measurement systems that use Nafion membranes to dry air samples, since the residual water vapor can be in the range of the where the largest biases occurred in our experiments (compare e.g. Verhulst et al., 2017).”
Revision: “Drying sample air to very low water levels, e.g. using a cryotrap, would eliminate the biases. However, the biases may affect measurement systems that use Nafion membranes to dry air samples due to residual water vapor. Stavert et al. (2018) reported that in their setup,

the Nafion membrane humidified calibration air to less than 0.015 % H_2O, while the humidity of the sample air was on average 0.2 % H_2O. This humidity difference could result in the maximum biases we observed. On the other hand, other studies reported smaller differences between the water levels of sample and calibration air after passing through Nafion (Welp et al., 2013; Verhulst et al., 2017). Eliminating differences between residual water vapor levels of sample and calibration air would remove the biases reported on here."

Comment:
Could the Picarro software correct this "internally"? If all pressure sensors have the same or a similar water vapor dependent bias, a correction should be possible.

Response:
Since we found as yet unexplained differences between instruments, we cannot give a "factory" correction of the pressure-induced biases.

Comment:
Section 3.1 is difficult to understand. I suggest adding a few words of explanation to the numbers given in Table 2, and discuss their meaning and relevance.

Response:
To improve clarity, we will exchange "slope" for "sensitivity". Furthermore, we will add an example to illustrate the magnitude:
Sect. 3.1:
Before: "… demonstrating that biases in cavity pressure directly affect mole fraction readings."
Addition: "For dry air mole fractions of 400 ppm CO_2 and 2000 ppb CH_4, a change of 1 hPa in cavity pressure makes a difference of 0.37 ppm CO_2 and 6.4 ppb CH_4 on average."

Comment:
Why are the water vapor readings not sensitive to pressure changes?

Response:
We think that the water vapor readings are also sensitive to cavity pressure, but that they were too variable in this experiment to detect the sensitivity based on our method. Since sensitivities of water vapor readings on cavity pressure that are undetectable at this level are irrelevant for the remainder of the paper, we did not investigate this further. To avoid confusion, we will remove the statement on the water vapor sensitivity from the manuscript.

Comment:
There is a large difference between droplet experiments shown in section 3.2.2. Experiments 2-4 shows a much faster decrease in H_2O compared to experiment 1. Were the conditions different for those experiments?

Response:
Experiments 2–4 were made on another day than experiment 1, and the setup was reassembled in between. The course of water droplet evaporation may have been affected e.g. by length and shape of the tubing between Tee piece and Picarro analyzer. We will add this information to the text (see below).

In the submitted manuscript, we generalized our results that droplets do not provide stable enough water vapor levels for deriving coefficients for the expanded water correction model by concluding that the droplet method in general is not suitable. However, the differences brought up by the referee in this comment, in particular the fact that the slowest-evaporating droplet yielded results closer to those from the experiment with stable water vapor levels, suggest that droplets may yet be suitable, but under the condition that they yield water vapor levels that vary slowly enough. We will acknowledge this with the suggestion to use the water trap-method for air stream humidification, which may be regarded as a droplet experiment with controlled evaporation (see above). Therefore, we will remove the generalizations that water droplets are not suitable in our evaluations of droplet results:
Abstract:
Before: "The commonly used droplet method does not fulfill this requirement."
Revision: "In our experiments with the commonly used droplet method, this requirement was not fulfilled".
Sect. 4.4.2:
Before: "Therefore, the droplet method proved unsuitable for correcting cavity pressure-related biases of CO2 and CH4 readings without independent cavity pressure monitoring. "
Revision: "Therefore, the results of our droplet experiments proved unsuitable for correcting cavity pressure-related biases of CO2 and CH4 readings without independent cavity pressure monitoring. However, droplet 1 evaporated slower than the others and the experiment yielded cavity pressure data closest to those from the experiment with stable water vapor levels. This experiment was performed on another day, and the setup was reassembled in between. The course of evaporation may have been affected by the length and shape of the tubing between droplet injection point and Picarro analyzer. Based on the results from this droplet, we speculate that droplet experiments with even slower evaporation may yield results from which coefficients for the expanded water correction model can be derived."

Sect. 5:
Before: "The commonly used droplet method is not suitable for correcting biases of CO_2 and CH_4 readings related to cavity pressure without independent cavity pressure monitoring, because in these experiments, water vapor can vary faster than it takes cavity pressure to adjust to a new water vapor level."
Revision: "The commonly used droplet method did not yield results suitable for correcting biases of CO_2 and CH_4 readings related to cavity pressure without independent cavity pressure monitoring. In these experiments, water vapor varied faster than it takes cavity pressure to adjust to a new water vapor level. Cavity pressure during the experiment where the droplet evaporated slowest was closest to the data from the experiment with stable water vapor levels. Therefore, we speculate that water droplets may be suitable for deriving coefficients for the expanded water correction model, provided that evaporation is sufficiently slow. However, our results do not determine the necessary equilibration time. Therefore, we recommend using methods that allow maintaining stable water vapor levels."
See also the referee comment above on simpler ways to account for the pressure-related biases in the field for paragraph on the water trap method added to this section.

Comment:
The WMO compatibility goal is interpreted by the authors as a allowed bias of ±0.05 ppm for CO2 and ±1.0 ppb for CH4. However, the compatibility goals of WMO are a "maximum allowed bias", and should therefore be ±0.1 ppm for CO2 and ±2.0 ppb for CH4. Please correct this in the text and figures.

