Atmospheric Measurement Techniques Discussions

Interactive comment on "Measuring variations of δ^{18}O and δ^2H in atmospheric water vapour using laser spectroscopy: an instrument characterisation study" *by* F. Aemisegger et al.

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Replies to the comments from referee 2

The reviewer's comments are repeated, followed by our replies. Specific comments are given for the printer-friendly version of the manuscript.

We would like to thank referee 2 for his/her constructive comments that helped to improve our paper. We address each comment point by point (see below) and performed structural changes in order to address the reviewer's general comment on conciseness. The structure is now as follows: Abstract 1) Introduction 2) Instruments 3) Delta scale

linearity 4) Water vapour mixing ratio calibration 5) Water concentration dependency of isotope measurements 6) Isotope measurement stability 7) Response time of the measurement systems 8) Comparative ambient air measurements 9) Conclusions

For each instrument characteristic, the experiments, results and discussion parts are now described together in a dedicated section. We think that this allows a clearer and more succinct presentation of the individual experiments. The different aspects are finally brought together and recommendations are formulated in the Conclusions section. This allows for a slight shortening of the text as suggested by referee 2. The section references, when citing the corrected text refer to this new structure.

The presentation of the results of the new instrument versions was kept in the individual instrument characteristic section. We added some results for the delta scale tests for completeness. For the response times the latest versions don't show any improvement. This is now mentioned but no results are presented.

1) P. 1597 L. 1: The title could be more specific by explicitly mentioning the commercial nature of the laser-based spectrometers and the comparative nature of the study: "... using two commercial laser-based spectrometers".

The title was changed to: "Measuring variations of δ^{18}O and δ^2H in atmospheric water vapour using two commercial laser-based spectrometers: an instrument characterisation study"

2) P. 1600 L. 14: The references to Baer 2002 and Crosson 2008 are inappropriate here, as they do not refer to water (vapor) isotope analyzers. I suggest referring instead to the company websites.

Corrected, the text was changed as follows: "Several research instruments (Webster, 2003; Kerstel et al., 2006; Sayres et al., 2009; Dyroff, 2010) and commercial measurement systems (Picarro, www.picarro.com; Los Gatos Research, www.lgrinc.com) based on cavity ring-down, cavity enhanced and tunable diode laser absorption spec-

troscopy have been proposed in the last decade."

3) P. 1601 L. 23: replace "permil" by "relative" and "approved" by "accepted".

Corrected as suggested, the sentence is now: "The heavy isotopic content of a given water vapour sample is generally expressed in terms of relative deviation of the isotopic mixing ratio from an internationally accepted standard."

4) P. 1602 L. 4-9: The formulation is imprecise: VSMOW is not just a reference standard, it is the internationally accepted primary standard defining the scale zero. $R_{standard}$ is not a reference standard but rather the relevant isotopic (atomic, not molecular) ratio of the primary standard VSMOW. SLAP is also a primary standard, used in combination with VSMOW to define the isotope scale (according to the IAEA guide lines), but it is not a normalization factor:

The sentence now reads: "The internationally accepted primary standard defining the scale zero is known as the Vienna Standard Mean Ocean Water (Gonfiantini, 1978) distributed by the IAEA. $R_{standard}$ is the isotopic ratio of VSMOW. When measuring the isotopic composition of water samples, the delta values have to be normalised according to the IAEA VSMOW2-SLAP2 scale as described in (IAEA, 2009), which corresponds to a two point calibration with a fixed zero point (VSMOW) and a second reference point (SLAP, Standard Light Antarctic Precipitation)."

5) P. 1602 L. 12-18: The term "atomic mass spectrometry" is inappropriate here, as in Isotope Ratio Mass Spectrometry (IRMS) the measurement is made on the molecular species. "Excitation energy levels" is a meaningless term when used without further qualification. What is different here is the rotational-vibrational energy level structure of the different isotopic molecules, leading to isotope characteristic transition frequencies in the near-infrared region of the spectrum. For completeness, a reference to reviews of the two methods could be given, for example the relevant chapters in the Handbook of Stable Isotope Analytical Techniques by De Groot.

