

## **Response to Reviewer 3 of manuscript “Continuous measurements of atmospheric water vapour isotopes in Western Siberia (Kourovka)”**

We thank Reviewer 3 very much for a thorough review of our manuscript and useful remarks and suggestions. We believe that taking the comments into consideration have improved the manuscript. Please find below our answers to individual comments.

### **Major comments:**

A) The motivation for studying water vapour isotopes in Western Siberian water vapour is not pointed out clearly enough in the paper. Please add more information on why such measurements at this location could be interesting and formulate the goals of this particular study more clearly. Is it finding an adequate calibration protocol for measurements performed at low humidity or is it understanding the driving processes behind the daily cycle in deuterium excess? Are these two aims somehow related (i.e. a good water vapour mixing ratio correction is essential to get good quality deuterium excess data since deuterium excess is so much dependent on the precision and accuracy of the  $^{18}\text{O}$  signal).

*Our study is part of a project investigating the water and carbon cycles in the permafrost and pristine peatlands of Western Siberia and their projected changes associated with climate change. In Kourovka we develop a reference site for continuous water isotope observations by different in-situ and remote sensing techniques. The observed isotopic composition variation dynamics at this monitoring site can serve as a good reference for analyzing large-scale West Siberian climate and hydrological cycle variations. The monitoring data are also used to validate and improve the global circulation models (LMDZiso, Risi et al., 2010; and ECHAM5-wiso, Werner et al., 2011) in order to make them better reproduce water isotope variability over the West Siberian area and*

*other regions with similar climate characteristics. This will allow to produce more accurate and reliable predictions of the water cycle and climate changes in the region of our interest and on the global scale as well.*

*The goals of this particular study we see in the following:*

- *Adaptation of the WS-CRDS isotope measurement system and the calibration and measurement protocol for the proper performance in low humidity conditions in order to obtain high quality data for  $\delta D$ ,  $\delta^{18}O$  and, especially, deuterium excess, despite the dry periods.*
- *Analysis of the diurnal variations of deuterium excess and its connection with meteorological conditions in order to understand the processes standing behind the phenomena of deuterium excess night decrease.*
- *Performance of the first long-term isotopic record of atmospheric surface water vapour on the territory of Russian Federation and provision of the final calibrated data for comparison with ground-based and remote sensing measurements (Gribanov et al., 2013) and simulation outputs from atmospheric general circulation models (Butzin et al., 2013; Gryazin et al., 2014).*

*We find these goals closely related to each other, as in order to get high quality isotopic data we need to have precise and accurate techniques, and in order to make a comparison with the other data we need to be sure of the reasons causing the variations observed.*

B) In my opinion the structure of the paper is weak, putting together many interesting but a bit loosely connected aspects of the water isotope measurements performed at Kourovka. Could you link the structure more clearly with the goals (see major comment A) and also organise your sections along the points mentioned in your proposed measurement protocol (section 3.2 is protocol step 5, section 3.3 is protocol step 3, section 3.4 is protocol step 4).

*We agree to put the structure of the paper more clearly and link it tightly with the main goals of the paper outlined in the previous answer. The sections along the points of the measurement protocol have been organized in the right order as well.*

C) The technical adaptations of the SDM made for low humidity measurements (change of the syringe pump, use of a dry air tank, maybe others?) should be described in more detail especially also since AMT is a technical journal. Could you describe the technical set up more precisely, e.g. with a schematic? Could you make clear what is standard in the SDM as provided by Picarro and what comes from your own adaptations? Could you mention what kind of product your glass pump is (manufacturer, characteristics like pumping rate range, precision). Same question for the dry air tank. How did you produce this dry air (mention again the manufacturer and the specs)

*An illustration of our calibration setup is shown on Figure S1. The liquid standard is drawn from container by syringe pump of the Picarro Standards Delivery Module (SDM) and transferred via capillary line into the Picarro injection head (C0105) of the Picarro vaporization module (A0211) which is set at 140°C. Evaporated standard is mixed with dried room-air pumped through the 450 cm<sup>3</sup> drying column filled with DRIERITE desiccant (Supplier No. 23001, W. A. Hammond Drierite Company, Ltd., USA, [www.drierite.com](http://www.drierite.com)). The change of the desiccant color from blue to pink indicates when its activity is depleted. Finally, the mixed standard water vapour is supplied into the Picarro analyzer.*

*The following technical improvements of the standard Picarro configuration have been made:*

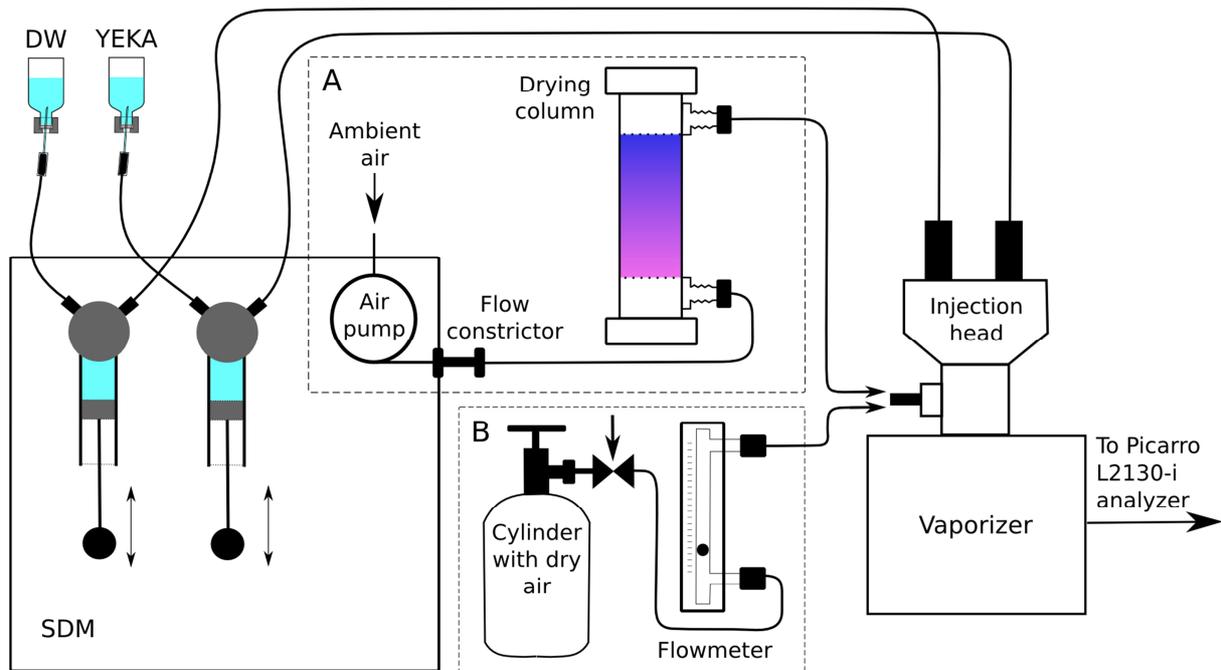
- *Substitution of the standard flexible metallized bags for reference water standards with the 15 ml glass bottles. This allows to visually control the absence of bubbles in the water, the absence of condensed water on the walls inside the bottle and the remaining amount of the water standard. Condensed water could be easily removed from the*

