

Author's note to editor: We learned a lot about these experiments from the first set and agreed with the reviewers' concerns that the experimental design could be improved. The revised manuscript is based on the following major changes.

1. We repeated the experiments using a new design. The air flow through the analyzer was increased to maximum flow rate of the external pump and we let the air flow through the tubing be controlled by the analyzer/external pump flow rate. This achieved the shortest turnover time of air in the analyzer and the slowest flow rate through the test tubing given our equipment which should allow the best conditions to identify differences between tubing material types and factors like length and inner diameter.
2. We added a curve fitting data analysis approach to help resolve memory differences between experiments. The new impulse function curve fitting analysis provides two additional memory metrics we discuss in the manuscript. We also kept the attenuation threshold time metrics and added another metric of the D-excess transient anomaly- the absolute value of the maximum D-excess signal peak.
3. We added a new tubing material, Bev-A-Line XX, which demonstrates a much longer memory effect and therefore provides an unacceptable material example.

These major changes mean that not all the previous reviewer comments are now applicable and are listed as such. Author responses are included in red text.

We appreciate the time, suggestions for improvement, and patience of editor Thomas Röckmann, the three anonymous referees, as well as Jonathan Keinan.

Reviewer 1 comments

This article compares the memory effect and lag times associated with laser-based water isotopic measurements for different tubing materials and dimensions. This article will be very useful for people involved in laser-based water isotopic measurements. The article is well written. My comments are relatively minor.

Note that I'm not an expert in laser-based isotopic measurements. Although I enjoyed reviewing this article, the comments by referees who are actually hands-in with such measurements will be very useful and probably more relevant than mine.

General: For readers who are not familiar with feet and inches, it would be helpful to systematically add between brackets the lengths in international units.

International units are added.

Figure 3 caption: d and e are not described in the caption. Try something like “Mean attenuation times $t_{95\%}$ for $\delta^{18}\text{O}$ (a) and δD (b) and $t_{63\%}$ for $\delta^{18}\text{O}$ (d) and δD (e) and t_3 ‰ for D-excess (c)”?

Also in this figure, how were the error bars estimated? Explain this somewhere in the data analysis section?

This figure has been removed in the revision. These memory quantification metrics and new ones are in the supplement. Error quantification is included in the methods section 2.4.1 specifically for threshold metrics, and 2.4.2 for impulse function metrics.

Section 4.2: I might be missing some basic elements to understand this section. Maybe giving a few more sentences of background or explanation would be useful:

- aren't the tubing cylindrical? If so why aren't the surfaces and volumes linear with length?

This discussion has been removed. Surface area and volumes are linear with length, but in that previous discussion, ID was also changing between short and long tubing.

- “the shape of the isotopic attenuation curves remained similar”: is it just the shape that remains similar? It looks like it's more than the shapes, the attenuation times remain similar as well, and this looks like the most important result.

“In this set of experiments we found that while overall memory metric differences exist, they are small in the materials and dimensions tested, and the operational impact among commonly used ¼ inch OD tubing inlets is expected to be limited.” In terms of attenuation curves, there are again small differences based on tubing dimensions and materials, but the operational impacted is expected to be limited.

- I 327: “However...”: why does it contradict the hypothesis that the isotopic memory mainly comes from the analyzer cavity?

No longer applies after we reduced the memory of the analyzer in the new experiments to better see differences between tubings.

- Why do the rates depend on the fraction of water adsorption sites that are out of equilibrium, rather than the number of sites? Could you give a simple equation (e.g. for the

first-order kinetic reaction) that would allow readers not familiar with this literature to understand this paragraph?

This discussion has been removed. There are now resolvable, but small, differences changing length and ID.

