Technical note: GUARD – An automated fluid sampler preventing sample alteration by contamination, evaporation and gas exchange, suitable for remote areas and harsh conditions

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Abstract. Automated water sampling devices adapted to field operation have proven highly useful for environmental research as well as in the public and private sector, where natural or artificial waters need to be tested regularly for compliance with environmental and health regulations. Such autosamplers are already available on the market in slightly differing versions, but none of these devices are capable of sealing the collected samples to prevent sample alteration by contamination, evaporation or gas exchange. In many sampling cases, however, this feature is essential, for instance for studying the hydrological cycle based on isotopes in rainwater, or for monitoring waters contaminated with toxic gases or other volatile compounds detrimental to biota and human health. Therefore, we have developed a new mobile autosampler, which injects water samples directly into airtight vials, thus preventing any sample alteration. Further advantages include low production costs, compact dimensions and low weight allowing for easy transport, a wide range of selectable sampling intervals as well as a low power consumption, which make it suitable for long-term applications even in remote areas and harsh (outdoor) conditions due to its heavy-duty water-proof casing. In this paper, we demonstrate 1) the sampler's mechanical functioning, 2) the long-term stability of the collected samples with regard to evaporation and gas exchange and 3) the potential of our device in a wide variety of applications drawing on laboratory and field experiments in different karst caves, which represent one of the most challenging sampling environments.

1 Introduction

Sampling natural waters (water bodies and rainwater), as well as artificial waters (including process and waste water) for subsequent hydro- and geochemical analysis, is indispensable for understanding the behaviour of natural and artificial waters, for determining their spatial and temporal variability (e.g. in the concentration of toxic compounds) as well as for determining their current state (e.g. Hiscock and Bense, 2014).A thorough monitoring of water is thus important, not only for scientific purposes but also to prevent adverse effects on human health and ecosystems, whether in the short, medium or long term.

However, the manual collection of water samples is not only time-consuming but also expensive and logistically challenging. This is particularly true in remote areas with poor or no infrastructure, where expenses for field trips and equipment transport to the sampling site and back are often significantly increased. Furthermore, in most cases the properties and composition of the water under investigation change with time, for instance, the concentration of pollutants like heavy metals or polycyclic aromatics (Appelo and Postma, 2005). In these cases, it is necessary to repeat water sampling multiple times at short intervals and over a sufficiently long time period, increasing the logistical constraints (e.g. Ahuja, 2013). When it comes to long-term monitoring of a site at relatively short intervals, manual sampling is definitely no viable option anymore (Chapin, 2015).

This impasse can only be overcome by automation: Autosamplers suitable for field operation, such as the portable sampler 3700C Compact (Teledyne ISCO, USA) are already available on the market and offer the opportunity to automatically and repeatedly sample water bodies (oceans, estuaries, lakes, rivers, groundwater, etc.). As they can be powered by batteries or solar panels these autosamplers do not need a connection to the grid and can, therefore, be applied even in remote areas.

Despite their suitability for a wide range of applications, available autosamplers lack the capacity to automatically seal the sample vials after collection. This, however, is absolutely essential in many sampling applications where any exchange of gases and/or volatile components between the sample and the ambient air needs to be prevented in order to preserve the sample's original properties until analysis. Examples are numerous and include cases of water being contaminated by toxic gases originating from anaerobic degradation of organics (e.g. CH_4 and H_2S) or by volatile organic compounds (VOCs), such as tetrachloroethene, benzene, MTBE or formaldehyde (e.g. Reemtsma and Jekel, 2010).

Sample vials also need to be gastight directly after sample collection where evaporation or condensation has to be impeded to prevent sample alteration, for example where non-volatile components like cations and anions need to be quantified. In such cases evaporation would cause erroneously augmented concentration values (Hiscock and Bense, 2014), especially in long-term monitoring schemes.

Similarly, the prevention of evaporation is paramount in all studies investigating the hydrological cycle based on the stable isotopes of hydrogen and oxygen (indicated as δD and δ^{18}O values). 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)." ~~The majority of such studies rely on rainwater samples collected manually at stations of the Global Network of Isotopes in Precipitation (GNIP) run by the International Atomic Energy Agency (IAEA) (e.g. Bowen and Wilkinson, 2002)~~. 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 ~~At these stations, rainwater is sampled at only low temporal resolution (≥ 1 month) because manual sampling~~

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2

~~at higher temporal resolution, such as rainfall-event-based sampling, is practically impossible as this would require round-the-clock stand by duty~~.

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~~Furthermore, sample alteration due to evaporation is prevented by sealing the water samples' surface with paraffin wax despite it causing technical problems with the standard method for water isotope analysis, i.e. Cavity Ring-Down Spectroscopy (CRDS).~~ This clearly illustrates the need for automated rainwater sampling with gastight sample vials. 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.

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.~~As there are currently no autosamplers available 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 fulfils all these requirements~~. In addition to fulfilling the former requirements, the GUARD autosampler offers further advantages including a low weight, low cost (~ 1,000 €), compact dimensions, easy transport, a wide range of selectable sampling intervals as well as a low power consumption, which permits either high-frequency sampling (e.g. every minute), long-term monitoring (e.g. 6 months), or medium-term monitoring at medium sampling frequency (e.g. daily sampling for 48 days)~~either high-frequency sampling, long-term monitoring, or medium-term monitoring at medium sampling frequency~~.

3

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Therefore, the GUARD autosampler is applicable for a wide spectrum of sampling purposes, ranging from studies on characterization of high-frequency variabilities to long-term changes in natural or artificial waters. By sealing the sample vials with septa (engineered membranes that permit the transfer of fluids without air contact, usually using a double-canula), not only undesired gas exchange and evaporation/condensation are prevented, but also any contamination that might

5   otherwise occur, especially in long-term monitoring projects where sample vials may need to stay at the sampling site for several months or longer. This protection is further ensured by a water-tight and airtight sampler case, which prevents damage from extreme weather conditions (e.g. water or dust ingress, high humidity, etc.) and also protects the samples from any external interference, e.g. from animal activity.

The setup and design of the GUARD autosampler are described in Sect. 2. In Section 3 we draw on test runs in the
10 "laboratory" and in a karst cave, one of the most challenging sampling environments, to demonstrate 1) the mechanical functioning and 2) the long-term chemical stability of the collected samples. In Section 4 we demonstrate the potential of our autosampler in a wide variety of applications by presenting the results of a 5-day case study at a sampling interval of only four hours, which would have been hardly possible without the use of our device. In Section 5 we compare our invention to already existing autosamplers suitable for field operation and conclude with highlighting potential sampling applications.

15 **2 Methodology: Autosampler set-up and design**

2.1 Hardware design and sampling process

The main components of the GUARD autosampler comprise an intake hose, a peristaltic pump, a mobile injection system and a vial holder (Fig. 1Fig. 1, Fig. 2Fig. 2, Tab. 1, Supplementary S5). To prevent any sample alteration resulting from contamination, evaporation, condensation and/or gas exchange during sample storage, the fluid samples (12 mL) are injected
20 into air/gastight vials using a peristaltic pump, at a user-defined date, time and interval.

At the beginning of the first sampling interval, 12 mL of fluid are sucked into the autosampler's tubing made of flexible and chemical-resistant FKM tubing that is hydraulically connected to the water under investigation (e.g. a lake). As the tubing is just long enough to accommodate precisely 12 mL (i.e. 1247 mm), the sample is not yet injected into the corresponding vial, but at first remains inside the tubing where it is already protected from gas exchange.

25 At the beginning of the subsequent sampling interval, two electric motors move the sampler's X- and Y-slide via toothed rubber belts until two separate end-switches are triggered that provide positioning calibration. Both slides are then positioned directly above the first sample vial. After a 2-seconds safety delay, a servo screwed to the sampler's Z-slide moves the Z-slide down, until a metal double cannula attached to the front end of the FKM tubing just barely pierces the rubber septum which keeps the vial permanently air/gastight. After another 2-seconds safety delay, the sampler's pump is reactivated and
30 the collected water is injected into the vial through one of the cannulas (the "sample cannula") while the subsequent sample is sucked into the sampler's tubing simultaneously. As a result of this design, the sample injection always lags the sample collection by one interval.

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As the sample vials are airtight, an overpressure builds up inside the vials during sample injection. Pressure equalisation is achieved via the second of the two cannulas which are soldered to one another. To achieve the maximum sample volume (here: 12 mL) this "pressure release cannula" is located 2-3 mm above the sample cannula, and the vials are filled with an overflow of several droplets. This setup avoids any unwanted interaction (e.g. gas or isotope exchange) between the
5 collected fluid sample and the supernatant air/gas left inside the vial. Subsequent to a 10-seconds safety delay implemented to allow for complete pressure equalisation and sample injection, the Z-slide with the double cannula is moved back up to its home position and the X- and Y-slides are positioned above the next sample vial. After another 2-seconds safety delay, the sampler enters a hibernation mode to minimise power consumption until the hibernation is interrupted with the start of the next sampling interval. After completion of a full sampling sequence, the Z-slide moves back up to its home position, the X-
10 slide moves to its end position and the sampler waits for input from the operator.

