Gas adsorption and desorption effects on cylinders and their importance for long-term gas records

M. C. Leuenberger, M. F. Schibig and P. Nyfeler

Climate and Environmental Physics, Physics Institute and Oeschger Centre for Climate Change Research, University of Bern, Switzerland

Reply to comments of Referee 1, 2 and 3

First of all, we would like to express our sincere thanks to the three referees. Their comments have been very helpful in considerably improving the manuscript. We are aware that the experiments that we have performed focusing on adsorption/desorption effects are only a small contribution to the very complex topic of the stability/instability of gas mixture in high pressure cylinders.

In the following we address all points raised by the reviewers point by point and hope that our answers are sufficient to publish the revised manuscript in ACP. The reviewers’ comments are given in italics and smaller size whereas our replies are written in normal style and size.

Referee 1:

This paper reports experimental results of the changes in the mole fraction of the trace gas components (CO2, CH4 and H2O) filled in the steel and aluminum cylinders in accordance with the changes in pressure and temperature. The CO2 and H2O mixing ratios in the cylinders increased with decreasing the pressure; the changes were accelerated at the low pressure and the changes are greater for steel cylinders than for aluminum cylinders. These changes are attributed to the gas adsorption/desorption effect on/from the inner wall of the cylinder. The authors explained the observed change associated with the pressure by adopting Langmuir’s adsorption isotherm. In the greenhouse gas measurement community, it is known by experience that the standard gases is more stable in the aluminum cylinders than in the steel cylinders and the mixing ratios in the cylinders are not reliable when the residual pressure is close to zero. This study is the first attempt to quantify the changes in the mole fraction in terms of the pressure-induced adsorption/desorption effect. The authors also examine the influence of the ambient temperature change on the adsorption equilibrium. Since these experimental results are useful for evaluating the stability of standard gas in cylinders, this paper is certainly worthy of publication in Atmospheric Chemistry and Physics. However, I think there are several mistakes in formulations and calculations and insufficient and ambiguous descriptions in the manuscript. Therefore, the manuscript is published after the authors and editors consider the following points.

We agree with the referee that the description of the experiments performed was not concise and partly incomplete or simply wrong. We have updated several parts to accommodate these shortcomings. See below.

General comments:
The amount of the adsorbed CO2 estimated from the emptying experiments is 0.3 ppm for aluminum cylinder and 9 ppm for steel cylinder. This result means that when CO2 standard gas is compressed into a cylinder, a significant decrease in the CO2 mixing ratio occurs due to the adsorption effect. It would cause serious problem on preparation of gravimetric standard gas; the CO2 mole fraction of the gravimetric standard gas, which is a mixture of pure CO2 gas and CO2-free ambient air prepared in an evacuated aluminum cylinder, would be by about 0.3 ppm lower than the CO2 mole fraction calculated from the masses of individual gases. The decrease in the CO2 mole fraction caused by the adsorption effect may be larger than 0.3 ppm because
smaller aluminium cylinders (~10L) are usually used for the gravimetric standard gas preparation and the volume-to-surface ratio decreases with the volume of the cylinder. However, such degradation of the gravimetric standard has not been reported, as far as I know. In addition, it is reported that the gravimetrically determined CO2 mole fractions agree well with those determined by the barometric measurement technique, which is another absolute measurement technique (Zhao and Tans, 2006, JGR, 111, D08S09, doi:10.1029/2005JD006003). These facts seem to indicate that the adsorption effect is no so large.

