Reply to the review of Anonymous Referee #2

The authors would like to thank anonymous referee for the valuable comments. In the following, referee's comments are given in bold and author's responses in plain text. Suggested new text is quoted in italics together with page and line numbers.

General comments: This paper investigates the trace gas stability of air stored in high pressure steel and aluminum cylinders with respect to adsorption/desorption surface processes. Experiments were designed to look at gas phase changes in CO_2, CH_4, CO and H_2O as functions of gas pressure and temperature.

The matter of trace gas stability in air standards is critical to atmospheric measurement programs. A better understanding of how surface processes affect trace gas concentrations could lead to better selection of cylinder materials and operating procedures.

This paper addresses these matters. It gives detailed descriptions of the experiments performed, which are new and informative, but the conclusions are somewhat vague. I am left with some unanswered questions.

To what extent are the results consistent with the Langmuir adsorption model?

We agree with our reviewer that this point needs further clarification. Our findings did not support the shape of the Langmuir adsorption isotherm as observed in the previous studies (Leuenberger et al. 2015, Brewer et al. 2018, Schibig et al 2018). The onset of the surface effects was not observed until sub-atmospheric pressures for the cylinders tested in this study.

In order to investigate whether the observed amount fraction changes can be explained by the Langmuir adsorption isotherm for monolayer coverage, we used a modified version of the Eqn. 5 from Leuenberger et al. (2015):

$$CO_{2,meas} - CO_{2,initial} + CO_{2,ads} = \Delta CO_2 = CO_{2,ads} \cdot \left(\frac{K \cdot (P - P_0)}{1 + K \cdot P} + (1 + K \cdot P_0) \cdot ln\left(\frac{P_0 \cdot (1 + K \cdot P)}{P \cdot (1 + K \cdot P_0)} \right) \right)$$

Where, $CO_{2,initial} + CO_{2,ads}$ is the mean of the measured amount fractions during the first hour for each experiment. Therefore, for P close to P_0, the left side of the equation will be close to zero and it increases with lower pressures. The left term on the right hand side of the above equation is always negative and the right term always positive. Increasing K or $CO_{2,ads}$ values increases the left term. Yet K increase is less pronounced compared to $CO_{2,ads}$ change. K determines the curvature whereas $CO_{2,ads}$ just stretch or compress the values.

In order to find the best possible fit, we have used R's inbuilt "optim" function with the setting Limited-memory Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm. Upper and lower bounds were set for each unknown ($CO_{2\ ads}$ and K) and the algorithm was run to minimize the sum of squared differences between the measured amount fractions and the modelled amount fractions. For $CO_{2,ads}$ lower and upper boundaries were set as 0.001 µmol mol^{-1} and 15 µmol mol^{-1}. We have set the first guess values for the algorithm to the lower boundaries. In Figure 1, we show the theoretical isotherms together with our experimental data. The purple points show measurement data from the 30 bar experiments of the aluminum cylinder, and the black lines show the Langmuir monolayer fit to the measurements with K values of 0.001 bar^{-1} and 1 bar^{-1} denoted by the solid and dashed lines, respectively. Fig 1.b shows a zoom-in to the region where the pressure in the cylinder is less than 3 bar. In order to find a better fit to the experimental data, we have further increased the upper limit of the K value up to 500 bar^{-1} (Table 1). At higher K values, the modelled curve fits better to the onset of the increasing amount fractions. The tendency of a higher K value in this study, contradicts to Schibig et al. (2018), where they have set the K value at 0.001 bar^{-1}. The difference between the estimated equilibrium constants in this study and Schibig et al. (2018) may be explained through the different surface properties (e.g. roughness or treatment of surface). Moreover, even by setting larger limits for all parameters, we did not find any K value which was able to fit the highest enrichments measured towards the end of the experiment. This might partly be related to the algorithm we have used and the limited number of data at the end of the measurements. However, the discrepancy for the highest enrichments can also be explained by another effect than desorption at low pressures. The reasonable range of K remains unclear. A more detailed analysis on model fitting is not within the scope of this experimentally focused study.