In the setup shown here the collected samples have a volume of 12 mL which is sufficient for most analyses, including isotope ratio mass spectrometry (IR-MS) and inductively coupled plasma mass spectrometry (ICP-MS). The pumping process takes only about 22 seconds and, thus, the collected sample represents the water under investigation at a given instant (integrated over 22 seconds). As one entire sampling step takes only 41 seconds (power consumption: 2.1 mAh), the
15 autosampler is capable of high-resolution fluid sampling with a minimum interval of one minute. This is valuable where high-frequency variations in the composition of the sampled fluid need to be resolved, for instance, in artificial tracer tests at the onset of the tracer breakthrough where samples are commonly collected at intervals as short as one minute (Leibundgut et al., 2009). If needed, the sample volume can be modified by changing the duration of the pumping step. For example, to obtain a 100 mL sample the pumping step would take about 3 minutes.
20 Using a 12 V battery with a capacity of 40 Ah the GUARD autosampler can operate off-grid for about 100 days without interruption at a 2-day interval (one full sampling sequence), thanks to the hibernation mode during which power consumption is reduced to 16.5 mA (we are currently working on further reducing the power consumption). On such long time spans the power consumed during the actual sampling process is practically negligible. If longer operation durations are necessary, multiple batteries can be connected in parallel to increase the total capacity. The sampler can also run on 12 V Li-
25 ion batteries if weight is an important constraint. Additionally, nearly discharged batteries can be replaced with fully charged ones without interrupting a running sampling sequence by using an electrical bypass. Of course, implementing an appropriate rectifier, the autosampler can also run on mains power in which case runtime limitations do no longer apply.

Fig. 2Fig. 2 shows the GUARD autosampler in detail and in operation during a 5-day case study (Sect. 4) focusing on the carbon isotope geochemistry ($\delta^{13}C_{DIC}$) of dripwater originating from a stalactite in a karst cave in northern Bavaria,
30 Germany.

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2.2 Electronic and software design

Most of the autosampler's electronic components are accommodated in the control unit (Fig. 1~~Fig. 1~~) inside an additional casing for protection. The centrepiece of the electronic design is the Arduino® Mega 2560 board which is based on an Atmel ATmega 2560 microcontroller. This microcontroller enables the autosampler to enter the hibernation mode during which power consumption is reduced 50-fold as compared to the power consumption during slide movement. It also contains a non-volatile 4 KB EEPROM memory in which the data (time and position) of the previous injection are saved temporarily. The interrupts of the hibernation mode at the beginning of each sampling interval are triggered by a real-time clock (RTC) chip that includes a separate 3V lithium button cell battery which ensures that the program controlling the sampler operation remains active, even if the main power supply may be interrupted. The electrical circuit diagram ~~is~~ as well as a Bill of Materials are given in the Supplementary (S1 and S6).

The program controlling the autosampler was constructed with the open-source software Arduino (version 1.8.3). The code is written in Java and can be uploaded to the board via a USB connection. A flowchart illustrating the operation of the GUARD autosampler is shown in Fig. 3~~Fig. 3~~.

3 Demonstration of the autosampler's functioning

3.1 X-Y-positioning

During and after the development of the GUARD autosampler we have conducted various indoor experiments to test the mechanical functioning of our prototype. One important requirement in that respect is a precise and reliable positioning of the X- and Y-slides at the exact locations of the sample vials. High precision is especially important for an efficient use of the space available for the sample vials which are arranged as close as possible to each other (yielding a capacity of 160 vials at the given casing dimensions). To achieve this high precision, all movements are executed by Computerised Numerical Control (CNC). The stepper motors for the slide movement in X- and Y-direction are programmed to turn in quarter-steps which correspond to a rotation of only 0.45 °. Consequently, the slide movements along the X- and Y-axis are accurate to less than 1 mm. As the pierceable area of the rubber septa is 7 mm in diameter, there is a more than sufficient error margin of about 350 %. This prevents the double cannula from hitting the sample rack during the Z-slide's downward movement which would cause the double cannula to deform and the respective sampling sequence to fail.

3.2 Sample injection

Another important aspect of an error-free mechanical functioning is a successful sample injection with an optimal use of the available sample volume. To demonstrate the fulfilment of this prerequisite we ran a complete sampling cycle comprising 48 tap water "samples" and analysed the size of the air bubbles remaining in the vials after sample injection. The results of this test are shown in Fig. 4~~Fig. 4~~: Most bubbles are 9.5 mm in diameter or less which confirms that the vials (internal diameter ≤

15 mm) are filled quasi-completely during sample injection. Assuming the bubbles were a perfect sphere, they would make up ≤ 0.45 mL (or ≤ 4 % of the inner vial volume). Considering that the bubbles are in fact strongly flattened, they more like make up ≤ 0.22 mL (or ≤2 % of the inner vial volume). Therefore, any sample alteration due to interactions between the fluid sample and the supernatant air/gas, for instance, due to isotopic exchange, is ~~effectively~~ prevented.

5 **3.3 First field test: Comparison of automatic and manual samples & long-term sample stability**

With respect to the quality of the samples collected by the GUARD autosampler, there are two main prerequisites: 1) Samples need to yield identical analytical results, whether they are collected automatically or manually, and 2) samples need to be unaltered and stable, even in the long term, which is ensured by the sample vials being air/gastight. In order to ascertain the fulfilment of both of these criteria, we applied our device in a first field experiment in a karst cave to automatically

10 sample the water at a specific drip site over the course of 33 days at daily intervals. For comparison, we collected 12 dripwater samples manually. We then analysed the oxygen isotopes in these water samples with cavity ring-down spectroscopy (CRDS) on a liquid water isotope analyser (LWIA-24d; Los Gatos Research). The standards used for calibration were LGR1A, USGS 46 and USGS 48. The accuracy (<0.07 ‰) was tested by repeated measurements of the control standard material LGR 2C. The average precision of the individual measurements (n = 124) was ±0.4 ‰. The isotope

15 data are shown in Fig. 5~~Fig. 5~~ and Fig. 6~~Fig. 6~~.

Fig. 5~~Fig. 5~~ demonstrates that the oxygen isotope results from the automatically and the manually collected samples are in

good agreement with each other, especially considering the respective analytical error ranges. In two cases (13th of December, around 3 pm and 22nd of December 2016, around 4 pm), $\delta^{18}O$ values do not seem to agree within error at first. However, as the manual samples had to be collected at least 15 minutes before or after the automatic collection in order to

20 allow for sufficient sample volumes (due to the low drip rate at this specific site), this seeming mismatch can be explained with the high-frequency variability of the dripwater $\delta^{18}O$ values at this drip site. This is best exemplified with the last two automatically collected samples in the left sub-plot in Fig. 5~~Fig. 5~~, where $\delta^{18}O$ values dropped from -10.05 ‰ to -10.24 ‰

within only 30 minutes. The sample collected manually exactly in between these two yields an intermediate $\delta^{18}O$ value of - 10.06 ‰ and is therefore consistent with the automatically collected samples. More importantly, there is no systematic

25 discrepancy between the automatically and the manually collected samples, with the respective arithmetic mean $\delta^{18}O$ values, calculated for the entire sampling period (both sub-plots of Fig. 5~~Fig. 5~~), differing by only 0.03 ‰.

In order to demonstrate that the sample vials are completely airtight and remain so even after the double cannula has pierced the rubber septa during sample injection, we measured the oxygen isotopic composition of nine different samples (stored in a fridge at 11.2~~8~~ °C) repeatedly over a time interval of six months. The results (Fig. 6~~Fig. 6~~) confirm the long-term stability of

30 the samples: If the vials were not airtight, evaporation would have led to a preferential removal of isotopically light water molecules from the water samples due to their higher vapour pressure (e.g. Hoefs, 2015) and, consequently, to an increase of the $\delta^{18}O$ value of the remaining water sample over time. Such a positive trend is not present in the data and the results from the repeated measurements agree well with the initial ones. The difference in $\delta^{18}O$ values between initial and repeated

measurements ranges from 0.00 ‰ (lt02-05) to 0.15 ‰ (between 2nd and 3rd measurement of sample lt03), but averages out at -0.01 ‰ over all measurements (median also -0.01 ‰) indicating that there is no systemic discrepancy between initial and repeated analyses. The results for δD are similar to the δ^{18}O results and also confirm the long-term stability of the samples (Supplementary S2).

To provide the reader with a notion of the effect of evaporation on the sample δ^{18}O values, we have calculated both evaporation and δ^{18}O change for the conditions prevalent in our fridge (temperature 8 °C, relative humidity 24 %) and assuming an opening of the sample vial of 5 % to imitate a minor lack of airtightness. The results of these calculations (Supplementary S4) demonstrate that even a small slit in a sample vial's rubber septum equalling only 5 % of the vial's inner cross section leads to a substantial shift towards higher δ^{18}O values in the residual water over time. After three months (90 days), for instance, δ^{18}O values would have risen from -10.1 ‰ by about 1.3 ‰ to -8.8 ‰. For comparison, the difference between the lowest and the highest δ^{18}O value in Fig. 6 is still below 0.3 ‰, while those data points span an even longer period of six months. Most importantly, there is no positive trend in the δ^{18}O values in Fig. 6 which illustrates that the sample vials are sealed properly, even after sample injection.

4 Case study: High-resolution drip sampling for speleothem science

The potential and usefulness of our autosampler are demonstrated in a first case study that would have been both too expensive and time-consuming to conduct without our device. The goal was 1) to prove the existence of high-frequency (daily) variability in the carbon isotope values (δ^{13}C) of dissolved inorganic carbon (DIC) in cave dripwaters and 2) to quantify its amplitude. This variability has important implications for the reconstruction of past environmental changes from speleothem δ^{13}C values as these are not only a function of the dripwater δ^{13}C signal originating from the surface environment, but also of the intensity of degassing of excess CO_2 from the dripwater (Fairchild et al., 2006). However, to date $\delta^{13}C_{DIC}$ variability has only been documented on the seasonal and annual scale (e.g. Spötl et al., 2005; Mattey et al., 2010), certainly also due to the lack of practical solutions for the high-frequency dripwater sampling in caves.

