Response to RC1:

Dear Dr. Hut,

Thank you very much for your thoughtful comments on our manuscript. Please find below your reproduced comments, followed by our responses.

COMMENT: I've read the paper "Technical note: A microcontroller-based automatic rain sampler for stable isotope studies" with great interest. I think it is highly relevant for the readership of HESS and recommend publishing it. I only have a minor suggestion that could (hopefully) make the article even more useful to the hydrological community.

RESPONSE: *Thank you for this positive and motivating evaluation. We are confident that your suggestions indeed improved our manuscript.*

COMMENT: On reproducibility: I applaud that the authors make their design completely open so the community can reproduce it for their own work. However, I have two issues with the way the material is presented. Firstly, providing a Bill of Materials, technical drawings, software and even an operation manual might not be enough for hydrologist to be able to re-produce the work of the authors. I would strongly recommend to add a "build guide" document to the (impressive) list of documents that the authors already provide. This build guide would detail, step by step, how to construct the sampler. For example, currently it is unclear what fabrication techniques to use in construction of the sampler. I recommend using a site like instructables.com for their comprehensive format and exporting the resulting instructable as a pdf.

RESPONSE: *We agree that the assembly of the collector parts is not fully self-explanatory and that a build guide is a useful addition to the material included in our initial submission. Hence, we have compiled such a build guide and hope that it will facilitate the construction for others.*

COMMENT: On archiving: Given the target of the authors "to enable reproduction" and the general nature of institute website designs (and corresponding URLs) to change every season, I would not advice to use an institute website as the main repository for the results of this work. I strongly urge the authors to make all material currently available on https://www.ufz.de/index.php?en=44048 (and the requested build guide, see above) available

- as supplementary material to this publication

- or publish it on Github and create a DOI through Zenodo

RESPONSE: *We now include all mentioned material in the supplement of the paper (instead of using github) to ensure that interested readers can obtain the paper and all related data from a single source. That said, we will maintain the initially mentioned website (https://www.ufz.de/index.php?en=44048) – not as an exclusive primary data source, but to announce updates, new developments, etc.*

As we have been contacted and asked for 3D files (for 3D printing of selected parts), we now also provide .stl files in the supplement.

COMMENT: on code, power consumption and re-usability: I understand the choice for C as a language to program the microcontroller, given the need for low power consumption. I've briefly scanned the code and it is well documented. I particularly like that the section on event based sampling instead of time based sampling is already present, but commented out for now. The C language however has a steep learning curve. Many hydrologist that work in making sensor systems use the Arduino ecosystem

for that reason. Since controlling a stepper-motor is the main action on the sampler, I believe that this could be achieved in the Arduino eco-system, at the cost of greater power consumption. Since there is ample room for a solar panel on top of the sampler, low power might not always be the main concern. I would like to ask the authors to add a sentence or two that the functionality of the sampler could be achieved with parts from the Arduino eco-system as well, although at the cost of greater power consumption.

Concluding, I really like the work presented, recommend it for publication in HESS with only a few minor changes suggested.

RESPONSE: *We also have the impression that Arduino microcontrollers are rather popular in the community. Hence, we followed your suggestion and added the following sentence in section 5 (Potential modificstions): "Although we used a Texas Instruments microcontroller, we can imagine that the functionality of the sampler could also be achieved with parts from the popular Arduino ecosystem, though probably at the cost of greater power consumption."*

Best regards,

Nils Michelsen (on behalf of the author team)

Response to RC2:

Dear Dr. Groening,

Thank you very much for your valuable comments on our manuscript. Please find below your reproduced comments, followed by our responses.

