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1 **Water isotope ratio ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) measurements in atmospheric**
 2 **moisture using an optical feedback cavity enhanced**
 3 **absorption laser spectrometer**

4 Rosario Q. Iannone,¹ Daniele Romanini,² Olivier Cattani,³ Harro A. J. Meijer,¹
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7 [1] Water vapor isotopes represent an innovative and excellent tool for understanding
 8 complex mechanisms in the atmospheric water cycle over different time scales, and they
 9 can be used for a variety of applications in the fields of paleoclimatology, hydrology,
 10 oceanography, and ecology. We use an ultrasensitive near-infrared spectrometer,
 11 originally designed for use on airborne platforms in the upper troposphere and lower
 12 stratosphere, to measure the water deuterium and oxygen-18 isotope ratios *in situ*, in
 13 ground-level tropospheric moisture, with a high temporal resolution (from 300 s down to
 14 less than 1 s). We present some examples of continuous monitoring of near-surface
 15 atmospheric moisture, demonstrating that our infrared laser spectrometer could be used
 16 successfully to record high-concentration atmospheric water vapor mixing ratios in
 17 continuous time series, with a data coverage of ~90%, interrupted only for daily calibration
 18 to two isotope ratio mass spectrometry-calibrated local water standards. The
 19 atmospheric data show that the water vapor isotopic composition exhibits a high variability
 20 that can be related to weather conditions, especially to changes in relative humidity.
 21 Besides, the results suggest that observed spatial and temporal variations of the stable
 22 isotope content of atmospheric water vapor are strongly related to water vapor transport in
 23 the atmosphere.

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 26 *J. Geophys. Res.*, 115, XXXXXX, doi:10.1029/2009JD012895.

27 **1. Introduction**

28 [2] To obtain detailed knowledge of the hydrological
 29 cycle, information on all three phases of water is required.
 30 Isotopic analysis of atmospheric trace gases provides a
 31 valuable tool for resolving their budgets because the phys-
 32 ical, chemical, or biological processes involved fractionate
 33 isotopically in unique ways and leave characteristic isotopic
 34 signatures in the trace gas. In particular, water vapor iso-
 35 topes provide information concerning the mechanisms of
 36 processes that occur in the water cycle, such as evaporation
 37 at the surface of the Earth and subsequent transport and
 38 phase changes in the atmosphere.

39 [3] The Global Network for Isotopes in Precipitation
 40 (GNIP), founded in 1958 by the World Meteorological
 41 Organization and the International Atomic Energy Agency
 42 (IAEA), has been surveying the isotopic composition of

precipitation water since 1961 [*Araguas Araguas et al.*, 43
 1996]. The network consists of about 100 sampling sites 44
 around the world, including marine, coastal, and inland sta- 45
 tions. Through those measurements, some information has 46
 already been obtained about the isotopic composition of 47
 atmospheric moisture, assuming that application of the 48
 Rayleigh condensation model is valid: the isotope distribu- 49
 tion in precipitation is an “equilibrium proxy” for the one in 50
 the vapor phase. This assumption is based on the concept of 51
 temperature-dependent equilibrium isotope exchange effects. 52
 However, because precipitation predominantly occurs as 53
 discrete events in both space and time, sampling of liquid 54
 water does not provide an estimate of vapor isotopic com- 55
 position with high temporal resolution, and it does not pro- 56
 vide information on changes occurring between precipitation 57
 events, or in areas with low or even zero precipitation. This 58
 has motivated new efforts to obtain more data on the spatial 59
 and temporal variation in the isotopic composition of 60
 atmospheric moisture. 61

[4] A second network was thus initiated by the IAEA in 62
 1994. This network was named Moisture Isotopes in the 63
 Biosphere and Atmosphere and it is intended to complement 64
 and expand the GNIP ([http://www-naweb.iaea.org/napc/ih/](http://www-naweb.iaea.org/napc/ih/MIBA/IHS_MIBA_current.html) 65
 MIBA/IHS_MIBA_current.html). 66

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67 [5] Water-vapor isotope measurements can be used to
68 reveal a possible relationship between water-vapor isotopes
69 and ambient moisture. In addition, atmospheric humidity
70 shows a diurnal pattern and it would be interesting to verify
71 the existence of this variation in the isotopes signal. Ulti-
72 mately, the information obtained in these atmospheric
73 moisture isotope studies can be used to improve the repre-
74 sentation of processes such as evaporation and condensation
75 in climatic simulations.

76 [6] Isotopic variations in H₂O vapor are usually reported
77 as delta values, expressed in per mil (‰), giving the devi-
78 ation of the ratio of the rare isotope to the most abundant
79 isotope, relative to a standard. The internationally accepted
80 standard material, used in hydrological applications, is
81 known as Vienna standard mean ocean water (VSMOW)
82 [Gonfiantini, 1978]. If we define R to be the ratio $[^2\text{H}]/[^1\text{H}]$
83 or $[^{18}\text{O}]/[^{16}\text{O}]$ in the sample or in the standard, we thus have

$$\delta = \left[\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right]. \quad (1)$$

84 Although the determination of the isotopic content of rain-
85 fall is a fairly straightforward process, measuring isotopic
86 ratios in the vapor is not easily performed and requires
87 sophisticated equipment.

88 [7] The conventional technique for this specific applica-
89 tion generally involves the use of cold traps cooled to
90 roughly -80°C in order to collect water vapor, followed by
91 laboratory isotope ratio mass spectrometry (IRMS) analyses.
92 *Jacob and Sonntag* [1991] recorded almost continuous time
93 series (sampling period of 1 or 2 days) of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in
94 atmospheric water vapor at Heidelberg (Germany) over a
95 time span of 8 years. We also cite the effort of *He and Smith*
96 [1999], who sampled water vapor from a light aircraft above
97 a forest in New England, Connecticut (United States), and
98 *Wang and Yakir* [2000], who measured water-vapor stable
99 isotopes to study evapotranspiration fluxes above canopies.

100 [8] Another option is to measure the water-vapor isotopic
101 distributions from space using a satellite-based spectrome-
102 ter. *Worden et al.* [2007] used the Tropospheric Emission
103 Spectrometer on board the Aura spacecraft to obtain a
104 characterization of the vertical profiles of $^1\text{H}^{16}\text{O}^2\text{H}$ and
105 H_2^{16}O in the tropical region. It is worth noting that both
106 cryogenic whole air sampling and satellite remote sensing
107 produce measurements with limited temporal resolution,
108 spatial resolution, or both.

109 [9] Optical spectroscopy enables long time series of onsite
110 measurements with high temporal coverage. *Lee et al.*
111 [2005] carried out continuous measurements of $\text{H}_2^{18}\text{O}/$
112 H_2^{16}O in atmospheric water vapor in New Haven, Connecticut
113 (United States), using a commercial Campbell-Scientific
114 tunable diode laser (TDL) gas analyzer. Later, *Wen et al.*
115 [2008], extended this study to include measurements of $\delta^2\text{H}$
116 using an upgraded version of the TDL analyzer. *Griffith et*
117 *al.* [2006] used a Fourier transform infrared (FTIR) spec-
118 trometer to perform measurements of $\delta^2\text{H}$ in an Australian
119 eucalypt forest near Tumberumba, New South Wales, in
120 southeastern Australia. Both these works describe systems
121 for measurement of atmospheric water vapor isotopes in real
122 time, based on infrared spectroscopy. Both the Campbell
123 Scientific and the FTIR instruments are fairly big and

require liquid nitrogen cooling for laser and/or detector 124
operation. 125

[10] Finally, very recently, measurements of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ 126
of atmospheric moisture were carried out by *Wang et al.* 127
[2009], whose aim was to calibrate an off-axis integrated 128
cavity output spectrometer, manufactured by Los Gatos 129
Research, Inc. (<http://www.lgrinc.com>). The precisions 130
achieved with this instrument were $\sim 0.1\%$ for ^{18}O and 0.4% 131
for ^2H , for an averaging time of over 500 s. Continuous 132
records of isotopic composition of water vapor were also 133
reported by *Galewsky et al.* [2009], who performed in situ 134
measurements at the Mauna Loa Laboratory in Hawaii. They 135
used three laser spectrometers, of which two were commer- 136
cial (Los Gatos Research, Inc., and Picarro, Inc., <http://www.picarro.com>), whereas the third laser-based spectrometer was 138
developed at the Jet Propulsion Laboratory. 139

