



**Airborne profiles of
HDO/H₂¹⁶O**

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Airborne in situ vertical profiling of HDO/H₂¹⁶O in the subtropical troposphere during the MUSICA remote sensing validation campaign

C. Dyroff¹, S. Sanati¹, E. Christner¹, A. Zahn¹, M. Balzer², H. Bouquet², J. B. McManus³, Y. González-Ramos⁴, and M. Schneider¹

¹Karlsruhe Institute of Technology (KIT), Institute of Meteorology and Climate Research (IMK-ASF), Karlsruhe, Germany

²Karlsruhe Institute of Technology (KIT), Institute for Data Processing and Electronics (IPE), Karlsruhe, Germany

³Aerodyne Research Inc., 45 Manning Road, Billerica, MA 01821, USA

⁴Agencia Estatal de Meteorología (AEMET), Santa Cruz de Tenerife, Spain

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Correspondence to: C. Dyroff (christoph.dyroff@kit.edu)

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Abstract

Vertical profiles of water vapor (H_2O) and its isotope ratio D/H expressed as $\delta\text{D}(\text{H}_2\text{O})$ were measured in situ by the ISOWAT II diode-laser spectrometer during the Multiplatform remote Sensing of Isotopologues for investigating the Cycle of Atmospheric water (MUSICA) airborne campaign. We present recent modifications of the instrument design. The instrument calibration on the ground as well as in flight is described. Based on the calibration measurements, the humidity-dependent uncertainty of our airborne data is determined. For the majority of the airborne data we achieved an accuracy (uncertainty of the mean) of $\Delta(\delta\text{D}) \approx 10\text{‰}$. Vertical profiles between 150 and ~ 7000 m were obtained during 7 days in July and August 2013 over the subtropical North Atlantic Ocean near Tenerife. The flights were coordinated with ground-based (Network for the Detection of Atmospheric Composition Change, NDACC) and space-based (Infrared Atmospheric Sounding Interferometer, IASI) FTIR remote-sensing measurements of $\delta\text{D}(\text{H}_2\text{O})$ as a means to validate the remote sensing humidity and $\delta\text{D}(\text{H}_2\text{O})$ data products. The results of the validation are presented in detail in a separate paper (Schneider et al., 2014). The profiles were obtained with a high vertical resolution of around 3 m. By analyzing humidity and $\delta\text{D}(\text{H}_2\text{O})$ correlations we were able to identify different layers of air masses with specific isotopic signatures. The results are discussed.

1 Introduction

The stable isotopologues of atmospheric water (H_2O) vapor contain information about its condensation history, because the isotopologue ratios are altered whenever H_2O is subjected to phase changes (Dansgaard, 1964). Evaporation and condensation leave a fingerprint in the isotopologue ratios due to differences in vapor pressure and kinetic diffusion properties of the isotopologues (Dansgaard, 1964; Merlivat, 1978; Jouzel and Merlivat, 1984). This fingerprint is mainly depending on temperature (vapor pressure), but it also contains information of relative humidity (kinetic effect) during evaporation.

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Mixing of different airmasses induces further changes of the isotopic composition of airmasses probed (Noone et al., 2011).

In this paper we discuss changes in the ratio $R_D = D/H$ in water vapor, which are expressed with respect to the Vienna Standard Mean Ocean Water (VSMOW) reference standard as $\delta D(H_2O) = R_D(\text{Sample})/R_D(\text{VSMOW}) - 1$ (typically given in ‰).

On a global scale, remote sensing measurements of $\delta D(H_2O)$, abbreviated herein as δD , can help to better constrain the condensation history and transport pathways from the ground to the sampling location. Tropospheric profile measurements have already been reported from ground and space by means of Fourier Transform Infrared (FTIR) spectroscopy or other techniques (Kuang et al., 2003; Zakharov et al., 2004; Worden et al., 2006; Frankenberg et al., 2009; Risi et al., 2010; Randel et al., 2012; Risi et al., 2012; Schneider et al., 2012). Since changes of δD are usually small, uncertainties in its determination (accuracy) may lead to misinterpretation of the physical processes involved in the H_2O transport.

Quality assessment of remotely-sensed δD has been performed theoretically (Worden et al., 2006; Schneider et al., 2006; Schneider and Hase, 2011; Lacour et al., 2012; Schneider et al., 2012; Boesch et al., 2013). So far empirical validation studies of tropospheric δD remote sensing products have been made with very few indirect references (Worden et al., 2011), or have used a δD reference that itself was not comprehensively validated (Schneider and Hase, 2011; Boesch et al., 2013). Recently Herman et al. (2014) presented reference data for space-based remote-sensing observations of the Tropospheric Emission Spectrometer (TES), which is an important progress. However their profile measurements were limited to the lower ~ 4500 m of the troposphere and did not fully cover the altitude range of the remote sensor's peak sensitivity.

Vertical profiles of calibrated in-situ δD measurements with well known accuracy are highly desirable in order to prove the quality of remotely sensed δD . Furthermore, highly resolved in-situ profiles can serve to study small-scale (10s to 100s of meters) processes related to tropospheric humidity, e.g. cloud formation (Bolot et al., 2013) and air mass mixing (Noone et al., 2011).

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In situ measurements have been performed airborne with different techniques and on various platforms (Webster and Heymsfield, 2003; Sayres et al., 2009; Iannone et al., 2009; Sodemann et al., 2013). With the exception of (Herman et al., 2014), these measurements were performed without what we believe is a critical component especially for a validation experiment: in-flight calibration. Only if one can prove that airborne measurements of a calibration-gas standard are reproducible within the stated instrument uncertainty, these measurements are an adequate source of data for remote sensing validation purposes.

In this paper we present high-resolution tropospheric vertical profiles of δD obtained in situ by the ISOWAT airborne tunable diode laser spectrometer during the MUSICA remote sensing validation campaign. We first describe our in-situ instrument, which has been adapted from a previous prototype to meet the requirements for the profile measurements. We discuss our calibration procedure, and derive the uncertainties of our airborne data. Then the MUSICA airborne campaign is introduced, and the vertical profiles are presented. In the last part we introduce how measurements of water isotopologues trace tropospheric transport processes.

2 ISOWAT II

2.1 Instrument setup

The ISOWAT II tunable diode laser spectrometer is based on the first prototype version (Dyroff et al., 2010), which is presently being operated onboard the IAGOS-CARIBIC passenger aircraft. ISOWAT II features a number of modifications that were implemented for the instrument operation during the MUSICA aircraft campaign. The basic instrument concept is reviewed briefly, and the modifications are discussed in the following section.

