Atmospheric Measurement Techniques Discussions

Interactive comment on "Evaluation of factors affecting accurate measurements of atmospheric CO_2 and CH_4 by wavelength-scanned cavity ring-down spectroscopy" *by* H. Nara et al.

Anonymous Referee #1

Received and published: 9 August 2012

The paper by Nara et al. investigates the sensitivity of cavity ring-down spectroscopy instruments to the measured air composition. It quantifies the impact of varying O_2, N_2, Ar, H_2O compounds in ambient air and the isotopic mixture of the analysis gases on the CO_2 and CH_4 measurement. This is a valuable contribution to the evaluation of the CRDS technique, which is increasingly used in greenhouse gas monitoring. I recommend the publication of the manuscript in AMT, after addressing my two main concerns and the subsequent comments:

(1) The manuscript may be used as a guideline for valid gas compositions for the WS-

CRDS technology; therefore, it would be nice to give an estimation of the investigated impacts not only for synthetic calibration gases, but also for ambient air measurements. The expected natural variations of O_2 etc. are probably too small to have an impact on CRDS measurements (see e.g. publications of R. Keeling at SCRIPPS, O_2 of 500 per meg ~100 ppm change. . .); however, this should clearly come out of the manuscript as well.

(2) The absolute H_2O calibration with a humidifier is indeed cumbersome. However, there is no need for an absolute calibration (last paragraph in Chapter 3 in [Chen et al., 2010]). It is sufficient to calibrate the analyzers to the same master instrument. Thus, the statement of the current manuscript is still true that the absolute calibration with the humidifier is too noisy for usage; however, a calibration of the three presented instruments to one scale of a selected analyzer might be more meaningful. As there is no need to repeat experiments, but a recalculation only, I recommend redoing the transferability analysis of the water correction function from this perspective. The new result will probably expand the suggested water vapor limit for ambient air measurements. (involves abstract page 5010/ lines 16ff, chapter 5 page 5025, and conclusions page 5028 lines 24ff)

More specific comments (page/line):

5009/1: The title might be not specific enough to reach the readers of interest. An alternative suggestion would be: "Effect of air composition (N_2, O_2, Ar, and CO_2-isotopes) on CO_2 and CH_4 measurement by cavity ring-down spectroscopy"

5011/1-16: The value of the introduction would increase by citing references for many statements (if not more specific ones can be found, IPCC may contribute), e.g. for the sparse network.

5011/28: (Heimann, 2009) does not fit in this measurement context here, maybe use in the first paragraph.

5012/4-17: Because you start with a general introduction before, and focus on the

WS-CRDS here only, the reader gets the impression WS-CRDS is the only new development in the field. I would appreciate a more general, brief transition to the new laser technologies (like cavity enhanced spectroscopy, quantum cascade laser, in situ FTIR); the Picarro analyzer is anyway presented in the sect. 2 in great detail.

5013/10-15: (see also discussion *(2)*) The sentence is contradicting. The H_2O scale of the instrument in [Winderlich et al., 2010] has not been calibrated directly to another Picarro instrument (end of sect. 2.2). However, following [Chen et al., 2010] in sect 3.2, the transfer of the water correction function works well, only if both instruments have been calibrated to the identical scale. Therefore, the incompatibility stated in the manuscript cannot be deduced here. I recommend to leave out both sentences.

5013/14: quantitatively > experimentally (there are also some quantitative numbers for isotopes in [Chen et al., 2010])

5014/22f: "the mole fraction is calculated ...", That is not exactly true. At this point, the absorption/transmission of the cell is only recorded for one wavelength setting. The mole fraction is calculated later from the spectral fit (as you write correctly later on). Please modify the wording.

5014/26: Is the resolution of the achieved spectrum really 0.0003 cm^{-1}? Is it possible that this number only states the resolution of the spectrometer (given by the wavelength monitor)? To my knowledge there are less points used for the spectrum underlying the fitting function (otherwise it would need more than 300 single measurement points to scan a spectral line width of ~0.1 cm^{-1}).

5015/5f: Please give the temporal scale for the given numbers.

5016/5ff: What does the first sentence say? Difficult to understand, maybe leave it out?

5019/1f: How long is the stabilization period approximately?