[11] Here we demonstrate that the infrared laser spec- 140
trometer we previously developed for airborne applications 141
[*Kerstel et al.*, 2006; *Iannone et al.*, 2009b] can be suc- 142
cessfully applied to the isotopic characterization ($\delta^2\text{H}$ and 143
 $\delta^{18}\text{O}$) of atmospheric, near-surface moisture through real- 144
time and continuous measurements with an accuracy and 145
precision comparable to that of cryogenic sampling and 146
IRMS, but with a much higher temporal resolution. The 147
instrument is lightweight (3 kg for the optical core, 148
excluding the computer and pump) and small (~ 25 L), has a 149
low power consumption (~ 150 W), and requires no liquid 150
nitrogen, making it ideally suited for field operation. It has a 151
large dynamic range of absorption measurement, a feature 152
in common with the commercial Los Gatos Research and 153
Picarro near-infrared water vapor isotope ratio spectrom- 154
eters. In addition, all three spectrometers are able to operate 155
autonomously, and the small size and the high degree of 156
portability make the analyzers easily transportable to the 157
field for use in in situ measurements. 158

[12] In the Los Gatos Research analyzer, the incoherent 159
coupling to a very dense cavity mode structure produces a 160
very low level of output signal compared to the other two 161
techniques and, consequently, requires a fairly high laser 162
power and a good signal detection system. Moreover, the 163
optical cell necessarily incorporates very large diameter 164
mirrors, which makes the gas cell volume large, and thus 165
increases the pumping requirement, if the gas exchange time 166
(which limits the instrument response time) must be kept 167
short. Our spectrometer and the Picarro analyzer share the 168
advantage of a very small cavity volume. An advantage of 169
the particular technique used in our spectrometer is the 170
inherent frequency calibration of the spectrum. For this 171
purpose, the Picarro analyzer is equipped with a proprietary 172
wavelength monitor module, which adds complexity and 173
cost to the instrument. Calibration of the (relative) frequency 174
scale is important in that it is a prerequisite for very precise 175
model fits to the spectral absorption features, which gener- 176
ally improve the long-term reproducibility of the absorption 177
measurements. 178

[13] We show preliminary measurements of water-vapor 179
isotope ratios in ambient air, sampled at the rooftop of the 180
Center for Isotope Research in Groningen, Netherlands (53° 181
 $13'\text{N}$, $6^\circ 33'\text{E}$) during two 1-week measurement campaigns, 182
when the instrument was not needed within its designated 183
project of airborne isotope ratio analysis of atmospheric 184
moisture. Although the spectrometer performance was 185

186 below its optimum (the noise equivalent absorption, NEA,
187 was almost a factor of 3 worse than what can be obtained
188 with the same setup and some sample introduction issues
189 were identified, as is discussed farther down), we use the
190 data here to show the wealth of information that can be
191 obtained with online continuous monitoring of atmospheric,
192 and thus relatively high water content, moisture, which does
193 not require the utmost sensitivity of the instrument. We
194 demonstrate that the results substantially surpass a conven-
195 tional offline cryogenic sampling strategy in terms of
196 information content.

197 2. Methods

198 2.1. Experimental Setup

199 [14] In recent years, several laser spectroscopic methods
200 have been proposed, developed, and optimized for isotopic
201 investigations, especially in the infrared region [Kerstel, 2004;
202 Kerstel and Gianfrani, 2008]. In this region, most molecular
203 species exhibit strong vibrational-rotational absorption bands.
204 This feature, combined with the use of diode lasers, enables
205 the resolution of single spectral lines of a molecule and to
206 discriminate between different isotopologues.

207 [15] The instrument used here was designed and con-
208 structed to use near-infrared diode laser absorption spec-
209 troscopy to detect water vapor isotopologues with a room
210 temperature, distributed feedback laser (Laser Components
211 GmbH) operating around $1.39 \mu\text{m}$ (7184 cm^{-1}). The laser is
212 tuned over a 1 cm^{-1} spectral range, enabling the nearly
213 simultaneous registration of H_2O isotopologue spectral
214 features, including rovibrational absorption lines belonging
215 to H^{16}OH , H^{17}OH , H^{18}OH , and $^1\text{HO}^2\text{H}$. The $\delta^{17}\text{O}$ mea-
216 surements are not considered here since they do not, and in
217 fact are not expected to, yield information beyond that
218 provided by $\delta^{18}\text{O}$ because of the relationship between ^{17}O
219 and ^{18}O observed in all tropospheric meteoric waters
220 [Meijer and Li, 1998]. In order to see deviations from this
221 behavior in tropospheric, evaporated water, extremely high
222 precision measurements of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ are required,
223 which are beyond the capabilities of this spectrometer
224 [Barkan and Luz, 2007].

225 [16] The device uses the sensitive technique of optical
226 feedback cavity enhanced absorption spectroscopy (OFCEAS)
227 and was developed in collaboration with the University of
228 Grenoble. Advantages of OFCEAS, compared to other laser
229 spectroscopic techniques, include the large dynamic range,
230 enabling isotope ratio measurements over almost three orders
231 of magnitude in the water-vapor mixing ratio, and a small gas
232 cell volume, enabling a fast gas exchange and spectrometer
233 response. For a detailed description of the experimental
234 apparatus we refer to a previous publication [Kerstel et al.,
235 2006], whereas its principle of operation is described by
236 Morville et al. [2005].

237 [17] The technique of CEAS yields a direct measurement
238 of the wavelength-dependent absorption coefficient a ,
239 which can be written as the product of the number density n ,
240 the normalized line shape function f , the line strength S , and
241 the absorption path length l :

$$a(\nu) = n(p, T)f(p, T, \nu - \nu_0)S(T)l, \quad (2)$$

where p and T represent the total pressure and temperature
of the sample in the spectrometer cavity, ν represents the
laser frequency, and ν_0 represents the line-center frequency.
Integration of the absorption coefficient over the entire line
profile f (i.e., the “line area”) directly yields the number
density of the associated species, assuming the line strength
is known. The line strengths of the absorption lines used in
this study, as well as their temperature and pressure
dependencies, are all tabulated in the HITRAN database
[Rothman et al., 2005]. The effective path length is deter-
mined by frequent calibration of the absorbance scale of the
spectrometer by means of cavity ring down measurements
[Kerstel et al., 2006].

[18] The mixing ratio is calculated assuming ideal gas
behavior. The isotope ratios, instead, are given by the super-
ratio of the absorption coefficients of the rare and abundant
isotopologues in the sample and a reference material
[Kerstel, 2004] and, thus, require no knowledge of the line
strengths. For example, in the case of oxygen-18,

$$\delta^{18}\text{O} = \frac{[a(\text{H}^{18}\text{OH})/a(\text{H}^{16}\text{OH})]_{\text{sample}}}{[a(\text{H}^{18}\text{OH})/a(\text{H}^{16}\text{OH})]_{\text{reference}}} - 1. \quad (3)$$

We note that equation (3) differs from equation (1) in the use
of molecular instead of atomic quantities. It can be shown that
the molecular isotopologue abundance ratios, $^2R_M = [\text{HO}^2\text{H}]/$
 $2[\text{H}_2\text{O}]$ for deuterium and $^{17/18}R_M = [\text{H}_2^{17/18}\text{O}]/[\text{H}_2^{16}\text{O}]$ for
oxygen-17/18, are in good approximation equal to their
atomic counterparts (such as $^2R = [^2\text{H}]/[^1\text{H}]$). This equiva-
lence of molecular and atomic values is an even better
approximation for the case of the “delta value” ($\delta = R_{\text{sample}}/$
 $R_{\text{reference}} - 1$) of equation (3) [Kerstel, 2004].

[19] The reference ratio of the absorption coefficients is
determined experimentally through periodic calibration
measurements on local standard materials that are well
characterized on the international, two-point VSMOW-
SLAP (standard light Antarctic precipitation) isotope scale
[Gonfiantini, 1984; Hut, 1987], as explained in more detail
in section 2.2.

[20] The whole setup is housed in an insulated aluminum
case, thermally regulated by two ribbon heaters (MINCO) to
a temperature of 32°C . To facilitate thermal exchange, two
ventilators are placed inside the box. A flow is established
inside the gas cell by means of a molecular drag pump. The
flow rate is adjusted via a manual valve, while the gas
pressure inside the cell is stabilized independently of the flow
by a forward pressure controller (Bronkhorst). The pressure
is therefore kept stable at a value of 40 mbar. The small gas
cell volume of $\sim 20 \text{ mL}$ ensures a fast gas cell exchange ($< 4 \text{ s}$)
with a very modest pumping speed of 150 mL/min (Alcatal
Drytel 1025) [Kerstel et al., 2006].