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We rephrased the sentences and added the suggested references. The passage now reads as follows: "Two physically different measurement principles allow to quantify the isotopic composition of natural waters. Isotope ratio mass spectrometry (IRMS) takes advantage of the differing mass-to-charge ratio of isotopes (Horita and Kendall, 2004). Laser spectroscopic systems use the difference in rotational-vibrational energy level structure of the different isotopic molecules, leading to isotope characteristic transition frequencies in the near-infrared region of the spectrum (Kerstel, 2004)."

6) P. 1602 L. 26: The reason that your laboratory has so far been working exclusively with the LGR analyzer is not a good reason to consider it the benchmark system. If anything, the "Golden Standard" in isotope ratio measurements is still IRMS, however imperfect (especially for water vapor measurements). In any case, both the LGR and Picarro systems are benchmarked independently from each other against a series of working standards, and there is also no need to express the performance of one in terms of that of the other.

The word benchmark was indeed misleading and was thus removed. The text now reads as follows: "The second type of laser systems, the water vapour isotope analysers (WVIA and WVIA-EP, DLT-100, version March 2011) by Los Gatos Research Inc. (LGR, Mountain View, CA, USA) are based on off-axis integrated cavity output spectroscopy (Baer et al., 2002)."

7) P. 1603 L. 6-10: Concerning the comment by referee 1: The cavity can be considered "high finesse" whether used in an on-axis or off-axis configuration. I have been informed that the finesse is defined for one family of transverse modes, not simply as the distance in frequency between neighboring transmission peaks (see, e.g., Ch. 14 of Lasers by A.E. Siegman). Thus even if the number of transverse mode families is increased drastically, the finesse of the cavity does not decrease, and neither does the width of the transmission profile. As the number of excited transverse mode families increases to the extent that neighboring peaks start to overlap within the width of the laser profile, the cavity becomes resonant irrespective of the precise wavelength of the

laser. This is facilitated by the use of astigmatic (not astigmatized!) mirrors.

Thank you for this explanation. We omit the term "high finesse" in the revised version to avoid confusion and now write: "In both systems, the sample gas is drawn through an optical cavity, in which pressure and temperature are precisely regulated. Laser light is injected into the cavity through a semi-transparent mirror. A photodetector, placed behind another mirror, measures the light intensity leaking out of the cavity. In the WVIA spectrometer, the optical cavity consists of two slightly astigmatic high reflectivity mirrors and the laser beam is coupled into the cavity in an off-axis alignment."

8) P. 1603 L. 13: When one is not thoroughly familiar with the operating principles of the techniques, it may be better to refer to the appropriate literature. However, the reference given here (Iannone 2009) is not a primary reference. The appropriate reference in this particular case appears to be Paul, Lapson, and Anderson, Appl. Opt. 40 (2001) 4904 (but note that they, and their figure 1 in particular, suggest the interpretation of the FSR as given by referee 1).

We changed the reference as suggested.

9) P. 1603 L. 21: I do not see why the pressure and temperature cannot be precisely regulated in the case of a fast gas exchange rate. It seems more likely that the Picarro systems operate with a low gas flow rate for rather different reasons; for example to avoid turbulence, which would induce noise on the spectra by its modulation of the refractive index and/or simply out of a desire to use a small, low power pump.

We removed the end of the sentence: "which limits the exchange rate in the cell".

10) P. 1604 L. 19: Lis et al. (2008) did not invent, or were the first to demonstrate, the combination of a liquid water autosampler and a laser-based water isotopic analyzer. This is again not a primary reference. At the very least, include "see, e.g., " in the reference.

Corrected as suggested: "Liquid autosamplers as used for liquid isotopic laser analy-

ses (see, e.g., Lis et al., 2008) are not optimal for calibrating vapour instruments as the produced calibration vapour quantity is very limited, making extended calibration runs of more than 5 min impracticable."

11) P. 1604 L. 23: For completeness include Lee et al. (2005) in the list of references.

The reference was added.

12) P. 1604 L. 24: replace "specific" by, e.g., "controlled" or "well-known".