walls by simple shaking, if needed. It is also easy to control the dryness of an empty bottle before filling it with the standard. The bottles are refilled to the 3/4 of the volume once per week and installed in an upside down position. The water intake needle is introduced in the lower part of the bottle through the hole in the cap.

- Usage of disposable silicon septa inside the bottle caps. This prevents bubble formation during insertion of a needle into the bottle.
- Replacement of ceramic syringe pumps with the newer Picarro glass syringe pumps equipped with the soft plunger sealing (Tecan Systems, Inc., Ball-end 250  $\mu$ l syringe, Ref. 19931 C X18A). This allows to avoid air bubbling in the sealing between the plunger and syringe walls.

Exclusively for the instrument humidity-isotope response calibration the air drying line (Fig. S1, A) have been substituted with the zero air gas supply from a 10 l tank cylinder (Fig. S1, B). A calibration gas mixture of  $N_2 + O_2$  (4:1) have been used (PGS-Service, Russia, [www.pgs.ru](http://www.pgs.ru)) with the following content of impurities:  $H_2 \leq 0.0001\%$ ,  $CO_2 \leq 0.0008\%$ ,  $CO \leq 0.0004\%$ ,  $CH_4$  and other hydrocarbons  $\leq 0.0005\%$ ,  $H_2O$  at normal conditions  $\leq 0.0002\%$ . The guaranteed dew point for the gas equals to  $-80^\circ C$ , which corresponds to approximately 0.5 ppmv of water vapour. For the flow rate control a purgometer Sho-Rate 1350 with 3-65 Glass Tube (Serv'Instrumentation, France) have been used. The gas flow rate was kept within the range 10-35 l/h.

The exact concentration of  $H_2O$  in the filled tank cylinder was measured in-situ as  $0.5 \pm 0.1$  ppmv.



Supplementary Figure S1. Illustration of the setup used for (A) routine calibrations and (B) humidity-isotope response calibration.

D) Cluster analysis in section 3.9: the section on the diurnal cycle of deuterium excess raises very relevant questions but it is too loosely connected with the rest of the paper in the current version of the manuscript. The clustering also needs to be introduced in more detail: did you normalise/detrend the data, if yes how? Did you take into account the seasonality of the deuterium excess signal? Why did you choose only 2 clusters, could be 3 or 4? Is there a physical motivation for choosing only 2 clusters? How did you choose the starting centroids in the clustering procedure (randomly)? Furthermore, this part needs additional analysis of the meteorological conditions associated with each cluster (e.g. typical wind conditions for each cluster as already proposed in the response to reviewer 1 but also surface fluxes, temperature, relative humidity, wind direction).

*We see the connection of section 3.9 with the rest of the paper in the importance of understanding the reasons of observed deuterium excess diurnal cycle – is it a natural behaviour of d-excess, or a sort of systematic error of the*

*instrument, or result of some third effect. In order to produce high quality data we need to be sure of the processes behind.*

*The k-means clustering algorithm is one of the most used methods for vector quantization. It is an iterative procedure which partitions “n” observations into “k” clusters trying to minimize the sum of the squared distances between each observation and corresponding cluster. At each iteration the center of mass is recomputed for each cluster obtained in the previous step and observations are redistributed between the clusters in accordance with which of the new center is nearer.*

*We chose not to normalize or detrend the data for this procedure. We just take deuterium excess daily data for the days with not less than 2/3 coverage by the measurements for the period from 08 May 2013 to 31 August 2013, average it on the 15 minutes basis and launch k-means clustering. We have not performed any seasonal partitioning inside this time period as we do not observe specific changes in d-excess cycles throughout it. Moreover, partitioned observations appeared to be equally distributed inside this period. The data outside of these dates have not been analyzed as there are no pronounced d-excess variations there.*