I 399: ". ." -> "." Corrected

Reviewer 2 comments

The manuscript by Meyer & Welp is a study aimed to show how different tubing materials affect the water vapor isotopic signal propagation inside tubings. The authors tested different kind of tubings by forcing the experimental setup with large isotopic step changes without changing the water vapor mixing ratio. The authors then discuss the shape of rising/falling edges and the timing characteristics of the step change curves (lag, rising time, t_{63} , t_{96} etc). The results show very similar characteristics for all the tubing materials tested, regardless of temperature (tested at ambient temperature and 60°C). This study can be highly relevant for the water vapor isotope community, since there is no clear evidence/agreement on what type of tubing is best suited for high frequency atmospheric measurements of water vapor isotope composition. In general the paper is well written and enjoyable to read. Results and concepts are clearly presented and discussed. Figures are of good quality and easy to interpret. However, there are some aspect of the design of the study and choices that I believe the authors must explain/address before the paper is accepted for publication. In conclusion, the manuscript requires a major revision in my opinion.

Major comment #1: I am not an expert of OA-ICOS but usually such instruments are equipped with large optical cavity. I will assume an optical cavity volume of ~830 ccm, following Aemisegger et al. (2012) . This volume is ~1.5 times larger than the inner volume of the largest tested tubes (100 feet, $3/16$ " ID). Moreover, the flushing rate of the instrument is $1/3$ of the flow rate in the tubings under test (in fast mode). Therefore, the experiment setup allow to spot only differences at very low frequencies. Indeed, all the high frequency components of the step change are dampened because of long average displacement of water molecules in the optical cavity. Therefore, the conclusion that all the tested tubing types are OK for water vapor analysis is valid only for low frequency analysis (e.g. hourly observations) but not for high-frequency

analysis (e.g. flux, aircraft etc). Since I don't know the characteristics of the TWIA I might be wrong. In case the cavity volume is smaller, please do not consider this comment.

We agreed with the reviewer and decided to repeat all the experiments using the shortest possible residence time of the TWVIA (~4s, Sect. 2.2). We hope the reviewer finds the results of this effort worthwhile.

Major comment #2: The plot reported in the supplement (S2) shows an unusual increase of the Allan variance at short averaging time (>~60 seconds). If the water isotope source is stable (invariant isotope composition with time) and the measurement system is stable (measurement noise is mostly white, instrumental drift is small) the minima in the curves should be found at longer averaging time and the drift (the increase in the adev curve) should be smaller. See e.g. Fig.7 in Aemisegger et al. (2012) or Fig.3 in Jones et al. (2017). **This suggests that the target value of the step change is not stable (i.e. the target isotope value is changing with time in the time frame of the analysis ~1 hour).** This might be due to the change in isotope composition in the source of water vapor? The authors already identify the DPG as a potential source of isotope variability. A correction of the source isotope composition using Rayleigh distillation might be necessary (mentioned at L119-120). It is not clear how large the fractionation of the standard water was during the tests .

Allan plot now presented shows data using the WVISS source which does not trend over time like the DPG source due to the nature of the vapor production. The stable 'end points' are now defined as the average of 600-1200 sec (10-20 min) to minimize the influence of any potential drift. This is a much faster stabilization than the previous experiments, where the 'end points' were 3400-3600 sec due to the slower analyzer flow rates. The new Allan plot shared in Figure S1 shows that the variance doesn't increase until ~200 sec in d18O and 1000 sec in δD which is more in line with expectations. Visual analysis of the hour-long experiments suggests that the drift is minimal within a sweepout, even with the DPG.

Because we normalize the transitions, it's not necessary to correct for small changes in the DPG source water over time. All source water values (uncalibrated) are given in Table S1. Source value differences change by 155.43 ± 3.43 ‰ (~2.2% variance) δD , 19.839 ± 0.463 ‰ (~2.3 % variance) $\delta^{18}O$, and 4.04 ± 3.610 ‰ (~89% variance) D-excess between experiments. See revised section 2.3 for a discussion of why calibration, water mixing ratio dependence, and instrument and source drift corrections are not necessary.

