

Author's response to:

'Interactive comment on "An improved water correction function for Picarro greenhouse gas analyzers" by Friedemann Reum et al. ' by Anonymous Referee #2

Friedemann Reum, Christoph Gerbig, Jost V. Lavric, Chris W. Rella and Mathias Göckede

Summary statement

The reviewer highlighted the need to include a more thorough estimation of uncertainties in our measurements. We present this information here alongside responses to the other comments of the review.

Reviewer's comment:

General

The results of the enhanced water correction function for CO₂ are not convincing. It will be helpful to summarize and list in a table all the factors that may cause a bias on the order of 0.037 ppm for CO₂ and 0.85 ppb for CH₄, and provide reasonable estimates of their associated uncertainties. For example, factors that may affect CO₂ on this order of magnitude include

1) tank regulator effects that cause CO₂ coming out of tanks drifting 2) uncertainties introduced by the sensitivity of CO₂ to cavity pressure, e.g. 0.502 ppm/Torr (Table 2) was derived for Picarro #3, and 0.466 ppm/Torr was reported by Filges et al., 2015; 3) solubility of CO₂ in water; 4) adsorption of CO₂ by magnesium perchlorate, especially under changing pressure.

Author's response:

As the reviewer points out, our results were in part inconsistent especially for CO₂. In the manuscript, we discussed this issue extensively and summarized our considerations in the abstract: "The magnitude of the effect varied across instruments and appeared to be negligible for some, and our experimental results were more robust for CH₄ than for CO₂. Thus, correction coefficients should be determined for each analyzer individually."

We thank the reviewer for the suggestions on possible causes of biases on the same order as the observed effect. We have considered such biases as reasons for the inconsistent CO₂ results, since they may have overshadowed the pressure effect presented here, resulting in the failure to detect said effect on CO₂ in two instruments. We discussed this subject only briefly in Sect. 4.3 and 4.4 of the manuscript. However, as pointed out therein, such a bias would either have systematically counteracted the pressure effect (which is unlikely), or the pressure effect of these instruments was smaller than for the other (in line with the statement on this issue cited above).

In the following, we provide error estimates for the effects suggested by the reviewer.

1) Tank regulator effects that cause CO₂ coming out of tanks drifting

We avoided probing water levels in only strictly ascending or descending order to minimize the effect of drifts of CO₂ and CH₄ on our results. We assess whether such drifts were present in the following paragraph.

Carbon dioxide and CH₄ measurements from three experiments (Picarro #3, #4 and #5) have been analyzed in the manuscript (the experiment with Picarro #1 and #2 were intended for characterizing the pressure effect only, and the trace gas data from these experiments were not suitable for analysis). Picarro #3 displayed the pressure effect on CH₄, #5 displayed the pressure effect on both CO₂ and CH₄, while #4 displayed neither. For Picarro #3, dry air measurements were obtained between wet air measurements, which can be used to assess drifts. During the experiments with Picarro #4 and #5, only one dry air measurement has been obtained. Hence, we use the temporal variations of residuals to the water correction fit to assess drifts for these two experiments here.

The summary of the drifts over the course of the experiments is provided in Table 1. No statistically significant drift of CO₂ has been observed. Only the drift of CH₄ during the experiment with Picarro #5 was statistically significant ($p < 0.05$). The drift has no considerable effect on the correction of the pressure effect, because the low water vapor levels relevant for the effect were all probed during one short period (e.g. Fig. 2 in author's response to Reviewer Comment 1 from July 7, 2017).

Table 1: CO₂ and CH₄ drifts during the water correction experiments. Picarro #3: Dry air measurements. Picarro #4 and #5: Water-corrected wet air measurements. The drifts are expressed as difference between the first and last observation based on a linear fit.