2.2. Calibration System

[21] Figure 1 represents a schematic of the gas handling
system used to calibrate the measurement of the atmospheric
water isotopes. The gas flow system basically has three
operational modes: ambient air inlet and either one of two
calibration gas streams. Outside ambient air was contin-
uously drawn through the system by means of fused silica-
coated (1/4-in. OD) tubing (O’Brien) leading from the
rooftop of our laboratory (line 3). As the flow inside the

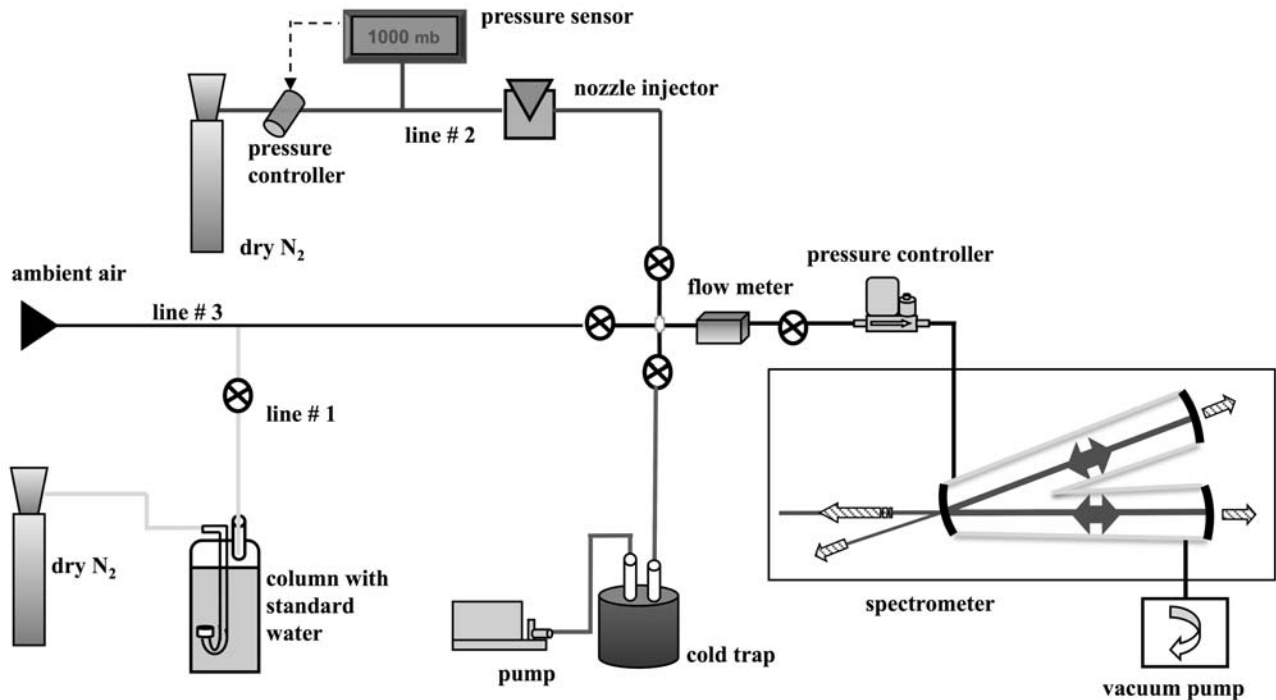


Figure 1. Sketch of the experimental arrangement used to calibrate the atmospheric measurements of water vapor isotope ratios. Three gas lines were used, one to lead atmospheric air to the laser spectrometer (line 3), and the other two for delivery of reference water vapor (lines 1 and 2), as explained in the text (section 2.2). The pressure controller establishes a pressure of 40 mbar inside the optical cell, whereas the flow was regulated to 150 mL/min by a metering valve at the exit of the spectrometer.

298 tube remains laminar, the length of the tube (10 m) does not
 299 noticeably alter the overall system response time, which
 300 was demonstrated to be 2 s in a series of measurements
 301 carried out by switching between synthetic air and labora-
 302 tory air. A 50 μm nylon filter was inserted at the beginning
 303 of the sampling line in order to eliminate particles from the
 304 airstream.

305 [22] The atmospheric measurements were interrupted
 306 once or twice daily for calibration measurements using two
 307 local isotopic standard waters. The use of two reference
 308 waters enables the calibration of the atmospheric moisture
 309 measurements to a two-point isotope scale in a procedure
 310 similar to the standard VSMOW-SLAP calibration proce-
 311 dure described by Gonfiantini [1984] and Hut [1987].

312 [23] Two calibration lines were installed. In the case of
 313 tropospheric water vapor characterized by a mixing ratio
 314 higher than 5000 ppmv, as encountered during measure-
 315 ments carried out in the month of July, calibration line 1 was
 316 used to obtain a reference moist airstream with a mixing
 317 ratio of 15,000 ppmv, comparable to that of the analyzed
 318 atmospheric air. In this case, two different reference waters
 319 of known isotopic composition, named GS-90 and GS-91,
 320 were stored in two tall (~ 1 m) and narrow columns with a
 321 volume of 2 L. The large volume of the bubblers guarantees
 322 that the isotopic composition change, due to the departure of
 323 water from the column in the form of vapor, is completely
 324 negligible. The isotopic composition of the GS-90 and
 325 GS-91 reference waters was determined by repeated

IRMS analyses in our Groningen laboratory. The isotope 326
 ratios are $\delta^2\text{H} = (-42.9 \pm 0.6)\text{‰}$ and $\delta^{18}\text{O} = (-6.34 \pm 0.02)\text{‰}$ 327
 for GS-90, and $\delta^2\text{H} = (-170.3 \pm 0.5)\text{‰}$ and $\delta^{18}\text{O} = (-22.37 \pm$ 328
 $0.02)\text{‰}$ for GS-91. A flow of dry nitrogen (grade purity 329
 5.0 UN 1066 nitrogen, water content < 1 ppmv), from a 330
 high-pressure tank, was passed ("bubbled") through the 331
 water after entering at the bottom of the column. The flow 332
 rate through the water column was set at 150 mL/min. The 333
 moist stream leaving the column, and subsequently diluted 334
 with nitrogen from the same tank in order to arrive at total 335
 water-vapor content similar to the analyzed air, was led 336
 through the laser spectrometer. The dilution ratio was 337
 determined by mass flowmeters, whereas the exact mixing 338
 ratio in this case was determined by the temperature and the 339
 gas pressure in the bubbler column. Using this scheme, the 340
 isotope ratio of the moist air exiting the column is thus not 341
 identical to the liquid water feed, but a fractionation factor 342
 that depends on the water-vapor temperature must be taken 343
 into account. The expected delta values for the GS-90 344
 standard in the moist stream are -16.05‰ and -121.3‰ for 345
 $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively, given the fractionation factors of 346
 -9.71‰ and -78.4‰ for ^{18}O and ^2H , in that order, at a 347
 temperature of 20°C [Majoube, 1971]. This is in good 348
 agreement with the experimental values determined by 349
 cryogenically collecting the GS-90 saturated water-vapor 350
 sample at the top of the column and analyzing it by IRMS: 351
 The reported isotope ratios in this case were $(-16.37 \pm$ 352
 $0.02)\text{‰}$ for $\delta^{18}\text{O}$ and $(-120.7 \pm 0.4)\text{‰}$ for $\delta^2\text{H}$. The actual 353

354 isotopic composition during the calibration cycles was
355 determined using fractionation factors corresponding to
356 the measured temperature in the climatically controlled
357 room.

358 [24] Gas line 2 was used for calibration of the spectrometer
359 at a mixing ratio value of 4,500 ppmv during the January
360 measurements when mixing ratios were typically <5000 ppmv.
361 This independent calibration scheme also served as a check
362 on the bubbler-generated, diluted calibration streams. It uses a
363 nozzle injector (Microdrop GmbH) to inject water droplets of
364 known size at a preset repetition frequency into a stream of
365 dry nitrogen or synthetic air. A detailed description of this
366 system is published elsewhere [Iannone et al., 2009a]. The
367 measurements were calibrated by the introduction of two
368 local water standards, in this case GS-48 and GS-50. The
369 GS-48 standard has an isotopic composition of $(-43.3 \pm 0.3)\text{‰}$
370 for $\delta^2\text{H}$ and $(-6.52 \pm 0.03)\text{‰}$ for $\delta^{18}\text{O}$, while the GS-50
371 standard has a value of $(-276.7 \pm 0.3)\text{‰}$ and $(-35.01 \pm 0.03)\text{‰}$
372 for $\delta^2\text{H}$ and for $\delta^{18}\text{O}$, respectively. Two nozzle injectors were
373 employed in order to switch more rapidly between the two
374 water standards.