Major comment #3: Please consider to change the step change into the impulse response by computing the derivative (see e.g. Jones et al., 2017, Steen-Larsen et al., 2014). This will let you to discuss how the signal is attenuated by e.g. fitting a normal distribution and looking at the standard deviation of the distribution, which is an indication of the average displacement of molecules inside your measurement system. For water vapor stable isotope analysis usually the impulses are not symmetrical, therefore a best fit of a log-normal distribution or of an exponentially modified Gaussian distribution should to the job.

We took the reviewer's suggestion and used Jones et al., 2017 as inspiration. The impulse responses of the data were not normal/gaussian nor skew-normal. They had longer memory tails than those models could fit. We fit a combination of a skew-normal and gaussian distributions to fit the experimental results and now report these metrics in the revised manuscript.

Minor comments:

- It is not clear how the start of the step change is detected. I think the switching of the 3-W valve is logged but how you detect the "start" of rising-falling edge to precise measure the lag?

The lag is the difference between the time the valve switched (recorded) and the time it takes the signal to propagate through the tubing to the analyzer which depends on length, ID (inner volume), temperature, and flow rate. We now utilize the location metric from the impulse response method as a metric to line up the sweepout curves. This is not the 'start', but it correlates well with a lag estimate from a breakpoint analysis also described in the revised manuscript. We also use a mean residence time metric that has been calculated based on temperature to adjust the threshold metrics, and this value also correlates well with lag time.

- A spectral analysis of the impulse response could be beneficial for understanding the limits of each tubing material for each application (e.g. by identifying the 3dB attenuation and the passband)

For our tubing comparisons, adding another memory metric to compare tubing performance like the 3dB attenuation and passband from a Fourier Transform does not immediately appear to add much additional value on top of the metrics we do provide, including the new impulse response function fit also suggested by reviewers. The 3dB attenuation and passband may be very valuable when characterizing a specific inlet + analyzer design in field studies and for developing back correction methods in the future, as suggested by Steen-Larsen et al., in their 2014 paper.

Steen-Larsen, H. C., Sveinbjörnsdóttir, A. E., Peters, A. J., Masson-Delmotte, V., Guishard, M. P., Hsiao, G., Jouzel, J., Noone, D., Warren, J. K., & White, J. W. C. (2014). Climatic controls on water vapor deuterium excess in the marine boundary layer of the North Atlantic based on 500 days of in situ, continuous measurements. *Atmospheric Chemistry and Physics*, 14(15), 7741–7756. <https://doi.org/10.5194/acp-14-7741-2014>

- L185 does this mean that the impulse response of your system is gaussian? Or at least, symmetrical?

Edited. The impulse response is shown in figure 2. It is not gaussian nor symmetrical.

- L344 Fairly slow? In respect to stable isotope analysis?

Correct- previous work has suggested the faster the air flow rate through tubing and analyzer, the less memory effect. Tubing air flow rates are often over 1 L/min and analyzer flow rates are generally 'as fast as possible'. Our new experiments minimize this concern.

- L494 Link to code/data is not working. Fixed

References

Aemisegger, F., Sturm, P., Graf, P., Sodemann, H., Pfahl, S., Knohl, A., & Wernli, H. (2012). Measuring variations of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in atmospheric water vapour using two commercial laser-based spectrometers: An instrument characterisation study. *Atmospheric Measurement Techniques*, 5(7), 1491–1511. <https://doi.org/10.5194/amt-5-1491-2012>

Jones, T. R., White, J. W. C., Steig, E. J., Vaughn, B. H., Morris, V., Gkinis, V., Markle, B. R., & Schoenemann, S. W. (2017). Improved methodologies for continuous-flow analysis of stable water isotopes in ice cores. *Atmospheric Measurement Techniques*, 10(2), 617–632. <https://doi.org/10.5194/amt-10-617-2017>