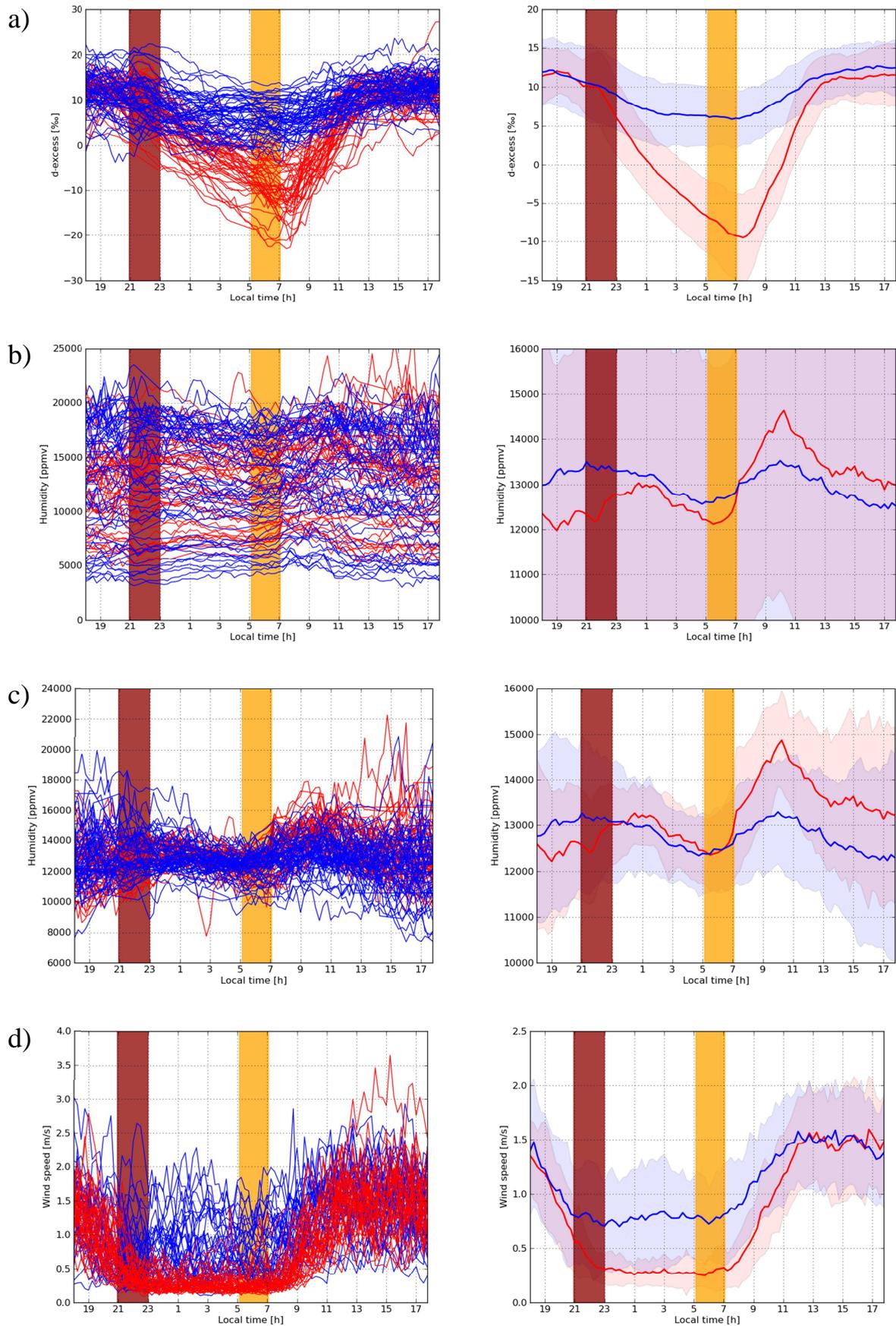
*The number of clusters is defined by user. We have tested different values, but have not obtained significant difference between the clusters when we try to partition the cycles into three and more clusters. Whereas for the test with two clusters the difference between the clusters minima have been almost 3 times larger than the standard deviation computed for the clusters. So, the motivation for choosing only two clusters is not physical, but statistical.*

*There is no need to choose the starting centroids in this clustering algorithm manually. The procedure automatically converges solution of the problem to a local optimum using efficient heuristic algorithms. The final result is reproducible and remains the same even if one sets specific starting conditions.*

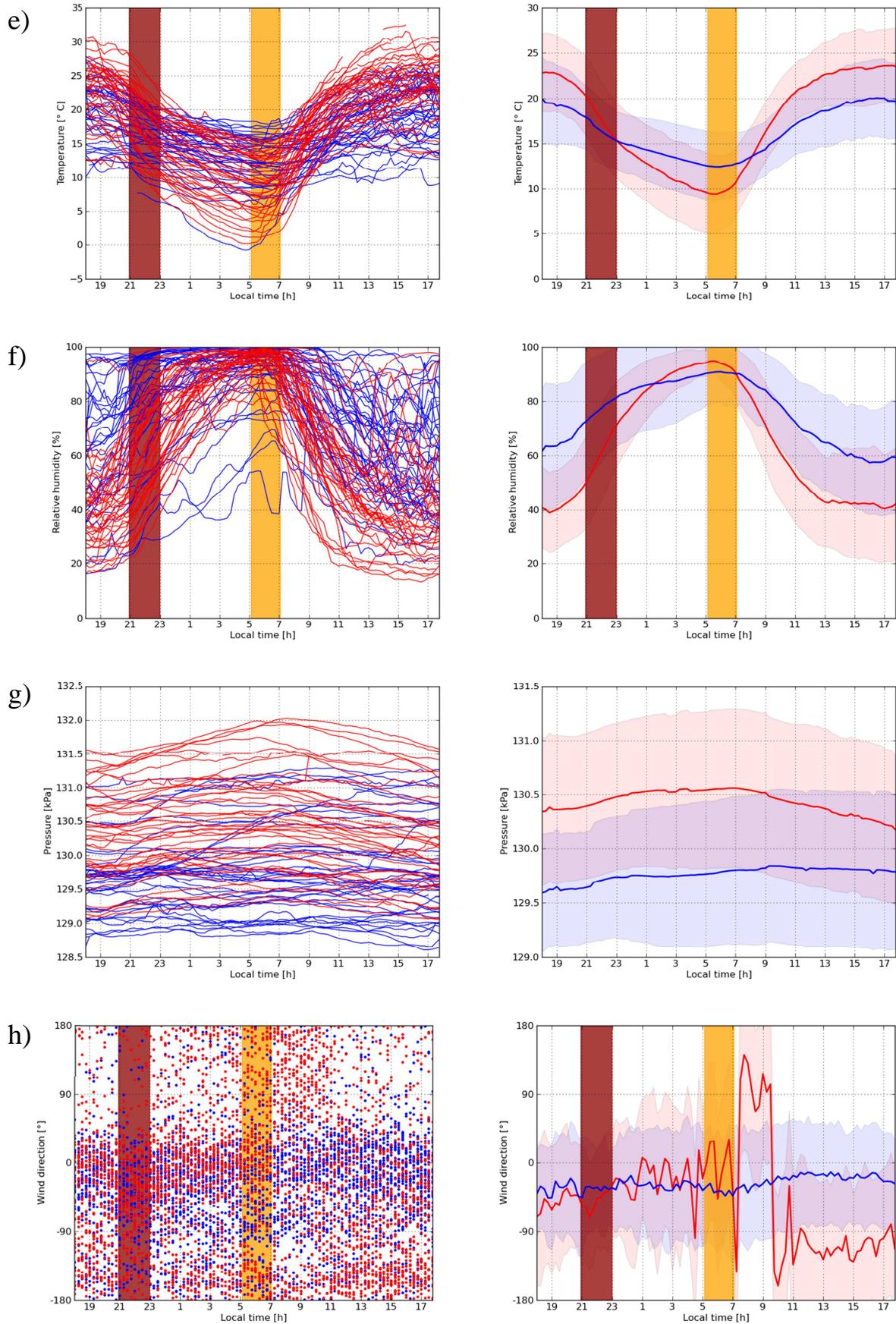
*We have performed an analysis of the meteorological conditions associated with each cluster (Figure S2). The stacked diurnal cycles for each parameter are shown on the left panels on Fig. S2 with the color indicating the corresponding d-excess cluster. Resulting clusters for each parameter are shown on the right panels on Fig. S2 with corresponding standard deviations shown by shading. The yellow bars show the time of sunrise and the dark red bars show the time of sunset. For each humidity cycle (Fig. S2, b) we have additionally subtracted the difference between its mean value and the overall mean value and juxtaposed the resulting centroids in the time interval between 05:00 LT and 06:00 LT (Fig. S2, c). This was done for better representation of the humidity morning burst difference and does not distort the clusters itself. All the other data were computed directly.*