COMMENT: Dear colleagues, I have read with interest this interesting manuscript on the design of an automated rain sampler minimising evaporation and therefore ensuring scientifically sound data for stable isotope process studies. The manuscript is well structured and provides a wealth of references to see the state of the art in recent efforts to ensure proper precipitation sampling for stable isotope analysis. I appreciate very much the details revealed by the authors to enable reproduction of such analyser in self-made mode, therefore probably minimising costs for most users having access to a workshop. The scientific findings are relevant, presented appropriately and comprehensively. The indicated very low energy consumption and use of cheap commercial batteries is a key advantage for successful application in many remote sampling scenarios. The setup may not be fully suitable for very cold conditions (anyway not below water freezing point). The experimental setting is solid and provides evidence of negligible isotopic fractionation due to minimal unavoidable evaporation. There are only few minor comments to potential users to improve the impact of the paper and minimise problems.

I did not find details on how to connect tubes through the caps into the individual bottles (two connections necessary per cap). This could be seen as very minor issue, but the connection through the cap needs to be completely air tight to atmosphere. One photo would suffice to clarify it.

RESPONSE: *Thank you for this positive and motivating evaluation. Concerning the tubing connections through the bottle caps, we have to admit that this crucial point was indeed not emphasized in our initial manuscript. We use cable grommets that also appeared in the bill of materials, but probably this aspect deserves more attention in the main text. We now added the following sentence:*

"All tubes are guided through the bottle caps by means of cable grommets (Fig. S2), ensuring a tight connection."

In the Supplement, we now provide additional details:

"Tubing-bottle connections

The water and air tubes are guided through the bottle caps by means of cable grommets. The used KAB SNAP 9 cable grommets (see bill of materials) are suitable for tubing diameters between 5.0 and 7.0 mm. They were installed by drilling two 16 mm bores into the bottle caps and pushing the conical part of the grommets through the bores."

Moreover, we now include a photograph.

COMMENT: One minor comment is related to the isolation of bottles after moving the upper disk to the next bottle position as discussed in section 2. This is the moment when each isolated bottle is keeping its actual air pressure at the time of closure, with its internal pressure not anymore being equilibrated via the tubing (page 3, line 15). The experimental data in Table 1 show in general an increased evaporation for hermetically closed bottles versus one bottle open to the atmosphere via a long tube (section 3.2.1, page 4 line 34). This could be caused by the atmospheric pressure fluctuations, resulting in periods of higher or lower pressure in the bottle versus the open atmosphere, and may induce pressure induced air flow and leakages (it is nearly impossible to keep a large area flat sealing pressure tight). The increase of losses with increased water amount could point to a solubility issue (slow penetration of liquid water according to filling height through plastic material).

RESPONSE: *We agree – it is very likely that pressure fluctuations (mostly triggered by the diurnal temperature regime) play a role, particularly if small leakages occur (very likely). Also the filling status of the blocked bottles seems to be relevant in terms of water losses. Hence, we have modified the corresponding paragraph in section 3.2.1 accordingly:*

"These data suggest that the diffusive loss through the tubing material of the connected bottles (two tubes per bottle, hence 0.28 g; see tubing loop data) is similar to the flux through the bottle material of Bottle 6 (0.24 g). As all connected bottles exhibited greater absolute mass losses, additional leakages, e.g. at the cable grommets in the bottle caps or at the distribution unit, seem likely. In this context, pressure fluctuations, induced by the diurnal temperature regime, probably play a role. It is also noteworthy that the blocked bottles 4 and 5, containing 300 and 400 mL of water, showed the greatest losses (> 2 g). This observation could point towards an influence of the bottle surface area in contact with liquid water on the diffusive water flux through the plastic. Nevertheless, the overall absolute losses are still rather small, particularly when compared to the worst case scenario, an unprotected bottle (Bottle 7)."

COMMENT: A second comment is related to the bottle types. I did not find an address for the provider of suitable bottles. However the quality of bottles is of major influence for such study. At the IAEA we have previously (2004) performed long term experiments with nearly 60 different bottle types used for regular water sampling, all filled with same water in triplicate and kept for 6, 12 and 18 months before analysis, recording the weight loss and isotopic shift. After 12 months more than half of bottle types showed evaporation losses above one percent of water weight, associated to delta18O changes of above 0.5 permille. Therefore the proper selection of bottle type is crucial for storage. Glass bottles could be perfect (however even some glass bottle types (!) caused evaporation by imperfect fitting of glass surface to plastic caps), but in most cases high quality HDPE bottles showed best performance at moderate price and robustness.