The ISOWAT instrument is a tunable diode laser absorption spectrometer to measure rotationally–vibrationally resolved absorption lines of the three main isotopologues of

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water, H₂¹⁶O, H₂¹⁸O and HDO at a wavelength of $\lambda = 2.65 \mu\text{m}$ ($\nu = 3765 \text{ cm}^{-1}$). In the spectrometer (Fig. 1), the beam of a distributed feedback (DFB) diode laser (Nanoplus GmbH) is collected by an anti-reflection coated $f = 25.4 \text{ mm}$ bi-convex CaF₂ lens. The beam is then focused and steered into an astigmatic-type multipass absorption cell (MPC, model AMAC-76-LW, Aerodyne Research, Inc.) by means of a spherical-mirror telescope comprising a $f = 250 \text{ mm}$ concave and a $f = -100 \text{ mm}$ convex spherical mirror. The MPC is aligned to $N = 110$ passes to achieve a total absorption pathlength of $l = 36.1 \text{ m}$ within a volume of $V = 0.5 \text{ L}$. The beam exiting the MPC is collected and focused by a $f = 100 \text{ mm}$ spherical mirror onto the thermoelectrically (TE) cooled HgCdTe sample detector (SD, model J19-TE4, Judson Technologies).

A fraction of the laser beam is picked off by a pellicle beam splitter (P-BS, 45 %/55 %) upstream of the MPC. This beam is split again by a second P-BS and it serves two purposes. One part is guided through a 10 cm long reference-gas cell filled with a high mixing ratio of H₂O. This beam is subsequently focused onto the TE-cooled InSb reference detector (RD, model J12-TE2, Judson Technologies). Spectra from the RD are used for active locking of the laser wavelength to the absorption lines of interest by applying a feedback to the laser-injection current I_{LD} . The second part of the beam is simply passing through the optical compartment of the instrument and is focused onto the TE-cooled HgCdTe background detector (BD, model J19-TE4, Judson Technologies). The BD is used to record spectra of residual water vapor present in the optical compartment. This open-path signal component is also accounted for in the SD spectra by including it in the fit.

In addition to recording the residual humidity using the BD, for ISOWAT II the optics compartment was sealed and it was actively dried to a relative humidity below 5%. To this end, a miniature pump (MP, 1410 Series, Gardner Denver Thomas GmbH) constantly circulated air from the compartment (Fig. 1). This air was dried in a desiccant cartridge containing molecular sieve (0.3 nm pore width) before it was re-directed into the optics compartment. Furthermore the optics compartment had an open port to ambient pressure (instrument surrounding) via a second desiccant cartridge. This

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was used as ventilation for the instrument as the aircraft cabin pressure during the campaign was varying between 1000 hPa at ground level and around 450 hPa at the highest flight level.

For ISOWAT II an entirely new digital data acquisition system has been developed.

This system has two main components. A compact embedded PC (KONTRON, model pITX-SP 2.5" SBC) provides a user interface to adjust all parameters for the laser control and data acquisition. These parameters are transferred to the second component, i.e. a digital data processing unit based on field-programmable gate array (FPGA, ALTERA, model Arria GX) technology.

In ISOWAT II we employ wavelength-modulation spectroscopy (WMS) with second harmonic detection. Thereby, the laser wavelength is scanned via the laser-injection current at a frequency of $f_{\text{scan}} = 10$ Hz across four absorption lines of interest using a triangular waveform (Fig. 2). In addition, the laser wavelength is modulated with a sinusoidal waveform at a frequency of $f_{\text{mod}} = 37.5$ kHz. All waveforms are generated by the FPGA, and are converted to analog voltages using a 16-bit digital-to-analog converter (DAC).

The detector signals of SD, RD, and BD are first filtered using individual analog band-pass filters (Sallen–Key filter of 4th order, $f_{c1} = 41$ kHz, $f_{c2} = 121$ kHz) with 10 dB/dec efficiency. The individual signals are then amplified using computer controlled low-noise amplifiers in order to utilize the full range of the 16-bit analog-to-digital converters (ADC). After digitization, three individual software lock-in amplifiers realized in the FPGA demodulate the detector signals at $2 \times f_{\text{mod}}$. The demodulated signals are then fed through software low-pass finite impulse response (FIR) filters with a cut-off frequency of $f_c = 500$ Hz. The second-harmonic spectra are then transferred to the embedded PC via USB connection for storage and further processing.

In addition to the second-harmonic spectra we record direct absorption spectra of the SD for power normalization purposes. To this end, the modulated analog SD signal used for the WMS is amplified and digitized by a 16 bit ADC. A software low-pass filter with $f_c = 500$ Hz in the FPGA equivalent to the one used for WMS signals further

conditions the signal. The spectral baseline is fit with a fourth-order polynomial (thick green line in Fig. 2). Furthermore the SD dark signal was measured every 10 min by switching off the laser diode for 10 s. The direct absorption signal was used to identify changes in the laser-power transmission through the MPC.

2.2 Calibration

Similar to the first version of ISOWAT (Dyroff et al., 2010), during MUSICA the instrument was equipped with a calibration gas source for in-flight calibration measurements. To provide a calibration gas mixture of known isotopic composition, a flow of 3.5 slpm (1 slpm = 1000 cm³ air at 1000 hPa) of ambient air was first dried to H₂O < 5 ppmv in a desiccant cartridge containing molecular sieve (0.3 nm pore width). A part (0.1 slpm) of this dry air flow was humidified by passing it through a small temperature-controlled bubbler ($T = 45 \pm 0.05^\circ\text{C}$) that contained a liquid-water isotope-working standard ($\delta\text{D} = -59.22 \pm 0.7\text{‰}$). The well-known fractionation factor for evaporation of the liquid water standard is $\alpha(T = 45^\circ\text{C}) \sim 1.06$, which leads to water vapor with $\delta\text{D} \sim -116\text{‰}$. The humidified flow was then mixed into the main dry air flow to produce a calibration gas with a (pressure dependent) humidity of around 3000 and 5000 ppmv at ground level and 6000 m flight altitude, respectively.

The calibration gas was fed into ISOWAT II 2 to 5 times per flight depending on flight situation. The MPC was first flushed with the calibration gas for 7 min to allow for complete isotope exchange. Then a calibration spectrum was recorded for 2 min, after which the MPC was flushed with ambient air for 7 min before continuation of ambient-air measurements.

In addition to the in-flight calibration unit we were using a larger unit for ground-based pre and post flight calibrations. Thereby dry synthetic air (Air Liquide, ALPHAGAZ 1) from a compressed cylinder was humidified in a 2 L volume bubbler filled with 500 mL of a liquid isotope working standard ($\delta\text{D} = -59.22 \pm 0.7\text{‰}$) at a temperature of 21 °C. This humidified air was subsequently diluted into a main flow of dry synthetic air. By adjusting the flow through the bubbler as well as the main dry air flow, the calibration

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humidity could be adjusted from a few hundred ppmv to more than 30 000 ppmv at $\delta D_{\text{CAL}} \sim -137\text{‰}$.

The relatively large amount of liquid isotope standard used in the ground-based calibration unit was replaced daily. This was effectively reducing drift in the isotopic composition due to evaporation of the bulk water source to $< 0.5\text{‰}$ in 4 hours of calibration. This drift was accounted for in the data analysis. The ground-based calibration unit was independently examined prior to the campaign using a laboratory-based Picarro water isotope analyzer in combination with a Standard Delivery Module (SDM). The repeatability was found to be better than 0.5‰ for δD , and the uncertainty in the measurement of the liquid standards was 0.7‰ . The in-flight calibration source was cross-calibrated by three measurements before and after each flight using this primary standard.

