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Atmospheric Measurement Techniques Discussions

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Design and performance of a Nafion dryer for continuous operation at CO_2 and CH_4 air monitoring sites

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Abstract

In preparation for the routine deployment of the Earth Networks greenhouse gas monitoring network, we have designed and tested a simple method for drying ambient air to below 0.2 % mole fraction H_2O using a Nafion dryer. The inlet was designed for use with a Picarro model G2301 cavity ring down spectrometer (CRDS) $CO_2/CH_4/H_2O$ analyzer. The analyzer measures water vapor mixing ratio at the same frequency as CO_2 and CH_4 and then corrects for the dilution and peak broadening effects of H_2O on the CO_2 and CH_4 mixing ratios. This analyzer is remarkably stable and performs well on water vapor correction tests, but there is potentially an added benefit of reducing the dependence on the H_2O correction for long term field measurement programs. Substantially lowering the amount of H_2O in the sample can reduce uncertainties in the applied H_2O corrections by an order of magnitude or more, and eliminate the need to determine an instrument-specific H_2O correction factor and to verify its stability over time. Our Nafion drying inlet system takes advantage of the extra capacity of the analyzer pump to redirect 30 % of the dry gas exiting the Nafion to the outer shell side of the dryer and has no consumables. We tested the Nafion dryer against a cryotrap (−95 °C) method for removing H_2O and found that it does not significantly alter the CO_2 and CH_4 dry mixing ratios of the sample gas. Systematic differences between the drying methods were at the level of 0.05 ppm in CO_2 and 0.1 ppb in CH_4 for the wet-air tests, well within the WMO compatibility guidelines.

1 Introduction

There is increasing interest in regional greenhouse gas emissions estimates as stakeholders aim to reduce and verify emissions at national, state and city levels (NRC, 2010). Two of the most important greenhouse gases of interest are CO_2 and CH_4. Atmospheric inversion methods provide a means of inferring emission rates based on atmospheric concentration measurements, but their usefulness at the regional level has

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been hampered by uncertainty in atmospheric transport (Houweling et al., 2010; Lin et al., 2006; Stephens et al., 2007) and sparse greenhouse gas monitoring locations (Butler et al., 2010; Gurney et al., 2002). Recently, Earth Networks, Inc. has proposed to greatly increase the density of atmospheric surface measurements by deploying a network of close to 50 continuous observation stations across the United States (http://www.earthnetworks.com/OurNetworks/GreenhouseGasNetwork.aspx). It is important that the data collected by this network is of high quality and meets or exceeds the WMO compatibility goals of 0.1 ppm CO_2 in the Northern Hemisphere and 0.05 ppm CO_2 in the Southern Hemisphere, and 2 ppb CH_4 (WMO, 2009).

Until recently, most highly accurate continuous CO_2 measurements were made using non-dispersive infrared (NDIR) spectroscopic analyzers (e.g. Bakwin et al., 1998). These analyzers require frequent calibration and drying the air prior to analysis. A newer approach using wavelength-scanned cavity ring-down spectroscopy (CRDS) has greater stability, reducing the frequency of calibration, and has the potential to eliminate the need for drying (Crosson, 2008). Water vapor interferes with CO_2 and CH_4 concentration measurements by diluting the mixing ratios in air and by broadening the spectroscopic absorption lines of other gases. The approach that Picarro, Inc. has taken with their CRDS analyzers is to concurrently measure H_2O of the sample and use experimentally derived algorithms to correct for the dilution and broadening effects (Crosson, 2008; Rella, 2010).

Since the Picarro CRDS instruments are fairly new, there have been limited studies published testing the stability and transferability of the water vapor correction algorithm for each instrument unit (Chen et al., 2010; Winderlich et al., 2010; Richardson et al., 2012). Chen et al. (2010) suggests that applying the same set of coefficients to multiple instruments can yield high quality data. They found the residual error after the water vapor correction is below 0.05 ppm for CO_2 and below 0.5 ppb for CH_4. Winderlich et al. (2010) concludes that the water vapor correction for an individual instrument is stable over a year and half and estimates the repeatability of the corrected measurements is within 0.03 ppm for CO_2 and 0.3 ppb for CH_4. Because of the limited testing on the

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transferability and long term stability of the water vapor correction coefficients, the manufacturer currently recommends experimentally calculating the correction coefficients for each individual instrument at the start of operations for best performance (Rella, 2010). The uncertainty analysis in (Rella, 2010) shows that using instrument-specific water vapor correction coefficients can reduce the uncertainty in the correction made to dry-gas mixing ratios by a factor of ~ 7 for CO_2 (0.36 to 0.048 ppm CO_2 at 4 % H_2O and 380 ppm CO_2) and ~ 11 for CH_4 (2.2 to 0.2 ppb at 4 % H_2O and 2000 ppb CH_4).

