Supplementary material

1. Water droplet test

Four sequential water droplet tests have been performed using the setup shown in Fig.S1. The whole experiment took ~ 7 hours. During the experiment, water droplets were injected into the inlet from a tee upstream of a particulate filter. The water droplet is to be held at the filter, and only water vapor can flow through. After air is humidified at the filter, it is split up into two paths, one with a chemical dryer (magnesium perchlorate), and the other without. The flow rate through the particulate filter is ~ 600 sccm (~450 sccm to CFADS 37, and ~150 sccm to CFADS109).
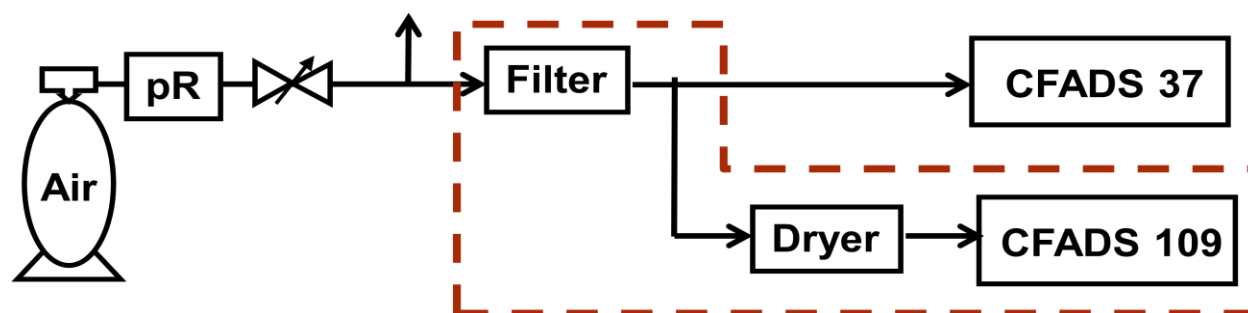


Fig.S1 Draft of the schematic of the water droplet tests.

The measurements of $CO_2$/$CH_4$/$H_2O$ by the two CRDS analyzers during the experiment are shown in Fig.S2. While the input of water vapor varies from 0 to 3.5%, the water vapor mixing ratios after the chemical dryer were measured between 0 and 0.008%, which causes deviations of less than 0.04 ppm for $CO_2$ and less than 0.2 ppb for $CH_4$ from their dry mole fractions due to the dilution and pressure-broadening effects. The deviations for $CO_2$ are accounted for by the default water corrections on the CRDS analyzer. The ph values of the water droplets are determined by a ph meter to be 4.0, 5.0, 6.3 (pure water), and 8.1 (tap water). Within the noise levels, there were no outgassing of $CO_2$ and $CH_4$ from the droplets except when tap water was used (Fig.S2).
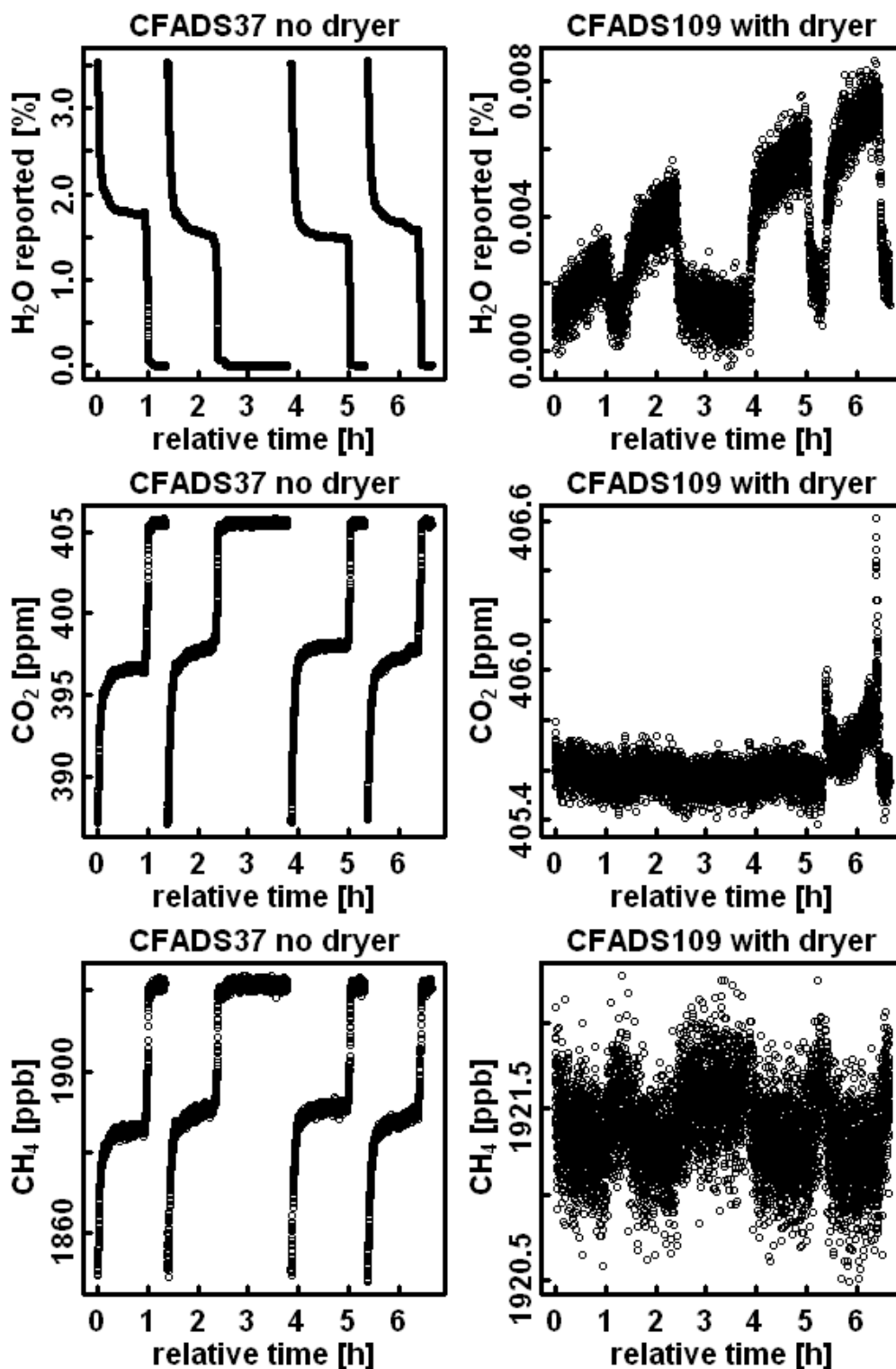
*Fig.S2 Measurements of CO₂/CH₄/H₂O mixing ratios by two CRDS analyzers, one with a dryer (left panel) and the other without (right panel), during four sequential water droplet tests with water droplets with the ph values 4.0 (acidified distilled water), 5.0 (acidified distilled water), 6.3 (distilled water), and 8.1 (tap water), respectively. The x-axis is relative to the starting time of the experiment. Note the scale differences on y-axes.*

