

## Responses to Review of Referee 1 (AMTD-8-8083-2015)

We would like to sincerely thank reviewer 1 for his excellent comments and suggestions. It improved the manuscript again by giving the reader more in-depth information about instrumental drift rates and their limited influence on our findings.

In the following we reply to every point raised by the reviewer 1. Our answers are given in red, whereas changes made to the manuscript are given in blue.

**Summary** This paper describes the results of laboratory experiments designed to probe the stability of CO<sub>2</sub> and other trace gases in high pressure, steel and aluminum gas cylinders. The authors performed two experiments: 1) high-flow decanting, and 2) low-flow measurement of trace gas mole fraction with temperature cycling of the gas cylinders. Their results suggest that surface adsorption of CO<sub>2</sub> can be modeled with a Langmuir-type isotherm. The effect of temperature on surface adsorption is significant for steel cylinders, but not for aluminum cylinders. Their results are not inconsistent with what has been previously reported.

**General Comments** Overall, the experimental design and data quality are only partially sufficient to support the conclusions. The results for the steel cylinder appear robust and reasonable. However, the results for the aluminum cylinder, although consistent with observations seen in our laboratory, could also have been influenced by analyzer drift. Inclusion of uncertainties would help justify the results. For the aluminium cylinders, the temperature sensitivity study is important to the field. Their results suggest that storing calibration cylinders at temperatures over the range -10 to 40 deg C has no appreciable affect on the CO<sub>2</sub> mole fraction. However, the fact that small increases in CO<sub>2</sub> were observed during the decanting experiments for aluminum cylinders, and the analyzers used are subject to drift unless calibrated during the experiment, raise questions about conclusions drawn from the data. The fact that the data fit the Langmuir isotherm could be coincidental.

Indeed drifts of the analyser could be a problem. We did not calibrate the instrument during a decanting experiment, however, during the temperature dependence experiment we did measure a reference gas (CA03901) as mentioned in the manuscript (p 8089, l. 9). This measurements done throughout the experiment showed rather constant values with a standard deviation 0.009 ppm. There is indeed a small trend of +0.0041 ppm/day. Excluding the trend, the standard deviation reduces to 0.006 ppm. Therefore, the trends seen in the steel and aluminium cylinder are most certainly not due to drifts of the analyser. Furthermore, there is no temperature dependence of the reference tank (CA03901) as expected since it was placed outside the climate chamber.

We added the following information to the revised manuscript in the results section where we discuss the second experiment:

The different sign of the dependencies for steel and aluminium cylinder is a first hint that these dependencies are not originating from instrument drift. This is supported by the measurements of cylinder CA03901 acting as a reference that was not exposed to the temperature variations but placed just beside the instrument in an anteroom. This measurements done throughout the experiment showed rather constant values with a standard deviation 0.009 ppm. There is only a small trend of +0.0041 ppm/day. Excluding the trend, the standard deviation reduces to 0.006 ppm. Furthermore, even with this small constant drift of the analyser, only the scatter of the data but not the temperature dependence itself would be affected. Actually, large instrument drifts could potentially be

estimated from the scatter of the data. Therefore, the temperature dependencies seen for steel and aluminium cylinders are most certainly not due to drifts of the analyser.

The authors should include information about how the cylinders were filled. For example : : : were the cylinders evacuated prior to filling? Were they conditioned to the same CO<sub>2</sub> mole fraction prior to filling? These issues could be important with respect to adsorption. Please describe how the cylinders were filled and any corresponding pretreatment or conditioning.

We agree with reviewer 1 and added the following information to the revised manuscript, also in response to issues raised by reviewer 2:

We ran two experiments in order to determine the pressure and temperature dependencies of gas adsorption on two different metal cylinder surfaces (steel and aluminium). We used 50 liter tempered steel (34CrMo4) cylinders equipped with a standard brass valve K44-8 from VTI with Peek as spindle sealing material. The regulator connection type is G 5/8" RH female thread from Carbogas Switzerland sealed with a PA disk. Gas wetted materials for these cylinders are steel, brass and Peek. The aluminium cylinders are new 30 liter Scott-Marrin Luxfer (AA 6061 T6) cylinders equipped with a brass valve D 202 from Rotarex with PA as spindle material. The regulator connection type is CGA-590. Gas wetted materials are aluminium, stainless steel, brass and PA. No additional pre-treatment of the inner surfaces were applied except these applied by the supplier and producer that we do not know in detail and these given above. The steel cylinders were filled by Carbogas according to their protocol. We do not know the filling history of these cylinders except that they are used for compressed air fillings only. The aluminium cylinders were pumped to roughly 10 mbars and then flushed and pressurised to 10 to 15 bars using dry compressed air with ambient concentrations three times and then filled with dry compressed air from another cylinder again at ambient concentrations. CB09877 prepared similarly at Empa and was additionally blended by a second compressed air. CA03901 was prepared at Boulder by NOAA/CMDL according their protocol.