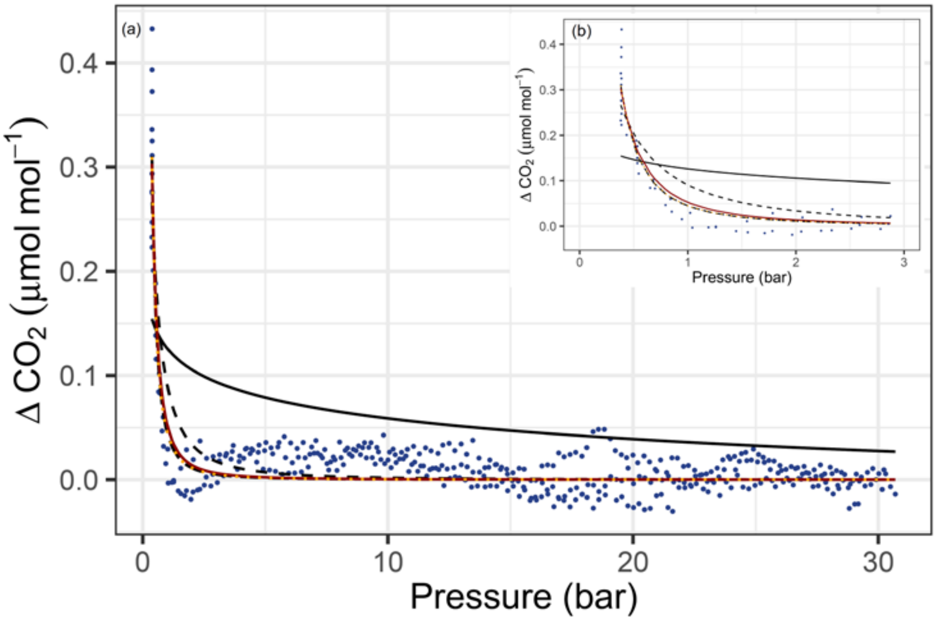

Figure 1: (a) Measured and modelled amount fractions of CO_2 for the aluminum cylinder filled to 30 bar. Purple points show measured data, black solid lines show the fit with K=0.001 bar^{-1}, black dashed lines show the fit K=1 bar^{-1}, dark red lines show the fit with K=10 bar^{-1}, and orange dotted lines show the fit K=100 bar^{-1}, and black long dashed lines show the fit K=379 bar^{-1} (b) Zoom-in to the region where the cylinder pressure is less than 3 bar.

Table 1: Model parameters for Langmuir adsorption isotherm for CRDS data

K (bar^{-1}) [1]	**$CO_{2,\ ads}$ (µmol mol^{-1}) [2]**
0.001	0.029
1	0.015
10	0.038
100	0.301
379 [3]	**1.116**

[1] Upper boundary for K is increased from 0.001 bar^{-1} to 500 bar^{-1} stepwise for each solution

[2] Lower and upper boundaries for $CO_{2,\ ads}$ 0.001 µmol mol^{-1} and 15 µmol mol^{-1}

[3] The best fit was not limited by the boundary conditions.

The following statement will be added at page 19 line 25:
"In contrast to the previous studies, the cylinders tested in this study showed enrichments only well below atmospheric pressures for the steel cylinder and the aluminum cylinder before heating. At sub atmospheric pressures, the enrichments followed a steep increase. This increase can only partly be fitted to the Langmuir adsorption isotherm if the equilibrium constant (K, the ratio between adsorption and desorption rates) are set to values higher than 1 (Supplementary material). Higher K values would correspond to higher surface coverage factors even at lower fill pressures. In comparison Schibig et al. (2018) have fixed the K value at 0.001 bar^{-1}*, corresponding to lower surface coverage even at pressures of 150 bar. The reasonable range of the equilibrium constant remains unclear. The differences in the cylinder interior characteristics such as surface roughness or treatment is highly likely the explanation of the discrepancy in the K values. A further investigation on the K value and modelling approaches is not within the scope of this experimental focused study."*

Figure 1 will be added to the supplementary material together with the information on the method used for the fit.

