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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.

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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 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: 1. "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.."

We agree on this issue and we thank the reviewer for pointing this out. However, as most isotope laboratories are still relying on earlier generation instruments, we believe that assessing also older generation instruments is an important part of this paper. In order to expand our comparative test with updated laser spectroscopes, we tested two new additional instruments, currently on the market (third generation Los Gatos Research 908-0008-3000 and second generation Picarro L2130-i) and added the results to the revised version of the manuscript. We modified Section 2.1 as follows: "The water samples were analyzed by six laser spectroscopes (three OA-ICOS: Delft University of Technology, the Netherlands, Czech Technical University in Prague and Czech Geological Survey, Czech Republic; three CRDS instruments: University of Trieste, Italy, University of Zürich, Switzerland, International Atomic Energy Agency, Vienna, Austria) and one mass spectrometer (University of Trieste), used as reference. Due to the rapid evolution of laser spectroscopy technology, we tested early and new generation instruments. The spectroscopes included: a) OA-ICOS: one Liquid Water Isotope Analyser, model DLT-100 version 908-0008 (first generation), one version 908-0008-2000 (second generation) and one version 908-0008-3000 (third generation), manufactured by Los Gatos Research Inc. (LGR, Mountain View, California, USA). These instruments

HESSD

9, C4053–C4063, 2012

are referred to as “LGR-1”, “LGR-2” and “LGR-3”, respectively. The volume of water for each injection was 750 nL. According to the manufacturer’s specifications (Los Gatos Research, Inc., 2008), the 1-sigma measurement precision was below 0.6 ‰ for d2H and 0.1 ‰ for d18O. b) CRDS: two Picarro L1102-i liquid analysers (first generation) and one L2130-i (second generation), manufactured by Picarro (Picarro, Mountain View, California, USA), named “PIC-1”, “PIC-2” (first generation) and “PIC-3” (second generation). The volume of water for each injection was 2 microL. The manufacturer reported the 1-sigma measurement precision below 0.5 ‰ for d2H and 0.1 ‰ for d18O (Picarro, Inc., 2008).”

2. “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?”

As mentioned in our response to comment #1, in this revised test we analyzed samples run with three LGR instruments (first, second and third generation spectroscopes named LGR-1, LGR-2 and LGR-3, respectively) and with three Picarro instruments, two of first generation (PIC-1 and PIC-2) and one just released second generation (PIC-3).

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

We used the default injection volume recommended by manufacturers, which is 750 nL for LGR instruments and 2 microL for Picarro instruments. We added this piece of information to the manuscript (Section 2.2).

4. “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,

HESSD

9, C4053–C4063, 2012

the 1 sigma precisions for d2H seem overly optimistic for external precision."

It's the external precision. All the internal standard prepared by the IRMS lab in Trieste are periodically calibrated against IAEA international standards and the lab participates at each IAEA inter-comparison exercises (the last one was WICO 2011). The Delta Plus analysis was done with the classical dual-inlet system. The CO2/H2 water equilibration was carried out using an on-line HDO equilibration device as specified in the text. We specified this in the revised version of the manuscript.

5. "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."

The results derived from the analyses of the most recent spectroscopes for both manufacturers provided new insight on the occurrence of memory effects (MEs). In addition to updating Fig. 2, we also added a new table (Table 3a, b) and expanded the discussion in the text. Particularly, the updated dataset revealed that a clear dependency of ME on analysis time did not occur. For instance, the third generation instrument (LGR-3) needed only 83 seconds to perform a measurement compared to 140 seconds of the second generation instrument (LGR-2) and to 245 seconds of the first generation instrument (LGR-1), but only the last one showed the lowest amount of ME. We agree with the referee about the presence of other potential influencing factors, such as the length of the transfer line, the heating of the transfer line and of the cavity, the amount of water per unit surface area of the laser cavity, the injection speed, the pump-out

