

## ***Interactive comment on “Technical note: GUARD – An automated fluid sampler preventing sample alteration by contamination, evaporation and gas exchange, suitable for remote areas and harsh conditions” by Arno Hartmann et al.***

### **Anonymous Referee #1**

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The manuscript by Hartman et al. presents a newly-developed automatic fluid sampler (GUARD) that fills the samples into septa-sealed vials to avoid sample alteration due to gas exchange, phase changes, or contamination. The performance of the GUARD system was evaluated with three experiments. In the first experiment, the remaining air in all sample vials was quantified. The authors conclude that the remaining air comprised less than 2% of the total inner volume of the vials and might thus not alter the sample. In a second experiment in a karst cave, the authors compared manually and automatically collected drip water samples and find only minor effects on the  $\delta^{18}\text{O}$

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values of the samples collected with the two different methods. Lastly, the authors repeatedly measured  $\delta^{18}\text{O}$  in water samples in nine vials that were initially pierced by the injection needle. The data suggest that the septum of the sampling vials remains air tight over a period of up to six months. Finally, a case study is presented as a practical application of the GUARD system. Drip water from a karst cave was collected over a period of five days at 4h-resolution to measure  $\delta^{13}\text{C}$  in the liquid water samples. The manuscript finishes with a short interpretation of the case study results and a technical comparison of the GUARD system with another automatic water sampler (3700C Compact from Teledyne ISCO, USA), which is already on the market. The paper is written and organized in a clear way; the quality of the figures is good. I believe that this technical note might be of great interest for the readers of HESS, since an innovative, field-deployable automatic liquid sampling system is presented that potentially allows flexible operation due to low energy consumption and easy handling. Before publication, however, I'd like the authors to address some critical points, which I have outlined below.

General comments: Carry-over effects: The manuscript describes how the sample (12ml) remains in the sampling tube until it is injected into the vial (P3 L27-31). Due to the under-pressure in the tube, a new sample fills the tube when the previous sample leaves it. I'm wondering about the carry-over effects due to the temporary sample storage in the tube, which might be significant, e.g. for instance for streamwater sampling when precipitation events cause drastically changing solute concentrations compared to baseflow conditions. Can you elaborate on potential carry-over effects in the tubing and what could be done about it (e.g., flushing with air or sample water)? If the sampling aims at analyzing organic constituents, biofilm growth inside the tube might alter the sample, especially when the sample interval is long, e.g. several days? What could be done to prevent biofilm growth?

Fractionation effects during sample storage: During the third experiment you conclude that no alteration of the sample occurred because of the constant  $\delta^{18}\text{O}$  values (Fig.

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6). Do you get the same results when using d2H? Since your samples were analyzed with a LGR, both isotopes should be measured simultaneously.

Check-standard during long-term sampling: In the case study, the GUARD system was operating over a period of 5-days and  $\delta^{13}\text{C}$  was measured in the 22 drip water samples. How can you be sure that the  $\delta^{13}\text{C}$  values you have measured were not affected by the sampling process or the storage? In order to quantify drift effects or alterations due to sample processing, it would have been ideal to regularly sample a check-standard with known  $\delta^{13}\text{C}$  in addition to the drip water samples. I would recommend to at least address this issue in the interpretation section of the results.

Harsh conditions: You state that the GUARD system is applicable in harsh (outdoor) conditions (title, P1 L19), which should include a wide range of air temperatures. However, there is no analysis of potential evaporation effects of the samples in very warm (and dry) environments. Instead, during the only long-term experiment that focused on the gas-tightness of the sampling vials, the samples were stored in the fridge at  $8^\circ\text{C}$  (P6 L29). In a warm (and dry) environment, I would expect the evaporative fractionation effect to be detectable, especially if the sample sits in the sampling tube for a while before it is injected into the vials. Could you please elaborate on this?

Specific comments:

P6 L10 and Fig. 5: You describe that you have collected one drip sample per day over a period of 33 days, however, in Fig. 5 only 14 data points from the GUARD system are shown, and these are clearly not in daily intervals. Please correctly state the used sampling interval in the text.

P6 L21-26 and Fig. 5: Why don't you show the remaining data points in Fig. 5 to support your claim that the isotopic composition in drip water can vary strongly over short periods? In this context, I would suggest to also provide the standard deviation to the arithmetic mean value in L25. If the standard deviation is substantial (which you suggest with your statement in L21-23), your conclusion based on the arithmetic

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means would be invalid.

P6 L2-3: Why didn't you simply weight the vials before and after filling in order to quantify the sample volumes?

P7 L 27: Sampling for 5 days, every 4 hours would yield 30 samples, not 22. What happened to the remaining 8 samples?

Fig. 5: Why are the error bars different for some points? Please indicate in the figure caption, what the errors pars represent (measurement uncertainty?). You should also report d2H values in Fig. 5 since they are measured anyway.

Fig. 6: In greyscale, the shading of the data points is difficult to distinguish (green versus light blue). I would suggest a different way to present these data, especially since some data points overlap with each other and the error bars.

Tab. 2: The sample volume can be smaller than 12ml in the GUARD system.

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