The existence of such high-frequency variability in $\delta^{13}C_{DIC}$ can be postulated based on the knowledge that cave air CO_2 concentrations can vary both strongly and quickly (e.g. Luetscher and Ziegler, 2012) as a response to ventilation processes (e.g. Tremaine et al., 2011): In general, strong ventilation of a cave system leads to an input of low CO_2 ambient air which (partly) replaces the CO_2 enriched cave air. The lowered CO_2 concentration causes enhanced degassing of excess CO_2 from the cave dripwater, which, in turn, results in increased dripwater $\delta^{13}C_{DIC}$ values, as isotopically light CO_2 transits preferentially from the liquid to the gas phase (Clark and Fritz, 1999).

4.1 Study area

This case study was carried out in the "Kleine Teufelshöhle" (N 49°45′17″, E 11°25′12″) in the Franconian Switzerland region in northern Bavaria, Germany. This cave is characterized by dynamic ventilation (forced convection). The mean

annual air temperature is around 8°C and the air humidity is close to saturation. This site warrants conditions suitable for a demanding field test due to 1) the lack of an electric supply network and to 2) the high relative humidity which poses challenges for electrical appliances in general. The GUARD autosampler was placed at a location adequate for sampling the dripwater from a specific group of stalactites, at drip site "DS4" (Fig. 2~~Fig. 2~~, right).

5 **4.2 Materials and methods**

Dripwater sampling was conducted automatically at 4-hour intervals over a period of five days yielding a total of 22 samples. The stable carbon isotopic composition of the dripwater DIC was determined at the University of Innsbruck using continuous-flow isotope ratio mass spectrometry following the method described in Spötl (2005). Calibration of the raw results versus the V-PDB scale is achieved using in-house calcite standards (subsequent to linearity correction) that have 10 been calibrated against NBS-18, NBS-19, CO-1 and CO-8 reference materials. The external precision calculated over 12 standards per run is typically ≤0.07 ‰ for $\delta^{13}C$.

Cave air CO_2 concentrations were logged every 30 minutes with a Vaisala GM70 hand-held unit equipped with a CO_2 probe optimised for the 0–2000 ppmV range (GMP222; accuracy: ± 1.5 % of the calibration value plus 2 % of the measured value). Cave air temperature (T) and relative humidity (RH) were logged at 10-minute intervals with a Tinytag TGP-4500 (Gemini 15 Loggers; accuracy: ± 0.5 °C at 8 °C and ± 3.0 % RH at 25 °C), while the combined drip rate of the stalactite cluster was logged with a Stalagmate Mark 3 (TGC-0011; Driptych) and integrated over 5-minute increments.

4.3 Results

Over the duration of the 5-day case study, RH was constant at 100 % and the drip rate oscillated between 26 and 28 drops per 5-min increment (5.2 to 5.6 drops/min). The results of the T, CO_2 and $\delta^{13}C_{DIC}$ analyses are summarised in Fig. 7~~Fig. 7~~. 20 Cave air CO_2 concentrations range from 520 to 1430 ppmV, with an average of 748 ppmV (n = 476) and a median of 710 ppmV, and $\delta^{13}C_{DIC}$ values range from -9.8 to -7.7 ‰, with an average of -8.8 ‰ (n = 22) and a median of -8.9 ‰. CO_2 concentrations peaked thrice (circled numbers in Fig. 7~~Fig. 7~~), with two smaller peaks of 910 and 1030 ppmV at the beginning of the monitoring period being followed by the most prominent and broad peak of 1430 ppmV that occurred during the night from the 2nd to the 3rd of May 2017. All three CO_2 peaks, particularly the last one, precisely coincide with 25 troughs in the $\delta^{13}C_{DIC}$ values, while CO_2 troughs coincide with $\delta^{13}C_{DIC}$ peaks, which results in a distinct negative correlation (Spearman's ρ = -0.88) of both geochemical signals. Temperature varies only very slightly, with both average and median being 8.6°C (n = 1425). Despite the low amplitude of T variations, T appears to correlate positively with $\delta^{13}C_{DIC}$, but only weakly (Spearman's ρ = 0.36).

4.4 Interpretations

30 The dripwater analyses obtained from the Kleine Teufelshöhle at 4-hour resolution over five days clearly prove the presence of a high-frequency variability in the $\delta^{13}C_{DIC}$, in addition to the already documented seasonal and interannual variability

(Spötl et al., 2005; Mattey et al., 2010). In this case, the maximum amplitude is 2.1 ‰ – a change that is great enough to be resolved by state-of-the-art isotope-ratio mass spectrometers (IR-MS). While this 2.1 ‰ change occurred over a period of almost two days (2017-05-02 01:00 to 2017-05-03 17:00), additional variability is observed on even smaller time-scales. For example, the difference in $\delta^{13}C_{DIC}$ values between the first local minimum (-9.04 ‰) and the first local maximum (-8.32 ‰)

5   came about in only 8 hours, with an amplitude of 0.72 ‰, suggesting rapid responses to even small changes in the ventilation regime.

The strong negative correlation between $\delta^{13}C_{DIC}$ values and CO_2 concentrations is consistent with ventilation events that lead to decreased cave air CO_2 concentrations: As high CO_2 cave air is partly replaced by low CO_2 ambient air degassing of excess CO_2 from the drip water is enhanced. As the process of degassing favours isotopically light CO_2 molecules, the

10 $\delta^{13}C_{DIC}$ values in the dripwater are increased during these ventilation events. This interpretation also seems to be confirmed by the measured T variations: Although they are very small, the positive albeit moderate correlation with $\delta^{13}C_{DIC}$ suggests that, during ventilation, part of the cave air is replaced by relatively warm low CO_2 ambient air. During winter months, it would be replaced by relatively cold but still low CO_2 ambient air.

In order to characterize the changes in the dripwater $\delta^{13}C_{DIC}$ with respect to the cave air CO_2 concentration, we have

15 determined the amplitude of the maxima/minima in $\delta^{13}C_{DIC}$ and CO_2 relative to their respective overall mean, simply by subtracting each maximum/minimum from the mean. This yields a total of six maximum/minimum pairs that plot very well along a linear regression line (Fig. 8~~Fig. 8~~). According to this regression, a change in cave air CO_2 concentration of about 435 ppmV produces a change in dripwater $\delta^{13}C_{DIC}$ of 1 ‰ that is then transferred to the $\delta^{13}C$ signal in the speleothem fed by this dripwater.

20 We note that potential drift effects or sample alterations that might be caused by the automatic sampling process have not yet been examined in detail. Corresponding tests using check-standards of known $\delta^{13}C_{DIC}$ values will be performed in future studies.

5 Summary and potential applications

With "GUARD" we have developed and tested an automated water sampler suited to field operation in remote areas and

25 harsh conditions that injects the samples into airtight vials in order to prevent sample alteration from contamination, evaporation/condensation and/or gas exchange.

In this paper, we have demonstrated its mechanical functioning, the long-term chemical stability of the collected samples and the potential of our autosampler in a wide variety of applications by presenting the results of a 5-day case study which would have been hardly possible without the use of our device. In this case study we have proven for the first time that cave

30 dripwater geochemistry varies on much smaller time-scales than has previously been established. Applying the GUARD autosampler we have collected enough dripwater samples at high temporal resolution to make a first contribution to

quantifying the effects of ventilation events on dripwater $\delta^{13}C_{DIC}$, which will help in using speleothem $\delta^{13}C$ as a proxy for palaeoenvironmental change.

To conclude we compare our prototype with the portable autosampler 3700C Compact (Teledyne ISCO, USA) which is, to our best knowledge, the only type of device similar to our prototype already available on the market. While there are also

5   other (bigger and heavier) models from Teledyne ISCO and similar devices offered by other companies, the 3700C Compact autosampler is representative of the technical state of the art.

The most relevant properties of both autosamplers are compared in Table 2. As might be expected when comparing a prototype with a market-ready product it is evident that the GUARD autosampler lacks specific features that enhance the end-user comfort, such as rinse cycles between samples, an automatic compensation for changes in hydraulic head and

10   different modes of sampling pacing. Both autosamplers are similar in weight and size. Almost a third of the GUARD's weight is due to the Pb-acid battery used in the presented setup. The battery can be transported separately from the autosampler or can be replaced with lighter Li-Ion batteries to reduce weight. Most importantly, however, the GUARD autosampler is capable of collecting gastight samples in a considerably higher maximum number of sample vials. Thanks to a wide range of selectable sample frequencies and its capacity to operate for extended periods of time, the GUARD

15   autosampler is well-suited for long-term sampling projects where a large number of samples need to be collected.

As existing autosamplers such as the 3700C Compact do feature neither gastight samples nor high numbers of sample vials, the GUARD autosampler is less competing with existing autosamplers as much as it closes a market gap in long-term monitoring where samples definitely need to be gastight with respect to air/gas exchange to prevent sample alteration. Within this sector, the GUARD autosampler offers many opportunities in various applications:

20   One example of such an application is the investigation of the hydrological cycle based on isotopes in all sorts of water bodies, including rainwater. ~~As mentioned in the Introduction, for this purpose the IAEA supplies researchers with isotope data generated from monthly composite samples of rainwater collected at the ~ 1,000 GNIP stations worldwide.~~ 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

25   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

30   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.

If these stations were equipped with GUARD autosamplers, the rainwater would not need to be collected manually anymore rendering the sampling process more economical. Furthermore, 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. In addition, paraffin wax would not be required anymore to prevent evaporation and would no longer cause technical problems with CRDS analyses. The GUARD autosampler could also be applied at the ~ 750 stations of the IAEA's Global Network for Isotopes in Precipitation (GNIR). 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.

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 S7). 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.

Another example for a promising application are dripwater monitoring schemes in karst caves that are necessary especially, if not exclusively, in speleothem science (Ford and Williams, 2007; Fairchild and Baker, 2012). The case study presented here illustrates well the GUARD's potential for offering new research opportunities. As most cave sites are located far from researchers' offices and are often difficult to get to, there is a great need for automation in dripwater monitoring studies. The sampler's application in high-frequency (short-interval) dripwater sampling will enable researchers to identify, resolve and quantify short-term variability in dripwater geochemistry and to better understand these complex cave systems – a prerequisite for reliable reconstructions of past climates and environments from speleothem proxies.

