Interactive comment on "Design and performance of a Nafion dryer for continuous operation at CO_2 and CH_4 air monitoring sites" by L. R. Welp et al.

Response by L. R. Welp et al.

Response to C. Gerbig (Referee)
Received and published: 7 September 2012

The paper describes the drying system designed for Earth Networks' greenhouse gas monitoring network. Various laboratory tests are presented, showing that the resulting measurement specifications are well within the compatibility guidelines as recommended by WMO. The paper is well written, and represents an important contribution as it describes the major elements of the sampling system setup used in a large and growing network of GHG observing stations. I recommend publication after the comments below have been addressed.

General comments:
Overall, the setup is well thought out, and I fully accept the decision to dry the sample rather than to apply water vapour corrections to a wet air measurement. However, it would have been a great opportunity for determining, based on a large number of analysers, if the water correction function coefficients are really instrument specific and if they really drift over time. As the authors note (P 5459, L 10) not enough is known about the differences in water vapour corrections for different analysers or their stability over time, and those observed differences could well be due to experimental artefacts. The experimental setup needed for determining instrument specific correction functions is in fact pretty much identical to the setup used for this study. But, as said before, I see that the decision had to be made and accept it.

(author response) We understand the reviewer's comment that we could have contributed to the growing database of water vapor correction coefficients for Picarro analyzers. We did in fact calculate the correction coefficients early on in our testing with pieces of the experimental setup presented here. We tested the water droplet method and a wet/dry stream method where we switched a cold trap in and out of a humid air stream. Our results differed depending on the experimental method used. The reason could have been because we had not acidified the DI water in the droplet method, but this was never confirmed. Another reason is because water vapor and CO2 'stick' to the stainless steel tubing walls and can compete for surface sites during periods of changing H2O. In part, it was the challenge of trying to verify the water vapor correction experimentally that lead us to choose to dry the sample air instead.

What I think should be stated a bit more clearly at the end is though, that there are not only advantages associated with this choice. Sample drying does eliminate the need to determine instrument specific
correction functions (or to proof experimentally that a universal correction is sufficient), but the choice is associated with a price. It adds to the system a number of elements: a Nafion tube, a pressure control loop, pump modifications, heated enclosure for dryer. All these are associated with additional cost, and additional (albeit probably low) maintenance. On the other hand, determining an instrument-specific water cor-

rection function would have added a few hours of lab testing once before deployment (and potentially after a year), and would have involved keeping track of correction coefficients for each instrument, which is also a burden. These "costs" associated with the choice for or against drying need to be weighed. May be this can be mentioned also in the conclusions, together with the advantages, to provide a more balanced view.

(author response) It is not our intention to make recommendations as to how other researchers should proceed in their own CRDS measurements. Rather, we present the design chosen for the Earth Networks deployments, show that it meets GAW specifications, and briefly justify the decision. The readers are left to make their own cost/benefit analysis for their individual situations to decide whether to dry the samples or not. Therefore we respectfully disagree that this discussion needs to be added to the conclusions.

I have a few issues with Table 2: When combining precision errors (first and second row of Table 2) with bias errors resulting from the water vapour correction and the Nafion effects (third and fourth row) to derive a resulting error as the quadrature sum of errors (last row), differences between the different application approaches become blurred, and depend on the integration time. Also the chosen integration time of 5 minutes seems short, given that usually hourly or longer averaging periods are applied when using ground-based observations. In addition, the values for instrument precision of the 5 min averages seem a bit large. Looking at the Picarro G2301 data sheet, the claimed upper limit is 0.025 ppm for CO2 and 0.022 ppb for CH4.

(author response) Given the high frequency capability of these analyzers, we believe an error analysis at the 5-min integration time is appropriate. The instrument precision values have been updated to reflect the revised G2301 data sheet, 0.025 ppm for CO2 and 0.22 ppb for CH4. (We had taken our numbers from an older version that Picarro has since updated.) However, if we were to use 1-hr instrument precision in our analysis, the error in all the approaches would be reduced by the same amount.

A further problem I see with
the second row of Table 6: The random noise in the H2O measurement is 30 ppm for 5 min averages (from the Picarro G2301 data sheet), which corresponds to 0.015 ppm CO2 or 0.075 ppb CH4. However, due to the weak nonlinearity of the water vapour correction this corresponding uncertainty in does only weakly depend on the water vapour level, and actually increases for lower water vapour. Thus it is unclear why in the table the corresponding numbers for CO2 are half for the setup with Nafion drying compared to the setup without drying. May be the authors have taken into account that the random noise in H2O is actually reduced at lower H2O mixing ratios, but than this should be stated.