Response:

The thresholds in our figures refer to the WMO internal reproducibility goals, which we have not explicitly pointed out in the manuscript. The WMO inter-laboratory compatibility goals refer to maximum allowed biased between laboratories, not between laboratories and the calibration scale. Therefore, keeping biases of a laboratory below these goals does not ensure the same level of compatibility to other laboratories. If one laboratory has a CO_2 bias of +0.1 ppm, and another has a bias of -0.1 ppm, the relative bias between these laboratories is 0.2 ppm, exceeding the compatibility goal. However, keeping biases to the primary scale below half of the compatibility goals ensures achieving the compatibility goals between laboratories. Therefore, we used these thresholds in the figures in our manuscript. The WMO calls these thresholds the "internal reproducibility goals", which encompass "not only instrumental imprecision, but also uncertainties in transferring the calibration scale from the highest level of standards to working standards and other uncertainties, for example related to gas handling, at the field station or laboratory" (WMO, 2016).
We will add the information on the internal reproducibility goals to text and figure captions.
Sect. 1:
Before: "… the World Meteorological Organization (WMO) has set compatibility goals for atmospheric CO2 and CH4 measurements to ±0.1 ppm for CO2 (±0.05 ppm in the southern hemisphere) and ±2 ppb for CH4 (WMO, 2016)."
Revision: "… the World Meteorological Organization (WMO) has set compatibility goals for atmospheric CO2 and CH4 measurements to ±0.1 ppm for CO2 (±0.05 ppm in the southern hemisphere) and ±2 ppb for CH4 (WMO, 2016) between laboratories. This compatibility between laboratories is ensured if individual laboratories keep uncertainties below half of these goals, which corresponds to the so-called internal reproducibility goals."
Addition to figure captions: "The dashed lines correspond to the WMO internal reproducibility goals, in the case of CO2 in the northern hemisphere (WMO, 2016). Keeping the bias between calibration scale and measurement within these goals ensures achieving the inter-laboratory compatibility goals."

Comment:
Page 4, lines 24-25: You state that the pressure of the external sensor was adjusted to be within a few hPa the same as inside the cavity by a needle valve. Please be more specific. How close was it?

Response:
The values were:
Droplet experiments (Picarro #1, type: flight-ready): -3.5 hPa
Stable levels, Picarro #1: -3.5 hPa
Stable levels, Picarro #2 (type: regular): +18.6 … 20.3 hPa
Stable levels, Picarro #3 (type: flight-ready): -12.5 hPa
The range given for Picarro #2 reflects the drift of the external pressure sensor readings during this experiment, which was larger than during the others.
The main reason for matching cavity pressure closely is that the inlet/outlet (regular/flight-ready analyzer, respectively) valve should not act as a choke, because otherwise the external sensor would not react to cavity pressure changes. The precise pressure difference is not important. Therefore, we will not add the values to the manuscript.

Comment:
The optimal position for an external pressure measurement would be either between the cavity and the inlet or outlet valve, which would allow for the measurement of the same

pressure as in the cavity without the influence of the loop feedback. Would that be feasible, and if yes, why was it not realized?

Response:
In principle, positioning the external pressure sensor between the regulating valve and the cavity would be possible, and we considered this option because of the advantages mentioned by the referee. However, opening tubing connections between these valves and the cavity would risk contamination of the cavity, which would be expensive and time-consuming to fix. This setup may also interfere with the temperature control of the cavity. The cavity and the connectors in question are located inside the so-called "hot box", and the temperature control mechanism of the cavity relies on a stable temperature around 45° inside the hot box. Installing the external pressure sensor between cavity and outlet valve would require extra tubing to leave the hot box, so it may have to be modified to minimize heat exchange with the surrounding. Due to these hurdles, we decided against this option and performed the experiments with the external pressure sensor mounted outside of the Picarro analyzers.

Comment:
Page 5, line 31: What was the reason for the drift of the external pressure sensor? Could this be identified?

Response:
We did not identify the reason for the drift of the external pressure sensor readings. One possible explanation is that the sensor may have reacted to ambient temperature variations, which may have affected the needle valves used as chokes. As stated in the manuscript, CO2 results may have been affected by dissolution in and outgassing from the water reservoir in experiments with stable water vapor levels, which may point to temperature fluctuations as well. However, ambient temperature data are not available and the experiments were conducted in an air-conditioned laboratory. The setup had an influence on the drift; it was significantly larger during the experiment with analyzer #2 (~1.6 hPa), where the external sensor was mounted upstream of the cavity instead of downstream, as it was the case with the flight-ready analyzers #1 and #3 (~0.1 and ~0.2 hPa). Ultimately, we did not answer this question because, as stated in the manuscript, the agreement of results based on the external pressure sensor with those derived from spectroscopic pressure measurements with the oxygen analyzer gives us confidence that the drift of the external sensor readings did not affect our conclusions.

Comment:
Page 18, section 3.4.3: Why is Picarro 4 performing better than others? Is it newer? Is it a different model (according to Table 1 G2401-mc; I could not find any information on a G2401-mc model on the Picarro website, only for G2401-m).

Response:
The "-c" stands for "custom engineering", which refers to modifications of cable harnesses or other details needed to make this instrument suitable for commercial flight. There is no difference between this analyzer and the other flight-ready analyzers that could affect the water correction.
To avoid confusion, we will edit the label to read "G2401-m".

Comment:
Page 15, Table 6: Should the range for CH4 be 0.41 –(-0.86) = 1.27 (instead of 1.30)?.

Response:
This is correct. The range was erroneously rounded to two significant digits. The actual range rounded to three digits was 1.27 ppb.

Comment:
Page 28, line 29: Reference of Stavert et al. is incomplete (journal is missing).

Response:
Thanks, we will fix this.

Comment:
Page 29, line 5: Link to report is wrong.

Response:
We cannot reproduce this error; the link takes us to the correct pdf-document.

References

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