However, these types of water vapor correction experiments are inherently tricky to perform because H_2O and CO_2 can interact with tubing walls in most experimental setups. Some amount of CO_2 can adsorb to the tubing walls, and increasing H_2O will displace that CO_2, creating an artifact in a dry/wet-air comparison. Simply reducing the H_2O in the sample by an order of magnitude or more would reduce the uncertainty in the corrected dry-gas mixing ratios by nearly the same amount as calibrating each individual instrument before network deployment. 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.

The Nafion membrane is known to be semi-permeable to water vapor and relatively impermeable to other gases (Leckrone and Hayes, 1997). Nafion dryers are designed with the semi-permeable membrane separating an inner sample gas stream from a stainless steel outer shell, with a counterflow purge gas stream. If the partial pressure of water vapor is lower in the purge gas stream, then water is removed from the sample gas stream. There are many different ways to supply the purge gas to Nafion dryers. Common methods include those with no consumables, like reusing the sample gas itself after passing through the inner Nafion membrane. And methods with consumables that must be replaced, such as using molecular sieve to remove all the water from the sample after the Nafion and before it is reused as the purge gas (e.g. Stephens et al., 2011) and dry air from a tank or generator. The choice depends largely on what the tolerance is for residual water in the sample gas.

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For the Earth Networks stations, we designed a simple drying inlet system for ambient air monitoring (Fig. 1) using a 72-inch long Nafion membrane dryer (PermaPure, Inc., model MD-050-72S-1). This inlet drying configuration takes advantage of the extra capacity of the external analyzer pump to redirect 30 % of the dried gas exiting the Nafion to the outer shell side of the dryer creating both a gradient in the H_2O partial pressure and total gas pressure across the Nafion membrane. This total pressure drop across the membrane enhances the drying capacity of the Nafion and conserves sample and reference gases.

This setup also unavoidably produces partial pressure gradients in CO_2 and CH_4 across the membrane that may allow small amounts of these gases to also permeate across the membrane (Ma and Skou, 2007). To reduce the influence of any such permeation on the sample measurements, the network sampling setup uses active pressure stabilization for all ambient air intakes and reference tank gases. This will ensure that the Nafion is exposed to sample and reference gases at identical total pressures, so that any direct effect of pressure-dependent permeation of CO_2 and CH_4 is canceled in the comparison between sample and reference gases.

Even with the pressure stabilization, however, one important difference still exists between samples and references, i.e. sample gas enters the Nafion with much higher moisture levels than calibration gases. The permeation of CO_2 and CH_4 through the membrane may be moisture-dependent (Ma and Skou, 2007), and this could lead to differential biases between sample and calibration gases that do not cancel.

Here we present results of tests that evaluate the performance of this particular setup. We show that the setup is very effective in reducing water to between 0.1 to 0.15 % levels, and show that any moisture-dependent changes in the permeation of CO_2 and CH_4 across the Nafion membrane are very small. We evaluated the setup both before and after 9 months of continuous usage to test for aging effects, and we quantify the time required for the Nafion system to stabilize after reference gases are introduced.

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2 Methods

The ideal inlet drying system removes H_2O without modifying CO_2 or CH_4. In this study, we test the performance of the inlet drying system by ensuring that any changes to CO_2 or CH_4 are negligible or correctable. This requires a humidified air source with known dry-gas mixing ratios of CO_2 and CH_4. It is difficult to humidify air without changing its dry-gas CO_2 mixing ratio slightly because of the propensity of CO_2 to interact with water adsorbed on tubing walls. For this reason, we compared our Nafion dryer system with a cryotrap at −95 °C using the experimental design in Fig. 2. Similar cyrotraps have been used in this community for decades and any effects on CO_2 and CH_4 are known to be very small. Thus, we believe showing that the Nafion system is as good as one of these cryotraps is a suitable performance benchmark.

The analyzer used for testing this application was a Picarro G2301 CRDS $CO_2/CH_4/H_2O$ gas analyzer, but this application may be used with any similar gas analyzer. The external pump used was a KNF pump unit supplied by Picarro, retrofit in order to make it leak-tight to ensure that the gas flow exiting the pump was identical to the gas flow through the CRDS analyzer. The same analyzers are used in the Earth Networks greenhouse gas network design but with a different external pump and a few slight changes to set air flow rates. Flow rates in the test system were controlled by manually adjusting needle valves at the CRDS inlet and in the Nafion counterflow loop (Fig. 2). In the deployed network design, the flow rates are set by replacing the default Picarro factory O'Keefe A-18-NY orifice with a smaller A-9-NY, and in the Nafion counterflow by an A-6-NY orifice (Fig. 1). For these orifices to work the downstream pressure has to be low to assure sonic velocity in the orifice. This is needed for the critical flow to be constant regardless of upstream pressure. It is also important to filter the gas upstream of the orifice to avoid getting it clogged.