*Only for the absolute humidity (Fig. S2, c) and wind speed (Fig. S2, d) do we observe a significant difference between the diurnal variations corresponding to the two d-excess clusters. However, we observe indications of slightly different meteorological conditions associated with the two d-excess clusters. For Cluster 1 (strong decrease in d-excess) we observe a more pronounced diurnal cycle in temperature (Fig. S2, e) and relative humidity (Fig. S2, f) and in general slightly higher pressure (Fig. S2, g). Cluster 2 (weak d-excess decrease) does on the contrary not show as strong diurnal cycle for these parameters and the atmospheric pressure is slightly lower. This indicates that Cluster 1 is associated with more stable atmospheric conditions, which allow the wind speed to become very small during the night creating a stratiform lower boundary.*

*The wind direction diurnal cycle (Fig. S3, h) appears to be not representative, as the wind speed values are usually quite small for the establishment of an appropriate wind direction signal.*



Supplementary Figure S2. Diurnal cycles and two centroids for (a) d-excess, (b) humidity, (c) humidity with subtracted mean value and (d) wind speed.



Supplementary Figure S2 (continuation). Diurnal cycles and two centroids for (e) temperature, (f) relative humidity, (g) pressure and (h) wind direction.

## **Specific comments:**

1) In the abstract you should mention somewhere that you use a commercial WS-CRDS instrument from Picarro (version L2130).

*Corrected*

2) p. 476, 1.18 You mention 30 permil depletion in deuterium excess is this an extreme case? Maybe you could mention the 20 permil decrease found on average in cluster 1, rather than the most extreme daily cycle case, or mention a range, e.g. 3-30 permil variation in deuterium excess in the course of one day. Is “depletion” really adequate here, I find it a bit misleading when speaking of deuterium excess.

*Yes, 30‰ is the maximum night decrease (32.8‰ exactly). As the minimum is around zero, we wrote “up to 30 ‰” that is the same as presenting the range 0-30‰. For better understanding we have added into the abstract the sentence mentioning the two clusters observed with the average values of deuterium excess decrease.*

*The word “depletion” has been replaced with “decrease”.*

3) p. 476, 1.20 Could you add the “accuracy” of the deuterium excess measurements, since this is a central parameter in your study. Is “accuracy” the right word here, or do you mean “total uncertainty”? If you want to use “accuracy” please explain what you mean by it in section 3.5.

*According to the uncertainty values for  $\delta D$  and  $\delta^{18}O$  given in section 3.5, the deuterium excess measurement uncertainty could be estimated as 2.3‰ at humidity levels above 1500 ppmv, 9.2‰ for the humidity range from 1000 to 1500 ppmv and 18.5‰ for the humidity range from 500 to 1000 ppmv. These values have been added in the abstract and section 3.5.*

*Yes, we mean total uncertainty, corrected.*

4) One of the main aims of your study is the adaptation of a measurement protocol very similar to the one published by Steen-Larsen et al., 2013 to very low humidity conditions. Can you point out clearly what is new in the protocol presented in this paper compared to the protocol proposed by Steen-Larsen et al 2013? I would appreciate a more in-depth discussion of the possibilities for calibration at very low humidities. Do you have an idea how you could improve your measurement and calibration procedure to reduce the uncertainty of your measurements below 1500 ppmv?

*Our adaptation of the protocol for low humidity conditions consists in the way we perform humidity-isotope response calibration. The standard configuration assumes the usage of the dried ambient air, but at humidity levels below 5000 ppmv we observe unreliable calibration results due to the residual water content of the dried air. Experiments with the usage of the dry gas showed consistent results and allowed us to perform humidity correction of the measurements properly. Now we are also looking for the other ways to perform calibration procedure at low humidities. The possible variants are: the usage of the cold traps for air drying (Ellehoj et al., 2013) or the SDM substitution with the bubbler system (Steen-Larsen et al., 2014b).*

*The other minor protocol modifications introduced in this work are: 1) pre-processing of the raw data in order to remove erroneous data and 2) data flagging depending on humidity levels.*

*We are largely limited by the instrument performance at humidity levels below 1500 ppmv (instrumental precision rapidly decreases with humidity, as was demonstrated on Figure 3 in the paper) – this we couldn't change. But we did improve the humidity correction uncertainty by the performed modifications and ultimately the total uncertainty of the measurements.*

5) p. 478, 1.10 and elsewhere, use Wavelength-Scanned Cavity Ring-Down.

*Corrected*

6) Section 2: I assume you normalise your data to the IAEA VSMOW-VSLAP scale? Mention this and reference the relevant IAEA document.

*Yes, as described in section 3.4, we correct all our measurements to the VSMOW-SLAP scale (IAEA, WICO report, 2012). We acknowledge that we should write VSMOW-SLAP and not just VSMOW slope as done in text. We have corrected this throughout the text.*

7) p. 480, 1.27 Please provide a much more detailed description of your calibration set up (see also major comment C), it is not clear how your standard vapour is produced from this one sentence description. Mention the version of the Picarro vaporizer used, how the dried ambient air is introduced into the vaporizer, how the dry air from the tank is introduced into the vaporizer (maybe different schematics for different set ups) and please mention the manufacturer and specs of the materials used (drierite, dry air, glass syringe pump).