375 [25] Finally, a comparison was made between our online
376 laser spectrometer and the cryogenic sampling technique
377 developed at the Commissariat à l'Énergie Atomique in
378 Paris (CEA). The CEA device uses a trap cooled with an
379 alcohol and dry ice slush and collects larger quantities of
380 water, thus requiring a substantially larger flow (~ 2 L/min)
381 than the laser spectrometer. Therefore, inlet line 3, which
382 carries the ambient air, was equipped with a Y split. One
383 part (150 mL/min) was led to the laser spectrometer, while
384 the remainder went to the cryogenic collection device.

385 [26] Water-vapor samples were collected between 17 and
386 23 July 2007. Air continuously circulated through glass
387 vapor traps immersed in an alcohol bath. The alcohol was
388 kept at -80°C by periodically adding liquid nitrogen or ice
389 slush. Samples were collected during time intervals lasting
390 between 10 and 13 h for a single sample.

391 [27] No more than a maximum of two samples per day
392 could thus be collected (e.g., between 1300 and ~ 2200 /
393 2330 h and between 2330 and ~ 1000 h of the following
394 day. The long sample time is due to the fact we wanted to
395 collect 2–3 ml of water, a requirement for precise IRMS
396 analyses at CEA. The calibration of the spectrometer using
397 the bubblers was then performed in the time interval
398 between 1000 and 1300 h and generally completed in less
399 than 1.5 h.

400 [28] The water collected in the traps was quantitatively
401 transferred to a small container by cryogenic vacuum dis-
402 tillation, within 12 h after collection. The collected water
403 was successively analyzed for its isotope ratios on IRMS
404 instrumentation at CEA. As an additional check, a small
405 fraction of a number of samples was transferred to different
406 vials and analyzed at the Centrum voor IsotopenOnderzoek
407 (Groningen, Netherlands) with the IRMS capabilities of the
408 biomedical laboratory (able to handle samples as small as
409 $10 \mu\text{L}$).

410 [29] Finally, during the intercomparison measurements,
411 temperature and humidity sensors (Tinytag, TGP-4500)
412 were mounted on the top of the building roof, close to our
413 air intake, in order to have a continuous registration of
414 these two atmospheric parameters. Furthermore, meteorolo-
415 gical data were taken from the Royal Netherlands

Meteorological Institute (KNMI) Web site (accessible at 416
<http://www.knmi.nl>). 417

3. Results and Discussion 418

[30] Figure 2 shows an example of data of the ambient 419
vapor isotope ratios for the period from 19 to 22 January 420
2007, in Groningen, Netherlands. Although the instrument 421
has a time resolution of a few seconds (determined by the 422
gas exchange rate), for these long time series we show one 423
data point per 5 min. With an averaging time of 300 s, the 424
measurement precision was determined to be 0.20‰ for 425
 $\delta^{18}\text{O}$ and 0.75‰ for $\delta^2\text{H}$ at a water mixing ratio of 426
 $\sim 15,000$ ppm. These values are comparable to those reported 427
previously for this spectrometer [Iannone et al., 2009a, 428
2009b], despite the relatively high value of the NEA, which 429
was determined to be approximately $10^{-9} \text{ cm}^{-1} \text{ Hz}^{-0.5}$, 430
whereas a more typical value for this OFCEAS spectrometer 431
is $4 \times 10^{-10} \text{ cm}^{-1} \text{ Hz}^{-0.5}$ [Kerstel et al., 2006]. 432

[31] For reasons of clarity, the calibration data are not 433
shown in the graphs but the corresponding periods are 434
clearly visible as gaps in the data record ($\sim 10\%$ of the 435
overall measurement time). 436

[32] In Figure 2a, the black line (top curve) represents the 437
relative humidity measured in our meteorological station of 438
Lutjewad (about 40 km to the northwest of Groningen), while 439
the shaded line (bottom curve) shows the ambient tempera- 440
ture. Figure 2b shows the amount of atmospheric water 441
detected by our infrared laser spectrometer. It is worth 442
noting how the spectrometer water-vapor mixing ratio fol- 443
lows a pattern consistent with the relative humidity, in 444
agreement with the observation of small and often correlated 445
variations in the outside temperature. Still, weather during 446
this period was very variable and the relative humidity (RH) 447
reached a maximum value of 93% between 19 and 20 January 448
(day 1 and day 2), with an amount of rain of 2 mm. Between 449
20 and 21 January (day 2 and 3), rainfall reached 10 mm. 450
The minimum value of 40% RH occurred by the end of 451
22 January (day 4), during a snow event. 452

[33] Over this 4 day period of measurements, $\delta^2\text{H}$ and 453
 $\delta^{18}\text{O}$ values also exhibited a high degree of variability, 454
attributed to the dynamic meteorological conditions. The 455
isotope values of deuterium span a wide range from -90‰ 456
to -150‰ , while the full range of variability of oxygen-18 457
measurements lies between about -16‰ and -33‰ . The 458
 $\delta^{17}\text{O}$ measurements are not shown here since they are not 459
expected to provide further information beyond that given 460
by $\delta^{18}\text{O}$ due to the very tight relation between $\delta^{17}\text{O}$ and 461
 $\delta^{18}\text{O}$ observed in all tropospheric water [see, e.g., Meijer 462
and Li, 1998]. In fact, the ^{17}O anomaly for our data, 463
defined as $\Delta^{17}\text{O} = \ln(1 + \delta^{17}\text{O}) - 0.528 \ln(1 + \delta^{18}\text{O})$, 464
assumes an average value of -0.4‰ , equal to zero within 465
the standard deviation of 1.6‰. 466

[34] Continuous measurements of atmospheric water- 467
vapor isotopes were also performed between 17 and 23 July 468
2007. At the time of recording the data, also 10 atmospheric 469
water vapor samples were collected by a cryogenic sample 470
method (see section 2.2). During the same period, time- 471
integrated rainfall samples were collected and subsequently 472
analyzed by mass spectrometry (see the discussion of 473
Figure 4b here below). As before, the daily averaged 474
weather conditions were taken from the KNMI Web site. 475

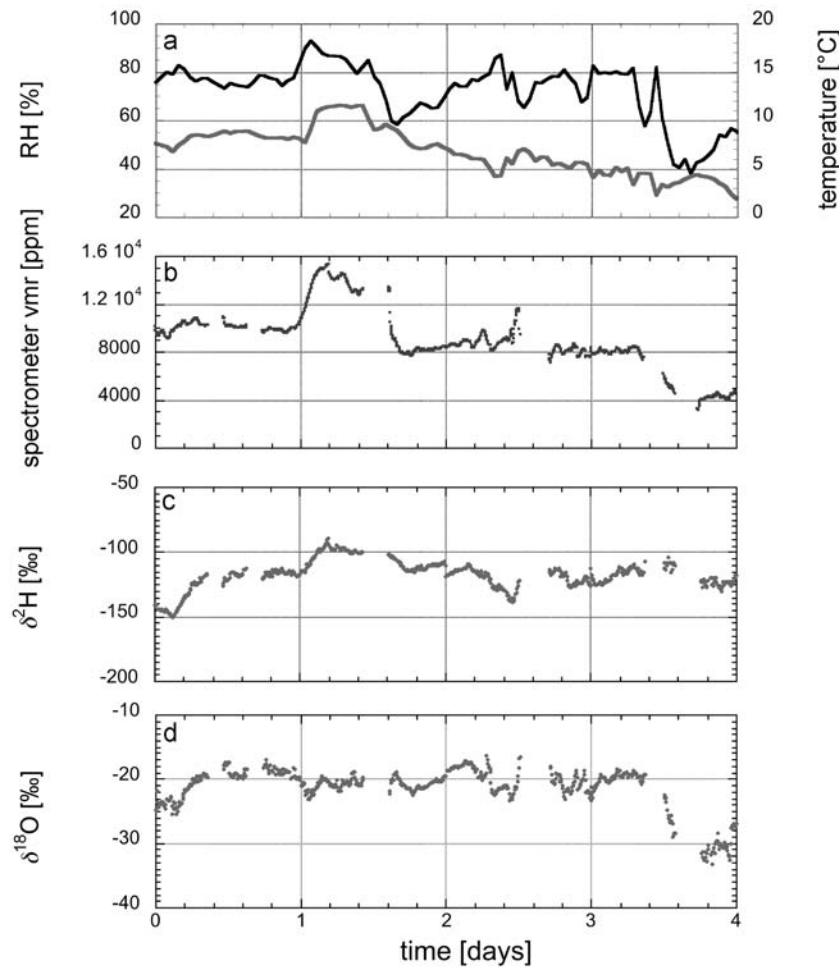


Figure 2. Continuous time series over 4 consecutive days with a 300 s time resolution: (a) ambient temperature and the simultaneously recorded relative humidity at the Lutjewad meteorological station (40 km NW of Groningen), (b) the volume mixing ratio of atmospheric air sampled from just outside the Groningen laboratory (53°N) as measured by the G2WIS spectrometer, (c) $\delta^2\text{H}$, and (d) $\delta^{18}\text{O}$. Two rain events and one snow event occurred during the 4 day measurement period (19–22 January). The horizontal arrows in Figure 2d indicate the precipitation events that occurred during these 4 days.