HESSD

9, C4053–C4063, 2012

rate. We mentioned all these factors in the revised version of the manuscript but a detailed analysis on their potential role on the occurrence of ME would be very difficult to decipher and would be out of the scope of this short Technical Note. To account for the reviewers suggestions we extended and modified section 3.1 as follows: “Figure 2 shows the ME for the transition between STD1 and STD3 (third triplet in the run), the situation when the highest isotopic difference between adjacent vials occurred. The ME was greater for hydrogen than for oxygen, as observed elsewhere (Gupta et al., 2009). For OA-ICOS instruments the maximum ME ranged approximately from 6 % to 14 % for d2H measurements and from 4 % to 9 % for d18O measurements. For CRDS instruments the maximum ME ranged approximately from 4 % to 6 % and from 2 % to 4 % for d2H and d18O, respectively. The analysis revealed that the first eight-ten injections were most affected by MEs for all instruments, whereas the final six-eight injections exhibited negligible MEs. This was confirmed by observing the average and standard deviation of ME computed separately for the first ten and the last eight injections (Table 3a, b). The dataset in this Table was formed by the 18 injections performed during each of the three transitions in an analysis run (considered together) between STD1 and STD3. Analysis of Table 3a, b clearly confirmed, for both isotopes and for all spectroscopes, the smaller MEs for the last eight injections out of 18 compared to the first ten injections. Overall, the average and the standard deviation of MEs ranged between 0.8 % and 3.0 % and between 0.8 % and 3.9 %, respectively, when considering the first ten injections. However, average values ranged from 0.1 % to 0.3 % for both hydrogen and oxygen isotope species and standard deviation values ranged from 0.1 % to 0.6 % when the last eight injections were considered. This suggests that, even for very high differences in isotopic composition of subsequent samples, discarding the first ten injections and averaging the remaining ones prevents the final delta value from being affected by MEs. Furthermore, Table 3a, b reveals that, on average, ME values were similar for both OA-ICOS and CRDS instruments, the only appreciable difference being the higher percentages of OA-ICOS spectroscopes for the first two or three injections (Fig. 2). It was worth noticing that ME values were, on average, slightly lower

HESSD

9, C4053–C4063, 2012

for the most recent spectroscope models, compared to early ones. Improvement in the reduction of MEs, reflected also in lower standard deviations of ME, was particularly evident in third generation OA-ICOS instruments (LGR-3), for which discarding six injections would provide an effective solution. Conversely, LGR-2 showed the highest percentage of ME (Fig. 2 and Table 3a, b), even higher than the first generation machine (LGR-1). This difference did not seem to be related to any specific variable, since all machines were routinely cleaned and maintained and the sampling conditions were the same for all instruments. An intrinsic variability for one specific instrument could be assumed, but further analyses are necessary to verify such behaviour. Theoretically, the difference in MEs between OA-ICOS and CRDS devices (Fig. 2) or the different amount of ME between instruments of various generations (Table 3a, b, especially for LGR machines), might be related to the different analysis time for each injected water sample. In fact, long analysis times (including longer between-sample cavity vacuum pumping) could facilitate the removal of water molecules of the previous sample from the system. Conversely, short analysis times could allow for the persistence of residual water molecules in the laser chamber. However, based on our analyses, a dependency on analysis time was not found. In general LGR-1 (first generation) took 245 seconds to inject and measure a sample, LGR-2 (second generation) took 140 seconds and LGR-3 (third generation) took only 83 seconds. Nevertheless, the highest values of ME were not observed for the "slowest" first generation machine, as might have been expected, and the "fastest" third generation spectroscope was not the one most affected by MEs (on the contrary, it had the lowest ME). Furthermore, CRDS lasers, that on average showed similar values of ME compared to OA-ICOS instruments, took 540 seconds (9 minutes) to perform a measurement, being more than two times, almost four times and more than six times slower than LGR-1, LGR-2 and LGR-3, respectively. Therefore, other influencing factors must explain the differences in ME between the three OA-ICOS generations and for the initial injections between the two technologies. For instance, the length of the transfer line (the longer the line, the higher are supposed the MEs), the heating of the transfer line and of the cavity (higher temperature helps

HESSD

9, C4053–C4063, 2012

the sample vaporization and likely reduces MEs), the amount of water per unit surface area of the laser cavity, the injection speed (the rate at which the water is injected into the instrument), the pump-out rate, the syringe deterioration, the variations in vaporizer temperature might all play some role in MEs. We do not have the appropriate technical insights and means to fully assess these aspects without involving the manufacturers, which is beyond the scope of this Technical Note."

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

We agree with the reviewer's suggestion and deleted the tables. In the revised version of the manuscript Table 3a and b were replaced with new tables showing the new results presented in section 3.1.

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

Yes, we agree with the reviewer's remark. In order to avoid confusion between "sample" and "standard" we insert this x-axis label: "number of injections per vial".

8. "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."

We thank the reviewer for this helpful remark and agree that the figure might be hard to understand. Therefore, we modified the figure as indicated by changing the x-axis label into "number of last averaged injections (out of 18)" and adding a horizontal line representing an acceptable precision (1 ‰ for hydrogen, 0.1‰ for oxygen). Moreover,

HESSD

9, C4053–C4063, 2012

the Figure was split in two Figures (a and b) to accommodate the two new instruments tested. The figure caption was significantly changed, as follows: “Figure 4a. Standard deviation for d2H for two laboratory measurement standards and one sample as a function of number of averaged injections. 18/18 indicates that all 18 injections of the same vial (either standard or sample) were averaged, whereas 17/18, 16/18, 15/18... indicates that only the last 17, 16, 15... injections were averaged (and the remaining discarded). The dotted horizontal line indicates currently acceptable reference precision for d2H (1 ‰. The legend depicts the difference between the isotopic composition of the standard/sample displayed and the isotopic composition of the previous vial analysed in the tray.” The same holds for Figure 4b.