5019/16: What does "identical to that in the atmosphere" mean? Atmosphere at

Hateruma in the year 2000 like in the Tohjima paper?

5019/17f: How large is the uncertainty estimate? The definition could also just be N_2 = 0.78%, O_2 = 21% and Ar = 1%, couldn't it? The uncertainty is the measurement uncertainty, as well as the uncertainty of the transfer of the 2000 results of N2 and Ar to your 2012 tank air (Regarding discussion *(1)* from above: How large is the expected atmospheric variability for these components?).

5020/25: Can you give the numbers from your results? They would be helpful to judge on the "reasonably well" agreement. In principle, the difference of the given numbers should be related to the coefficients in Table 1, right?

5021/1-6: It is a circular reasoning: First you calculate the coefficients from your data with a linear fit, than you calculate the linear relationship with these coefficients, than it fits to your data? Please rewrite.

5022/14: What are the expected impacts, when using pressurized ambient air, without the described purification process, and dehumidification only (see discussion *(1)* above)?

5026/15: Why do you use % by volume? CO_2 and CH_4 are detected as molar fraction, the H_2O should also be detected as such. Do you have a special reason for that change?

5027/9-5028/2: The calibration of two analyzers to one master analyzer will reduce the uncertainty in the water scale transfer. See discussion *(2)*. What was the accuracy of the dew point measurement? 0.2 degree would be well enough for the low water range, but the change in absolute water vapor amount at e.g. 20 to 20.2 degC is far beyond the needed accuracy for the calibration of the CRDS analyzer.

Figure 1: Do you have a flow restriction in the uppermost line downstream the humidifier? A flow resistance with the same restriction as the parallel drying agents would reduce the pressure changes after switching. The pressure changes can be the reason

for increased CO_2 absorption/desorption in $Mg(ClO_4)_2$.

Figure 2+3: How did you transfer the mentioned uncertainty of the flow meter (in x-direction) to an error bar in y-direction? How large is the uncertainty in your lower x-axis (that refers to my question on page 5019, line 17f) May you add "PBE" into title on the y-axis to be consistent with the formulas in the text?

Technical corrections (page/line):

Abstract: 5010/9: The statement "Ar<O_2<N_2" is simply true for ambient air. The intended meaning is clearly something else, but it is not clear for somebody reading the abstract only. Please rephrase.

5012/7: decay rate of a laser > decay rate of laser light

5012/11: (Santa Clara, CA) > (Santa Clara, CA, USA)

5013/10: under the single calibration scale for the water vapor. > if calibrated to the same scale of water vapor.

5013/24-27: It is difficult to read that Eq. (1) is used as numbering within the sentence. Maybe change to: ... we investigated a) the impact ... ; b) ...; c) ...

5014/17: 140 ± 0.05 > 140.00 ± 0.05, and 40 > 40.00

5015/12: CO_2 molecule > CO_2 molecules

5015/11ff: *"This bias results from absorption line-broadening and -narrowing of CO_2 molecule due to random thermal motion of the molecules, collisions between molecules, and velocity-changing collisions (Varghese and Hanson, 1984). Random thermal motion and intermolecular collisions produce line-broadening effects (referred to as Doppler and Lorentzian broadening effects, respectively), while the velocity-changing collisions produce line-narrowing effects (a kind of Dicke narrowing), which diminish the Doppler broadening effects (Dicke, 1953)."* > "This bias results from absorption line-broadening and -narrowing of CO_2 molecules due to random thermal mo-

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tion, and collisions. Random thermal motion and intermolecular collisions produce line-broadening effects (referred to as Doppler and Lorentzian broadening effects, respectively), while the velocity-changing collisions produce line-narrowing effects (a kind of Dicke narrowing), which diminish the Doppler broadening effects (Dicke, 1953; Varghese and Hanson, 1984)."

5016/1: molecule are > molecules, and are **5016/1f**: skip "in WS-CRDS measurement" **5016/2**: remained > remain

5016/21: are subject to > depend on the composition of the

5016/26: c is mole fraction > c is the mole fraction

5017/2: maximum value > the maximum value; line-shape > the line-shape

5023/20: were > ranged

5024/21: For the comparison > For this comparison