6 Data availability

All data used in this study are available upon request from the corresponding author.

Kommentar [AH15]: Reader 1 comment 7 and Reader 2 comment 3

Kommentar [AH16]: Reader 1 comment 5 and Reader 2 comment 4

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Kommentar [AH17]: Reader 1 comment 7 and Reader 2 comment 3

Kommentar [AH18]: Reader 1 comment 1

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Kommentar [AH19]: Reader 2 comment 1

Kommentar [AH20]: Referee 2 comment 3

Kommentar [AH21]: Reader 2 comment 1
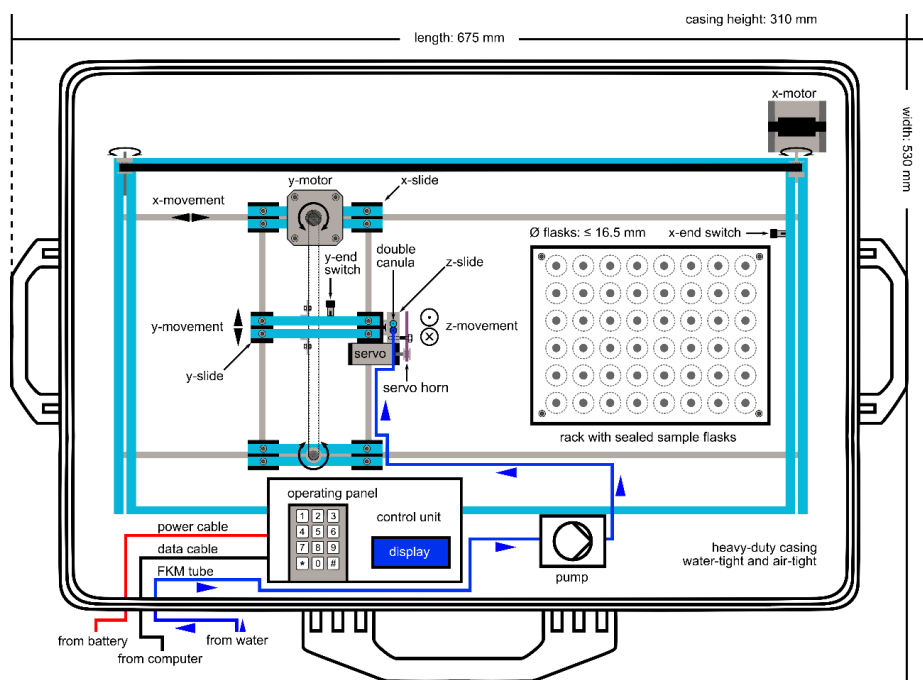
Fig. 1.Hardware design of the GUARD autosampler (top view, schematical). Water samples are pumped directly into vials that are permanently gastight by rubber septa. The shown set-up comprises 48 sample vials but the autosampler can be equipped with up to 160 sample vials at the given casing dimensions.

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Fig. 2. The automated fluid sampler GUARD in detail (left) and in operation (right) during a 5-day case study (Sect. 4carried out in the cave "Kleine Teufelshöhle" in the Franconian Switzerland region, Germany. At a 4-hour interval, a total of 22 dripwater samples were automatically collected for subsequent analysis of the carbon isotope values ($\delta^{13}C_{DIC}$) of the dissolved inorganic carbon (DIC).

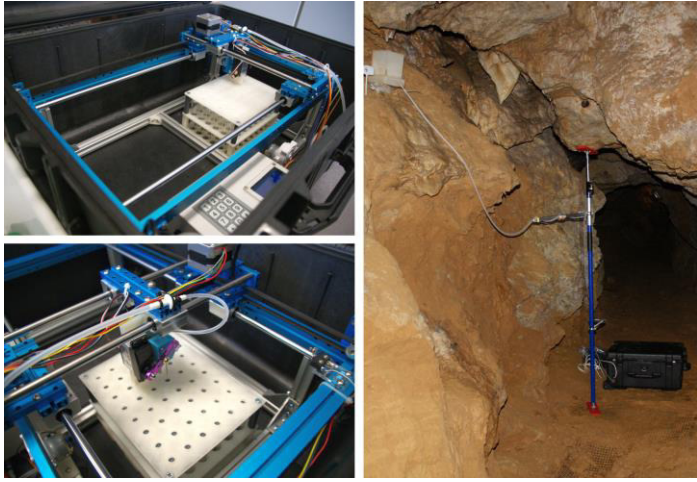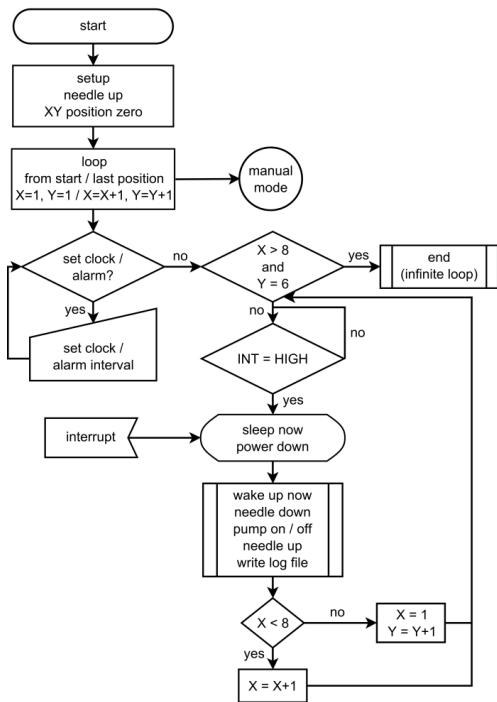**Fig. 3.** Flowchart illustrating the autosampler's operation for a setup comprising 48 sample vials in total, arranged in lines (X direction) of 8 and columns (Y direction) of 6 vials, respectively. Once the last sample has been collected, the program enters an infinite loop and waits for input from the operator.
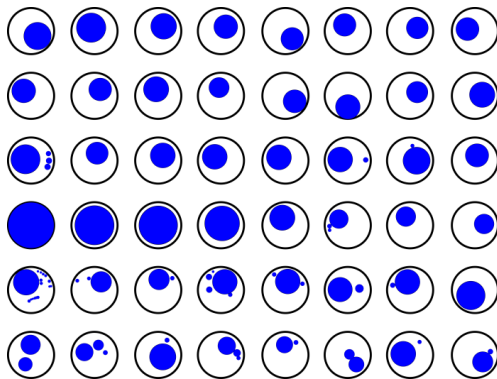
Fig. 4. Top view (digitised facsimile) of the sample vials (black circles) turned upside down in order to illustrate the air/gas bubbles (blue circles) remaining in the vials after sample injection.
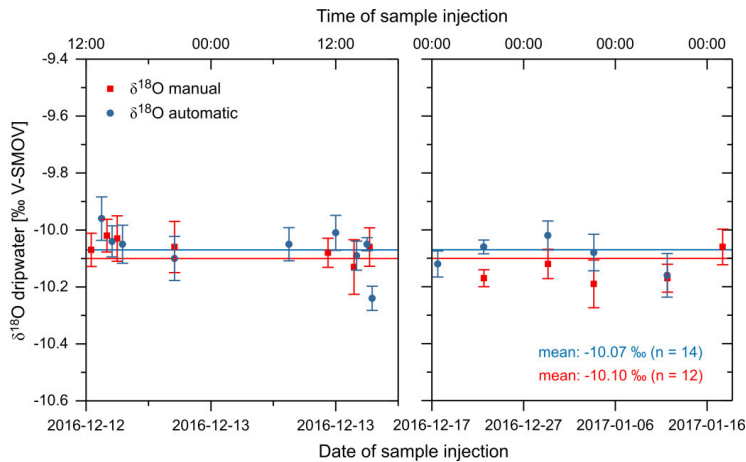
Fig. 5. First field testing of the GUARD autosampler: Oxygen isotope values (indicated as δ¹⁸O relative to the international standard V-SMOW) in dripwater samples from a specific drip site in the karst cave „Laichinger Tiefenhöhle" in the Swabian Alb region, southern Germany. Samples were collected automatically (blue circles) over the course of 33 days (December 13, 2016, to January 14, 2017) and supplemented by 12 samples collected manually (red squares) for comparison of both methods. **Error bars represent measurement uncertainty.** Blue and red horizontal lines indicate the overall arithmetic mean of each data set. Note the difference in scale of the x-axes of the two sub-plots. **Not all of the 33 samples were analysed for isotopic composition.**
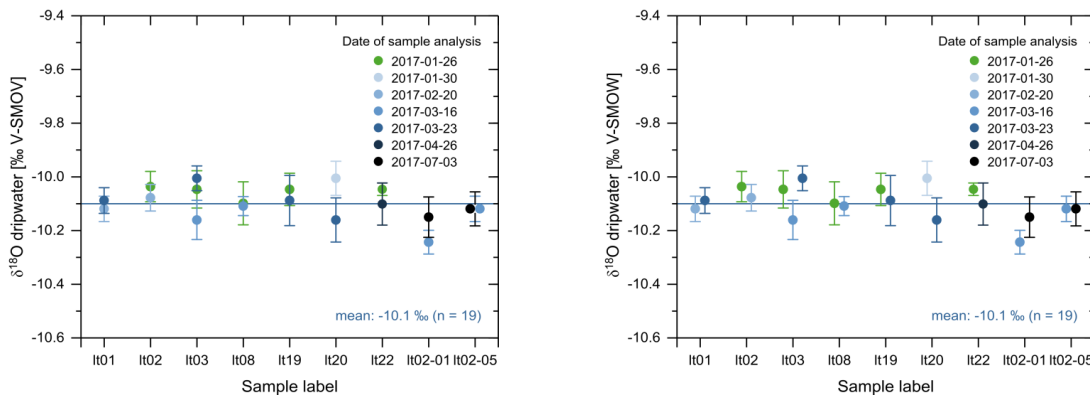
Fig. 6. Results of repeated δ¹⁸O measurements (circles in tones of blue) measured in the automatically collected samples together with the original δ¹⁸O data from ~~Fig. 5~~**Fig. 5** (green circles) plotted against their respective label ("lt" stands for Laichinger Tiefenhöhle). The darker the tones of blue, the later the respective measurement was repeated. **For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.**
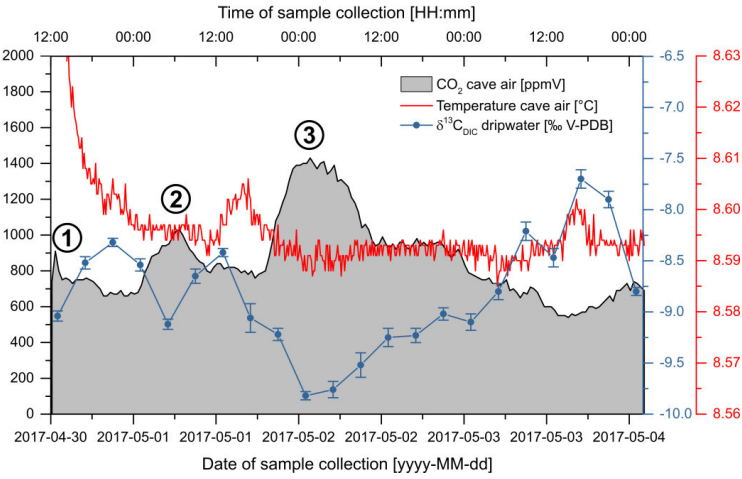
Fig. 7. Time series of T, CO_2 and $\delta^{13}C_{DIC}$ generated during a first case study applying the GUARD autosampler (units are given in the legend). Cave air CO_2 concentrations and dripwater $\delta^{13}C_{DIC}$ values correlate negatively. Main CO_2 peaks are highlighted with circled numbers.