Dry air from a standard tank was passed through a temperature-controlled bubbler style humidifier in wet-air tests or bypassed in dry-air tests (Fig. 2). The resulting wet-air (or dry-air) was split between the Nafion dryer and the cyrotrap, each constantly flowing

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at ~ 70 scc min^{-1}, and alternately sampled by the Picarro analyzer, or sent to a waste pump. The cyrotrap was stainless steel, with a $\frac{1}{2}''$ outer tube and a $\frac{1}{8}''$ inner dip tube. Air flowed in through the outer tube, and 3 mm glass beads at the bottom reduced the chance of ice crystals entering the inner tube along with the airflow out of the cryotrap. We also added heat tape to the top of the cryotrap, above the chiller, to discourage liquid water build up at the top of the trap. The H_2O mixing ratio of the humidified air was adjusted by changing the temperature of the water bath surrounding the humidifier and by changing the gas pressure inside the humidifier. Delivery pressure to the Nafion dryer and cyrotrap was maintained at 600 Torr by an MKS 640 pressure controller in order to simulate conditions appropriate for routine sampling of ambient air.

The experiments using this test set up of the Nafion drying system were conducted at ambient laboratory temperature of ~ 24 ± 1 °C over the course of each experiment. The drying systems deployed by Earth Networks are in an enclosure warmed to ~ 45 °C in order to minimize the chance of condensation forming in the inlet system and to buffer temperature changes. This temperature increase makes the Nafion less efficient at removing water (Leckrone and Hayes, 1997), by approximately 0.01 % (or 0.1 mmol mol^{-1}) based on side-by-side operation of the test system described here and a network system sampling air from the SIO pier. However, we do not expect the warmer temperatures to affect the CO_2 and CH_4 permeability tested here.

Three types of experiments were completed at the start of operation: one dry-air run (Exp. 1), one wet-air run (2.1 % H_2O, Exp. 2), and two wet-air runs (2.1 % H_2O) with a secondary cyrotrap after the Nafion dryer to eliminate the need to apply the water vapor correction (Exp. 3). The secondary cryotrap was placed immediately before the CRDS. This secondary cryotrap used a "cold finger" design similar to that of the primary cyrotrap, but smaller, $\frac{1}{4}''$ stainless steel outer tube and $\frac{1}{16}''$ inner tube, with no glass beads.

In all these experiments, gas was constantly flowing through the Nafion system at 100 scc min^{-1} (with 30 scc min^{-1} of that redirected to the counterflow purge) and the cryotrap at 70 scc min^{-1}. We used the CRDS changeover valve (Fig. 2) to alternately

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switch the CRDS intake between the Nafion and cryotrap, quantifying any differences in the CO_2 and CH_4 mixing ratios between the two treatments.

For the wet-air runs, the H_2O values were 2.1 %, which were as high as we could achieve with the bubbler humidifier at 20 °C and maintaining an operating pressure greater than 600 Torr and keeping the test system at laboratory temperature. Since the Nafion-dryer treatment without the secondary cyrotrap did not completely remove all of the water from the air, and in the case of the dry-air run, it added water to the air, we applied the water vapor correction from Chen et al. (2010) as recommended by Rella (2010) to the data as needed (Appendix A). These corrections are on the order of 1.0 ppm CO_2 and 3.7 ppb CH_4 for 0.2 % H_2O.

For these tests, we switched the changeover valve every 60 min. Preliminary tests using 15-min switching intervals showed drifting CO_2 values presumably because of different flow resistances between the Nafion system and the cryotrap causing small pressure changes that in turn caused CO_2 to be adsorbed or desorbed on the walls after switching.

After completing a first round of tests as described above, the Nafion dryer inlet system with the CRDS was used continuously for nine months of routine air measurements from the pier at the Scripps Institution of Oceanography (SIO). We then repeated the dry gas Exp. 1 and wet gas Exp. 3 to see if the aging of the Nafion over the nine-month period had any impact on the permeability of CO_2 and CH_4.

All data was processed on 1-min running means, discarding the first 30 min of data after switching. There was no evidence of drift in CO_2 or CH_4 in the last 30 min of data for each treatment. The number of switching intervals varied in each experiment, as the primary cryotrap would plug with ice after several hours of use, thereby ending the experiment. Biases between the Nafion and cryotrap treatments were calculated as the differences between Nafion and the mean of the two cryotrap treatments before and after, i.e. the mid-point difference, and then averaged over the total number of sampling pairs. In Table 1, we report the mean and standard deviation of the mid-point differences.

