

## ***Interactive comment on “High-accuracy continuous airborne measurements of greenhouse gases (CO<sub>2</sub> and CH<sub>4</sub>) during BARCA” by H. Chen et al.***

### **Anonymous Referee #2**

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The publication by Chen et al. describes laboratory measurements of mixing ratios of CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O, employing a commercially available detector (Picarro Inc.) which is based on cavity ring-down (CRD) spectroscopy. The motivation for the study was an airborne mission BARCA (Balanco Atmosferico Regional de Carbono na Amazonia - Phase B) in May 2009 in Brazil, during which a Picarro Inc. analyzer was flown alongside a non-dispersive infrared (NDIR) detector. The objective of the study is to evaluate the mixing ratio accuracy in conjunction with data acquired during BARCA. The authors characterize the reliability and (long term) stability of the Picarro detector in comparison with the NDIR detector performance for future airborne atmospheric

missions on the detection of green house gases. Experimental details, objectives and general achievements of BARCA are not given.

The main aspects of the paper concern the corrections of data due to the presence of water, collisional broadening and isotope effects, but also the investigation of stability criteria on basis of measurements with calibration standards. Since the work presented mainly concerns the performance of the Picarro analyzer, this paper is mainly of interest to (potential) Picarro customers.

## GENERAL COMMENTS

The authors repeatedly refer to the 'measurement of CO<sub>2</sub>' in a casual way, rather than to the 'measurement of CO<sub>2</sub> mixing ratios' or 'CO<sub>2</sub> concentrations'. Even though the context usually provides enough information to avoid confusion the measured quantity should always be stated in my opinion.

Generally more attention to detail would have been desirable. Should mixing ratios not be given in ppmv (by volume) rather than ppm?

## SPECIFIC COMMENTS

The title of the paper does not appear to summarize the content of the paper in an appropriate way, since mixing ratios of CO<sub>2</sub> and CH<sub>4</sub>, as they were acquired during the BARCA campaign are not discussed. This, however, is the expectation generated using the present title. I recommend that the authors consider a new title.

### Section 1

P3129, L1: A reference(s) should be given after "...since the 1930s."

### Section 2

P3130, L22-24: The sentence should be rephrased. "... thus providing parts-per-billion concentrations ..." -> "... thus typically providing parts-per-billion mixing ratio ..." "... which is unaffected by the initial strength of the light source." -> "... which are in good

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approximation independent of the intensity fluctuations of the excitation light source."

P3130/31: Details of the ring-down setup have been published previously (Crosson 2008). In my opinion the main technical features and specifications of the setup, that are of interest to the reader in the context of the present study, are inadequately summarized here. Also no spectroscopic information is given in section 2. Which cross-sections were used for gas concentration retrieval - (refs?). How are cross-sections affected by the temperature - was that taken into account? Only in section 6 it is stated that, after fitting a profile to a line feature, the peak height was used to determine the mixing ratio of CO<sub>2</sub> in air. Why were concentrations not obtained from integrated spectra?

The choice of the term "partially reflecting mirror" (in two places) is somewhat unlucky considering the fact that the cavity mirrors' reflectivity was  $R > 0.99995$ . The wavelength ranges and line assignments for the retrieval of CO<sub>2</sub> and CH<sub>4</sub> mixing ratios ( $\sim 1603$  nm for CO<sub>2</sub>, and  $\sim 1615$  nm for CH<sub>4</sub>/H<sub>2</sub>O according to (Crosson, 2008)) are not stated. It is of interest to have more spectroscopic information in this paper, because the effective independence of the approach from potential H<sub>2</sub>O interferences is claimed to be one of the major achievements here.

Since some of the improvements listed at the end of section 2 can only be fully appreciated if sufficient detail is given on the CRD analyzer - more information should be provided; perhaps in Figure 1. Please note that AMT is a journal that reaches an audience with significant technical interest.

### Section 3

Please explain to the reader what is meant by the "dilution effect"?

#### Section 3.1

Figure 1 does not contain enough details and the corresponding caption should be improved.

P3132, L8: Ambient air in a tank was supplied to the humidifier. Where was the ambient air taken from - laboratory air, outside air?