A dew-point hygrometer (Edge Tech, model DewMaster) was occasionally connected in parallel to ISOWAT on the ground in order to perform absolute humidity measurements that served as calibration of the H_2^{16}O and HDO absorption line fit.

2.3 Data handling

Ten second-harmonic ($2f$) spectra are averaged in 1 s and normalized by optical power at the sample detector (P_{LD}). We therefore use the spectral baseline of the simultaneously recorded direct absorption channel together with the detector zero signal. The latter is linearly interpolated between measurements taken every 10 min where the laser was switched off for 10 sec. The normalized $2f$ spectra are then divided into windows around the individual absorption lines.

For the strong H_2^{16}O line we determine the peak-to-peak amplitude $A_{\text{H}_2^{16}\text{O}}$ based on the signal at line center and the minima of the two negative lobes of the $2f$ absorption line. This is then compared to $A_{\text{H}_2^{16}\text{O}}$ from a previously recorded calibration spectrum in order to derive the H_2O mixing ratio. The shape and amplitude of the strong H_2^{16}O line are considerably affected by absorption-line self broadening (Burch et al., 1962).

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The other absorption lines are much less affected by line broadening, and in each fit window a linear least squares fit is performed using singular value decomposition (SVD) (Dyroff et al., 2010). The SVD fit includes constant and linear baseline terms, as well as the line component from the calibration spectrum, and it yields the mixing ratio of the individual isotopologues. From the mixing ratios the isotopologue ratios are determined.

First we transferred the peak-to-peak absorption-line signal $A_{\text{H}_2^{16}\text{O}}$ onto a humidity scale based on the humidity calibrations performed using the dew-point hygrometer. Then we determined the humidity dependent correction functions $\text{CF}(\text{H}_2\text{O})$ for the raw isotopologue ratio $R_{\text{D}}^* = \text{HDO}/\text{H}_2^{16}\text{O}$ as depicted in Fig. 3a. For the $\text{CF}(\text{H}_2\text{O})$ of the strong H_2^{16}O line we use an empirical 6th-order polynomial, and for the $\text{CF}(\text{H}_2\text{O})$ of the weak line a first-order polynomial (black traces in Fig. 3).

In order to transfer the raw R_{D}^* to δD on the VSMOW scale, we first divide the individual R_{D}^* measurements by the daily average $\text{CF}(\text{H}_2\text{O})$. We then multiply by the isotopologue ratio of the calibration gas $R_{\text{CAL}} = R_{\text{VSMOW}}(\delta\text{D}_{\text{CAL}} + 1)$, where $R_{\text{VSMOW}} = 3.10693 \times 10^{-4}$, and obtain δD by solving

$$\delta\text{D} = \frac{R_{\text{D}}^*}{\text{CF}(\text{H}_2\text{O})} R_{\text{VSMOW}}(\delta\text{D}_{\text{CAL}} + 1) - 1. \quad (1)$$

Figure 3b depicts this procedure for the calibration measurements of 25 July 2013. The black dashed lines indicate the uncertainty range, which is defined as the range of data in which 1σ of the data fall.

Note that we have defined a transition interval between 10 000 and 12 000 ppmv in which we make use of both the strong and the weak H_2^{16}O absorption line. In this interval, the individual fit results are used in a humidity-weighted manner in order to achieve a smooth transition between the two fit regimes.

2.4 Uncertainty estimate

The uncertainty of our δD measurements was derived from the calibration measurements that were performed on every flight day before and after each flight as described in Sect. 2.2. We define the uncertainty as the SD of all daily calibrations to the daily mean humidity correction function for a given humidity interval h :

$$\Delta(\delta D)_h = \sqrt{\left[\frac{1}{n-1} \sum_{i=1}^n (\delta D_i - \delta D_{\text{CAL}})^2 \right]_h} \quad (2)$$

The uncertainty was determined in humidity intervals (h) of 10 ppmv between 100 and 25 000 ppmv, and it is depicted for all flight days as black traces in Fig. 4.

Any differences in the instrument response before and after the flight was assigned to instrumental drift. Even though the instrument temperature was greatly stabilized, the drift was most likely caused by changes in the temperature of not well temperature-stabilized components (see Sect. 2.5 for detailed discussion).

In addition we have used the in-flight calibration measurements to verify that our uncertainty estimate was justified. The difference of these calibration measurements to the expected δD of the in-flight calibration gas standard is depicted as blue diamonds in Fig. 4. These differences are generally better or equal to the uncertainty estimation. We are thus confident that the instrumental uncertainty of our flight measurements is equal to or better than the stated uncertainty estimate.

2.5 Sources of uncertainty

We have identified two main factors that define the measurement uncertainty of ISOWAT II. They are differently effective throughout the investigated humidity range.

At humidities below ~ 1000 ppmv, optical interference fringes superimposed onto the measured absorption spectra become relevant as the measured absorption signal becomes weak. The fringes in our system during the MUSICA campaign were with

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OD $\sim 1\text{--}2 \times 10^{-4}$ about 1.5–3 times higher than currently in ISOWAT-I (Dyroff et al., 2010), and their free spectral range were such that they could not easily be distinguished from the absorption lines by our absorption line fit. The phase of the fringes was also changing due to slight changes in instrument temperature, which prohibited the recording of the fringes once for later subtraction while sampling dry air (background spectrum). The fringes affected mostly the HDO line at dry conditions as well as the weak H₂¹⁶O line below 15 000 ppmv. For example, the fractional absorption of HDO at 200 ppmv and $\delta D = -400\text{‰}$ is around 4.2×10^{-4} , i.e. a signal to fringe ratio of $\sim 2\text{--}4$.

An array of residual spectra is depicted in the lower panel of Fig. 5. By repeatedly modulating the temperature of the anti-reflection coated $f = 25.4$ mm CaF₂ collection lens (top panel in Fig. 5) we were able to identify this lens as the source of the most dominant fringe.

In a laboratory test after the campaign, replacement of this lens by a reflective mirror objective has reduced the overall fringe level by a factor of 2. Importantly, the fringe free-spectral-range (FSR) has become shorter by a factor of 3 to 4. This will potentially make fitting of the fringe structure easier for future measurements. We plan to carefully re-design the optical setup of ISOWAT based on the results using the mirror objective.

The second factor affecting the instrumental uncertainty was related to slight changes in the temperature of the laser-gain medium. In the present instrument, this temperature is set to a constant value ($\sim 28^\circ\text{C}$). Then the laser emission wavelength (λ_{LD}) is tuned by sweeping the laser-injection current (I_{LD}). Despite setting T_{LD} to a constant value, T_{LD} was drifting during instrument operation. We actively control the DC component of I_{LD} in order to maintain the wavelength scan in the spectral window around the absorption lines of interest (line lock). Adjusting the DC component of I_{LD} changes the operating point of the laser. This affects the nonlinear response of laser power (P_{LD}) and λ_{LD} to a sweep of I_{LD} . Changes in P_{LD} are accounted for by normalizing the second-derivative spectra by the direct-absorption spectra. Changes in the wavelength tuning of the laser lead to a distortion of the recorded spectra. As we determine

mixing ratios and δD by fitting of ambient spectra to a previously recorded calibration spectrum, this distortion of the spectra adds uncertainty to the fit.

