Authors' response to short comment 1

Reader Comment:

Hartmann et al. present an automatic battery-operated sampler that takes water samples at pre-programmed time intervals and seals them to prevent atmospheric contact. The suggested method, i.e., the injection of water with a double-cannula into septum-sealed vials (arranged in an X-Y-grid), is rather elegant. Additionally, the number of vials (currently 48, but up to 160) is substantial. Hence, I share the authors' view that the presented device has great potential in hydrology, which warrants publication in HESS.

Nevertheless, there are a few minor points that I would like to mention:

The authors emphasize several times that available autosamplers do not seal collected samples (e.g., page 2, line 13-14; page 2, line 32-33) and selected one commercial device for comparison. Indeed, this sampler (ISCO 3700C Compact) does not prevent atmospheric contact. However, autosamplers that are capable of sealing samples after collection do exist. The following list might not be complete, but these are devices I have stumbled upon in the course of my own literature review (disclaimer: I am currently involved in the design and testing of an automatic rain collector):

1. OPEnSampler by OPEnS Lab (http://www.open-sensing.org/opensampler/; see review by Rolf Hut)
2. Lisa Liquidsampler by Lukas Neuhaus (https://www.liquidsampler.de/)
3. Sequential, time-integrating precipitation collector by Coplen et al. (2008; see Supporting Information)

The first two devices have apparently not been formally published and the second website is currently only available in German. Although it may be quite easy to miss these models in a literature review, they do exist and I would like to suggest that they be mentioned in the paper for the sake of completeness. Including them will not diminish the value of the authors' contribution. Although there are a few other devices (with somewhat different specifications), the sampler by Hartmann et al. is still a useful addition to those already in existence, particularly if presented in a way that enables reproduction (see review by Rolf Hut).

Authors' response: We thank Mr. Michelsen for notifying us of the existence of other similar liquid autosamplers being developed by other groups. Indeed, we seem to have missed these devices in our own literature research. In response to the comment of Rolf Hut (referee #2) with regard to the OPEnSampler we have already suggested to change the manuscript and to mention and to cite the sampler in our manuscript. However, in view of the fact that the OPEnSampler is not the only device similar to the GUARD autosampler, we suggest a more comprehensive change to the manuscript in order to give appropriate credit to other groups for their sampler developments.

As the mentioned liquid autosampler prototypes are not (yet) available on the market, we argue that our comparison of the GUARD autosampler with the commercially available autosampler 3700C Compact (Teledyne ISCO, USA) in Section 5 of the manuscript is still relevant and thus advocate not omitting this comparison from the manuscript.

Changes to the manuscript: On page 2 in line 31, insert "Furthermore, the need for automated liquid sampling in general is demonstrated by a number of technical developments by multiple groups with the aim of creating automated liquid samplers capable of sealing the samples after collection. For instance, researchers at Oregon State University have developed the "OPEnSampler" (Nelke, Selker and Udell, 2017; http://www.open-sensing.org/opensampler/) that comprises an array of 24 solenoid valves, allowing the 24 sampling containers to be sealed from the environment after sample collection. Lukas Neuhaus has developed the "Lisa Liquidsampler" (not published) that fills 48 sample vials sealed by septa (engineered membranes that permit the transfer of fluids without air contact, usually using a double-canula) using a vacuum pump via 48 separate transfer tubes. Applying a new automated precipitation collector obtaining 96 sequential 15-mL samples, Coplen et al. (2008) were able to measure a strong decrease of 51% in the hydrogen isotope ratio (δD) of precipitation over only one hour resulting from the landfall of an extratropical cyclone along the coast of California. Evaporation and subsequent isotopic fractionation was minimised by a Teflon-coated vial cover, thus sample vials are not sealed individually."

To harmonise the rest of the manuscript with this change, we suggest to replace the sentence on page 2 in line 32 with "In addition to these newly developed liquid autosamplers that are 1) suited for field operation in remote areas and under harsh (outdoor) conditions and 2) capable of sealing the sample vials (gastight) directly after sample collection, we have designed, constructed and tested a new autosampler ("GUARD") that also fulfils these requirements, but can be equipped with up to 160 sample vials due to its space-efficient design."

Reader Comment: Additionally, the section on potential applications attracted my attention. I am a bit confused about the authors' idea to use their sampler in the Global Network of Isotopes in Precipitation (GNIP; see Section 5). Currently, it sounds as if they suggest replacing the current cumulative collectors with their automatic sampler. As far as I know, the main aim of GNIP is to collect integral samples, i.e., samples that represent the entire precipitation occurring during the collection period (usually a month). The samples are then routinely analyzed for $\delta^{18}O$, $\delta^{2}H$, and partly ^{3}H. I am not sure how this could be achieved with the model described in the manuscript. In the current setup, one "collected sample represents the water under investigation at a given instant (integrated over 22 seconds)" (page 4, line 15-16). Maybe the authors could provide more details on the potential deployment as part of GNIP.