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Fig. 8. Relationship between cave air CO_2 concentrations and dripwater $\delta^{13}C_{DIC}$ quantified based on the six maxima/minima recorded during the case study (black circles). The relationship can be fitted very well with a linear regression (red line).

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Tab. 1. Detailed description of the autosampler's integral components.

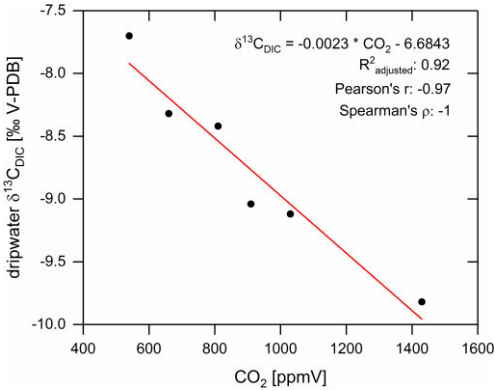| COMPONENTS	DESCRIPTION
Mechanical	
Casing	Peli®, model 1610, heavy-duty, water-tight and airtight, including a valve for automatic pressure purge
Z-movement: servo	Reely® Standard RS-610 MG, operating voltage 6.6 V, attached to the Z-slide containing the double-cannula via an elongated hole in the servo's horn
X-/Y- movement: motors	Sanyo Denki®, bipolar hybrid stepping motors, 1 A, 24 V, 1.8°/step, 0.265Nm, 4 wires
Pump	Peristaltic (flexible-tube) pump, model AP-40; operating voltage 12 V,
Sample vials	Labco Exetainer® 738W, soda glass, 12 mL, flat bottom, height (vial + cap) ≤ 101 mm; external ø ≤ 15.5 mm; internal ø ≥ 13.2 mm; including rubber septa with a thickness ≥ 3 mm
Tubing	Deutsch & Neumann®, FKM (synthetic rubber, "Viton"), Shore hardness 75, external ø ≤ 6.2 mm, internal ø 4 mm
Double cannula	Braun Sterican®, metal, external ø 0.60 mm; length excluding Luer-Lock connector 30 mm
Electronic	
Battery	Panasonic®, valve regulated Pb-acid battery 12 V, 20 Ah, maintenance-free, non-spillable, low self-discharge, 5.8 kg, 76 x 167 x 181 mm; ~~the sampler can also run on 12 V Li-ion batteries if weight is an important constraint~~
Microcontroller board	Arduino® Mega 2560 including an Atmel ATmega 2560 microcontroller with 54 digital I/O pins, 16 analogue inputs, 6 interrupt inputs, 4 serial interfaces, 1 I^2C interface and 4 KB EEPROM memory (non-volatile); hibernation mode-enabled
Real-time clock	RTC PCF8563 powered by a separate 3V lithium button cell battery as a buffer battery
Display	Liquid crystal display (LCD) with 2 lines à 16 characters
Other electronic components	operating voltage 5 V; 3 DC/DC converters; 2 stepping motor driver carriers: Pololu® A4988; relay board including 2 relays; keypad comprising the characters 1 to 9, * and #

Kommentar [AH26]: Referee 2 comment 8

Tab. 2. Comparison of the GUARD prototype with conventional autosamplers available on the market, represented here by the 3700C Compact from Teledyne ISCO (information retrieved from the manufacturer's website: www.teledyneisco.com)

PROPERTIES	"3700C COMPACT"	"GUARD"
gastight samples	No	Yes
sample frequency	1 min to 99 h 50 min	1 min to 168 h
estimated operating time (at a 2-day interval)	< 70 days	100 days
maximum number of samples vials	24	160
sample volume	0.375 to 9.45 L	< 12 mL
weight (incl. battery; excluding samples)	11.3 kg	13 kg (+5.8 kg battery)
weight (incl. battery and samples)	15.8 to 23.3 kg (depending on sample size and number)	18.8 to 20.7 kg (depending on sample number)
total outer dimensions	H: 70.5 cm; ø: 45 cm; V: 0.14 m³	H: 31 cm; L: 67.5 cm; W: 53 cm; V: 0.11 m³
rinse cycle(s) between samples	Yes, up to three	No
Liquid presence detector (automatic compensation for changes in hydraulic head)	Yes	No
Different modes of sample pacing (e.g. time, flow)	Yes	No

Kommentar [AH27]: Referee 1 comment 12

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General comments:

Referee Comment 1: <u>Carry-over effects</u>: 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)?

Authors' response 1: Carry-over effects might occur with the device setup as presented in our paper, in particular, as referee #1 points out, when the chemical composition varies strongly between consecutive samples. Carry-over effects could be effectively prevented by thoroughly flushing the tubing with sample water, either prior to sample pre-collection, or prior to sample injection. If such a flushing step is implemented, sample pre-collection becomes obsolete. During development of the presented device we regarded minimizing both the power-consumption and the technical complexity as a higher-priority requirement than preventing carry-over effects through flushing. However, a flushing step could still be implemented without the need of any fundamental changes to the current system. It is important to bear in mind that, in some sampling scenarios, flushing is not a viable option, especially in scenarios where the sample water is not provided in sufficient quantity or continuity, for example during rainwater or cave dripwater sampling. In sampling scenarios focussing on water isotopes, carry-over effects are likely to be minor as the water molecules to be analysed for oxygen isotope composition do not strongly bond to the tubing's wall, but are readily flushed out of the tubing during sample injection. Furthermore, the isotopic composition of natural waters is unlikely to change drastically between consecutive samples.

Referee Comment 2: If the sampling aims at analysing 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?

Authors' response 2: As the tubing is contained within a sealed case protecting the tubing and sample vials from sunlight, the probability of biofilm growth is already diminished compared to a system exposed to light. As some microorganisms are capable of forming biofilms in the absence of light, to further prevent the formation of biofilms, antimicrobial coatings could be applied to the inner walls of the tubing, such as antibiotics, biocides or colloidal silver coatings that are commonly used on medical devices to prevent infection (e.g. Ramasamy & Lee, 2016). The most practical solution to the potential problem of biofilm growth is probably the use of silver plated metal tubing instead of the FKM tubing presented in the paper.

Referee Comment 3: <u>Fractionation effects during sample storage</u>: During the third experiment you conclude that no alteration of the sample occurred because of the constant $\delta^{18}O$ values (Fig. 6). Do you get the same results when using d^2H? Since your samples were analysed with a LGR, both isotopes should be measured simultaneously.

Authors' response 3: Yes, the δD results (see Fig. 6b) also confirm the long-term stability of the samples: Again, if the vials were not airtight, evaporation would have led to a preferential removal of isotopically light water molecules from the water samples due to their higher vapour pressure (e.g.

