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 #1 (6 July 2017)

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

Summary:

Among some other points, the main concerns of the reviewer are (1) the influence of the drying cartridge, which was used for shielding the external pressure sensor against water vapor changes, especially on CO2, and (2) the validity of the relationship between external pressure sensor reading and Picarro cavity pressure, due to certain components of the experimental setup (drying cartridge, needle valves). As we explain below in replies to the reviewer's specific comments, concern (1) is unfounded due to our experimental setup. Concern (2) requires more attention and we acknowledge that there are uncertainties in the external pressure readings (however, these are discussed in the manuscript). We address all comments of the reviewer below.

After reading the review, we believe that in our efforts to write a concise paper we may have kept certain sections too brief. In a revised manuscript, we will add the clarifications given in the responses below in the cases where they were not present in the manuscript that we initially submitted.

However, we would like to emphasize at this point that the uncertainties regarding the external pressure measurement have no influence on the main message of our study, i.e. improving the empirical water vapor correction for CO2 and CH4 readings of Picarro GHG analyzers. One of our major results was that coefficients for the improved empirical water correction can be obtained even without external pressure measurements. The external pressure measurements were mainly used to infer whether or not the observed shortcomings of the traditional water vapor correction – i.e. systematic, water-dependent biases in the corrected CO2 and CH4 data – were artifacts of water correction experiments and should thus be ignored. Even though there are uncertainties associated with the use of the external pressure sensor, the information obtained from this instrument served very well for this specific purpose: Our experiments with external pressure monitoring revealed that the shortcomings of the traditional water vapor correction can be linked to pressure changes in the cavity of the Picarro analyzer, and therefore should be corrected for. Accordingly, as the main objective of the presented study we provided a way to correct for the effect.

This summary statement and the more detailed comments below aim at clarifying the rather minor role of the accuracy of the external pressure measurements. We believe that the concerns raised by the reviewer regarding this element of our study should not put the validity of the overall findings into question.

Reviewer's comment:

The paper's topic is interesting, and may be an important contribution for the atmospheric greenhouse gas measurement community. However, I feel that the manuscript unfortunately suffers from redundancy, unclear writing, bad organization, and confusing data analysis. All these problems make it extremely difficult to follow. Furthermore, significance of the measurement biases due to the water vapor interference on the cavity pressure measurements was

inconsistent across the instruments. I am uncertain of this study, and therefore I think it would be better to revise the experimental methodology carefully and needs further investigation. I am very afraid, but I suggest rejection of this manuscript from AMT. I encourage the author to rewrite the manuscript from scratch with the help of the coauthors for clarity after consideration of my comments.

Author's response:

The reviewer made a general statement about "redundancy, unclear writing, bad organization, and confusing data analysis" of/in the manuscript, and suggested "to rewrite the manuscript from scratch with the help of the coauthors for clarity after consideration of [his/her] comments". We would hereby like to emphasize that before submission the manuscript went through numerous draft iterations, involving input and feedback from all coauthors. All persons listed on the author list fully agreed with the content of the manuscript, and the way it was presented. We acknowledge that it is always possible to improve the presentation of a text by further polishing certain aspects. Still, we find the structure and writing of the manuscript are of adequate quality to deliver the scientific message behind our study. We are open to constructive suggestions how to further improve the presentation, and therefore would like to ask the reviewer for more specific criticism which aspects of our text need revision.

The fact that the observed effect had different magnitudes for the individual instruments was addressed in the manuscript. As described in sections 3.4 and 4.4 of the manuscript, this observation has but one consequence for the main point of our study, which is that coefficients for our improved empirical correction have to be obtained per instrument (as opposed to using common coefficients for all instruments). The underlying reasons for the differences between instruments may be subject to future research.