(author response) The values appeared to be half in the Nafion-drying case because of rounding to the nearest hundredth. In our revision, we've left these values in the thousandth decimal place to avoid this confusion. The reviewer is right that there is a weak nonlinearity in the water vapor correction, but it decreases at lower water vapor. (The equation in the Rella et al. discussion paper in this same special issue was in error and has been corrected in the final paper.)

In summary, when taking these modified precision estimates
into account, and when using hourly integration periods, the quadrature sum of errors in case of instrument specific water correction without drying is 0.02 ppm (instead of

0.06 ppm) for CO2, and in case of a universal correction with Nafion drying is 0.05 ppm (instead of 0.07 ppm) for CO2. I find this a more appropriate method for comparing the different sampling approaches.

(author response) We have edited Table 2 to reflect the referee's comments on precision versus bias errors. However, we argue that since it is impossible to know the sign of the water vapor correction bias for any individual instrument, that it should still be added in quadrature. Since we do know the sign of the Nafion bias, we now add it in (not in quadrature).

Specific comments:

P5455 L18: The paper by Ma and Skou (2007) cited by the authors indicates that there is a dependence of the permeability on temperature, as one would expect, albeit their experiments were done using a different gas matrix. Is there any evidence for assuming that increasing temperatures from 24 to 45C does not change the permeability? Has a final experiment with a similar setup been performed for the system setup as it is now deployed in the field?

(author response) It is true that the results of Ma and Skou (2007) predict an increase in the permeability of CO2 at higher temperatures. Using the relationship they found, we can expect a loss of 0.025 ppm of CO2 at 25 deg C, and 0.031 ppm at 45 deg C given the conditions in our experimental setup. A difference of only 0.006 ppm of CO2 across this temperature range.

We have repeated our experiments with the heated CalBox and revised the manuscript accordingly. We do find higher rates of CO2 permeability with the Earth Networks field module both at room temperature and elevated temperature.

Figure 2: please indicate in the figure that the secondary cryotrap is optional and not used in two of the three experiments

(author response) Clarified

P5457 L 9: As the difference between treatments was calculated based on ten half hour measurements with both treatments, the 5-minute measurement precision is not relevant. Also, the manufacturers specifications represent upper limits, and thus should not be used to assess if the observed differences are significant. I suggest using an estimate of the uncertainty of the mean difference that is based on the (scattering) observations themselves.

(author response) The uncertainty given with the differences is just what the reviewer suggests. I've removed the comment about the manufacturer specifications, as it is misleading.

Figure 4: It would make more sense to plot the 5-min ensemble averages at the mid-point rather than at the end-point

(author response) The new version is now plotted at mid-point.

Response to J. Winderlich (public comment)
Received and published: 2 October 2012

The paper is presenting a nice Nafion dryer setup. I like many of the thoroughly thought ideas, but still like to commend on some parts that might become critical for a measurement network.

The maximum error in CO2 of 0.05 ppm is worrisome. This number is a negative bias to the network, introducing artificial carbon sinks (in comparison to non-biased stations).
For the southern hemisphere this is already not compliant with the WMO recommendations, especially because random errors, calibration errors and the remaining water correction introduce further (random) uncertainties. In contrast, the wet measurement with a full H2O correction would mainly result in random errors.

(author response) The southern hemisphere 0.05 ppm WMO target is ambitious and it is not clear if any method at the moment achieves that level of precision. There is also the possibility that the water vapor correction method could result in bias errors resulting from experimental artifacts. In that case, a measurement network relying on individual instrumental water correction calibrations runs the risk of introducing spurious offsets within the network. A small negative bias introduced by the Nafion drying at every network station could be corrected for when comparing to data from other networks.

It is mentioned in the paper, that parts of this error are compensated by sending the calibration gases through the Nafion dryer as well. Unfortunately, the dryer will react quite differently for dry air; [Ma et al., 2005] report a strong preference of CO2 diffusion compared to O2 with increasing water content (almost exponential dependence). Thus, the presented setup will probably compensate the negative bias only very little (as it is also written on p. 5453, line 19ff).