Overall the paper is of excellent quality and should definitively be accepted. Best regards, Manfred Gröning m.groening@iaea.org

RESPONSE: *In our initially submitted manuscript, we mentioned our supplier, but admittedly quite late – in section 3.1 where we describe the methodology of our evaporation experiment. In section 2 outlining the design, we had tried to keep out suppliers to not impede reading flow and because the section was meant to only describe the principle of the collector. However, we agree that suitable bottles are crucial and hence added the following sentence upon first mention of the bottles, i.e., in the Design section:*

"With respect to the bottles, we recommend thick-walled HDPE bottles that effectively reduce diffusive water losses (Spangenberg, 2012; personal communication Manfred Gröning, IAEA, https://doi.org/10.5194/hess-2019-93-RC2). For our purposes, we selected 500 mL HDPE wide-mouth bottles by Labsolute (Renningen, Germany; wall thickness approx. 1.7 mm)."

Initially we had only cited Spangenberg (2012) in this regard. Since the IAEA has apparently carried out such experiments much earlier, we now also refer to your comment as personal communication and provide the DOI of your review. We hope you agree with this.

Best regards,

Nils Michelsen (on behalf of the author team)

Additional changes

Apart from the changes requested by the reviewers (see above; manuscript and supplement), we made a few additional modifications:

- We added two new references to our manuscript (Zannoni, et al. 2019; Ankor et al., 2019). Both papers appeared in the course of the review process and we felt the need to mention them in our introduction. While the former is only briefly mentioned, the latter deserves a whole paragraph.
- We also added a sentence to the acknowledgements because we wanted to thank 1) the reviewers for the valuable comments and 2) the Open Access Publishing Fund of Technische Universität Darmstadt.

The mentioned changes are highlighted in red in the following.

Technical note: A microcontroller-based automatic rain sampler for stable isotope studies

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Abstract. Automatic samplers represent a convenient way to gather rain samples for isotope ($\delta^{18}O$ and $\delta^{2}H$) and water quality analyses. Yet, most commercial collectors are expensive and do not reduce post-sampling evaporation and the associated isotope fractionation sufficiently. Thus, we have developed a microcontroller-based automatic rain sampler for timer-actuated collection of integral rain samples. Sampling periods are freely selectable (minutes to weeks) and the device is low-cost, simple, robust, and customizable. Moreover, a combination of design features reliably minimizes evaporation from the collection bottles. Evaporative losses were assessed by placing the pre-filled sampler in a laboratory oven with which a diurnal temperature regime (21-31°C) was simulated for 26 weeks. At the end of the test, all bottles had lost less than 1 % of the original water amount and all isotope shifts were within the analytical precision.

These results show that even multi-week field deployments of the device would result in rather small evaporative mass losses and isotope shifts. Hence, we deem our sampler a useful addition to devices that are currently commercially available and/or described in the scientific literature. To enable reproduction, all relevant details on hard- and software are openly accessible.

1 Introduction

The stable isotopes ^{18}O and ^{2}H represent nearly ideal tracers that are frequently applied in hydrology and other disciplines. Yet, most applications require data on the isotope composition of precipitation (Bowen and Revenaugh, 2003; Hughes and Crawford, 2013).

Although isotope analyzers have become field-deployable, enabling high-resolution on-site rain analyses (Berman et al., 2009; Herbstritt et al, 2018a; Munksgaard et al., 2011, 2012; Pangle et al., 2013; von Freyberg et al., 2017; Windhorst et al., 2017), many researchers hesitate to take their analyzer to the field due to the risk of damaging the expensive device and due to logistical constraints such as high power demand (Herbstritt et al., 2018b). Hence, most samples are still obtained in more traditional ways for subsequent analysis in the laboratory. They are collected manually (e.g., in intra-event studies; Conroy et al., 2016; Michelsen et al., 2015), with cumulative rain collectors (summarized in Michelsen et al., 2018), or with automatic samplers.