We fully agree with the reviewer. Indeed, our eq. (4) of the ACPD manuscript is approximately describing the change of the CO2 concentration of the decanted gas as a function of pressure. We used the term “approximately”, since eq. (4) does not take into account that the measured value at high pressure is already influenced by the adsorbed CO2 amount, but only mirrors the change of the decanted gas mixture. By doing this the parameter CO2, ad does actually not correspond to the adsorbed CO2 amount at high pressures but the change of observed CO2 in the decanted gas mixture at low pressure. This can be illustrated by the fact that eq. (4) reduces to CO2, meas. on the right-hand side for high pressures since KP is by far exceeding 1 and to CO2, meas. – CO2, ad (1- 0.6/1.6) for the pressure of 1 bar. CO2, ad should correctly be name as ΔCO2, corresponding to the measured CO2 change in the decanting gas at pressure zero. This is different to what we tried to express. Equation D of reviewer 1, does exactly what we tried to do and we fully agree with his derivation. This also brings the information with already present knowledge in agreement with our measurements done with these decanting experiments.

I think the Eq. (4) in the manuscript does not express correctly the change in the CO2 mole fraction in the cylinder for the emptying experiment because the equation does not take the influence of the released air into account.....

Yes, we agree with reviewer 1 that our eq. (4) does not describe that process correctly but is an approximation for the term CO2,ad does not correspond to the adsorbed CO2 but to the CO2 change at pressure zero (see above). We slightly adapted eq. D into the new eq. (4) as follows:

\[
\text{CO}_2^{\text{meas.}} = \text{CO}_2^{\text{ad}} \cdot \left[ \frac{\text{K} \cdot (P - P_0)}{1 + \text{K} \cdot P} + (1 + \text{K} \cdot P_0) \cdot \ln \left( \frac{P_0 \cdot (1 + \text{K} \cdot P)}{P \cdot (1 + \text{K} \cdot P_0)} \right) - 1 \right] + \text{CO}_2^{\text{known}} \quad (\text{eq. 4})
\]

Using eq. D, the amount of CO2 adsorbed for experiment 1 correspond to 0.41 ppm for the steel cylinder and 0.047 ppm for aluminium cylinder.

Specific comments
1) P. 19294, L. 14-15: The amounts of the absorbed H2O on the inner wall of the steel and aluminum cylinders (0 ppm and 30 ppm) are not discussed in the text. And the amount of the absorbed CO2 for the steel cylinder is 6 ppm here, but is 9 ppm in the following text. Which value is correct?

Indeed the adsorbed amounts of H2O have not been mentioned in the ACPD main text. However, we discussed Figure 3 briefly that displays the close linear relation of H2O and CO2 changes during the decanting experiment of a steel cylinder. The CO2, ad Value (0.41 ppm) has now changed since eq. 4 was altered to actually express the adsorbed rather than the CO2 change in the decanted gas, which amounts to 6 ppm. We altered the corresponding sentences as follows:
It is interesting to note that the adsorbed water is about five times stronger (<2.5 ppm) as shown by an equal pressure behaviour of desorption (Figure 3) than for CO2 (0.41 ppm).”

“Dislike the steel cylinder, aluminium cylinder did not show any desorption effect for H2O and CO and a hardly visible effect for CH4 as displayed in Figure 5."

2) P. 19296, L. 13-14: “Freundlich and Küster (1894)” is not listed in Reference.

The reference Freundlich and Küster (1894) is incorrect, it does not even exist and will be removed in the updated manuscript. In 1894, Herbert Freundlich was aged 14 only and no publication is listed under his name at that time. Equation 1 in the manuscripts is named after Freundlich H.[1906], however, he obviously was not the first that has used such a mathematical fit to observations. He was mentioning Küster’s work. Prof. F.W. Küster has released the first edition of the Handbook “Logarithmische Rechentafeln für Chemiker “ in 1894. Most probably Freundlich meant this Handbook but did not properly reference it in his publication of 1906. On the Web the Freundlich and Küster (1894) appears many times but without any reference given.

3) P. 19297, L. 25-26: I think that the surface condition of the cylinders also affects the adsorption ability as well as storage stability. How was the inner surface of the cylinders washed and treated? Such information is useful to the community of the greenhouse gas measurements.