9. “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.”

Yes we agree, the sentence was removed in the revised manuscript, also new comments were added covering the two new instruments included in the test.

10. “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.”

Due to the new results added to the manuscript, conclusion 2 was too long to be merged with conclusion 4, so we left them separated. Point 2 was modified as follows: “Overall, the maximum ME ranged from 4 % to 14 % for d2H and from 2 % to 9 % for d18O measurements. The first ten injections out of the 18 were most affected by ME, with average MEs ranging between 1.1 % and 3.0 % for hydrogen and between 0.8 %

HESSD

9, C4053–C4063, 2012

and 2.4 % for oxygen. However, when discarding the first ten injections and considering only the last eight, MEs were negligible for all instruments (average ME ranged between 0.1 % and 0.3 % for both hydrogen and oxygen). On average, ME values were similar for both OA-ICOS and CRDS instruments, with a significant improvement in the reduction of ME for the most recent generation of spectroscopes (especially OA-ICOS)."

We agree and thank the referee for the suggestion to report the range of standard deviations when the first injections are discarded. We changed point 4 accordingly, as follows: "Standard deviations for the final reported value were unsatisfactorily high (up to 7.5 ‰ for d2H and 0.54 ‰ for d18O measurements for extreme cases) when the all measurement injections were used, including those affected by ME. However, for samples characterized by only small isotopic differences with respect to the previous vial in the tray or when rejecting the first six or eight injections, a marked precision increase was noted, with standard deviations in the range of 0.1 ‰1.0 ‰ for d2H and 0.05 ‰0.17 ‰ for d18O."

11. "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.

We thank the reviewer for this suggestion that significantly helped to improve the manuscript. We made efforts to give the reader some short but clear practical indications that could be helpful for other users of laser spectroscopy. We completely rewrote this section, changing the text as follows: "In this test we assessed the MEs of differ-

HESSD

9, C4053–C4063, 2012

ent laser spectroscopy instruments under standard operating conditions. Specifically, we quantified the MEs and assessed the impact of MEs on measurement precision. Given the practical perspective of this Technical Note and our experience as users of laser spectroscopes for hydrological and environmental applications, we can outline some operational solutions (a-c in the list below) or post-processing data analysis (d-e) that might be adopted by other users of laser spectroscopy in order to avoid the occurrence of MEs or to reduce their influence on the final reportable d values. Most of these suggestions consist of practical and basic laboratory procedures and, as such, they do not claim to eliminate the problems derived by the influence of ME. However, given a simple application, these approaches can be easily followed by users of laser spectroscopy.

a) Samples for laser spectroscopy analysis should ordered or grouped in order of isotopic compositions, as this can often be estimated ahead of time, with the aim to analyse samples with similar isotopic ratios in the same analysis run. Furthermore, if possible, laboratory measurement standards should closely bracket the expected range of sample isotopic composition. Additionally, ordering samples according to expected increasing or decreasing isotopic ratios might help to avoid high differences between adjacent unknown sample vials. b) If samples are truly unknown, group them according to the same water source, sampling location and region of origin. However, keep in mind that, even at the small spatial scale, different water sources (e.g., liquid precipitation, solid precipitation, surface waters, groundwater, soil water etc.) might have significantly different isotopic ratios. Moreover, some physical processes such as seasonal effects and altitudinal effects might result in markedly different isotopic compositions of the same water sources. c) If a broad range of isotopic composition of unknown samples is suspected, a preliminary run with a wide range of reference standards (very depleted and very enriched) could be carried out. This would allow to analyse samples exhibiting very high differences in isotopic ratios separately. The disadvantage of this approach is additional screening time and analysis cost. d) It is often advisable to adopt an analysis scheme (e.g. the one suggested in IAEA, 2009b

HESSD

9, C4053–C4063, 2012

or similar) so that six or nine injections are performed and the first two or four are discarded. However, as demonstrated and reported elsewhere (GrÓğning, 2011), there are cases when rejecting two or three injections might be insufficient to eliminate ME. Thus, as a quick and preliminary assessment of possible occurrence of ME, check for increasing or decreasing variations (according to the value of the previous sample) in d values of subsequent samples that exceed the typical instrumental precision by two or more times. If necessary, run a few samples and apply the procedure presented here in order to decide a proper number of injections to perform and a threshold number of injections to reject. e) If it is not possible to employ the solutions listed above, post-analysis memory correction calculations, as the ones reported in Gupta et al. (2009) and GrÓğning (2011), can be applied."

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

Thanks, corrected!

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