Reply to the review of Anonymous Referee #3

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 describes a series of experiments aimed at comparing the adsorption of some atmospheric trace gases in various materials. Experiments were planned in a very structured way to allow meaningful observations. The study was part of a larger study on adsorptions, and it is clear that authors chose to limit this paper to one main variable: the surface material. A good number of different materials were chosen, and all of them appear to be of interest to the community. The paper is generally well written, well-structured, clear, and provides a number of details on the instruments and methods, with some further details missing. However, the discussion part of the paper is quite limited. The results need to be put in perspective with other published work, in particular on CO_2 with aluminium. It also misses explanation and assumptions on the phenomena at work. Previous work by Leuenberger included a complete model with an attempt to fit the results during similar experiment in large cylinders. This paper should at least summarise this effort and explain if such attempt was also made here, and why it does not appear. Considering the type of comments provided below, I recommend a major revision before the paper can be published.

We would like to thank our reviewer for the insights and opinions. As already stated by the reviewer, this study focuses on surface material. The previous study on these small cylinders (Satar et al. 2019, 10.5194/amt-2019-197) have already concentrated on comparing the newly built small cylinders with the existing literature. In the presented work, we aimed at going a step further and have used the aluminum cylinder as the measurement chamber. We'll include a separate discussion section (presented as well in the replies to anonymous referee #1). Regarding a model of fit for the results presented in this study, the observed maximal deviation from the initial amount fraction for the blank cylinder was as low as 0.05 µmol mol^{-1} making modelling of this increase extremely difficult. For the material loadings, adsorbed amounts should be distributed between the blank cylinders and the material blocks. However, subtracting the maximal amount fraction difference of the glass loaded cylinder from the material loaded cylinder resulted in amount fractions in the order of the standard deviation of the measured data. Therefore, for the majority of the materials fitting the Langmuir isotherm is not reasonable (presented as well in the replies to anonymous referee #1).

Please see point by point comments for the comparison between this work and the previous studies.

Specific comments by section:

Section 1. Introduction:

-Cylinders volume in this study compared to others: the introduction mentions this difference but does not state the potential impact on observations. In Schibig 2018 it is explained that cylinders smaller than 30 L should present larger effects, due to the surface to volume ratio. This should be observed and reflected through the introduction and the rest of the paper, in terms of the magnitude of observed effects compared to cylinders commonly used as standards.

Despite our efforts of increasing the surface area the material effects were minor, the geometric surface to volume ratio in the material experiments were 71.4, whereas this ratio is only 25.4 in Schibig et al. (2018). Our study with various different materials have revealed that even by increasing the

surface areas the desorbed amount at the end of the experiment until sub-atmospheric pressures is not significant for the materials except Dursan and DLC.

In the discussion part the following paragraph will be added (already presented in the replies to anonymous referee#1):

"The presented setup enabled the investigation of surface effects under "extreme" conditions which favored adsorption/desorption. Compared to common usage in the atmospheric measurement and gas metrology communities, our study has differed in cylinder size, geometric surface to volume ratios, pressure and temperature ranges. Previous studies (Leuenberger et al. 2015, Brewer et al. 2018, Schibig et al. 2018) investigating surface effects in compressed gas cylinders have used (50 L, 10 L, or 29.5 L) cylinders. The geometric surface of the small (5 L) aluminum cylinder used in this study is 0.18 m^2, which results in a surface to volume ratio of 35.7 for the unloaded cylinder. Compared to 29.5 L Luxfer cylinders, the small cylinders are estimated to be more prone to adsorption by 40 %. Inserting material blocks into the aluminum cylinder further increased the surface area. Therefore, the setup allows to test materials under increased surface to volume ratios in which the surface effects should be stronger and dominant. However, despite our efforts of increasing the surface material effects were minor."

Section 2.1:

-Small chambers in aluminium and steel cylinders were designed, but this study only reports observations with the aluminium cylinder. The rationale behind this choice should be added. Was it after the conclusions of the other paper?

For the material experiments we have chosen to use the cylinder with the smallest background effect. We will add the following on page 3 line 14:

"Since the aluminum cylinder showed smaller effects with respect to surface effects in the previous study (Satar et al, 2019), we have chosen to use the aluminum cylinder only for the material experiments in order to minimize the background effect related to the measurement chamber."

-The analyser is mentioned line 27 without a description. Please add the model and the performances which are relevant to the study. In particular one needs to pay attention to the sensitivity for the compounds measured, to demonstrate that observations are meaningful (or not). The claimed repeatability of the instrument appears sometimes on the same order as the changes measured during the study.

