Atmospheric
Chemistry
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Discussions

Climatic controls on water vapor deuterium excess in the marine boundary layer of the North Atlantic based on 500 days of in situ, continuous measurements

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Abstract

Continuous, in situ measurements of water vapor isotopic composition have been conducted in the North Atlantic, Bermuda Islands (32.26° N, 64.88° W) between November 2011 and June 2013, using a cavity-ring-down-spectrometer water vapor isotope analyzer and an autonomous self-designed calibration system. Meticulous calibration allows us to reach an accuracy and precision on 10 min average of δ^{18}O, δD, and d-excess of respectively 0.14‰, 0.85‰, and 1.1‰, verified using two parallel instruments with independent calibration. As a result of more than 500 days with 6 hourly data the relationships between deuterium excess, relative humidity (rh), sea surface temperature (SST), wind speed and direction are assessed. From the whole dataset, 84 % of d-excess variance is explained by a strong linear relationship with relative humidity. The slope of this relationship (-42.6 ± 0.4‰ % (rh)) is similar to the theoretical prediction of Merlivat and Jouzel (1979) for SST between 20 °C and 30 °C. However, in contrast with theory, no effect of wind speed could be detected on the relationship between d-excess and relative humidity. Separating the dataset into winter, spring, summer, and autumn seasons reveals different linear relationships between d-excess and humidity. Changes in wind directions are observed to affect the relationships between d-excess and humidity. The observed seasonal variability in the relationship between d-excess and relative humidity underlines the importance of long-term monitoring to make accurate conclusions.

1 Introduction

Water stable isotopes in the atmosphere are key tracers of physical processes within the hydrological cycle. Since the 1950s, water stable isotopes of precipitation and their imprint in many different natural archives have been measured by mass spectrometry and understood in relation to processes controlling evaporation and evapotranspiration, moisture transport and condensation (Epstein and Mayeda, 1953; Dansgaard, 1954;

Rozanski et al., 1993). The founding works of Dansgaard (1964) and Craig and Gordon (1965) have shaped the last ~ 50 yr of research using water isotopes. The knowledge of hydrological cycle processes is fundamental for the implementation of water stable isotopes in conceptual Rayleigh distillation models or atmospheric regional or general circulation models, and their various applications such as the quantitative interpretation of ice core records (Johnsen et al., 1989; Jouzel et al., 1997). Here, we will focus on the basis of the atmospheric water cycle: the relation between $H_2^{18}O$ and $HD^{16}O$ compared to $H_2^{16}O$ in the marine boundary layer near the ocean surface. We will use the delta-notation introduced by Craig (1961a):

$$\delta^* = \left(\frac{R_{sample}}{R_{VSMOW}} - 1 \right) \times 1000,$$

where δ^* represents either $\delta^{18}O$ or δD, and R_{sample} and R_{VSMOW} is respectively the isotopic ratio of the sample and the Vienna Standard Mean Ocean Water.

As noted by Craig (1961b), the relationship between $\delta^{18}O$ and δD reflects the imprint of kinetic and equilibrium fractionation processes. The second order parameter d-excess has been defined by Dansgaard (1964) in order to highlight the isotopic variability, which is not driven by equilibrium fractionation that otherwise leads to a linear relationship between $\delta^{18}O$ and δD with a global mean slope of 8 (‰/‰) (Majoube, 1971):

$$d \text{ excess} = \delta D - 8 \times \delta^{18}O$$

Without large changes in temperature (which alter the slope of 8 due to the temperature-dependence of the equilibrium fractionation coefficients), changes in d-excess are dominated by kinetic fractionation. As qualitatively explained by e.g. Dansgaard (1964), the kinetic effect during evaporation arises from the different diffusivities of the water isotopes $H_2^{16}O$, $HD^{16}O$, and $H_2^{18}O$ in the air. This kinetic fractionation during evaporation was formally described by Merlivat and Jouzel (1979) (hereafter MJ79)

under an idealized "closure assumption" implying no advection of moisture. They formulated theoretical relationships between d-excess, sea surface temperature (SST) and relative humidity of the air compared to the saturation vapor pressure at the ocean surface (rhSST). We will in the following refer to rhSST as relative humidity normalized to SST. The relationships were expected to depend on the wind regime affecting molecular and turbulence mixing at the ocean surface, following the evaporation theory of Brutsaert (1975). Assessing the validity of MJ79 calculations requires long-term monitoring of water vapor isotopes in the marine boundary layer in order to separate the effect of the different influencing factors.

During the past decades only a few observations of surface water vapor isotopes have been conducted in the marine boundary layer due to the analytical challenges associated with cryogenic sampling. Gat et al. (2003) conducted cryogenic sampling of water vapor in the eastern Mediterranean and reported high d-excess values, due to strong kinetic effect produced as dry air transported from Europe moved across the warm Mediterranean Sea, a finding further supported by the study of Pfahl and Wernli (2009). Similarly, in another study, high d-excess values measured in several Arctic areas were attributed to high kinetic effect produced by dry polar air at the sea ice margin (Kurita, 2011; Steen-Larsen et al., 2013). Uemura et al. (2008) cryogenically collected 60 samples of water vapor onboard a research vessel during a one-month crossing of the Southern Ocean from Australia to Antarctica and back to South Africa. Consistent with the theory of MJ79, a strong relationship was observed between d-excess and rhSST (with a slope of −58‰ per % rhSST), but a strong correlation between rhSST and SST did not allow identifying the impact of SST alone. Pfahl and Sodemann (2013) used data from Gat et al., Pfahl and Wernli, and Uemura et al. to propose a globally applicable interpretation of d-excess in precipitation based on the overall linear relationship between surface vapour d-excess and rh. A recent support for the strong relationship between d-excess in the marine boundary layer water vapor and rh was obtained from a one-month campaign in the eastern North Atlantic by Bennetti et al. (2014) (slope of −45‰ per % rhSST). The difference between findings from Ue-

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mura et al. (2008) and Bennetti et al. (2014) open questions about both temporal and spatial variability in the relationship between d-excess and rh.

With the availability of commercial laser water vapor isotope analyzers (Crosson et al., 2002; Baer et al., 2002), it has recently become possible to perform accurate and continuous in situ measurements, provided that correct protocols are implemented for the calibration of the measurements. Further developments have allowed the setup of autonomous systems in remote field sites in regions spanning from Greenland to Niger, producing records of the variability of surface water vapor isotopic composition over seasons to years (e.g. Steen-Larsen et al., 2013; Bonne et al., 2013; Tremoy et al., 2012). With the goal of performing year-round measurements of water vapor isotopic composition in the North Atlantic marine boundary layer, we have focused on the Bermuda Islands. The location was chosen due to warm SST as a result of the nearby Gulf Stream current, and because this area is expected to be a key moisture source for the North Atlantic sector. Indeed, part of our motivation was to characterize the isotopic composition at the source of moisture for Greenland and therefore to improve the understanding of the processes governing Greenland water stable isotopes and the interpretation of d-excess from Greenland ice core records (e.g. Steen-Larsen et al., 2011; Johnsen et al., 1989; Fisher, 1992; Masson-Delmotte et al., 2005; Jouzel et al., 2007). For this purpose, we have designed a water vapor isotope system with the goal of being completely autonomous for periods of several months and able to perform frequent drift-calibrations in order to have high accuracy for the d-excess. Section 2 presents the setup of this system and our protocol for calibration of our measurements. Using two water vapor isotope analyzers calibrated independently of each other allows us to estimate the accuracy and precision of our observations. Section 3 is devoted to the investigation of statistical relationships and drivers for the observed variability in the d-excess: seasonality, wind direction, and wind speed as well as effect of averaging over different number of days.

