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Atmospheric Measurement Techniques Discussions

Interactive comment on "High-accuracy continuous airborne measurements of greenhouse gases (CO_2 and CH_4) during BARCA" *by* H. Chen et al.

Anonymous Referee #1

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General Comments

H. Chen *et al.* present a well written and structured report on their new analyzer based on cavity ring-down spectroscopy (CRDS) technique. Since this commercially available instrument from Picarro, *Inc.* is significantly gaining interest from a large spectrum of scientists, technical papers dealing with validation, characterization and testing of such analyzers are very useful mainly for people interested in purchasing and applying the CRDS instruments. In the paper, special emphasis is placed on the laboratory investigation regarding the influences of various physical parameters (like temperature, pressure, humidity, isotopic composition, etc) on the analyzer. This work

is motivated by the flight campaigns over Brazil in which the instrument was used to continuously measure CO_2 and CH_4 concentration at impressive level of precision and accuracy. I found the manuscript's technical content very useful and recommend it for publication after the few comments and suggestions listed below are addressed.

Specific Comments

The title as well as the abstract is misleading, because in the paper the authors do not present any data from their BARCA airborne campaign. The manuscript has mainly a technical nature and should be introduced as such. Revising the title and the abstract is recommended.

Unfortunately, the paper has a major shortcoming in the way the authors have discussed the pressure broadening effect. This topic needs to stand on its own. For example, the line profile definition is critical to the pressure broadening effect discussion, but one cannot understand that from reading this paper alone. The Fig 4 shown in the manuscript only represent simple simulations of the normalized Galatry profile in function of changing the y parameter by unrealistically large amounts. Except the illustrative character, this has rather little in common with real-life conditions. Moreover, the authors do not communicate the pressure values used in their experiments, although this parameter is crucial for the topic and would allow the reader to do some back-of-the-envelope calculations. This could be performed relatively easy since all the pressure broadening coefficients for CH_4, CO_2 and H_2O are known at 1.6 μm. Actually, the authors should use these coefficient values to confine their fit, more so, because as stated "the uncertainty ... is mainly caused by the noise in the y parameter due to imperfect mathematical fit". Also the whole procedure of standard gas correction for pressure broadening effect is unclear, because of the following: The CRDS analyzer uses the peak height obtained from the fit of the spectral line

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to determine the mixing ratio of total CO_2, but since its exact value is not known (see isotope composition issues), one ends up with two unknown parameters in the fit result: one is the real concentration or the absolute height and the other is the pressure broadening coefficient. How exactly did the authors solve this?

On the other hand, the section about isotope correction is presented in a too detailed manner, although, this issue is well known in the laser spectroscopy community and not only, see *e.g.*, Bowling *et al.*, Agricultural and Forest Meteorology 118 (2003) 1–19 and Griffis *et al.*, Agricultural and Forest Meteorology 135 (2005) 44–60; It is also needless to make a lengthy discussion on this issue, as the absolute values regarding the isotope composition of the CO_2 are not known in the present study and only a good guess about their expected value is used.

I would suggest that prior to any important flight campaign the standard gases that are going to be employed for calibration should be analyzed and characterized by mass spectrometry for their composition, including not only the species in interest, but also the background gas fractions (N_2, O_2) and, when necessary, then also for isotopic species. The logistic and analytical expenses are negligible in comparison to a flight campaign organized abroad. This will assure the highest accuracy of the data, make any inter-comparison straightforward and avoid comments as above.

P3130 Line 1: "...highly accurately" is not a common term, I would recommend the use "of high accuracy" instead.

P3130 Line 1 and 2: "...without the need to dry the sample air or to employ in-flight calibrations. It was necessary to perform in-flight calibrations and careful air drying techniques ..." The logical connection between the two sentences is missing and the two statements are actually in contradiction. Please rephrase it.

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P3130 Line 20: “CRDS is a technique which introduces a gas sample into a high-finesse optical cavity . . .” There are many techniques which introduce the gas sample into a high-finesse optical cavity. I recommend rewriting the sentence as follows: “In the CRDS technique the gas sample is analyzed in a high-finesse optical cavity . . .”

P3131 Line 1: “light at a specific wavelength”. The value is known, so why not use it? Near-infrared region at 1.6 μm.

P3131 Line 8: write “are” instead “is determined”.

P3131 Line 19: “solid state memory” I would rather call it as solid state drive (SSD) or RAM drive. These devices are of course based on solid state memory, but in the computer you install the drive which has to emulate a hard disk drive interface.

P3132 Line 8: replace “from an ambient air tank” with “from a pressurized ambient air tank”

P3133 - P3134: In my opinion, the accuracy of the water dilution experiment significantly suffered by the fact that the humidity content of the gas entering into the CRDS analyzer is not known in absolute values. The authors also do not specify the humidifier type and its accuracy. The water signal of the CRDS should be calibrated for exact dilution determination, which is rather complicated since one has the significant pressure self-broadening effect also for the water. Nevertheless, the authors should inform the reader about the quantitative values of the dilution effect and the pressure broadening effect due to the humidity. This would be very useful in judging the magnitude of such corrections and eventually comparing them with other existing analyzers.

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A linear correlation between two instruments obtained at a given time is not a sufficient prove for the transferability of the water correction functions. Such statements may lead to confusions and probably to false assumptions in follow-up water correction/calibrations attempts. Referencing an instrument to another without any real calibration is giving cause for concern.

P3133 Line 19: “subsequent text” should not read as “subsequent test”?

P3134 Line 23: “The water vapour measurements of the two analyzers are linearly correlated”. This clearly indicates that there should be something more than just dilution and pressure broadening effect, otherwise one would expect that the analyzers measuring the same gas at the same conditions should not only linearly correlate, but rather give the same result. Therefore the word “water calibration” should be replaced by correction, correlation or scaling factor in this section.

P3134 Line 5: replace “single stable H_2O spectroscopic feature” with “single H_2O absorption line”

P3134 Line 22: “we applied temperature and pressure variations that typically occurred during flight.”
The authors highlight the main characteristics of the analyzer which are important for measurements on board aircraft. However, there is still another factor which would be interesting to investigate. This is the “mechanical stress due to shock and vibration” as stated in the introduction. Any thoughts here?

P3138 Line18: “the CRDS analyzer might have drifted since the calibrations were made 4 months before the campaign.” This assumption disagrees with the statement on P3134 Line 12, where the authors expect a drift of 0.5 ppm over two years, which is clearly much less than the 0.2 ppm in four months.

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P3138 Line 2: “the Lorentzian broadening parameter was measured as part of the field campaign, and that data, along with a laboratory investigation of the dependence of the peak height of the absorption lines on Lorentzian broadening, were used to correct the calibration tank data reported by the CRDS analyzer.”

I cannot see any link between the “Lorentzian broadening parameter measured during the field campaign and the laboratory investigation of the dependence of the peak height of the absorption lines on Lorentzian broadening”. The effective pressure broadening is a sum of individual pressure broadening coefficients weighted by the partial pressure of each gas component. Therefore, the pressure broadening of humid ambient air will be different from the pressure broadening caused by a dry and synthetic air.

P3142 Line 12: replace “The CRDS analyzer performed highly stably under” with “The CRDS analyzer demonstrated high stability under”

P3142 Line 22: replace “The CRDS analyzer performed highly stably without” with “Highly stable operation of the CRDS analyzer was found even without”.

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 3127, 2009.