*The full answer was given in comment C.*

8) p.481, l. 1 What dry air flow rates did you use? Indicate numerical range.

*Dried room-air is pumped at a constant rate of 12 litre-per-hour.*

9) p. 481, l. 7 Change “exact isotopic values” to “reference values normalised to the VSMOW-SLAP scale”.

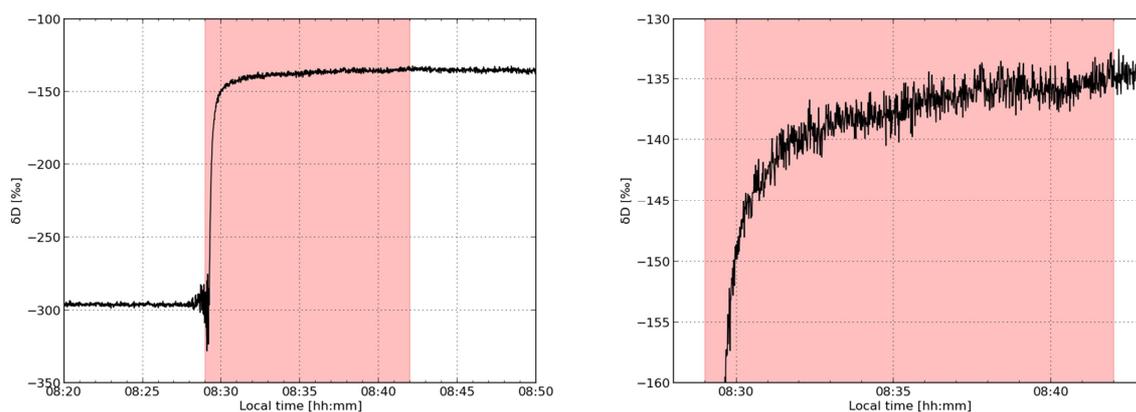
*The full sentence was corrected as follows: “The isotopic values of these reference waters in the VSMOW-SLAP scale were measured at LSCE...”*

10) p.481, l. 9 Why do you remove 13 min of ambient air measurement, this seems a very long time period for an instrument for I would not expect such long response times. Please justify in more detail, mention the pumping rate and the size of the cavity.

*During the first 13 minutes after the calibration procedure the instrument contains residuals of the calibration water vapour. The pumping speed is about*

30-40 ml/min, but we do not know the size of the cavity as it is inside the Picarro analyzer. Figure S3 shows an example for  $\delta D$  measurements during the instrument switching from calibration to ambient air measurements (the first 13 minutes are shown in red). The switching occurs at 08:29 LT, the mean ambient  $\delta D$  value equals to  $-134.4\text{‰}$ . At 4 minutes after the switching the instrument shows  $-138.7\text{‰}$  (3.2% error), at 8 minutes it shows  $-136.2\text{‰}$  (1.3% error) and at 12 minutes it shows  $-135.1\text{‰}$  (0.5% error). Such an effect occurs each time the instrument switches between the samples with largely different isotopic composition (more than 150‰ in this case). We found it appropriate to remove the first 13 minutes of the measurements after each calibration cycle.

We have added these figures in the supplementary material because we find it very important to communicate this to the community.



Supplementary Figure S3. Example of  $\delta D$  measurements during the instrument switching from calibration to ambient air measurements (left) with a zoomed region (right). Red – discarded part of the measurements (13 minutes).

11) p. 481 l. 13 Steen-Larsen et al., 2013 did not study the water vapour mixing ratio dependency in great detail, other earlier studies could be cited here (e.g. Sturm and Knohl, 2010, Rambo et al., 2011, Aemisegger et al., 2012).

*In the work of Steen-Larsen et al., 2013 a full detailed examination of this effect is performed. Results are presented in the supplemental material (<http://www.atmos-chem-phys.net/13/4815/2013/acp-13-4815-2013->*

*supplement.pdf*). The work of Sturm and Knohl, 2010, Rambo et al, 2011, and Aemisegger et al., 2012 does not treat the isotopic dependency at very low humidity levels. Steen-Larsen et al. uses a semi-continuously humidity variation between 500 ppmv and 6000 ppmv to characterize the instrumental performance at these low humidities. Sturm and Knohl and Aemisegger et al. has one data point below 5000 ppmv while for Rambo et al. the minimum humidity was 5000 ppmv.

12) p. 481, l. 19 See comment 6) → mention here the characteristics of the dry air from the tank cylinder.

*We use a calibration gas mixture of  $N_2 + O_2$  (detailed characteristics were given in comment C).*

13) p. 481, l. 21 Explain in more detail, e.g. with a schematic what you mean with the “utilization of septa for water intake from vials with needles”, do you mean as a standard water reservoir? How are these reservoirs connected to the syringe pumps?

*The sentence was rewritten for better understanding (see comment C). Water reservoirs are connected to the syringe pumps by means of the standard Picarro tubing with a needle at the bottle end. This needle is introduced through the septum inserted at the bottle cap in an upside down position of the bottle.*

14) p. 481, l. 23, See comment 6) → mention manufacturer and specs.

*We use Picarro glass syringe pumps. The full answer was given in comment C.*

15) p. 481, Section 2.4 these data processing steps largely overlap with the ones presented in Steen-Larsen et al., 2013. I do not see the point of repeating them here if they are the same. Only mention the differences.

*Corrected. The protocol itself is not new and we therefore do not repeat all the steps in the article, but refer the reader to Steen-Larsen et al. 2013 for details. The section 2.4 has been removed and all remaining information has been moved to the relevant places in the text.*

16) p. 482, l. 17 The section title for section 3.1 is somewhat unspecific. “Instrument performance” is too general. What you describe in this section is actually only the problems you had with the SDM between April and September 2012. As you only show and further discuss the isotope measurements from September 2012 to August 2013, leave out the discussion of the problems with the SDM between April and September 2012, this does not provide any useful information to the reader. You can mention the advantages of the glass syringe in the methods.

*The title has been removed together with the discussion of the problems between April and September 2012. Remaining information has been moved to the other parts of the manuscript.*

17) p. 483, l. 8, What does “have been validated” mean? Flagged as good following your protocol?