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2 Materials and method

2.1 Meteorological observations

As shown in Fig. 1, our water vapor isotope monitoring system was installed at the Tudor Hill Atmospheric Observatory in Bermuda (32.26° N 64.88° W). Air temperature and relative humidity (rh) were recorded using a Campbell Scientific CR1000 logger (± 0.1 °C and ± 2 % rh) and wind direction and speed using a RM Young propeller-type vane ($\pm 3°$ and ± 0.3 m s^{-1}). Distribution of wind direction and speed is shown in Fig. 1d indicating that the wind is predominantly straight in from the ocean (~ 65 % occurrence). Surface pressure data values are obtained from the meteorological observations taken by the Bermuda Weather Service at Bermuda's L. F. Wade International Airport nearby. During the few days when we had meteorological data gaps at Tudor Hill, we used the airport observations by the Bermuda Weather Service. Monthly sea surface temperature data (SST) was obtained by averaging daily MODIS-aqua satellite observations over a ~ 600 km $\times$ 800 km area centered on Bermuda (Haines et al., 2007; Acker and Leptoukh, 2007). Mean monthly air temperature data ranges from 17.7 °C (February, mean daily high/low: 19.8 °C/15.5 °C) to 27.2 °C (August, mean daily high/low: 29.8 °C/24.5 °C). Monthly mean sea surface temperatures vary from 18.4 °C to 28.2 °C (minimum/maximum: March/August). Monthly climatology data 1949–1999 (Air temperature and SST) were obtained from the Bermuda Weather Service. Other measurements carried out at the tower consist of sampling for the Global Atmosphere Passive Sampler Network, continuous lower atmosphere ozone measurements and discrete greenhouse gas sampling for NOAA's Earth System Research Laboratory, continuous measurements of aerosol optical depth for NOAA's Aerosol Robotic Network, and continuous solar radiation measurements for NOAA's Baseline Surface Radiation Network.

2.2 Setup

We installed in November 2011 a water vapor isotope analyzer from Picarro inc. (Model # HBDS-2120) at the Tudor Hill Atmospheric Observatory in Bermuda, where the base of the meteorological tower is at $\sim 29\,\mathrm{m\,a.s.l.}$ (meters above sea leve) and sit-
uated $\sim 30\,\mathrm{m}$ from the coast. The instrument is installed inside a temperature regulated box ensuring daily temperature variability $< 0.2\,°C$, which itself is placed inside an air-conditioned container where diurnal temperature variability is $< 2\,°C$. The setup of the system (Fig. 1c) is similar to the setup previously deployed above the Greenland ice sheet (Steen-Larsen et al., 2013). Three inlets were initially installed on the
tower at a height of $\sim 20.5\,\mathrm{m}$ above ground ($\sim 49\,\mathrm{m\,a.s.l.}$), $\sim 13.1\,\mathrm{m}$ above ground ($\sim 42\,\mathrm{m\,a.s.l.}$), $\sim 5.8\,\mathrm{m}$ above ground ($\sim 35\,\mathrm{m\,a.s.l.}$). In June 2013 we installed a separate fourth inlet $\sim 2.5\,\mathrm{m\,a.s.l.}$ The top inlet placed $\sim 49\,\mathrm{m\,a.s.l.}$ is well above local vegetation (scrub) and provides the measurements, which are the focus of this paper.

Air sampling is performed using copper tubing, as laboratory experiments showed
copper to cause less smoothing of the signal compared to for example stainless steel and PTFE. All inlet tubes were placed inside Armaflex[®] closed cell tube insulation and heated to above $50\,°C$ using self-regulating heat trace from Raychem[®]. To prevent rain from being sucked into our air sampling tubes, the entrance of the inlets was placed inside Nalgene[®] bottles with their bottoms removed and substituted by a wire mesh
screen to prevent intrusion of foreign objects, such as insects. An extra shield was placed above the inlets for protection against frequent intense precipitation events. A $10\,\mathrm{L\,min^{-1}}$ air pump ensures a quick transport of the air from the start of the inlet and into the analyzer. An extra $5\,\mathrm{L\,min^{-1}}$ air pump maintains a constant flow in the tubes not being sampled. Inside the temperature-regulated box, a manifold operated by the
analyzer controls which inlet is being measured. A three-way valve controls whether the analyzer measures ambient water vapor, or water vapor from the calibration unit. The purpose of the calibration unit is to supply the analyzer with water vapor of known isotopic composition. This is achieved by using a similar vapor source as described by

Ellehøj et al. (2013). Dry air is let to slowly bubble through water of known isotopic composition kept at constant temperature inside a glass bottle (5 L). Ellehøj et al. (2013) showed that the water vapor isotopes are stable over flow rates up to $150\,mL\,min^{-1}$, which is well above the flow rates used here ($\sim 30\,mL\,min^{-1}$). As the temperature of the system is very stable, the known isotopic composition and temperature of the water are used to calculate the isotopic composition of the generated water vapor under the assumption of isotopic equilibrium. This saturated water vapor is instantly diluted with dry air (humidity level below 200 ppmv generated from Drierite®) as it leaves the glass bottle to prevent any condensation in the tubes and thereby isotopic fractionation. We used this vapor generation system to perform humidity-isotope response calibrations and for drift corrections, as introduced in Steen-Larsen et al. (2013) and described hereafter.

2.3 Calibration

As described in Steen-Larsen et al. (2013) it is necessary to perform a humidity-isotope response calibration of the analyzer, and correct the raw measurements. Following the protocol described in Steen-Larsen et al. (2013), water vapor with a constant isotopic composition is introduced into the instrument at different humidity levels, obtained by diluting the saturated water vapor coming out of our bubbler-system. We vary the humidity in steps of 10 min, but start and finish the sequence at the same humidity level in order to correct for drift of the system. The drift is assumed to be linear between the start and stop of each sequence. To assess the stability of the humidity-isotope response through time, calibrations were repeated at different dates (Fig. 2). Small but significant drifts in the humidity-isotope response curve are observed over the monitoring period. To correct for this observed drift of the humidity-isotope response, we assume the drift to be linear between two consecutive humidity-isotope response calibrations.

To reference our measurements against the international IAEA VSMOW-SLAP scale, we measured standards of known isotopic composition. Between 3 and 10 differ-

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ent standards, which varied between ~ 0 and $\sim -39\,\text{‰}$ in $\delta^{18}\text{O}$ and between ~ 0 and $-310\,\text{‰}$ in δD, were used each time we carried out a VSMOW-SLAP calibration. The standards used were referenced by respectively the Institute of Arctic and Alpine Research at University of Colorado, Centre for Ice and Climate at University of Copenhagen, and Laboratoire des Sciences du Climat et de l'Environnement in Gif-sur-Yvette, and calibrated against the IAEA VSMOW-SLAP. The standard deviation of the residuals between the VSMOW-SLAP value of the standards and the calculated values based on best linear fits is $\sim 0.1\,\text{‰}$ for $\delta^{18}\text{O}$ and $\sim 1.1\,\text{‰}$ for δD. We carried out VSMOW-SLAP calibrations in November 2011, August/September 2012 (most intensive period of calibrations, with 6 calibrations within 3 weeks), and June 2013 (Table 1). Table 1 rules out short-term variability for the VSMOW-SLAP slope but shows long-term changes in the slope, similar to values reported by Bastrikov et al. (2014). We assume that the VSMOW-SLAP slope varies linearly between the calibration periods. This observed drift is small, and has no impact on our data quality. The range of observed atmospheric water vapor isotope variability is less than $\sim 10\,\text{‰}$ in $\delta^{18}\text{O}$, and much smaller than the range of the standards. An un-accounted drift of 0.01 in the VSMOW-SLAP $\delta^{18}\text{O}$ slope would for example result in a maximum bias of only $0.1\,\text{‰}$ in $\delta^{18}\text{O}$ of the measured atmospheric water vapor isotope signal.