Reviewer's comment:

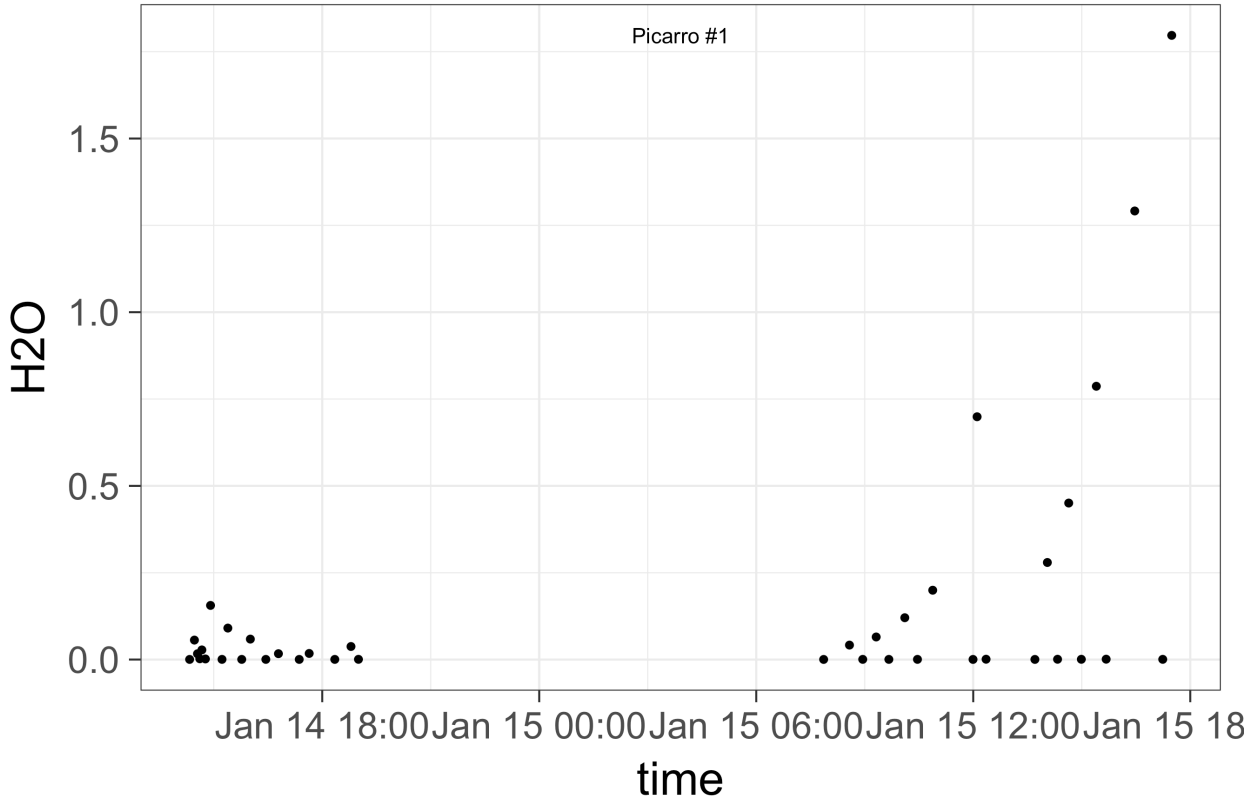
Specific comments (Major comments)

I have great concern about the experiment for the estimation of the quantitative relationship among the readings of external pressure sensor, CO2, CH4, and internal pressure sensor. The author used the Mg(ClO4)2 cartridge to shield the external pressure sensor from humidity change. The external pressure sensor measurements can also be biased by the presence of water vapor? Then I wonder why the author did not use the pressure sensor independent of the water vapor presence for the experiments. Since the experimental system can be highly complex due to the installation of the Mg(ClO4)2 cartridge, I have no idea what the external pressure sensor measures. In addition, there are several other concerns as described below:

Author's response:

The reviewer raises the question whether the relationships between the readings of external pressure sensor, CO2, CH4, and internal pressure sensor were valid over the course of a whole experiment, focusing on the validity of the external pressure measurement. These questions were addressed in sections 3.1, 4.1.2 and 4.3 of the manuscript. We kept especially sections 3.1 and 4.1.2 short in order to focus on the major results of the study, and will provide more details here in a revised manuscript version. The relationships the reviewer refers to may change slightly with time and/or water content. Still, as presented in section 3.1 of the manuscript, the relationships were not considerably affected by water vapor in the measured air, and moreover were very similar across instruments. Regarding changes of the relationships with time (e.g. due to

saturation of the drying agent with water) we randomized the order of water levels probed in one experiment (Picarro #3, mentioned in sect. 2.1 of the manuscript). With this setup, a drift of the external pressure sensor would have been visible in random biases of the pressure versus water level. This was plotted in Fig. 2 of the manuscript, and the residuals to the fit were small compared to the observed effect. Therefore, if a drift such as the one suggested by the reviewer was present, it was smaller than the signal. To illustrate the different probing strategies, we present the order in which water levels were probed for all instruments with external pressure measurement in the figure below.



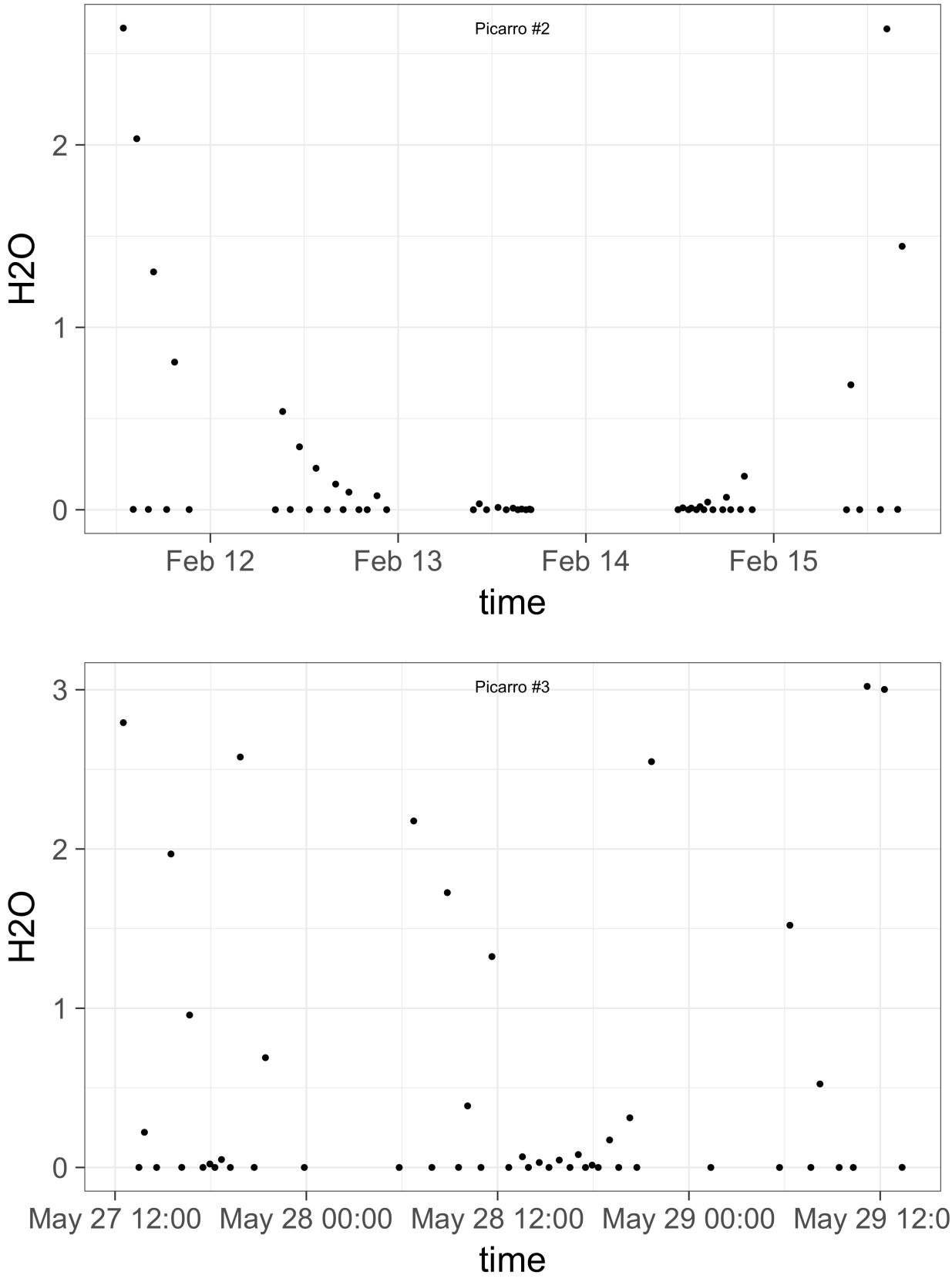


Fig. 1: Water levels probed during the experiments with external pressure monitoring.

These considerations do not address whether there was a bias present in the external pressure measurement during wet air measurements. On the one hand, we reported that the slope of internal cavity pressure versus external pressure measurement was independent of water vapor (sect. 3.1 of the manuscript). On the other hand, we cannot exclude a water-dependent offset based on our data. Given that the shape of the pressure changes – in particular the "pressure bend" – was consistent between pressure and CH4 data, we omitted this in the discussion of the uncertainties of the external pressure measurement. Instead, we concluded this discussion by emphasizing that uncertainties in the external pressure measurement are insignificant for the water correction of CO2 and CH4, since all parameters can and should be derived from the CO2 and CH4 data directly (sect. 4.1.2. in the manuscript). Furthermore, we only briefly discussed such a bias as a potential reason for observed discrepancies between the external pressure data and trace gas data (sect. 4.3. in the manuscript). We explained why this hypothesis is less likely than another one. However, in a revised manuscript, we will include the statement that a water-dependent offset may nonetheless be present, although it is unlikely to explain the discrepancies discussed in sect. 4.3 of the manuscript.