*No, it means that for the period from 21 September 2012 to 31 August 2013 we have 82% coverage with the final calibrated data. The other 18% consists of the instrument malfunctioning time or calibration periods.*

18) p. 483, l. 10 See general comment B on the structure of the paper, maybe start with your protocol point 1.

*Restructured*

19) p. 483, l. 15 I do not understand why a third order polynomial is chosen here, the relation shown in Figure 2 looks linear to me. What is the motivation behind your choice of the humidity calibration function? Is there any physical

motivation for this choice? Did you compare the residuals of the fit when using a linear vs. your third order polynomial function?

*You are right, the difference is negligible. There is no specific motivation to use polynomial function, the fitting has been changed to linear in the paper.*

20) p. 483, l. 18 “For periods when the analyser was not performing air measurements, the meteorological station data is used” I do not understand this sentence. What does this imply? During instrument failures or calibration periods you do not have isotope measurements either.

*During the isotope analyzer failures or calibrations we can use humidity measurements from the meteorological station data. But in the context of this paper we really do not analyze the meteorological data without the isotope data. The sentence has been removed.*

21) p. 484, Section 3.3 mention the range of measured water vapour concentrations, from Figure 5 it is not visible what the lowest water vapour mixing ratio values are. Furthermore, you should shortly explain, where the “humidity-isotope response” comes from, what is the physical reason for this humidity dependency in isotope measurements. Such an explanation is really important, since the “humidity-isotope response” is one of the central aspects in this study.

*The range of humidity variations is indicated in Section 3.6 (from 250 ppmv in winter up to 23 000 ppmv in summer).*

*The humidity-isotope response is determined in order to characterize the instrumental dependence on the measured isotopic value from the absolute water concentration. The cause of this dependence is related to the spectral baseline being dependent on the height of the  $H_2^{16}O$  spectral peak. Non-perfect correction in the Picarro software for this influence means that a “manual” on-site characterization is needed.*

22) p. 484, l. 14 Mention here that “the overall humidity dependency is significantly less pronounced for the range 800-5000 ppmv” Since below 800 ppmv you have no data from the drierite carrier gas experiment.

*Corrected*

23) p. 484, l. 25 To justify why you use the humidity-isotope dependency obtained with dry air from your tank for the ambient air you really need to indicate the exact chemical composition of the dry air.

*The exact chemical composition of the dry air was given in comment C.*

24) p. 484, General remark on part 3.3: it is known from several other studies (e.g. Galewsky et al., 2011) that hydrocarbons like for example methane can interfere with laser measurements of water vapour isotopes and become very important at low water concentrations (also discussed in Aemisegger et al., 2012). Could it be that such an effect affect your measurements? Do you have methane and CO<sub>2</sub> measurements at your measurement site or at some nearby location? Actually the L2130 Picarro instrument version provides methane measurements as well.

*Yes – it is correct that large variations in, for example, methane can influence the measurements. This is automatically corrected for by the Picarro software.*

25) p. 485 Section 3.4 I would call this section “Normalisation of the isotope data to the VSMOW-SLAP scale” or something similar, calibration is somewhat vague.

*The suggested version refers to the data, whereas in our version we refer to the instrument. And what we do with the instrument in this step is exactly its calibration using known-isotopic vapour standards. We suggest to keep the current title.*

26) p. 485, l. 3 V-SMOW slopes should be VSMOW-SLAP slopes, with one reference standard you do not get a slope.

*Corrected*

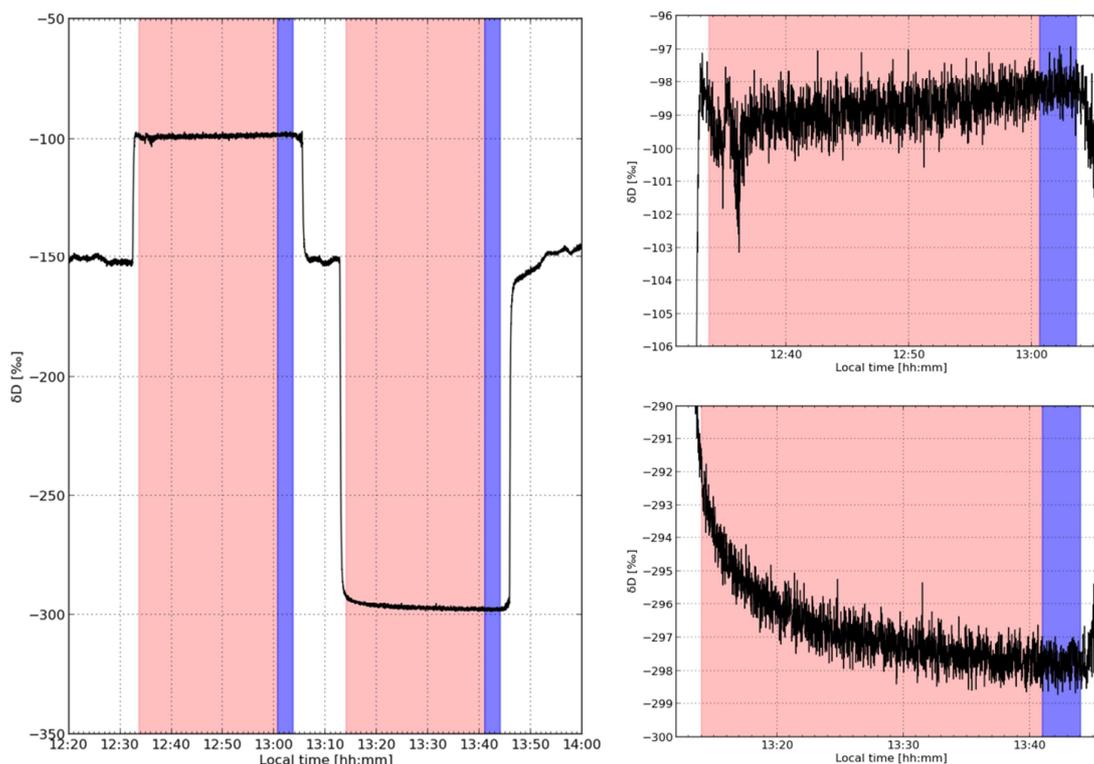
27) p. 485, l. 6 Do you calibrate at regular 6 hour intervals? If yes, do I understand this correctly: you calibrate each standard for 30 min and remove 13 min after the calibration run → use 63 min every 6 hours. You thus lose 4h of measurement time for your calibration. Could this impact the quality of your daily cycle if you have missing measurements at regular 6h time intervals? Could this calibration procedure be optimised? Measuring a standard for 30 min but only using the last three minutes (10% of the data) does not seem very efficient to me.