To account for the drift of the measured atmospheric water vapor isotope signal, we measure every 6–12 h water vapor with a known isotopic composition. This is carried out using our bubbler system described above. We have monitored the isotopic composition of the water inside our bubbler by taking samples regularly for measurements on an IRMS-system. As expected from the minor removal of water vapor ($\sim 0.03\,\text{g/drift}$ calibration) and large water body (5 L), no change in the liquid water isotopic composition was detected. The water vapor from the bubbler is measured for 30 min of which the first 15 min are discarded due to memory effects. The raw measurements are corrected using our humidity-isotope response correction (Fig. 2). They are then calibrated against VSMOW-SLAP using the slopes presented in Table 1 and drift corrected using the measurements of the vapor from the bubbler and the expected isotopic composi-

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tion of the water vapor calculated from the equilibrium fractionation coefficient and the liquid water isotope value.

Figure 3 shows the long-term drift of the system, characterized respectively for $\delta^{18}O$ and δD by a ~ 3‰ increase and a ~ 7‰ decrease over the ~ 1.5 yr measurement period. The associated ~ 25‰ drift of d-excess stresses the uttermost importance of this correction. No apparent reason for this drift could be determined. The stable isotopic measurements of water samples taken from the bubbler rule out a drift of the standard itself. We note a long-term correlation between the drift and the temperature of the calibration system and analyzer (Fig. 3). However, abrupt changes in the temperature do not seem to induce any response of the system. A 48 h running mean (black line, Fig. 3) is used to drift correct the measurements of the atmospheric water vapor isotopes.

The Picarro humidity measurements are calibrated against the estimated absolute humidity (ppmv) from the Campbell humidity sensor showing a strong linear relationship (Fig. 4). Hereafter, we use the corrected Picarro humidity values.

2.4 Signal smoothing due to the experimental setup

Due to the length of the introduction line (25 m of tubing), we expect the signal to be smoothed through mixing and interactions with the inside tube wall (Massman and Ibrom, 2008). By using a 10 L min^{-1} pump to transport the sample quickly from the inlet to the analyzer we try to minimize the smoothing of the signal from the interactions between the water vapor and the walls of the tubing. In order to quantify this effect, two sets of experiments were performed. We first injected air with two significantly different water vapor concentrations (~ 1000 ppmv and $\sim 30\,000$ ppmv) and secondly injected air containing the same concentration of water vapor, but with two significantly different water vapor isotopic compositions ($\delta^{18}O$: ~ -56‰ and ~ -17‰). The observed step changes in the humidity and isotope values are shown in Fig. 5. The normalized response functions for the shifts in humidity, $\delta^{18}O$, and δD together with the averaged time derivative of the normalized response functions are shown in Fig. 6. A log-normal distribution gives a good fit (not shown) to the time derived normalized response func-

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tions. The lag time for the signal to arrive at the analyzer (defined as the time at which 0.5 % of the normalized response has been reached) is shorter for the humidity ($\sim$ 40 s) than for the isotopes ($\sim$ 50 s). Similarly, 95 % of the normalized response is obtained after respectively $\sim$ 225 s, $\sim$ 650 s, and $\sim$ 1200 s for the humidity, δ^{18}O, and δD sig-

5 nal. This smoothing of the signal between the inlet and the analyzer causes different memory effects on each parameter. Since the performed step changes can be approximated by a Heaviside step function for the humidity and isotopic change, the first time-derivative of the original humidity and isotope signal becomes a Dirac delta function. The transfer function (i.e. the dampening of the signal at different frequencies)

10 of the complete set-up can therefore be estimated from the Fourier transform of the time derivative of the normalized change. This is shown in Fig. 7 for humidity (black lines), δ^{18}O (blue lines), and δD (red lines). A signal with a periodicity of $\sim$ 100 s will be attenuated by $\sim$ 85 % in humidity, 98.5 % in δ^{18}O, and 99.7 % in δD. However, it is potentially possible to record humidity signals with a periodicity down to $\sim$ 30 s. Due to

15 a compensation between larger smoothing and lower noise level for δD (compared to δ^{18}O), it is possible to observe signals in both δD and δ^{18}O with a periodicity down to $\sim$ 60 s. Using the estimated transfer function for δD and δ^{18}O and the fact that the measured signal is equal to the original signal convoluted by a log-normal function, it could be possible to perform a back-smoothing correction and recreate the original high

20 frequency signal using similar techniques as applied to ice core water stable isotope records or eddy-covariance analysis (Johnsen, 1977; Johnsen et al., 2000; Spank and Bernhofer, 2008).

2.5 Instrumental inter-comparison and inter-site variability

During autumn 2012, a second Picarro inc. analyzer was installed in parallel with the

25 original analyzer for a short period of time. Each analyzer was calibrated independently using the above procedure. The comparison of the two records allows us to directly estimate the uncertainty of the measured water vapor isotope signal, including the uncertainty of each of the calibration steps. Based on 10 min averaged calibrated data from

the two analyzers, spanning a period of 5 days (Fig. 8), the inter-instrument differences are normally distributed with a mean and standard deviation of 0.05 ± 0.14 ‰ (δ^{18}O), -0.15 ± 0.85 ‰ (δD), and 0.3 ± 1.1 ‰ (d-excess). The mean he mean deviation for δ^{18}O, δD, and d-excess being close to zero rules out any systematic bias between the two analyzers. Following Steen-Larsen et al. (2013), the standard deviation of the inter-instrument differences is used as a conservative estimate for our precision. Our obtained precision of 1.1 ‰ for d-excess far exceeds the precision of water vapor cryogenic trapping capabilities and reaches the precision achieved by IRMS.

In order to investigate the regional coherency of the observed water vapor isotopes, we have implemented the second analyzer at the opposite end of the Bermuda Islands, located 20 km away from Tudor Hill observatory (Fig. 1) for a period of $\sim$ 3 days beginning of autumn (Julian day 249–252 of 2012). The comparison of the two records (Fig. 9) depicts a gradient in humidity levels, probably due to the altitude at which measurements were conducted ($\sim$ 15 m a.s.l vs. $\sim$ 49 m a.s.l. for Tudor Hill). Altogether, a very good agreement is observed between observations at either end of the island. During an event at which the wind blew parallel with the axis formed by the two stations, at day 251.1, we observe a 1 h delay between the first increase of humidity and water vapor isotopic composition at the northern site (Fig. 9, black solid line), and the same signals recorded at Tudor Hill (20 km away). This is fully consistent with air mass transportation at the mean wind speed of about 20 km h^{-1} without any significant difference in the magnitude of the water vapor isotopic signal between the two sites. Based on this short comparison, we conclude that the signal measured at Tudor Hill is representative of a regional signal, without any significant regional effect along the Bermuda Islands.

3   Results and discussions

During the > 500 days measurement period the SST is found to vary between $\sim$ 20 °C and $\sim$ 28 °C with maximum and minimum occurring respectively around mid-March and mid-July. (Fig. 10, light blue curve). Figure 10 shows our corrected records of humidity

(green), relative humidity normalized to SST (red), δ^{18}O (blue), and d-excess (black) for the period between November 2011 and June 2013 (6 h data). Thanks to limited prolonged data gaps our data coverage is 95 %. The first gap in the data ($\sim$ 2012.25) was due to a flooded inlet caused by heavy rain, while the second gap ($\sim$ 2012.4) was
5 due to a failure of a vacuum pump.

The full year of data from 2012 allow us to compute the annual mean value for the humidity, δ^{18}O, δD, and d-excess: $\sim$ 20 500 ppmv, 70 % (rhSST), −11.81 ‰, −80.8 ‰, and 13.7 ‰. We find for 2012 a well-defined maximum (minimum) for δ^{18}O (d-excess) to occur in July (−10.0 ‰ and 7.3 ‰), while the months November–February
10 have roughly similar minimum (maximum) δ^{18}O (d-excess) mean values (−12.5 ‰ to −12.8 ‰ and 16.8 ‰ to 17.7 ‰). Figure 10 clearly shows July–August to have less variability (standard deviation (σ) of the 6 h data) in δ^{18}O and d-excess: $\sim$ 1.03 ‰ and $\sim$ 3 ‰ than January–February ($\sigma(\delta^{18}$O) and $\sigma(d$-excess): $\sim$ 1.8 ‰ and $\sim$ 9 ‰). We notice the absence of a significant diurnal variation in the humidity and isotopes indicating
15 the absence of local diurnal processes related to the boundary layer and plant transpiration (Welp et al., 2012; Berkelhammer et al., 2013).