Hoefs, 2015) and, consequently, to an increase of the δD value of the remaining water sample over time. Such a positive trend is not present in the δD data and the results from the repeated measurements agree well with the initial ones. The difference in δD values between initial and repeated measurements ranges from -0.30 ‰ (lt20 and lt23) to 0.70 ‰ (lt02-05), but averages out at 0.0 ‰ over all measurements (median also 0.0 ‰) indicating that there is no systemic discrepancy between initial and repeated analyses (Fig. 6b).
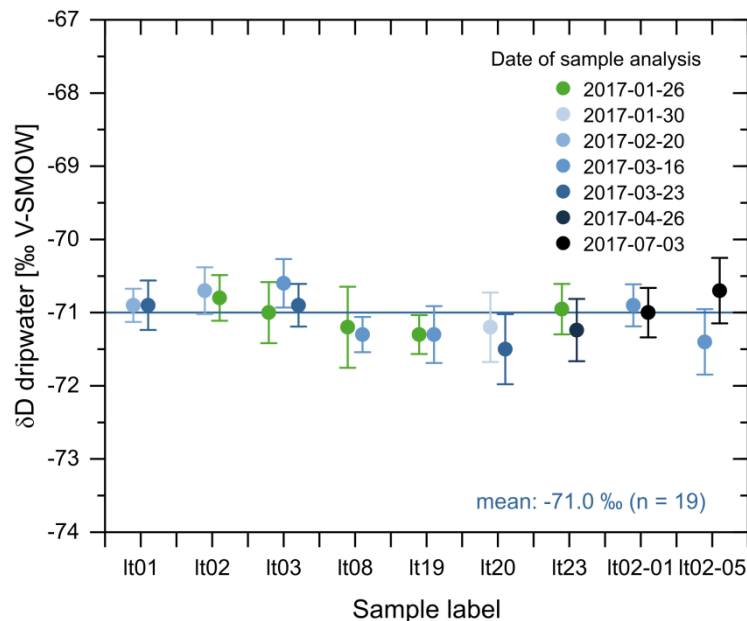

Fig. 6b: Results of repeated δD measurements (circles in tones of blue) measured in the automatically collected samples together with the original δD data from Fig. 5 (green circles) plotted against their respective label ("lt" stands for Laichinger Tiefenhöhle). The darker the tones of blue, the later the respective measurement was repeated.

Changes to the manuscript: Insert Fig. 6b in the Supplements and include a reference to Fig. 6b in the text.

Referee Comment 4: Check-standard during long-term sampling: In the case study, the GUARD system was operating over a period of 5-days and $\delta^{13}C$ was measured in the 22 drip water samples. How can you be sure that the $\delta^{13}C$ 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 $\delta^{13}C$ in addition to the drip water samples. I would recommend to at least address this issue in the interpretation section of the results.

Authors' response 4: The purpose of the case study performed in the cave "Kleine Teufelshöhle" was to monitor the changes in dripwater $\delta^{13}C_{DIC}$ values with varying cave pCO_2 after the dripwater had equilibrated with the cave atmosphere via CO_2 degassing. Therefore, if potential drift effects or alterations in dripwater $\delta^{13}C_{DIC}$ values caused by sample processing were to be examined using a check-standard of known $\delta^{13}C_{DIC}$, this standard would have to be treated exactly as the sampled dripwater, i.e. allowed to degas prior to sampling. This would however alter the $\delta^{13}C_{DIC}$ value of the standard, depending on the varying pCO_2 difference between dripwater and cave atmosphere, thus inevitably hampering the use of the check-standard as a control with known $\delta^{13}C_{DIC}$. However, an aliquot of the CO_2-equilibrated check-standard could be sampled manually and injected into an airtight sample vial with a double-cannula syringe, shortly before another aliquot of the check-

standard is collected automatically by the GUARD autosampler. Comparison of the $\delta^{13}C_{DIC}$ values of both "samples" should enable for detecting any potential sample alterations during automatic sampling. In agreement with the comment of referee #1, we will address the issue of potential sample alterations in section 4.4.

Changes to the manuscript: Insert at the end of section 4.4: "We note that potential drift effects or sample alterations that might be caused by the automatic sampling process have not yet been examined in detail. Corresponding tests using check-standards of known $\delta^{13}C_{DIC}$ values will be performed in future studies."

Referee Comment 5: <u>Harsh conditions</u>: 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°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?

Authors' response 5: The statement that the GUARD autosampler is applicable under harsh conditions mainly refers to its rugged water-tight casing and its ability to prevent damage from extreme weather conditions (e.g. water or dust ingress, high humidity, etc.) and to protect the samples from any external interference, e.g. from animal activity. However, this statement can be expanded to include the samples, too: Once, the samples are injected in the airtight vials, evaporative fractionation as well as other forms of sample alteration are effectively prevented, regardless of ambient air temperature or temperature fluctuations. It is certainly true that the sample is most prone to change during pre-storage in the FKM tubing. During this phase of the sampling, evaporative fractionation is at least minimised through two mechanisms: First, the FKM tubing is highly impermeable to gases and thus impedes evaporation and/or gas exchange through its walls. Second, evaporation can only occur over a very small surface of only about 12.6 mm^2 thanks to the small inner diameter of the tubing of only 4 mm. Furthermore, sample pre-storage inside the tubing is not necessary if sample water is provided in sufficient quantity and continuity, for instance, when sampling water from rivers, lakes or the ocean. In these cases, the sample can be injected directly into the sample vial and is therefore almost instantly sealed from the surrounding atmosphere.

Specific comments:

Referee Comment 6: 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.

Authors' response 6: The sampling interval is correctly stated as daily, however, not all of the 33 samples were analysed for $\delta^{18}O$ values.

Changes to the manuscript: Add at the end of the caption to Fig. 5: "Not all of the 33 samples were analysed for isotopic composition."

Referee Comment 7: 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 means would be invalid.

Authors' response 7: While all of the manually collected samples were analysed for $\delta^{18}O$ values, not all of the hourly samples collected by the autosampler were measured. However, the sum of 16 samples over a period of 26.5 hours is sufficient to establish that there is a certain variation in dripwater $\delta^{18}O$ values on time scales as short as 30 minutes. The (absolute) standard deviation for the 14 automatically collected samples is 0.07 ‰ and 0.06 ‰ for the 12 manually collected samples. Based on the small difference of only 0.03 ‰ between the arithmetic mean $\delta^{18}O$ values calculated for both sample types, we concluded that there is no systematic discrepancy between the automatically and the manually collected samples. This conclusion holds true even if dripwater $\delta^{18}O$ values vary on time scales as short as 30 minutes as this variation includes both positive and negative excursions from the long-term mean values.

Referee Comment 8: P6 L2-3: Why didn't you simply weight the vials before and after filling in order to quantify the sample volumes?

Authors' response 8: Weighing the vials before and after sample injection is another way of quantifying the sampled volumes. As the sample vials were almost entirely filled during the various test runs we conducted, quantifying the sampled volumes by means other than visually confirming that only small air bubbles remained after sample injected simply did not seem necessary.

Referee Comment 9: P7 L 27: Sampling for 5 days, every 4 hours would yield 30 samples, not 22. What happened to the remaining 8 samples?

Authors' response 9: The remaining 8 samples could not be successfully collected during the case study due to an imprecise positioning of the sample slide and double-cannula at the position of sample 24. We have already been able to trace this positioning error to a faulty motor driver. We have therefore installed a new motor driver and achieved both precise and reliable positioning results since this change.

Referee Comment 10: 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.

Authors' response 10: The error bars represent the precision of each individual measurement. It includes the precision of the ten internal sweeps performed by the mass spectrometer on a single sample and the precision of multiple (two to three) measurements of the same sample. The error is propagated using the formula x= (a^2+b^2)^0.5, with x being the propagated error and a and b representing the two error types outlined above.

Changes to the manuscript: We will include the measured δD values in the Supplementary.

Referee Comment 11: 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.

Authors' response 11: We have changed Fig. 6 so that the data points do not overlap any more. As 7 different measurement dates need to be illustrated in this figure, indicating the different measurement dates with different data point symbols or shadings is neither practical nor intuitive in this case. We suggest to include in the figure's caption "For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper."

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

Authors' response 12: That is correct. The sample volume can be defined by changing the duration of the pumping step during sampling. Headspace is minimal if the vials are filled to the maximum.

Changes to the manuscript: We will include a ≤ sign in Tab. 2.

References

Ramasamy, Mohankandhasamy; Lee, Jintae (2016): Recent Nanotechnology Approaches for Prevention and Treatment of Biofilm-Associated Infections on Medical Devices. In: *BioMed research international* 2016, S. 1851242. DOI: 10.1155/2016/1851242.

Authors' response to short comment 2

Reader Comment 1:

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 1: 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 2: 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 2: 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 3: (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 3: 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 4: (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 4: 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).
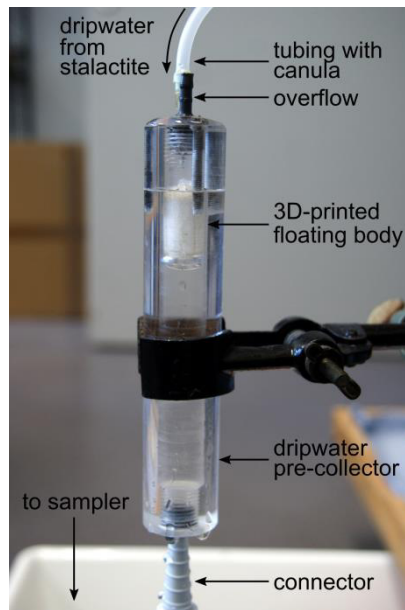
Fig. 1: Pre-collector used during the case studies.

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 S6). 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 5: 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

Referee Comment 1:

    I.   **Validity and claims:**

The authors claim that their device prevents contact with the environment, including evaporation of the sample, after the sample is taken. They demonstrate in their fieldwork in the karst cave that their samples are statistically identical to manual samples. They furthermore show that their samples do not deteriorate over time by repeating the measurements. The question I have:

    1.   I would expect an autosampler to take measurements at regular intervals. However, in Figure 5 the samples seem to be taken at rather random times. Can the authors explain why this is?

Authors' response 1.1: The karst dripwater samples for which Fig. 5 shows the $\delta^{18}O$ values, have been collected automatically using the GUARD autosampler at (regular) hourly intervals from 13:30 o'clock on December 12, 2016 to 07:30 o'clock on December 13, 2016 and from 12:00 o'clock to 15:00 o'clock and at daily intervals from December 13, 2016 to January 14, 2017. However, not all of the collected samples were analysed for isotopic composition. This is why the samples seem to be unevenly spaced in time. As referee #1 deduced an incorrectly stated sampling interval, we will mention at the end of the caption to Fig. 5 that not all of the collected samples were also analysed.