We will mention the name of the analyzer earlier on page 3 line 27:

"On the measurement line between the pressure regulator and the Picarro Cavity-Ring Down Spectroscopy analyzer (CRDS) G2401 either an electropolished stainless steel 1/4'' tubing ,…"

On page 5 at line 3, we will add the following:

"The experiments were conducted using a Picarro G2401 CRDS analyzer enabling measurements of CO_2, CO, CH_4 and H_2O. According to the specification sheet of the analyzer, 5 minute, 1-σ standard deviation is <0.02 µmol mol^{-1}, <1.5 nmol mol^{-1}, <0.5 nmol mol^{-1} and <50 µmol mol^{-1} for the species CO_2, CO, CH_4 and H_2O, respectively. In order to investigate the material's pressure dependency, the cylinder was filled through expansion from the mother cylinder to around 15 bar, and was evacuated through the Picarro analyzer."

-Compressed air used for the study: more details on the composition are clearly needed, at least nominal values provided by the company. The water content in particular is under question, as some

of the observed differences are of the order of 70 µmol/mol. Does this mean the water amount fraction was even higher than this? This is important to clarify, considering that the work of Brewer et al. showed how water can be preferably adsorbed on surfaces, decreasing the adsorption of other compounds such as CO_2.

The observed differences of the 70 µmol mol^{-1} were not related to the water content of the mother mixtures, but were related to the equipment or material involved in the experiments. This is already explained on page 9 at lines 14-18 for the runs with mass flow controller.

On page 4 at line 4 the following will be added:

"After spiking the mother mixture, the composition of LUX3575 was 428.59 µmol mol^{-1}, 1083.73 nmol mol^{-1}, 2132.93 nmol mol^{-1} and <15 µmol mol^{-1} for CO_2, CO, CH_4 and H_2O."

On page 9 at line 18, we will add the following:

"Similar to the CO_2 response of Dursan loading, the increase in H_2O amount fraction is most probably a combination of both desorption of newly adsorbed molecules and, desorption from the coated layer. It is unlikely that the enrichment of H_2O is related to the mother mixture since all other materials resulted in significantly lower amount fraction differences."

Section 2.2:

-Flow rate: previous studies of Schibig et al. and Brewer et al. mentioned an influence of the flow rate at which cylinders are being emptied. How was this taken into account? What was the flow rate during the measurements? Some consideration on this point should be provided.

Schibig et al. (2018) and Brewer et al. (2018) have conducted their measurements at high and low flow rates. In Schibig et al. (2018), low and high flow conditions were 0.3 L min^{-1} and 5.0 L min^{-1}, whereas in Brewer et al. (2018) the low and high flow rates were 0.7 L min^{-1} and 5.5 L min^{-1}, respectively. The flow rate in the presented experiments in this study as well as Satar et al. (2019) are comparable to the low flow conditions. In contrast to the above-mentioned previous studies, there was no excess flow prior to the analyzer. 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 of Satar et al. (2019). Since we have conducted the measurements at low flow conditions, other fractionation effects due to a temperature gradient in the cylinder are not expected.

We will add the following flowrate information on page 6 line 1:

"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 decreased to 15 mL min^{-1}."

-Pressure values during temperature studies: table 1 shows that the pressure could change when changing the temperature. Consider explaining the reason and potential impact on the results.

We think there was a misunderstanding in the interpretation of the values presented in Table 1. The three pressure values shown in the table only show the starting pressures of each experiment, and does not give information on pressure change related to temperature change. Regarding pressure changes during the temperature experiments, these changes can be estimated using the ideal gas equation. For example, for a filling of 15 bar pressure and 20 °C temperature a pressure of 18.1 bar at 80 °C and 13.5 bar at -10 °C is expected. At these ranges, no pressure effect is expected. This point is already taken into account and discussed for the temperature experiments (on page 10 line 6).

For clarification, we will add the following in the caption of Table 1:

"The pressure values indicate the pressure in the small cylinder at the beginning of each replicate run."

-It is explained that in this study, all reported values are in amount fraction difference. It can be assumed that this choice was made to plot all data together and be able to compare different observations. This might be a good reason, but absolute values should also be provided, at least once, to be able to compare the results in this study with others.

Indeed, similar to other studies we have preferred to plot our results in amount fraction differences. This approach enables to compare different observations and also highlights the measured differences. The mother cylinder content is compressed natural air. We have added the composition of the cylinder to section 2.1.

-Temperature cycle: please clarify that the container was refilled at the beginning of each new temperature step. This information could also be added on figure 3.

We think that there is a misunderstanding at this point. The cylinder was not filled at the beginning of each new temperature step. The cylinder was filled to about 15 bar at the beginning of the temperature cycle (Fig. 3) and refilled after a full temperature cycle.