It was found after the campaign that the major source of temperature drift was a temperature-dependent potentiometer (100 ppm K^{-1}) on the commercial laser-driver unit. The resistance of this potentiometer changes due to changes in ambient temperature, which in turn changes the temperature setpoint of the laser-temperature control loop. Replacing this potentiometer with a fixed resistor with low temperature coefficient (2 ppm K^{-1}) will minimize the change of the temperature setpoint.

Meanwhile, we have developed an improved stabilization of the laser-operating point by implementing a second control loop. In this approach we additionally control the temperature of the aluminum mount of the laser diode using resistive heaters. The temperature of the mount is adjusted such that λ_{LD} is maintained stable, which is determined by analyzing the position of the absorption lines within the reference-detector spectra. This in turn allows to maintain the DC component of I_{LD} constant. Consequently the laser operating point is stabilized. First tests in the laboratory have shown that this approach minimizes the drift of the laser-temperature setpoint by a factor of 11 even when using the temperature-sensitive potentiometer.

3 MUSICA aircraft campaign

3.1 Objective and realization

The primary goal of the MUSICA airborne campaign was to perform validation measurements for two remote sensing instruments, (i) the satellite-borne Infrared Atmospheric Sounding Interferometer (IASI) instrument on both the MetOp-A and -B satellites, and (ii) a ground-based Fourier Transform Infrared (FTIR) spectrometer at the Izaña meteorological observatory (IZO). The second goal was to investigate transport and processing of water vapor in the North Atlantic free troposphere.

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Seven research flights were conducted from Las Palmas Airport (LPA), Canary Islands, Spain. The Canary Islands are located in the subtropical North Atlantic approximately 200 km west off the coast of Morocco at 28° N latitude (Fig. 6). The flights were coordinated in time and location with the morning overpasses of the MetOp-A and -B polar-orbiting satellites (Klaes et al., 2007). Both satellites are equipped with an IASI instrument as scientific payload (Blumstein et al., 2004). IASI measures nadir radiance spectra from which tropospheric H₂¹⁶O, HDO and δD vertical profiles are retrieved (Schneider and Hase, 2011). MetOp overpasses took place on a trajectory from north-east to southwest, where IASI scanned transversal to its flight direction. The individual spectra were filtered based on data quality and cloudiness as described in (Wiegele et al., 2014). The ground location of all quality-filtered vertical profile measurements obtained during the campaign is depicted as circles in Fig. 6.

The aircraft flights were performed in the line of sight of the ground-based FTIR instrument stationed at IZO. The FTIR measures solar absorption spectra to retrieve vertical profiles of H₂¹⁶O, HDO and δD in the troposphere (Schneider et al., 2012). The blue lines in Fig. 6 indicate the line of sight for the beginning and the end of the profile flight on 24 July 2013. The aircraft flight track of this day is shown as red trace in Fig. 6.

The flights started with a relatively fast ascent to the ceiling altitude of the aircraft (~ 6800 m). The aircraft crew was then waiting for the overpass of the satellites before performing a slow cascaded descent with up to ten selected levels. The levels were held for 5 min. Each flight took around 3.5 h.

3.2 Aircraft and instrumentation

For the campaign, several research instruments were mounted in a CASA C-212-200 (Fig. 7) of the Instituto Nacional de Técnica Aeroespacial (INTA). The C-212 is a medium-sized transport aircraft powered by two turboprop engines. It has an unpresurized cabin and can reach a maximum ceiling altitude (depending on payload) of

around 23 000 ft (7000 m) with the requirement for oxygen use by the pilots and operators.

ISOWAT II was mounted in the foremost position of the aircraft cabin. Ambient air was sampled by a rearward facing stainless steel inlet with 0.25 inch (6.35 mm) outer diameter mounted on top of the aircraft fuselage (Fig. 7). A flow through the inlet line of around 15 slpm (1 slpm = 1000 cm³ air at 1000 hPa) at ground level and around 6 slpm at the aircraft ceiling level was established by a membrane pump (MD1 VARIO SP, vacuubrand GmbH) downstream of the ISOWAT II instrument. Inside the aircraft, heated ($T = 40^{\circ}\text{C}$) electropolished stainless-steel tubing (ULTRON, Dockweiler AG) was used to connect the inlet system to the instrument. A flow of 1.5 slpm was branched off the main flow and fed into the ISOWAT II instrument for isotope ratio measurements.

3.3 Meteorological conditions

Two different meteorological conditions were encountered during the MUSICA campaign, which also mark the predominant conditions at the Canary Islands in summer.

During the days 21 July 2013, 25 July 2013, and 30 July 2013 the marine boundary layer (MBL) was well separated from the free troposphere (FT) by a temperature-inversion layer at an altitude of around 1100 m. This inversion is a consequence of large-scale subsidence in the downward branch of the Hadley circulation (Cuevas et al., 2013). The subsiding air is adiabatically warmed as it reaches lower altitudes, thus yielding a well developed temperature-inversion layer. In the MBL, winds from North East were encountered, while in the FT the wind came from North West. We refer to these meteorological conditions as North Atlantic owing to the airmass origin in the FT.

During the days 22 July 2013, 24 July 2013, 31 July 2013, and 01 August 2013 warm and mineral-dust laden air reached the Canary Islands from the east in a layer of variable thickness at an altitude of approximately 2 to 5 km. This Saharan Air layer (SAL) was positioned above a layer of MBL air, and it presumably originated from the African Boundary Layer (Rodríguez et al., 2004; Alonso-Pérez et al., 2011; Cuevas et al., 2013). We refer to these conditions as Sahara.

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Figure 8 shows satellite images of the Moderate Resolution Imaging Spectroradiometer (MODIS) instrument of the days 21 July 2013 (a) and 31 July 2013 (b). In Fig. 8b one can observe the dust-laden air as the hazy area in the right half of the image. Note that the images are daily composites and may not reflect the conditions during the actual hours of flight. The flight tracks are depicted as red traces.

4 Results

Figure 9 presents an overview of the vertical profiles of H₂O and δD as well as the estimated total uncertainty of the isotope ratio $\Delta(\delta D)$ (see Eq. 2) with a temporal resolution of 1 s. The black symbols show all in-flight calibration measurements that were performed during the campaign. We note that the uncertainty of the in-flight calibrations is in most cases smaller than $\Delta(\delta D)$. This provides good evidence that our uncertainty estimate can be understood as an upper limit.

For better clarity we only show in Fig. 9 the data of the descending branches of the flights. Ascent and descent took place at different times, and more importantly at slightly different longitudes. We noticed strong longitudinal gradients in some of the flights, which prohibits averaging of the ascent and descent profiles. Good agreement of ascent and descent data is found where longitudinal gradients were low or sampling locations coincided.

For a more detailed analysis we shall have a closer look at the measurements during the descending branch of the flight on 31 July 2013. Figure 10 shows the corresponding vertical profiles of temperature (T), H₂O mixing ratio, and δD .

Studying the vertical profile in Fig. 10 reveals large spatial gradients in humidity and isotopic composition. We can divide the profile in 5 different layers.