(author response) We tested for this very effect. The Nafion moisture level in this network application is a much smaller range that that tested by Ma et al., 2005. Our Table 1 gives one an idea of how big this effect may be. Although it is an upper bound because those dry air experiments were done with an extremely dry Nafion membrane, much drier than it ever gets in the network application where the dry reference gases are run for 3 hours at the most or could easily be run at different times for shorter durations to reduce the wet/dry Nafion bias as much as possible.

Moreover, [Leckrone et al., 1997] report quite strong temperature dependency of
Nafion membranes: with increasing temperature a higher storage of H2O in the membrane results in higher H2O concentration (in contrast to p. 5455 line 18f). At 45 degC the Nafion may lose some drying capabilities.

(author response) I does, but it's not that important because we still apply the Chen water correction.

My largest concern is caused by the observations described on page 5456 line 11ff.
The long stabilization time and the observed temporal drift (within the first 30 min) after wet/dry switching implies a strong sponge effect of the Nafion membrane also for changing ambient conditions, which are not yet taken into account. In my eyes, it would be helpful to run an analyzer with your suggested setup in parallel to another analyzer with a cryotrap or with a fully verified water correction. Another possibility without additional experiment might be a purely mathematical estimate: A response function of the Nafion dryer might be calculated from the data

shown in Fig. 4 to convolve it with a typical ambient signal. This might give a first estimate of the magnitude of the Nafion sponge effect on the observations.

(author response) We calculated a first-order exponential response function to the data in Figure 4 as per the reviewer's suggestion and forced the function using observed H2O for the month of July 2011 (H2O = 1.5 – 2%). The bias caused by the instrument response due to changes in H2O contributed an additional noise of less than 0.003 ppm. The 10-minute stabilization time therefore is not expected to significantly bias the CO2 data. Changes in the moisture and temperature of ambient air can also affect CO2 adsorption on the inlet lines (e.g. up the tower) and have been largely ignored by the community. On the hourly time scale or longer, those relevant for background air measurements, these inlet line sponge effects average out anyway due to mass balance. For urban or local air measurements, we aren't concerned with changes as small as 0.1 ppm anyway.

Some more specific comments:
p. 5452, line 8ff: The CO2-H2O interaction is still true in the rest of the inlet line.

(author response) I think you mean downstream of our inlet selector valve, but that's not really the point here.

p. 5453, line 7f: "conserves sample and reference gas" is not really true, as you show in the following paragraph.

(author response) The approach conserves total air volume. Perhaps not CO2 mixing ratios in that air.

p. 5454 line 12 ff: Is it possible to quantify the additional measurement uncertainty due to the application of the same water correction parameters for different analyzers for H2O < 0.15%?

(author response) We updated this discussion using values for 0.15% from Rella et al. (AMT, 2013).

References: Leckrone, K. J., and Hayes, J. M.: Efficiency and Temperature Dependence of Water Removal by Membrane Dryers, Analytical chemistry, 69(5), 911-918, 1997.
Ma, S., Odgaard, M., and Skou, E.: Carbon dioxide permeability of proton exchange membranes for fuel cells, Solid State Ionics, 176(39-40), 2923-2927, 2005

Response to Anonymous Referee #2
Received and published: 7 December 2012

The submitted manuscript presents the design of a sampling and drying setup for continuous carbon dioxide and methane observations with a cavity ringdown spectrometer. The experiments are carefully designed and performed. The paper is scientifically sound and well written. The manuscript is definitely within the scope of 'Atmospheric Measurement Techniques' and is of sufficient originality to merit publication in this journal. There are only minor comments that might be considered by the authors before publication in AMT:

General comments
The authors cite several times Rella (2010), especially in the introduction. Rella (2010) is a non-reviewed Picarro report. Please refer to the newer, more elaborate and peer- reviewed publication Rella et al., 2012, AMTD (reference below) wherever possible. **(author response) Done.**

I miss a clear statement if the influence of the remaining water will be corrected during the continuous monitoring and if all analyzers within the Earth Networks network use the same correction parameters. While it is mentioned that there was an application of the H2O correction during the described experiments, it isn't really clear to me how it will be done during the continuous operation within the network. So far it is only mentioned 'The simple, partial drying technique we present here does not eliminate the water vapor influence, but reduces the water vapor correction by an order of magnitude or more, thus eliminating the need to characterize the water vapor correction on each instrument before deployment.' (page 5452) and 'The setup eliminates the need for establishing the H2O correction on each analyzer and monitoring its stability over time. It also reduces post-processing of the data.' (page 5460). Why does it reduce post- processing of the data? Does it mean that there is no H2O correction planned?

