Authors' response to short comment 2

Reader Comment:

Hartmann et al. present a novel water autosampler which indeed excels over similar devices in the number of samples to be collected without supervision and also in its evaporation-protective properties (indeed most products seem to focus on dissolved constituents or their radioactivity and less on the water itself being the carrier medium). Their particular efforts to design a relatively small device in a ruggedized casing look promising for unsupervised sample collection even in remote and/or poorly accessible locations.

Key technical aspects have already been assessed by reviewer 1 and 2 (carryover effects of the peristaltic pump, eventual vulnerability towards evaporation within the tubing prior to injecting into the vial, storage effects in the Exetainer vial [note that the vendor specifications of the OA-ICO spectrometer state a typical drift of up to 0.2 per mil d18O; hence almost all tested and retested samples fall within instrument specifications]).

In line with reviewer 2 (and recognizing a number of parts in Fig. 2 from various online 'makershops)' we encourage the authors to make their work accessible to the broader scientific community in a reproducible manner, recognizing a number of additional applications after small modifications.

Notwithstanding the above, we'd like to make three remarks for the authors' kind consideration:

(1) The necessity to establish a local precipitation isotopic baseline (pg. 2 line 23-31) is undisputed and we appreciate that the Global Network of Isotopes in Precipitation (GNIP) is listed as the key resource. However, the authors present some vague assumptions regarding GNIP:

a. not all these samples are collected manually, including some of them being totalized in active or passive devices (there are a number of devices compliant with the GNIP sampling guidelines).
b. GNIP is *coordinated* by the IAEA, while sampling efforts are undertaken through dedicated partner institutions in IAEA or WMO Member States.
c. To properly cite the GNIP database, pls. see http://www-naweb.iaea.org/napc/ih/IHS_resources_gnip.html (scroll down to 'obtaining and citing GNIP data'; note that Bowen and Wilkinson 2002 refer to a derivative isoscape product).
d. Whilst the GNIP database includes sections for data sampled at other temporal resolutions than monthly, this remains the default sampling frequency to assure the worldwide compatibility of GNIP data from different sources. In settings where no permanent staffing is available at GNIP stations, a number of totalizers have been tested to compensate for this deficiency (see the GNIP manual http://www-naweb.iaea.org/napc/ih/documents/other/gnip_manual_v2.02_en_hq.pdf or Terzer et al. 2016)

Authors' response: We agree with all of the above statements and suggest the following changes to the manuscript:

Changes to the manuscript:

Replace the sentence on page 2, lines 24-26, with "The majority of such studies rely on rainwater samples (mostly) collected manually at stations of the Global Network of Isotopes in Precipitation (GNIP; IAEA/WMO, 1994) coordinated by the International Atomic Energy Agency (IAEA) with the sampling performed by dedicated partner institutions in member states of the IAEA or the World Meteorological Organisation (WMO).

Replace the sentence on page 2, lines 26-28, with "At these stations, rainwater is generally sampled at monthly resolution to ensure worldwide compatibility of GNIP data from different sources. While most of these samples are collected manually, a number of active or passive totalizers compliant with the GNIP sampling guidelines (Terzer et al., 2016) are in operation at GNIP stations without permanent staffing. Manual sampling at higher temporal resolution, such as rainfall event-based sampling, is practically impossible as this would require round-the-clock stand-by duty."

Reader Comment: As a side note, paraffin wax is never used for sealing water samples during passive totalization (we assume the authors referred to paraffin oil) and its deleterious effects on laser spectrometry are subject to debate (e.g. Wassenaar et al. 2018 found that the laser spectrometry data are more vulnerable to VOC contamination; however increased spectrometer maintenance is of relevance).

We recommend to the authors to shorten the corresponding paragraph to highlighting the importance of establishing an isotope baseline for meteoric waters, to mentioning the spatial and temporal discontinuity in the GNIP database as a problem statement, and to acknowledging that sealants other than paraffin are advisable for the ease of handling and reduced need for spectrometer maintenance.

Authors' response: We agree with the above statement and suggest the following changes to the manuscript:

Changes to the manuscript: Replace the sentence on page 2, lines 28-31, with "Furthermore, sample alteration due to evaporation is commonly prevented by sealing the water samples' surface with paraffin oil despite it causing an increased need for maintenance of the standard instrument for water isotope analysis, i.e. Cavity Ring-Down Spectroscopy (CRDS).