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3 Results and discussion

3.1 Testing at the start of operation

In the first dry-air experiment, Exp. 1.1 (Fig. S1), we ran dry tank air with a CO_2 dry gas mixing ratio of ~ 506 ppm and CH_4 of ~ 4787 ppb, switching between the Nafion and bypass. In this case, the cyrotrap was in-line but not chilled, rather at ambient laboratory temperature since the air was dry already. The mean mid-point difference of the Nafion and bypass treatments was -0.01 ± 0.01 ppm for CO_2 and -0.07 ± 0.27 ppb for CH_4 (summarized in Table 1). Negative values mean that there was slightly less CO_2 and CH_4 after the Nafion treatment than the cryotrap treatment. The measured difference between treatments was within the manufacturer-specified uncertainty; a 5-min measurement precision of < 0.15 ppm CO_2 and < 50 ppb CH_4.

In the first wet-air experiment, Exp. 2.1 (Fig. S2), we humidified tank air with a CO_2 dry gas mixing ratio of ~ 393 ppm CO_2 and ~ 1874 ppb CH_4 to 2.1 % H_2O. The Nafion dryer reduced the H_2O in the humidified sample down to 0.12 %, and we applied the water vapor correction to this data to calculate dry gas mixing ratios for CO_2 and CH_4, Eqs. (A1) and (A2). We then compared the Nafion dryer treatment with the cyrotrap and found a mean mid-point difference over 4 pairs of Nafion/cryotrap switching of -0.03 ± 0.01 ppm for CO_2 and -0.08 ± 0.05 ppb for CH_4 (Table 1).

The final two wet-air experiments, Exp. 3.1a (Fig. 3) and Exp. 3.1b (Fig. S3), used the additional cryotrap to completely remove the residual water that makes it through the Nafion. The CRDS confirmed that the air was dried to below 0.00002 %, and no water vapor corrections were applied. The largest mean Nafion minus cyrotrap differences were -0.05 ± 0.01 ppm of CO_2 and 0.1 ± 0.05 ppb of CH_4 (Table 1). In this set of wet-air experiments, the cold trap plugged with ice after 3 to 5 pairs of Nafion/cryotrap switching.

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3.2 Testing after 9 months of operation

After nine months of continuously monitoring ambient air from intakes on the SIO pier, we repeated similar tests to see if age or use affected the permeability of the Nafion to CO_2 and CH_4. We repeated the dry-air experiment, Exp. 1.2, using a different dry air tank with approximately 393.6 ppm CO_2 and 1873 ppb of CH_4, again, leaving the cryotraps at room temperature (Fig. S4). We applied the water vapor correction to account for the small amount of water added from the Nafion treatment. The mean of 14 pairs of Nafion minus cyrotrap mid-point differences was 0.01 ± 0.01 ppm for CO_2 and -0.05 ± 0.1 ppb for CH_4 (Table 1).

We also repeated the wet-air experiment, Exp. 3.2 (Fig. S5) using the same dry air tank as in Exp. 1.2, but humidified to 2.2 % H_2O. We used the secondary cyrotrap, which eliminated the need to apply the water vapor correction. The mean of 10 pairs of Nafion minus cyrotrap mid-point differences was -0.03 ± 0.01 ppm of CO_2 and 0.08 ± 0.06 ppb of CH_4 (Table 1). These results are similar to Exp. 3.1a and 3.1b, run prior to routine operation, and show no sign of age effects on Nafion after nine months.

3.3 Transition times

We were also interested in addressing how much time is required for the system to stabilize under routine conditions when the intake selector switches from wet ambient air to dry reference tank air. The previous experiments focused on identifying potential steady state offsets caused by the Nafion. It is possible that when humidity changes rapidly in the Nafion when switching from moist air to a dry reference tank, that there are transient offsets in CO_2 and CH_4 while the Nafion dries out. In Fig. 4 we show the ambient air to dry tank transitions from one month of routine operation in April 2012. The water vapor correction in Appendix A was applied to this data. The humidity of the reference gas exiting the Nafion decreases from about 0.12 % to 0.08 % as the Nafion slowly dries. After switching, it takes the CRDS measurements about 10 min to stabilize.

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4 Conclusions

We have tested a setup for drying air using a Nafion dryer in conjunction with a CRDS analyzer. We find that the permeation of CO_2 and CH_4 through the Nafion membrane in both dry-air and wet-air experiments, relative to a −95 °C cryotrap, is within the precision of the analyzer measurements, 0.05 ppm CO_2 and less than 0.1 ppb CH_4. When comparing approaches for dealing with water in CRDS analysis, we estimate that the expected precision in the CO_2 and CH_4 measurements at 2 % ambient H_2O utilizing the Nafion dryer with a universal water vapor correction is comparable to not drying the sample air and characterizing an instrument-specific water vapor correction (Table 2). Although, it should be noted that it is not really known statistically what the differences are in water vapor correction coefficients among different analyzers. At least part of the range in coefficients reported by different laboratories could be the result of experimental artifacts and may not reflect actual response differences among analyzers. More testing is needed to determine the uncertainty in the water vapor correction across many analyzers.