*Not exactly. We calibrate after every 6 hours of ambient air measurements. We thus lose 73 min every 7.2 hours. Calibration intervals are not regular on the day scale, but are shifted throughout the measurement period, so the missed part is different for each daily cycle.*

*We chose to have more reliable and accurate observation, but then instead lose about 1 hour every 7 hours. It is important to notice that to have accurate vapor isotope measurements it is very important to treat the memory of the standard measurements correctly and consistently. This is something which we feel everybody who makes field measurements of water vapor isotopes should realize and act according to. We make the assumption that during the ~1 hour without measurements we can linearly interpolate any changes in the atmospheric water vapor.*

*Figure S4 shows an example of  $\delta D$  measurements during the two-standard calibration. Calibration intervals (30 minutes) are shown in red with the last 3 minutes shown in blue. On the zoomed fragments (Fig. S4, right panel) it can be seen that representative measurements are established only in the very end of calibration interval. With the larger isotopic difference between the two adjacently measured samples the effect becomes more pronounced. We find it*

*reasonable to calculate the resulting value of each successful calibration over the last three minutes in a steady plateau area.*



Supplementary Figure S4. Example of  $\delta D$  measurements during the calibration time-series (left) with zoomed regions (right). Red – calibration period (30 minutes), blue – representative part (3 minutes).

28) p. 485, l. 10 It would be important to know the data acquisition time of the raw data, are these standard deviation computed on 1Hz data?

*Yes, the data acquisition time is  $\sim 1$  Hz (0.85 Hz exactly), this information has been added in section 2.3. And yes, these standard deviations were computed on the data with that frequency.*

29) p. 485, l. 13 I am not convinced by your argumentation that always calibrating at 12000 ppmv is a better approach than calibrating at the ambient humidity level. Of course the uncertainty of your calibration run impacts the total uncertainty of your isotope measurements but your humidity correction is affected by a similar uncertainty and your ambient air measurements are

performed at a humidity level with a similar instrumental noise. I find it more honest to calibrate at the ambient humidity level. You then also know what the current instrumental noise level is from your calibration run and you can use it to compute the total error affecting your measurements.

*We do not really agree on this. We can determine the humidity-isotope response calibration very reliable by making numerous measurements at several different humidity levels. The aim of the drift-measurements is to establish the drift of the system. It is therefore important that we get the most reliable estimate of this. With the larger noise level at lower humidity levels we also will have higher noise level on the mean value of the drift estimate. As we will have to correct both the ambient air measurements and the drift measurements to the same reference level we do not see the added value of making the drift measurements at a level of ambient humidity.*

*Furthermore, using the “SDM + DRIERITE” configuration for every-day calibrations, we strongly recommend not to run calibrations at the humidity levels below 5000 ppmv. As it was demonstrated on the Figure 3, the response of this configuration is unreliable at low humidity. Besides, the calibration run uncertainty is not similar with the air measurement uncertainty, as in the first case we have an additional systematic error related to the incomplete air drying in the DRIERITE column that becomes significant at low humidity levels. Note also, that for the ambient air measurements we use correction obtained for “SDM + dry gas” configuration. So, applying two different corrections for calibrations and air measurements would actually increase the total uncertainty. That is why we have decided to calibrate at 12 000 ppmv always.*

30) p. 485, l. 18, Are these drift values computed over 1 year? So is it < 2permil/year?

*Yes, exactly. The instrument reveals a very good stability.*

31) p. 485, l. 19, Use VSMOW-SLAP slope.

*Corrected*

32) p. 485, l. 20 Instrument accuracy is a bit unspecific, is it total measurement uncertainty that you mean, maybe explain which uncertainty sources you include in the “instrument accuracy”.

*Yes, we mean total uncertainty, corrected.*

33) p. 485, l. 21 It is not clear here what the “conservative instrument uncertainty estimate” by Steen-Larsen et al., 2013 is. What is it based on, what does it encompass? Since you did an independent characterisation study, why not use your own data to estimate the total uncertainty of your isotope measurements. I do not find it adequate to use the “conservative uncertainty estimates” from Steen-Larsen et al., 2013 since you use a much newer version of the Picarro instrument here (L2130 vs L1102 in Steen-Larsen et al., 2013). Indicate also the uncertainty of deuterium excess measurements.

*On the base of our study we can determine “precision” of our measurements (dispersion of the measurements within the mean measured value), but not “accuracy” (closeness of the measured value to the true value). The instrument precision is shown graphically on Figure 3 in the manuscript (error bars correspond to plus-minus one standard deviation of the measurements). But in our work we are rather interested in the absolute error of our measurements. We do not have a possibility to determine it by ourselves, as for this we should have an independent calibrated instrument. Thus, we use the results from the work of Steen-Larsen et al. 2013, where such an estimation has been performed. As we use a newer version of the instrument we can be confident that its accuracy is not worse than that for the previous generation. This is why we speak about a “conservative estimate” as the real error should not be higher than these values and also because we do not measure it by ourselves.*

34) p. 486, l. 25 Are the 3 permil variations in deuterium excess an average over the whole year, or for winter? This is probably within the uncertainty range of the deuterium excess measurements?

*This is an average for the whole year. But we meant variations from one day to another, **excluding** strong night drops during summer. In the next sentence we conclude that in contrast to this mean value, the summer deuterium excess variability is much larger at the diurnal scale. The word “however” has been replaced in the text with “opposite to this” for better understanding.*

*And yes, this is within the uncertainty for deuterium excess measurements that equals 2.3‰ at “normal” humidity and reaches 18‰ at 500 ppmv, for example.*

35) p. 487, l. 1 “Our observed seasonal cycles in isotopes...”

*Corrected*

36) p. 487, l. 7 To study what exactly? Give more motivation and scientific questions that are relevant in this context. Why should we expect a deuterium excess maximum in autumn?