476 Figure 3a shows the 1-week time series of the relative
 477 humidity and ambient temperature, and the spectrometer
 478 water vapor content variation in the atmosphere, $\delta^2\text{H}$, and
 479 $\delta^{18}\text{O}$ are shown in Figures 3b, 3c, and 3d, respectively. For
 480 clarity of presentation, the precipitation data are not shown.
 481 Over this week, there was considerable variability in the
 482 isotope ratios of $\delta^2\text{H}$ and $\delta^{18}\text{O}$. The maximum values of $\delta^2\text{H}$
 483 and $\delta^{18}\text{O}$ were about -79‰ and -7.0‰ , respectively, and
 484 the minimum values were -135‰ and -23‰ , respectively.
 485 [35] In Figure 3 the horizontal bars represent the δ values
 486 determined by the cryogenic trap described in section 2.2.
 487 The extent of the bars corresponds to the sampling period.
 488 [36] To be able to compare the results of the cold trap and
 489 the laser spectrometer methods, mass-weighted average
 490 $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are obtained by weighing the delta
 491 values with the corresponding spectrometer water-vapor
 492 mixing ratios. The summation is over all delta values
 493 determined within the time frame of the cryogenic collection
 494 in question. The data are reported in Table 1. We notice
 495 that the overall deviation, given by the mean value of the

residuals, is -1.3‰ (1.7‰) for $\delta^{18}\text{O}$ and $+1.0\text{‰}$ (7.7‰) for
 $\delta^2\text{H}$, where the values in parentheses give the standard
 deviation ($n = 10$). No clear correlation is observed between
 the residuals of ^{18}O and ^2H . Similar differences between the
 isotope ratio measurements obtained by means of laser and
 those obtained by cryogenic collection and subsequent IRMS
 analysis have been reported previously by other authors.
 First, Lee *et al.* [2005] found an average difference of
 -1.77‰ (1.75‰) for their ^{18}O measurements. This differ-
 ence reduced to -0.36‰ (1.43‰) after correcting the data
 for incomplete cryogenic collection. Later, Wen *et al.* [2008]
 observed a disagreement between their TDL and cryogenic
 sampling techniques of up to -10.4‰ and $+4.9\text{‰}$ for deu-
 terium and oxygen-18, respectively. Also, no correlation
 among the residuals of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ could be seen [Wen
et al., 2008]. The authors attributed these differences to the
 difficulties of condensing out all sample water vapor passing
 through the cryogenic traps, as well as a combination of
 errors in both the laser spectrometer and IRMS analyses.

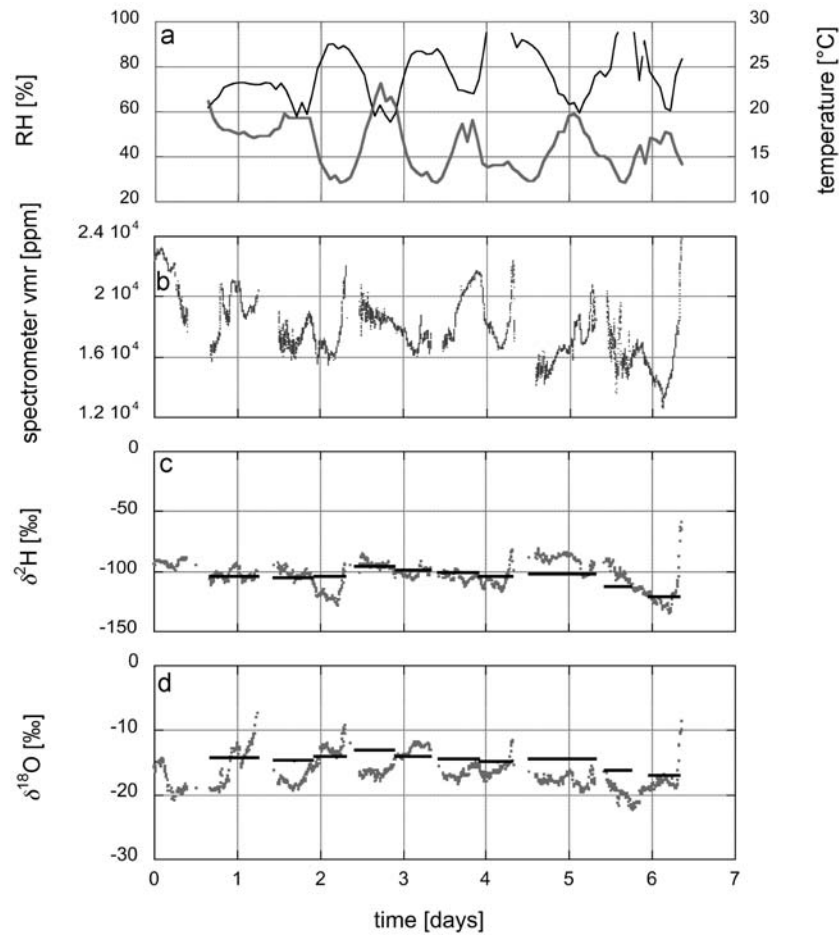


Figure 3. Time series of 300 s isotope composition of ambient water vapor measured with the laser spectrometer during the week of intercomparison with the cold-trap method (17–23 July 2007): (a) ambient temperature and the simultaneously recorded relative humidity just outside the Groningen laboratory (53°N, 6°E), (b) volume mixing ratio of atmospheric air as measured by the G2WIS spectrometer, (c) $\delta^2\text{H}$, and (d) the $\delta^{18}\text{O}$. The horizontal bars give the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values determined by the water-vapor cryogenic sampling system, with the horizontal extent of the bars indicating the sampling period.

515 [37] In our case, the discrepancy is most likely caused by
 516 condensation and the subsequent evaporation within the
 517 ambient air gas-inlet line. In particular, during the early
 518 morning hours the air temperature can drop below the

dewpoint temperature, causing a phase change within the
 519 sampling stream and consequently altering the vapor isotope
 520 content. Although an attempt was made to heat the tubing
 521 line during the measurements, this failed to heat the total
 522

t1.1 **Table 1.** Comparison of the Water Vapor Mixing Ratio-Weighted $\delta^2\text{H}$ and $\delta^{18}\text{O}$ Values of the Atmospheric Water Vapor as Measured
 t1.2 by G2WIS, and by Cryogenic Collection Followed by IRMS Analysis, for the Data Shown in Figure 3 (Collected from 17 to 23 July
 t1.3 2007)^a

t1.4	Samples	$\delta^2\text{H}_{\text{IRMS}}$ (‰)	$\delta^2\text{H}_{\text{LS}}$ (‰)	$\Delta^2\text{H}_{\text{LS-IRMS}}$ (‰)	$\delta^{18}\text{O}_{\text{IRMS}}$ (‰)	$\delta^{18}\text{O}_{\text{LS}}$ (‰)	$\Delta^{18}\text{O}_{\text{LS-IRMS}}$ (‰)	$v_{\text{H}_2\text{O}}$ (ppm)
t1.5	1	-104.2	-102.9 (4.6)	-1.3	-14.3	-14.9 (3.3)	0.6	19098
t1.6	2	-105.7	-104.5 (4.5)	-1.2	-14.8	-17.2 (1.2)	2.4	17449
t1.7	3	-104.5	-117.9 (7.5)	13.4	-14.2	-13.0 (1.5)	-1.2	17300
t1.8	4	-95.8	-96.1 (3.8)	0.3	-13	-16.1 (1.0)	3.1	18164
t1.9	5	-99.9	-102.1 (3.3)	2.7	-14.1	-12.7 (0.9)	-1.4	17108
t1.10	6	-101.3	-104.9 (3.4)	3.6	-14.5	-16.6 (0.9)	2.1	19786
t1.11	7	-104.8	-107.6 (8.0)	2.8	-15	-16.1 (1.3)	1.1	18543
t1.12	8	-102.6	-91.4 (6.1)	-11.2	-14.5	-17.9 (0.8)	3.4	16671
t1.13	9	-112.9	-99.3 (6.0)	-13.6	-16.2	-19.2 (1.0)	3.0	16907
t1.14	10	-121.9	-116.3 (13.7)	-5.6	-17	-17.3 (2.3)	0.3	15962
t1.15	Mean			1.00			-1.3	
t1.16	Standard deviation			7.8			1.7	
t1.17	Standard error			2.4			0.55	

t1.18 ^aThe standard deviations are given in parentheses. IRMS, isotope ratio mass spectrometry; LS, laser spectrometer.