Steen-Larsen, H. C., Sveinbjörnsdóttir, A. E., Peters, A. J., Masson-Delmotte, V., Guishard, M. P., Hsiao, G., Jouzel, J., Noone, D., Warren, J. K., & White, J. W. C. (2014). Climatic controls on water vapor deuterium excess in the marine boundary layer of the North Atlantic based on 500 days of in situ, continuous measurements. *Atmospheric Chemistry and Physics*, 14(15), 7741–7756. <https://doi.org/10.5194/acp-14-7741-2014>

Reviewer 3 comments

The manuscript of Meyer and Welp details a comparison experiment of tubing types at two temperatures. The work deals with the common issue of memory effect in water isotope analysis and aims to minimize this effect by finding the most appropriate material. While in general the experimental setup is logical and the text reads well, **I have some major points that I feel are not addressed well. Also, the text and figures need refining to more clearly communicate the findings.**

Major comments:

My main concern about this paper is highlighted in figure 4, where fast and slow analyser flow modes are compared. Based on the text, fast analyser mode increases the flow of air through the optical cavity (x2.5). During fast analyser flow, the MFM was removed, but test tubing was kept. Also, flow rates upstream of the analyser before the venting T, passing through the tested tubing itself, remained constant. Given that your study was designed to test tubing attenuation, and nothing changed in the tubing or flow through the tubing, no difference would be expected between slow and fast analyser modes. Still, Figure 4 indicates a 10x smaller memory effect duration for fast analyser flow compared to slow analyser flow. This suggests that all (equally large) attenuation times found in slow analyser mode, the mode in which all tubing was tested, were predominantly caused by attenuation in the instrument or, as the authors suggest, in the MFM. Thus, not by tubing itself. **How can reliable conclusions be drawn on tubing material type then?**

We agree with the reviewer's concerns and repeated the experiments.

I would highly recommend including dekabon as an additional tubing material. In the introduction you clarify that it is known that dekabon causes attenuation. If you can show it also does using your setup, you can be more confident about the attenuation times you find for the other materials. In the current state, open questions about the setup cast doubt on your finding that attenuation times are independent on tubing material and temperature.

We did not have Dekabon on hand and it is not commonly used in the field anymore. We did include a test of Bev-A-Line XX which showed the extremely long memory time the reviewer wanted to see.

Intuitively, tube length and tube ID impact attenuation, as indicated by your measurement setup. You don't observe this and defend your findings claiming the exchange is a "first-order kinetic reaction" (Sect 4.2). I miss a simple, interpretable, explanation on this, given the context

of tube attenuation, possibly including a figure. Please clarify in your explanation why the following train of thought would be incorrect:

- with 20x longer tubing, 20x more exchange sites are present, all occupied by isotopic composition 1 just before the switch.
- after the switch to isotopic composition 2, exchange sites are swapped with a constant rate for each isotopologue, independent of tubing length.
- as the longer tube has a 20x higher net amount of isotopic composition 1, it will take longer for the output signal to consist of 95% isotopic composition 2.

The reviewer makes logical comments on how to think about this. We don't disagree. It's clearly not a sequential process that all the sites at the beginning of the tubing have to exchange before ones at the end of the tubing. The new experiments with the shorted analyzer residence time are now able to resolve small differences due to length and tubing ID. We looked to the gas-wall partitioning theory presented in Pagonis et al. (2017) to help to explain the differences that we see between the same material and length and only changing ID and the keeping everything same and only changing length. We think the ID sensitivity makes sense based on their predictions. The length effects are a bit difficult to resolve given the additional residence time of the analyzer cavity, we might not be accurately characterizing the short tubing response.

You indicate in your introduction (e.g. L. 60) that temperature and air flow rate (and tubing material) have a known "great effect" on attenuation based on various previous studies. Still, your results replicate none of these effects (effective air flow rates through tubing material was changed by wall thickness variations in your experiment). I feel that section 4.1 and 4.2 don't currently provide convincing arguments for why you don't find the known dependencies with temperature or flowrate.