Picarro	CO2 drift [ppm]	CO2 drift p-value	CH4 drift [ppb]	CH4 drift p-value
#3	-0.014	0.08	-0.18	0.09
#4	0.010	0.54	-0.36	0.08
#5	0.003	0.79	-0.47	1.5e-5

2) Uncertainties introduced by the sensitivity of CO₂ to cavity pressure

We agree that the total uncertainties of the relationships between external pressure measurement and CO₂ and CH₄ mole fractions are larger than the standard errors reported in Table 2 of the manuscript (see also our response to the next comment of the reviewer, below). We performed two such calibrations for Picarro #3, one with dry air and a second one with wet air. The results differed by a few percent (manuscript Sect. 3.1):

(CO₂: +5 %, CH₄: -2 %, cavity pressure: +1 %). We concluded from these numbers that no systematic differences between dry and wet air are present in these relationships (see manuscript). The effect of these uncertainties on observed mole fractions is negligible, since the relative differences translate to relative differences of the absolute size of the pressure effect (i.e. 0.037 ppm CO₂ and 0.85 ppb CH₄ in our experiments). Hence, they are on the order of 0.002 ppm CO₂ and 0.02 ppb CH₄ for ambient mole fractions. These uncertainties, and the uncertainty of the pressure scale were not observable in our experiments and too small to explain the differences in the effects observed between instruments.

We will add this information to the revised manuscript by making the following change to Sect. 3.1:

Original (page 4 lines 20-21):

“The slopes in wet air (3 % H₂O) were measured for Picarro #3 and were very similar to the slopes in dry air (CO₂: +5 %, CH₄: -2 %, cavity pressure: +1 %).”

Changed to:

“The slopes in wet air (3 % H₂O) were measured for Picarro #3 and were very similar to the slopes in dry air (CO₂: +5 %, CH₄: -2 %, cavity pressure: +1 %). The effect of these uncertainties on observed mole fractions is negligible, since the relative differences translate to relative differences of the absolute size of the pressure effect (i.e. 0.037 ppm CO₂ and 0.85 ppb CH₄ in our experiments; see Sect. 3.3 and 3.5.1). Hence, the uncertainties are on the order of 0.002 ppm CO₂ and 0.02 ppb CH₄ for ambient mole fractions. These uncertainties, and the uncertainty of the pressure scale were too small to be observable in our experiments.”

The reviewer remarked that the sensitivity of CO₂ to cavity pressure changes we found was different from the one in Filges et al. 2015. This is not the case, since the difference is due to the fact that we reported the sensitivities with respect to different mole fractions than Filges et al., with respect to the external pressure measurement instead of cavity pressure, and for another instrument. However, a direct comparison can be made since in fact Picarro #1 is the instrument used by Filges et al. To avoid confusion, we switch to reporting the sensitivities as fractional changes as in Kwok et al. 2015. In Table 2, we report the sensitivities of the instruments in our study, the findings of Filges et al. 2015, and the results of Kwok et al. 2015. Our results for Picarro #1 are very well compatible with those by Filges et al. 2015. The mostly small differences between the sensitivities obtained for the different instruments may be due to differences in the absolute pressure calibration of the internal pressure sensors of the analyzers. Only the sensitivity of CH₄ from Kwok et al. differs strongly from the other results. This is likely due to uncertainties of the experiment by Kwok et al. (C. W. Rella, personal communication). We did not explore the differences further in our study.

We will update the way we reported the sensitivities of CO₂ and CH₄ to pressure in Table 2 of the manuscript with the information presented here.

Table 2: Sensitivities of CO₂ and CH₄ to changes of internal cavity pressure.

Picarro	$\frac{\Delta\text{CO}_{2,frac}}{\Delta P}$ [Torr ⁻¹]	$\frac{\Delta\text{CH}_{4,frac}}{\Delta P}$ [Torr ⁻¹]
#1	$(1.20 \pm 0.02) \times 10^{-3}$	$(4.26 \pm 0.06) \times 10^{-3}$
#1 (Filges et al. 2015)	1.20×10^{-3}	4.3×10^{-3}
#2	$(1.258 \pm 0.002) \times 10^{-3}$	$(4.372 \pm 0.002) \times 10^{-3}$
#3	$(1.200 \pm 0.002) \times 10^{-3}$	$(4.326 \pm 0.005) \times 10^{-3}$
(Kwok et al. 2015)	1.3×10^{-3}	3.5×10^{-3}