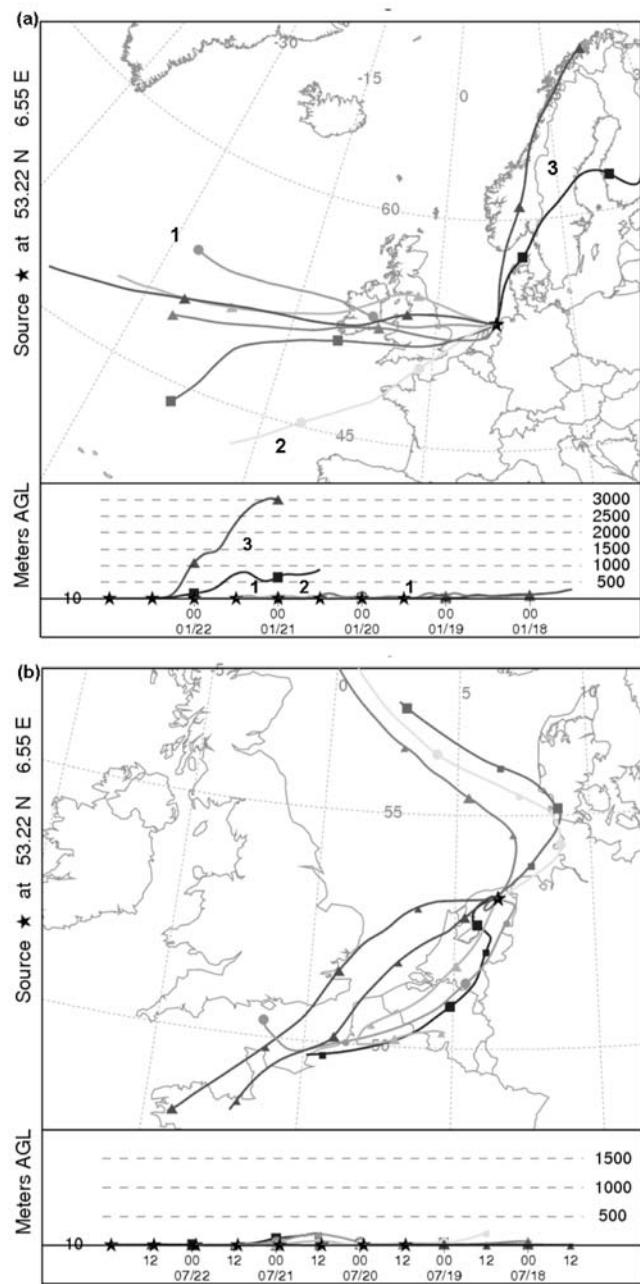


Figure 4. Twenty-four-hour-long backward trajectories produced by the NOAA HYSPLIT model. Two trajectories were calculated per day, one ending at 1200 and the other at 2400, for the two measurement periods: (a) 19–22 January and (b) 17–23 July 2007. Individual trajectories can be identified by their end time as is done in the bottom of each of Figures 4a and 4b. Trajectories start at 10 m above the ground. The boundary layer extended from 10 to 3000 m and from 10 to 1500 m for the months of January and July, respectively.

523 length of the inlet tube to temperatures above the high
524 summertime temperatures registered on some of the days.
525 The condensation of water vapor inside the inlet line is
526 particularly apparent in Figure 3 during the early morning
527 hours of days 2, 3, 5, and 7 by a rapid increase in the

measured mixing ratio beyond that predicted by the relative
528 humidity and temperature records, and sharply increasing
529 isotope ratio signals (especially visible in the ^{18}O record).
530 We believe that these excursions are due to the fact that the
531 liquid water, which formed earlier in the gas line during
532 periods of high outside temperatures, starts to evaporate
533 faster when the atmospheric water content decreases during
534 periods that combine a low outside temperature with a low
535 RH. Since, in all cases, these periods of excessively high
536 observed values of the volume mixing ratio are followed
537 immediately by a calibration cycle of the spectrometer, the
538 instrument is, as it were, reset. The flushing of the spec-
539 trometer with dry air, as part of the calibration cycle,
540 effectively removes the excess humidity in the inlet line.
541 The remainder of the data set is therefore believed to be still
542 largely representative of outside atmospheric moisture.
543

[38] When comparing the data between January and July,
544 a first difference to highlight concerns the variations in the
545 RH. During most of the days in the winter period the water
546 vapor content is fairly constant, whereas consistently higher
547 water-vapor mixing ratios are observed during daytime than
548 during nighttime in the summer season. This clear diurnal
549 variation is not observed in the January data, in agreement
550 with a strong diurnal temperature signal during the sum-
551 mertime measurements, which is absent in the winter
552 set.
553

[39] It is noteworthy, however, that also during the winter
554 experiment, the RH reached high values (on one occasion as
555 high as 93%), and the absence of a diurnal cycle in this case
556 can be explained by large-scale transport and mixing of air
557 masses rather than the local meteorological conditions. This
558 interpretation of the data finds its origin in Figures 4a and
559 4b, which show backward trajectories computed using the
560 NOAA Hybrid Single Particle Lagrangian Integrated Tra-
561 jectory (HYSPLIT) model (available at <http://www.arl.noaa.gov/HYSPLIT.php>) [Draxler, 1992; Draxler and Hess, 1998]. The figures show that, during winter, air originates
564 from both the western and southern Atlantic Ocean (area 1
565 and 2, respectively), as well as on some occasions from land
566 regions in Norway (area 3). During summer, although the
567 origin of air masses is variable, the direction of the majority
568 of the back trajectories is toward the south.
569

[40] The variations of the deuterium and oxygen-18 isotope
570 ratios in the atmospheric moisture are shown in Figures 5a
571 and 5b, which show $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ for the January and
572 July measurements, respectively. In Figure 5, the global
573 meteoric waterline (GMWL) is shown together with an
574 evaporated waterline, with a slope of 4.5, intended here as a
575 point of reference for the measured isotope ratios.
576

[41] The GMWL describes the globally averaged stable
577 isotope composition of precipitation. During the evaporation
578 of meteoric water, relative humidity is the major factor
579 determining the isotopic composition of the atmospheric
580 vapor besides temperature and wind speed. Humidity affects
581 oxygen and hydrogen differently, such that the slope of the
582 evaporation line varies due to changes in water-vapor
583 mixing ratio content. This occurs because evaporation is
584 partly a nonequilibrium process and, particularly, because
585 lower relative humidity leads to a faster rate of evaporation
586 and, consequently, the kinetic fractionation will be greater.
587

[42] From Figure 5a, it is clear that the individual δ values
588 of ^2H and ^{18}O are located slightly above the GMWL. The
589