This wording has been removed. In the previous experiments, the analyzer memory was sufficiently large to limit the resolution of tubing differences. We repeated the experiments using faster flow through the analyzer and slower flow through the tubing and found slight effects of temperature and effective flow velocities. See revised Section 3.

Minor comments:

Graphics

Fig 1. Please add the flowrate coming from the WVISS. Is this exactly 1.1L/min? Otherwise, why doesn't it need an overblow? Also, given that only mass flow meters (not controllers) are used

according to the scheme and text, how is the 1.1 L/min set. Explain in the text if the rotameters were used to set the flows.

New experiments removed all in-line elements including rotameters, MFM, and filter, and the flow rate through the tubing and the analyzer is now set by the analyzer/external pump, which is at maximum speed. Flows were verified at the start of the experiments using a Bios Definer 220.

Fig 2. Add a theoretical e-folding time based on sample cell mixing. I derive a 25sec residence time based on a 500ml cell (which I think your LGR has) with 100ml/min flow. It shows the reader whether analyser mixing can cause attenuation (seems non-dominant) but generates questions on how the analyser flowrate adjustment has such a large effect.

The previous experimental design had a long analyzer residence time compared to the tubing residence times, so we repeated the experiments using improved conditions to address reviewer concerns. We've included a calculation of the analyzer (sample cell) residence time which is ~4s in the new experimental design (based on an estimated 0.925L volume at 40 Torr and 0.635 L/min flow rate). We now indicate temperature adjusted mean residence times. The short thick-walled FEP tubing has a residence time of 1.0 ± 0.09 s. Long thick-walled tubing (different materials with 1/8 inch ID) has a residence time of 19.7 ± 1.6 s, and the long thin-walled tubing (different material with 3/16 inch ID) has a residence time of 45.2 ± 2.5 s.

Fig 4. This figure should be remade. The panel labels are in the wrong order compared to the description. The y-label of current panel b is wrong (ΔD). The legend is unclear as it looks like one large legend while each column has its own.

This figure has been replaced with the new experimental results and care has been taken to ensure the labels are correct

Tab S1. Tubing lengths are only occasionally mentioned, include this everywhere and make units uniform (foot or '). Also, I notice that the WVISS dilution setting was not constant, seemingly affecting the H₂O concentration of the mixture generated, why wasn't the dilution constant?

Tubing lengths have been added to the supplemental table S1. The nebulizer flows seem to change slightly over time, likely due to partial clogging. If the dilution flow was changed, it was to match the WVISS output H₂O mixing ratio between experiments. In this round the nebulizer was cleaned at one point and replaced with a new nebulizer at another time so dilution flow was adjusted at times. The goal was to keep H₂O mixing ratios as close to constant as possible across experiments.

General

I noticed frequent incoherent sentence structures, sometimes making it challenging to get the point. I recommend going over the document to improve this.

We have attempted to simplify and clarify sentence structure.

You are in a low flow laminar regime ($Re \ll 3000$) through a long tube, yet within-tube flow rate differences, which are roughness dependent, were not explicitly considered as a cause for signal attenuation. I think it would be a valuable point to add (even if effects are non-dominant).

We have calculated Reynold's numbers for the tubing diameters and reported these in the paper and edited the discussion to include the potential effect of tubing roughness.

"The flow in all experiments was laminar with Reynold's numbers calculated between 579 and 870." section 2.3

"The overall attenuation curves of the tested tubing material types, lengths, and temperature conditions had effectively the same reverse sigmoidal shape after fitted location time adjustment. The slight differences in signal attenuation could be due to errors in normalization and location adjustments between experiments, differences in tubing internal roughness, and analyzer noise." section 4.5

Text

L.104 "fast" and "slow" analyser suggests you used multiple, which I understand was not the case. Also, it would help the reader to explicitly state whether the flowrate through the tested tubing changed (I understand it didn't) under both analyser regimes. Lastly, why multiple flow speeds through the analyser and not only maximal instrument flow? Increasing instrument attenuation complicates your setup not helping to answer your research question.