We are not certain about what the reviewer means by "why the author did not use the pressure sensor independent of the water vapor presence for the experiments". We measured the pressure of the air measured by the Picarro analyzer, so the external pressure sensor had to probe the wet air stream. To minimize influence of water vapor on the external pressure sensor, it was installed with the drying cartridge in a dead end branched from the air stream. If there are ways how to circumvent this issue, we are certainly open to more specific suggestions by the reviewer.

Reviewer's comment:

1. What was temperature control for the humidification unit? The slight temperature change will affect the solubility of CO2 and CH4 in the de-ionized water which results in change in the mole fractions of CO2 and CH4 in the sample air, especially for CO2.

Author's response:

We did not discuss temperature stability in detail in the manuscript for the sake of brevity. Instead, we briefly described the strategies for avoiding the impact of temperature effects and other drifts, and will provide more information below.

As the reviewer stated, the solubilities of CO2 and CH4 vary with temperature. This would lead to outgassing or dissolution of the trace gases in the water reservoir in our experiments, thus changing the mole fractions of the gases in air. However, CO2 and CH4 in the air stream would only be affected until the water reservoir reached equilibrium with the air stream. The equilibration time depends on several factors, among them the efficiency of the mixing of the air stream with the water reservoir, the flow rate of the air stream, the volume of the water reservoir, and in our experiments the head space of the gas washing bottle. In the manuscript, we acknowledged that equilibration effects may have gone unobserved if they occurred on a timescale much longer than an hour (sect. 4.3). However, we employed two strategies to exclude impacts of effects related to equilibration or drift of any kind (temperature, pressure in cavity, external pressure measurement, outgassing and dissolution). One strategy was to wait for stabilization of CO2, CH4 and external pressure readings before using the data to obtain a data point (hence the different probing times per water level, see sect. 2.1 of the manuscript). The other strategy was to vary the order in which different water vapor levels were probed during the

experiments (see sect. 2.1 of the manuscript and Fig. 1 in this response). In particular, one experiment (Picarro #3) was carried out using a random sequence of water vapor levels. It is unlikely that a temperature or any other drift correlated with this sequence (see sect. 4.3 of the manuscript).