3) Solubility of CO₂ and CH₄ in water / drifts

As explained in the manuscript and further elaborated on in our response to Reviewer Comment 1 (July 7, 2017), the strategies to avoid effects of dissolution in or outgassing from the water reservoir were to wait for stable signals and vary the order in which water vapor levels were probed. We acknowledged the possibility that equilibration processes might have affected our results and gone unnoticed if they were on timescales much longer than one hour. In the following paragraph we look for such equilibration processes by analyzing drifts in the available data. In particular, we analyzed drifts of CO₂, CH₄, H₂O and pressure during the intervals that were used for further analysis and looked for correlations with residuals of the water correction fit. If a drift that affected the mole fractions were detectable, it would have a negative correlation with the fit residuals, since a downward (upward) trend would mean the recorded mole fraction was too high (too low). As can be seen from Fig. 2, no such trend could be detected. However, we did find correlations between CO₂, CH₄ and external pressure measurement drifts (Fig. 3). Hence, these correlations are due to drifts of cavity pressure, meaning that perfect stability was not reached. Despite this relationship, we could not find evidence that these drifts affected our results in a systematic way, as they were random with mean effects near zero and they did not explain the residuals of the water correction fit (Fig. 1 and Fig. 2). Furthermore, we investigated the drifts during the experiment with Picarro #3 more closely. The drifts depended on the data selection used for analysis; the last 10, 15 and 20 minutes of each probing interval were tested (Fig. 4). This indicates that these drifts were not part of a longer-term trend, but short-term variations. This is supported by the similarity of the pressure effect of the three experiments despite these different drifts (manuscript Sect. 3.2). Nonetheless, we will stress in a revised manuscript that there may be effects on longer timescales than those probed here, and encourage future research on this issue:

Original (page 12 lines 1-3):

“If this explanation were true, the systematic difference between dry air and wet air trace gas mole fractions would have precisely compensated for the pressure bend, which seems unlikely.”

Changed to:

“If this explanation were true, the systematic difference between dry air and wet air trace gas mole fractions would have precisely compensated for the pressure bend, which seems unlikely. Nevertheless, to exclude that such equilibration effects influence the water correction, we encourage future research on this topic.”

To estimate the contributions of different error sources to the overall error of our CO₂ and CH₄ measurements, we use the relationships between mole fraction drifts and pressure drifts as a measure for uncertainties associated with cavity pressure equilibration. Furthermore, we assume that the residual drift after subtracting the pressure equilibration drift was associated with other effects such as equilibration with the water reservoir,

potentially due to temperature instability. The uncertainties obtained in this way are summarized in Table 3.

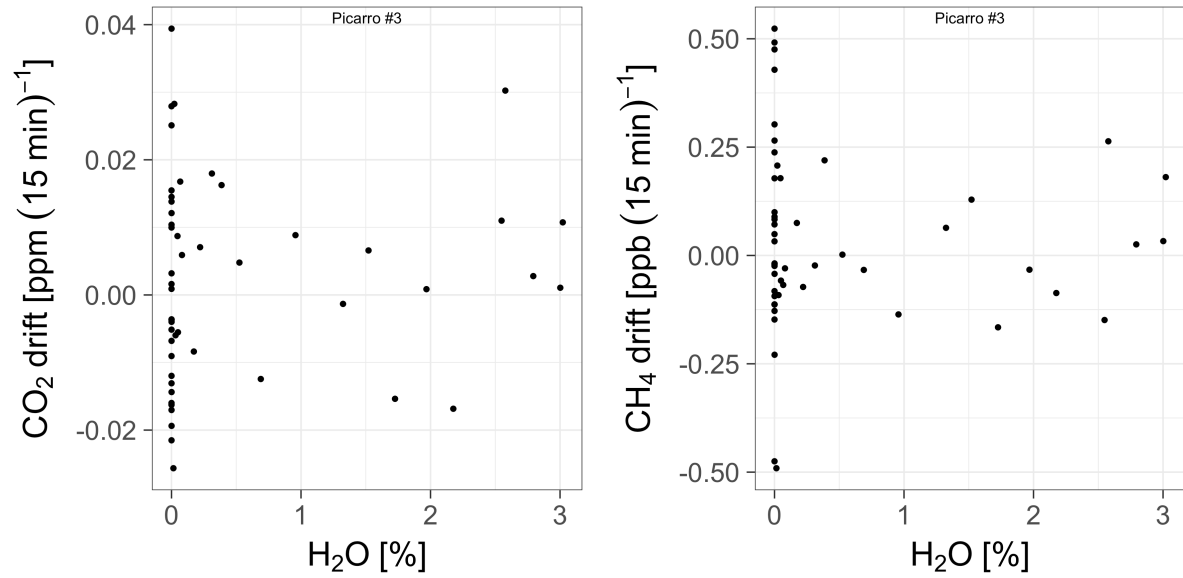


Fig. 1: Drifts of data during the interval used for analysis (last 15 minutes of each probing interval) vs H₂O (Picarro #3).