Establishing an isotope baseline for meteoric waters is crucial for research in hydrology, meteorology and other scientific fields. While remarkable progress has been made thanks to GNIP data, the network is still spatially and temporally discontinuous, among other reasons due to the practical constraints on rainwater sampling in remote areas. Automated rainwater sampling could help solve this issue and increased maintenance of spectrometers could be avoided by applying gastight sample vials."

Reader Comment: (2) In line with the above, we find the authors' comments regarding potential applications at GNIP stations pretty presumptuous (pg. 10 line 8 ff.):

a. the 1,000 sites mentioned are not temporally continuous, and the network is *coordinated* by IAEA, however the sampling is carried out by partner institutions in IAEA or WMO Member States, and the choice of equipment is subject to their respective organizational context as long as it is compliant with the GNIP sampling guidelines.
b. as indicated, the presently active GNIP stations employ an array of sampling methods (yet compliant with the protocol), not all of which rely on daily retrieval of the rainwater and not all totalizing stations employing paraffin oil as a sealant.

We agree however that a coordinated effort of sampling at higher frequency may be beneficial to a number of especially meteorological and climatological assessments; however the resulting analytical effort needs to be kept in mind.

Authors' response: We agree with the above statements and suggest the following changes to the manuscript:

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."

Reader Comment: (3) On the technical side, we see that the sampler in its present form may certainly be applied to sample continuously flowing media (drip waters, groundwaters, surface waters, leachates etc.), however given the discontinuous nature of precipitation in both timing and intensity, and the resulting need to integrate into discrete, timed samples (regardless of whether samples are taken on a sub-hourly, daily, or monthly basis), the device in its present form is not undisputedly suited as a precipitation sampler since it lacks (a) a precipitation trigger to end hibernation mode, and (b) appropriate means to totalize precipitation, safe from evaporation, over the sampling interval prior to dispensing into the vial.

Based on (2) and (3) we suggest to the authors to shorten the paragraph on potential applications, and we strongly advise to state that the device in the form presented is not capable of collecting discontinuous media such as precipitation (but this could be added as an outlook).

Authors' response: As with a similar comment by reader #1 (Mr. Michelsen) we agree with the above statement and suggest the following changes to the manuscript already suggested in the authors' response to the comments of reader #1:

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).

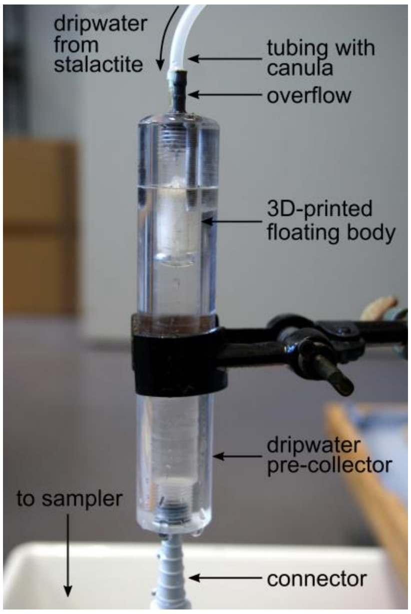

Fig. 1: Pre-collector used during the case studies.

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 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: To conclude, we congratulate the authors on their achievements with the development of an autosampler for continuously flowing media, and we look forward to see the concept expanded into discontinuous media as well.

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.

IAEA/WMO, 1994, Global Network for Isotopes in Precipitation (GNIP) Database. IGBP PAGES/World Data Center-A for Paleoclimatology Data Contribution Series # 94-005. NOAA/NGDC Paleoclimatology Program, Boulder CO, USA.

Terzer, S., et al., 2016. An assessment of the isotopic (2H/18O) integrity of water samples collected and stored by unattended precipitation totalizers. Geophysical Research Abstracts, 18, EGU2016-15992.

Wassenaar, L.I. et al., 2018. Seeking excellence: An evaluation of 235 international laboratories conducting water isotope analyses by isotope-ratio and laser-absorption spectrometry. Rapid Communications in Mass Spectrometry 32, 393-406