The QCLAS measurements at sub-ambient pressures were presumably done to test the adsorption model under extreme pressure conditions. Did the experimental results support the model?

Indeed, these measurements were conducted to test the adsorption model under extreme conditions. Moreover, these measurements can also be useful for measurement systems operated at low pressure conditions. The experimental results supported the Langmuir model, however, the enrichments occurred in the region where the pressure correction function required extrapolation (page 11 line 19). Therefore, these data should be interpreted carefully. Our aim when conducting the QCLAS experiments was to find the lower limit under which CRDS measurements would be reliable. Nevertheless, we have conducted a similar analysis as presented above in order to determine model fit parameters. We add the Langmuir fit (Figure 2) to supplementary material.

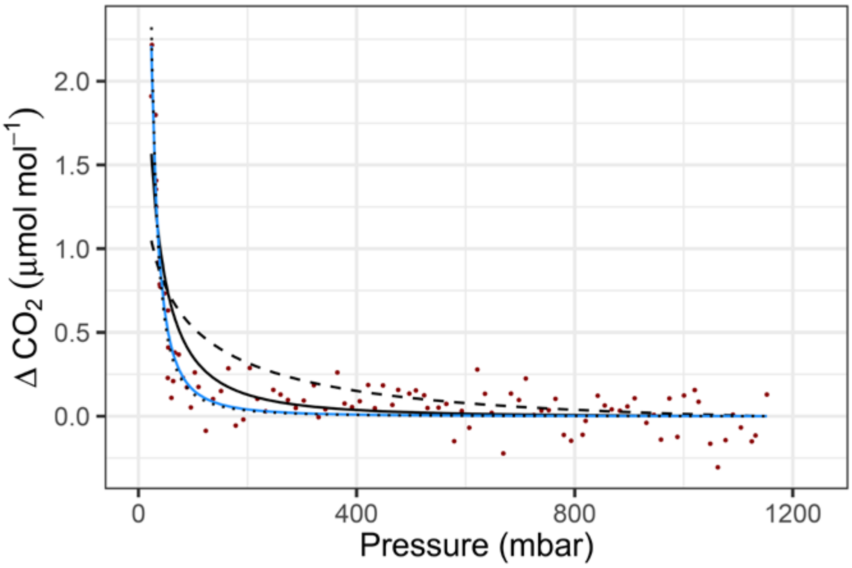

Figure 2: Measured and modelled amount fractions of CO$_2$ for the aluminum cylinder from the QCLAS setup. Red points show measured data, black dashed lines show the modelled fit with K=0.001 bar^{-1}, black lines show the modelled fit with K=0.01 bar^{-1}, blue lines show the modelled fit with K=0.152 bar^{-1} and black dotted lines show the modelled fit with K=1 bar^{-1}

Table 2: Model parameters for Langmuir adsorption isotherm for QCLAS data

K (bar^{-1}) [1]	**$CO_{2,\ ads}$ (µmol mol^{-1}) [2]**
0.001	0.185
0.01	0.149
0.152 [3]	**0.454**
1	2.387

[1] Upper boundary for K is increased from 0.001 bar^{-1} to 1 bar^{-1} stepwise for each solution

[2] Lower and upper boundaries for $CO_{2,\ ads}$ 0.001 µmol mol^{-1} and 15 µmol mol^{-1}

[3] The best fit was not limited by the boundary conditions.

Was the observed temperature dependency consistent with the model?