The fact that both sample air and reference gases pass through the Nafion before the analyzer makes any drying bias due to permeation through the Nafion even smaller in routine operation, i.e. the bias will cancel out after applying the CO_2 and CH_4 calibrations to the sample air based on reference gas analysis. Also, because the Nafion dryer has a slow response time for H_2O, it will humidify dry tank air such that the reference gases will have a similar humidity to the sample air when they enter the analyzer, and uncertainty in the water vapor correction will further cancel out (Richardson et al., 2012).

The Nafion dyer system was quite effective at removing water vapor from the ambient air sampled from the SIO pier. For example, the Nafion reduced the mean H_2O in the ambient air during April 2012 to 0.11 % on average. This inlet system is entirely self-sustaining and required no intervention over the nine months it was in operation. We also find that the performance of the system is not subject to problems from degradation

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of the Nafion, at least over a 9-month time frame. The time to achieve stable gas readings after switching from ambient gas to sample gas is on order of 10 min.

The setup eliminates the need for establishing the H_2O correction on each analyzer and monitoring its stability over time. It also reduces post-processing of the data. This method more fully capitalizes on the ability of the CRDS to provide high quality measurements with reduced calibration activities, and thereby saving labor costs for deployments involving an extensive network of analyzers such as that planned by Earth Networks.

Appendix A

Water vapor correction

The water vapor correction from Chen et al. (2010), as recommended by Rella (2010), is summarized in Eqs. (A1) and (A2).

$$\frac{(CO_2)_{wet}}{(CO_2)_{dry}} = 1 + aH_{rep} + bH_{rep}^2 \quad \text{(A1)}$$

$$\frac{(CH_4)_{wet}}{(CH_4)_{dry}} = 1 + cH_{rep} + dH_{rep}^2 \quad \text{(A2)}$$

where H_{rep} is the reported H_2O mixing ratio by the analyzer, $(CO_2)_{wet}$ and $(CH_4)_{wet}$ are the measured mixing ratios of the wet gas, $(CO_2)_{dry}$ and $(CH_4)_{dry}$ are the true dry-gas mixing ratios, $a = -0.012000$, $b = -0.0002674$, $c = -0.00982$, and $d = -0.000239$.

Supplementary material related to this article is available online at: http://www.atmos-meas-tech-discuss.net/5/5449/2012/amtd-5-5449-2012-supplement.pdf.

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References

Bakwin, P., Tans, P., Hurst, D., and Zhao, C.: Measurements of carbon dioxide on very tall towers: results of the NOAA/CMDL program, Tellus B, 50, 401–415, 1998.

Butler, M. P., Davis, K. J., Denning, A. S., and Kawa, S. R.: Using continental observations in global atmospheric inversions of CO_2: North American carbon sources and sinks, Tellus B, 62, 550–572, doi:10.1111/j.1600-0889.2010.00501.x, 2010.

Chen, H., Winderlich, J., Gerbig, C., Hoefer, A., Rella, C. W., Crosson, E. R., Van Pelt, A. D., Steinbach, J., Kolle, O., Beck, V., Daube, B. C., Gottlieb, E. W., Chow, V. Y., Santoni, G. W., and Wofsy, S. C.: High-accuracy continuous airborne measurements of greenhouse gases (CO_2 and CH_4) using the cavity ring-down spectroscopy (CRDS) technique, Atmos. Meas. Tech., 3, 375–386, doi:10.5194/amt-3-375-2010, 2010.

Crosson, E. R.: A cavity ring-down analyzer for measuring atmospheric levels of methane, carbon dioxide, and water vapor, Appl. Phys. B, 92, 403–408, doi:10.1007/s00340-008-3135-y, 2008.

Gurney, K., Law, R., Denning, A., Rayner, P., Baker, D., Bousquet, P., Bruhwiler, L., Chen, Y., Ciais, P., Fan, S., Fung, I., Gloor, M., Heimann, M., Higuchi, K., John, J., Maki, T., Maksyutov, S., Masarie, K., Peylin, P., Prather, M., Pak, B., Randerson, J., Sarmiento, J., Taguchi, S., Takahashi, T., and Yuen, C.: Towards robust regional estimates of CO_2 sources and sinks using atmospheric transport models, Nature, 415, 626–630, 2002.

Houweling, S., Aben, I., Breon, F.-M., Chevallier, F., Deutscher, N., Engelen, R., Gerbig, C., Griffith, D., Hungershoefer, K., Macatangay, R., Marshall, J., Notholt, J., Peters, W., and Serrar, S.: The importance of transport model uncertainties for the estimation of CO_2 sources and sinks using satellite measurements, Atmos. Chem. Phys., 10, 9981–9992, doi:10.5194/acp-10-9981-2010, 2010.

