Author's reply to comments from anonymous referee #1

We would like to thank the referee #1 for his/her interest in our work and helpful comments to improve our manuscript. Listed below are our replies to the referee's comments and suggestions, which we have revised our manuscript according to.

Main comments

(1)

<Referee> It would be nice to given 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; however, this should clearly come out of the manuscript as well.

<Reply> Based on our experiments, we estimate that natural variation of oxygen has little impact on the magnitude of PBEs on the CO_2 and CH_4 measurements. Since the seasonal amplitude of oxygen is 200 ppm at most, corresponding impact of PBEs is ±0.01 ppm for CO_2, ±0.01 ppb for CH_4. We have added this discussion into section 3-2.

(2)

<Referee> The absolute H_2O calibration with a humidifier is indeed cumbersome. However, there is no need for an absolute calibration. 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, 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.

<Reply> According to the referee's advice, we have reconsidered the discussion on the water correction described in section 5. In the section, we evaluated the transferability of the water correction function among three WS-CRDS instruments correctly (as referee #2 H. Chen suggested). We also showed difference of water correction values from three WS-CRDS instruments as well as from previously reported water correction values in Chen et al. (2010) and Winderlich et al. (2010). As a whole, we did not prove the transferability in this study, but we found that water correction values from all reported correction functions agree within typical analytical precision of WS-CRDS for water vapor concentration of <0.4 %V for

CO_2 and <0.6 %V even under individual water vapor measurement scale. Please check our reanalysis described in section 5.

More specific comments

<Referee> P5009/1: 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”

<Reply> We have changed the title to “Effect of air composition (N_2, O_2, and Ar) on CO_2 and CH_4 measurement by cavity ring-down spectroscopy: calibration and measurement strategy”

<Referee> P5011/1-16: 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.

<Reply> We have added more references appropriately in Introduction.

<Referee> P5011, L28: (Heimann, 2009) does not fit in this measurement context here, maybe use in the first paragraph

<Reply> We have excluded this reference.

<Referee> P5012/4-17: 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.

<Reply> We have added brief introduction of optical measurement history for CO_2 and CH_4 in section 1 (Introduction).

<Referee> P5013, L10-15: (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.

<Reply> We have revised the paragraph accordingly.

<Referee> P5014, L22f: “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 spectral fit. Please modify the wording

<Reply> We have revised the manuscript appropriately.

<Referee> P5014, L26: 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}).

<Reply> As is indicated, “0.0003 cm^{-1}” is a wavelength resolution of the wavelength monitor. We have revised the sentence to avoid ambiguous wording.

<Referee> P5016, L5ff: What does the first sentence say? Difficult to understand, maybe leave it out?

<Reply> We have revised the sentence accordingly.

<Referee> P5019, L1f: How long is the stabilization period approximately?

<Reply> It typically took approximately 3 min. We have added this information into the manuscript.

<Referee>P5019, L16: What does “identical to that in the atmosphere” mean? Atmosphere at Hateruma in the year 2000 like in the Tohjima paper ?

<Reply> It means that atmospheric abundances of Ar, and other noble gases does not change significantly since 2000. We have clarified our text .

<Referee>P5019, L17f: How large is the uncertainty estimate? The definition could also just be N_2 = 0.78%, O_2 = 0.21%, 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 N_2 and Ar to your 2012 tank air (Regarding discussion ***(1)*** from above: How large is the expected atmospheric variability for these components?)

<Reply> This section has been modified. We calculated O_2 mole fraction by assuming mole fractions of Ar and other noble gases. We think that mole fractions of these gases do not show significant difference between 2000 and 2012. Thus the uncertainty of O_2 mole fraction is subjected to the uncertainty from the measurement. As described in our manuscript, the uncertainty for this O_2 determination is approximately 10 ppm.

<Referee> P5020/25: 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?

<Reply> Yes, it should be so. But, unfortunately, pressure broadening coefficients have different physical dimension, requiring measurement parameters like FWHM (full width at half maximum), HMDL (half width at half maximum) fitted with the same function. Therefore we can't calculate exact values of the pressure broadening coefficients simply. However the relation of the magnitude of these coefficient values will be the same with that for our results. That's why we cited Nakamichi et al. (2006) here. If our discussion citing is still ambiguous, we will remove this discussion.

<Referee> P5021, L1-6: 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.

<Reply> Thank you for your keen indication. We have revised the manuscript accordingly.

<Referee> P5022, L14: What are the expected impacts, when using pressurized air, without the described purification process, and dehumidification only (see discussion **(1)** above)?

<Reply> First of all, impact of natural variation of oxygen on the WS-CRDS measurements is negligible as mentioned above in our reply to main comments (1). During the compression of natural ambient air, oxygen can be dissolved into condensed water pool in our air compression system due to cryogenic dehumidification. We have checked that the oxygen decrease resulting from the dissolution is only a few tens of ppm. Thus we conclude that compressed natural air does not bias the CO_2 and CH_4 measurements by WS-CRDS. We have added above discussion into the section 3-2, and corresponding revision has been done.

<Referee> P5026, L15: 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?

<Reply> Because the WS-CRDS instrument outputs measured H_2O concentration in % volume.

<Referee> P5027,/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.r. 20 to 20.2 degC is far beyond the needed accuracy for the calibration of the CRDS analyzer.

<Reply> We did reanalysis of the water correction. In the improved discussion, we evaluated the transferability of water correction function for G-1301 under the water vapor measurement scale of G-1301, avoiding the propagation of the dew point measurement. Please check our revision in section 5.

<Referee> 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 $Mg(ClO_4)_2$.

<Reply> Thank you very much for your indication. Yes, we carefully setup our sample humidification unit according to the report by Chen et al., (2010). We used a back-pressure valve to prevent the pressure fluctuation. As we did not describe and draw usage of the valve in the manuscript, we have added the sentence regarding the back-pressure valve and corrected schematic of the sample humidification unit in Figure 1.

<Referee> 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?

<Reply> The mole fractions of N_2, O_2, and Ar in the compressed air were calculated based on the O_2 measurement (209326 ±10 ppm) by assuming that the mole fraction of Ar is unchanged significantly in the year between 2000 and 2012. The Ar mole fraction in 2000 was reported by Tohjima et al. (2005), and current Ar mole fraction would be 9333 ±5 ppm. Thus the error of X lower axis in Figure 2 and 3 is attributed to the error from the dynamic dilution process. The error during dynamic dilution on the mole fraction of inert gases (N_2, O_2, and Ar) can be calculated from empirically determined error of the flow rate for the compressed air and the inert gas (F_{comp} and F_{inert} in Eq. (10)). For example, relative error during the dynamic dilution for N_2 is typically less than 0.4%, corresponding to the maximum error of ±20 ppm against excess N_2 of 5000 ppm. This dilution error and the standard deviation of WS-CRDS measurement of CO_2 and CH_4 is then propagated on the Y axis values based on the Eq. (9) and (10).

Technical corrections

<Referee> P5010, L9: 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.

<Reply> We have revised the sentence to be reasonable.

<Referee> P5015, L5f: Please give the temporal scale for the given numbers.

<Reply> The measurement precisions were given for 5 min.