P3132, L18/19: Experiments were performed above room temperature to avoid water vapour condensation in the inlet line. How does that compare with the in-flight conditions? What inlet losses could be expected during the airborne mission.

P3132, L22/23: A linear or exponential drift of CO<sub>2</sub> mixing ratios as determined downstream from the humidifier is reported due to the 'interaction' between CO<sub>2</sub> and H<sub>2</sub>O. A significant drift is not apparent in Fig. 2a,b; The blue line appears constant over the time interval shown. Do Figs. 2a,b show already corrected mixing ratios? Can the drift be quantified? Can the nature of the interaction be specified - chemical reactions?

P3133, L6/7: The quadratic dependence of the concentration ratio  $[\text{CO}_2\text{wet}]/[\text{CO}_2\text{dry}]$  on the water concentration  $[\text{H}_2\text{O}]$  is empirically described by virtue of parameters denoted a, b (for CO<sub>2</sub>), c and d (for CH<sub>4</sub>). The values given should carry a unit.

### Section 3.2

From the first sentence in this section the reader gets the impression that the temporal constancy of the parameters a to d was to be investigated, and not the transferability of the parameters from one analyzer to another. If the temporal constancy of a,b,c and d is the main aspect in this section, then the following assumption of the authors is not clear to me: "The assumption is that if the coefficients are transferable between instruments, they are also likely to not change over time." How can the long term time stability of an instrument be compared with the performance of two setups at the same time? This requires further justification.

P3133, L20: 'Similar experiments' are not specified sufficiently.

P3133, L23/24: The way how two analyzers are connected to the humidifier is not shown, a separate part in Fig. 1 for instance would be appropriate.

P3134, L5-8: The authors state that, "Because the water vapor measurement by the C1202

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analyzer is based on a single stable H<sub>2</sub>O spectroscopic feature which is spectrally close to the CH<sub>4</sub> spectral feature, we expect the measurement of the water vapor to exhibit the same highly stable performance over time that has been demonstrated on both CO<sub>2</sub> and CH<sub>4</sub>." Since there are two lasers in the device the long term stability for the detection of CO<sub>2</sub> and CH<sub>4</sub> / H<sub>2</sub>O may be different. Furthermore, in the last part of the section the performance on CO<sub>2</sub> detection is used to estimate the expectation of instrument stability for H<sub>2</sub>O. Is it possible to apply some Alan variance type of analysis to data to quantify the long term stability of the instrument in this context?

P3134, L13: "In CO<sub>2</sub>, these analyzers appear to drift less than 0.5 ppm (Richardson et al., 2009) over two years of operating time,..." Under what operational conditions of the analyzer? What does "appear to drift" mean in this context. The reference is practically not traceable and hence not helpful in this context.

#### Section 4

P3134, L24: The analyzer was placed in an environmental chamber to simulate flight conditions of a non-pressurized aircraft cabin. No details are given on the "environmental chamber".

P3135, L8: What is meant by 'undisturbed stability'? In Figure 3 there are mixing ratio spikes apparent at ca. 51500, 54000, 55900, 57000 s for CH<sub>4</sub> and at ca. 54200 and 55900 s for CO<sub>2</sub>. Is there an explanation for these?

P3135, L24/25: "The time delay between the time air enters the inlet until it reaches the sample cell varies according to the bypass flow and relevant volumes." What is the 'bypass flow' and what are the 'relevant volumes' - no experimental details are given here?

#### Section 5

This section compares the mixing ratios of CO<sub>2</sub> obtained with the CRD analyzer and an NDIR CO<sub>2</sub> analyzer aboard the aircraft during the BARCA campaign. At first ar-

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guments on the timing of the measurements are made and finally a mean difference (0.22+/-0.09 ppm) and standard deviation (0.23+/-0.05 ppm) are stated. The order in which arguments and data are presented here was difficult to follow, since the purpose of initially comparing the timings of the duty cycles in the CRD and NDIR analyzer only becomes obvious in the last sentence of the section. The correlation optimization should be included much earlier in the text or the order in which various aspects are presented should be rearranged altogether. The caption of table 1 is too short. It does not even mention that the data refer to CO<sub>2</sub>. Details on the timing are also not included in the table. Column 2 or the caption should contain a year as well. Why was flight 001 removed from the average (not stated in the main text)?