Section 3:

-It is said several times that changes observed with CO_2 are significant only for Dursan. However, differences of the order of 0.15 µmol/mol were observed with other materials and this is comparable with the compatibility goal within GAWG. In other studies, similar changes were not considered negligible. Some analysis in view of already published work should be added and made more consistent.

We thank our reviewer for pointing this out. It should be noted that the differences observed in this study were observed at sub-atmospheric pressures, other studies including Leuenberger et al. (2015), Schibig et al. (2018) and Brewer et al. (2018) observed these differences at an earlier onset at higher pressures. In our opinion, this study should be seen independently from the existing literature due to the following reasons: (i) the experimental setup used in this study is not comparable to previously published work in terms of inserting different materials in a measurement chamber, (ii) an introduction into the blank cylinders and their comparison to existing literature is already presented in detail within the scope of Satar et al. (2019), (iii) the surface to volume ratios in the current study is increased on purpose to increase adsorption/desorption effects.

In the previous study in which the cylinders were introduced (Satar et al., 2019), a discussion on how the small cylinders behave in comparison to other studies has already been included for the blank cylinders. In our opinion the focus of the presented work is to understand the effects of different materials. Nevertheless, we suggest to add the following the paragraph to discussion (presented as well in the replies to anonymous referee #1):

"The presented setup enabled the investigation of surface effects under "extreme" conditions which favored adsorption/desorption. Compared to common usage in the atmospheric measurement and gas metrology communities, our study has differed in cylinder size, geometric surface to volume ratios, pressure and temperature ranges. Previous studies (Leuenberger et al. 2015, Brewer et al. 2018, Schibig et al. 2018) investigating surface effects in compressed gas cylinders have used (50 L, 10 L, or 29.5 L) cylinders. The geometric surface of the small (5 L) aluminum cylinder used in this study is 0.18 m^2, which results in a surface to volume ratio of 35.7 for the unloaded cylinder. Compared to 29.5 L Luxfer cylinders, the small cylinders are estimated to be more prone to adsorption by 40 %. Inserting material

blocks into the aluminum cylinder further increased the surface area. Therefore, the setup allows to test materials under increased surface to volume ratios in which the surface effects should be stronger and dominant."

Regarding the significance of 0.15 µmol mol^{-1}, we clarify as follows on page 9, at line 10 (presented as well in the replies to anonymous referee #1):

"For CO_2 measurements, the amount fraction differences for all materials except Dursan were less than 0.17 µmol mol^{-1}, with slight differences among the various loadings. Of this difference, 0.05 µmol mol^{-1} is related to the blank cylinder (background effect). The blank cylinder corresponded to the "14 bar after heating" case presented in Satar et al. (2019). More information on the blank cylinder and its filling history is provided in the above-mentioned publication. It is also crucial to consider that during all material block experiments, glass pieces were also present in the small measurement chamber. When the material runs were compared to the experiments with glass, except the DLC loading, the remaining differences were in the order of 0.02 µmol mol^{-1}, which corresponded to the 5-minute standard deviation of the measured data."

-The "empty" case needs further clarification. First on the term itself which is badly chosen as the container is always filled with gas. Second on the values compared to the other paper of the authors. They are apparently those of the case "aluminium, filled at 14 bar, after heating". This should be clarified and related to the choice of this material (best results?).

In order to avoid this misunderstanding, we have changed *"empty"* to *"blank"* as suggested by the anonymous reviewer 2.

Aluminum cylinder was chosen as a measurement chamber for the presented study, since aluminum is the commonly used material in the atmospheric measurement community. Since all material experiments were conducted after the temperature experiments presented in Satar et al. (2019), we have naturally used the "aluminum cylinder after heating". The choice of the cylinder is already clarified above (Section 2.1), and the blank results are linked to the 14 bar after heating case in the discussion section (please see the suggestions above).

-The "steel" results can be confusing when compared to the other paper, where a difference of 0.5 µmol/mol was observed. The setup is of course not the same, but this would need some consideration and some assumptions to explain those discrepant results.

We thank our reviewer for his/her attention. The discrepancy between the two steel result is most likely related to the different composition of steel used in these two studies. In the presented study stainless steel blocks of (316L) are used, whereas the previous study uses a steel cylinder of hardened and tempered steel (1.7218 / 25CrMo4 EN AW-6061) This information is already presented at the respective papers.

-Results on water: figure 4 shows up to 60 µmol/mol changes, which would mean quite large water content to start with. Was it the case? If not, where does the water come from?

