Hydrology and Earth System Sciences Discussions

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.

Anonymous Referee #1

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Comments on Technical Note: On the memory effects in the analysis of d2H and 18O water samples measured by different laser spectroscopes

This technical paper takes a closer look at the well-known inter-sample memory effects inherent in the isotopic analysis of liquid water samples by laser spectroscopy, which users have seen expressed as higher variance for samples that have exceptionally low deuterium contents (e.g. glacial ice, high latitude snow samples). The authors used early generation instruments from two primary suppliers in order to test what users may encounter using off-the-shelf to laser spectroscopy regarding inter-sample

memory effects. The experimental tests were appropriately designed and overall the paper is well written.

Specific Comments:

Page 5299 Section 2.1. I think the authors should point out that laser spectroscopy for water isotope analyses is still a rapidly evolving analytical and technological field, compared to IRMS. Hence the findings of this work are, in part, addressing a moving instrumental target. For example, all of the instruments used in this paper are currently obsolete. LGR now sells its 3rd OA-ICOS generation instrument, and Picarro sells its second generation series instrument. Both companies claim improvements in the area of memory and throughput.

Page 5299 Line 10 – Can the authors explicitly indicate which generation each of the LGR instruments are? (Generation 1 or 2) I note it's mentioned later as the "upgraded model" (faster pumping), but is that a second generation?

Page 5299 Line 15 – ditto above – Picarro 1st generation?

Methods – authors do not mention the volume of water per injection used for each instrument –please add.

Page 5299 Line 23 – It's not clear if authors mean instrumental (internal) precision of the Delta Plus itself, or the precision of the gas bench for water equilibration assays. It is not even mentioned if the Delta Plus analysis was done by classical dual- inlet analysis or by continuous flow methods (e.g. Gasbench). Please clarify. In either case, the 1 sigma precisions for d2H seem overly optimistic for external precision.

Page 5303 Lines 10-15 – Authors need to explain this section more clearly other than by "slow" or "fast" analyses based on time. For example, it seems to me one should discuss also the amount of water per unit surface area of the laser cavity (heated or un- heated) and pump-out rate. The heated Picarro laser chamber is only 35 ml in volume, yet the LGR chamber is about 500 ml (?) and unheated, at least in first two generation

instruments. The transfer line on the Picarro is hot, but not on the LGR. Intuitively, one would assume that a larger unheated chamber would have a much higher memory effect, yet that is not what is seen, proportionately. Any other explanation? Based on these conditions one would expect the Picarro to have far less of a memory effect.

Table 3 (strongly consider combining 3a and 3b into a single Table) – or deleting them altogether – the text is good enough.

Figure 1, 2 – x-axis should be "# of injections per sample"

Figure 4 – This figure is a bit confusing for the reader at first glance, and looking at the caption. I had to look at it for a while to "get it". Authors may need to more clearly specify that it's the average number of the "last" injections. For example, on the x-axis 18 means 18/18 injections were averaged, and 4 means the final 4/18 injections averaged. It would also be useful to draw a horizontal line showing an acceptable precision (SD) – possibly +/- 1.5 permil for d2H and +/- 0.2 permil for d18O. This will enable the quickly reader to see at what point the memory inflections affect outcomes beyond what are considered acceptable precisions.

Page 5304 Line 25 (referring to Fig 4). "The range of SD values was generally lower for CRDS…" This statement can be taken the wrong way by a reader – especially since that statement is only true when 16 or more out of 18 are averaged (e.g. rejecting only the first 2 injections or less). I do not see any difference in the SDs between the CRDS or OAICOS when one rejects 4 or more of the first injections.

Page 5305 (Conclusions) Consider merging conclusion 2 and 4 into a single bullet. Also consider reporting the range of SDs when the first 4-6 injections are ignored – I know of no labs that would not average all analyses without rejecting the first 3-6 (!!) , nor is that even recommended in the manufacturers literature! So it seems a curious statement to make.

The final concluding paragraph (the most useful outcome of the paper) falls quite a

bit short of offering clear recommendations and so needs to be completely re-written. Last paragraph appeared to be hastily written compared to the rest of the paper. The authors mention 3 solutions: avoid, reduce and mitigate. Please give clear usable examples of each of these solutions, using one per paragraph. For example, "avoid" might be to run samples with 8 injections, and reject the first 5 injections. Give some useful examples of analysis templates that would overcome the memory problems.

Currently, the numbering of points in the previous paragraph draws far more attention to the problems observed than to the proposed solutions.

Running header: "…d2H and d18O of water samples."

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