(author response) I've clarified this. We do apply the Chen correction. This approach eliminates the need to monitor the water correction over time and apply any resulting time-dependent post-processing which is more complicated to trace and document.

The authors use the parameters proposed by Chen et al. (2010) for the H2O correction.
Chen et al. used an older model, a G1301 Picarro analyser in his study. According to my knowledge, the H2O outputs of the G1xxx and the G2xxx series analyzers are processed differently in Picarro's data acquisition software, leading to non-identical H2O readings and, thus, to different corrections functions. Did you try to reproduce Chen's approach to retrieve individual parameters for the analyzer used in the present study?

(author response) We did not. See previous comments to referee #1.

There are two differences between the setup used for the tests presented here and the setup to be operated in the network: flow restriction with the needle valves and critical orifices, respectively, and Nafion dryer temperatures of 24C and 45C, respectively.
No guess is made if the different approaches of flow restrictions could influence the results. The temperature influence is only covered by one sentence: 'However, we do not expect the warmer temperatures to affect the CO2 and CH4 permeability tested here.' (page 5455). Did the authors repeat any of the experiments shown here with one of the final setups to be employed in the Earth Network network?

(author response) We tested an Earth Networks inlet module and have included the results in this revision.

Specific comments:
Page 5450, lines 18 – 20: I agree that the systematic differences are well within the WMO compatibility goals for CH4 but it is not the case for CO2 since the compatibility goals (at least for the Southern Hemisphere) are 0.05ppm, i.e. as large as the observed bias.

(author response) Clarified to Northern Hemisphere goal.

Page 5451, lines 6 – 9: The statement about the data quality requirements doesn't only hold true for the Earth Networks network but for all greenhouse gas monitoring networks.

(author response) Done.

Page 5452, lines 28 – 29: The choice also depends on the presence of skilled local operators and the frequency of maintenance visits.

(author response) Done

Page 5453, lines 1 – 8: did the authors also try other setups? E.g. to use the exhaust flow of the analyser as Nafion counterflow. This setup would allow directing only 70 ml/min through the Nafion. Please elaborate why the present setup was chosen.

(author response) We didn't try any modifications of this setup. One reason for not directing the CRDS exhaust to the Nafion purge is that it is at lower pressure and makes it more difficult to optimize the purge flow.

Page 5454, lines 14 – 16: what was done to leak-tight the pump?

(author response) The connections on the KNF pumps were tightened or replaced with better sealing versions.

Page 5457, line 11: according to the current specsheet for a G2301 analyzer available on the Picarro webpage, the respective precisions (5-min averages) are 25ppb for CO2 and 0.22ppb for CH4. An analyser with a 5-min precision of 50ppb for CH4, as stated in the present manuscript, wouldn't be suitable for monitoring purposes trying to meet the WMO compatibility goals.

(author response) Updated these values to reflect Picarro's new spec sheet.

Page 5457, line 19, Figure 3: was the CRDS analyser calibrated for H2O? If not, it is misleading to provide numbers such as 0.00002%. H2O readings shown in Figure 3 are negative.

(author response) The CRDS analyzer was not calibrated for H2O. The air was thoroughly dried with secondary cyrotrap, such that no water correction was required for CO2 and CH4. We've removed the H2O panel from the figure as it does not contain any information anyway.

Technical corrections:
Page 5452, line4: 'Rella, 2010' is an in-text citation. **(author response) Removed**
Page 5452, lines 25 – 28: incomplete sentence; rephrase it. **(author response) Done**
Page 5455, line 18: explain acronym 'SIO' first time it is mentioned. **(author response) Fixed**

References: please add weblink for Rella, 2010. **(author response) Rella 2010 is replaced by Rella et al (2013)**
Table 1: 24 May 2011 and 30 May 2011 should read 24 May 2012 and 30 May 2012. **(author response) Fixed.**
Figure 3, top panel: reduce y-axis range. **(author response) The detail at that level doesn't really matter and will be more of a distraction. We just removed that panel.**

Reference:
Rella C. W., H. Chen, A. E. Andrews, A. Filges, C. Gerbig, J. Hatakka, A. Karion, N. L. Miles, S. J. Richardson, M. Steinbacher, C. Sweeney, B. Wastine, C. Zellweger, 2012. High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air, Atmospheric Measurement Techniques Discussion, 5, 5823-5888