Valid point, corrected in new experiments

L. 108 Indicate in this section if any calibrations were performed and if not, why. This should also clarify whether the isotopic compositions you mention are raw analyser outputs or independent compositions.

Corrected in Sect. 2.3.

L. 124 If possible, indicate a range instead of the "approximately" as the consistency of the 100 foot length seems essential for your tests! E.g. +/- 10 foot or 0.1 foot?

Now listed in Supplementary Table S1

L. 134 Clarify how the temperature was measured and guaranteed? In case 60C was the maximum heating temperature of the self-regulating heating tape, real temperatures could have been much lower (often a linear wattage decrease with no heat emitted at 60C, and hardly any at 50C. Given a heat loss through the insulation, a $W_{in} = W_{out}$ at 40C might also have been realistic).

The thermocouple probe was placed inside the insulation on the side of the tubing opposite of the heat tape, ~3 inches (~7.6 cm) from the end closest to the analyzer inlet. Differences in the insulation properties of the two materials used and likely differences in thermocouple placement relative to unavoidable gradients in temperature resulted in differences in average temperatures for each experiment, ranging from 48.6 to 75.2 °C. Specific temperatures are listed in Table S1. More precise control of temperature was not possible with the equipment in our lab. Even so, we believe the results are useful in testing performance and are likely similar to common field inlet installations.

L. 138 You mention multiple errors for the 1.1L/min flowrate. Is it 0.15, 0.45, or the combination? Relatively, errors seem large given your dependence on a consistent setup.

Omega is no longer used to determine flow rates. We instead use the Bios Definer 220.

L. 148 Explain why the filter was needed. The dry air source and dryrite are likely already filtered, and standards used were likely demineralized. It seems like an extra uncertainty that is not evidently needed.

It was a standard part of field inlet setups out of an abundance of caution and we wanted to represent that. It's removed in the new setup.

L. 209 Be more explicit about the nature of this breakpoint analysis. Is it the time from switch to any "new isotopic signal" hitting the analyser?

Yes- noted now in methods

L. 248 The contents of this paragraph are near identical to the contents of the paragraph before it in another wording, consider merging both.

We have separated results into visual and memory metric sections to prevent repetition of results.

L. 323 The “shape” of the attenuation curve was not expected to differ, but the attenuation time is expected to differ. Remove “shape” in the text to prevent this confusion for the reader.

We have kept in most mentions of “shape” of the attenuation curve to highlight that while the shape is similar, the exact coordinates of the attenuation curve and hence the attenuation times differ.

L. 327 If instrument influence is “likely” much larger than the tubing, the paper loses its merit, and the conclusions can’t be made. If this is indeed a real concern this discussion point should be expanded, or experiments should be repeated.

Experiments were repeated at faster flow rate

L. 350 Unclear argument. Was the flowrate adjusted in the “with omega / without omega” experiment in the appendix? It seems like it was, making it odd to say the omega was the cause of the attenuation, and not increased analyser flow.

This is corrected in the new experiments.

L. 355 The arguments presented for MFM attenuation suggest that material type and additional volume are key, seemingly contradicting the presented conclusions stating that neither tube length (i.e. volume) nor material type impact attenuation. Please attempt to reconcile why this could be.

It could be a different material not tested. For example, the new Bev-A-Line tubing tested has a very large influence on memory. But the omega is removed in the new experiments.

L. 369 Mention this residence (or turnover) time in the methods together with your instrument and flow details. Also, the 8-12 seconds seems to be based on the 0.2-0.3 flowrates while 0.1L/min was used for most tests.

This has been added.

“This air flow rate led to an analyzer residence time of 3.97 s. Temperature adjusted tubing mean residence times were 1.0 ± 0.09 s for short thick-walled FEP, 19.7 ± 1.6 s for long thick-walled tubing, and 45.2 ± 2.5 s for long thin-walled tubing.” Section 2.2

L. 370 Unclear sentence. Define "this" (2x). you seem to suggest in-line elements impact the analyzers turnover time, but the analyser regulates its own inlet speed, correct?