We agree with the referee that surface conditioning might also be important for the adsorption results, however in our case no pre-treatments have been applied neither for steel nor aluminium cylinders. We added this information by modifying sentence to:

“In the first experiment we decanted 5 liters per minute from either a steel (50 liter steel cylinder from Carbagas, Switzerland) or aluminium (30 liter Scott-Marrin Luxfer aluminium cylinder) cylinder without any additional pre-treatment of the inner surfaces and monitored the mole fractions of CO2, CH4 and H2O by a Picarro G2311f and G2401, in which case CO was measured in addition.”

Furthermore, we added a paragraph about the ratio of effective to geometric surface area:

“Hence, it seems plausible to question the validity of our assumption that the exposed adsorption surface corresponds to the geometric surface. Due to surface roughness the adsorption surface might be significantly larger than the geometric measure. This is known in literature as rugosity. Values may range from 1 to more than 10 in the case of a sponge. For metals surface roughness is more often expressed as Ra, i.e. the arithmetic mean of the surface height changes. Our experimental results suggest that the rugosity value to be at least significantly above unity for steel cylinders.“

4) P. 19299, L. 2-20: In this paragraph (the first paragraph of Section 3), only result of the emptying experiment for the steel cylinder is discussed. Therefore, the first sentence of the paragraph, “Figures 2 and 4 display … cylinder”, should be changed to like “Figure 2 displays the CO2 … for a stainless cylinder.” Following this change, it would be good to cite Figure 4 in the first sentence of the second paragraph of Section 3.
5) P. 19299, L. 15-16: I think there is an error in calculation. The number of CO2 molecule corresponding to 9 ppm change in the steel cylinder is about $1.2 \times 10^{21} (= (50 \times 100/22.4) \times 9 \times 10^{-6} \times 6.02 \times 10^{23})$. But, the number of the CO2 molecule occupying the inner surface of 1.09 m² with the diameter of 3.4 \times 10^{-10}m is about $1.2 \times 10^{19} (=1.09/(1.7 \times 10^{-10})^2 \times 3.14))$, which is by two order smaller than above number.

We agree with the referee that our calculation is indeed not completely correct since the 9 ppm, quoted in the Discussion version, does actually not correspond to the adsorbed CO2 but the maximal CO2 deviation at pressures close to zero (i.e. close to the total usage of the gas). We agree that the derived equation D from the reviewer comment 1 is correct. By following this equation the CO2 corresponds to 0.41 ppm at a pressure of 105 bar for the steel cylinder decanting experiment. This corresponds to a 2.15 milli-liter CO2 STP or $5.8 \times 10^{19}$ CO2 molecules and hence is about five times larger than the inner geometrical surface area of the steel cylinder. However, as pointed out by referee #2, the surface area (in particular untreated surfaces as it is the case in our study) is often larger than the geometric estimate. We added a description about the so-called rugosity and the surface roughness.

6) P. 19299, L. 25-26: Did the authors use two different aluminum cylinders for the two emptying experiments with the different decanting rates? Are those cylinders listed in Table 1? If the only one aluminum cylinder was used, it would be better to explain the difference in the estimated K values, 2 bar-1 and 10 bar-1.

Yes, we used two different aluminium cylinders for the emptying experiments. Only one cylinder was mentioned in the original table 1 because it was also used in the temperature experiment. Therefore, the different K values are representing the different cylinders used. For clarification we updated table 1 such that it lists all cylinders used for the two experiments.

7) P. 19300, L. 1-2: Was the instrument (CRDS) calibrated against other standard gases 5 to detect the trends during the emptying experiments or, at least, before and after the experiments?

We calibrated the instrument by measuring laboratory standards that have been calibrated against a set of NOAA standards before and after the experiments. However, during experiment no calibration was done, therefore we cannot exclude a drift of the concentration over time. Yet, the trend seen in the decanting experiments using the aluminium cylinder (Figure 4 lower panel) might be due to the Joule-Thomson temperature effect (see explanation in the updated manuscript version).