From the 6 hourly data, d-excess is strongly correlated with rhSST ($n = \sim$ 2100, $R =$ −0.93); with a slope of −42.6 ± 0.4 ‰ per % (Table 2, Fig. 11a). For the remainder of this section, we further investigate the stability of the relationship between d-excess
20 and rhSST, comparing the results obtained under different wind regimes, and different seasons (based on SST values).

The observed relationships are compared to theoretical calculations based on MJ79 performed for a smooth surface (wind speed below 6 m s^{-1}) and a rough surface (wind speed around 10 m s^{-1}) and for SST of 20 °C and 30 °C. The best linear fit to our ob-
25 servations is extremely close to MJ79 predictions for a smooth surface, and bracketed by calculations for SST between 20 °C and 30 °C. It is also found that the predictions corresponding to a rough surface and SST of 20 °C constitute a lower bound for the observations.

Note that this comparison relies on the implicit assumption that Tudor Hill winds and relative humidity (measured at about 49 m a.s.l.) are representative of meteorological conditions of the lower boundary layer. Based on the similarity of humidity variations (despite a systematic offset) with the other end of the Bermuda Islands (Fig. 1), and the lack of a strong diurnal variability, which could be driven by changes in the marine boundary layer height, we assume this implicit hypothesis to be valid.

In order to investigate if the observed relationship depends on the wind regime, Fig. 11b shows the subsets of observations corresponding to wind conditions associated with a smooth surface (wind speed $< 6\,\mathrm{m\,s^{-1}}$ – blue dots) and a rough surface (wind speed $> 7\,\mathrm{m\,s^{-1}}$ – red dots). We made the separation according to the discontinuity in the kinetic fractionation factor defined by MJ79. A small difference between the two subsets appears for rhSST < 0.6, with smooth conditions associated with higher ranges of d-excess. The slope of the relationship between d-excess and rhSST is slightly more negative (-43‰ per % vs. -42‰ per %) for data corresponding to low winds. However, this observed difference is much smaller than inferred from MJ79 (from -42.7 to -28.5‰ per % when shifting from smooth to rough surface). This indicates that either the wind regimes defined in MJ79 might not be appropriate for this area or the observed d-excess of the local water vapor is affected by past wind conditions.

3.1 Seasonal d-excess vs. rh

We now investigate whether the relationship between d-excess and rhSST varies as a function of SST and season. The winter period is defined for SST below 21.0 °C, summer for SST above 26.0 °C, and spring and autumn for SST between 23.0 °C and 25.0 °C. Figure 11c and d show the d-excess vs. rhSST for the different periods as well as the best linear fits (summarized in Table 2). The average rhSST for both the complete data set and for the winter subset data is around 60–65 %. Comparing for this rhSST the absolute values of the best fit shown in Fig. 11 and in Table 2 reveal the winter d-excess to be about 1‰ lower compared to that for the complete data set (~ 17‰ compared to ~ 18‰). This offset is consistent with the theory of MJ79 and the

dependency of d-excess on SST: 3 °C colder winter SST is expected to decrease winter d-excess by approximately 1 ‰. With similar SST and rh ranges, we also observe that d-excess is systematically higher in autumn than in spring, which also translates into different intercepts of d-excess vs. rhSST regressions (Fig. 11d, Table 2). This feature, which cannot be explained by local meteorological parameters (i.e. SST), points to a change of moisture source region(s) and/or condition between spring and autumn. The validation of this hypothesis requires specific investigations such as moisture back trajectory calculations, or water tagging using atmospheric general circulation models, which are beyond the scope of this manuscript.

Finally, Fig. 11c and d and Table 2 highlight that the slope between d-excess and rhSST is much more negative in summer than for other seasons. The distribution of the summer d-excess data shows a subset of points for rhSST > 0.65 which are aligned on the same d-excess vs. rhSST relationship as for the winter season. However, a subset of abnormal high summer d-excess data corresponding to rhSST < 0.65, and dominant northwesterly winds, lead to a much more negative slope with respect to local rhSST. Section 3.3 will systematically investigate the influence of wind direction on the d-excess.

3.2 d-excess vs. rh on different time scales

Figure 10 clearly depicts enhanced winter variability in surface humidity and isotopic composition. This is supported by a wavelet analysis showing significant power in the variability of the humidity and isotopes with periodicities between 3 to 8 days from mid-November to mid-February. During the summer months (mid-April to mid-September), no period with a significant power show up. This is consistent with the build-up and westerly shift of the Bermuda-Azores high pressure system during summer. This prevents frontal systems to pass through the area compared to the winter period when the high pressure system is weaker and frontal systems are able to move across Bermuda (Huang et al., 1999; Portis et al., 2001). As different weather systems dominate the isotopic variability during different seasons, we used a wavelet coherence analysis to char-

acterize the relationship between d-excess and rh in the frequency and time domain (not shown). It confirms that d-excess and rh time series are strongly anti-correlated over the full data period on time scales between ~ 1–2 days and up to 2 months (the length of dataset does not allow this analysis to be extended on longer time scales). The lack in correlation on time scale below 1–2 days may be due to the analytical limitation, and the too low signal to noise ratio of our d-excess measurements.

Due to the strong anti-correlation between d-excess and rhSST on time scales of days to months, it is possible to investigate the relation between d-excess and rhSST for different averaging time scales. We divide the record into separate non-overlapping periods ranging from one day and up to one month. The estimated slope of the daily to monthly averaged d-excess vs. rhSST values is shown in Fig. 12 as function of the averaging period. We find that the slope for d-excess vs. rhSST changes from $\sim$-43.6 $\pm$ 0.7 ($R^2 = 0.86$, $n = 494$) to $\sim -52.0 \pm 3.3$‰ per % ($R^2 = 0.86$, $n = 36$) when increasing the averaging time from 1 day to 2 weeks. Increasing the averaging time further from 2-weeks to 1 month does not significantly affect this slope further. We note that time averaging allows for ntegration across synoptic systems, and therefore also implies as spacial averaging throughout air masses passing along the island. While the daily slope is consistent with that of MJ79, increasing averaging time causes the slope to deviate from the theoretical slope of MJ79 and to becomes closer to the value found by Uemura et al. (2008) from their transect across the Southern Ocean. As the theoretical slope of MJ79 is based on the closure assumption, we speculate that deviation from this slope with increased averaging time (averaging across synoptic systems) reflect that this assumption is no longer valid. Further studies are required to support this speculation. Future comparisons between observations and results from atmospheric general circulation models should clearly include the analysis of the relationship between d-excess and rhSST along different frequencies, as shown in Fig. 12.

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3.3 Influence of wind direction on d-excess

In previous sections, we have reported several findings, which suggest that changes in moisture advection (and moisture sources) might affect the variability of the d-excess measured in Bermuda. Figure 13 depicts the distribution of d-excess (contours) as a function of relative humidity (x-axis) and wind direction (y-axis), for summer (upper panel) and winter (lower panel), and the differences in relationships between d-excess and rhSST for subsets based on specific sectors (subjectively defined) of wind direction. In summer, we find that the d-excess vs. rhSST obtained during wind from the western sector has a very negative slope of -56.7 ± 2.2‰ per %. We conclude that westerly winds cause high summer d-excess levels, possibly due to high kinetic effect induced by warm, dry air masses coming of the American continent (Pfahl and Sodemann, 2013; Gat et al., 2003). In winter, differences in slopes are also identified for specific wind sectors, the southwestern sector (wind directions 200–250°) leading to the most negative slope and the highest d-excess levels for a given rhSST (Table 2). The dependency of the slope of d-excess vs. rhSST against wind direction illustrates the limitation of the closure assumption and the need for long-term monitoring in order to deduce the drivers of the d-excess in the marine boundary layer.

