

## Review of

*“The stable isotope composition of water vapour above Corsica during the HyMeX SOP1: insight into vertical mixing processes from lower-tropospheric survey flights”*

by H. Sodemann et al.

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**General comments** This paper presents airborne in situ measurements of the stable water isotope (SWI) ratios  $\delta D$ ,  $\delta^{18}O$ , and the second order isotope parameter deuterium excess from 21 flights over the Mediterranean. Thanks to the relatively high temporal resolution of the measurements, the study is able to reveal highly variable and well-structured SWI profiles as well as a very variable relation between specific humidity and SWI ratios. The mean values and the variability of the vertical SWI profiles are in good agreement with sparse existing airborne SWI measurements and are discussed with respect to condensation, air mass mixing, and processes related to evaporation. Based on the evolution of the SWI ratios during four days the authors find that both large-scale transport and vertical mixing within separated layers are responsible for the observed variable and well-structured vertical SWI profiles. This is supported by a backward trajectory analysis, which confirms the relation between the observed SWI ratios and air mass origin and transport.

Especially the observations of deuterium excess are unique with respect to the amount of data and temporal resolution and of high interest for atmospheric studies on transport and isotope microphysics and the validation of isotope-enabled models. The data is complemented by a comprehensive and convincing interpretation. I recommend publication of this innovative, very well-written paper after my following major two concerns regarding measurement uncertainty have been addressed:

1. In my opinion, a central assumption of this publication regarding the measurements of deuterium excess is stability of the deuterium excess-humidity response of the instrument. The applied deuterium excess-humidity response correction was determined after the campaign. The fact that this response is individual for each Picarro Isotope Analyzer may indicate that the response is related to the alignment of optical components or other parameters that could change with time or in consequence of mechanical stress. Because the magnitude of the applied humidity correction for deuterium excess (Fig.A3c) is of the same order of magnitude as the observed range of observations of deuterium excess (Fig.6b) this may introduce significant systematic uncertainty to the observations. The authors mention additional calibrations of the SWI-humidity response during the campaign. Could you add them to Fig.A3 to demonstrate stability of the SWI-humidity response correction?

2. Uncertainty estimates for the SWI measurements are based on the standard deviation of calibration standard measurements in the lab (Fig.A4). However, this estimate does not account for (a) memory effects of the inlet tubing and other effects responsible for the observed hysteresis of SWI measurements, (b) potentially increased instrumental drift in consequence of mechanical stress during the flights, and (c) systematic uncertainty of the applied SWI-humidity response correction. Could you quantify these three uncertainty terms e.g. for humidity levels of 1000, 5000, and 10000 ppmv:

- (a) The observed hysteresis of SWI measurements should be consistent with the stated measurement uncertainty. Could you quantify the observed mean hysteresis of the SWI measurements for different humidity levels?

In my opinion, not only changes in cavity pressure but also memory effects of inlet tubing and analyzer are reasonable explanations for the observed strong hysteresis of the SWI measurements. The 123 cm of inlet tubing closest to the isotope analyzer were not flushed by the TF2 flushing pump. Considering the small air stream of  $0.11 \text{ min}^{-1}$  through this part of the tubing, the relatively strong adsorption of water on PTFE surfaces, and encountered strong gradients of specific humidity memory effects may play an important role. This seems to be supported by the differences between SWI measurements during ascent and descent, which appear to be especially pronounced during dry conditions and smaller during moist conditions. Compare e.g. Fig9g: dry conditions above 1700 m a.s.l. are related to a strong hysteresis of  $\delta D$ , wet conditions below 1700 m a.s.l. are related to a small hysteresis of  $\delta D$ .

With respect to memory effects of the measurement system the authors state time constants of 2.4s, 1.7s, and 1.3s for  $\delta D$ ,  $\delta^{18}O$ , and  $H_2^{16}O$ , which are within the applied averaging time of 15s. These time constants were determined in Aemisegger [2013]. As I understand it, Aemisegger [2013] derived the time constants by measuring the instrument response to changes of specific humidity of 1000 ppmv between 12000 and 22000 ppmv. I assume that these time constants may be substantially larger for drier conditions and larger humidity steps e.g. from 5000 to 500 ppmv.

- (b) During the campaign SWI calibrations were performed before and after the flights. However, most of the calibrations before the flights had to be discarded because stabilization of the instrument was not completed. Could you estimate typical drift of the isotope analyzer during the flights based on the few days with successful calibrations before and after a flight?
- (c) Do the error bars in Fig.A3 state the total uncertainty of the SWI-humidity response calibration? Could you underpin stability of the SWI-humidity response calibration by measurements during the campaign?

### Specific comments

- p.2,L.8: In my opinion, stating the definition of the  $\delta$ -notation or citing e.g. [Coplen, 2011] would be helpful.