Since analyzer drift may impact experiment 1, it calls into question the results of experiment 2 as well. The authors need to provide evidence that their results are robust and not an artefact of analyzer drift.

See answer above regarding the drift and the corresponding changes made in the revised version of the manuscript.

Prior to publication, some text and figures could be improved.

Specific Comments  
Tables and Figures

Figure 4: You mention that the analyzers were calibrated at the beginning and end of the decanting experiment. This leaves room for analyzer drift. According to the manufacturer's website, the Picarro 2401 is subject to drift of up to 0.1 ppm CO<sub>2</sub> in 24 hours, and the drift specification for the 2311f is up to 0.25 ppm CO<sub>2</sub> in 24 hrs. These drift rates are comparable to the changes in CO<sub>2</sub> you observed in the high-pressure region. It seems likely that the change in CO<sub>2</sub> at low pressure is related to adsorption, but are you sure the downward trend in the lower panel, before the cylinder reaches 5 bar, is not related to analyzer drift?

We agree with reviewer 1 that Picarro lists these drift rates, however, our experience is that the drifts are less under laboratory conditions. As described above, this is supported by the drift rate measured during experiment 2 on cylinder CA03901 of 0.041 ppm/24h. Nevertheless, we cannot completely rule out that drift rates were different during experiment

1 and could have potentially influenced the negative trend observed for the low flux decanting experiment. Therefore, we added a sentence mentioning this possibility. However, we judge it to be less secured. We modified the text discussing the low flow experiment as follows:

In particular the slightly decreasing mole fractions in the low flow (0.25 liters per minute, Figure 4, lower panel) decanting experiment on the aluminium is most probably a result of the Joule-Thomson effect though instrumental drifts may play a role. However, our observation of drift rates under laboratory conditions with the instruments in use does not strongly support this.

Fig 4 caption: “cannot determined” change to “could not be determined”

done

Table 1: In the caption you say that no steam cleaning was applied. Are you sure? Do you know what was done by the manufacturer or supplier? What about cylinder conditioning? Were the cylinders conditioned to similar mole fractions of CO<sub>2</sub> and H<sub>2</sub>O for some time before being filled the final time?

We agree that we do not know what has been done by the supplier, therefore, we added the following sentences in the Table 1 caption.

Note that no pretreatment of cylinders has been applied by us, i.e. no steam cleaning, surface conditioning or finishing except those applied by the supplier (see main text).

Table 2: Since the temperature dependencies of CO and CH<sub>4</sub> could not be detected, I suggest removing these columns from the Table and including a note in the caption: such as “temperature dependencies for CO and CH<sub>4</sub> could not be detected within experimental uncertainties”.

Good point, thank you.

applied

Figure 6: This figure is not very helpful. I assume that you are showing the best fit lines rather than individual data because there is a lot of scatter in the data. This information would be better presented in a table, with slope, uncertainty, and r<sup>2</sup> values for each cylinder.

Here, we disagree with reviewer 1. First of all, it is not true that there is a lot of scatter in the data, except maybe for the aluminium cylinders that represents very small variations in the range of the measurement uncertainty of the instrument. Second, we are convinced that it visualised the important fact that there is indeed a very large dependence on individual cylinder regarding the temperature dependencies. Furthermore, it highlights easily that difference between steel and aluminium cylinders. However, we suggest to add a pointer to the corresponding axis for the two cylinder types for improved visibility.

Changes will be applied to the final Figure 6.

Figures 7, 8: Displaying the fit equations leads to confusion. It is not clear that the middle equation is the average of the two (I think). I suggest you report desorption energies in the caption, in units of kJ/mol, and limit to a few significant figures, such that 15096 J/mol becomes 15.1 kJ/mol, unless you really believe the additional digits. In the caption, I suggest replacing “temperature gradient” with “increasing/decreasing temperature”.

We agree with reviewer 1. We changed temperature gradients in “increasing/decreasing temperature”, corrected the y-axis title and moved the desorption energies to the captions after removing it from the Figures.

done

Also, the y-axis labels in Figures 7 and 8 have different numbers of parenthesis. Which one is correct?

done

Introduction

P8085, L10: replace “addressed” with “attributed to”

Since you focus only on the Langmuir isotherm, much of the theory is unnecessary. You could shorten this section by eliminating the BET discussion. Further, the IUPAC definition, P8086 lines 21-24 are not helpful in this context.

Yes, we agree with the reviewer 1 and skipped the IUPAC definition as well as the BET discussion. The corresponding section reads now.

The four assumptions listed by Langmuir are often not fulfilled, in particular assumption (iv), yet in our experiments we found a good agreement with this simplified adsorption theory.

