Supplementary Information

A   Instrumental Water Cross-Sensitivity Correction

Previous studies have found a cross-sensitivity of reported mixing ratios of gases to atmospheric water vapour with the OA-ICOS in two separate ways; through dilution and pressure broadening effects (Chen et al., 2010). The effect of H_2O on the gas mixing ratios that is specific to each instrument and was determined by changing humidity added to the gas standard stepwise from $0 - 26,000$ ppm of H_2O. Multiple stepwise H_2O tests were run on the instrument, where the average of the values at each step of H_2O was used to calculate a correction factor shown in Equation 1.

$$[CH_4]_{dry} = [CH_4]_{CP} + \left(1.4667 \times 10^{-11} \times [H_2O]_{CP}{}^2\right) + (2.0233 \times 10^{-6} \times [H_2O]_{CP}) - 6.3502 \times 10^{-5} \quad [1]$$

One example of these tests is shown in Figure S1, where the difference between the uncorrected wet (light gray) and dry mole fraction (dark gray) is attributed to dilution effects because the wet mole fraction is calculated by the number of moles of the atmospheric species is divided by the number of moles in wet air. The remaining difference between the uncorrected and corrected dry mole fraction (green) is attributed to pressure broadening effects, where the corrected mixing ratio was calculated from Equation 1. In total, there was a ~3% discrepancy between the wet mixing ratio and corrected dry mixing ratio at 26,000 ppm H_2O.
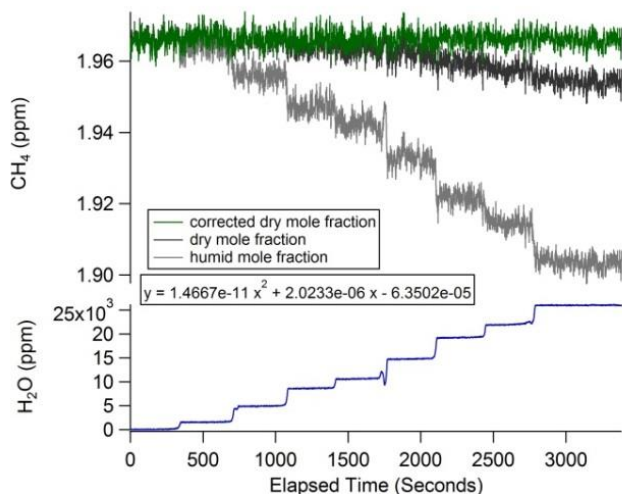

Figure S1: One stepwise test of CH_4 where moisture was added over 8 different levels from $0 - 26,000$ ppm with the uncorrected (gray) and corrected (green) mixing ratios.

The instrument was also tested for its accuracy in measuring water using a dewpoint generator (model LI-610, LI-COR Inc., Lincoln, Nebraska) which was attached to the inlet line similarly to the calibration gas tests. The measured H_2O mixing ratio was plotted against the set dew point temperature converted into ppm of H_2O in Figure S2. The FGGA underestimated the

mixing ratio of H_2O as relatively humidity was increased, although there was still a linear correlation ($R^2 = 0.9994$). As the accuracy of the dew point generator could not be properly determined, the accuracy of the FGGA was simply judged by the relative values shown in Figure S2 and the underestimation of H_2O was not corrected for within the FGGA. The absolute value of the H_2O mixing ratio was not important in the calculation of the fluxes, although the relative mixing ratio of H_2O to CO_2 and CH_4 was used to correct for dilution and pressure broadening effects.
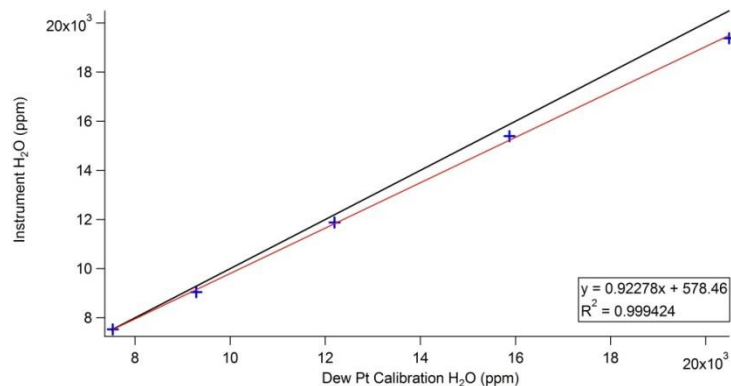

Figure S2: Calibration of water measurements using a Dew Point Generator.