4 Conclusions

In order to monitor the drivers of marine boundary layer d-excess of the subtropical North Atlantic, we have presented continuous long-term observations of surface water vapor isotopic composition over a ~ 1.5 yr period between November 2011 and June 2013 from the Bermuda Islands. Thanks to meticulous independent calibration protocols, the inter-comparison of two parallel analyzers shows that the accuracy and precision of 10 min averages of δ^{18}O, δD, and d-excess is respectively 0.14‰, 0.85‰, and 1.1‰. Tests on our monitoring system show that isotopic signals can be accurately retrieved with a temporal resolution down to 1 min intervals. During a few

days, parallel measurements recorded by separated water vapor isotope analyzers on each end of the Bermuda Islands show a common signal within these 20 km, suggesting limited effect of the island. We conclude that the signal is dominated by the marine boundary layer moisture.

5   The accuracy and precision of the *d*-excess measurements allow us to document and investigate the controls on the *d*-excess variability. In accordance with theory, *d*-excess variability is driven by the relative humidity of the air normalized to sea surface temperature. However, we could not identify any shifts in relationship with wind speed. In Bermuda, the relationship between *d*-excess and relative humidity depends on the

10 season, and thereby SST. Moreover, specific wind directions (western winds in summer, and southwestern winds in winter) lead to unusually high *d*-excess values for a given humidity level, and a higher negative slope between *d*-excess and humidity. This feature stresses the limitation of the closure assumption and calls for long-term monitoring in order to characterize the complete set of processes controlling the vari-

15 ability of surface moisture *d*-excess. Such long-term monitoring indeed allows to evidence processes other than relative humidity (e.g. SST, wind direction...), which act on *d*-excess. We have clearly demonstrated the change of *d*-excess vs. relative humidity slope as a function of the averaging period (from 1 day to 2 months). Extending our record in time will allow for the investigation of the drivers of *d*-excess at the inter-

20 annual scale. A next step will be to diagnose changes in moisture source and remote evaporation conditions, using back trajectory calculations and water tagging within atmospheric models in order to take into account the advection effects highlighted by the impact of wind directions. Our dataset will in the future be used to test the validity of deuterium retrievals based on remote sensing (Lacour et al., 2012), and to benchmark

25 atmospheric general circulation models equipped with water stable isotopes (Werner et al., 2011; Risi et al., 2010; Yoshimura et al., 2008).

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Table 1. Slope between IAEA VSMOW-SLAP values and measured values of standards.

Date	Slope		Standard deviation slope		Mean slope		Standard deviation mean slope	
	δ^{18}O	δD	δ^{18}O	δD	δ^{18}O	δD	δ^{18}O	δD
27 Nov 2011	1.0708	1.0685	0.0206	0.0104	–	–	–	–
28 Aug 2012	1.0713	1.0915	0.0029	0.0055	1.0733	1.09315	0.0052	0.0078
31 Aug 2012	1.0756	1.0886	0.0062	0.0047				
4 Sep 2012	1.0690	1.0949	0.0033	0.0033				
6 Sep 2012	1.0812	1.1081	0.0203	0.0051				
10 Sep 2012	1.0756	1.0883	0.0023	0.0100				
15 Sep 2012	1.0669	1.0875	0.0026	0.0064				
13 Jun 2013	1.0527	1.0759	0.0044	0.0049	1.0547	1.0756	0.0022	0.0003
2 Jul 2013	1.0571	1.0753	0.0014	0.0024				
3 Jul 2013	1.0543	1.0755	–	–				

Table 2. The slope and intersect of d-excess vs. relative humidity for the complete data set as well as seasonal, wind direction, and wind speed subsets.

		Slope [‰ [rh^{-1}]]	Intercept [‰]	R^2	N
All data		−42.6 ± 0.4	43.5 ± 0.3	0.86	1926
	High wind speed (> 7 m s^{-1})	−42.0 ± 0.5	42.9 ± 0.4	0.89	679
	Low wind speed (< 6 m s^{-1})	−43.0 ± 0.6	43.9 ± 0.4	0.82	1016
Summer data		−51.9 ± 1.5	50.8 ± 1.1	0.76	398
	Wind direction 0–180°	−45.2 ± 2.1	46.3 ± 1.5	0.69	208
	Wind direction 180–360°	−56.7 ± 2.1	54.1 ± 1.6	0.80	180
Winter data		−40.7 ± 0.5	41.4 ± 0.4	0.88	738
	Wind direction 0–200°	−41.7 ± 0.8	42.5 ± 0.6	0.88	287
	Wind direction 200–250°	−49.1 ± 1.0	48.6 ± 0.8	0.92	164
	Wind direction 250–360°	−38.7 ± 1.1	39.8 ± 0.6	0.82	275
Autumn data		−37.4 ± 1.1	41.8 ± 0.7	0.90	135
Spring data		−39.1 ± 1.8	40.0 ± 1.4	0.85	90

