

Reply to the *Interactive comment* by anonymous Referee #2 on the manuscript “Modeling the dynamic behavior of a droplet evaporation device for the delivery of isotopically calibrated low-humidity water vapor” (<https://doi.org/10.5194/amt-2020-428>).

I would like to start with thanking the reviewer (in fact: both reviewers) for the constructive comments that will undoubtedly make for a much better paper. As outlined here below, these will be implemented in the final manuscript where applicable. Here below I will copy the text of the review in black text, then provide my reply in blue, indented text, immediately following each item of the review.

The author presents a mathematical model to calculate the water isotope ratio which has been measured with a new developed calibration instrument described recently in another work published by Leroy-Dos Santos et al. (2020) in AMTD. The results of the presented simulations fit quite well with the measurements of that particular calibration device. I think it would have been more suitable to publish this work as an add-on to the published paper mentioned above. I don't see the unique selling point of this work and the added value of it for the community. Therefore I suggest a major revision.

We (i.e., the authors involved in the Leroy-Dos Santos paper and the current manuscript) have collectively chosen to submit the modeling effort in a companion paper to the experimental paper by Leroy-Dos Santos *et al.* (2020) for a number of reasons:

Firstly, the theoretical understanding of the dynamic behavior has enabled the identification of the droplet evaporation device as an independent tool to investigate isotope fractionation factors involved in liquid-vapor transitions, as well as isotope fractionation occurring during the process of evaporation of cloud water droplets. The same is true for the determination of the evaporation rate of nano- and micro-liter-sized droplets, which has been the subject of a large body of research, starting with the fundamental work of Maxwell and Langmuir, and more recently in the fields of drying, painting and patterning technologies, dehumidification, cooling technologies, desalination, DNA synthesis, etc. In our opinion, this alone merits separate publications in order to reach as many of the potentially interested researchers as possible.

Secondly, we need to mention that the actual instrument used to produce the data for the current paper is different from the one presented in the companion paper. The simulations have not been performed to fit the data presented by Leroy-Dos Santos *et al.* ... In fact, the data used here in section 3.2 for confrontation with the model could not even be produced with the new instrument, as it was expressly (re-) engineered to eliminate the non-ideal behavior that allowed demonstrating the success of the model in simulating the instrument behavior under very different operating conditions. It was also never equipped with evaporation chambers of different dimensions, as was needed to produce the distinctly different behavior of section 3.1 versus section 3.2. Partly as a consequence of this, a different combination of authors contributed to the work described in the two papers.

Finally, we also felt that adding the model to the experimental paper would make the paper unwieldy long. Also, it would have been very awkward, and most likely

confusing for the reader, having to describe the older, prototype instrument in the same paper that describes the newly designed, re-engineered device in order to be able to present the data of section 3.2.

In conclusion, and especially considering that the experimental paper by Leroy-Dos Santos and colleagues (2020) has now been accepted for publication, and its final version has been submitted, we remain of the opinion that the model paper should be published separately, and preferably as a companion paper.

In any case I have several comments the author should consider to incorporate into the manuscript before publication. Major issues:

1) For a better understanding the author should briefly describe in the introduction why the measurement of the water isotope is important and what insights you gain from it.

I thank the reviewer for this suggestion, as it will indeed be useful for a reader who is not from the isotope community to see some justification for the importance accorded to water isotope measurements. I thus suggest to add a more general explanation at the beginning of the Introduction along the lines of:

“Water is arguably the most important molecule in Earth’s atmosphere. The large enthalpy change associated with the evaporation and condensation of water causes it to dominate the global redistribution of energy by tropospheric transport of latent heat. Water vapor is also the most important greenhouse gas. The natural atmospheric greenhouse effect warms Earth’s surface by 33 K to hospitable temperatures of on average 15 °C. About 75% of this temperature increase is generated by water vapor and clouds, as a feedback effect driven by the non-condensable greenhouse agents, and foremost carbon dioxide [Lacis2010]. This feedback effect, in turn, is a superposition of a multitude of large and (especially as clouds are involved) complex individual processes that partially cancel each other. Due to this complexity, water, in the form of water vapor, as well as liquid and crystal phase water inside clouds, is by far the largest unknown in current climate models [IPCC2014]. Atmospheric data of relevant tracers, which may help to disentangle and quantify the many relevant processes, are desperately needed. Of these, the isotopic composition of water is arguably the best candidate (in particular the isotope ratios D/H and $^{18}\text{O}/^{16}\text{O}$), as all processes in which water is involved are isotope-dependent. Therefore, water isotope ratios enable identification of different moist air masses and following of their mixing; they also reflect the evaporation and condensation history of the moist air in question. In the journal *Nature*, the climate researcher Gavin Schmidt actually called the water isotopes “the most super-duper fantastic thing ever” [Tollefson2008].”