1. The lowest layer between sea level and ~ 440 m is characterized by a rather constant T , H₂O, and δD .

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2. Above this layer we observed a well defined temperature inversion, which came along with a sharp negative gradient in both H₂O and δD . At its minimum at an altitude of ~ 900 m, H₂O decreased to less than 2000 ppmv (relative humidity $\sim 8\%$) at $\delta D < -300\%$.
3. A third layer starts at ~ 1025 m with a sharp positive gradient of H₂O and δD , which is then followed by relatively constant humidity and slightly increasing δD until an altitude of around 1900 m.
4. The fourth and thickest layer is characterized by a column of high humidity and high δD , which stretches nearly 3.5 km between around 1900 m and 5350 m altitude. It is a weakly stable layer with a temperature lapse rate of 8.6 K km^{-1} .
5. At an altitude of around 5350 m we encountered an abrupt decrease in both H₂O and δD as the aircraft flew at constant altitude in easterly direction. Above we measured the lowest humidity at around 430 ppmv and $\delta D \approx -370\%$.

In order to investigate the processes that may have lead to the observed humidity distribution, we depict δD as a function of H₂O (Fig. 11). By doing so it becomes immediately evident that δD measurements provide additional information, because we observed a rather large range of δD for similar humidity, especially when between around 1000 ppmv and 8000 ppmv. We may now be able to identify individual hydration processes by comparing our measurements with model calculations. The Rayleigh model describes an atmosphere in which water vapor condenses at a relative humidity of 100% and the condensate is immediately removed from the atmosphere by precipitation. The isotopic composition of the condensed phase is defined by the temperature-dependent vapor-pressure isotope fractionation (Dansgaard, 1964). The heavy isotopologue HDO condenses preferentially over H₂¹⁶O due to its lower vapor pressure. The remaining vapor is becoming more depleted in HDO as the air becomes dryer.

Here we consider ocean water as the major source of atmospheric vapor. Around the Canary Islands, the ocean water has $\delta D_{\text{ow}} \approx +7\%$ w.r.t. VSMOW (Benetti et al.,

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2014). The sea surface temperature (SST), which is used to derive the initial isotope fractionation during evaporation, was around 22.5°C (NOAA_OI_SST_V2 data, <http://www.esrl.noaa.gov/psd/>). Assuming a relative humidity w.r.t. SST of $RH_{SST} = 80\%$, the initial vapor has $H_2O \approx 23\,000$ ppmv and $\delta D_{ev} \approx -70\text{‰}$ with respect to the liquid source reservoir. The gray shaded area in Fig. 11 depicts a range of Rayleigh models for $\delta D_{ow} = 0\text{‰}$ (lower boundary) and $\delta D_{ow} = +7\text{‰}$ (upper boundary).

First consider the most humid measurements (layer 1) marked with (1) in Fig. 11. These measurements were taken at an altitude of less than 440 m above the ocean, and they are around 20‰ above the Rayleigh model. The elevated δD may be due to the evaporation of a fraction of sea spray into the lower atmosphere, i.e. a process suggested e.g. by Benetti et al. (2014).

We note that on this particular day the wind above the ocean was strong, and the lowest atmospheric layer was very hazy. This was confirmed by particle concentration measurements (not shown), which showed elevated concentrations of small particles (size < 3 μm) below 500 m altitude.

If the droplets evaporate (even partially), δD of the vapor becomes less negative (Gat et al., 2003; Benetti et al., 2014). We can estimate the fraction F of sea spray that evaporated without fractionation and mixed with evaporated ocean water by solving

$$\delta D = F\delta D_{ow} + (1 - F)\delta D_{ev}. \quad (3)$$

Here $\delta D = -50\text{‰}$ was measured and $\delta D_{ow} = +7\text{‰}$ as well as $\delta D_{ev} = -70\text{‰}$ are assumed. Consequently $F = 0.26$, i.e. 26% of the total water vapor may have originated from the evaporation of sea spray without significant fractionation. Analyzing H₂O vapor samples for their δD , Gat et al. (2003) concluded that in this particular study up to 50% of the H₂O vapor may have originated from evaporated sea spray.

Above this humid layer we observed a very sharp humidity gradient, where the humidity decreased by more than one order of magnitude. This data (layer 2) remains close to the theoretical Rayleigh model (blue data in Fig. 11). This suggests that the dehydration of this air occurred predominantly close to isotopic equilibrium as the air-

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mass was lofted and cooled. These observations were taken in the (locally) warmest layer, where the lowest humidity suggests a temperature of last condensation of around -12°C at the sampling pressure. This in turn leads to the conclusion that this air mass must have originated from much higher than the sampling altitude. Descent and adiabatic warming lead to a strong decrease of relative humidity vs. ice (RH_i) to $\text{RH}_i \sim 8\%$ (not shown), a process termed subsidence drying (Sherwood et al., 2010). The altitude of origin of this air mass was above 5000 m.

At an altitude between 1000 and 1900 m (layer 3), we observed a steady increase of δD , while the humidity remained relatively constant at around 3000 ppmv. This transition is well defined in Fig. 11 and shows a very tightly correlated group of data (medium blue).

In layer 4 extending between around 1900 m and 5400 m, we observed a relatively compact distribution of δD and humidity. There, δD is significantly elevated with respect to the Rayleigh model. This suggests that a considerable fraction of the water content is originating from processes other than slow ascent and dehydration of boundary layer air. A model based on the method described by Noone et al. (2011) that describes mixing of moist air typical of the marine boundary layer (MBL; $\text{H}_2\text{O} = 22\,900$ ppmv, $\delta\text{D} = -75.6\text{‰}$) and dry air from the upper troposphere (UT; $\text{H}_2\text{O} = 1100$ ppmv, $\delta\text{D} = -385\text{‰}$) excellently fits our observations (solid line (4) in Fig. 11).

Layer 4 also showed elevated concentrations of dust (not shown) which originated from the Sahara desert (see Fig. 8). This suggests that the observed air mass is likely a mixture of MBL air, continental Saharan boundary layer (BL) air, and dry air of the UT. The range of humidity and δD suggest that we observed different fractions of moist and dry air. At the top of this layer we observed an abrupt change towards dry UT air with δD close to the Rayleigh model.

Above 5400 m (layer 5) we observed a dryer layer spanning a large range of δD between -200 and -380‰ . The measurements could be fit to a mixing model line between a low-altitude reservoir of $\text{H}_2\text{O} = 4900$ ppmv and $\delta\text{D} = -133\text{‰}$, and a higher-altitude reservoir with $\text{H}_2\text{O} = 500$ ppmv and $\delta\text{D} = -373\text{‰}$ (solid line (5) in Fig. 11).

5 Conclusions

In this paper we present details of an instrument and methods to perform measurements of δD . The instrument and methods were successfully applied in vertical-profile flights during the MUSICA airborne research campaign at the Canary Islands in the summer of 2013 (Schneider et al., 2014). The campaign mainly focused on the validation of remote sensing measurements from ground and space by performing simultaneous in-situ measurements. The airborne sampling measurements were performed with the ISOWAT II tunable diode laser spectrometer. Modifications to ISOWAT (Dyroff et al., 2010) were implemented prior to the campaign aiming to provide measurements with better accuracy and well-defined uncertainty.