## Section 6

Was there a specific reason to use exactly four tanks of synthetic air? What determined that number?

P3137, L24: Why were absorption cross-sections not obtained from integrated spectra. The corresponding information would be better placed in the experimental section.

### Section 6.1

P3138, L14: Why was the z parameter not independently established during the measurements in Brazil - was there a specific reason?

Fig. 4 shows modeled profiles according to the Galatry model (Varghese and Hanson, 1984). The authors should consider showing experimental results here. Especially since on P3139 it stated that the uncertainty in the correction is mainly caused by the uncertainty in the y parameter owing to the fit error.

P3138, L19: ... normalized peak height and the width of the spectral profile... -> ... height and the width of the spectral profile ... The discussion on the pressure broadening appears too short. The conclusions in the last paragraph of the section seems not well supported by the information provided in section 6.1

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## Section 6.2

When referring to the isotope ratio in the sample or reference mixture parenthesis should be used around the symbols. It should be made clear that mixing ratios are meant here throughout. Hence ... $^{13}\text{C}/^{12}\text{C}$ \_sample ... -> ...( $^{13}\text{C}/^{12}\text{C}$ )\_sample ... and ... $^{13}\text{C}/^{12}\text{C}$ \_reference ... -> ...( $^{13}\text{C}/^{12}\text{C}$ )\_reference ... and ... $^{18}\text{O}/^{16}\text{O}$ \_sample ... -> ...( $^{18}\text{O}/^{16}\text{O}$ )\_sample ... and ... $^{18}\text{O}/^{16}\text{O}$ \_reference ... -> ...( $^{18}\text{O}/^{16}\text{O}$ )\_reference ...

P3140, L18: Please explain GLOBALVIEW-CO2C13.

P3140, L20: What logistic difficulties are referred to here?

P3141, L3: Corrections due to variation of the delta $^{13}\text{C}$  and delta $^{18}\text{O}$  of 0.14 to 0.16 ppm are claimed to be small in comparison to the pressure-broadening impact. This does not seem to be the case. They seem to be within the same order of magnitude (-0.22 ppm to 1.68 ppm on Page 3139).

Table 2 should be explained better. The caption is cryptic and I recommend to improve the column titles.

## Section 7

P3142, L6: ... Of green house gases during ... -> ... Of the green house gases  $\text{CO}_2$  and  $\text{CH}_4$  ... ->

### SUGGESTED TECHNICAL CORRECTIONS

P3129, L7: ...aircraft -> ...aircrafts

P3129, L10: ...on board aircraft ... -> ... on board an aircraft ...

P3129, L28: ... and  $\text{CH}_4$  with ... -> ... and  $\text{CH}_4$  concentrations with ...

P3130, L3: ...in all in situ ... -> ... in all previous in situ ...

P3131, L4: ...off the laser ... -> ... off the lasers ... (probably plural since there are two lasers).

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P3131, L7: ... spectrum ... -> ... spectra ...

P3131, L26: ... CO2 better ... -> ... CO2 to be better ...

P3134, L17: ... to just drift of ... -> ...to a drift of ...

P3134, L27: The analyzer measured a standard gas during ... -> The analyzer measured mixing ratios of standard gases CO2 and CH4 during ...

P3135, L9: ... compared to under normal ... -> ... compared to normal ...

P3135, L12: ...aboard research aircraft or aboard commercial ... -> ...aboard a research aircraft or aboard a commercial ...

P3137, L10: ... very linear ... -> ... linear ...

P3137, L17: ... one year's storage ... -> ... aone year storage period ...

P3137, L19: ... we try ... -> ...we tried...

P3137, L20: ... we use the ... -> ... we used the...

P3138, L22: Delta Peak is not defined in the text.

P3139, L11: ... total CO2 by ... -> total CO2 concentration by ...

P3141, L7: ...as well since ... -> ... as well, since ...

P3143, L10: Remove line break.

## References

P3144, L32: ...filed... -> ...field...

## Figures

The time scales in Figs. 2a,b and 3 seem arbitrary - what is the relevance of the times on the axes?

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