8) P. 19300, L. 6-9: Table 1 should be referred to here.

Done

9) P. 19300, L. 17-22: I think that Eq. (5) is derived from Eq. (3), but it cannot be obtained simply by taking the natural logarithm of Eq. (3). So, it should be explained how to obtain Eq. (3). Similarly, it would be better to briefly explain how to calculate the desorption energies from the slopes in Fig. 8 and Fig. 10.

The reviewer is correct that we cannot directly derive eq. (5) from eq. (3). Starting with equation 4 extended with the temperature dependence of K, corresponding to the ratio of adsorption and desorption rate constants ($k_0$, $k_1$), i.e. $K=K_0 \exp(-E_{des}/RT)$, one can calculate the ratio of the CO2 difference obtained as a function of temperature from a reference temperature to the adsorbed CO2 concentration. According to the new eq. 4 (eq. D of reviewer 1) one can calculate the CO2 difference between a variable condition with temperature $T$ and
pressure \( P \) \((CO_{2,\text{meas}}(T))\) and a reference temperature (\( T_{\text{ref}} \)) corresponding to a \( P_{\text{ref}} \) \((CO_{2,\text{meas}}(T_{\text{ref}}))\). One can set \( P_{\text{ref}} \) to \( P_{\text{min}} \) and \( T_{\text{ref}} \) to \( T_{\text{min}} \) such that eq. 4 correspond to \( CO_{2,\text{known}} - CO_{2,\text{ad}} \), which is cancelled by the same part of the \( T, P \) condition. Assuming that the gas in the cylinder respond as an ideal gas, the pressure under the temperature \( T \) corresponds to

\[
K \cdot \frac{(P - P_{\text{min}})}{1 + K \cdot P} = (1 + K \cdot P) \cdot \ln \left( \frac{P_0 \cdot (1 + K \cdot P)}{P \cdot (1 + K \cdot P_0)} \right)
\]

The second term on the right-hand side can be approximated by

\[
\frac{CO_{2,\text{meas}}(T) - CO_{2,\text{meas}}(T_{\text{ref}})}{CO_{2,\text{ad}}} = -\frac{(P - P_0)}{P_0 \cdot (1 + K \cdot P)}
\]

With \( K = K_0 \cdot e^{-\frac{E_{\text{des}}}{RT}} \)

\[
\frac{CO_{2,\text{meas}}(T) - CO_{2,\text{meas}}(T_{\text{ref}})}{CO_{2,\text{ad}}} = -\frac{(P - P_0)}{P_0 \cdot (1 + K_0 \cdot e^{-\frac{E_{\text{des}}}{RT}} \cdot P)}
\]

Taking the logarithm and since \( K_0 \cdot P > 1 \), we get

\[
\ln \left( \frac{CO_{2,\text{meas}}(T) - CO_{2,\text{meas}}(T_{\text{ref}})}{CO_{2,\text{ad}}} \right) = -\ln \left( \frac{P - P_0}{P_0 \cdot K_0 \cdot P} \right) - \frac{E_{\text{des}}}{RT}
\]

\[
R \cdot \ln \left( \frac{CO_{2,\text{meas}}(T_{\text{ref}}) - CO_{2,\text{meas}}(T)}{CO_{2,\text{ad}}} \right) = -E_{\text{A,des}} \cdot \frac{1}{T} - R \cdot \ln \left( \frac{P - P_0}{P_0 \cdot K_0 \cdot P} \right)
\]

With the slope \( E_{\text{A,des}}(\Theta) \) and the intercept \( R \cdot \ln \left( \frac{P - P_0}{P_0 \cdot K_0 \cdot P} \right) \).

\[
E_{\text{A,des}}(\Theta) = -R \cdot T \cdot \ln \left( \frac{CO_{2,\text{meas}}(T_{\text{ref}}) - CO_{2,\text{meas}}(T)}{CO_{2,\text{ad}}} \right)
\]

10) P. 19300, L. 25-26: I’m not sure what the sentence “This might point to ...(Keeling et al., 2007)” mean. Please explain why the authors consider the influence of thermal diffusion is small.