During the MUSICA campaign seven flights were performed during which vertical profiles of δD in the troposphere in the subtropical North Atlantic near Tenerife were measured. The profiles were ranging between sea level and around 7 km altitude. The flights were coordinated in time and space with δD remote-sensing measurements from ground by the FTIR spectrometer at Izaña, Tenerife, as well as from space by the IASI instruments onboard the MetOp A and B polar orbiting satellites.

With ISOWAT II we demonstrated δD measurements in-situ with a temporal resolution of 1 s. This translated to a horizontal resolution of around 75–95 m and vertical resolution of around 3 m. This allowed resolving even very sharp vertical gradients found both in humidity and δD . A rather extensive calibration protocol allowed determining a robust uncertainty estimate of our δD measurements, i.e. a mandatory requirement for validation measurements. The uncertainty is depending on humidity. For most conditions during the campaign the uncertainty was around 10%. Only in the arid upper troposphere the uncertainty was somewhat higher.

Using one flight as an example, five different airmass layers could be identified. Their humidity could be analyzed based on the H_2O and δD measurements, as well as using relatively simple models for dehydration and airmass mixing. Further data analysis is

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presently being done to better describe both large and small-scale atmospheric processes based on our measurements.

In a recent paper by Schneider et al. (2014), the ISOWAT II in-situ measurements presented here were used for a first validation of space and ground-based remote sensing measurements of δD . We aim to enlarge the data set for this purpose by performing regular profiling of the troposphere with a new version of ISOWAT onboard the IAGOS-CARIBIC passenger aircraft (Brenninkmeijer et al., 2007).

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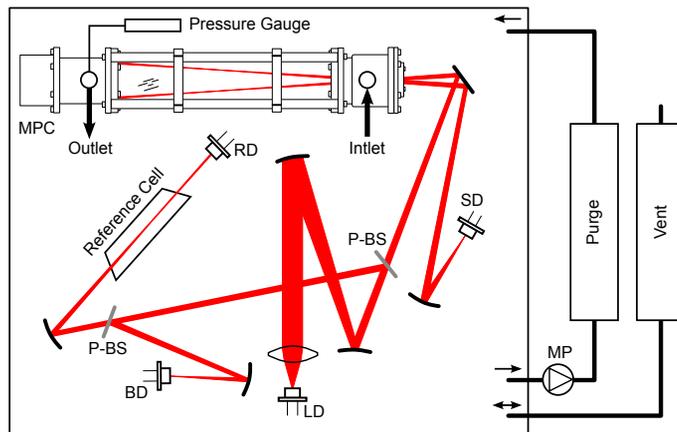


Figure 1. Optical system of the ISOWAT II spectrometer. LD: laser diode; P-BS: pellicle-beam splitter; MPC: multipass cell; SD: sample detector; RD: reference detector; BD: background detector; MP: miniature pump.

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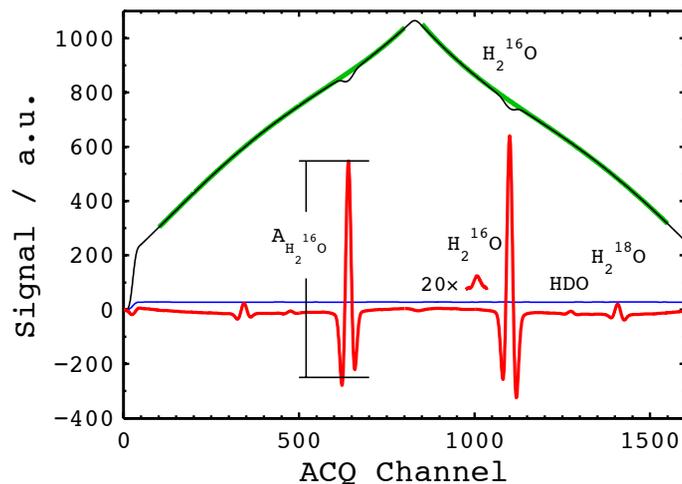


Figure 2. Example spectra of ISOWAT II showing the up and down scan across the absorption region of interest. Polynomial baseline (green trace) of the direct absorption spectra (black trace) as well as detector zero signal (blue trace) are used to normalize the second-harmonic absorption spectra (red trace). $A_{\text{H}_2^{16}\text{O}}$ is the peak-to-peak amplitude of the strong H_2^{16}O absorption line. The weak H_2^{16}O line used in humid conditions is depicted 20× enlarged.

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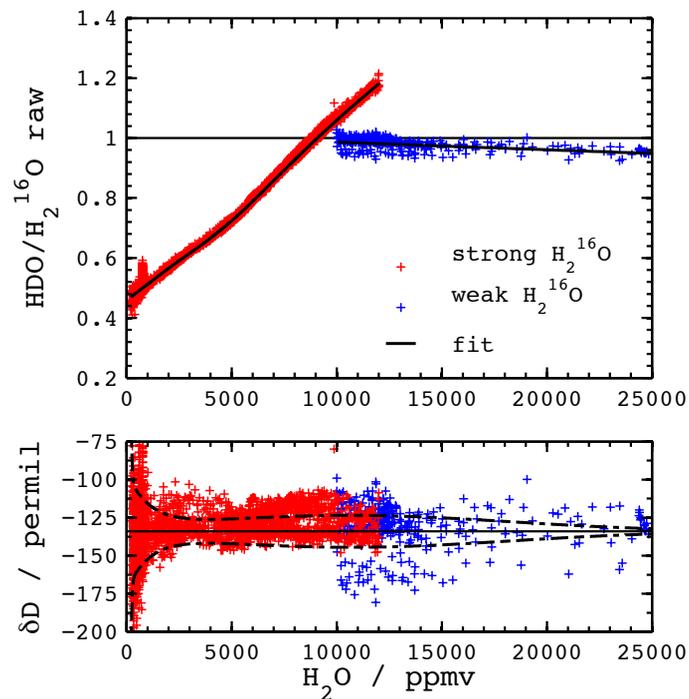


Figure 3. (a) Individual calibration measurements on 25 July 2013 prior and post flight together with the daily average calibration functions for strong (red) and weak (blue) H₂¹⁶O line fit. (b) Calibration measurements on VSMOW scale corrected for nonlinear response. Dashed lines indicate the 1σ confidence band.

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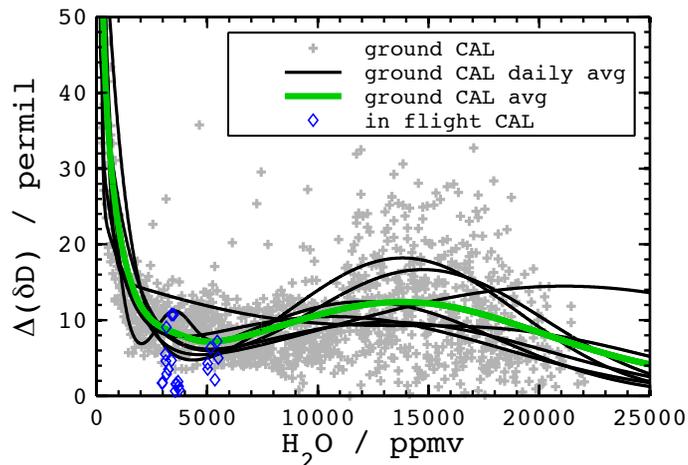


Figure 4. Uncertainty analysis for all flight days. Grey symbols: deviation of individual 1 Hz calibration measurements from calibration standard; black lines: daily fit of $\Delta(\delta D)$ (Eq. 2); green line: campaign average of $\Delta(\delta D)$. In-flight calibrations are depicted as the difference to the daily mean (absolute value) by the blue symbols.