- p.6,L.1: “...changed after the installation of a replacement pump...” Slope and offset between CRDS humidity measurements and HCLY measurements were stable between flights, but changed after the installation of a replacement pump. Does this change indicate memory effects of the inlet tubing, whereby the impact of these effects changed in magnitude in consequence of an adjusted air flow?
- p.6,L.10-28: See my first point in the general comments.
- p.6,L.30-p.7,L.10.: SWI measurements with the Picarro isotope analyzer are based on linear two-point calibrations at  $\delta D = -78.68\text{‰}$  and  $-166.74\text{‰}$ . Aemisegger et al. [2012] show significant non-linearity of this correction for an older version (L1115-i) of the Picarro isotope analyzer. As many of the observations with high d-excess are related to  $\delta D$  ratios smaller than  $-166.74\text{‰}$  (Fig.4) it might be of interest to quantify respective additional measurement uncertainty at small isotope ratios.
- p.7.,L.15-L.18: The required measurement accuracies of  $\text{H}_2^{16}\text{O}$ ,  $\delta D$ , and especially of deuterium excess are of different order of magnitude. A drift of the CRDS  $\text{H}_2^{16}\text{O}$  calibration by  $10\text{‰}$  would be almost undetectable if comparing the CRDS and HCLY humidity measurements. However, changing  $\delta D$  and  $\delta^{18}\text{O}$  by  $10\text{‰}$  would shift the deuterium excess even for  $70\text{‰}$ . I therefore think that a small observed drift of the CRDS  $\text{H}_2^{16}\text{O}$  calibration does not necessarily confirm a small drift of the SWI calibration.
- p.7,L.22-24: Dyroff et al. [2015] used a different measurement principle. For this reason please skip this sentence.
- p.7,L.26-28: “From laboratory experiments with the inlet system...” Please add a description of this experiment to the Appendix. See my point 2a in the general remarks.
- p.9,L.33: Could you explain in more detail what you mean by non-linearity of the delta scale.
- p.9,L.31-p.10,L.1: “The high d-excess ... is therefore not an indication of insufficient data quality, but a real feature ... in the atmosphere”: I agree that the high d-excess encountered is not an indication of insufficient data quality, but I don’t think that agreement with the observations of Galewsky et al. [2011] and Samuels-Crow et al. [2014] alone justifies the conclusion that the SWI composition presented here is a real feature. I would rather treat this agreement as further evidence for reliable observations. Please rephrase this sentence.
- p.12,L.6: “a very dry and depleted free tropospheric air mass”: The free tropospheric end member you assume for the green mixing curve is drier but less depleted than the free tropospheric end member corresponding to the orange curve. Can the free tropospheric end member corresponding to the green mixing curve be explained by condensation alone or do the specific humidity of  $0.5 \text{ g kg}^{-1}$  and the  $\delta D$  of  $-220\text{‰}$  imply earlier mixing?

- p.14,L.34: As mentioned above I would appreciate a quantification of the memory effects regarding uncertainty of the SWI measurements.
- p.15,L.33-34: “Reproducibility was good ... except for the dry intermediate layer”. To me this seems like further evidence for a humidity-dependent and not a cavity pressure-dependent hysteresis of the SWI measurements.
- p.20,A1: Was temperature in the non-pressurized cabin stabilized? Did you heat the tubing to avoid condensation?
- p.21,L.3-5: I wouldn’t use the standard deviation of calibration standard measurements as measure for the total uncertainty of the observations during the campaign as this value doesn’t consider the effects causing the observed hysteresis of SWI measurements, potentially increased instrumental drift during the flights in consequence of mechanical stress, and systematic uncertainty of the humidity response correction. See my second point in the general remarks.
- p.21,L.18-20: “Possible causes of this hysteresis... due to observed changes in the cavity pressure”: What about memory effects causing the hysteresis?
- p.21,L.32-p.22,L.4: The authors refer to SWI calibrations bracketing each flight ensuring stability of the SWI measurements. This is in contrast to p.7,L.6-7: “...with very few exceptions only the calibration runs after the daily flight operations were used...”. Maybe you could add a figure demonstrating the stability of SWI measurements based on the few days with successful calibrations before and after the flights. Otherwise I would skip the sentence p.22,L.2-4 “...calibration during flight would not improve data quality substantially in our case...”
- Fig2a: What is the meaning of the red and black lines.
- Fig2, Fig3, Fig6, Fig9, Fig10, Fig11, Fig12, FigA3, FigA4, FigA5: I would appreciate consistent use either only of ppmv or only of  $\text{g kg}^{-1}$  for stating humidity in the different figures and in the text.
- Fig6b: Could you add systematic uncertainty of the deuterium excess measurements (resulting e.g. from uncertainty of the SWI-humidity response correction) to this figure?
- Fig.A3: Do the error bars show statistical uncertainty from measurement noise? What is the meaning of the red crosses?

### Technical corrections

- p.7.,L.30: CRDS
- p.8,L.4: “1.17”: Table 3 states an uncertainty of 1.18‰ for d-excess.
- p.11,L.31: “relatively moist”: Do you mean relatively dry?

- p.11,L.35: “magenta line”: The respective line is orange.
- p.21,L.4: “Figure A5”: Figure A4?
- Fig9: “black or solid ... grey or dashed lines”: There are no dashed lines visible in this figure.
- Fig10: “red stippled”: not shown
- Fig.A5: “red”: magenta; “blue”: green

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