Leckrone, K. J. and Hayes, J. M.: Efficiency and temperature dependence of water removal by membrane dryers, Anal. Chem., 69, 911–918, doi:10.1021/ac9610220, 1997.

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Lin, J. C., Gerbig, C., Wofsy, S. C., Daube, B. C., Matross, D. M., Chow, V. Y., Gottlieb, E., Andrews, A. E., Pathmathevan, M., and Munger, J. W.: What have we learned from intensive atmospheric sampling field programmes of CO_2?, Tellus B, 58, 331–343, doi:10.1111/j.1600-0889.2006.00202.x, 2006.

Ma, S. and Skou, E.: CO_2 permeability in Nafion® EW1100 at elevated temperature, Solid State Ionics, 178, 615–619, doi:10.1016/j.ssi.2007.01.030, 2007.

NRC: Verifying greenhouse gas emissions: Methods to support international climate agreements, 124 pp., 2010.

Rella, C. W.: Accurate greenhouse gas measurements in humid gas streams using the Picarro G1301 carbon dioxide/methan/water vapor gas analyzer, 1–18, 2010.

Rella, C. W., Chen, H., Andrews, A. E., Filges, A., Gerbig, C., Hatakka, J., Karion, A., Miles, N. L., Richardson, S. J., Steinbacher, M., Sweeney, C., Wastine, B., and Zellweger, C.: High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air, Atmos. Meas. Tech. Discuss., in review, 2012.

Richardson, S. J., Miles, N. L., Davis, K. J., Crosson, E. R., Rella, C. W., and Andrews, A. E.: Field testing of cavity ring-down spectroscopy analyzers measuring carbon dioxide and water vapor, J. Atmos. Ocean. Tech., 29, 397–406, doi:10.1175/JTECH-D-11-00063.1, 2012.

Stephens, B. B., Gurney, K. R., Tans, P. P., Sweeney, C., Peters, W., Bruhwiler, L., Ciais, P., Ramonet, M., Bousquet, P., Nakazawa, T., Aoki, S., Machida, T., Inoue, G., Vinnichenko, N., Lloyd, J., Jordan, A., Heimann, M., Shibistova, O., Langenfelds, R. L., Steele, L. P., Francey, R. J., and Denning, A. S.: Weak northern and strong tropical land carbon uptake from vertical profiles of atmospheric CO_2, Science, 316, 1732–1735, doi:10.1126/science.1137004, 2007.

Stephens, B. B., Miles, N. L., Richardson, S. J., Watt, A. S., and Davis, K. J.: Atmospheric CO_2 monitoring with single-cell NDIR-based analyzers, Atmos. Meas. Tech., 4, 2737–2748, doi:10.5194/amt-4-2737-2011, 2011.

Winderlich, J., Chen, H., Gerbig, C., Seifert, T., Kolle, O., Lavrič, J. V., Kaiser, C., Höfer, A., and Heimann, M.: Continuous low-maintenance CO_2/CH_4/H_2O measurements at the Zotino Tall Tower Observatory (ZOTTO) in Central Siberia, Atmos. Meas. Tech., 3, 1113–1128, doi:10.5194/amt-3-1113-2010, 2010.

WMO: Report of the 15th WMO/IAEA meeting of experts on carbon dioxide, other greenhouse gases, and related tracers measurement techniques, Jena, Germany, 7–10 September 2009, GAW Report No. 194, WMO TD No. 1553, 2009.

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Table 1. Mid-point differences between Nafion and cyrotrap treatments (Nafion minus the mean of cryotrap measurements before and after).

Date	Exp.	Description	n[a]	CO_2 mean (ppm)	CO_2 stdev[b] (ppm)	CH_4 mean (ppb)	CH_4 stdev[b] (ppb)
29 Jul 2011	1.1	Dry-air	11	−0.01	0.01	−0.07	0.27
1 Aug 2011	2.1	Wet-air, 2.1 %	4	−0.03	0.01	−0.08	0.05
2 Aug 2011	3.1a	Wet-air, 2.1 %, 2nd cryotrap	5	−0.05	0.01	−0.02	0.10
18 Aug 2011	3.1b	Wet-air, 2.1 %, 2nd cryotrap	3	−0.03	0.01	0.10	0.05
24 May 2011	1.2	Dry-air	14	0.01	0.01	−0.05	0.10
30 May 2011	3.2	Wet-air, 2.2 %, 2nd cryotrap	10	−0.03	0.01	0.08	0.06
		Maximum Differences		−0.05	0.01	0.10	0.27

[a] Number of Nafion intervals measured; [b] standard deviation of the mid-point differences.