Such automatic samplers, initially mostly developed for precipitation chemistry studies, cover a broad range of designs (see reviews by Krupa, 2002; Laquer, 1990; Robertson et al., 1980). Simple versions of the "linked collection vessels" type (Robertson et al., 1980), featuring a set of serially connected bottles that are consecutively filled, are inexpensive and easy to construct. They have no moving parts and collect samples on a volume basis (Laquer, 1990). Particularly the designs by Kennedy et al. (1979) and Vermette and Drake (1987) are still used nowadays (Fischer et al., 2016, 2017; Hervé-Fernández et al., 2016; Muñoz-Villers and McDonnell, 2013; Saffarpour et al., 2016), albeit sometimes with modifications (Buda and DeWalle, 2009; Qu et al., 2017). Drawbacks of this sampler type comprise the lack of an efficient evaporation reduction

mechanism, possibly causing post-sampling fractionation (Fischer et al., 2017) and a potential for cross-contamination of samples.

More complex "automatically segmenting samplers" (Robertson et al., 1980) are commercially available, but usually expensive (several thousand €; Tauro et al., 2018). Further, they often do not minimize evaporation sufficiently (Hartmann et al., 2018; Tauro et al., 2018; Williams et al., 2018). To overcome the latter problem, researchers have occasionally added paraffin oil to the collection bottles of such commercial samplers (Birkel et al., 2011; van Huijgevoort et al., 2016; Sprenger et al., 2017; Tunaley et al., 2017), as recommended by Fergusson (1921). However, a quantitative oil removal is not easy and oil traces might cause problems during laboratory analyses (Gröning et al., 2012), particularly in laser spectroscopy (IAEA, 2014). Fischer et al. (2016) thus explicitly avoided the oil method and preferred to empty their automatic samplers directly after rainfall events.

The isotope community also developed various custom-made automatic samplers, mostly for high-resolution sampling of rain and/or surface water (e.g., Camacho Suarez et al., 2015; Conroy et al., 2016; Coplen et al., 2008; Muller et al., 2015; Neuhaus, 2016, 2018; Siebert, 2015; Terzer-Wassmuth et al., 2018; Zannoni et al., 2019). While some of these collectors are outlined in the corresponding patent specifications (Coplen, 2010; Neuhaus, 2016; Siebert, 2015), several others are only briefly described or not at all. We can imagine that, at least in some of these cases, the researchers did not provide details, because they saw their collectors as means to an end, i.e., as tools helping to generate data on which they eventually concentrated.

Notable exceptions in this context are Hartmann et al. (2018) and Nelke et al. (2018), who do provide sufficient details on their devices to enable reproduction. The former authors use a peristaltic pump to inject water directly into air-tight vials. Nelke et al., by contrast, utilize two peristaltic pumps to direct water into aluminium-lined bags using solenoid valves. Both collectors apparently focus on continuously flowing media (e.g., dripwater, surface water; instead of discontinuous media such as precipitation) and take discrete "snapshot" samples (instead of integral samples) of small to moderate size (12 and 250 mL, respectively). Moreover, their designs have in common that they are rather sophisticated. Yet, complexity can be a double-edged sword. While their technical solutions are certainly elegant, the advanced designs might be somewhat difficult to reproduce.