We did not discuss temperature stability in the manuscript and will do so in the following paragraph.

The strategy for temperature stability was to keep the temperature in the whole laboratory stable. Reasons for focusing the temperature stabilization not only on the humidification unit were the risk of condensation between the gas washing bottle and the Picarro analyzer, and the possibility of different rates of heat exchange between the air flowing through the gas washing bottle and the water reservoir due to different flow rates over the course of each experiment. Experiments with Picarros #1–#4 were carried out in an air-conditioned laboratory, but unfortunately there is no temperature data available for these experiments. However, we do have data of the room temperature during the experiment with Picarro #5. Temperature stability during this experiment was difficult to achieve, as it took place at a remote site in Siberia, and we managed to keep the room temperature within ± 0.3 K. Below, we plotted the corrected CO2 and CH4 data and air temperature against time (Fig. 2). A temperature effect should be reflected in the dry air mole fractions of CO2 and CH4. The figure shows that the magnitude of CO2- and CH4 variations was well below the magnitude of the effect we corrected using the improved water correction function (0.037 ppm CO2 and 0.78 ppb CH4, see sect. 3.5.1 of the manuscript). This means that even if a temperature effect was at play, its effect was small compared to the bias corrected by applying our correction.

Despite all our efforts to minimize the effects of temperature on our measurements, we discussed this effect as a potential explanation for the inconsistent results for CO2 in sect. 4.3 in the manuscript, and concluded that, although it does not explain the observations perfectly, is the most likely of the explanations we considered. Related to this is the following statement from sect. 4.4 of our manuscript (page 12, lines 11-13):

“In some cases, the effect on CO2 (two out of three instruments) and CH4 (one of these two instruments) even appeared negligible. In those cases, it may be possible that a small effect exists but is masked by random fluctuations.”

To summarize, we already acknowledged the possibility of effects on CO2 related to its high solubility in water (compared to CH4) in sect. 4.3 of the manuscript. To further clarify the potential impacts of this effect on the results obtained within the context of this study, in a revised version of the manuscript we will expand this section and section 4.4 with the remarks on temperature from this response.