Corrected as suggested: "For example, with a dew point generator as a calibration system, dry air is bubbled through a water reservoir at a controlled temperature and the liquid water is continuously enriched in heavy isotopes, following a Rayleigh distillation process."

13) P. 1604 L. 28: "... are precisely regulated or measured". BTW: knowledge of the pressure is only required for an estimate of the water mixing ratio, not for the vapor phase isotope ratios.

We changed the text as follows: "The isotopic composition of the vapour can be determined if the initial and the residual water isotopic composition are known and if the temperature in the water reservoir is precisely regulated or measured."

14) P. 1605 L. 15-20: The Picarro standards delivery module (SDM) introduces a continuous stream of water into the vaporizer. Evaporation occurs at the meniscus of the water surface at the end of the needle. There is no droplet formation!

Corrected as follows: " The standards are filled into collapsible bags (B1, B2). The liquid standards are then pumped by syringe pumps (SP1, SP2) via capillary lines (C1, C2) to the injection head (H) of the vaporiser. The injection system consists of two needle ports (P1, P2) and a carrier gas inlet (A). The head of the needles penetrates the vaporisation chamber (C), the temperature of which is regulated at 140°C to ensure immediate and full evaporation of the liquid standard introduced through the needles."

15) P. 1606 L. 2: Note that Figure 1(a) gives the wrong liquid water flow rate.

Thank you. We corrected Fig. 1. The unit in Fig. 1 now reads "l/s" instead of "l/min".

16) P. 1606 L. 21: Given that the LGR WVISS allows for only one standard delivery at a time, it is at least curious that this device was used instead of the two standards delivery module of Picarro, which would allow for changing the second standard (bag) for another during the delivery of the first standard. a) What characteristics made you decide to use the WVISS?

The WVISS was used in the delta scale experiment because we wanted to measure the produced vapour samples in parallel with the Picarro and LGR instruments. The quantity of vapour delivered by the SDM is insufficient to be measured in parallel by different instruments. We made the choice of the calibration unit for the different experiments clearer by adding a short comment in section 2.3, where the calibration systems are presented: " However, in contrast to the Picarro system, it allows for stable production of large quantities of calibration vapour over several days. Therefore, in the experiments conducted in this study the WVISS was used to measure the same standard in parallel with the Picarro and LGR instruments.

Furthermore to clarify which instruments were tested in parallel we added the following sentence at the end of Sec. 2.2: "The tests presented here were done simultaneously for L1115-i, WVIA and WVIA-EP, the same experiments were then repeated later only for L2130-i, when the new version of the Picarro water vapour analyser was available."

b) How much time does the changeover take? 5 min

c) How long does it take for the WVISS to purge the delivery lines and was this time included in the two minutes of discarded data at the beginning of each cycle, or does it still need to be added to this? Yes this time is included in the two minutes of discarded data, the time to purge the line and the cavity of each instrument depends on the response time of the instruments.

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d) Ten times 10 minutes represents only about 20 percent of the tot al of 8 hours used for each calibration run. What happened in between?

We measured each standard for 10 minutes: 10 standards shown in this paper, the 3 IAEA standards and 2 other standards not included in the paper. Due to a problem with the capillary line in 3 cases we required more time than normally for the purging and resetting of the system. The main message here is that we measured all the standards on the same day. There were some breaks in between, which did not allow us to do all the measurements one after the other. The term "continuously" is misleading. We changed it as follows: "All measurements were done twice (run 1 and run 2), each time within a time period of a day."

17) P. 1606 L. 26: If I understand correctly, the so-called "drift" standard was not used to remove instrumental drift from the measured data, since these were after all known (working) standard values. Rather, its use was to purge the WVISS water delivery lines. If this is indeed the case, I suggest using a different name for this purge liquid.

We used the drift standard as both a "purge" standard to "reset" the measurement system and as a drift standard to monitor changes in the calibration settings of the instruments. The text now reads as follows:

"Furthermore, between two working standard calibration runs we measured a drift standard for three minutes in order to remove memory effects from the calibration unit and to monitor the behaviour of the measurement system over the whole calibration experiment."