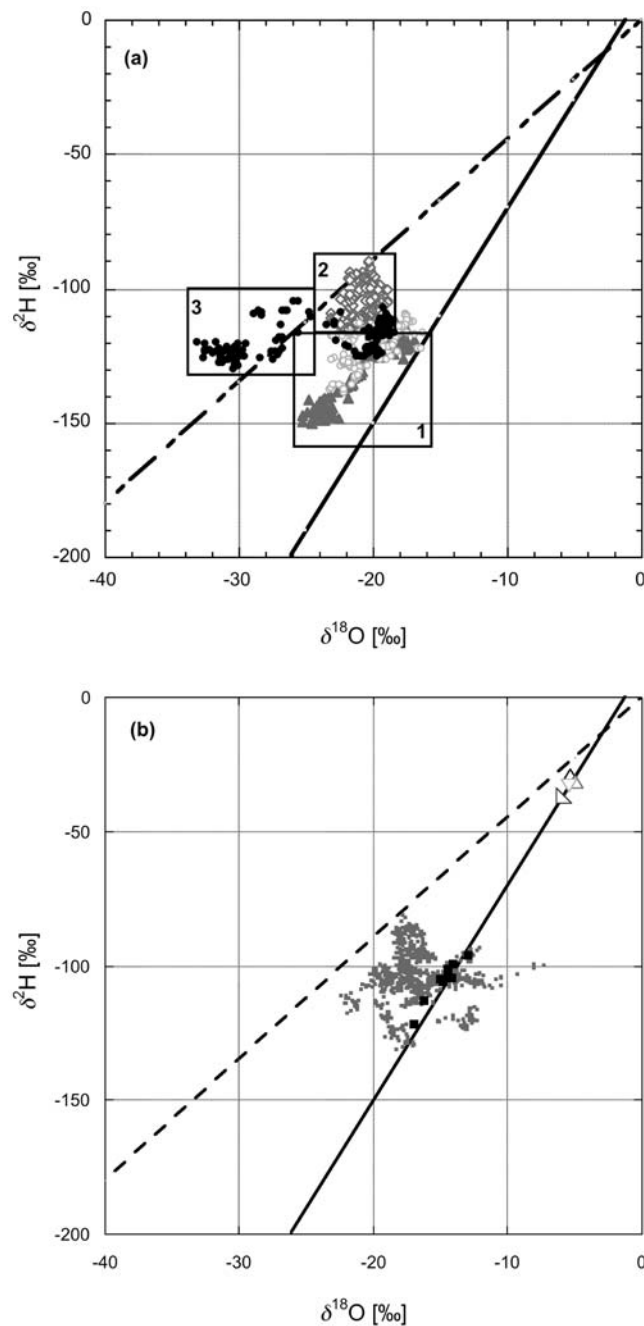


Figure 5. The meteoric relationship for ^{18}O and ^2H in water vapor (a) between 19 and 22 January 2007 (19 January 2007, solid triangles; 20 January 2007, open diamonds; 21 January 2007, open circles; 22 January 2007, solid circles) and (b) between 17 and 23 July 2007. In Figure 5a the three rectangular shapes indicate three different groups of data, each corresponding to a different humidity ranges (40%–60%, area 3; 60%–80%, area 2; and finally 80%–100%, area 1). Data suspected of condensation in the gas line are excluded from Figure 5b. Furthermore, in Figure 5b, the open triangles represent the isotopic composition of the rain events of this week, whereas the solid squares give the isotopic composition of the atmospheric samples collected by the cryogenic sampling system. For comparison, the GMWL (continuous line) and the evaporated water line (dashed line) are shown.

isotope measurements are identified by day: 19 January 590
2007 (solid triangles), 20 January 2007 (open diamonds), 591
21 January 2007 (open circles), and 22 January 2007 (solid 592
circles). Three different groups of data can be identified, each 593
corresponding to a different source area, which becomes 594
apparent when the data are correlated with the back trajec- 595
tories of Figure 4a. In fact, on 19 and 21 January, the air 596
masses are originating from the western Atlantic Ocean 597
(area 1); on 20 January, the back trajectory has its origin 598
over the southern Atlantic Ocean (area 2); whereas on 22 599
January, the air comes from Scandinavia (area 3). The dif- 600
ferent source regions of the air masses are also reflected in 601
the local RH level, which is clearly not determined by the 602
local temperature only (cf. Figure 2, top). In fact, the three 603
different areas correspond to three RH ranges: from 40% to 604
60% (area 3), from 60% to 80% (area 2), and finally from 605
80% to 100% (area 1). The plot of $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ yielded 606
a significant ($r = 0.92$) straight-line relationship for the data of 607
area 1. As well, the linear regression equation for the data of 608
the second area shows a positive correlation ($r = 0.68$) 609
between the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of the water vapor. Finally, a 610
similar but slightly lower correlation ($r = 0.56$) is observed 611
between deuterium and oxygen-18 in the data belonging to 612
the third area. 613

[43] Figure 5b shows, besides the measured atmospheric 614
moisture $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope ratios, the four collected rain 615
samples (triangles). The solid squares represent instead the 616
isotopic composition of the atmospheric water vapor mea- 617
sured by cryogenic collection and subsequent IRMS analysis. 618
Both the laser spectrometer and the IRMS data lie 619
significantly closer to the GMWL compared to the data of 620
January. In particular, as for the laser spectrometer data, the 621
IRMS data are also found above the GMWL. The best fit 622
through the IRMS data defines a slope $\delta^2\text{H}/\delta^{18}\text{O}$ equal to 623
 $6.3 (\pm 0.6)$. This is a consequence of the higher RH. During 624
this summer week, the humidity level reached values of 625
about 96% in a strong diurnal cycle, and rain events 626
occurred during the night from 17 to 18 July, and on 20, 21, 627
and 22 July. These precipitation events are the main cause of 628
variation of $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Precipitation leads to a more 629
negative isotopic composition of the remaining vapor, while 630
the increased humidity reduces the evaporation of local 631
surface water. Moreover, rain events are generally linked to 632
the arrival of different (warmer) air masses. 633

[44] It should be noted that the laser spectrometer isotope 634
data show significantly higher variation than the cryogeni- 635
cally collected samples. This is mostly due to the fact that 636
the cryogenic collection method suffers from a strong bias 637
toward high water content periods, especially given the 638
extremely long sample collection times that were required to 639
collect an amount of liquid water sufficiently large for iso- 640
topic analysis at the CEA laboratory in Paris. 641

[45] Figures 5a and 5b are thus in good agreement with 642
theoretical considerations according to which high levels of 643
humidity result in a better isotope equilibrium between 644
liquid and vapor and a MWL with a slope closer to 8 [Clark 645
and Fritz, 1997]. 646

[46] In addition, it is possible to observe the influence of 647
air originating from land regions in Scandinavia on the 648
isotopic signature during the week in January. In particular, 649
the arrival of these relatively dry air masses from north- 650
westerly regions results in strong changes in the $\delta^{18}\text{O}$ of 651

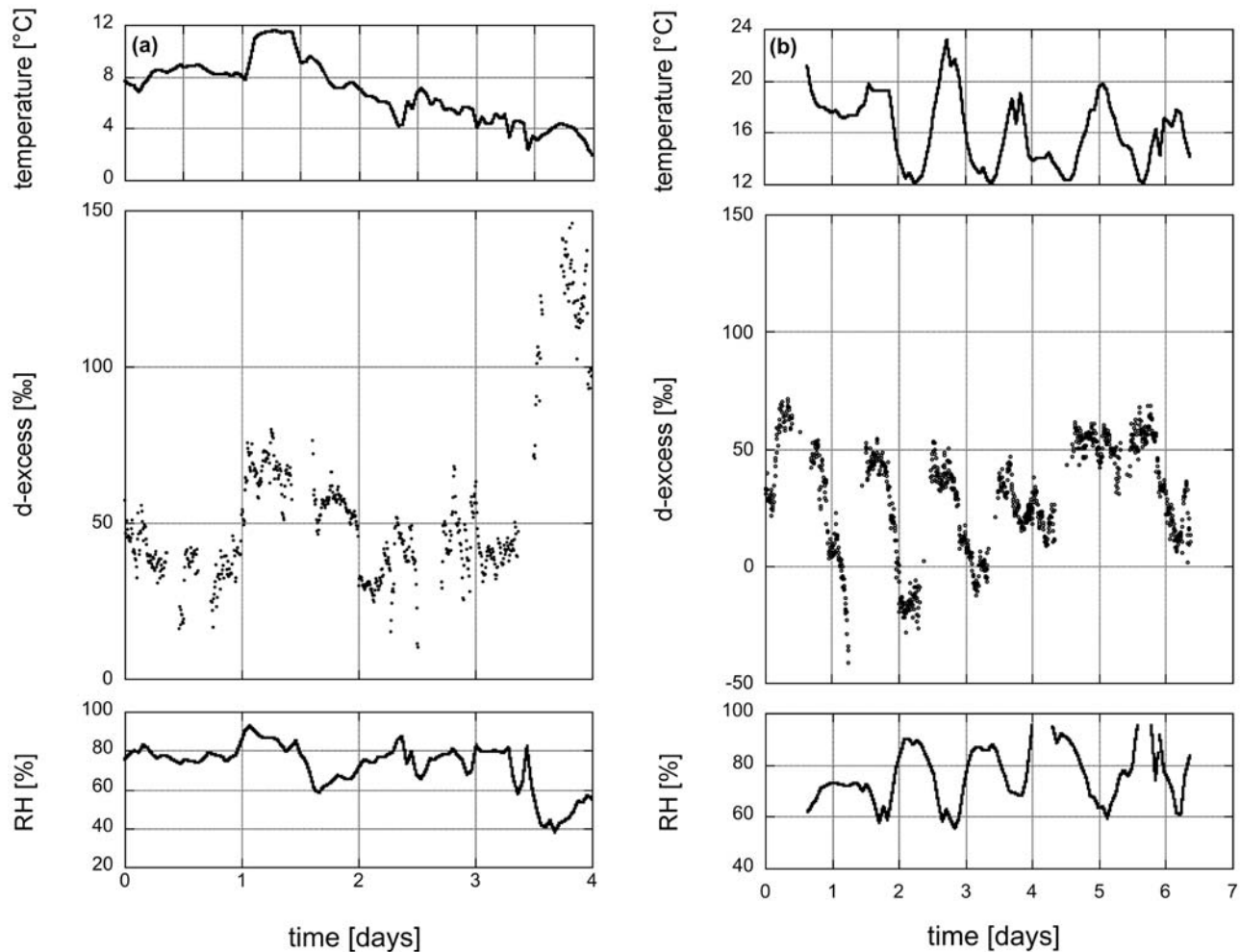


Figure 6. Time series of d excess based on the laser spectrometry method for (a) 19–22 January and (b) 17–23 July 2007: (top) ambient temperature and (bottom) relative humidity.

