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.

1 General comments

This manuscript deals with adsorption/desorption of trace gases in air on various metal surfaces. While many existing studies have focused on real cases, testing types of cylinders in use in the atmospheric measurement community, this manuscript on the contrary describes experiments performed using specifically designed test cylinders, filled with an air mixture and various materials, to study potential adsorption phenomenon of gases (CO_2, CO, CH_4, water vapour) on the tested surfaces. The results presented in this manuscript represent many hours of preparation and measurement, and are surely of value for the community measuring trace gases in the atmosphere and preparing reference gas mixture for this purpose. In particular, this study reports detectable and quite large effects for the coating Dursan for CO_2, which was unexpected, Dursan being advertised as a passivation treatment. Irreversible alteration of the amount fraction for most species and materials at temperatures equal or above 80 °C are also reported. In many other cases, no clear adsorption/desorption effect can be seen, which is at the same time a bit disappointing for process analysis but also good news from the user's point of view. The manuscript is well organised and figures in particular have been prepared with great care and display the results very clearly. Some descriptions in the text may gain in clarity (suggestions hereafter under 'specific comments').

2 Specific comments

What is your method's limit of detection, i.e. the smallest adsorption/desorption effect that could be detected using the chosen measuring instrument? What does the thresholds of 0.2 µmol/mol you mention for CO_2 p. 9 l. 9, 6 nmol/mol for CO and 1 nmol/mol for CH_4 (p. 7 l. 15) represent? If these questions are answered in the companion paper, please cite it.

We agree with our reviewer that this point needs further clarification. The word "threshold" is not correctly used in this context, therefore we replace it with the following phrasing on page 9 line 10:

"*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.*"

For the presented experiments, we have used a Picarro G2401 CRDS analyzer. According to the specification sheet, the 5-minute, 1-σ precision of the instrument is <0.02 µmol mol^{-1}, <1.5 nmol mol^{-1} and <0.5 nmol mol^{-1}, for CO_2, CO and CH_4, respectively. The numbers presented in our study (0.17 µmol mol^{-1}, 6 nmol mol^{-1} and 1 nmol mol^{-1}, for CO_2, CO and CH_4, respectively) were reported to highlight that the observed changes have not exceeded these values but are higher than instrument precision stated in the specification sheet. These values can further be compared to the 5-minute standard deviation of measured data for CO_2, CO and CH_4 which in our case corresponded to 0.02 µmol mol^{-1}, 5 nmol mol^{-1}, and 0.2 nmol mol^{-1}, respectively. For CO_2 measurements, an explanation is already provided to clarify the significance of the observed changes within the reply to the anonymous referee#1. For CO and CH_4 considering the standard deviation of the measurements and the specifications of the analyzer, the observed maximal amount fractions are not significant and do not show material dependency.

We will add and rearrange the paragraph on page 7 line 13:

"For CO and CH_4, the maximum difference in the amount fractions did not exceed 6 nmol mol and 1 nmol mol^{-1}, respectively. According to the analyzer (Picarro G2401) specification sheet, the 5-minute, 1-σ precision of the instrument is <1.5 nmol mol^{-1} and <0.5 nmol mol^{-1}, whereas the 5-minute standard deviation of measured data corresponded to 5 nmol mol^{-1} and 0.2 nmol mol^{-1}, for CO and CH_4, respectively. Therefore, we have concluded that no significant change was observed in the final amount fractions for any of the materials during the course of the pressure experiments for the species CO and CH_4."

For the pressure tests in particular, very little adsorption/desorption effect is seen, making likely very hard to actually estimate a number of molecules adsorbed per unit of surface area and/or to compare with theoretical adsorption curves (even if, from the user's point of view, this is actually good news). This stated, it seems also clear that a new design allowing to cause larger adsorption effect would demand a substantial work and is beyond the scope of this manuscript. Still, how would you design a new test chamber / test material or how would you conceptually modify the present equipment to provoke a larger effect that could then be better analysed? I would suggest to add a few lines discussing this in the discussion and/or conclusion.

We thank our reviewer for appreciating the difficulty of estimating the number of adsorbed molecules. In order to increase adsorption, we would recommend inserting materials of very high surface areas into the measurement chambers. Some ideas would be using thin metal plates, metal spheres or metal pieces resulting from manufacturing processes (e.g. metal chips).

We will add the following statement at the end of the discussion:

"Moreover, in order to observe significant surface effects, materials of very high surface areas can be inserted into the measurement chamber. Some ideas would be using thin metal plates, metal spheres or metal pieces resulting from manufacturing processes (e.g. metal chips)."