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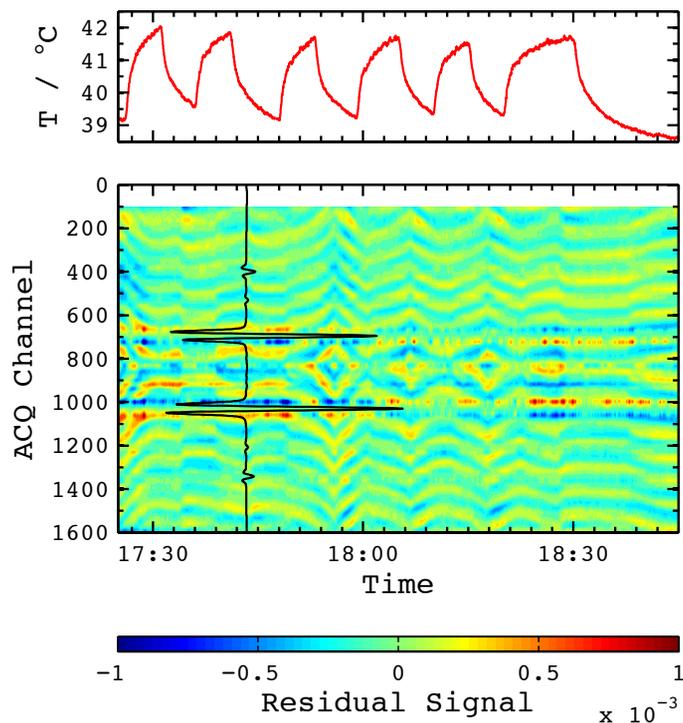


Figure 5. (a) Temperature recording of the mount of the $f = 25.4$ mm collection lens. (b) Array of spectral residuals recorded in the laboratory while repeatedly modulating the temperature of the $f = 25.4$ mm collection lens. The color code represents the residual amplitude scaled to optical density. The black trace depicts a second-harmonic spectrum recorded at 1 s integration time.

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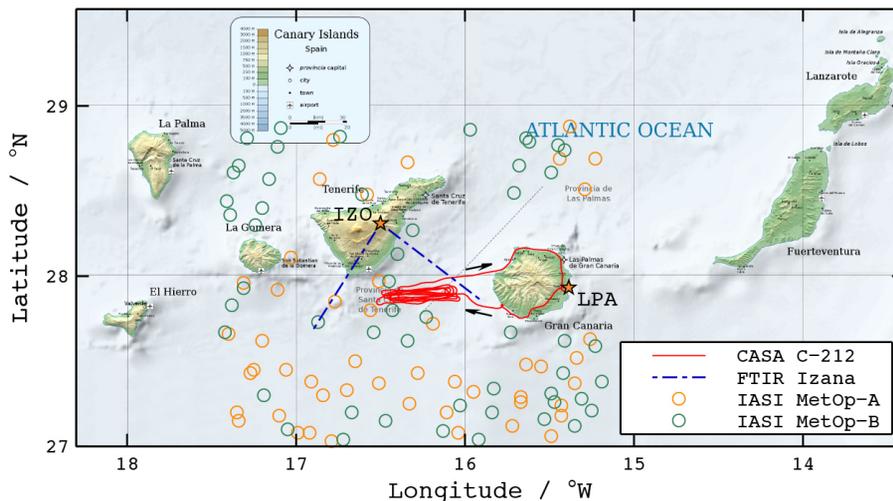


Figure 6. Aircraft flight track (red) of 24 July 2013 departing from Las Palmas Airport (LPA). Also shown are all Metop A and Metop B measurements (symbols) obtained during the campaign after a data-quality filter was applied. The FTIR line of sight (blue lines) for 10:30 and 13:00 UTC (start and end of profile measurements) at Izaña (IZO) is indicated. (Map source: http://en.wikipedia.org/wiki/File:Map_of_the_Canary_Islands.svg)

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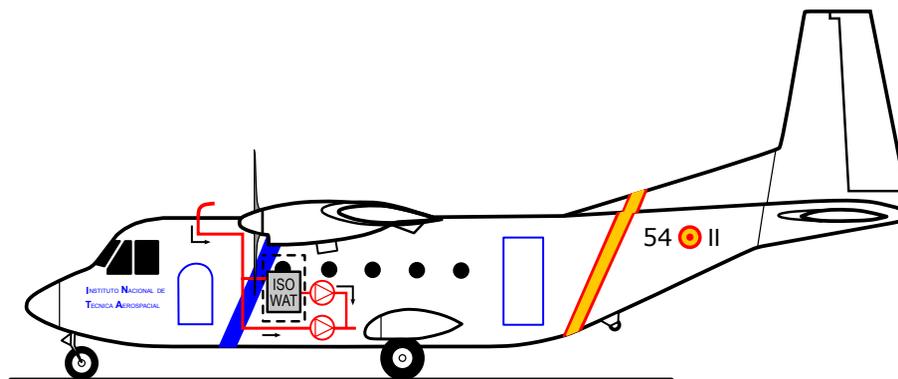


Figure 7. CASA C-212 aircraft of Instituto Nacional de Técnica Aeroespacial (INTA). The rearward-facing ambient air inlet was located on top of the fuselage. The inlet line was flushed at a high flow using a membrane pump. ISOWAT was mounted in the foremost position of the aircraft and was equipped with a second pump to establish the gas flow through the instrument.

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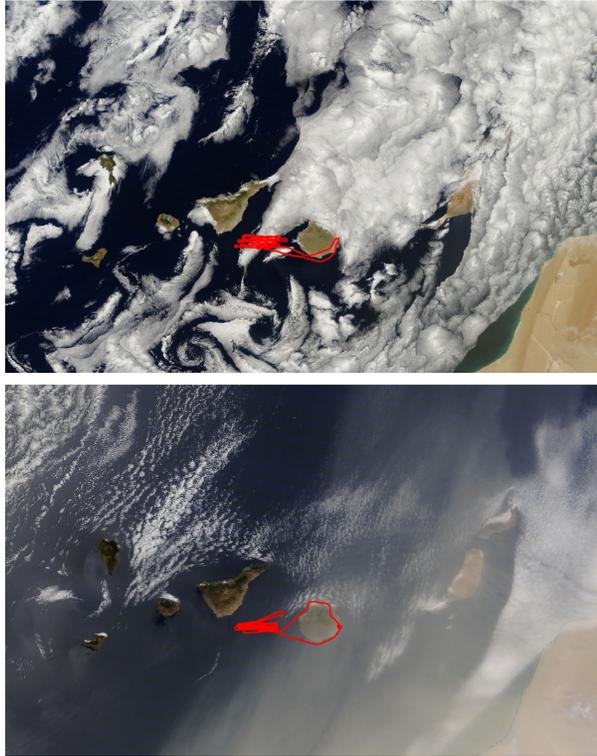


Figure 8. Satellite images of the Canary Islands of 21 July 2013 (top) and 31 July 2013 (bottom), which are representative of “North Atlantic” and “Sahara” conditions, respectively (explanation, see Sect. 3.3). Images are daily composites of data of the Moderate Resolution Imaging Spectroradiometer (MODIS) aboard the NASA Terra and Aqua satellites (source: <https://earthdata.nasa.gov/labs/worldview/>). The aircraft flight tracks are depicted as red traces.