Removed tests on in-line elements. The analyzer does regulate its own inlet speed. The MFM was influencing the isotopic attenuation time (or memory effect).

L. 388 It is not entirely clear how you defined your lag time using the breakpoints. The unexplained lag time is similar to the order of magnitude of the sample cell residence time I found for 0.1l/min flow (25s).

We have included a clearer explanation of how breakpoint analysis is conducted by looking for a change in slope of the curve (Sect. 2.4.1). A section comparing lag, temperature adjusted mean residence time, and new location times extracted from an impulse response analysis has also been included (Sect. 3.1).

L. 445 The recommendation to use short inlet tubing seems to contradict your own findings that inlet tube length does not matter for isotope attenuation times. Clarify that recommendation if you chose to keep it.

We have clarified recommendations based on the results of our new experiments.

L. 475 Your experiment with reduced tube ID effectively increased the air flow rate in the test tube and you found no difference in attenuation whatsoever. Stating in your conclusion that "higher air flow rates will minimize the memory effect" seems opposed to this. Please explain this better earlier in your text or adjust the sentence.

We have clarified recommendations based on results and other previous work. It is clear that the higher flow through the analyzer is important.

L. 482 To keep the conclusion short, remove "While differences..." as this sentence has no different message than the sentence before.

We have removed repetition.

Community comments

Review of the manuscript entitled "Water vapor stable isotope memory effects of common tubing materials"

This article compares the memory effect lag times associated with laser-based water isotopic measurements for different tubing materials and dimensions and will be very useful for people involved in laser-based water isotopic measurements. Since water isotopes in vapor are a common measurement in atmospheric sciences, and dealing with the memory effect is a major analytical challenge, this manuscript is suited for the scope of the journal.

My general impression is that this is a good paper with important conclusions. Flow rate is more important than material being used and that the optical cavity of the system which generally cannot be modified is the largest contributor of the memory effect. This is crucial information.

Major comments

I would add more literature describing analytical methods used to reduce memory effect other than Vallet-Coulomb et al. 2021 such as (Guidotti et al., 2013; Schauer et al., 2016; Pierchala et al., 2019; Qu et al., 2020; de Graaf et al., 2020; Hachgenei et al., 2022)

Edited to include de Graaf and Hachgenei. This is just an example list and not meant to be an exhaustive list of studies on reducing memory influence in liquid water injection systems.

The use of feet and inches is confusing. I would remain with the metric system.

Edited to include both imperial and metric units.

Figure 3 shows that heated tubing has longer attenuation times (effectively similar within measurement error but still slightly longer). This should be addressed. It is counterintuitive – I would expect higher temperature to decrease the attenuation time. I would also suggest trying an even warmer temperature like 90 degrees.

Obtaining the equipment to do higher temperature experiments was outside the scope of this project. Heating the tubing decreased lag, residence, and location times. We also thought that higher temperatures would decrease the memory times. The new experiments now show residence time adjusted attenuation times are similar or shorter in the heated tubing, in general. "When adjusted for location, heated experiments often appear to have a less steep δD slope and intercept the $t_{63\%}$ metric later than unheated experiments. We see this specifically in the δD signal for all tubings in the enriched-to-depleted direction with the exception of long thin-walled FEP, and for copper and HDPE in the depleted-to-enriched direction. Location adjusted attenuation curve slopes for $\delta^{18}O$ intercept the $t_{63\%}$ metric later and are shallower for the heated experiments for PFA in the enriched-to-depleted direction and PTFE and copper in the depleted-to-enriched direction (Fig. 3 and S3)." The old experiments didn't have the resolution

needed to see these slight changes in attenuation times. We attempt to address this in Sect. 3 and 4.

