A Low-Maintenance Drying System for Ambient Air Greenhouse Gas Monitoring

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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 0.1\% mole fraction H\textsubscript{2}O using a Nafion model MD-050-72S-1 dryer. We tested the prototype inlet drying system on a Picarro model G2301 Cavity Ring-Down Spectroscopy CO\textsubscript{2}/CH\textsubscript{4}/H\textsubscript{2}O analyzer. The analyzer measures water vapor mixing ratio at the same frequency as CO\textsubscript{2} and CH\textsubscript{4} and then corrects for the dilution and peak broadening effects on the CO\textsubscript{2} and CH\textsubscript{4} mixing ratios. This analyzer is remarkably stable and performs well on water vapor correction tests, but we believe there is an added benefit of reducing the dependence on the H\textsubscript{2}O correction for long-term field measurement programs. Unlike CO\textsubscript{2} and CH\textsubscript{4} measurements, which can be calibrated in the field with compressed gas standards, the H\textsubscript{2}O correction is not easily calibrated in the field. Substantially lowering the amount of H\textsubscript{2}O in the sample can reduce uncertainties in the applied H\textsubscript{2}O corrections by an order of magnitude or more, and reduce the need to verify the H\textsubscript{2}O correction algorithm stability.

Our Nafion drying inlet system takes advantage of the extra capacity of the external Picarro analyzer pump to redirect 30\% of the dry gas exiting the Nafion to the outer shell side of the dryer. This method has no consumables and does not appear to alter the CO\textsubscript{2} and CH\textsubscript{4} concentrations of the sample gas within measurement precision. We restrict sample flow through the G2301 analyzer to 70 cc/min to conserve calibration gases during routine deployment. It is difficult to humidify air without changing its dry-gas CO\textsubscript{2} mixing ratio slightly because of the propensity of CO\textsubscript{2} to interact with water adsorbed on tubing walls. For this reason, we compared our Nafion dryer system with a proven cold trap at -95°C. Dry air from a standard tank was passed through a humidifier in the wet-gas test (or bypassed in the dry-gas test) and then alternately directed through the Nafion or cold trap at 15-min intervals. Differences between the Nafion dryer and cold trap in the dry-gas and wet-gas tests were less than the targeted precision of the measurements. Systematic differences between the drying methods were at the level of 0.01 ppm in CO\textsubscript{2} and 0.007 ppb in CH\textsubscript{4} for the wet-gas test (Fig 1) and 0.01 ppm in CO\textsubscript{2} and 0.04 ppb in CH\textsubscript{4} for the drygas test.

\textbf{Figure 1.} Time series of wet-gas experiment showing 1-min running means of the analyzer’s 1-sec sampling. Tank air was humidified to 2.2\% H\textsubscript{2}O (mole fraction) and either passed through the cold trap (blue) or Nafion (red) in 15- min switching intervals. The first 2 min and last 1 min of each 15-min interval were excluded from the analysis because of transient artifacts. The moisture content of the Nafion-dried stream increased from 0.004\% to 0.016\% over the course of the experiment. CO\textsubscript{2} and CH\textsubscript{4} have been corrected for water vapor using factory default settings on the analyzer. Blue and red horizontal lines are means of cold trap intervals and Nafion intervals respectively over the entire experiment. The cause of the small drift in CH\textsubscript{4} is unknown, but is subtracted in these tests.