Methods

Please describe how the cylinders were filled and any corresponding pre-treatment or conditioning.

done

P8086, L13 replace “from either a steel or aluminum” with “both steel and aluminum”

done

P8089, L3: It is not clear from the text that experiment 2 involved lower flow rates. This should be clearly stated at the beginning of this section. i.e. “The purpose of this experiment was to determine the temperature dependence of the adsorb/desorb process. Gas usage in experiment 2 was designed to be far less than that in experiment 1”.

done

P8089, L8: “six horizontally” : : : this is the first mention of six cylinders. The number of cylinders studied should be mentioned earlier: ie. “Eight cylinders (5 steel, 3 aluminum) were tested over a temperature range of -10 to 50 deg C : : :”

done

P8089, L23: Are the calibration coefficients actually relevant here? I would think that to resolve very small CO<sub>2</sub> differences, analyzer repeatability and drift rate are the relevant terms.

Yes, this is correct. Since the experiments are designed to be short-term measurements indeed the repeatability and drift rate are the most important terms. The repeatability can be accessed by the short-term measurement variability and corresponds to < 0.01 ppm (averaged over 5 minutes) whereas the drift rate has been estimated from the standard

cylinder CA03901 to be 0.0041 ppm/day. We added the following part just after the calibration coefficients.

Though, of more importance for these experiments that are designed to be short-term measurements are the repeatability and drift rates. The repeatability can be accessed by the short-term measurement variability and corresponds to < 0.01 ppm (averaged over 5 minutes) whereas the drift rate has been estimated from the standard cylinder CA03901 to be 0.0041 ppm/day (see also Result section).

P8090, L23-24: Do you mean “can be determined experimentally from a fit to the measured mole fraction”?

Yes

applied

P8091, L20: I would simply use this information to justify using the Langmuir model. I think it is well known that the actual surface area is likely greater than the geometric area.

Yes, we agree and re-formulated the last sentences that reads now:

This considerations justify using the Langmuir model.

P8092, L16: Could this be due to analyzer drift?

Very unlikely, see discussion above about the drift influence on thermal dependencies.

P8093, L19: This is a creative way to determine the desorption energy. However, I think more explanation is needed. I can see that you plotted the LHS of eq 6 vs  $(1/T-1/T_0)$ , and found the energy E from the slope. And the method is outlined in the Appendix. However, I think a clear explanation should also be included in the main document. Were values for  $CO_{2,ads}$ ,  $K(T_0)$ , and E determined simultaneously, or iteratively? Also in figure 7, the y-axis label is  $R \cdot \ln(1-dCO_2/CO_{2,ads}) + b$ . What is “b”, and how was it determined?

Equation 6 can be rearranged by moving the second term on the right hand-side, denoted as  $R \cdot \ln(b)$  in Figure 7 and 8, to the left. Therefore, the dependence of the term on the left handside to  $E \cdot (1/T-1/T_0)$  must go through zero and the slope of it corresponds to E.

$$R \cdot \ln \left( 1 - \frac{CO_2(T_0, T) - CO_2(T_0)}{CO_{2,ad}} \right) + R \cdot \ln \left( \frac{\frac{T_0}{T} + P_0 \cdot K(T_0) \cdot e^{\frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)}}{1 + P_0 \cdot K(T_0)} \right) = E \cdot \left( \frac{1}{T} - \frac{1}{T_0} \right)$$

$$b = \left( \frac{\frac{T_0}{T} + P_0 \cdot K(T_0) \cdot e^{\frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)}}{1 + P_0 \cdot K(T_0)} \right)$$

$$R \cdot \ln \left( \left( 1 - \frac{CO_2(T_0, T) - CO_2(T_0)}{CO_{2,ad}} \right) + b \right) = E \cdot \left( \frac{1}{T} - \frac{1}{T_0} \right)$$

The values of  $K(T_0)$ ,  $CO_{2,ad}$  and E were optimized by minimizing the square root differences from observations, iteratively.

From this graph or through eq. 6 we now can estimate  $\text{CO}_{2,\text{ad}}$ ,  $K(T_0)$  and  $E$  by minimising the squared differences of using eq. 6, iteratively with initial values obtained from experiment 1 for steel and aluminium cylinders, respectively.

P8094, L2: Are these values really known to 1 J/mol? I suggest using kJ/mol and limiting to 1 or 2 decimal places, consistent with actual uncertainties.

Yes, we agree

applied

Appendix:

P8095, L23: Do you mean "Derivation of equations 5 and 6"?

Yes, of course. Thank you

applied

Equation (A2): what is "a", area?, number of surface sites? Please define.

In equation (A2), "a" corresponds to the adsorbed amount of  $\text{CO}_2$  (unit moles) scaled by the inverse of the Langmuir dependence. It has nothing to do with an area, or a number of surface sites.

Assuming that  $\text{CO}_2$  adsorption/desorption follows eq. 2 and eq. 3, the Langmuir's adsorption isotherm, the amount adsorbed at pressure  $P$ ,  $n_{\text{ad}}$ , is expressed in relation to the inversely scaled adsorbed amount at pressure  $P_0$ ,  $a$ , according to...(A2).

P8096, L6: "change in the adsorbed amount" : : : Is this the correct term? Or do you mean the "amount adsorbed at pressure, P"

done