Changes to the manuscript: Add at the end of the caption to Fig. 5: "Not all of the 33 samples were analysed for isotopic composition."

    2.   The authors substantiate their claim that the samples are kept airtight by placing them in a fridge for a considerable amount of time. However, there is no control to compare against, i.e. no open samples that are exposed to evaporation in that fridge. It is hard for the readership to judge the amount of expected evaporation had the samples not been properly sealed. I would find it unreasonable to ask the authors to redo their experiments, but would like to ask them to provide the readership with an estimate of expected evaporation in the setting of their fridge (8 °C, high humidity I guess?) based on literature values. This will help to show that indeed, their samples are sealed properly.

Authors' response 1.2:

We agree with referee #2 that we could have demonstrated the airtightness of the sample vials after sample injection even better had we implemented control samples that are not entirely sealed from the atmosphere and thus exposed to evaporation. To compensate for that caveat and to provide the readership with a notion of the effect of evaporation on the sample $\delta^{18}O$ values, we have calculated both evaporation and $\delta^{18}O$ change for the conditions prevalent in our fridge. Despite being set to 8 °C, the temperature in the fridge was measured to be 11.2 °C, relative humidity was 24 % according to measurements. Based on these conditions and assuming an opening of the sample vial of 5 % to imitate a minor lack of airtightness, evaporation was calculated using a formula that has proven adequate for inactive indoor swimming pools that are not influenced by direct sunlight or wind (Smith, Löf and Jones, 1994) using a water density of 1 g/cm^3:

$$\frac{\dot{m}}{A} = \frac{(30.6 + 32.1 * v_w)(P_w - P_a)}{\Delta H_v}$$

where $\dot{m}/A$ is the evaporation rate [kg/(m^2 hr)], v_w is the air velocity over the water surface [m/s],

P_w is the saturation vapour pressure at the water temperature [mm Hg], P_a is the saturation vapour pressure at the air dew point [mm Hg] and ΔH_v is the latent heat of water at the pool temperature [kJ kg].

The $\delta^{18}O$ value of the residual water remaining at each given time was calculated on the basis of a fractionation factor α between water and vapour according to the following formula (e.g. Clark and Fritz, 1999):

$$1000\, ln \propto_{water-vapour} = 1.137\left(10^6/T_k^2\right) - 0.4156(10^3/T_k) - 2.0667$$

where T_k represents the temperature of the phase change [K] and on the following relationship (e.g. Hoefs, 2015):

$$\frac{R_w}{R_{w0}} = f^{(\frac{1}{\propto}-1)}$$

where R_w is the isotope ratio of the water at a given time [‰ V-SMOW], R_{w0} is the initial isotope ratio of the water [‰ V-SMOW], and f is the fraction of the residual water [-]. The results of these calculations (Fig. 1) demonstrate that even a small slit in a sample vial's rubber septum equalling only 5 % of the vial's inner cross section leads to a substantial shift towards higher $\delta^{18}O$ values in the residual water over time. After three months (90 days), for instance, $\delta^{18}O$ values have risen from -10.1 ‰ by about 1.3 ‰ to -8.8 ‰. The difference between the lowest and the highest $\delta^{18}O$ value in Fig. 6 of the manuscript is still below 0.3 ‰, while those data points span a longer period of six months. Most importantly, there is no positive trend in the $\delta^{18}O$ values in Fig. 6 of the manuscript which illustrates the sample vials are sealed properly, even after sample injection.
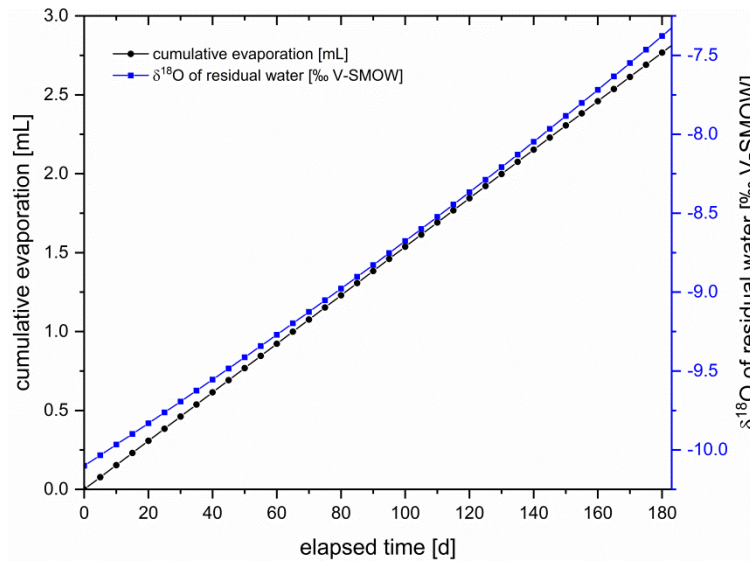
Fig. 1: Effect of evaporation on the $\delta^{18}O$ value of the residual water in a 12 mL sample vial at a temperature of 11.2 °C and a relative humidity of 24 %.

Changes to the manuscript: We will add Fig. 1 in the authors' response to the Supplementaries including the corresponding explanations as above. In the manuscript, we will insert a shortened version of these explanations at the end of Section 3.3 (page 7, line 3).

Referee Comment 2:

II.   Open Science and reproducibility:

HESS is a fully Open Access journal and the editors also actively advocate for Open and Reproducible Science in general. In this spirit I think that although the article as it now stands informs the readership about the existence of the new autosampler, it does not allow hydrologists to start using it. The provided technical details are insufficient to rebuild the GUARD using just this article. If the authors intended this (because they maybe want to pursue manufacturing the GUARD commercially?) then I think that HESS might not be the ideal outlet to promote it, it is after all a non-for-profit Open Access Scientific journal, not a commercial advertisement leaflet.

I hope the authors did intend the GUARD to be re-buildable by other hydrologists, which would be completely in the spirit of Open Hardware, the movement spearheaded by the Arduino which the authors use as main CPU. By providing a flowchart of their code and their electrical circuitry the authors do hint that this is their intention. For the GUARD to be fully re-buildable I would ask the authors to add:

1. A detailed technical drawing of the physical device, including sizes of all components

Authors' response 2.1: Any user of the GUARD autosampler would benefit from it the most if the sampler's dimensions are precisely adapted to the user's specific requirements. Therefore, the exact dimensions of the GUARD device presented in the manuscript are not relevant as the device dimensions should be regarded flexible rather than fixed. The necessary minimum dimensions mainly depend on the number of sample vials needed. In the setup presented in the manuscript the GUARD autosampler comprises 48 sample vials, but can be equipped with up to 160 sample vials at the given casing dimensions by maximising the dimensions of the sample rack (to the left side in Fig. 1 in the manuscript) and by reducing the space between adjacent sample vials to zero. If a higher number of sample vials is needed, the sampler dimensions need to be adapted accordingly. Only few components of relevant size have fixed dimensions (Table 1). All x-profiles and guides that form the framework within which the x- and y-slides move have to be cut to fit into the chosen casing.

Table 1: Integral components of the GUARD autosampler of relevant size

COMPONENTS	Description	Dimensions
Mechanical		Length x Width x Height
Z-movement: servo	Reely® Standard RS-610 MG, operating voltage 6.6 V, attached to the Z-slide containing the double-cannula via an elongated hole in the servo's horn	40x20x42 mm
X-/Y- movement: motors	Sanyo Denki®, bipolar hybrid stepping motors, 1 A, 24 V, 1.8°/step, 0.265Nm, 4 wires	42x42x24 mm
Pump	Peristaltic (flexible-tube) pump, model AP-40; operating voltage 12 V,	55x50x42 mm

Changes to the manuscript: Add Table 1 in the authors' response to the Supplementaries.

2. A Bill of Materials akin to their Table 1, but with more detail. At least the price and an (online?) location where the parts can be bought at the time of publishing should be included.

Authors' response 2.2 / Changes to the manuscript: We will add the following Bill of Materials to the Supplementaries