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Table 2. Summary of errors for different CRDS application approaches.

Water correction type Nafion drying	Universal No (2 % H_2O)		Instrument-specific No (2 % H_2O)		Universal Yes (0.15 % H_2O)	
	CO_2 (ppm)	CH_4 (ppb)	CO_2 (ppm)	CH_4 (ppb)	CO_2 (ppm)	CH_4 (ppb)
Instrument precision[a]	< 0.05	< 0.7	< 0.05	< 0.7	< 0.05	< 0.7
Random noise in H_2O measurement[b]	0.02	0.1	0.02	0.1	0.01	0.1
Uncertainty in instrument specific H_2O correction[c]	0.16	1.1	0.02	0.1	0.01	0.1
Nafion-induced uncertainty[d]	N/A	N/A	N/A	N/A	0.05	0.1
Quadrature sum of errors[e]	0.17	1.3	0.06	0.7	0.07	0.7

[a] 5-min mean from the Picarro G2301 manufacturer specifications sheet. [b] Based on Rella et al. (2012). [c] Interpolated from values in Rella (2010). [d] From this experiment. [e] The quadrature sum of errors = $\sqrt{(a^2 + b^2 + c^2 + d^2)}$. This was used assuming that the errors are not correlated and do not act in the same direction.

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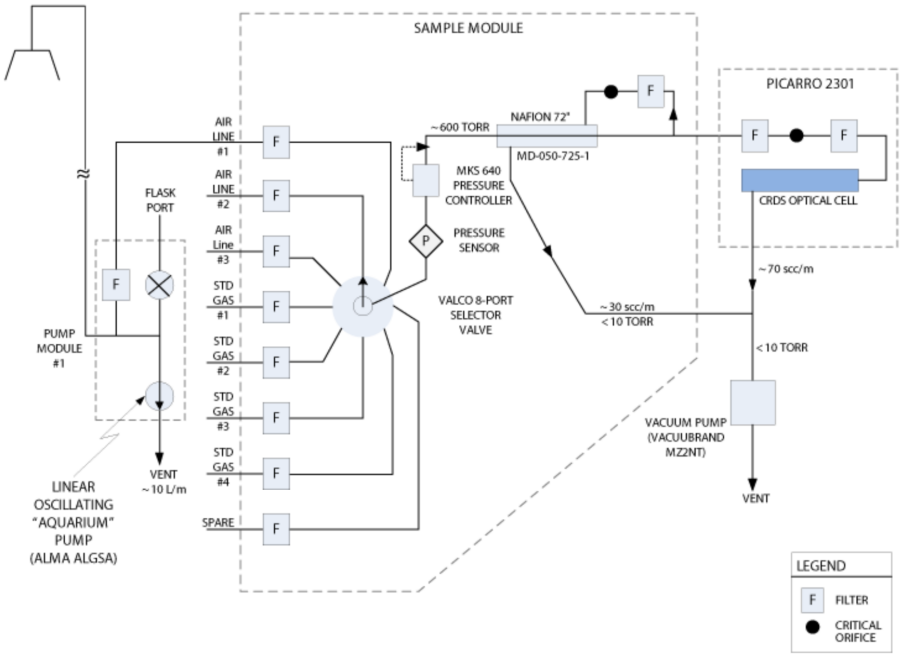

Fig. 1. The gas-handling design for the Earth Networks greenhouse gas monitoring stations. The "Sample Module" houses the Nafion dryer inlet system. All ambient air and reference gases pass through the Nafion dryer.

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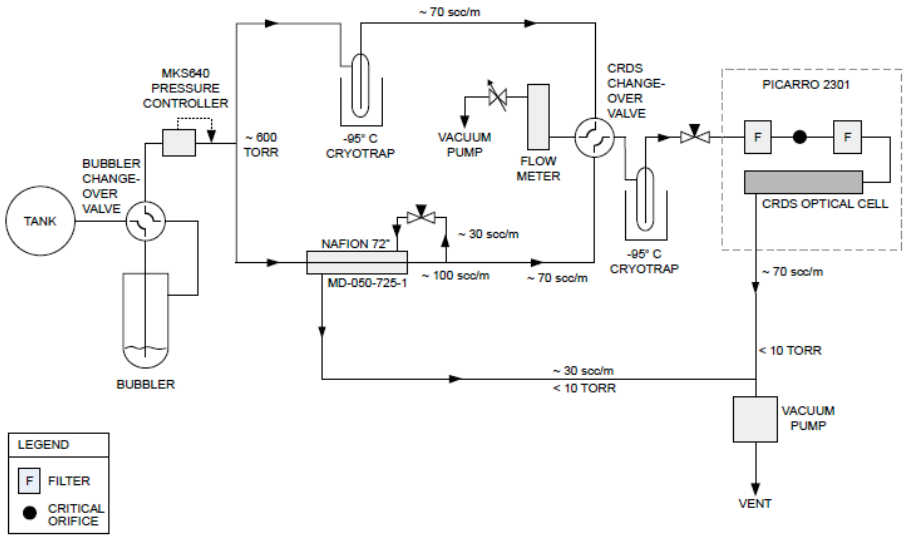