The observed temperature dependency was not consistent with the Langmuir adsorption isotherm at least above 80 °C. The temperature dependencies observed in the presented study are irreversible and not related to a physical adsorption. Within the scope of other studies (Leuenberger et al., 2015 and unpublished data), reversible temperature responses are measured until 80 °C, however these differences were an order of magnitude smaller than the presented enrichments in this study at 180 °C. Therefore, we are confident that the observed differences, above 80 °C are not related to a reversible adsorption process. The discussion on page 18 starting from line 14 explains other relevant hypotheses on the observed enrichments.

Four different gases were measured but analysis of the results focuses on CO_2. This may be because CO_2 showed the strongest signals, but the authors should comment on why this is the case, and provide some more discussion of what the results say about the other gases. For example, do the gases differ in their sensitivity to adsorption on account of their molecular properties? Can this explain the different pressure and temperature dependencies observed for the different gases?

We agree with our reviewer that more information on other species is necessary. The reason that our study concentrate on CO_2 is indeed related to the strong amount fraction response of CO_2.

The following paragraph will be added at page 19 after line 31:

"This study also showed that the measured gases CO, CO_2, CH_4 and H_2O had different sensitivities with respect to surface processes. We have observed surface effects for CO_2 and H_2O. Observed effects of H_2O during the pressure experiments were an order of magnitude larger than CO_2 (not shown here). One of the explanations that CO_2 and H_2O are more prone to surface effects might be due to their high boiling points. CO_2 sublimates at -78.5 °C, and the boiling point of H_2O is 100 °C. Whereas for CH_4 and CO, boiling points are -161 ° C and -191.5 °C, respectively. Since CO is a reactive compound, it might be argued that it would be more prone to surface effects. However, our results have shown that CO in atmospheric air was not affected by surface interactions at short time scales (in the order of days). This is highly likely related to the competitive adsorption between species. The ratio between the amount fraction of CO and CO_2 would be 1 to several hundreds. In order to understand competitive adsorption to its full extent, experiments focusing on a range of amount fractions would be useful. Moreover, when discussing adsorption properties, polarity is also an

important criterion. Therefore, the non-polar structure of CH_4 makes it less prone to adsorption, whereas the polar geometry of H_2O enables it to be more adsorptive."

What conclusions can be drawn for how air standards should be prepared and used?

The air standards should not be stored at high temperatures. However, high temperatures might be useful for pre-treatments of cylinders. Aluminum cylinders are well suited to store greenhouse gases such as CO, CO_2 and CH_4, whereas usage of stainless steel cylinders are more suited for standards of halogenated compounds.

I think the paper could be suitable for publication in AMT if these questions are addressed.

Specific comments:

It is unclear in some parts of the text if quoted gas pressures are absolute or relative to ambient atmospheric pressure. There is potential for more confusion when referring to cylinder and cell pressures.

We agree with our reviewer this point need clarification. Cell pressures are consistently reported as absolute pressures, whereas cylinder fill pressures for CRDS measurements are consistently reported relative to the ambient pressure. We make the following additions to the manuscript in order to prevent confusion:

On page 1, line 9:
"This extensive dataset revealed that for absolute pressures down to 150 mbar the enhancement in the amount fraction of CO_2 relative to its initial value (at 1200 mbar absolute) ..."

In Table 1 on page 6,
"[bar relative to atm]"

On page 7, line 16:
"Therefore, we filled the aluminum cylinder to 1200 mbar (absolute)"

On page 10, caption of Figure 5:
"Reported pressure data show absolute pressure values."

On Page 11, line 17:
"At the point where the cell pressure started to fall below the target pressure (150 mbar absolute- Fig. 5c) …"

On page 12, caption of Figure 6:
"x-axes show the absolute pressure values in the sample cylinder."

On page 19, line 5:
"The independent QCLAS measurements on the aluminum cylinder has not shown any effect down to absolute pressures as low as 150 mbar."

On page 20, line 11:
"The results showed that for absolute pressures above 150 mbar… "

Page 8, line 4 – It should be noted here that CH_4 decreased while the other three gases increased in concentration. What does this say about the favored explanation of outgassing?