In the revised version we added the standard deviation of the drift measurements in the caption of Table 4: "The standard deviation of the drift standard measurements over the individual runs was 1.2‰ (0.7‰ for δ^2H of L1115-i (WVIA) and 0.3‰ (0.3‰ for δ^{18}O of L1115-i (WVIA)."

18) P. 1607 L. 8: Why would you use different calibration materials for the laser and

IRMS measurements?? I cannot think of any good reason to do so. Nor can I think of any good reason to use the precious VSMOW and SLAP primary standards directly in the laser instruments, as this goes directly against all IAEA guidelines, and makes no sense considering the use of WS11 and WS12 for the IRMS analyses. It practically invalidates the intercomparison of laser and IRMS, at least outside the interval spanned by WS11 and WS12.

Following your comment and two similar ones by referee 1 (comment 11 and 12), we measured the standards again with IRMS and used the IAEA standards to calibrate the measurements. We adapted the text and the results accordingly.

Our thinking by using the VSMOW2 and SLAP2 standard was that, these are well-known standards and they cover nearly the whole range of the delta scale in which we are interested. We don't do our daily calibration with IAEA standards, but for an independent IRMS - laser instrument comparison study using standards, which span a large range of delta values, we thought it was appropriate to use them. Furthermore the IAEA standards provide a direct link to the VSMOW-SLAP scale with a traceability chain that is as short as possible. With this experiment we can thus compare the measurements by IRMS and by the laser spectrometers in an independent way.

19) P. 1608 L. 2 and L. 22: Why do you revert to the Picarro SDM for the measurements of section 3.3 and then back again to the LGR WVISS in section 3.4? In the manuscript I found no better argument than the nice alternation between the two. But what if you had decided to present the isotope stability measurement before that of the water concentration dependency...? I think that most readers, like myself, are rather curious to learn what motivated your choice of calibration unit for each specific task. In fact, it would be very interesting to compare the performance of the calibration units, in addition to that of the analyzers themselves. Without some kind of deliberation, this choice appears completely random and illogical. After all, unless all measurements are made with the "best" calibration unit, the only logical choice would be to test the analyzer with the calibration unit of the same manufacturer, which is very likely the

most common configuration found with other end-users.

As mentioned in our response to comment 16 a), we made the choice of the calibration unit for the different experiments clearer in the revised version by adding a short comment in section 2.3, where the calibration systems are presented. The SDM cannot be used in combination with the LGR instruments because it does not deliver enough calibration vapour. We used the WVISS for all the instruments in the cases where we wanted to conduct parallel measurements. The water vapour mixing ratio test was done with the Picarro calibration unit for the Picarro instrument because this is a fundamental calibration issue. It is thus necessary to conduct this test with the calibration unit designed for the Picarro instrument as this is the way most other users will do their tests. The goal of the delta scale linearity test was rather the comparison of controlled measurements of the same vapour by the different instruments. We made this point clearer in the manuscript by the change described in our reply to comment 16 and by the following 2 sentences in the water vapour mixing ratio section:

"Because water vapour mixing ratio effects directly affect calibration, we tested the water vapour mixing ratio dependency of the L1115-i system using the SDM. Furthermore, this is the set up we use during the comparative field experiment (Sec. 8)". And to make clear that the water vapour mixing ratio characterisation could not be done with the SDM for L2130-i: "The SDM was not available when the experiments with L2130-i were performed."

20) P. 1609 L.12 (Figure 8):

a) It would be most instructive to present the Allan plots of Figure 8 together with the time series data used for its calculation. In fact, for anybody who has generated such figures him- or herself it is evident that the shape of the curve depends, sometimes significantly, on the exact beginning and end point of the time series, as well as its exact length.