Fig. 2. Experimental setup for testing the Nafion dryer. Dry tank air is humidified with a bubbler. The Nafion and cryotrap portions are continuously flowing and the CRDS changeover valve allows the CRDS analyzer to alternately monitor each of the treatments. The second cyrotrap downstream of the CRDS changeover valve was added in some experiments to remove the residual water exiting the Nafion and eliminate the need to apply any water vapor correction. In the dry-air experiments the cyrotraps were left at room temperature.

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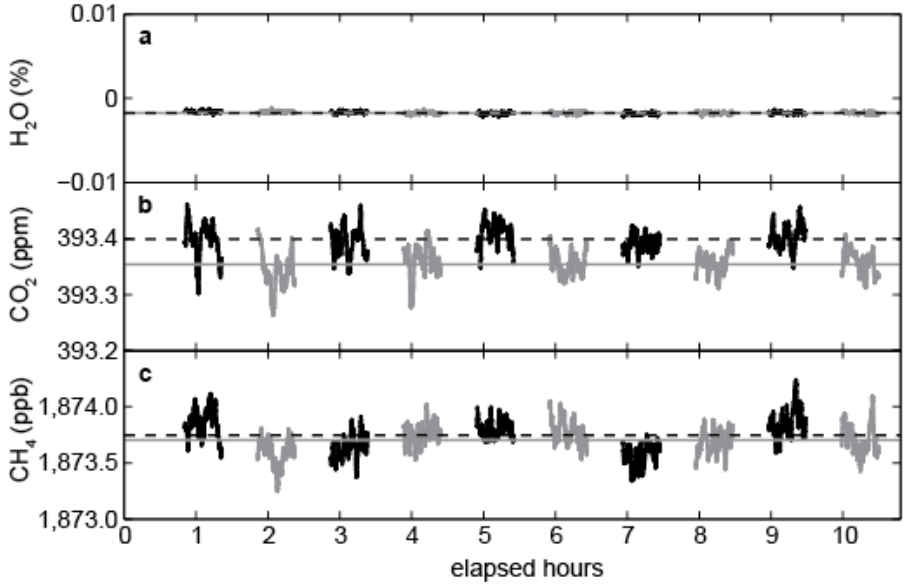

Fig. 3. Wet-air Exp. 3.1a on 2 August 2011. The cryotrap treatment is shown in black and the Nafion treatment is in grey for **(a)** H_2O, **(b)** CO_2, **(c)** CH_4. The first 30 min of data were excluded for each treatment. The straight lines are mean values for the cryotrap (black dashed) and Nafion (solid grey) over the entire experiment. The cryotraps plugged up with ice, ending the experiment after approximately 11 h. The secondary cryotrap was used in this experiment, so no water vapor correction was applied.

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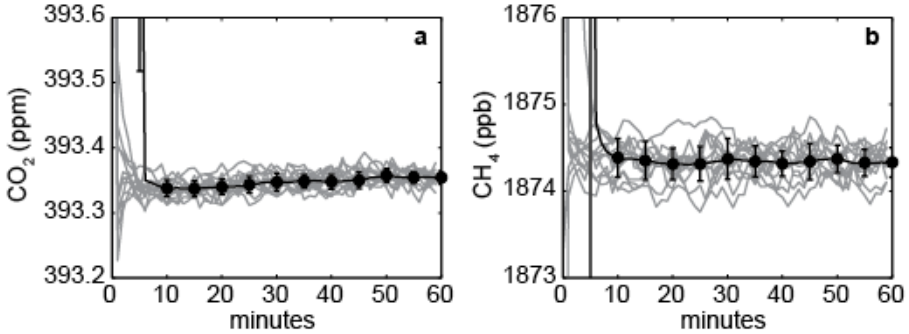

Fig. 4. Grey lines are the 1-min averages of the first reference tank switched to after ambient air during the daily reference tank checks for **(a)** CO_2 and **(b)** CH_4. This tank was sampled for 1 h. The 5-min ensemble averages over every daily tank run are shown in black, plotted at the end-point, along with 1-standard deviation error bars. This data was collected during the month of April 2012. The Nafion wets the dry reference gas to similar levels during ambient monitoring. On average, the water level started at 0.12 % and dropped to 0.08 % by the end of this hour. It shows that after switching from wet ambient air to a dry reference tank, the CO_2 and CH_4 values stabilize by 10 min.

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