652 atmospheric water vapor. In fact, data of the second half of
 653 the day on 22 January (Figure 5a) have $\delta^{18}\text{O}$ values that are
 654 consistently far from the GMWL. As a matter of fact, this
 655 necessarily indicates that (isotope fractionation in the
 656 hydrologic cycle during this part of the day is not governed
 657 by liquid-vapor equilibrium. *Jouzel and Merlivat [1984]*
 658 proposed that nonequilibrium condensation becomes sig-
 659 nificant when sublimation on ice crystals occurs. These data,
 660 in fact, come from a period of a cold front passage during
 661 which snowfall occurred, corresponding to a sharp
 662 decreasing of the humidity as shown in Figures 2 (top) and 4a.
 663 This snow event explains why $\delta^{18}\text{O}$ is so much lower com-
 664 pared to the previous period.

665 [47] During these particular meteorological conditions, the
 666 decrease in the $\delta^2\text{H}$ value is less remarkable than that for
 667 ^{18}O . This can be explained in terms of higher deuterium
 668 excess, defined as $d = \delta^2\text{H} - 8 \cdot \delta^{18}\text{O}$ [*Dansgaard, 1964*], due
 669 to a strong kinetic evaporation, which takes place into
 670 unsaturated air. Vapor generated under low-humidity con-
 671 ditions has a high deuterium excess, as a result of the fact
 672 that the relative contribution of kinetic fractionation is larger
 673 for ^{18}O than for ^2H [*Araguás Araguás et al., 2000*]. This is
 674 very visible in Figure 6a, where the deuterium excess, for
 675 the January week, is graphed with the ambient temperature

and the RH. Typical values of d excess in rain samples in
 the Groningen region vary between 10‰ and 30‰. In our
 case, since the data define a $\delta^2\text{H}/\delta^{18}\text{O}$ slope < 8 , the d excess
 shows higher values. During the week in January, the deu-
 terium excess ranged between +20‰ and +75‰ for most of
 the measurements period, except for the second half of the
 last day (22 January), where d excess reached values up to
 +125‰, indicating extreme low-moisture conditions. High
 values of d excess were also found by *Angert et al. [2008]*.
 In their publication they discuss results of measurements of
 the isotopic composition of atmospheric water vapor per-
 formed over 9 years (1998–2006). Although the temporal
 resolution is not very high, they report d excess values up to
 +50‰ during wintertime. The measurements were carried
 out in Israel, at which latitude one would normally expect to
 see lower deuterium excess values than at the higher latitude
 of our study. More important, the cryogenic collection
 method of the Israeli study is strongly biased toward high
 humidity (since during periods of high humidity more water
 is collected than during equally long low-humidity periods)
 and, thus, low deuterium excess, exacerbated by the long
 data collection times. From Figure 6a, we thus conclude that
 the d excess increases as the RH under which the evapora-
 tion occurred decreases. A plot of the d excess versus the

700 local RH shows a statistically significant correlation ($r =$
701 0.60) under dry winter conditions. In addition, air masses
702 with different moisture characteristics, due to their different
703 origins, have higher d excess values and the d excess value
704 can provide specific information to identify the mixing of
705 evaporated air in the atmosphere.

706 [48] Figure 6b shows d excess for the week in July
707 compared with temperature and humidity. During these
708 summertime measurements, the d excess was negatively
709 correlated with the RH with a correlation coefficient of 0.48.
710 If the humidity is low, d excess values are high. In contrast,
711 d excess values corresponding to high humidity are low.
712 Again we see that the d excess may give insight into the RH
713 deficit in air masses.

714 [49] These observations are in good agreement with the
715 work of *Uemura et al.* [2008], who determined deuterium
716 excess of atmospheric water vapor above the Southern
717 Ocean in order to provide detailed knowledge of ocean
718 surface conditions.

719 4. Conclusion

720 [50] We have applied our instrument, originally designed
721 for the in situ isotope analysis of stratospheric water vapor,
722 to continuous, ground-based atmospheric water-vapor
723 isotope measurements.

724 [51] Two approximately 1 week long data sets were
725 recorded, one in January and the other in July 2007. The
726 July data set was compared to IRMS analyses on moisture
727 samples collected simultaneously by a cryogenic technique.
728 Differences between the two different measurement strate-
729 gies are attributed to condensation in the inlet line that affects
730 mostly the laser measurements, as well as to incomplete
731 sample collection in case of the cryogenic method. Thanks to
732 the high time resolution of the laser method, as well as its
733 continuous measurement nature, the inline condensation
734 events are easily identified in both the volume mixing ratio
735 and the isotope ratio records. The data sets also make it very
736 apparent that the cryogenic technique is strongly biased
737 toward high-water-concentration data and thus misses many
738 of the most interesting features at low-water-volume mixing
739 ratios visible in the continuous, high-resolution record.

740 [52] A strong positive relationship is observed between
741 the isotopic composition of the water vapor and its mixing
742 ratio, suggesting that the RH is the main meteorological
743 parameter controlling the isotope distribution near the sur-
744 face, as has been demonstrated previously in other related
745 studies [*Angert et al.*, 2008; *Jacob and Sonntag*, 1991;
746 *White and Gedzelman*, 1984].

747 [53] Even with the relatively small data set of this study,
748 interesting differences between the behavior of the isotope
749 signals in the winter and summer seasons are apparent. In
750 particular, we observe that in summer the evaporation and the
751 precipitation processes affect both deuterium and oxygen-18
752 simultaneously. High temperatures and high levels of
753 humidity result in a near-isotopic equilibrium between air
754 moisture and precipitation. Furthermore, the summer data
755 show a clear diurnal cycle, in contrast to the winter data. In
756 the wintertime, on the contrary, the interaction of fresh dry
757 air from northwest of Groningen with western Atlantic
758 Ocean air masses makes the change in the deuterium and
759 oxygen-18 isotopes decoupled to a larger extent than is the

case in the summer season. For this reason also, the atmo- 760
spheric moisture shows a large deuterium excess in winter. 761

[54] Nowadays, measurements of water vapor isotopes 762
have become a significant topic in several fields of research, 763
for example, in hydrology and ecology. With the introduction 764
of laser technology, it has become increasingly possible to 765
perform simultaneous in situ measurements of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ 766
in water vapor, making the optical isotope ratio technique 767
definitely competitive with IRMS. Water-vapor isotope 768
samples obtained with a cryogenic system, and subsequently 769
analyzed with IRMS, can provide only an episodic picture of 770
the weather conditions, which may turn out to be insufficient 771
for reliable conclusions concerning changes in atmospheric 772
water vapor. 773

[55] So far, the calibration of a laser spectrometer to 774
measure water-vapor isotopes in near-surface atmospheric 775
air has been most commonly done by means of a dew point 776
generator [*Lee et al.*, 2005; *Wen et al.*, 2008]. This requires 777
the knowledge of temperature-dependent isotope fraction- 778
ation factors since the isotopic composition of the vapor is 779
related to that of the liquid in the reservoir, and the need of 780
relatively large quantities of water involved makes this 781
procedure relatively expensive and quite unsuitable for field 782
applications. The microdrop method developed by us can be 783
easily extended to higher volume mixing ratios and is likely 784
to become an important alternative to the dew point gener- 785
ator [*Iannone et al.*, 2009a]. The problems encountered with 786
condensation in the inlet tubing during the summertime 787
measurements in this preliminary study are easily resolved 788
by properly heating the entire length of the inlet tube (e.g., 789
by Ohmic heating) or by reducing the pressure in the inlet 790
tube immediately after the air intake. 791

[56] Monitoring the stable isotope composition of atmo- 792
spheric water vapor can provide a continuous record of 793
valuable data on the atmospheric hydrological cycle. This 794
will help to further understand the functioning of, and in- 795
teractions between, the water cycle and other biogeochemi- 796
cal cycles, which in combination with retrieved observations 797
by satellites will enable global mapping of the water cycle. 798

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