This can then be followed by the specific argumentation, as we put forward in the Leroy-Dos Santos paper that there is a strong need for a reliable means of calibrating optical spectrometers for low-humidity applications, as in Antarctica, using liquid standards.

Tollefson, Jeff. 2008. “Vapour Spies to Reveal Climate Clues.” *Nature* 455 (7214): 714–714. <https://doi.org/10.1038/455714a>.

2) It would be good to describe the meaning of δ for the readers not so familiar with the subject.

Thank you for pointing this out. I will include a brief description in the Introduction of the delta-value as a relative deviation of the isotope ratio in a sample with respect to the same ratio in a standard material. The definition of the delta-value should appear much earlier in the paper than at L100, as is now the case.

3) The derivation of the formulas are not always easy to follow, please prepare a better description.

It is disappointing to read this as I had the manuscript already proofread by more than one colleague, and had made modifications following their suggestions ... In the absence of more detailed comments, I will re-read the entire paper again with special attention to this issue, and in the process ask for additional input from different colleagues to be incorporated in the final version. At this point I can think of two clarifications that may be useful to some readers:

L89: Add an intermediate step: "expressing both the droplet size ... and the evaporative water flux $\Phi_e(t)$ as a function of $V_d(t)$, and to subsequently calculate both as function of the time-dependent input water flux $\Phi_0(t)$ by numerical integration of Eq. (3)."

L90-100: Mention that the factor $(1+R)$ in the denominator of Eqs. (9) to (11) arises from a conversion from isotope ratio to isotope concentration (requiring that one divides by the sum of the isotopologues, not just the abundant isotopologue).

4) Generally please replace 'water concentration' with 'water vapour concentration'..

This will be done. See also the comment on this topic by David Walton (Referee 1).

5) All figures should be enlarged. The legend of the figures are too small..

Thank you for this suggestion; will be implemented in the final version. Please note that the current type setting is imposed by the TeX style document provided by AMT. The definition of the images is more than sufficient to allow for larger figures. For the manuscript I set the figure sizes manually, but I expect that these will be overruled in the journal's final type setting process.

6) The colours of the graphs changes from one figure to the next. The author should consider to use the same colour for the simulation in all figures.

Thank you for pointing this out. Whereas the color coding: Black for concentrations, Red for Oxygen-18, and Green for Deuterium has been followed throughout, Figures 4 and 6 should have their color coding inversed with respect to experimental data (should be gray) and simulation (one of the above colors for the isotopes). This will be easy to correct for the final version.

7) Figure 4 why does $\delta^2\text{H}$ oscillate so much more than $\delta^{18}\text{O}$. Please give an explanation.

Thank you for this observation. I will add an explanation to the text to mention that the larger fractionation for deuterium compared to oxygen-18 leads to a larger excursion of the d2H signal compared to d18O. At the same time the noise on the d2H signal is much larger than that of d18O because of the lower signal-to-noise ratio of the deuterium feature detected by the infrared spectrometer, directly related to the lower abundance of $2\text{H}16\text{O}1\text{H}$ (0.031%) with respect to $1\text{H}18\text{O}1\text{H}$ (0.20%) in our natural water sample.

Minor issues: 1) line 66-69 the use of numbers in brackets could lead to the misunderstanding that the author refers to the number of the appropriate formulas, consider using other annotations. 2) line 136 The standard waters used were left-over? Consider a better formulation.

Thank you for pointing out the potential for misreading the numbers in lines 66-69. I will itemize the three points using the letters *a*, *b*, and *c* instead. Considering the “left-over” in line 136, I refer to my response to Dr. Walton’s question concerning the type of water used (with Lines 60-70). I propose to mention the origin of the water as an older standard water of the Center for Isotope Research in The Netherlands.