*The motivation for such a study is to investigate the moisture origins over Siberia. Kurita (2011) reported high d-excess values in autumn in Siberian five-year time series, which were attributed to increased kinetic effects due to the Artic-origin air mass contribution during this time period. However, in our one-year long record this feature does not appear. Comparison with the data from the following several years will allow to understand whether we have such a contribution over our site or not.*

37) p. 487, l. 15-20 Can you give a more detailed interpretation of these slopes?

*The lower slope values in spring and summer reflect the increased d-excess variability during these seasons, which we discuss in later sections. We attribute*

*it to the contribution of the local recycling processes being dominant over the large-scale transport processes.*

*Obtained slope values are comparable to the 6.8 value reported by Bonne et al. (2013) for the 1.5 year monitoring data in southern Greenland and the 6.5 value reported by Steen-Larsen et al. (2013) for NW Greenland in summer. In the last work a separation of high d-excess measurements from the full data also leads to the higher slope values (7.4 for high d-excess measurements and 7.2 for non-high d-excess measurements), which are the same as ours.*

*Another important point is that the strong correlation observed between  $\delta D$  and  $\delta^{18}O$  serves as an indirect verification of our data quality.*

38) p. 487, l. 27 What kind of processes do you allude to?

*We allude to the local processes leading to the strong deuterium excess decrease during the night. In this section we have showed that the daytime measurements do not detach from the overall strong correlation between  $\delta D$  and  $\delta^{18}O$ , unlike the night values. The reasons for this effect are discussed in section 3.9.*

39) p. 488, l. 15 Can you compare your isotope-temperature slopes with literature values? Why do you expect an isotope-local temperature dependency? Rayleigh distillation would be more a process that happens during water vapour transport. You say that this slope is about half the relation expected from Rayleigh distillation, can you help the reader to understand how you come to this 50% value? Which other process does influence this slope?

*For Rayleigh distillation the slope between isotopic composition and temperature is  $0.8 \text{‰ } ^\circ\text{C}^{-1}$  for  $\delta^{18}O$  and  $6 \text{‰ } ^\circ\text{C}^{-1}$  for  $\delta^{18}D$ . Bonne et al. (2013) have analyzed relationship between  $\delta^{18}O$  in vapour and local temperature for southern Greenland and obtained a slope of  $0.37\text{‰ } ^\circ\text{C}^{-1}$ , which is also half the relationship expected from Rayleigh distillation, as in our observations.*

However, Steen-Larsen et al. (2014a) observed the  $0.81 \text{ ‰ } ^\circ\text{C}^{-1}$  value for the slope during the summer period in NW Greenland.

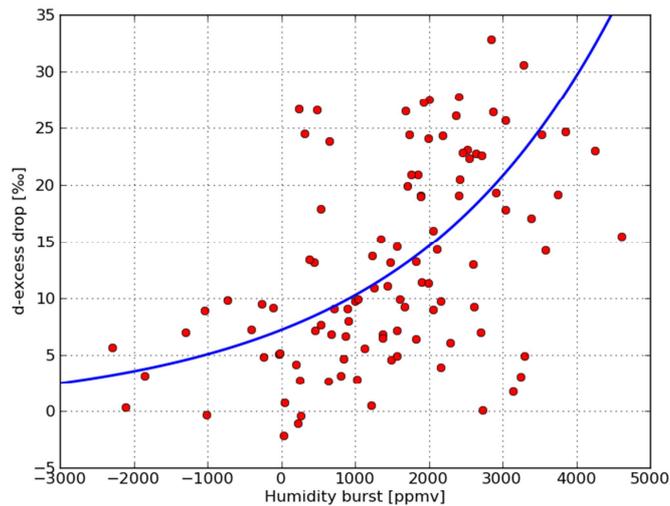
*From the close relationship between temperature and logarithm-of-humidity we could expect an isotope – local temperature dependency, because the values of local temperature and logarithm-of-humidity are also connected with each other.*

40) Section 3.9 see my major comment D.

*Answered in comment D and corrected*

41) p. 490 l. 4, I don't understand when the inverse correlation between deuterium excess and humidity occurs.

*The inverse correlation is observed between the magnitude of deuterium excess shift from the day value to the night value (which is negative) and release of humidity in the morning (which is positive). The sentence have been reformulated using another parameter in order to have a positive correlation and accompanied by Figure S5: “Within all the diurnal cycles, we observe a positive correlation ( $R = 0.49$ , Fig. S5) between the amplitude of d-excess drop (difference between d-excess mean value for the interval from 15:00 LT to 18:00 LT and mean value for the interval from 07:00 LT to 08:00 LT) and humidity value increase during the morning burst (difference between humidity mean value for the interval from 09:30 LT to 10:30 LT and mean value for the interval from 05:00 LT to 06:00 LT).”*



Supplementary Figure S5. Deuterium excess drop vs. morning humidity burst.

42) p. 490 l. 8 I don't understand your argument with the dewfall.

*We refer the readers to the detailed description proposed by Berkelhammer et al., 2013 regarding the interaction between the isotopic compositions measured in the canopy and the formation of dew. In general we propose that there is a positive correlation between amount of dew formed and the magnitude of the humidity burst. The drop in d-excess is according to Berkelhammer related to formation of dew, we therefore expect (as our data also show) a positive correlation between the magnitude of the d-excess drop and the release of humidity in the morning.*

43) p. 490, l. 13 Use WS-CRDS as everywhere else in the paper.

*Corrected*

44) p. 490, l. 15 The protocol you present has already been published earlier on (Steen-Larsen et al., 2013), please reformulate. E.g. a measurement protocol has been adapted.

*Corrected*

45) p. 490, l. 21 Mention the humidity range of your measurements.

*A new sentence have been added in conclusions: “During the monitoring period the isotopic composition varies in the ranges from –100‰ to –300‰ for  $\delta D$ , from –15‰ to –40‰ for  $\delta^{18}O$  and from +25‰ to –25‰ for d-excess with the humidity concentration being in the range 250-23 000 ppmv.”*

46) Figure 3: how did you standardise your data? I assume the y-axis shows a bias with respect to the measured value at some reference humidity level (e.g. 12'000 ppmv?).

*Yes, exactly. The following sentence has been added in the Section 3.3 and Figure 3 caption: “The y-axis shows a bias with respect to the mean value measured at 12 000 ppmv.”*

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