Authors' response: In our manuscript, we do not suggest replacing the cumulative collectors of the GNIP by GUARD autosamplers. We rather imply that "the application of GUARD samplers would be a cost-effective solution to supplement GNIP and/or GNIR stations" (page 10, line 16). Only in the case of "new stations too remote for regular manual sample collection" (page 10, line 17), we suggest that the GUARD autosampler "might even facilitate the installation" (page 10, lines 16-17), of additional GNIP/GNIR stations.

The predominantly monthly rainwater sampling interval applied at GNIP/GNIR stations offers the advantage of compatibility of the isotopic data from different stations. Therefore, we do not advocate ceasing this kind of operation. However, we stated that with the GUARD autosampler or similar autosamplers capable of high-frequency sampling, "much shorter sampling intervals would become possible which would enable researchers to investigate shorter-term variability in precipitation isotope systematics to improve our understanding of the underlying processes" (page 10, line 11-13). Investigating processes acting on short time-scales requires high-frequency sampling of (rain)water. To achieve this in hydrology/meteorology sampling frequency has to be at least high enough to resolve different precipitation events ("event-based" sampling). For instance, only by using such event-based data Celle-Jeanton et al. (2001) were able to demonstrate characteristic differences in the isotopic composition of rainwater in the Mediterranean coastal region of France the authors attributed to different types of synoptic weather systems. As the synoptic weather situation can change rather quickly, monthly rainwater isotope data would have most likely been of insufficient temporal resolution to identify this relationship between isotope composition and synoptics. Interpretations on monthly rainwater isotope compositions alone can even be misleading as demonstrated by a case study conducted by Treble et al. (2005) : While monthly rainwater isotope compositions on Tasmania suggested a control by temperature (positive correlation), a 6-yr-long daily record revealed a strong amount effect as the actual mechanism controlling the isotopic composition of individual rainfall events.

Reader Comment: Would they still use a peristaltic pump or would the rainwater flow into the vials by gravity?

Authors' response: Yes, we would still use a peristaltic pump because pumping (by under- or overpressure) is necessary to inject the sample liquid into the septa-sealed sample vials as these are airtight and need to be filled through a double-canula with a small diameter for the double-canula to be able to pierce the septa. Sample injection by gravity alone is not possible due to the flow resistance exerted by the small-diameter canula.

Reader Comment: Would they use the same vial number (48) and size (12 mL)?

Authors' response: The maximum benefit from the application of the GUARD autosampler is achieved if it is equipped with the maximum number of sample vials, i.e. 160. The sample volume of 12 mL, however, is sufficient for most analyses, including isotope ratio mass spectrometry (IR-MS) and inductively coupled plasma mass spectrometry (ICP-MS).

Reader Comment: How would they approach programming collection intervals, without knowing when it will rain?

Authors' response: The temporally discontinuous nature of rainfall poses a fundamental challenge to automatic rainwater sampling. In general, in order to prevent the pump from running dry and to avoid insufficient sample volumes during sample collection, rainwater needs to be pre-collected in a suitable container. In our case studies in karst caves we applied a specifically designed pre-collection container ("pre-collector") with an internal volume of exactly 12 mL. During dripwater pre-collection a 3D-printed floating body (volume considered) inside the pre-collector would rise until it seals the pre-collector once it is completely filled with dripwater. Any dripwater in excess of 12 mL spills over through a small hole at the top of the pre-collector (Fig. 1).

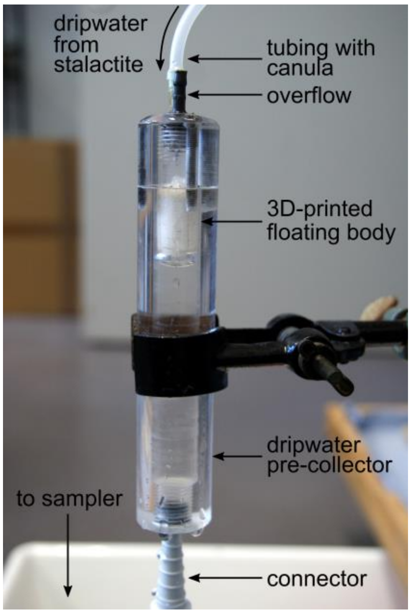

Fig. 1: Pre-collector used during the case studies.

Changes to the manuscript: Add Fig. 1 in the authors' response to the Supplementaries and insert a brief description of its purpose and design similar to above.