During the experiment 2, the decanting rate of a cylinder (filled to 100 bar) was about 250 ml/min when it was measured otherwise zero. This gas flow lead only to very small temperature changes of the pressure regulator attached to the cylinder following the Joule-Thomson effect and corresponds to about 1 Kelvin (a cooling of -27 Kelvin of the gas corresponds to a about a decrease of 1 Kelvin on the regulator assuming steady state conditions, i.e. power loss (about 0.15 W) compensated by heat uptake from the environment
after Stefan Boltzmann). Temperature changes on the cylinder itself are even significantly smaller. The heat capacity and in particular the conductivity of the tanks (steel as well as aluminium) is high enough to compensate for any gas flow induced temperature changes on the cylinder. The regulator, however, is exposed to cooling that in turn is dependent on the gas flow, i.e. about 1 Kelvin for 0.25 l/min (power loss 0.15 W) and about 15.5 Kelvin for 5 l/min (power loss 3 W) in experiment 1 using the Joule-Thomson coefficient for air (-0.27 K/bar) and assuming a surface area of 0.03 m² for the regulator. This effect decreases linearly with pressure due to the Joule-Thomson coefficient dependence on pressure.

11) P. 19303, Table 1: There is no mention of Table 1 in the manuscript. Are the values of the second decimal place significant?

Done, see above

12) P. 19308, Fig. 4: Is the blue curve in the top panel expressed only by Eq. (4)? Isn’t it the combination of Eq. (4) and a linear function corresponding to the gradual increasing trend?

Yes, it corresponds only eq.4 (now in an updated version), no gradual increasing trend is overlaid.

13) P. 19308, Fig. 4 caption: How were the desorption energies (EA,des) calculated from the emptying experiments?

In exactly the same way as for experiment 2, since for the aluminium cylinders we had temperature recordings available in contrast to the steel cylinder measurements.

14) P. 19311, Fig. 7 caption: Does the steel cylinder 5a correspond to the cylinder 5 (LK548528)?

Yes, cylinder 5a corresponds to LK548528. We omitted “a” since it is not listed like this in table 1.

15) Fig. 6, 7, and 9: There is no mention of these figures in the manuscript.

Done, we reference every figure in the updated manuscript.

Anonymous Referee #2

The manuscript by Leuenberger et al. from the Climate and Environmental Physics department in Bern presents results from experiments designed to characterize the dependence of gas concentrations upon emptying high pressure cylinders. The problem of changing concentrations during withdrawal of air from such cylinders is well known and of particular importance for the long term cylinders characterizing the respective international trace gas scales. Experience teaches that below a certain threshold the concentrations become unreliable. However, the threshold varies from laboratory to laboratory and largely depends on the treatment of the cylinders. Systematic studies of the corresponding effects are scarce and details need to be characterized in a more quantitative fashion in order to avoid artifacts in the high-precision measurements of atmospheric trace gases. The experiments by Leuenberger et al. are an important step in this direction.

The major factors causing concentration changes are thermal fractionation during gas withdrawal, the type of cylinder (aluminium, stainless steel), surface treatment before filling, adsorption of trace gases on cylinder walls, reactions with the wall material, residual moisture, diffusion through cylinder or valve gaskets and more. According to Keeling et al. (Tellus 59B, 3, 2007), the largest effects are thermal fractionation, corrosion and leakage. Desorption effects account for less than 5 % of the total uncertainty. Other laboratories have reported
much larger effects, which mainly have been attributed to cylinder handling (cylinders kept horizontally or standing upright, with consequences for the temperature distribution).

