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Interactive comment on “Gas adsorption and desorption effects on cylinders and their importance for long-term gas records” by M. C. Leuenberger et al.

Anonymous Referee #1

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Manuscript No.: acpd, 14, 19293-19314, 2014 Title: "Gas adsorption and desorption effects on cylinders and their importance for long-term gas records" Authors: M. C. Leuenberger, M. F. Schibig, and P. Nyfeler

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 ef-

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fect 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.

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 causes 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 aluminum 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

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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.

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. For accurate discussion, I define values as follows: Standard air with known CO₂ mole fraction, CO_{2,0}, is compressed into a cylinder to pressure of P₀. After reaching the adsorption equilibrium, the CO₂ mole fraction in the cylinder is reduced to CO_{2,1} and the difference (CO_{2,0}-CO_{2,1}) is denoted by CO_{2,ad}. Here, the CO₂ amount in the gas phase of the cylinder, Q, is expressed as a product of the pressure P and the mole fraction CO₂ (Q=P×CO₂). Assuming that the CO₂ adsorption/desorption follows Eq. (2) (Langmuir's adsorption isotherm), the change in the adsorbed amount, Q_{ad}, is expressed according to

$$Q_{ad} = (1 + KP_0) \times CO_{2,ad} \times P / (1 + KP), \quad (A)$$

where K represents the equilibrium constant ($K = k/k_{-1}$). Thus, the change in the CO₂ amount in the gas phase of the cylinder according to the pressure change is expressed by the following differential equation:

$$dQ/dP = Q/P - [(1 + KP_0)CO_{2,ad}] / (1 + KP)^2. \quad (B)$$

Note that it is assumed that the desorbed CO₂ from the inner wall is mixed quickly and homogeneously in the cylinder. The first term on the right hand-hand side of Eq. (B) represents the effect of the gas release, and the second term represents the effect of the CO₂ desorption from the inner wall, which is derived from the derivative of Eq. (A) (-dQ_{ad}/dP). Solving the differential equation (A) with the boundary condition Q(P₀) = P₀ × CO_{2,1} yields

$$Q = P \{ CO_{2,ad} \times [K(P - P_0) / (1 + KP) + (1 + KP_0) \ln \{ P_0(1 + KP) / \{ (1 + KP_0)P \} \}] + CO_{2,1} \} \quad (C)$$

Therefore, the measured CO₂ mole fraction of the cylinder gas during the emptying experiment (CO_{2,meas}=Q/P) is expressed according to

$$\text{CO}_{2,\text{meas}} = \text{CO}_{2,\text{ad}} \times \left[\frac{K(P - P_0)}{(1 + KP) + (1 + KP_0) \ln \left[\frac{P_0(1 + KP)}{(1 + KP_0)P} \right]} \right] + \text{CO}_{2,1} \quad (\text{D})$$

The Eq. (D) can reproduce well the experimental results shown in this paper for the pressure range from 100 to 1 bar (Fig. 1). Roughly evaluated CO_{2,ad} and K values by matching the curves based on Eq. (D) with the curves based on Eq. (4) with the CO_{2,ad} and K values reported in the manuscript (the blue curves shown in Fig. 2 and Fig. 4 in the manuscript) are also shown in Fig. 1 together with the reported values in this study. The CO_{2,ad} based on Eq. (D) are considerably small, especially for the aluminum cylinders. This result, suggesting that the adsorption effect is insignificant for the preparation of gravimetric standard gases as long as the aluminum cylinders are used, seems to be consistent with our experience of the standard gas preparation. Therefore, I think the authors should re-examine Eq. (4) and re-analyze the experimental results of this paper.

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

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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 1.2×10^{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 3.4×10^{-10} m is about 1.2×10^{19} ($= 1.09 / \{ (1.7 \times 10^{-10})^2 \times 3.14 \}$), which is by two order smaller than above number.

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.

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

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

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.

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.

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

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?

13) P. 19308, Fig. 4 caption: How were the desorption energies ($E_{A,des}$) calculated from the emptying experiments?

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

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

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/14/C5928/2014/acpd-14-C5928-2014-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 19293, 2014.

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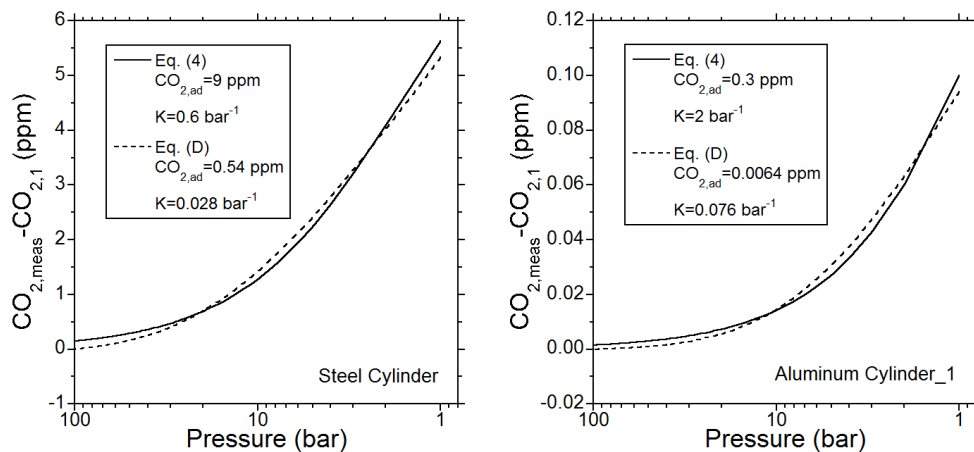


Fig. 1. Estimated changes in the CO₂ mole fraction during the emptying experiment for (left) the steel cylinder and (right) the aluminum cylinder. The solid curves are expressed by Eq. (4) and broken curves

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