Water corrections from each of the four water tests are derived based on two different dry values: 1) actual dry values measured by the CRDS analyzer after a chemical dryer; 2) assumed constant dry values. Instead of showing the water correction functions, we give the differences corresponding to the influences for $CO_2$ and $CH_4$ at atmospheric levels between these functions and their means (Fig.S3). When actual dry values are used, the variability of four water tests is shown to be less than 0.1 ppm for $CO_2$ and less than 1 ppb for $CH_4$ (Fig.S3a,d); when assumed constant dry values are used, the variability of the tests excluding the one using tap water (ph=8.1) is comparable to those derived based on actual dry values. The differences between the mean functions derived based on the two different dry values are less than 0.05 ppm for $CO_2$ (excluding the tap water test) and 0.5 ppb for $CH_4$.
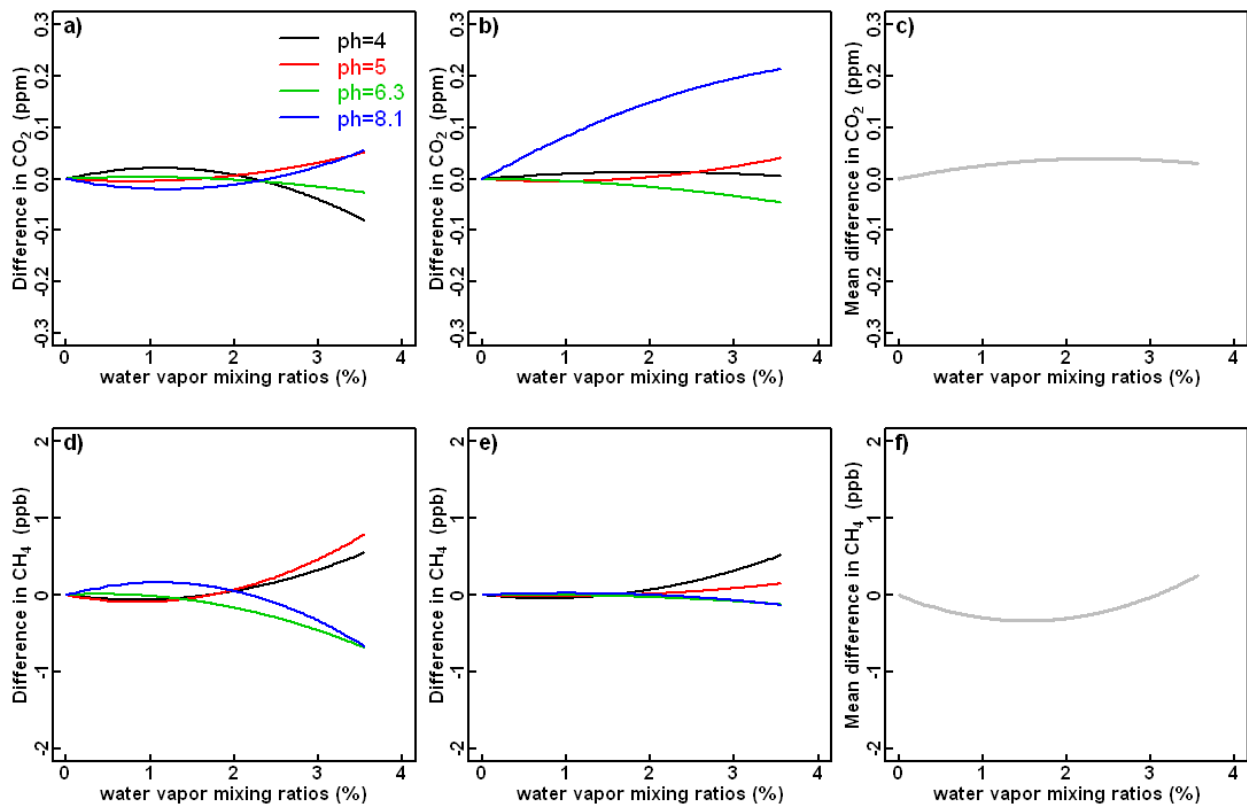


*Fig.S3 The differences corresponding to the influences for $CO_2$ and $CH_4$ at atmospheric levels between water correction functions and their means: a) and d) actual dry values are used; b) and e) assumed constant dry values are used. The ph values of the water droplets are given in the legend of a). The differences between the mean functions derived based on the two different dry values are shown for $CO_2$ (c) and $CH_4$ (f).*

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A theoretical calculation of the total amount of $CO_2$ in low salinity water (<2 ppt salinity) gives ~20 μmol $CO_2$/L when ph equals 6, and ~500 μmol $CO_2$/L when ph equals 8 (Millero et al., 1987), which corresponds to an increase of ~0.01 ppm and ~0.32 ppm in the $CO_2$ mixing ratios of the air stream when the water vapor mixing ratio is at 3.5%.

It <mark>may</mark> be critical whether the particular filter of the CRDS analyzer is clean or not. Additional $CO_2$ could be generated when the organic matter on the filter interacts with water or water vapor, especially when the water is acidified.