Components	Description	quantity	cost/unit	total cost	company	purchase order no.
Mechanical						
Casing	Peli®, model 1610, heavy-duty, water-tight and airtight, including a valve for automatic pressure purge	1	252.35 €	252.35 €	Waterproof-Cases	-
Z-movement: servo	Reely® Standard RS-610 MG, operating voltage 6.6 V, attached to the Z-slide containing the double-cannula via an elongated hole in the servo's horn	1	12.60 €	12.60 €	Conrad Electronic	1365925 - 05
X-/Y- movement: motors	Sanyo Denki®, bipolar hybrid stepping motors, 1 A, 24 V, 1.8°/step, 0.265Nm, 4 wires	2	38.95 €	77.90 €	RS Components	829-3499
Pump	Peristaltic (flexible-tube) pump, model AP-40; operating voltage 12 V,	1	19.90 €	19.90 €	Gemke Technik GmbH	APE40CD12V
Sample vials	Labco Exetainer® 738W, soda glass, 12 mL, flat bottom, height (vial + cap) ≤ 101 mm; external ø ≤ 15.5 mm; internal ø ≥ 13.2 mm; including rubber septa with a thickness ≥ 3 mm; 48 vials of 300 in a packaging unit	1	22.28	22.28 €	IVA	IVA738W
Tubing	Deutsch & Neumann®, FKM (synthetic rubber, "Viton"), Shore hardness 75, external ø ≤ 6.2 mm, internal ø 4 mm	3	12.90 €	38.70 €	häberle Shop	9.205 765
Double cannula	Braun Sterican®, metal, external ø 0.60 mm; length excluding Luer-Lock connector 30 mm	2	3.40 €	6.80 €	häberle Shop	7.079 505
Framework for slide movement	Makeblock XY Printer	1	269.95 €	269.95 €	Eckstein	MB90014
Electronic						
Battery	Panasonic®, valve regulated Pb-acid battery 12 V, 20 Ah, maintenance-free, non-spillable, low self-discharge, 5.8 kg, 76 x 167 x 181 mm; the sampler can also run on 12 V Li-ion batteries if weight is an important constraint	1	75.03 €	75.03 €	Voelkner	S167901
Microcontroller board	Arduino® Mega 2560 including an Atmel ATmega 2560 microcontroller with 54 digital I/O pins, 16 analogue inputs, 6 interrupt inputs, 4 serial interfaces, 1 I^{2}C interface and 4 KB EEPROM memory (non-volatile); hibernation mode-enabled	1	21.99 €	21.99 €	Conrad	1409778 - 05
Real-time clock	RTC PCF8563 powered by a separate 3V lithium button cell battery as a buffer battery	1	10.91 €	10.91 €	Conrad	1195070 - 05
Display	Liquid crystal display (LCD) with 2 lines à 16 characters	1	9.87 €	9.87 €	Conrad	183045 - 05
Other electronic components:	relay module	1	8.52 €	8.52 €	Exptech	EXP-R25-187
	drivers for stepping motors	2	7.95 €	15.90 €	Exptech	EXP-R25-001
	casing for control panel	1	5.28 €	5.28 €	Conrad	522641-99
	DC/ DC converter 12V	1	12.00 €	12.00 €	Conrad	154170-05
	DC/ DC converter 5V	1	2.65 €	2.65 €	Conrad	157954-05
	DC/ DC converter 6,5V	1	5.82 €	5.82 €	Conrad	156674-05
	CR2032 3V lithium button cell battery as a buffer battery	1	2.26 €	2.26 €	Conrad	1086225-05
	USB service interface FrontCom® Micro IE-FCM-USB-A Weidmüller	1	20.35 €	20.35 €	Conrad	746885-05
	Membrane keypad Matrix 1 x 12 SU709948	1	11.11 €	11.11 €	Conrad	1341283-62
	3D print-outs (sample rack, connectors, double-canula adapter)	1	15.00 €	15.00 €	-	-
	Aluminium slot profiles 20x20 mm Slot 5 (m)	1	2.94 €	2.94 €	Motedis	19586
	Sliding nuts Slot 5 100 pieces	1	21.42 €	21.42 €	Motedis	96214
	Screw DIN 7984 M4x10 Slot 5	100	0.12 €	12.00 €	Motedis	-
	Bracket 20x40 I-type Slot 5 10 pieces	3	7.50 €	22.50 €	Motedis	093W202N05
	Swivel Feet. Series 10 PA; foot 40, threaded rod 5x60 4 pieces	4	1.00 €	4.00 €	Motedis	-
	Miniature sliding rail IGUS drylin TK-04	1	10.16 €	10.16 €	IGUS	TS-04-07
	CNC Aluminium Servo Horn 60mm for Futaba servos 25 teeth	1	6.90 €	6.90 €	Ebay	251439671553
	Cable gland PG7 Polyamide black (RAL 9005) KSS EGRWW7 water-tight	1	0.34 €	0.34 €	Conrad	533738-05
	zip ties different sizes 200 pieces	1	3.80 €	3.80 €	Conrad	541665-62
	USB cable PC/Sampler	1	4.29 €	4.29 €	Conrad	1592198-62
	Merck® silicone grease for sealing 100gr.	1	68.70 €	68.70 €	häberle Shop	1.07746.0100
	Hose fitting, straight, 4040	10	2.15 €	21.50 €	häberle Shop	9.207 801
	Total			**1,095.72 €**		

3. A step by step build guide. This could be hosted on an external website like instructables.com and linked to in the article, it could also be provided as supplementary material

Authors' response 2.3: We find the idea of referee #2 of a step-by-step build guide highly intriguing and would like to provide such a guide in the near future, being aware of the potential benefit it might have for researchers and other users who want to build their own GUARD autosampler. However, considering the complex process required building the GUARD autosampler with its many steps and including multiple custom adaptions involving 3D-printouts, we hope that the referees and the editors of HESS understand that a complete step-by-step build guide is clearly beyond the scope of this journal article, even for the Supplementaries. As we certainly do intend to make the GUARD autosampler available to potential users in research and other fields and bearing in mind the complexity of the building process, however, we would like to offer these users our advice during their building process until a step-by-step guide can be provided. As another way of making the GUARD autosampler accessible for the scientific community and other groups, we might lend our device to interested users, of course free of charge. We hope that the referees and the editors of HESS can accept one or both of the offered solutions.

Minor points:

Referee Comment 3: The opens lab at OSU is also working on an autosampler, with a completely different setup. Might be worth citing their work: http://www.open-sensing.org/opensampler/. They have a paper forthcoming, but did present it at the AGU fall meeting (where I spotted it). Maybe that abstract can be cited.

Authors' response 3: We will mention the OPEnSampler and cite the conference abstract, as suggested.

Changes to the manuscript: Insert at the end of page 2: "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".

Referee Comment 4: On line 3 of page 3 the terms "high frequency, long term monitoring" etc. are used. What constitutes high frequency of long term is very dependent on the field of science one is in. Please make this more specific to the GUARD.

Authors' response 4: We will specify the time scale referred to in the manuscript.

Changes to the manuscript: On page 3 in line 3 replace line by "either high-frequency sampling (e.g. every minute), long-term monitoring (e.g. 6 months), or medium-term monitoring at medium sampling frequency (e.g. daily sampling for 48 days)."

Referee Comment 5: On page 3, line 6: I had to look up what "septa" is. Maybe this is because I'm not a native English speaker. If septa is considered a technical term, please explain it once you introduce it for the first time.

Authors' response 5: We will define the term upon its first appearance in the manuscript.

Changes to the manuscript: On page 3, in line 6 insert after "septa": "(engineered membranes that permit the transfer of fluids without air contact, usually using a double-canula)"

Referee Comment 6: On page 4, line 24: Future work might be better placed in the discussion, although mentioning it at both places is also fine.

Authors' response 6: Connection multiple batteries in parallel, replacing discharged batteries using an electrical bypass and operating the GUARD autosampler on mains power using an appropriate rectifier are options viable for any battery-powered autosampler. Therefore, these options mentioned on page 4, in line 24, do not distinguish the GUARD autosampler from any other autosampler such as the 3700C Compact from Teledyne Isco. For that reason, we think that mentioning these options again in the discussion (Section 5) would be redundant and inappropriate.

Referee Comment 7: On page 6, line 4: "effectively prevented" assumes certain demands from applications. I suggest replacing it with something like: "prevented for most common use cases".

Authors' response 7: As there might be applications we might not have considered, we agree to change the passage.

Changes to the manuscript: On page 6, in line 4 delete "effectively".

Referee Comment 8: On page 18, table one: Sentences like "the sampler can also run ... ... important constraint" are more suited in the discussion.

Authors' response 8: We agree with referee #2 and will remove the indicated sentence.

Changes to the manuscript: On page 18, in Table 1 in line "Battery" remove the remark "the sampler can also run on 12 V Li-ion batteries if weight is an important constraint" and insert it on page 4 in line 29 at the end of the paragraph.

References

Clark, Ian D.; Fritz, Peter (1999): Environmental isotopes in hydrogeology. [2. print., corr.]. Boca Raton: Lewis Publ.

Hoefs, Jochen (2015): Stable isotope geochemistry. 7. ed. Cham: Springer (Earth Sciences).

Nelke, Mitch; Selker, John, S.; Udell, Chet (2017), The OPEnSampler: A Low-Cost, Low-Weight, Customizable and Modular Open Source 24-Unit Automatic Water Sampler, Abstract H41J-1596 presented at 2017 Fall Meeting, AGU, New Orleans, LA, 11-15 Dec.

Smith, Charles, C.; Löf, George; Jones, Randy (1994): Measurement and analysis of evaporation from an inactive outdoor swimming pool. In: Pergamon 1994, pp. 3-7.

Authors' response to short comment 1

Reader Comment 1:

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 1: 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 2: 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 $\delta^{18}O$, δ^2H, and partly ^3H. 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 2: 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 <u>supplement</u> 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 3: Would they still use a peristaltic pump or would the rainwater flow into the vials by gravity?

Authors' response 3: 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 4: Would they use the same vial number (48) and size (12 mL)?

Authors' response 4: 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 5: How would they approach programming collection intervals, without knowing when it will rain?

Authors' response 5: 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).
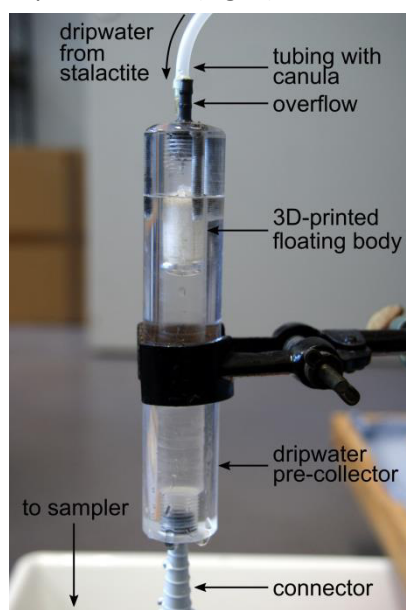

Fig. 1: Pre-collector used during the case studies.

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 S6). 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 6: Could their sampler also be used at GNIP sites exhibiting harsh conditions (i.e., a warm and arid climate)?

Authors' response 6: 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 7:

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 7: 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.