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Atmospheric Measurement Techniques Discussions

Interactive comment on "Continuous measurements of atmospheric water vapour isotopes in Western Siberia (Kourovka)" *by* V. Bastrikov et al.

Anonymous Referee #3

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This paper presents a 1.3 year measurement time series of stable water isotopes in atmospheric water vapour in Western Siberia (Kourovka) using the L2130 version of the commercial cavity ring-down spectrometer of Picarro. Due to the location of the measurement site in a cold continental region the challenge for isotope measurements with such an instrument lies in the very low water vapour concentrations that can occur particularly in winter in this region. An optimised measurement protocol very similar to the one presented in Steen-Larsen et al., 2013 for these cold conditions is proposed.

A central and very challenging aspect discussed in this paper is how the humidity dependency of water vapour isotope measurements should be corrected. This is an important topic for the growing isotope measurement community using commercial laser spectrometers. Furthermore, I think this paper raises very interesting questions about the processes dominating water vapour isotope variability in continental boundary layer air. However, in the current form it is difficult for the reader to filter out the truly novel aspects and the scientific motivation behind this study. I summarised my major concerns in the following 5 major comments that should be addressed by the authors:

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 18O signal).

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).

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 glas 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)

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).

Specific comments:

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

2) p. 476, l.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.

3) p. 476, l.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.

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?

5) p. 478, l.10 and elsewhere, use Wavelength-Scanned Cavity Ring-Down.

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

7) p. 480, l.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, glas syringe pump).

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

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

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.

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).

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

from the tank cylinder.

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?

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

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.

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.

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

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

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?

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.

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.

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.

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.

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 CO2 measurements at your measurement site or at some nearby location? Actually the L2130 Picarro instrument version provides methane measurements as well.

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.

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

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 loose 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.

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?

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.

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

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

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".

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.

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?

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

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?

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

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

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?

40) Section 3.9 see my major comment D.

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

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

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

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.

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

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?).

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