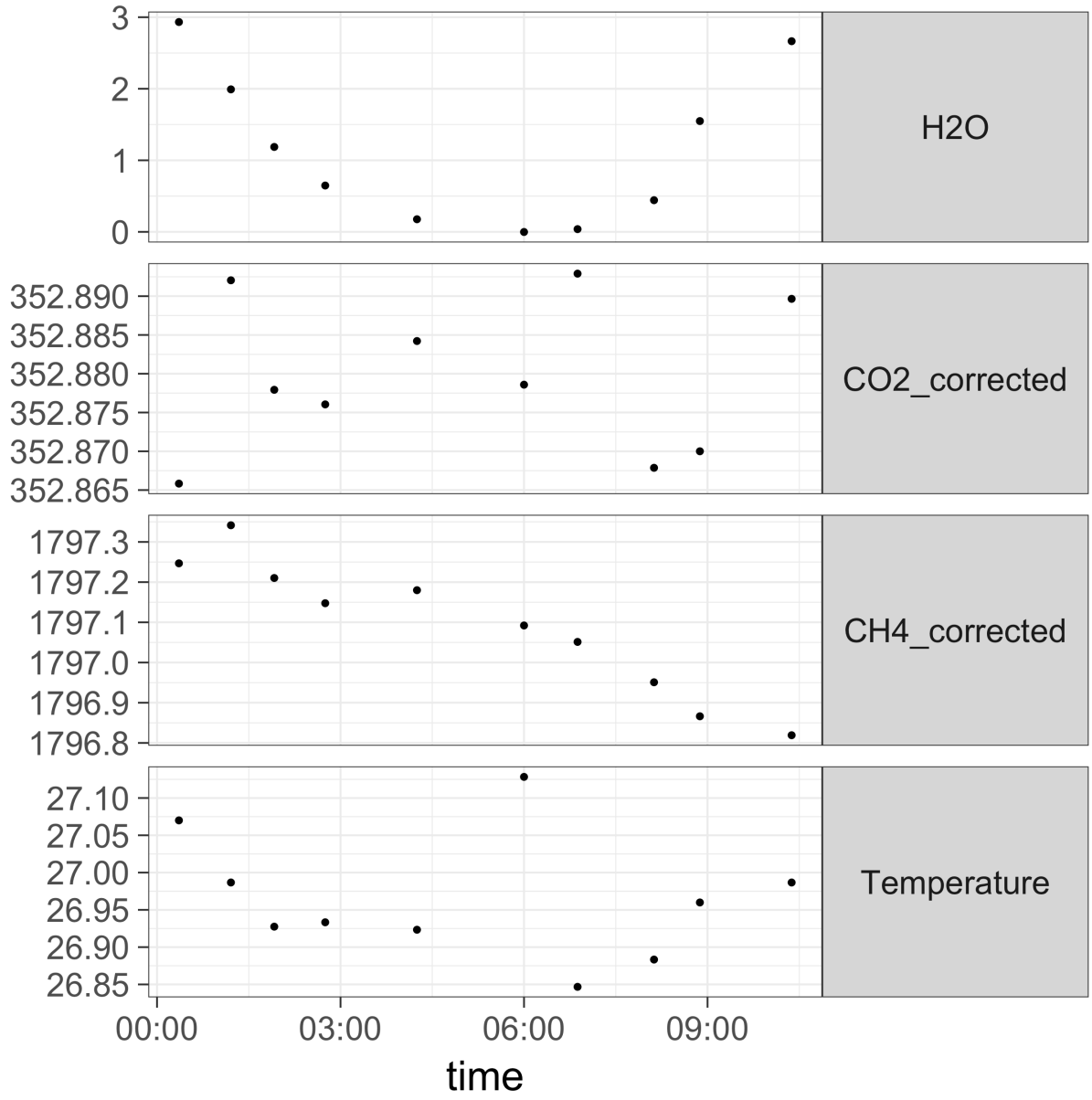


Fig. 2: Water vapor, corrected CO2 and CH4 data and Temperature vs time during the experiment with Picarro #5

Reviewer's comment:

2. There is no detailed information for the Mg(ClO4)2 reagent, but the author used CO2-saturated Mg(ClO4)2 reagent to avoid CO2 loss on the reagent?

Author's response:

Before we address this comment, we would like to make sure there was no misunderstanding about the experimental setup: this and other comments by the reviewer suggest he/she had in mind a setup where the air stream measured using the Picarro analyzer flowed through the drying cartridge. To exclude a misunderstanding, we stress that the cartridge was instead installed in a dead end branch (see also sect. 2.1 and Fig. 1 in the manuscript). More importantly regarding this particular comment in the context of our manuscript, the experimental results that could have

been affected by the drying cartridge – the ones from which we interpreted the CO2 (and CH4) data – were either performed without external pressure measurements, and thus no drying cartridge was installed at all (Picarros #4 and #5), or the cartridge was installed downstream of the Picarro analyzer (Picarro #3). Thus, the cartridge could have no direct effect on CO2 and CH4 mole fraction measurements of the Picarro analyzers in our experiments.

The effect the reviewer pointed out in this comment may become relevant when external pressure readings are obtained using ground-Picarros, since the dead end branch containing the drying cartridge would be upstream of the Picarro analyzer (see Fig. 1 of the manuscript). However, since the drying cartridge would be installed in a dead end branch, even with such a setup we would expect very little influence on CO2 and CH4 mole fractions in the air stream measured by the Picarro analyzer, especially since the distance between the measured air stream and the drying cartridge can be increased by using longer tubing.