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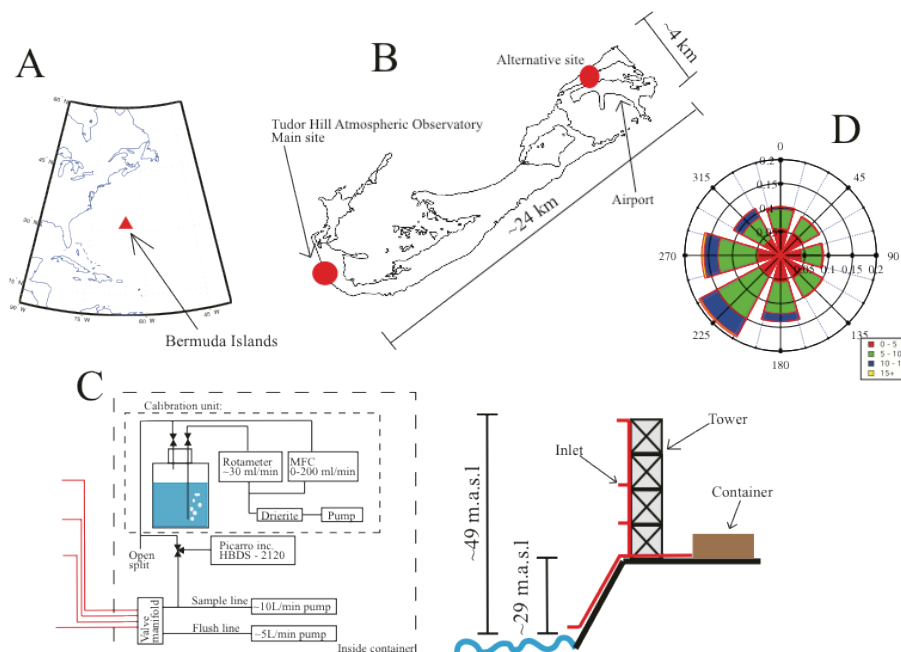
Fig. 1. Illustration of the position of the Bermuda Islands **(A)**, map of the sites where observations have been performed at Tudor Hill Atmospheric Observatory and on the other site of the island **(B)**, system setup **(C)**. The wind rose (6 hourly observations) indicates that the wind is predominantly arriving to Tudor Hill directly from the ocean **(D)**.
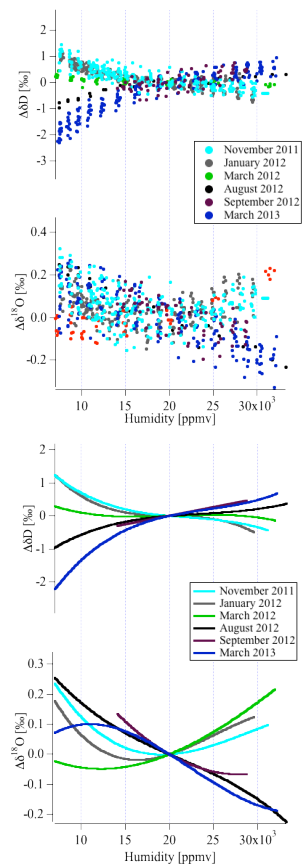
Fig. 2. Humidity-isotope response calibrations of the analyzer performed at different dates during the monitoring period. The lower panel represents the best fit using either a second or third order polynomial to the observations.
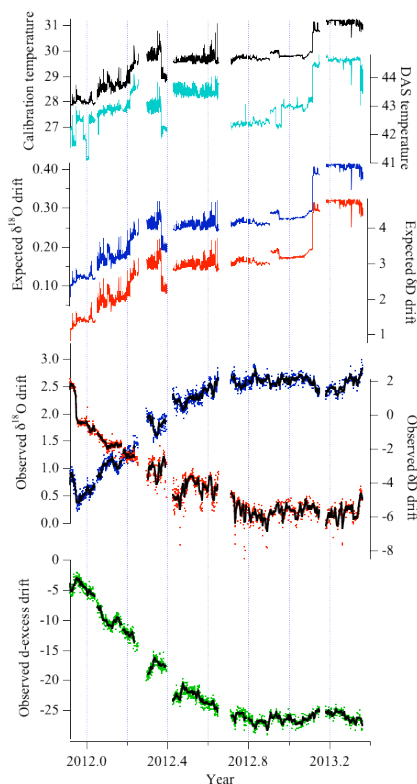
Fig. 3. Drift on the measured isotopic values. The top panel shows the temperature of the water body in the bubbler system. Below is shown the internal temperature of the Picarro analyzer (DAS temperature). The theoretical drift of the calibration water vapor isotopes is calculated, based on the drift of the calibration temperature. The observed drift in δ^{18}O, δD, and d-excess is shown for individual measurements in blue, red, and green dots. The 48 h running mean is shown using a black solid line.
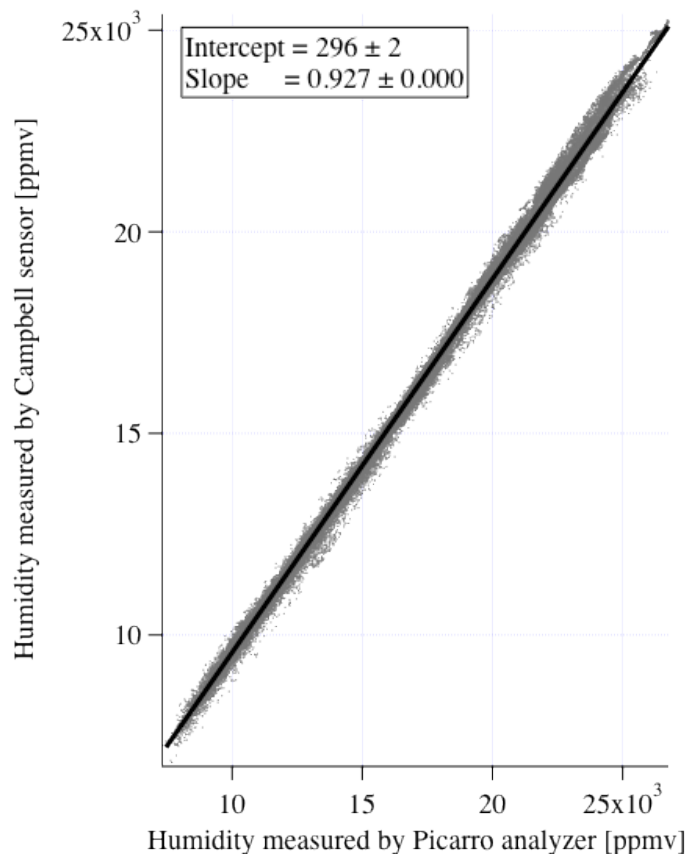
Fig. 4. Relationship between the observed absolute humidity by the Campbell humidity sensor (y-axis) and the measurement by the Picarro analyzer (x-axis). This relationship is used to correct the Picarro humidity measurements.

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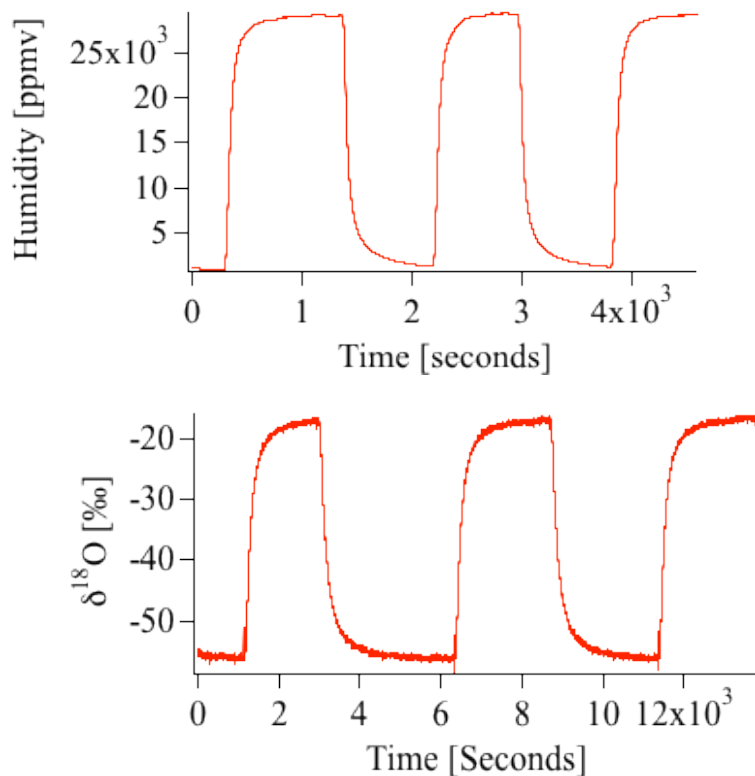
Fig. 5. Results of experiments conducted to characterize the response time of the system. Step changes of humidity followed by step changes in $\delta^{18}O$ were performed. Note that the steps are not of equal length as the experiment was performed on an ad-hoc field setup on top of the tower.

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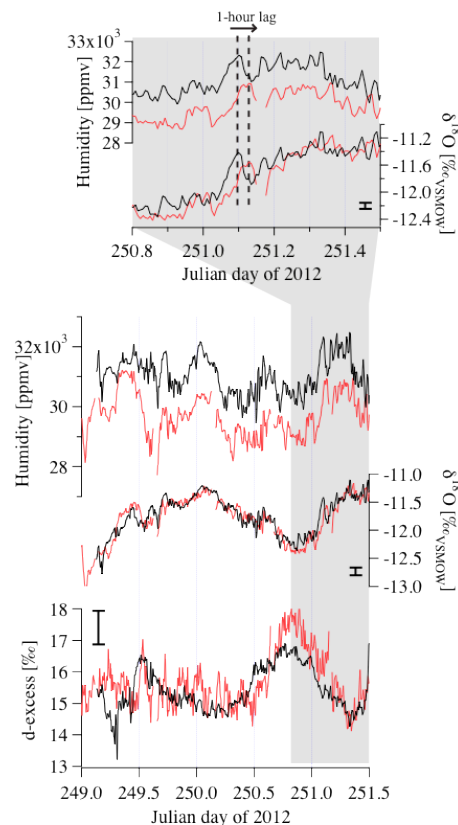Full Screen / Esc