Authors' response (continued): One issue is that collection of rainwater needs to be initiated automatically as soon as a sufficient sample volume is available, or later, but not earlier. To ascertain that a sufficient sample volume is indeed available a detector is needed that ends hibernation and triggers sample collection. This could be achieved by implementing a photo sensor or some other kind of detector. As such a detector was not required for our case studies in karst caves but is needed for the automatic sampling of rainwater we suggest to highlight that the GUARD autosampler, at its current setup, is not suited for rainwater sampling as also proposed by Mr. Stefan Terzer-Wassmuth (reader #2).

Changes to the manuscript: Insert on page 10, line 17: "Due to the temporally discontinuous nature of rainfall automatic rainwater sampling requires 1) sample pre-collection for temporary storage of rainwater until a sufficient sample volume is available while minimising or even preventing evaporation and 2) a detector such as a photo sensor to end hibernation and trigger sample collection once a sufficient sample volume has been provided by rainfall. For the case studies in karst caves presented in this paper we applied a specifically designed pre-collection container ("pre-collector") with an internal volume of exactly 12 mL (Supplementary C). During dripwater pre-collection a 3D-printed floating body inside the pre-collector would rise until it seals the pre-collector once it is completely filled with dripwater. Any dripwater in excess of 12 mL spills over through a small hole at the top of the pre-collector. It is important to note that, at its current setup, the GUARD autosampler does not comprise a sample volume detector and is therefore not suited for rainwater sampling. As automatic rainwater sampling would be beneficial in numerous applications, such a detector certainly represents a useful future extension to the current GUARD system."

Reader Comment: Could their sampler also be used at GNIP sites exhibiting harsh conditions (i.e., a warm and arid climate)?

Authors' response: Yes, due to ruggedized design and the airtight sample vials we do not see a reason why the GUARD sampler should not be applicable in warm and/or arid climates, especially for sampling continuously provided media that does not require sample pre-collection. For sampling discontinuous media such as rainwater, the pre-collector should be installed inside the casing to minimise evaporation.

Reader Comment:

Alternatively, the authors could phrase their idea more carefully, for example by suggesting the addition of their device to the cumulative collectors at GNIP stations (instead of replacing them).

I hope these minor comments are helpful and perhaps contribute to further improvement of the manuscript, which is already a good contribution in presenting a useful automatic sampler.

Authors' response: To further clarify that we propose adding GUARD (or similar) samplers to the GNIP and especially the GNIR, rather than replacing the collectors currently in operation, we suggest the following changes to the manuscript as also suggested in the authors' response to reader #2 (Mr. Terzer-Wassmuth):

Changes to the manuscript: Replace the sentences on page 10, lines 9-14, "As mentioned in the Introduction, for this purpose the GNIP supplies researchers with isotope data generated from (mostly) monthly composite samples of rainwater collected at the ~ 1,000 GNIP stations worldwide.

If these stations were supplemented with GUARD autosamplers, much shorter sampling intervals would become possible which would enable researchers to investigate shorter-term variability in precipitation isotope systematics to improve our understanding of the underlying processes. To achieve this, sampling frequency needs to be at least high enough to resolve different precipitation events ("event-based" sampling). For instance, only by using such event-based data Celle-Jeanton et al. (2001) were able to demonstrate characteristic differences in the isotopic composition of rainwater in the Mediterranean coastal region of France the authors attributed to different types of synoptic weather systems. As the synoptic weather situation can change rather quickly, monthly rainwater isotope data would have most likely been of insufficient temporal resolution to identify this relationship between isotope composition and synoptics. Naturally, the increased number of samples generated by high-frequency sampling needs to be considered.

In addition, paraffin oil would not be required to prevent evaporation and increased maintenance of CRDS instruments could be avoided. The GUARD autosampler could also be applied at the ~ 750 stations of the Global Network for Isotopes in Precipitation (GNIR), also coordinated by the IAEA. Especially in very remote areas, the application of GUARD samplers would be a cost-effective solution to supplement GNIP and/or GNIR stations and it might even facilitate the installation of new stations too remote for regular manual sample collection."

References

Celle-Jeanton, H., Travi, Y., Blavoux, B., 2001. Isotopic typology of the precipitation in the Western Mediterranean region at three different time scales. Geophysical Research Letters 28, 1215–1218.

Coplen, T. B., Neiman, P. J., White, A. B., Landwehr, J. M., Ralph, M.; Dettinger, M. D. (2008) Extreme changes in stable hydrogen isotopes and precipitation characteristics in a landfalling Pacific storm, Geophys. Res. Lett., 35, L21808.

Treble, P., Budd, W.F., Hope, P.K., Rustomji, P.K., 2005b. Synoptic-scale climate patterns associated with rainfall delta O-18 in southern Australia. Journal of Hydrology 302, 270–282.