The manuscript by Leuenberger et al. concentrates on adsorption effects. The experiments are described quickly: High-pressure cylinders filled with ambient air are emptied using a continuous bleed with a variety of flows, thereby monitoring gas concentrations (CO2, CO, CH4 and H2O). Seven cylinders were studied, some were aluminium, some stainless steel tanks. The temperature was changed between -10 and +50 C. The CO2 concentrations change considerably with temperature, with a large scatter of the data for the steel tanks. The aluminium tanks show a much smaller dependence. It would have been nice to read a discussion of the possible causes (like heat conductance of the materials), which has not been made.

We agree with the reviewer that the discussion of the possible causes was short. We have calculated the influence of heat conductance for both materials and found it to be marginal. This is actually visible in the Figure 1, since the actual temperature is in good agreement with the measured temperature on the cylinder, however both are offset by 2.75 hours to the set temperature of the climate chamber. This is reasonable considering the size of the climate chamber which is about 10 x 4 x 3 meters. The cylinders were lying horizontally on a wooden tray. Therefore, the heat exchange of the cylinders must be through the air temperature. Using heat conductivity and heat capacity values for steel and aluminium lead to equilibration times which are significantly shorter than the lag of the climate chamber to the set temperature.

All experiments are interpreted mainly in terms of adsorption / desorption. The flow rates are rather high (up to 5 L / min). Some important information is not provided: - position of the cylinders before and during the experiments (horizontal or vertical) - temperature gradient - surface roughness and treatment prior to filling - CO2 adsorption as a function of moisture.

The cylinders were lying horizontally on wooden trays during the experiment, before they were placed vertically in our laboratory about 10 km away from the climate chamber location. We do understand what the reviewer meant with temperature gradient? Figure 1 displays the applied temperature gradient and based on the heat conductivity the temperature of the cylinders follow the climate chamber temperature timely. All cylinders were not exposed to treatment prior to fillings – at least not to our knowledge. The cylinders were filled by the CarboGas company, the institute’s gas supplier.

The sometimes artificial distinction between physisorption and chemisorption is rather simplistic and not discussed specifically for the different species involved. CH4 could be expected to have little chemical activity and therefore be described using physisorption only. H2O in contrast will exhibit mainly chemisorption, thereby providing a liquid surface where gases like CO2 might dissolve in at varying degrees depending on the local pH. These effects are not discussed in the manuscript at all.

Based on the energy range found from experiment 2 (below 15 kJ/mol), we have little evidence that chemisorption (100 – 1000 kJ/mol plays a major role in what we have observed. We rather interpret our findings for all species with physisorption (1-10 kJ/mol) alone. Our results suggest about 5 mono-layers of CO2 adsorption and about 10 mono-layers of H2O adsorption. This amount will not be enough to act as liquid like layer and hence the reviewer’s suggestion is not adequate. Therefore, local pH is expected to play a negligible role.

The surface area is given as a geometric term only. However, untreated surfaces often are a lot larger than the pure geometry might suggest. Hence, before calculating the number of adsorbed layers, the surface area must be known with some accuracy.
We fully agree with the reviewer’s comment that the geometric area is most probably significantly underestimating the effective surface exposed to gas molecules for adsorption. Indeed, in future experiment the surface roughness or rugosity should be investigated in parallel. We mentioned this issue in the updated manuscript.

The reported adsorbed CO2 amounts (up to 9 ppm for a steel tank) seem very high and need to be confirmed independently. A simple experiment would be to fill a tank and measure the corresponding air concentrations simultaneously. The adsorbed gas would decrease the gas concentrations in the cylinder. Hence, there should be a difference of 9 ppm between the gas measured during filling and the gas withdrawn from the (steel) cylinder afterwards. I expect a missing amount of no more than 0.2 ppm, but I may be wrong.

The statement in the ACPD manuscript is misleading. The 9 ppm increase does not correspond to the CO2 amount adsorbed but the change observed on the decanting gas at low cylinder pressures. The comment by reviewer 1 also concerns this issue and he suggested modifying equation 4 to equation D given in his comment. We fully agree with this equation D and this leads to a CO2 amount absorbed of <0.5 ppm for the steel and <0.05 ppm for aluminium cylinders. Therefore, you are completely correct with your intuition that the adsorbed CO2 concentration is in the range you stated.

