Hydrology and Earth System Sciences Discussions

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Interactive comment on "Technical Note: On the memory effects in the analysis of δ^2H and δ^{18}O water samples measured by different laser spectroscopes" *by* D. Penna et al.

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We thank the anonymous referee for her/his comments, which helped to clarify some points and improve the revised version of the paper. The reviewer's comments are quoted above the authors responses.

General Comments: "This paper investigates the memory effects commonly observed with laser spectroscopic isotope ratio measurements of depleted liquid water samples. A sequence of ten depleted snow water samples and several reference standards is analyzed using eighteen injections for each water. This is done for two CRDS and

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OA-ICOS instruments, respectively, with an IRMS serving as reference. Conclusions are then drawn regarding the magnitude of memory effects encountered as a function of the number of repetitive injections of individual waters and the isotopic separation of successive waters. The title of the manuscript is somewhat misleading in my opinion as it may imply a broader and more in-depth investigation of memory effects in laser spectroscopic isotope ratio measurements while the focus of the paper is quite narrow. The paper is generally well written and technically sound. The employed statistical and experimental techniques are not particularly innovative yet overall adequate and presented clearly. There is a need for systematic investigations of and guidance on the practical problems encountered in the field of laser spectrometric isotope ratio measurements. As such, the scope of the paper is commendable and a practical contribution to the field is made. A few shortccomings exist that should have been avoided to make the paper relevant to more users of laser spectrometers. Most of all, this refers to the use of older generation laser spectrometers only and a lack of directly transferable solutions."

We thank the reviewer for underlining our effort to give a practical contribution to the knowledge of the relatively new laser spectroscopy technology. The aim of the Technical Note was intentionally specific and focused on the most common situations that lead to the occurrence of memory effects and on some simple, practical laboratory procedures to prevent such effects. We accept the suggestion given by the referee about the potentially misleading title and changed it into "Evaluation of between-sample memory effects in the analysis of d2H and d18O of water samples measured by laser spectroscopes." As for the use of older generation spectrometers and the lack of directly transferable solutions, please, refer to responses given to specific comment #1 and #6.

Specific comments: 1. "P5299, L7-17: As noted by the other reviewers, testing of current generation laser spectrometers would have been important for the practical relevance of the paper. Also, given some variations between instruments and set ups,

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testing of several laser spectrometers of the same type could have been worthwhile. This could have helped to provide more reliable and transferable conclusions. Other users will likely need to conduct a similar analysis to the one presented in this work to derive suitable procedures for their labs (as suggested by the authors on P5306, L11-12)."

As replied to the first reviewer, we absolutely agree on this point. Therefore, we looked for owners of more recent instruments and were able to include two new generation spectroscopes in our test. These instruments comprise of a third generation Los Gatos Research 908-0008-3000 and a second generation Picarro L2130-i. We believe that the additional results that were obtained from the analysis of the updated machines greatly helped to improve the manuscript.

2. "P5300, L25-27: Why have they tried to minimize the isotopic differences between sub-sequent samples? A broader range of isotopic differences could have been interesting."

This sentence indeed did not fully reflect our intention and we changed it as follows: "We took advantage of the wide isotopic range of the samples and measurement standards in designing the analysis sequence template presented in Table 2, where some adjacent vials were very close in isotopic composition, whereas others differed markedly. This allowed us to test the performance for a broad range of differences in isotopic compositions between adjacent vials (the lowest absolute difference between the heaviest and lightest water was approximately 2 ‰ for d2H and 1 ‰ for d18O, whereas the highest absolute difference between the isotopically heavier and lighter water was approximately 201 ‰ for d2H and 25 ‰ for d18O (Table 2)."

3. "P5302, L7 et seq.: Rather than analyzing selected individual results, I believe it would be more informative to present more holistic plots or tables indicating the expected magnitude of memory effects and standard deviations as a function of the inter-vial range and of the part of injections considered. This could serve as a basis for

practical decisions when the maximum inter-vial isotopic difference can be anticipated. Such basis is not provided when only results for some extreme cases are provided."

In this short paper we want to give evidence to the occurrence of memory effects when analysing samples that are characterized by markedly different isotopic compositions and, at the same time, to suggest simple practical procedure to assess such effects and to mitigate or prevent them. Given the number of six tested machines, the different measurement technologies involved (OA-ICOS vs. CRDS) and their different stage of technological development (first, second or third generation instruments), resulting in different tendencies to memory effects, it would have been difficult and in a sense potentially misleading to provide holistic information on the expected magnitude of memory effects as a function of the various variables considered. In fact, this would lead to averaging results and inevitably to mask and smooth out the inter-machine variability. On the contrary, we believe that showing a few, representative cases can better inform the reader about the possible occurrence/not occurrence of memory effects and the potential performance of each instrument regarding this issue.

4. "P5303, LL20: Given the sequence of samples chosen, have the authors observed a dependency of memory effects on the direction of the gradient of isotope ratios of subsequent sample waters? That is, are the same memory effects observed for positive and negative isotopic differences of subsequent sample?"

During the data processing we also analyzed the occurrence of memory effects when moving from a very depleted (very negative) to a significantly more enriched (less negative) sample and vice versa but we haven't noticed any appreciable difference. We added a sentence dealing with this question in section 3.1.

5. "P5303, L25-27: I agree with reviewer#2 in that an evaluation of memory effects as a function of analysis time would be more meaningful in terms of instrument performance and could be included. However, from a standard user point of view the evaluation as a function of number of injections is still relevant."

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Yes, we think that the analysis of ME as a function of number of injection is important from a practical perspective. However, as mentioned in detail in the response to comment 5 by referee #1, we also extended the discussion on the role of analysis time on ME in the revised version of the manuscript.

6. "P5306, L1-14: Although some useful arguments are made, the recommendations provided in this paragraph partially lack decidedness reflecting a lack of direct transferability of results. Particularly given the narrow scope of this technical work more definitive guidance should be offered. For example, the authors could have applied the cited post-analysis correction calculations."

As mentioned in the response to comment #11 of the first referee, we completely rewrote this part, in order to present simple but effective practical solutions that might be easily adopted by other users of laser spectroscopy. These suggestions encompass a list of single or possibly integrated operations that can help to avoid the occurrence of ME or to reduce the ME influence on the final reportable delta values. We also suggested, as one of last possible solution, to follow some post-analysis correction procedures reported in the literature. However, we have not applied them to our dataset evaluating their effectiveness since we believe that this is beyond the scope of this Technical Note.

7. "P5305, L3-5: The acronyms are already defined on P5298."

This issue was corrected in the manuscript.

8. "Figure 4: In the figure caption and on P5304, L8-9, it is stated that results are shown for two samples and one standard. This is in disagreement with the legend."

Yes, that was a mistake. We corrected it.

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