We do not think that such a plot gives much information to the reader. We performed

an Allan test and chose the stationary part of the measurements, i.e., the period when the calibration system was in steady state. We of course left out the start and the end of the calibration run to avoid any influence from the calibration unit warm up or valve switch. The goal here is to characterise the instrument precision and drift in an ideal set up. The following figure shows the δ^2H measurements by L1115-i:

b) The curves tend to change from measurement to measurement, which is not captured in the given plots, as they lack an error estimate. In the absence of a proper, analytical error estimate the best one can do is to calculate the Allan deviation for a linear instead of logarithmic time step. Although in the latter case neighboring data points will be correlated, at least the spread in the Allan deviation values becomes visible. Including a correct estimate of the error on the determination of the (minimum) Allan deviation will have repercussions for the "optimal" numbers reported in Table 6, which are without a doubt too optimistic. In fact, a hint of this is given by the sharp and very fast fluctuations seen in figure 9. Some of the fast and large changes in the "bias correction" value appear to occur on a time scale comparable to that of the optimum averaging times reported in Table 6. If such a sharp transition were included in the time series used for the calculation of Figure 8, the reported short-term precision would be rather worse.

We changed the Allan plots. Fig. 8 now shows the Allan deviations computed with a linear time step. We adapted the optimal numbers of Table 6 and in the text.

We also performed some Allan variance analysis on our long-term stability test data and did not find substantially different drift patterns and Allan deviations than in the short-term.

We added the following sentences in Section 4.4.3 (discussion paper version): ""It has to be emphasised that these precision values were obtained in ideal laboratory conditions with well controlled environmental parameters and thus represent an optimal case. They characterise the stability of the measurement system and do not account

for the uncertainties introduced by water vapour mixing ratio biases discussed in Sec. 5."

c) How do I interpret the results of Figure 9 in light of the two incidental calibration curves of Table 4? The latter shows that the raw d2H VSMOW values reported by the L1115-i differ by some 11 per mil between the two calibration runs. This is about 10 times larger than the largest excursion seen in Figure 9! For SLAP the situation is another factor of 5 worse still, given the large differences in normalization slopes. Based on the results of Table 4, the 3-day calibration curve of Figure 9(a) could be expected to be dramatically worse than that of Figure 9(b). That this is not the case may indicate a problem with the calibration performed for Table 4. It seems plausible that due to its slow response, the Picarro analyzer is more prone to memory effects. If this is the case (you subscribe to this in section 4.1, P 1613, L. 18), the measurement strategy should have been adapted to take this effect into account and the conclusion would also be that the Picarro analyzer cannot be used to faithfully capture fast (< 1 min) isotopic ratio variations.

We checked the results shown in Table 4 and still think they are ok. We now point out the large change in the δ^2H calibration factors of the L1115-i instrument more clearly and changed the text as follows: "For L1115-i the normalisation factors as well as the intercepts were different in the two runs. In the case of the δ^2H the change in the zero point was large with 11‰ difference. For WVIA we found that the normalisation factors remained within the uncertainty range, the intercept however changed slightly. As L1115-i, WVIA and WVIA-EP were connected to the WVISS in parallel, the large change in the δ^2H signal calibration factors L1115-i must come from the instrument itself."

This point is now also mentioned in Sec. 6.2: "These bias correction amplitudes may be larger for δ values at the edge of the VSMOW-SLAP scale. The long term stability experiment was only done with WS6 at δ^2H=-79‰ but the results shown in Tab. 4 (compare b1 and b2 for L1115-i) and discussed in Sec. 3 suggest that changes of up

to 10‰ in the measurement bias of δ^2H can occur over several days at δ^2H=0‰."

21) P. 1609 L. 16: best or optimal precision is minimum precision, not maximum precision.

We replaced "maximum" by "best".

22) P. 1609 L. 23 (and P. 1622 L. 25): I cannot agree with the statement that the Allan variance analysis is not a useful tool for very long averaging times. All depends on the time series, and especially its length, used to perform the Allan variance. Beyond the optimal averaging time the Allan plot generally shows the onset of instrumental drift, which provides extremely useful information! In fact, in order to assure the most precise, as well as most accurate measurements over longer periods of time, it is essential that the complete calibration procedure (i.e., both sample and reference material (working standard) measurements, and any necessary purging or cleaning of the delivery lines and analyzer) needs to be completed within the optimal averaging time determined by an Allan variance analysis. This was also the consensus of the EGU Workshops on laser-based isotope ratio methods, organized by Kerstel, Gianfrani, and Werle in 2009 and 2011. If the actual averaging time extends beyond the optimal value, the Allan plot provides an estimate of the increased standard deviation of the measurement due to the effect of drift. I would argue that this is highly useful information. For example, the δ^2H Allan plots predict by extrapolation that the precision of data averaged over approximately one day (10^5 sec) will be of the order of 0.3 per mil, due to instrumental drift. This is indeed in agreement with the general trend observed in Figure 9. However, it is also clear that the Allan plots of Fig. 8 present by far too optimistic values of the achievable precision. If these plots were representative of the overall performance of the instruments under all laboratory conditions encountered during the tests of Figure 9, than one would not expect to see such large and rather rapid (some appear to occur on the time scale of 0.5 hour) changes in the bias corrections of Figure 9. This stresses the importance of including an error estimate in the Allan plots, preferably determined by repeated determination of the Allan plot using different time