Perhaps we did not state clearly enough in the manuscript that some experiments were performed without external pressure measurement. This information was contained in Table 1. We will add a paragraph to section 2.1 about the experiments that were performed without external pressure measurement.

Reviewer's comment:

3. The author used the needle valve to adjust the pressure readings close to those of the internal pressure sensor, but what was the stability of the sample pressure downstream the needle valve? The pressure change can cause the increased CO2 absorption/desorption on Mg(ClO4)2 reagent.

Author's response:

Regarding part one of this comment: We indeed observed a drift of the external pressure sensor over time (see Fig. 3 below). The needle valve in question may play a role in this context. The drift was only briefly mentioned in the manuscript, alongside the mitigation strategy: we took dry air measurements between wet air measurements and used the pressure differences as measurement points (this was described in section 2.1 of the manuscript). This procedure relies on the assumption that the slope of internal pressure change versus external pressure reading (sect. 3.1) was not significantly affected by the drift of the external pressure reading. This assumption was not verified in a separate experiment, but discussed in section 4.1.2 of the manuscript. In this section, we established that the difference in the slope of the external pressure sensor readings versus internal cavity pressure between dry and wet air measurements was negligible (sect. 3.1). As outlined in the response to first specific comment of the reviewer, this does not exclude a water vapor-dependent offset during wet air measurements. As stated in said response, we will include a statement about this possible offset in a revised manuscript.

An argument for why pressure stability was sufficient with respect to time (not water vapor), which was not contained in the manuscript, was the magnitude of the drift, which was 0.1 Torr during two experiments (Picarro #1 and #3). This was less than the pressure difference between dry and wet air (0.4 Torr). Therefore, we argue that pressure drift with time, which may be attributable to the needle valve, had no considerable influence on the external pressure readings. During the experiment with Picarro #2, the external pressure reading drifted with a larger magnitude, 1.2 Torr. For this instrument, the argument above may not hold, but we observed only

small differences irrelevant to our findings between the pressure readings from this experiment and the ones from the other two.

