



Interactive comment on “Technical Note: On the memory effects in the analysis of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ water samples measured by different laser spectrometers” by D. Penna et al.

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We thank Dr. Baer for participating in the open discussion and for sharing his comments, which helped to clarify some points and to improve the revised version of the paper. Dr. Baer's comments are quoted above the authors responses.

General Comments: “The memory effects on laser-based instruments to measure 2H and 18O are well known. As the authors note, both instrument manufacturers recommend ignoring the first few injections to alleviate memory effects. For example, the standard LGR procedure for analyzing samples with as wide a range of isotopic ra-

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tios as has been analyzed in the present paper would involve injecting the unknown water sample repeatedly for 10 times, discarding the first 6 injections, and averaging the values obtained in the last 4 injections. As the authors note, this procedure essentially eliminates any memory effect in the sample measurement. It is also important to note, as the authors have, that since the instruments from the different manufacturers have different injection rates, the memory effects also vary with the respective injection timing.”

Specific comments: 1. “Specifically, the following plot recasts the data presented from Figure 1 (2H of Std 3) so that the variation of 2H is a function of total measurement time (not number of injections) using the analysis times stated in the manuscript. This plot shows that the entire analysis has been completed on some instruments before the memory has been eliminated on other instruments primarily due to the differences in the measurement rates.”

The updated Fig. 2, that now includes results from the latest version of both OA-ICOS and CRDS instruments, shows that even for extreme differences in isotopic composition of subsequent samples, discarding the first few (approximately eight-ten) injections reduces the amount of memory effect to negligible values for both types of devices. Particularly, a clear improvement in the overall performance regarding memory effect is observable for the third generation instrument of LGR, for which discarding the only first 6 injections proved to be effective. These results were statistically confirmed by the new Table we inserted in the revised version of the manuscript (Table 3a, b).

2. “In addition, when memory effects are evaluated, it is important to consider all of the components in the sampling system. In particular, how was the memory of the syringes accounted for in this investigation? Were syringes with identical performance used on all instruments? In our testing at LGR, we have found significantly worse memory with gas-tight syringes, particularly in ^{18}O measurements, which is why LGR recommends zero-dead-volume syringes instead of gas-tight syringes.”

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Yes, we agree that a global view on the system should be considered when assessing the machine performance. In this context, we used, for all instruments, the syringes recommended by the manufacturers, that are zero-dead volume syringes. We specified this in the revised version of the manuscript (Section 2.1)

3. “An additional point of note: based on the data extracted from the manuscript, it appears as though the LGR instruments are exhibiting uncharacteristically large memory, with $1/e$ values greater than 1 injection – normally LGR instruments should exhibit values closer to 0.8 injections or less). We suspect that this could be due to the syringe and/or a dirty injection block. So, if the injection block was cleaned and/or syringe was changed, the observed memory on the LGR instruments could be even smaller.”

As reported in the Section 2.1 of the revised manuscript, we made sure the system was clean before running each analysis. Therefore, we cannot really explain the uncharacteristically large memory effect for instrument LGR-2 (version 908-0008-2000), which could be due to the intrinsic variability of the instrument itself (behaviour noted in our previous test, see Penna et al., 2010). Conversely, instrument LGR-3 (version 908-0008-3000) showed on average the lowest percentage of memory effects among the six tested machines (see Fig. 2 and Table 3a, b).

4. “Finally, as the first reviewer noted, the authors used a first-generation and second-generation LGR Liquid Water Isotope Analyzer in this investigation. LGR’s current models represent “third-generation” instruments that incorporate several improvements including redesigned injector (or evaporator), refined plumbing, faster pumping speed, faster measurement timing and comprehensive thermal control. The general result is significant improvement in speed, precision and overall performance compared with older models.”

As mentioned, we included in the revised analysis the most recent versions of both manufacturers. Given the specific aim of the paper, we did not evaluate the accuracy and the overall performance of these new machines. However we can confirm that,

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particularly for LGR instruments, according to our analyses, a general lower percentage of memory effect and a higher precision compared to earlier models was noticed.

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