Another noteworthy open source device is the autonomous rainfall sampler by Ankor et al. (2019), which collects daily and monthly samples. Here, the water flows by gravity through the partly 3D printed system and is elegantly guided by a split tipping bucket and a "water switch" into the daily and monthly bottles having volumes of 225 mL and 2 L, respectively. Unfortunately, a 13-week field test (mean temperature: 25.3°C) revealed evaporative losses from the pre-filled bottles, resulting in remarkable $\delta^{18}O$ changes. The latter ranged from about 1.10 to 2.63 ‰, depending on the bottle cap material. Only when paraffin oil was used the collection bottles (see above), the isotopic changes were acceptable (approx. 0.14 ‰ for $\delta^{18}O$). To mitigate the evaporation effect, the authors suggest a coupled hydrologic-isotopic model that takes advantage of the combined daily and monthly sample collection and allows a back-calculation of the original sample volumes and isotopic compositions. Although such an approach might be an option, we think it would be more straightforward to minimize evaporation from the collection bottles in the first place.

Here, we describe a complementary automatic rain sampler. Our simple, robust, and low-cost collector allows the timer-actuated collection of integral rain samples, with time intervals ranging from minutes to weeks. A combination of design features effectively reduces post-sampling evaporation. In the spirit of Open Science (cf. Ankor et al., 2019; Hartmann et al., 2018; Nelke et al., 2018), we provide a detailed description of our customizable collector and its components. Moreover, we present the results of a 26-week test addressing the evaporation reduction capacity of the device in a warm climate.

2 Design

The following section gives an overview of the sampler design. Further details (bill of materials, technical drawings, circuit diagram, code, and manuals) enabling reproduction are provided in the supplement and on the website https://www.ufz.de/index.php?en=44048 (section Documentation).

The sampler collects rain by a funnel from which the water flows into a distribution unit, the core of the device (Fig. 1). It consists of two custom-made uniaxial discs (separated by a 2 mm neoprene rubber seal) with drill holes that are positioned opposite of each other. The upper disc (PTFE) is the rotor (rotates clockwise) and has two drill holes fitted with push-in ports. The outer port is the rain inlet and the inner port is the air outlet. The lower disc (PVC-U) is the stator (remains static) and features 36 ports that are arranged in two circles. The ports of the outer circle are connected to water tubes and the ports of the inner circle are connected to air tubes (LDPE; see section Pre-test of tubing materials in the supplement, incl. Fig. S1, Table S1).

Water coming from the funnel flows through the rain inlet into the distribution unit and then through a water tube, into the first 500 mL sampling bottle. All tubes are guided through the bottle caps by means of cable grommets (Fig. S2), ensuring a tight connection. With respect to the bottles, we recommend thick-walled HDPE bottles that effectively reduce diffusive water losses (Spangenberg, 2012; personal communication Manfred Gröning, IAEA, https://doi.org/10.5194/hess-2019-93-RC2). For our purposes, we selected 500 mL HDPE wide-mouth bottles by Labsolute (Renningen, Germany; wall thickness approx. 1.7 mm).

To minimize post-sampling evaporation, we adapted the concept of an evaporation-free cumulative collector (Gröning et al., 2012), which has been successfully tested under hot and arid conditions (Michelsen et al., 2018) and is advocated by the IAEA (2014). In this concept, an inlet tube extends to the bottom of the bottle. A few millimeters of rainfall are sufficient to cause a water level rise into the tube, thus decoupling the bottle headspace from the atmosphere. This process can be amplified by inserting the end of the inlet tube into a small container (cf. Gröning et al., 2012; or a short piece of bent tubing, see Fig. 1), reducing the amount of rain needed to decouple the air in the bottle from the atmosphere. The air displaced by the inflowing water leaves the bottle through the air tubing that, unlike the inlet tube, extends just below the bottle cap. The air tubing leads from the bottle cap back to the distribution unit. Here, the air is pushed through the air outlet into a 15 m long pressure equilibration tube (cf. Gröning et al., 2012, IAEA, 2014).