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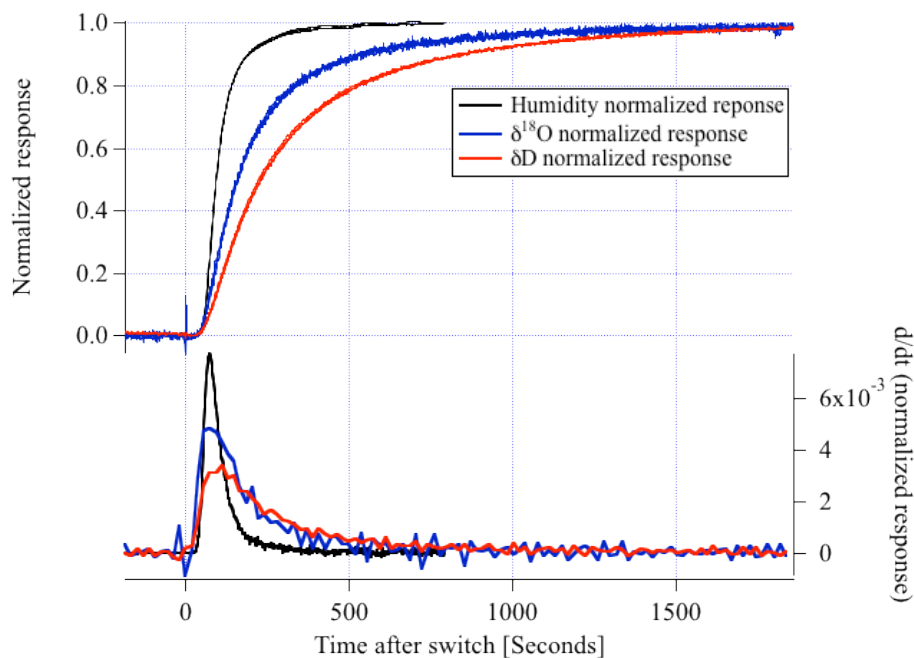
Fig. 6. Normalized response function for humidity, $\delta^{18}O$, and δD (upper panel). Time-derivative of the normalized response functions (lower panel).
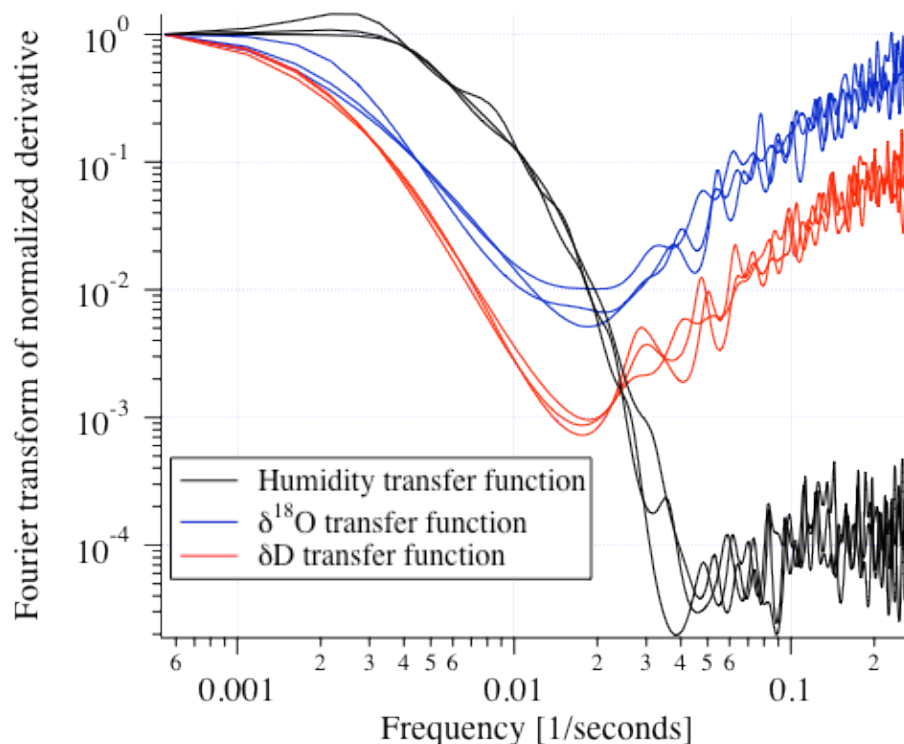
Fig. 7. Fourier transform of the time-derivative normalized response functions for humidity, $\delta^{18}O$, and δD. The transfer functions of the humidity and isotopes are estimated for each of the 3 steps shown in Fig. 5.
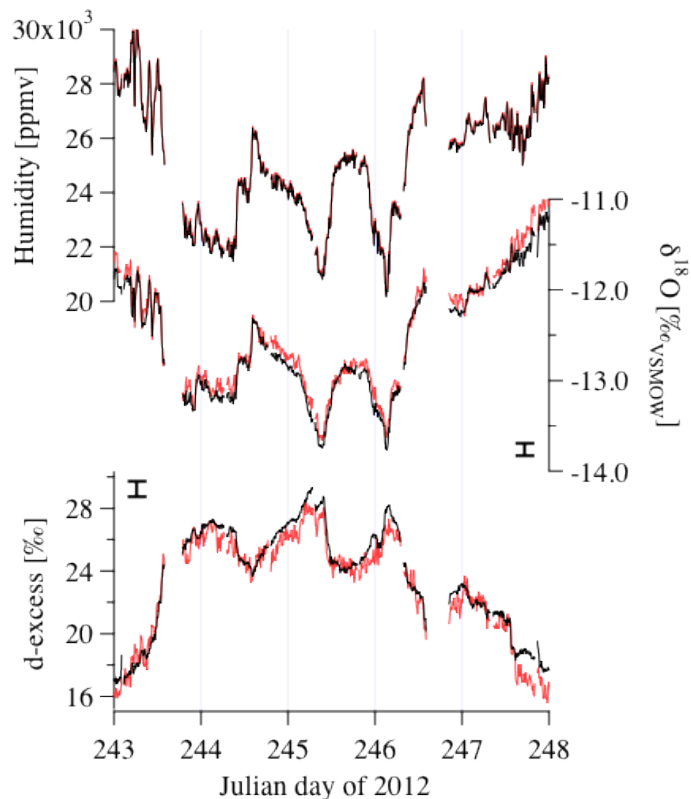
Fig. 8. Observed humidity, $\delta^{18}O$, and d-excess by two independently calibrated water vapor isotope analyzers installed in parallel using the same inlet on the tower. The observations are reported as 10 min averages. The estimated uncertainties for $\delta^{18}O$ and d-excess based on the standard deviation of the inter-instrument anomaly (0.14‰ and 1.1‰) are indicated next to the axes.

Fig. 9. Humidity, δ^{18}O, and d-excess measured by two water vapor analyzers separated to opposite ends of the island. We highlight an event where an increase in humidity and δ^{18}O is first recorded at the northern site and 1 h later at Tudor hill as expected by surface wind direction and wind speed during this period. The estimated uncertainties for δ^{18}O and d-excess (0.14 ‰ and 1.1 ‰) are indicated next to the axes.
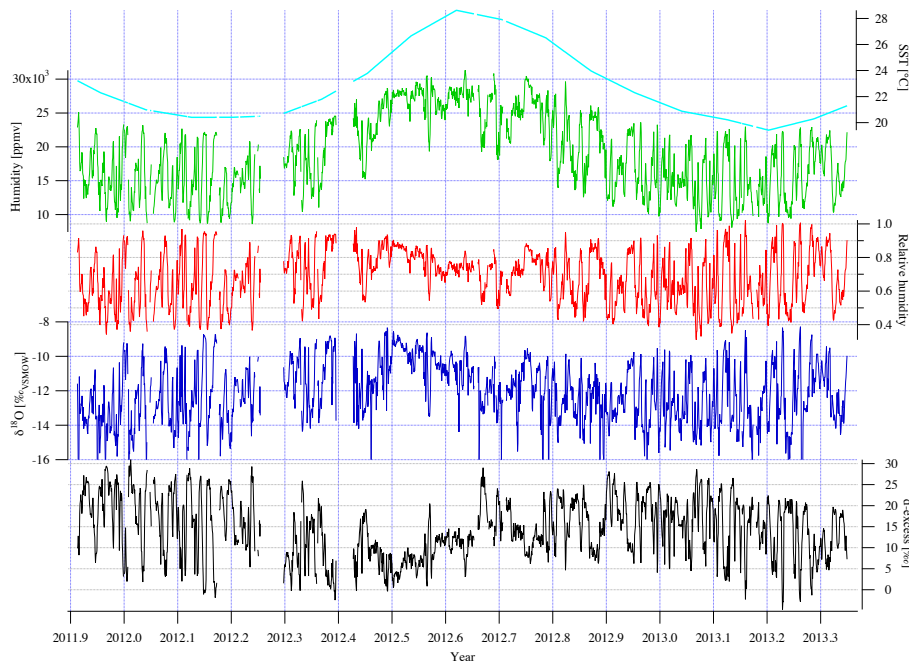
Fig. 10. SST, humidity and water vapor isotopic composition monitored between November 2011 and June 2013. From top to bottom are shown the sea surface temperature [˚C] (cyan), humidity [ppmv] (green), the relative humidity normalized to sea surface temperature (red), the water vapor δ^{18}O [‰] (blue) and d-excess [‰] (black).