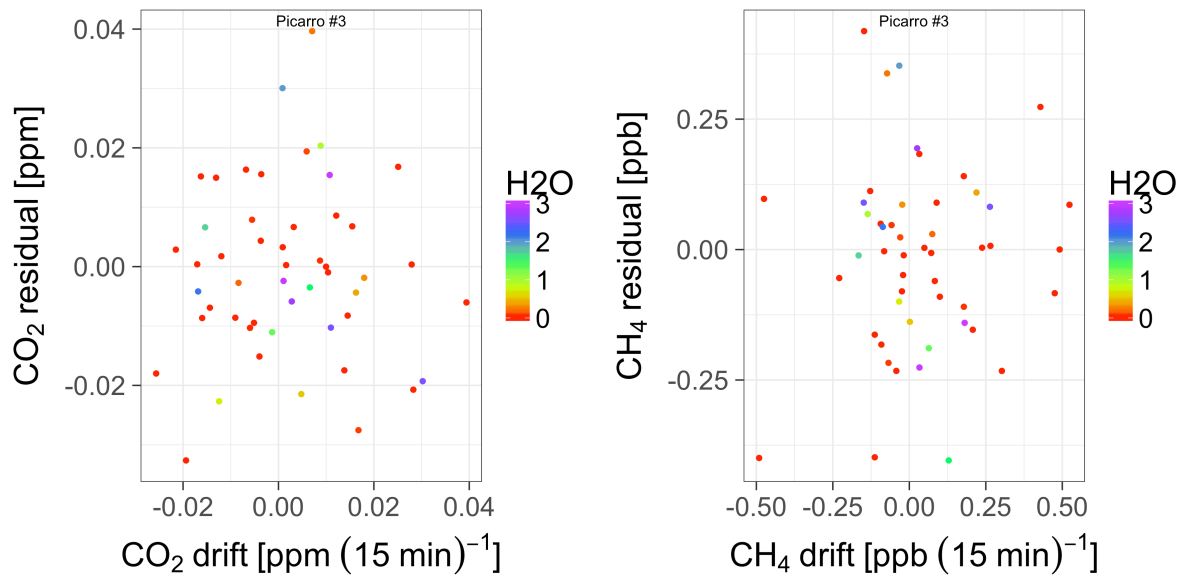


Fig. 2: Water correction fit residuals vs drifts (data as in Fig. 1)