B   Instrument Accuracy and Precision

The instrument was tested for its stability, accuracy, and precision before being deployed at the field site, during the field campaign, and after being brought back to the laboratory. A calibration gas (Linde Canada Ltd., Brampton, Ontario) certified at 2010 ± 100 nmol mol^{-1} for CH_4 was used to test the accuracy of the instrument. Before the instrument was brought to the field, 20 audits were conducted over a period of three months with a range in mixing ratios between $1990 - 2004$ nmol mol^{-1}. When the instrument was brought back from the field, three audits were run on the instrument with mixing ratios ranging between $1998 - 2000$ nmol mol^{-1} showing good agreement with audits run before the field campaign. An example of one high-flow audit run over 30 minutes is shown in Figure S3 conducted prior to the field campaign, where the instrument reported an average mixing ratio with the standard deviation 1876 ± 20 nmol mol^{-1} respectively using a different calibration gas with a mixing ratio of 1900 ± 95 nmol mol^{-1}. The stability of the instrument during this high-flow audit showed decreasing Allan variance over the integration times with no significant increase in Figure S4.
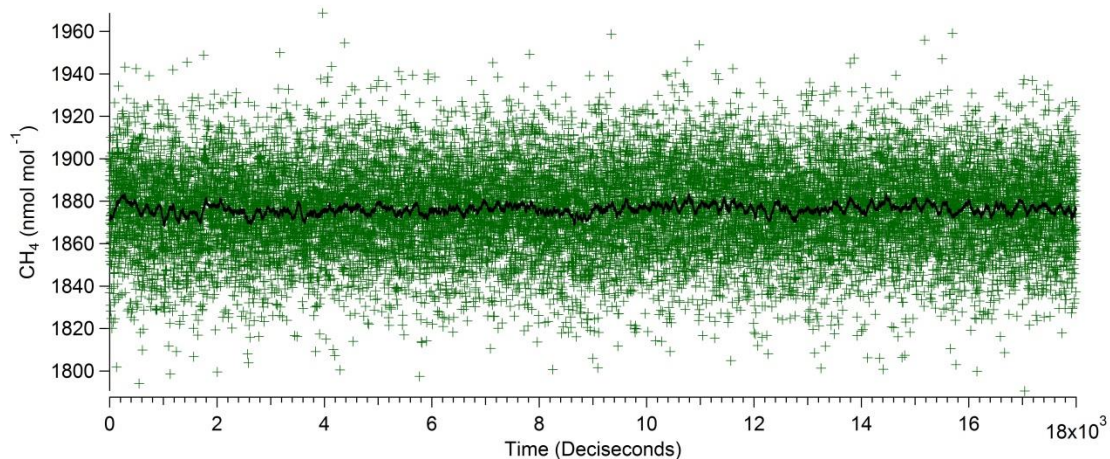
Figure S3: Time series of one audit at 10 Hz (green crosses) using high flow setting after the instrument was brought back from the field overlaid with a 10 second average.
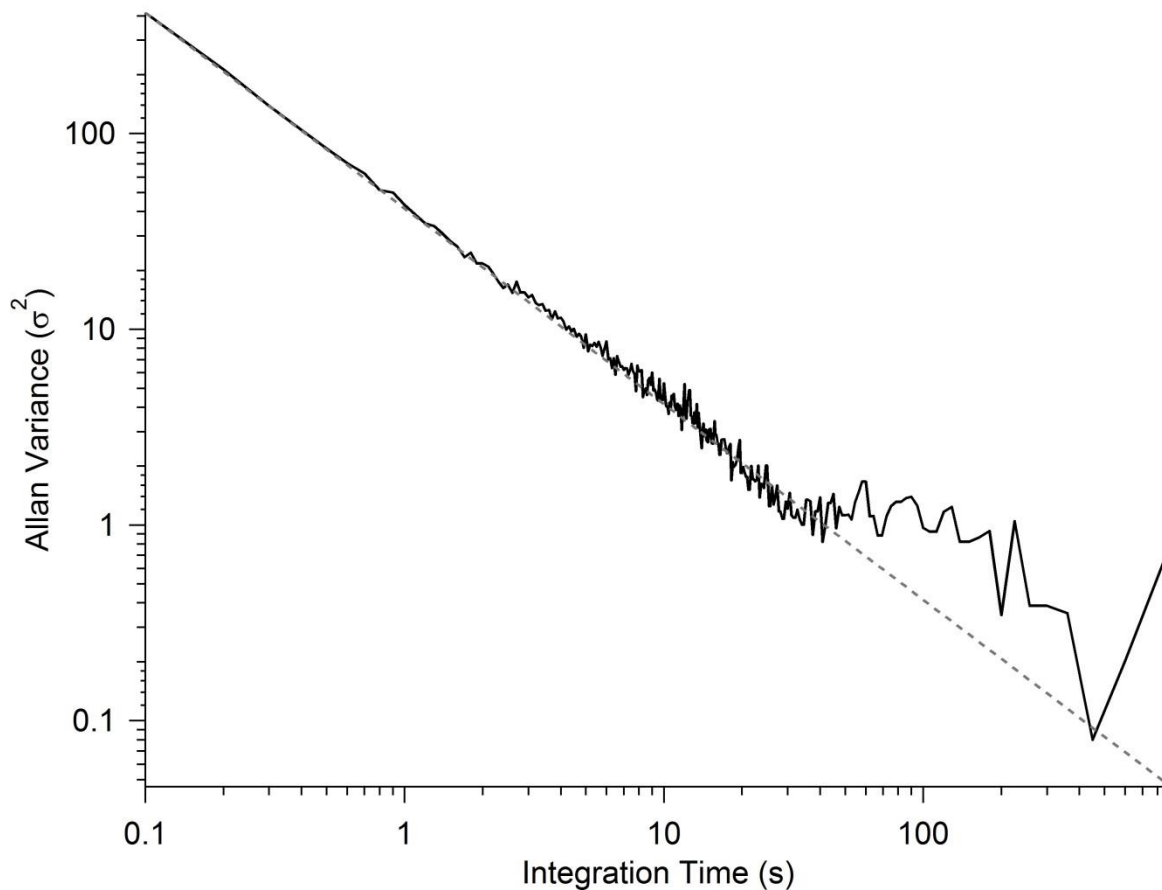

Figure S4: Allan variance plot of CH_4 with a line of slope -0.5 indicating the region of uniform spectral density Gaussian noise. Units of the y-axis are $(nmol\ mol^{-1})^2$.