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series. Figure 9: It should be pointed out that the flat appearance of the L1115-i 3-day bias correction curve is purely accidental. If the calibrations had been carried out on days 3, 6, and 9.5 (instead of on days 4, 7.5, and 11) the curve of the L1115-i would have shown a peaked appearance, whereas that of the WVIA would have appeared flat. Both instruments appear to exhibit roughly the same long-term behavior.

The description of the short and long term stability experiments was misleading in the original version of the paper. We also think that the Allan variance analysis provides useful information on the drifts and on the optimal calibration procedure for the instruments. We performed the following changes: a) We now introduce the stability section as follows: " The stability of a laser spectroscopic system is an important characteristic, which allows to quantify the precision of the measurement system for given averaging times, the instrument internal drifts as well as the optimal inter-calibration time. In this section we investigate the effects of drift and choice of inter-calibration time on precision and accuracy of the isotope measurements in two different experiments. First, we show the results from a stability test performed at the timescale of 1 day (Sec. 6.1). Then, we discuss a slightly different experiment, which was designed to analyse stability over a period of 14 days (Sec. 6.2)."

b) We now introduce the section on long-term stability as follows: "A stability analysis for time scales of several days is conducted as a complement to the short-term stability test to investigate changes in the instrument calibration at the time scale > 1 day and as complementary information for finding the ideal calibration scheme. "

c) As mentioned in our response to comment 20 b), we now use a linear time step in the Allan plots of Fig. 8, which better reflects the uncertainty in the computed Allan deviations.

23) P. 1610 L. 22: The lag time for the L1115-i instrument is given in the text as 88 sec, whereas the figure shows a time lag of approx. 130 sec. Also, the lag times are about equal for the Picarro and LGR instruments for the same length of inlet tubing.

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This is not what I would expect based on the 20 times higher pumping speed of the latter instrument.

We corrected Fig. 2 in the revised version of the manuscript.

The lag times are nearly equal, because the set up was such that the heated tubing was the same until the short separation tubes leading to the two instruments. This was not clear in the manuscript and will be added. The text was changed as follows: "In the setup used here τ_{lag}=88 s for the L1115-i instrument and 75 s for the WVIA system with a common 12 mm PFA sample line length of 15 m. The separation tubings leading to the individual instruments was 0.5 m long. Due to the difference in pumping rate of the two instruments these short individual lines were not purged at the same rate. The flow in the common sampling line was 1 l/min. This explains the small difference in the lag times."

24) P. 1616 L. 15: The measurement precision decreases (= improves!) with increasing mixing ratio.

We replaced "increase" by "improve" and "decrease" by "deteriorate".

25) P. 1616 L. 24: I don't understand the reference to Helliker (2010). The spectral features are reported in HITRAN, whereas the first water isotopic ratio measurements in the spectral ranges used in these commercial instruments were reported by Kerstel et al. (Spectroc. Acta 2002) and Gianfrani et al. (Opt. Ex. 2003).

The suggested references were added. The text now reads as follows: "The absorption peak of $\delta^{18}O$ is stronger than the one of δ^2H (Kerstel et al., 2002; Gianfrani, 2003; Rothman et al., 2009)."

26) P. 1617 L. 25: It should be noted that the uncertainties in the parameters of Eq. (6) and (7) (presumably corresponding to the shaded areas around the curves in Figure 7) propagate into the uncertainties of the isotopic ratio measurements. These uncertainties are certainly not negligible and ought to be quantified. The paper by Rambo et al.