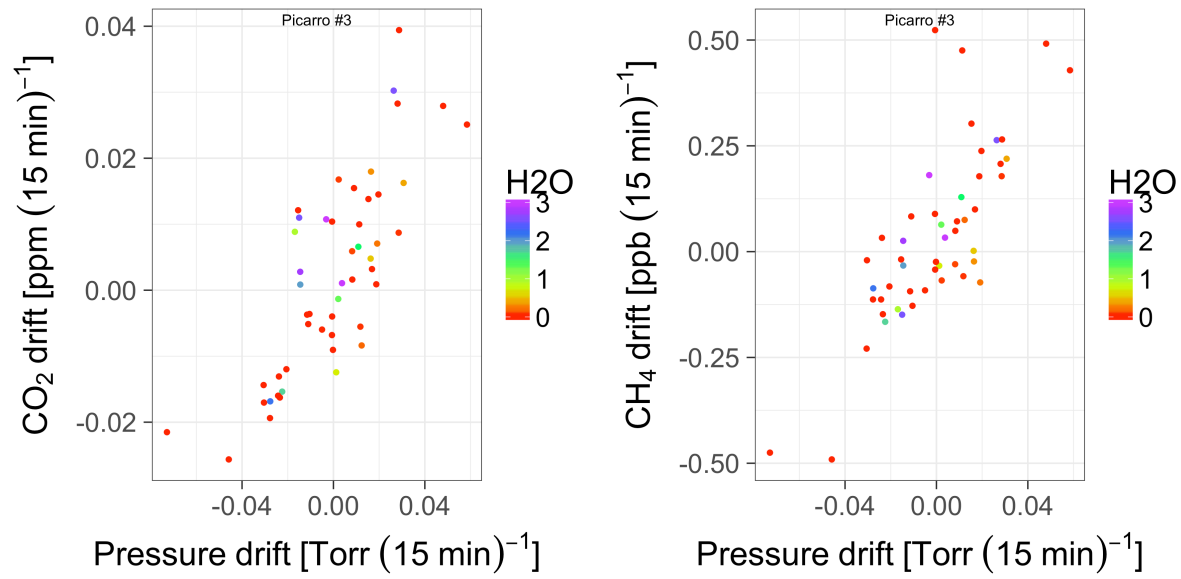
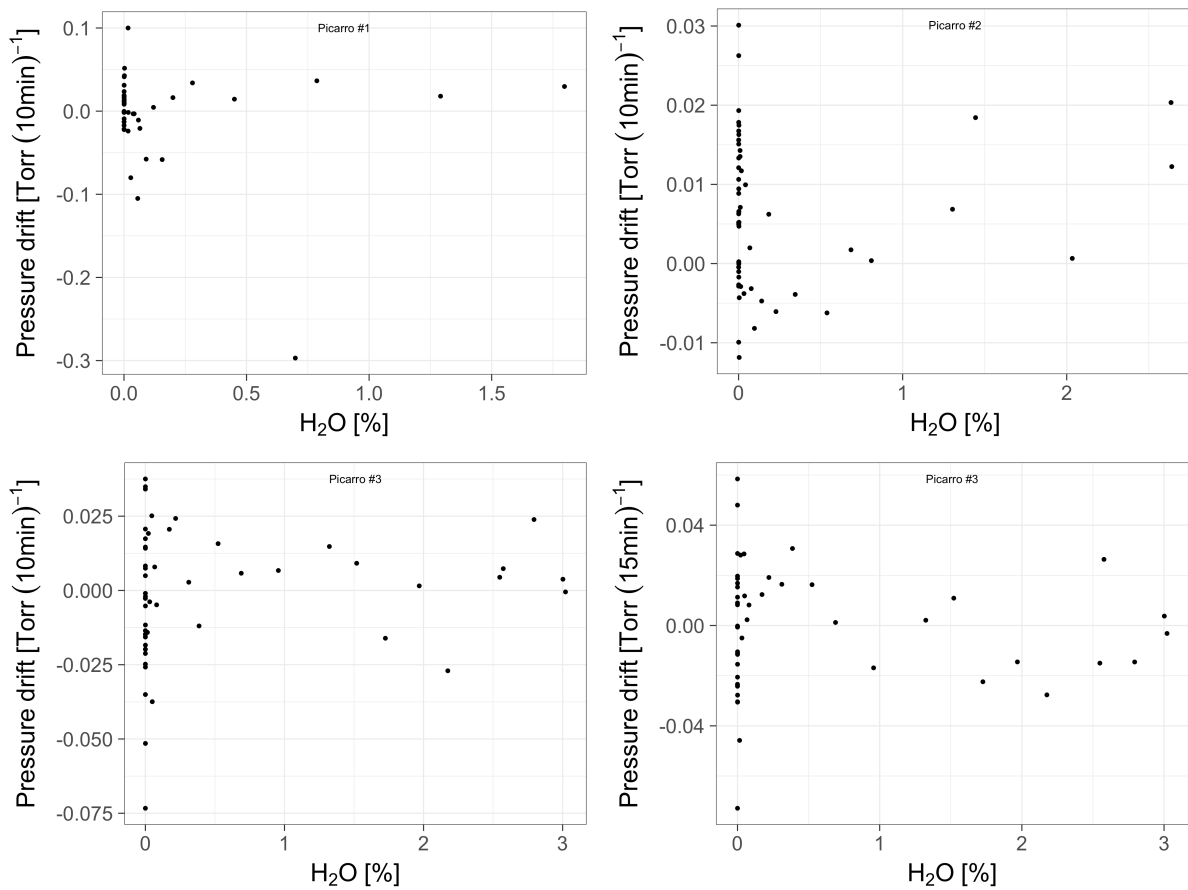