Distinction container/content: I would suggest making clear reference to a gas mixture when writing of measuring, spiking or being adsorbed (e.g.: working gas, mother mixture), and to a gas container when writing of evacuating, cleaning, connecting, etc. (e.g.: working cylinder, mother cylinder). A few examples:

p. 3 l. 29: The fillings were done using compressed air from high pressure 50 l aluminum cylinders (LUX3586 and LUX 3575). – text modified accordingly

p. 3 l. 29-30: These two cylinders are called the mother cylinders and their air content the mother mixture from here on. – text modified accordingly

p.3 l. 31: In addition to the mother mixture, another mixture of comparable content and from a cylinder of comparable material and equipment to the mother cylinder was measured [...]. – text modified accordingly

p. 3 l. 33: This mixture (from cylinder LUX3579) is refereed to as the working gas. – text modified accordingly

p. 4 l. 2-4: [...], the mother mixtures we spiked [...] using another compressed air mixture as carrier gas. – text modified accordingly

Please check that this distinction is clear through the manuscript.

p.5 l. 6: 'empty cylinder': it is stilled filled using the mother mixture so it is not empty strictly speaking. Maybe 'blank cylinder' (with the same meaning as 'blank measurement') would be more precise. Please modify through the manuscript (text, Tables, Figures).

We understand the concern of our reviewer, we have changed *"empty cylinder"* to *"blank cylinder"* throughout the manuscript.

p. 7 l. 12: 'end amount fraction': I would suggest replacing by 'final amount fraction'. Please check through the text. – "end amount fraction" was changed to "final amount fraction" in the manuscript.

3 Technical corrections, phrasing

Abstract: a direct mention of adsorption right at the beginning would be more clear. Suggestion: A critical issue [...] employed. Both measuring and preparing reference gas mixtures for trace gases are challenging due to e.g. adsorption/desorption of the substances of interest on surfaces; this is particularly critical at low amount fraction and/or for reactive gases. Therefore, to ensure [...]. This study focuses on testing potential adsorption/desorption effects for different materials [...].

We agree with our reviewer that an earlier mentioning of adsorption is essential, we have changed the text accordingly.

Abstract l. 10: [...] to investigate the pressure dependency of adsorption up to 15 bar, and its temperature dependency [...]. – text modified accordingly

p. 1 l. 18, suggestion: In order to achieve a high level of compatibility for data obtained at different sites and/or at different time, the World Meteorological Organisation [...]. – text modified accordingly

p.1 l. 22: [...] but also by limiting any cause of molar fraction alteration. – text modified to *"but also by limiting any cause of amount fraction alteration."*

p. 1 l. 22: maybe mention an order of magnitude for the lifetime of a standard cylinder?

On page 1 at line 22, the sentence is modified accordingly:

"During their relatively long lifetime in the order of decades, standard gas cylinders […]"

p. 2 l. 8: larger volume – text modified accordingly

p. 2 l. 18: we aim at distinguishing these effects – text modified accordingly

p. 2 l. 28: on various surfaces. – text modified accordingly

p. 2 l. 30: According to the current literature, – text modified accordingly

p. 2 l. 34: the adsorption loss on the stainless steel surface – text modified accordingly

p. 3 l. 14: [...] we used the aluminium cylinder only. – text modified accordingly

p. 3 l. 17: [...] used in the atmospheric measurement community. This custom-made[...] – text modified accordingly

p. 5, legend of Fig. 2: related to the cleaning procedure – text modified accordingly

p. 7 l. 2: For the data analysis, for each temperature step the first 10 minutes of the measurements were not included in order to allow time for equilibration; the mean of the remaining 25 minutes was calculated. – text modified accordingly

p. 9 legend of Fig 5: whereas in the second and third panels – text modified accordingly

p. 9 l. 10 For example, [...] analyser showed [...] pressure run, whereas the mass flow[...]. – text modified accordingly

p. 10 l. 6: Based on the results of the pressure tests, the temperature experiments were conducted within a pressure range for which no pressure effect should occur, [...]. – text modified accordingly

p. 10, legend of Fig. 6: The x-axes correspond to the temperature cycles (cf. Fig. 3), – text modified accordingly

p. 10, legend of Fig. 6: does the y-axis show the amount fraction differences relative to the first measurement bloc done at 20◦C? (There are three measurement blocs done at 20◦C.)

We thank our reviewer for pointing this out. We changed the legend accordingly:

"the y-axes show the amount fraction differences relative to the first measurement block at 20 °C."

p. 10 l. 7: In order to graphically distinguish [...] – text modified accordingly

p. 11 l. 9: remove 'Please' (check through the text). – text removed accordingly

Suggestion: displaying Fig. 6 and 7 on the same page.