Our reviewer points out an interesting point, however, the underlying mechanism of the instrument related effects are unclear. The decrease in CH_4 might partly be related to a dilution caused by the increase of other compounds in the cavity.

Page 12, line 2 – It is claimed that CO and CH_4 dependency on pressure was not significant, but in Figure 6 for CH_4 at least, the "Steel before heating" and "Aluminum after heating" plots show elevated CH_4 at low pressures. Is this an analytical artefact or a real bias? If real, it requires some comment. The authors should also comment on why there is a clear effect for CO_2 and H_2O but not for CO and CH_4.

We thank the reviewer for pointing this out. We relate these changes to an analytical artefact likely related to a drift in CH_4 measurements and the cavity pressure instabilities which occurred towards the end of the experiments. Since the onset of this increase is not the same for the conducted experiments and the observed differences are not consistent through the replicates, we do not relate these effects to adsorption / desorption processes. Fig. 7c clearly shows the differences among the replicates of steel cylinder, and the aluminum after heating experiments.

Please see the text above for explanation of the adsorptive properties of all measured species.

Page 15, Section 3.3.2 – It appears that all four gases are correlated in their response to temperature changes. If so this should be made clear. Is there a reason why the figures and the table consider only correlations between the pairs CO_2 – CH_4 and CO– H_2O?

We agree with the reviewer that this point needs clarification. Indeed, all pairs are correlated, for easier visibility only two pairs at a time was shown. The species were paired by highest coefficient of determinations.

The reason behind such correlations might be chemical reactions following fixed ratios of production, however it is highly questionable if it is feasible to produce methane under 180 °C and slightly over 10 bar. This is already explained on page 18 lines 14-18.

The readability of the paper is fairly good, but could be improved in places with a little attention from a proficient English speaker. Maybe the editor could help with this. Some specific suggestions are included below.
We thank our reviewer for his attention, the technical corrections noted below are changed at the respective places.

Technical comments:

Page 1, line 9 – replace “until pressures as low as 150 mbar” with “for pressures down to 150 mbar” – text modified accordingly

Page 1, line 17 – reword to “measurements of CO2 were made at Mauna Loa, Hawaii in the late 1950s...” – text modified accordingly

Page 1, line 19 – “with an increasing number” - corrected

Page 1, line 21 – Global Atmosphere Watch - corrected

Page 2, line 13 – has received attention - corrected

Page 2, line 18 – amount fractions - corrected

Page 2, line 25 – gas cylinder usage - corrected

Page 3, line 3 – reword to “enables placement of test materials...” - corrected

Page 3, line 31 – interpret - corrected

Page 4, lines 1-2 – Provide some more detail about the flow rate used and the length of time required to obtain reliable measurements. Was there significant change in cylinder pressure?

The flow rate during the pressure experiments is shown in Fig. 4a. The flow rate into the cell of the CRDS analyzer is between 15 mL min^{-1} and to 220 mL min^{-1}, regulated by the outlet valve as explained in Sect. 3.1.1. Regarding the time required, the measurement setup has 1/4″ tubing which is 30 cm long. Prior to the experiment, the tubing and the pressure regulator were flushed 3 times. For the analysis the first 10 minutes of data was not taken into consideration. 10 minutes of measurements with 220 mL min^{-1} would correspond to a 0.4 bar decrease in the pressure of the small cylinder. Since the observed effects in the cylinders does not start until pressures less than atmospheric pressures, the change is not significant for the presented experiments.

For clarity we include this information also in Page 4 line 3:

“There was no flow regulation after the pressure regulator prior to the analyzer inlet. At the beginning of the experiment the flow rate was 220 mL min^{-1} (STP) and towards the end of the experiment it was 15 mL min^{-1}(STP). More information on flow rate is included in Sect. 3.1.1. The measurement setup had 1/4″ tubing of 30 cm. long. Prior to the experiment, the tubing and the pressure regulator were flushed 3 times. For the analysis the first 10 minutes of data was not taken into consideration.”