Fig. 3: CO₂ and CH₄ drifts vs pressure drift (data as in Fig. 1)



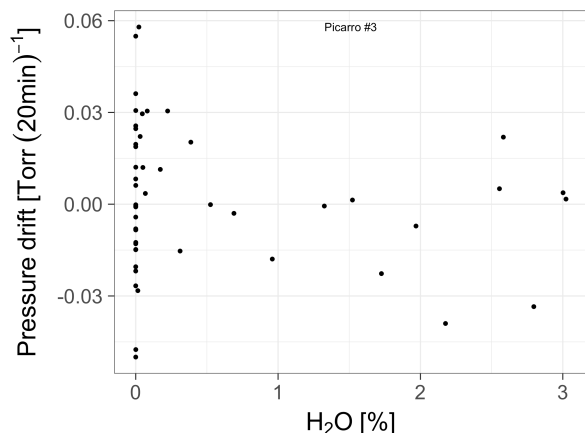


Fig. 4: Pressure drifts vs H₂O. From top left to bottom: Picarro #1, #2, #3 (10 min), #3 (15 min), #3 (20 min). The times refer to the amount of data at the end of each probing interval used.

Table 3: Error estimates based on drifts of trace gas and pressure in the data used for analysis (last 15 minutes of the probing intervals). The total errors are very similar to the estimates based on fit residuals (manuscript Sect. 3.3), confirming their validity.

	CO ₂ [ppm]	CH ₄ [ppb]
Pressure equilibration	0.012	0.16
Other, incl. solubility	0.009	0.13
Sum	0.015	0.21
Comparison: fit residuals	0.014	0.17

4) Adsorption of CO₂ by magnesium perchlorate, especially under changing pressure.

As explained in our response to Reviewer Comment 1 (July 7, 2017), the magnesium perchlorate cartridge was never installed upstream of the Picarro analyzer during the experiments from which we analyzed the CO₂ and CH₄ mole fraction data. Therefore, there is no error associated with adsorption of CO₂ by magnesium perchlorate in our analyses.

Reviewer's comment:

In addition, the specified standard errors in the existing tables provide little information, as they are derived from the fit assuming statistical noise only, and are usually much lower than the overall uncertainties associated with the numbers.

Author's response:

We agree that the standard errors of the fit parameters reported in Tables 2-5 of the manuscript may underestimate the uncertainties of the quantities presented. This is the reason why these uncertainty estimates were not used for the key quantities of the paper, and thus have little significance in the first place. In our opinion, the best estimate of the uncertainties of an instrument calibration such as the water correction presented here is to repeatedly perform calibration experiments and use the differences between individual calibrations to derive the uncertainties associated with the calibration. This approach is necessary to quantify uncertainties that are not detectable from a single calibration

experiment, such as variations with time and environmental conditions. Thus, the full uncertainty estimate of the water correction must be assessed for instruments individually, while the scope of this paper is to provide a method to correct one specific effect.

In our manuscript, we recommended one parameter, the pressure bend position h_p , for use with water correction functions of other analyzers in the absence of sufficient data to constrain it. In line with our statement about uncertainties above, we estimated the uncertainty of h_p as the standard deviation of the estimates for the three individual instruments, reflecting the variability of this quantity. The error associated with this parameter and its usage for other instruments was extensively discussed in Sect. 3.5.1. Therefore, we do not think it is necessary to change the uncertainties reported in Tables 2-5 of the manuscript.

Reviewer's comment:

Detailed comments:

Page 3 Line 9 The considerable amount of water used (500 ml) here will affect CO₂ mole fractions. Has this effect been characterized?