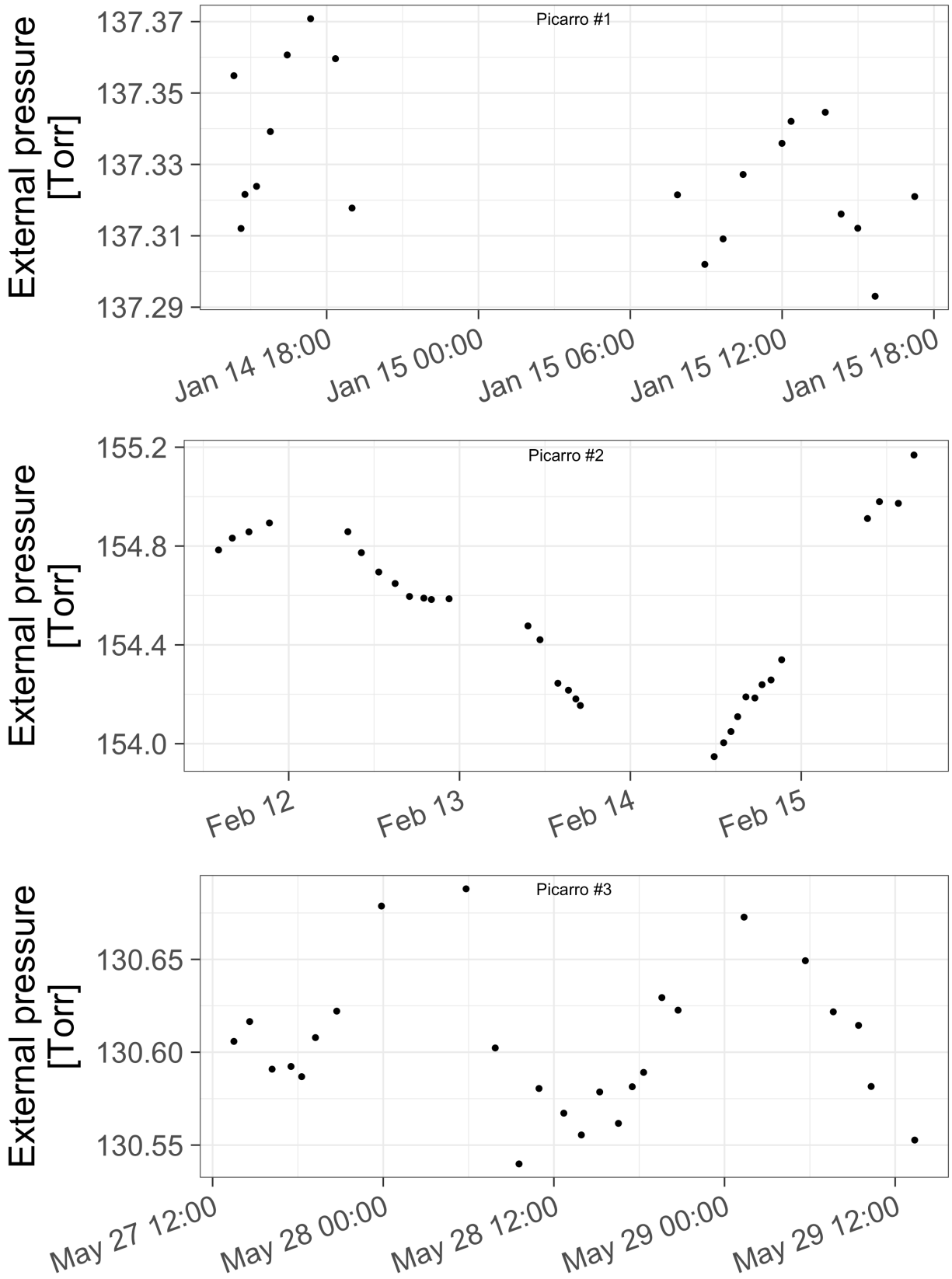


Fig. 3: Drift of the external pressure measurement during dry air measurements for all experiments with external pressure measurement.

Part two of this comment was addressed in the answer to comment #2 of the review (see above): the drying cartridge was never in contact with air before it was measured by the Picarro analyzer for those experiments from which we analyzed the CO2 and CH4 readings, so it could not have had an effect via absorption/desorption.

Reviewer's comment:

4. Depending on the water vapor absorption on the Mg(ClO4)2 reagent, magnitude of the pressure loss in the Mg(ClO4)2 cartridge may be changed, resulting in the pressure gradient between up- and downstream the cartridge.

Author's response:

We already discussed the influence of the drying cartridge and other factors on the external pressure measurement in detail in the answers to the other comments above, and stated that we will include these statements in a revised version of the manuscript.

This comment may be understood as suggesting the possibility that the drying cartridge caused pressure changes in the cavity of the Picarro analyzer. This is impossible, since the pressure stabilization of the instrument compensates external pressure changes. Thus, an effect of the drying cartridge on CO2 and CH4 via pressure variations can be excluded. To underline this statement, the systematic water-dependent biases of CO2 and CH4 were also present when no drying cartridge was installed (Picarro #5).

Reviewer's comment:

5. The author checked complete removal of water vapor behind the Mg(ClO4)2 cartridge at the external pressure sensor?

Author's response:

This is another possibility for inaccuracies of the external pressure measurement. We did not check for complete removal of water vapor behind the drying cartridge, and will include this alongside the other considerations raised by the reviewer and discussed in this response as stated above.

We would like to conclude by stating again that uncertainties of the external pressure sensor would not influence CO2 and CH4 readings of the Picarro analyzer, and that external pressure measurements are not necessary to achieve the main objective of this study: a better water correction for CO2 and CH4 for Picarro GHG analyzers.