Overall, the line between temperature related diffusion and adsorption / desorption effects is difficult to draw given the set of experiments. Some of the effects are unusually large. The effect of water adsorbed to the surfaces needs closer inspection.

We agree with the reviewer that further experiments are necessary related to the issue of water adsorption, but also related to temperature issues at the regulator. The latter is especially important when working of low decanting flows that might allow diffusion driven fractionation.

The manuscript may be published, but only after paying close attention to effects that may be caused by temperature inhomogeneities and associated (very slow) diffusion and effects that can clearly be attributed to surface phenomena. The latter also requires a minute characterization of the surfaces involved.

We included now a discussion about the potential distinction of adsorption/desorption versus diffusion driven processes. Due to the high gas flows we are convinced that diffusion driven processes cannot be the prime cause of our observations. However, several influencing factors requires further attention.

Anonymous Referee #3

The manuscript by Leuenberger et al. presents results from a study of the effects of adsorption onto the inner wall of steel and aluminum cylinders, and the effect of cylinder pressure on the adsorption. This effect has been suspected for many years, and seen by National Metrology Institutes when attempting to create high precision gas primary standards for carbon dioxide. The practice of filling cylinders with dried air and letting them sit to equilibrate is also brought into question, as the subsequent lowering of the cylinder pressure through removal of gas for analysis, brings into play the pressure effects investigated by this paper. Thus while the methods and scope of this paper are limited, it is important to bring these issues to the forefront so users are aware of the risks when using cylinder standards in their work. As this paper just scratches the surface of this problem, it does open the discussion for more work to be done and published to properly define this potential bias, and the uncertainty of the bias, so it may be properly accounted for in the data collected, and in the preparation of gravimetric primary standards. The two previous referee comments make very valid points, and I support their comments as well. However I recommend publishing this paper after the authors have considered all the specific comments. Specific Comments: This is a very limited study, only three cylinders composed of aluminum and
steel. In our experience this effect is very cylinder dependent, and can very quiet a bit due to cylinder treatment. Cylinder treatment is not considered in this report, and the treatment of cylinders investigated was not listed in the method section. The water measurements are below the lower bounds published in the Picarro literature. Are these values reliable? From our own Picarro instruments, water values in the ppm range <200 ppm are questionable. The conclusions are overstated, as these results are applicable to the cylinders tested only, and may not be extended to all cylinder treatments for all specialty gas sources. The larger concern is when using aluminum cylinders to prepare gravimetric standards, as this bias is very large and must be evaluated fully to prepare SI traceable gravimetric primary standards. There the source of the cylinder can largely dictate the amount of bias possible. In our experiments the bias can be as high as 0.8 ppm and as low as 0.1 ppm depending on the cylinder treatment of 30 L aluminum cylinders. The choice of Scott Marin cylinders is relevant only as the WMO community has standardized on that source, a dangerous practice, as it relies on a commercial company continuing in business. The temperature dependence may also be cylinder dependent, however this has not been rigorously tested.

We agree with the reviewer’s view that our experiment does only scratch the complex topic of gas instabilities in gas cylinders or during its decanting process. Since we have experienced many effects in our laboratory that are still requiring proper explanations, we started with such preliminary experiments. Of course, we would like to continue this path with additional and more focussed work using improved pre-defined conditions, that were not present – at least in some parameters – during the presented study. The calibration of the Picarro instrument related to water vapour determination remains an issue especially at the low concentration levels. However, we have quite good confidence that the values are realistic. Nevertheless, we will state in the updated manuscript that this requires further investigations. Indeed, many of the effects changing the gas composition within the cylinder or during the gas decanting process are cylinder or pressure regulator dependent and therefore require further testings.

References: