Supplemental Information for

Isotopic measurements in water vapor, precipitation, and seawater during EUREC[4]A

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Contents

Introduction

This supplement provides additional information about the sampling designs and/or calibration procedures for water vapor isotopic analyzers installed at the Barbados Cloud Observatory (BCO), aboard the ATR aircraft, and aboard the P-3 aircraft. Additional information is provided about the uncertainty estimates derived from the P-3 analyzer calibrations.
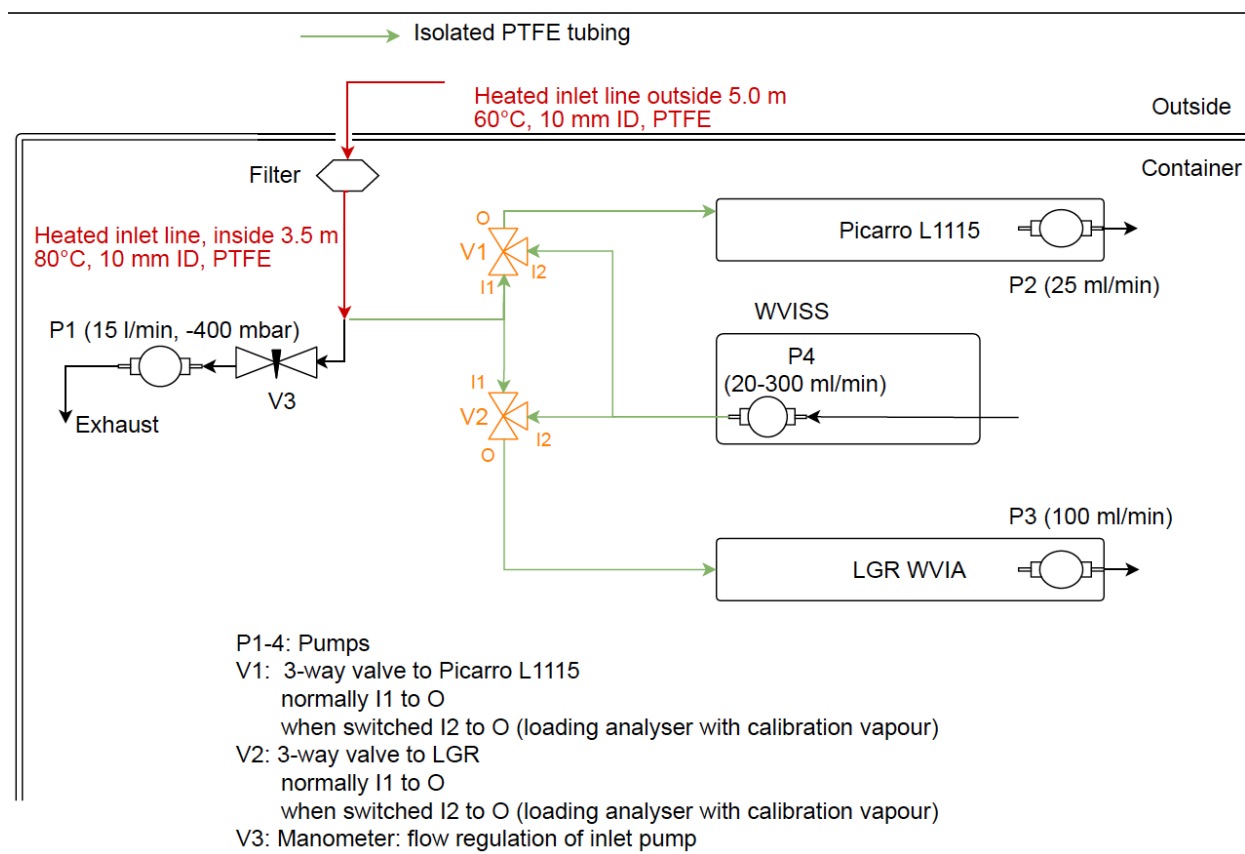

Figure S1: BCO sampling schematic. Red arrows depict the heated line that pulled ambient air into the instrument container at a rate of 15 L min⁻¹. Green arrows depict the isolated PTFE tubing through which the two water vapor isotopic analyzers – a Picarro L1115 analyzer using cavity ringdown spectroscopy (CRDS) and a Los Gatos Research (LGR) analyzer using off-axis integrated cavity output spectroscopy (OA-ICOS) – picked off sub-samples of this flow. Three-way valves (labeled V1 and V2) allowed the analyzers to alternate between measuring ambient water vapor and calibration gases, which were generated using an LGR water vapor isotope standard source (WVISS).
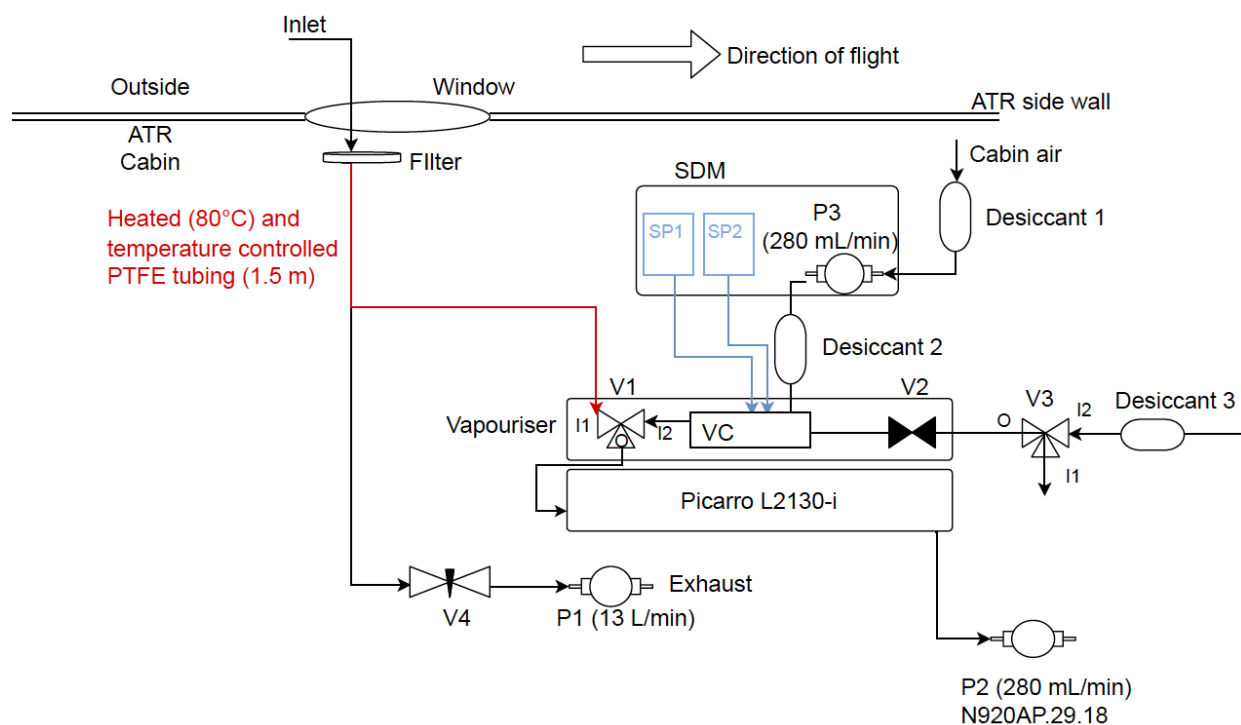
Figure S2: ATR sampling schematic. The red arrow depicts the sample flow from the inlet to a Picarro vaporizer, which was attached to the Picarro L2130-i water vapor isotopic analyzer on the aircraft. Valves inside the vaporizer determined whether the analyzer sampled ambient water vapor or calibration standards, which were pumped into the vaporizer by a Picarro Standards Delivery Module (SDM). SP1 and SP2 represent the two liquid standards delivered by the SDM.

Text S1. BCO calibration results

Calibration measurements, standard deviations, and target (reference) values for the oxygen and hydrogen isotope ratios of the two water vapor isotopic analyzers installed at BCO are provided in the accompanying spreadsheet *BCO_Cals.xlsx*. *L115* refers to the Picarro CRDS system, and *LGR* refers to the Los Gatos Research OA-ICOS system. Other abbreviations include *m* for measured, *s* for standard deviation, *cal* for calibrated, *err* for error, *diff* for difference, and *ref* for reference.

Text S2. ATR calibration results

Calibration measurements, standard deviations, and target (reference) values for the three standard waters (*STD*) run on the water vapor isotopic analyzer installed aboard the ATR are provided in the accompanying spreadsheet *ATR_Cals.xlsx*. Abbreviations are the same as described in Text S1. Functions to correct the isotopic dependence on humidity (*WVDC*), to normalize the isotope ratios to the VSMOW-SLAP (Vienna Standard Mean Ocean Water - Standard Light Antarctic Precipitation) scale, and to correct the measured water vapor concentrations are also provided. A schematic of the bubbler system used to determine the humidity-dependence correction is provided in Fig. S3.
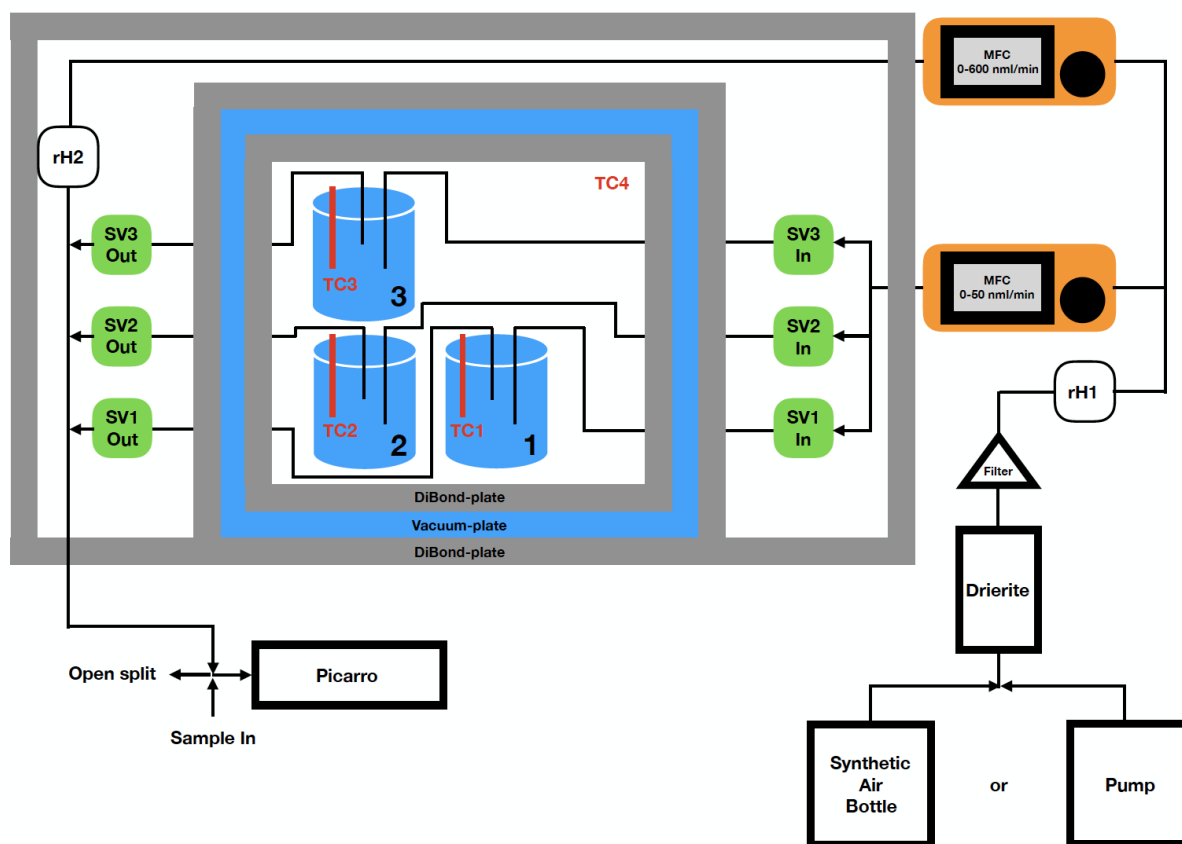

Figure S3: ATR calibration bubbler schematic. In the black pearl bubbler system used to test the humidity dependence of the isotopic measurements of the ATR analyzer (Picarro), dry air is pumped through a Drierite drying unit and separated into two streams, whose flow is controlled by two mass flow controllers (MFC, orange). One dry air stream is directed through one of three 2 L liquid standard bottles (blue). Upon passage through the bottles, the air becomes saturated in water vapor. The temperature at various points (TC 1-4) inside an isolated box, made of DiBond plates (gray) with vacuum in between, is measured to keep track of potential changes in fractionation coefficients. The saturated stream is then mixed with various amounts of dry air from the second stream, whose relative humidity is monitored at location rH2. rH1 serves as a measurement of the background humidity level.

Text S3. P-3 calibration results and uncertainty estimates

The humidity dependence of the isotopic measurements made on the P-3 aircraft was tested by diluting a moisture source of known isotopic composition to varying degrees with dry air. The dependence was checked twice before the EUREC⁴A winter 2020 field deployment, three times shortly following the deployment, and once just over one year later. Although substantial deviations in the measured isotope ratios were detected for water vapor concentrations less than 1000 ppmv, the direction and magnitude of the deviations varied depending on the isotopic composition of the calibration source relative to the isotopic composition of the water vapor sampled immediately prior. Because these variations (some of which transpired within a single 24-hour period) could be approximated crudely using a simple linear mixing model, we hypothesize that the reference gases used to test the humidity dependence were contaminated with water vapor that had desorbed from the tubing and valve surfaces of the calibration system. Such contamination prevented an accurate characterization of humidity-dependent isotopic biases.

Following guidance from the National Institute of Standards and Technology (NIST, 2021) for situations in which an "inconsistent" bias is detected, no humidity-dependent correction was applied to the P-3 isotopic field measurements. Instead, the spread in the calibration measurements was used to estimate uncertainty in the humidity dependence of the field data. To quantify this spread, the residual standard deviation (in units ‰) was calculated for humidity bins with centers at 50, 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1200, 1400, 1600, 1800, 2000, 2400, 2800, 3200, 3600, 4000, 4400, and 4800 ppmv. Modified third and second order polynomials were then fit to these standard deviations (as a function of the natural log of water vapor concentration) and then flattened for humidity values exceeding 1000 and 2000 ppmv, for $\delta^{18}O$ and δD, respectively. The polynomial fits were then used to predict uncertainties at all humidity values measured in the field.

Normalization of the P-3 isotopic measurements to the VSMOW-SLAP scale was accomplished by fitting a linear regression between the measured and known values of four liquid water standards, which were introduced to the analyzer soon after the field deployment. These standards had values of -45.41, -22.38, -14.15, and -0.28 ‰ for $\delta^{18}O$ and -355.18, -163.50, -111.65, and 1.60 ‰ for δD. Each standard was injected into a Picarro vaporizer multiple times. To minimize biases associated with hysteresis, the first 5-to-6 injections of each standard were ignored and the remaining 4-to-8 averaged to produce a single measured value. Only the last ~2 minutes of each injection were considered in the averaging. The calibration resulted in the following linear normalization functions:

$$\delta^{18}O_{cal} = 0.7848114 + 1.137206 \text{ x } \delta^{18}O_{meas} \tag{1}$$

$$\delta D_{cal} = -4.083203 + 0.9359169 \text{ x } \delta D_{meas} \tag{2}$$

where the subscripts *cal* and *meas* represent the calibrated (normalized) and measured isotope ratios, respectively. The residual standard deviations of the linear regression fits are 0.08 ‰ for $\delta^{18}O$ and 0.73 ‰ for δD.

Linear correction functions derived from normalization checks performed in the field were only used to evaluate uncertainty rather than to adjust the isotopic measurements. Liquid standards used during the in-field calibration checks were the same as those used in the post-campaign calibration except for the most enriched standard (whose in-field value was -2.17 ‰ in $\delta^{18}O$ and -8.60 ‰ in δD). Much like before, the first 2-to-3 injections were ignored and the subsequent 2-to-4 injections aggregated to derive a single calibration measurement. However, because a leak was suspected in the vaporizer used in the field, only the first minute of each injection was considered for analysis, and the median (rather than mean) was used to produce a single measured value. Comparing the normalization curves derived post-campaign with those suggested by the in-field checks resulted, over the range of standard values, in maximal (absolute) correction differences (i.e. *max_difference*) of 0.99 ‰ in $\delta^{18}O$ and 3.19 ‰ in δD. The potential errors in the normalization are thus taken as $\frac{1}{\sqrt{3}} \times$ *max_difference*. Adding these errors in quadrature with

the residual standard deviations from the humidity-dependent tests provides an estimate of total uncertainty in the P-3 calibrations. Because (normalization) corrections are applied to the sample-rate data, total calibration uncertainties are propagated (and reduced) when the sample-rate data are averaged to 1 Hz.

In addition to the reported calibration uncertainty associated with each 1 Hz isotope ratio (e.g. $\delta^{18}O_u$), there is also a standard error associated with averaging the sample-rate measurements. This standard error of the mean can be calculated from the standard deviations (e.g. $\delta^{18}O_{sd}$) and number of sample-rate points per average (*n*) provided in the 1 Hz data files. Data users wishing to be especially cautious in their analyses may wish to combine the calibration uncertainties with the 1 Hz standard errors as shown as follows for $\delta^{18}O$:

$$\delta^{18}O_{u.combined} = [\ \delta^{18}O_u^2 + (\delta^{18}O_{sd}/\sqrt{n})^2 \ ]^{-1/2} \tag{3}$$

Calibration uncertainties and standard errors can be combined equivalently for δD.

Water vapor concentrations from the P-3 isotopic analyzer were corrected independently by applying the following correction function, derived from the calibration measurements:

$$H_2O_{cal} = 1.615 \times 10^{-2}(H_2O_{meas}) - 1.574 \times 10^{-6}(H_2O_{meas})^2. \tag{4}$$

Uncertainties in the water vapor concentration were estimated from the standard errors of prediction associated with the quadratic fit.
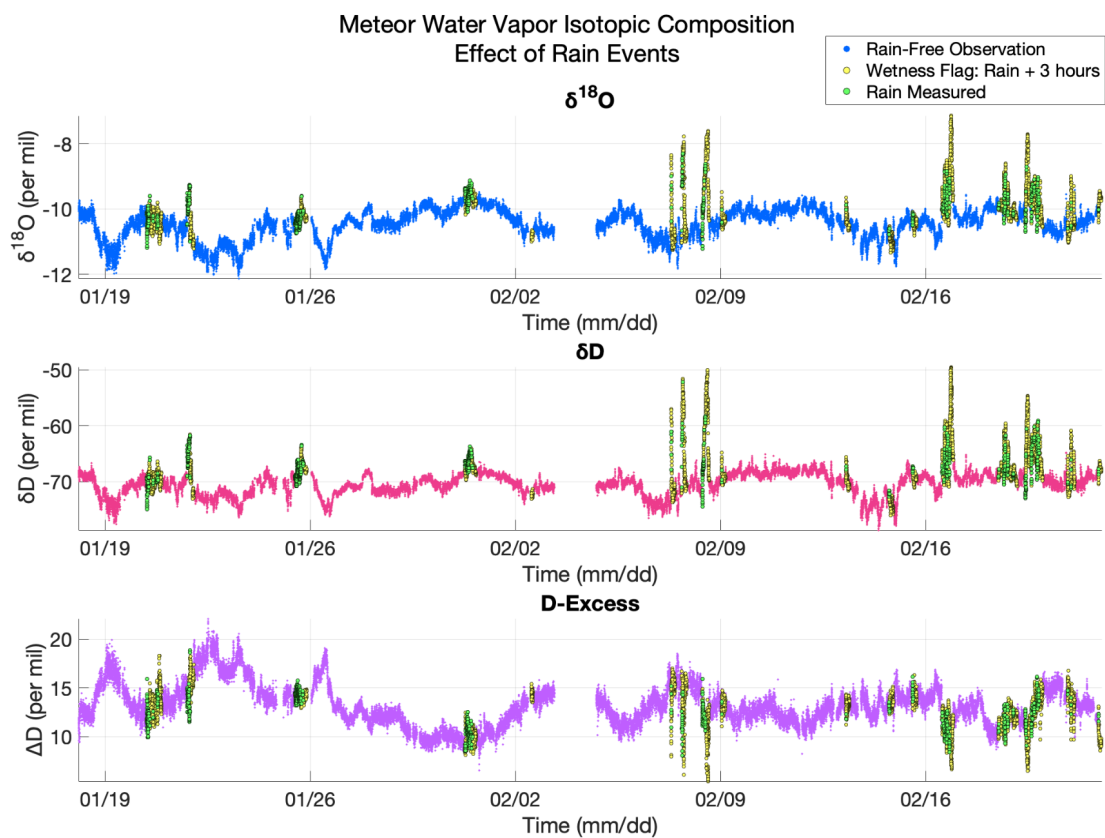
Figure S4: Meteor wetness flag evaluation. Data marked with a wetness flag in the Meteor water vapor dataset (yellow circles) exhibit atypical isotope ratio values for up to three hours following periods of rainfall (green circles).

References

NIST/SEMATECH e-Handbook of Statistical Methods, https://doi.org/10.18434/M32189, 2021.