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(2011) shows that these amount corrections, in their case for the WVIA, are not stable and vary significantly and in a random manner on an hour-to-hour basis.

The text now reads as follows: "Fig. 7 shows the uncertainty range of these corrections. This uncertainty of the water vapour mixing ratio correction propagates into the isotope measurement uncertainty. Similar dependencies were found by Schmidt et al. (2010) for the L1102-i version of the water vapour isotope instrument by Picarro. Since the correction can be different for every instrument, this characterisation step has to be done individually for every instrument. Rambo et al. (2011) found that this dependency on water vapour mixing ratio varies significantly in time for WVIA. In our case the dependency remained of similar amplitude and shape, when the experiment was repeated later on. However, regular calibration of the instrument at different water vapour mixing ratios spanning the ambient air measurements is necessary to ensure that the bias is correctly removed."

27) P. 1618 L. 22: Please note that a hydrocarbon trap typically does not remove methane, which is know to be an important interfering species, especially at low water concentration. See, e.g., Hendry et al. (Anal. Chem. 2011).

The text now reads as follows: "Effects due to hydrocarbons or different CO2 composition can be excluded, since filtering ambient air with a CO2 absorber and a hydrocarbon trap did not remove the difference between the measurements. However, the effect of methane cannot be excluded and is known to be an important interfering species especially at low water vapour mixing ratios (Hendry et al., 2011)."

28) P. 1620 L. 22: The important point to note is that for such mesoscale meteorological measurements, one may thus assume that the natural variations are larger than the instrument precision, and larger than the instrumental drift over the averaging time period.

This point was made clearer. The text was changed as follows: "For mesoscale meteorological applications an averaging time range of 15 min to 6 h is useful and thus

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precision values of the order of the numbers indicated in Tab. 6 for $\sigma_A^{T_0}$ can be expected. Natural variations in water vapour isotopic composition associated with mesoscale weather phenomena are much larger than the precision values and drift amplitude obtained here (see Sec. 8)."

29) P. 1620 L. 25: For standard Eddy covariance measurements, a measurement rate of typically 20 Hz is required. Even though the update frequency of the analyzers may be of the order of 2 Hz, their actual response time does not even come close to this number because of pumping speed and memory effect constraints (see Table 7). In fact, in the case of the L1115-i analyzer, even the 5-s averaging time is not useful, as the analyzer is not able to capture variations at this time scale. With either of these analyzers, only relaxed Eddy accumulation provides a realistic option for flux measurements, but is cumbersome to implement because of its requirement of conditional sampling.

We removed the remark on eddy flux measurements.

30) P. 1625 L. 22 and 28: How are these accuracy numbers to be reconciled with the accuracy statements made on P. 1623 L. 5 and 8? I believe this merits a thoughtful discussion, especially considering that WS6 and 7 do not span an extremely large isotope range.

The calibration uncertainty values obtained in the field are now shortly discussed: "These values compare well with the uncertainty estimates obtained in Sec. 3 in the delta-scale laboratory experiment. The optimum precision values described by the Allan deviation (Sec. 6.3) should however not be compared directly to these sample standard deviations."

31) P. 1626 L.7:

a) When comparing the time series obtained by two different instruments with rather different time responses, it is crucial to first put the time series on the same time sam-

pling axis. That this was indeed done, is only mentioned in the caption of Figure 13, but given its importance should also be mentioned in the text.

For clarity, this information has been added as suggested in the text, but as we compare hourly data this time shift correction does not affect the comparison results substantially.

b) Have the measurements also been weighted with the water mixing ratio, in order to account for the over-representation of the high mixing ratio values in the L1115 time series due to its longer response time (see, e.g., Iannone et al. J. Geophys. Res. 2010)?

Because we compare data at an hourly time scale, the water vapour mixing ratio weighting does hardly influence the result. The differences in response time and water vapour mixing ratio signal of the instruments are too small to have an effect at the hourly time scale. Furthermore, if such a weighting is computed, the uncertainty of the water vapour mixing ratio measurement is introduced as well into the isotope data and increases the isotope signal uncertainty.

Fig. 1.

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