The two cases with high water changes were already explained in the manuscript on page 9 at line 14 and with the suggestions above. It is important to note that the big differences in the amount fractions are observed towards the end of the experiments where desorption is expected to be at play. We relate the high water content with the mass flow controller and the Dursan blocks. For the remaining runs, considering the low flow rate and the duration of the high water vapor content episodes, the

integrated amount of water vapor is reasonable since there is a trace amount of water available in the mother cylinder which will be adsorbed at high pressures.

Comments on figures:

Figure 5: consider splitting in different figures to allow a larger front. This is currently far too small.

We understand the reviewer's concern. We will increase the font size, but will keep all subfigures.

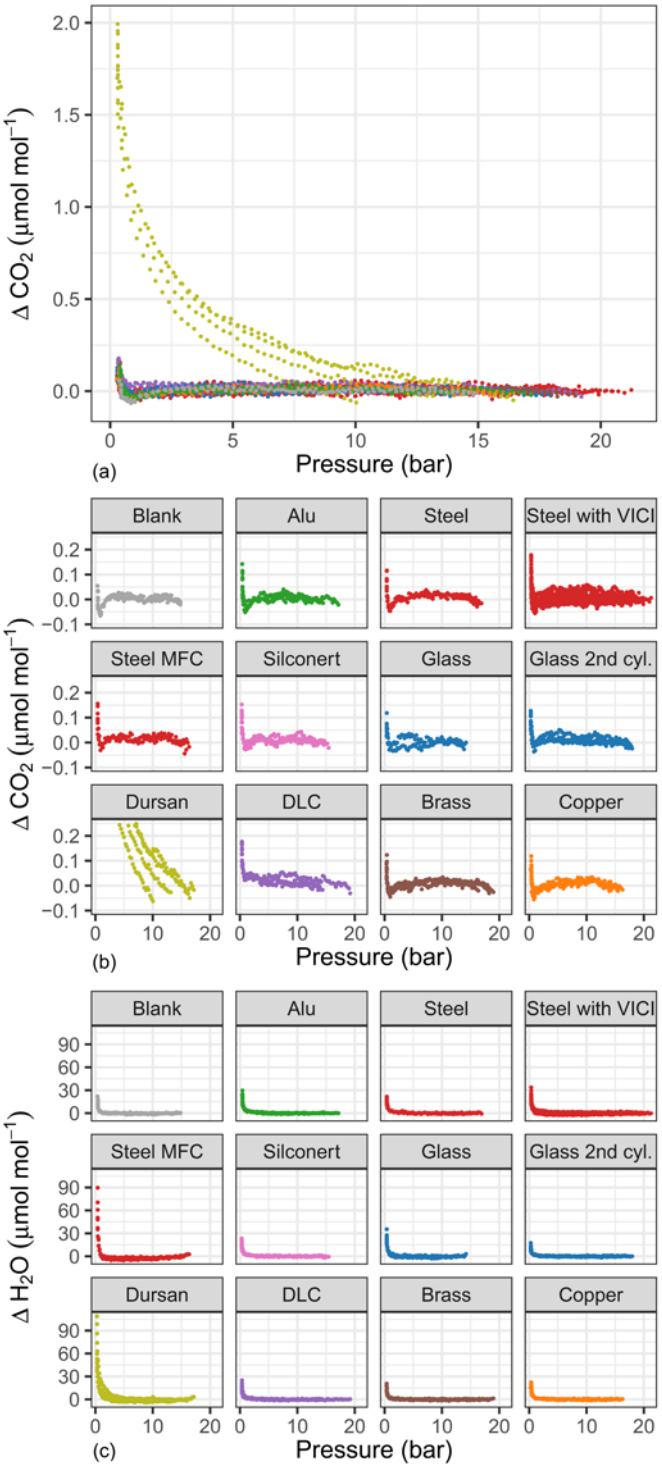

Figure 5. Amount fraction difference relative to the start of the experiment for (a, b) CO_2 and (c) H_2O with respect to pressure for all tested materials. The first panel shows all materials together, whereas in the second and third panels, each material is plotted separately. Consistent color codes are used throughout the study.

Figures 6: the x-axes is very disturbing, even after the highlight in the text noting that it indicates the temperature cycle, which is why the scale is not linear. There is some logic in this choice, but it discards the possibility to clearly see the temperature effect. Consider plotting with a linear temperature scale using a color code or different shapes to show the time. Another option is to use time as x-axes and superpose the temperature cycle.

We respect our reviewers view on Figure 5 and Figure 6. However, in our opinion the plots are clearly showing both the reversibility (e.g. H_2O) and the irreversibility (e.g. CO and CO_2) of the temperature effect. Superposing a temperature cycle would pack more information on already full plots especially in the case of group 1 plots (Fig. 6a).