We agree with our reviewer and combined the two figures into one.

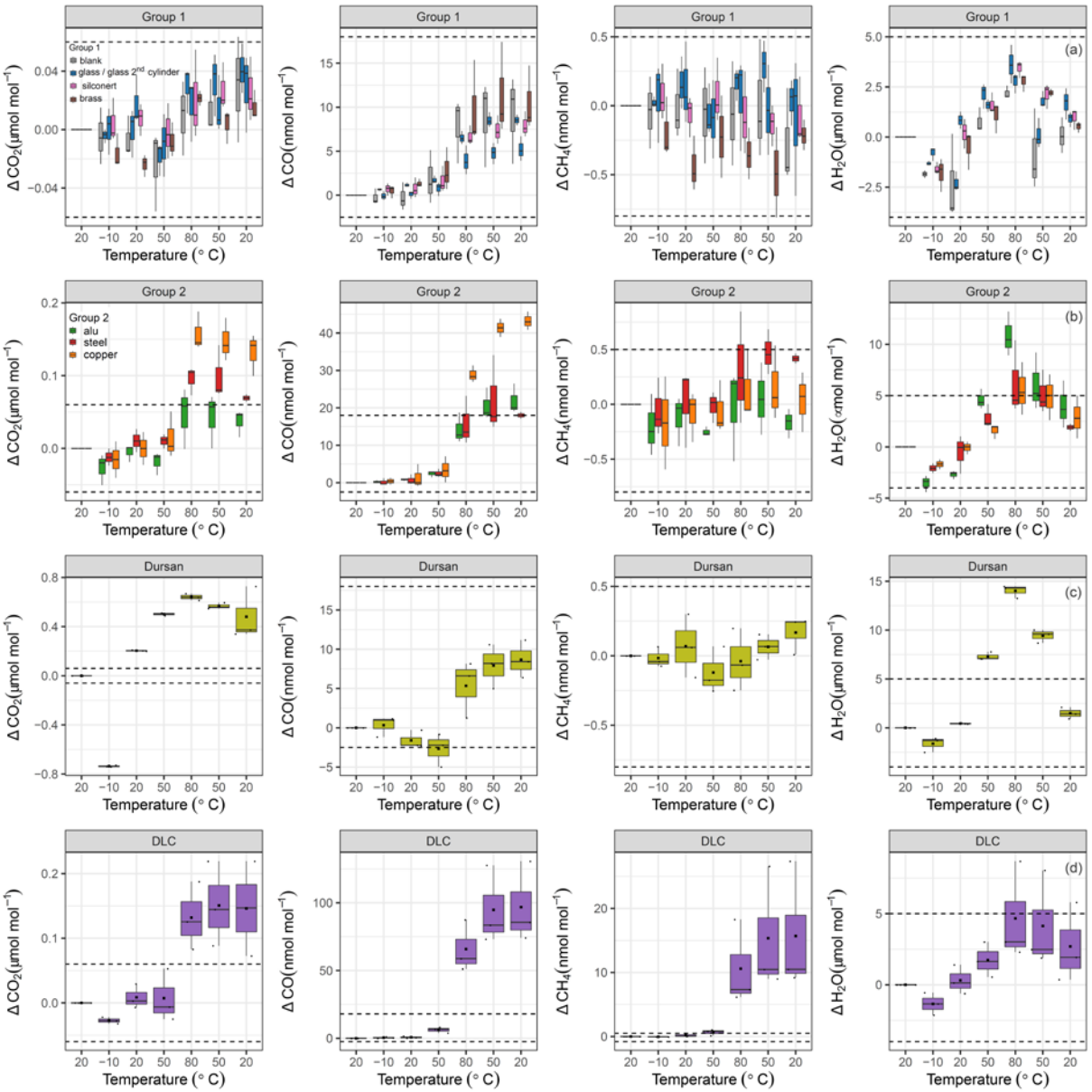

Figure 6. Temperature experiments grouped according to temperature response. (a) Group 1 materials are blank cylinder (gray), glass (blue), SilcoNert®2000-coated steel (pink), and brass (brown). (b) Group 2 materials are aluminum (green), stainless steel (red), and copper (orange). (c) Dursan® (light green) and (d) DLC (purple) coatings on stainless steel. Dashed lines indicate the same ranges for each species. The x-axes correspond to the temperature cycles (cf. Fig.3), and the y-axes show the amount fraction differences relative to the first measurement block at 20 °C.