Author's response:

In the manuscript we failed to clarify which amount of water was used for which experiment. During experiments from which CO₂ and CH₄ mole fractions were analyzed and presented, the amount of water used was considerably smaller than 500 ml. In the experiment with Picarro #3, 15 ml were used, with Picarros #4 and #5 the amount was about 40 ml. The 500 ml have been used in experiments from which only pressure data was interpreted (Picarros #1 and #2). We will clarify this by making the following change in Sect. 2.1 of the manuscript:

Original (page 3 line 8-9):

“Air in the other line was directed through a gas washing bottle (glass) containing deionized water (depending on bottle size, about 15 ml to about 500 ml were used in the experiments presented here).”

Changed to:

“Air in the other line was directed through a gas washing bottle (glass) containing deionized water. The amount of water used varied. In the experiments from which only pressure data were interpreted (Picarros #1 and #2), 500 ml of deionized water were used. In the experiments from which trace gas data were interpreted, the amount of water was reduced to ensure faster equilibration of the water reservoir with the air stream. In the experiment with Picarro #3, 15 ml were used, and in the experiments with Picarros #4 and #5 the amount was 40 ml.”

As the reviewer pointed out, streaming air through liquid water alters the mole fractions of the gas stream by dissolution or outgassing until equilibrium is reached. The equilibrium shifts with temperature and pressure. In his/her comment from July 6, 2017, Anonymous Referee #1 raised questions about temperature and pressure stability during our experiments as well. We addressed these questions together with equilibration of the gas

stream with the water reservoir in the gas washing bottles and the effects they might have had on our findings on pages 5-10 of our response to Reviewer Comment 1 (July 7, 2017). We conclude that temperature and pressure stability were sufficient and did not affect our findings.

Reviewer's comment:

Page 4 Line 22 Was there no offset in the cavity pressure compared to the external pressure measurement?

Author's response:

Yes, as mentioned in Sect. 2.1 (page 3, line 26-27), there was an offset between cavity pressure and external pressure measurement. The transformation of external pressure readings to cavity pressure was explained in Sect. 3.2 of the manuscript. To clarify the procedure, we will make the following change in this section:

Original (page 4 line 26 – page 5 line 3):

“To calculate a “corrected cavity pressure” from the external pressure measurement, pressure readings for dry air before and after each wet air measurement were interpolated to the times of the wet air measurements. The deviations between the wet air pressure values and the interpolated dry air pressure values were multiplied with the slope described in Sect. 3.1, and added to the dry air cavity pressure of 140 Torr.”

Changed to:

“As explained in Sect. 3.1, the external pressure measurement was modeled as a linear function (slope and offset) of internal cavity pressure. Therefore, to calculate a “corrected cavity pressure” from the external pressure measurement, pressure readings for dry air before and after each wet air measurement were first interpolated to the times of the wet air measurements. Then the deviations between the wet air pressure values and the interpolated dry air pressure values were multiplied with the slope, and added to the dry air cavity pressure of 140 Torr.”

Reviewer's comment:

Page 9 Section 3.5.2 Which model was used? III or IV?

Author's response:

The water correction used was that described in Sect. 3.1. It was model (iv) in that a fixed value for the pressure bend position h_p was used. To clarify this, we will make the following changes:

Original (page 7 line 29-30):

“Therefore, we used the mean h_p from the three experiments with external pressure monitoring, Eq. (4), and investigated the uncertainty associated with this procedure.”

Changed to:

“Therefore, we used model (iv) with h_p fixed to its mean value from the three experiments with external pressure monitoring, Eq. (4), and investigated the uncertainty associated with this procedure.”

Original (page 9 line 4-5):

“In this section, we describe the impact of the improved water correction on hourly averages of CO₂ and CH₄ data from Ambarchik over the years 2015 and 2016”

Changed to:

“In this section, we describe the impact of the improved water correction, which was derived in Sect. 3.5.1, on hourly averages of CO₂ and CH₄ data from Ambarchik over the years 2015 and 2016”

Reviewer’s comment:

Page 13 Line 17 – 18 It is not clear what is said here. Rephrase the sentence.

Author’s response:

We will make the following change to clarify this sentence:

Original (Page 13 Line 17 – 18):

“The results indicated small impacts of observation biases considerably larger than the WMO goals on annual flux budgets at continental scales. “

Changed to:

“In some cases, the observation biases assessed in these studies were considerably larger than the bias corrected by using the improved water correction presented here. The studies indicated small impacts even of these comparatively larger observation biases on annual flux budgets at continental scales. “