Minor comments

Line 60-61: the authors cite references claiming air flow rates and temperatures affect attenuation times, yet their results do not replicate this. I think this should be discussed

In the previous experiments, the analyzer memory was sufficiently large to limit the resolution of tubing differences. We repeated the experiments using faster flow through the analyzer and slower flow through the tubing and found slight effects of temperature and effective flow velocities. See revised Section 3.

Line 80: This definition is not accurate. The physical reason for the ME is that water molecules adsorb onto surfaces due to hydrogen bonding, which is a well-known phenomenon in vacuum technology. Replacing ordinary hydrogen with deuterium increases binding energy and, consequently, also the residence time of deuterated water molecules on internal surfaces of vacuum systems. This is why the memory effect is stronger for δD compared to $\delta^{18}O$ as stated in line 81. The delay in the speed at which the isotopologues move through the tubing" is relevant only for diffusive transport, not for air flow.

Thank you for pointing this out- we have changed the wording.

Line 120: can delete "following Rayleigh fractionation".

We have removed this phrase.

Line 134: Specify how the temperature was measured and guaranteed. If this is the temperature of the heating tape the real temperature could have been much lower within the tubing. Especially for different flow speeds. I am concerned the fast flow rate experiment was at a lower temperature than the slow flow rate.

All flow rates through the tubing were the same. Flow should not bias tubing temperature. Different insulations do bias tubing temperature though and some of this variability is noted in the supplementary table S1 and text.

"Differences in the insulation properties of the two materials used and likely differences in thermocouple placement relative to unavoidable gradients in temperature resulted in differences in average temperatures for each experiment, ranging from 48.6 to 75.2 °C (Table S1). All heated

experiments (average 60 ± 8 °C) are significantly warmer than ambient temperature experiments (average 24 ± 1 °C). "

Line 161: why normalize? I think there should also be comparisons for different isotopic values

We normalize to compare across experiments and avoid the need to adjust for source water and analyzer drift over time. The isotopic differences between experiments were

155.43 ± 3.43 ‰ (~2.2% variance) δD , 19.839 ± 0.463 ‰ (~2.3 % variance) $\delta^{18}O$, and 4.04 ± 3.610 ‰ (~89% variance) D-excess.

Line 248- 260: This paragraph can be significantly shortened to be more comprehensible. For instance L251: "the measured $t_{95\%}$ values for $\delta^{18}O$ range from 33–34 seconds, with uncertainties ranging from 32–36 seconds" can be shortened to "the measured $t_{95\%}$ values for $\delta^{18}O$ are $33-34 \pm 2$ seconds"

We use this presentation in the new manuscript.

L255: either "from... to" or "between... and". Don't use "from... and"

Adjusted when describing ranges of values.

L260: Why is a second attenuation metric for judging D-excess not appropriate? This sentence is unclear.

The second attenuation time (similar to that of $\delta^{18}O$ and δD) for D-excess is not appropriate as the shape of the attenuation curve is not a unidirectional transition. We chose a time to achieve within 3 per mil based on common analyzer precision metrics. We note this more clearly in Sect. 2.4.1.

L327: Why does this disprove that the analyzer optical cavity and internal plumbing which are likely much larger than tubing effects is the dominant factor being more significant than tubing type and dimensions?

We agree with the reviewer's concerns and repeated the experiments.

L329: "the exchange rate of water molecules from the vapor to the inner tubing surface can be considered a first-order kinetic reaction". Also the exchange rate of water molecules from the

vapor to the analyzer cavity and internal plumbing. In this case the internal cavity is much warmer than the tubing and may have different rate of water adsorption/desorption.

This is a true statement. However, we have removed references to reaction kinetics in this round of the manuscript.

L445: If the tubing length is not an issue according to your findings why is the recommendation to use short inlet tubing logical? It seems to contradict your findings that inlet tube length does not matter for isotope attenuation times. This should be clarified.

We have clarified recommendations based on new results and other previous work.

L495: The given link to figure data, scripts and workup code doesn't work

Fixed

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