Supplementary material

1. Water droplet test

Carbon dioxide is highly soluble in liquid water, and can form carbonates as well, which means that the liquid water used in the droplet experiments represent a potential virtual source and sink of carbon dioxide (and to a lesser extent methane) which can affect the measurements of the correction coefficients. To investigate these effects, we have performed a series of experiments designed to probe the effect of dissolved gas in liquid water. Four sequential water droplet tests have been performed using the setup shown in Fig.S1. The whole experiment took about 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).
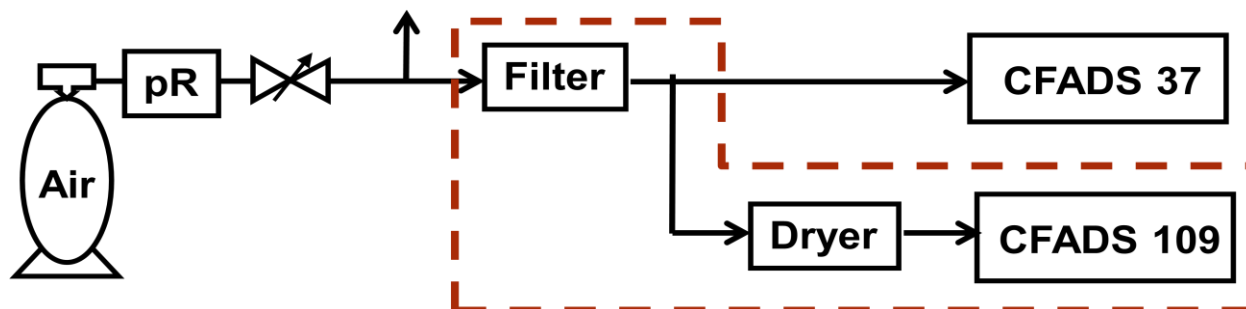

Fig.S1 Draft of the schematic of the water droplet tests.

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).
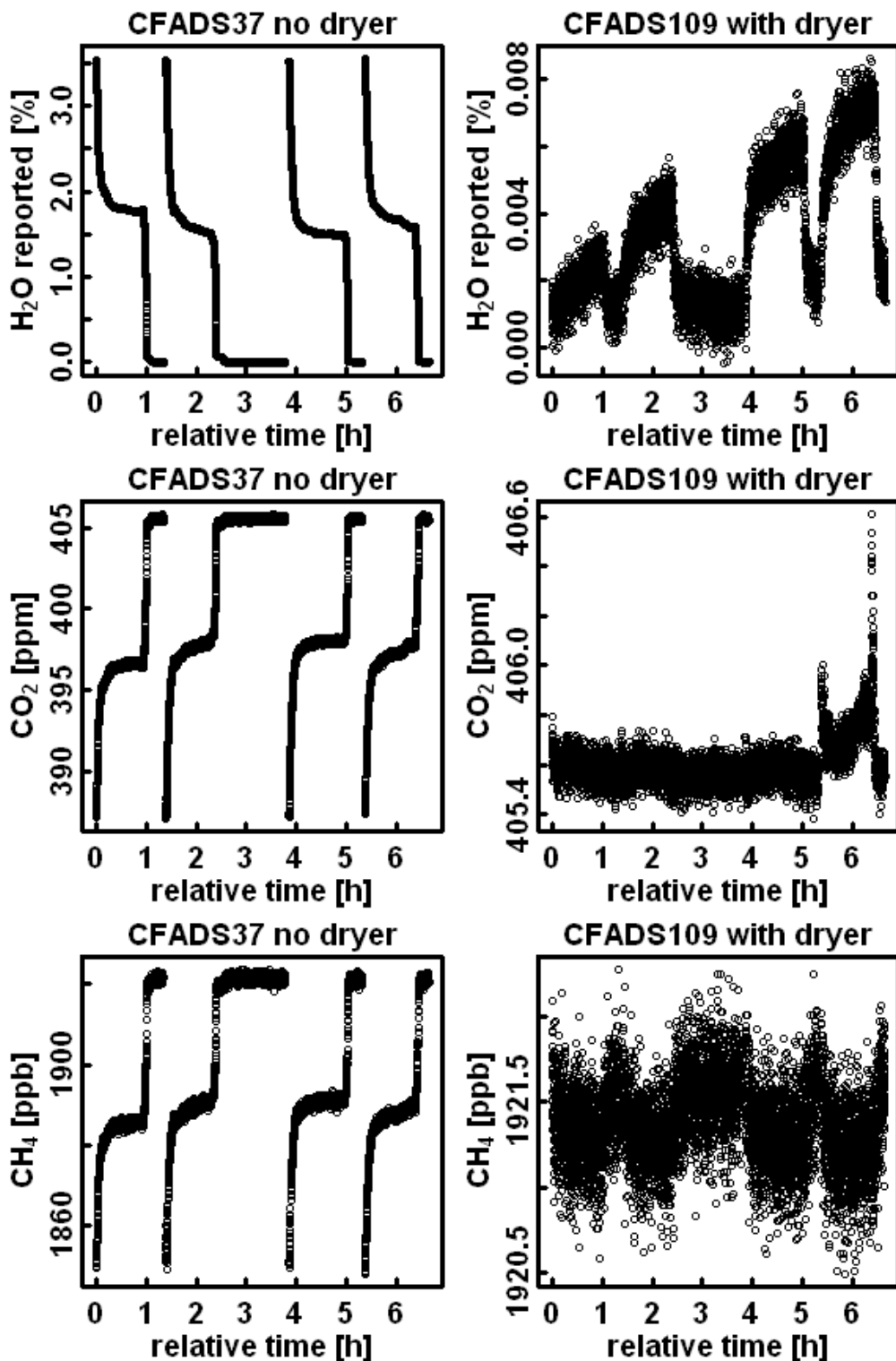
Fig.S2 Measurements of CO_2/CH_4/H_2O mixing ratios by two CRDS analyzers, one with a dryer (right panel) and the other without (left panel), during four sequential water droplet tests with water droplets with the ph values 4.0 (acidified distilled water), 5.0 (acidified distilled water), 6.3 (distilled 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. The additional of each droplet to the dry

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gas stream brings a rapid rise of the water concentration followed by a slow and irregular return to zero. Outgassing from the last droplet is visible from the tap water in the right center panel at t = 5.5 – 6.5 h.

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.
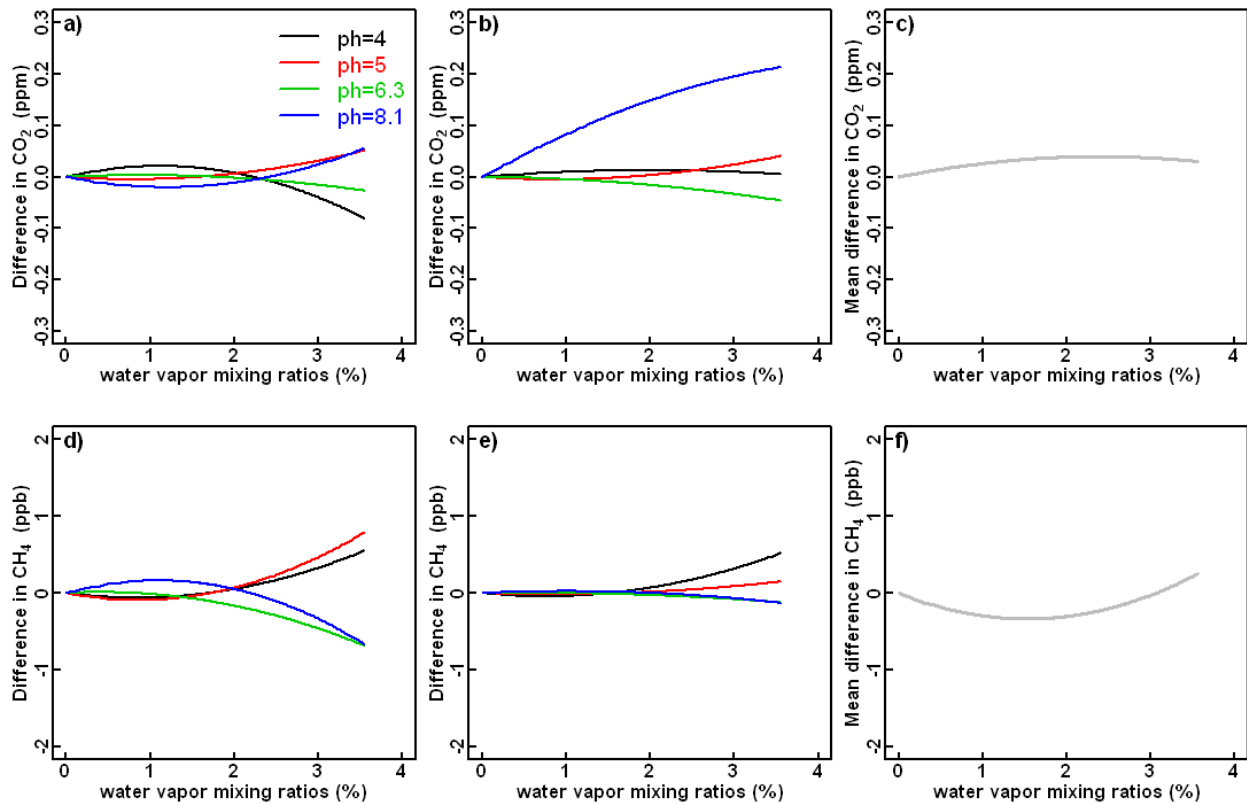

Fig.S3 The differences corresponding to the influences for CO_2 and CH_4 at atmospheric levels between water correction functions and their means: a) and d) actual dry values are used; b) and e) assumed constant dry values are used. The ph values of the water droplets are given in

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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).

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 may be critical whether the particulate 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.