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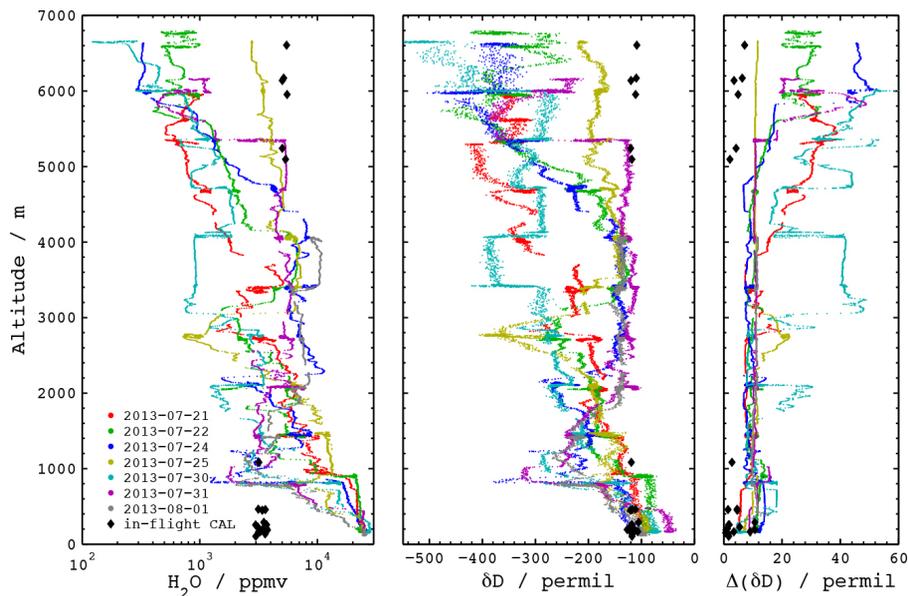


Figure 9. Vertical profiles of H₂O (left), δD (center), and instrumental absolute uncertainty (right) of all flight days evaluated at 1 Hz. For better clarity we show here only data with aircraft descending. Black symbols denote the respective quantities of the in-flight calibration measurements.

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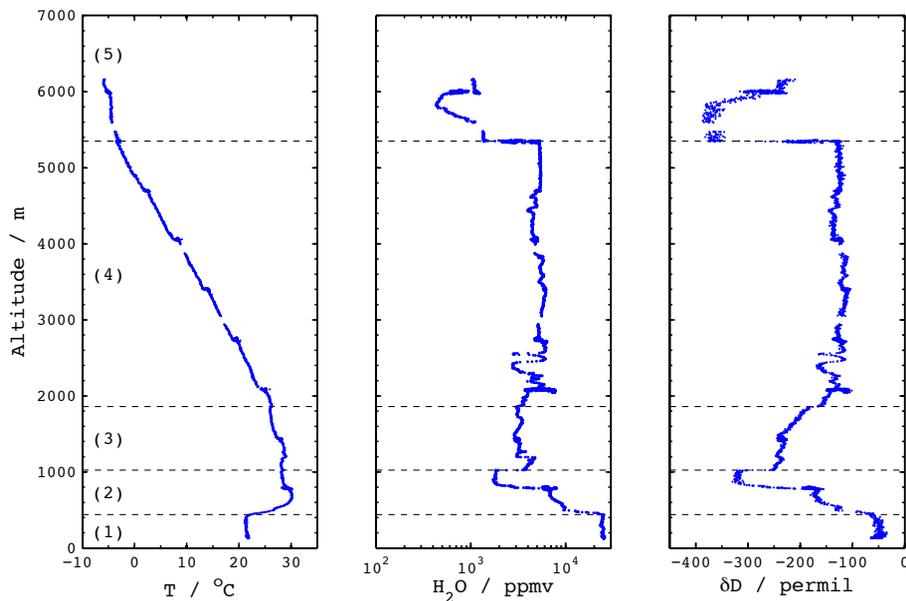


Figure 10. Measurements of temperature (T), H₂O mixing ratio, and δD taken with 1 s averaging on 31 July 2013. The profile is divided into 5 layers for interpretation.

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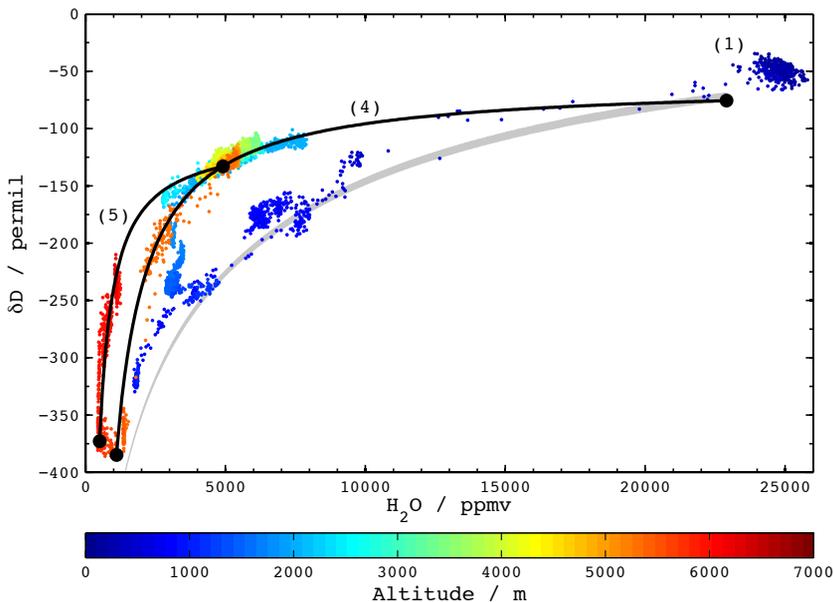


Figure 11. Distribution of H₂O and δ D measurements (1 Hz) during the descending branch of the flight on 31 July 2013. The color code represents the sampling altitude. The grey shaded area depicts a range of possible Rayleigh models assuming SST = 22.5 °C and RH = 80 % for ocean water with δ D = 0 ‰ (VSMOW, lower boundary) and δ D = +7 ‰ (upper boundary). The solid lines represent air mass mixing of (4) MBL and UT air, and (5) air at intermediate altitude and UT air (numbers according to levels in Fig. 10).

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