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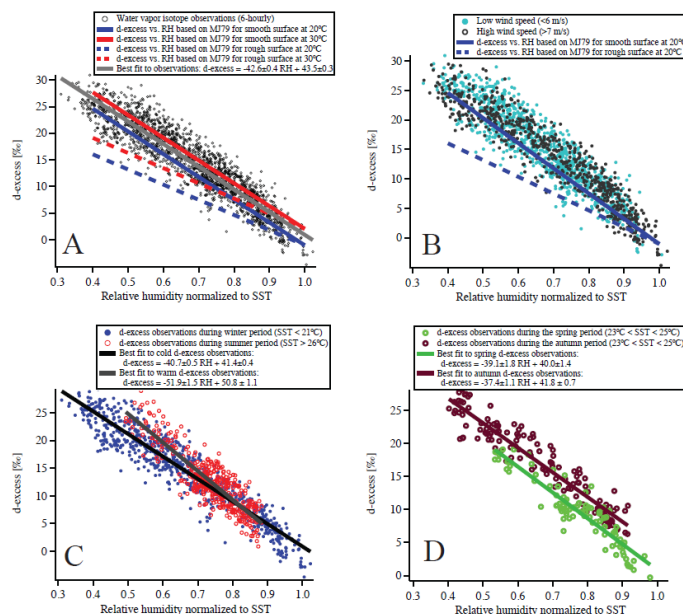
Fig. 11. (A) Complete set of 6 hourly observations of *d*-excess vs. relative humidity (rhSST) normalized to sea surface temperature (black dots), with a best fit (grey line). Results from the theory of MJ79 are displayed for respectively a rough and smooth surface, and for SST of 20 °C and 30 °C. **(B)** The complete set of 6 hourly observations of *d*-excess vs. rhSST separated into calm ($< 6\,\mathrm{m\,s^{-1}}$ – cyan dots) and strong winds ($> 7\,\mathrm{m\,s^{-1}}$ – grey dots). MJ79 calculations are shown for a rough and smooth surface at 20 °C. **(C)** Observations collected during winter (defined as SST < 21 °C – blue dots) and summer (defined as SST > 26 °C – red dots) period. The best linear fits to winter and summer observations are shown as respectively black and grey solid lines. **(D)** Observations collected during spring (23 °C $<$ SST < 25 °C – green dots) and autumn (23 °C $<$ SST < 25 °C – brown dots) period. Best linear fits to respectively the spring and autumn period are shown as green and brown solid lines.
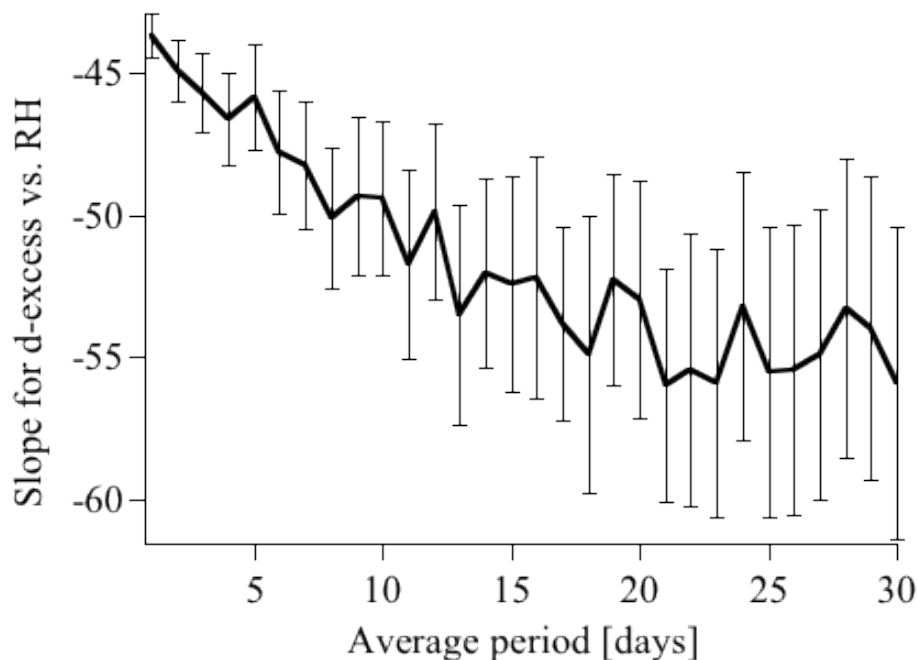
Fig. 12. Slope of *d*-excess vs. RH for different averaging periods varying from 1 day to 30 days.
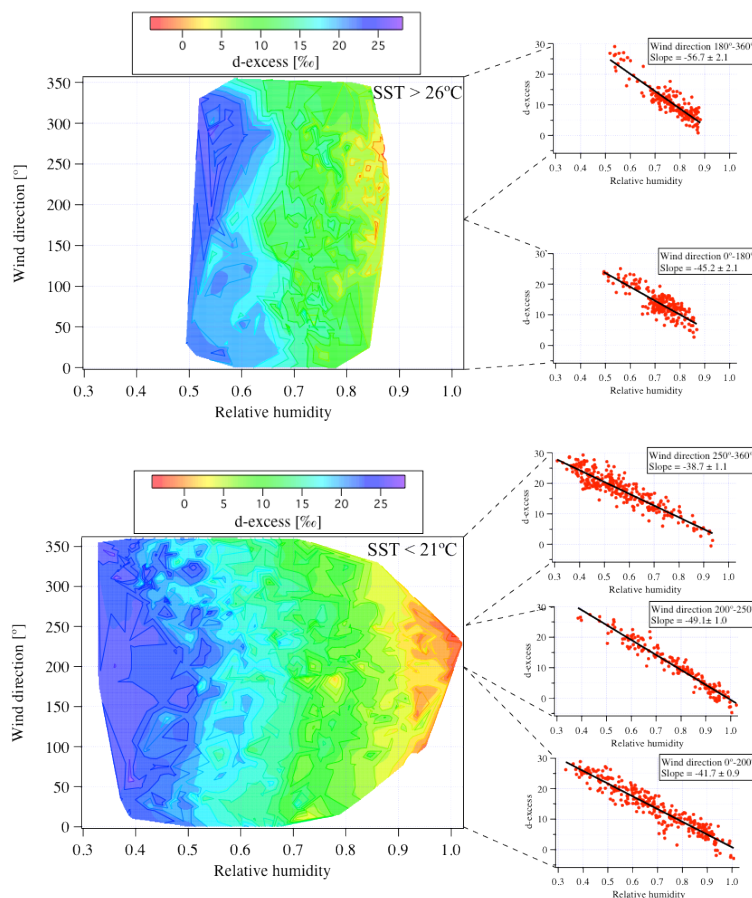
Fig. 13. *d*-excess as function of wind direction and relative humidity for summer period (SST > 26 ˚C) (upper panel) and for winter period (SST < 21 ˚C) (lower panel).

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