At the end of the freely selectable sampling interval, a microcontroller (Texas Instruments; for details, see supplement) triggers a stepper motor to turn the rotor of the distribution unit by 20°. Through this rotation, the first sampling bottle is isolated from the atmosphere – the rotor disc closes the water and air tubes of this bottle. In turn, rain can now flow into the second bottle. The air thus displaced from the second bottle is pushed into the aforementioned pressure equilibration tube, i.e., this tube is shared by all bottles. A tight fit of the rotor is ensured through a spring above the disc, providing sufficient pressure to avoid leakages.

The microcontroller features a display and buttons for convenient programming, avoiding the necessity of a notebook during field setup or maintenance. Moreover, the microcontroller has a set of low power modes that are excessively used. In fact, the microcontroller and the accompanying stepper motor driver are only active during initial setup and between sampling periods, while the distribution unit is driven to the next sampling port. The fact that the distribution unit consumes virtually no power during sampling, allows for week-long sampling periods on just two AA batteries for the logic unit and another eight AA batteries for the stepper motor.

The stepper motor and the control unit (microcontroller with accessories and batteries) are each located in a dust- and water-proof enclosure and connected by a water-proof cable (IP68). This robust design loosens the requirements for the overall enclosure. For field deployments (not presented here), a simple plastic storage box was chosen to be sufficient to house the sampling bottles and the automatic collector.

3 Evaporation experiment

3.1 Methods

After initial tests targeting the functional capabilities of the sampler (timing, rotation angles, etc.), we studied the evaporation reduction efficiency of the device.

To this end, five HDPE bottles (500 mL; Labsolute, Renningen, Germany) were partially filled with water of known isotopic composition ($\delta^{18}O$=-8.53 ‰, $\delta^{2}H$=-60.7 ‰ related to Vienna Standard Mean Ocean Water, V-SMOW) and connected with water and gas tubing to the distribution unit (Table 1). The latter was not coupled to the microcontroller unit, i.e., the rotor did not move during the test.

Bottle 1 (filled with 100 mL) was connected to the open ports, i.e., its water and air tubes led to the ports beneath the rain inlet and the air outlet, respectively (Fig. 2). A 2 m long rain tube (without funnel) was connected to the rain inlet and a 15 m long pressure equilibration tube was connected to the air outlet. With this bottle, we wanted to assess how long a sampling bottle can be left "exposed" to the atmosphere (exposed via the rain tube and the pressure equilibration tube).

Bottles 2 to 5 contained different water amounts (100, 200, 300, and 400 mL) and their water and air tubes led to stator ports that were blocked by the rotor disc. Here, the goal was to determine how long a sample can remain in the collector without undergoing critical evaporative mass loss.

This setup was placed for 26 weeks (cf. Hartmann et al., 2018) in a laboratory drying oven (T 6120 by Heraeus, Hanau, Germany) with which a diurnal temperature regime was simulated (Michelsen et al., 2018). A socket timer triggered a daily 12 h heating period (31°C). After this phase, the oven was allowed to cool down to room temperature (approx. 21°C). To accelerate this cooling process, the oven was opened daily for three hours. Temperature and relative humidity in the oven were logged in 10 min intervals (DK320 HumiLog ruggedPlus by Driesen + Kern GmbH, Bad Bramstedt, Germany).

For comparison, two additional bottles were placed into the oven – Bottles 6 and 7 (both filled with 100 mL). Bottle 6 was closed, thus representing a best-case scenario. With this approach, potential diffusion through the bottle material was tested. Bottle 7, by contrast, was "open", i.e., it featured two holes (diameter 6 mm) in its cap, to represent the worst case (no evaporation suppression).

Moreover, three identical HDPE tubing loops (häberle LABORTECHNIK, Lonsee-Ettlenschieß, Germany) were included in the oven experiment. They were partially filled with 0.5 mL of water and the tubing ends were connected to each other with a connector. All three loops had a circumference of 25 cm, which corresponds to the lengths of the tubing between the bottles and the distribution unit. This allowed for an estimate of diffusive water fluxes through the tubing material.

To determine evaporative mass losses during the experiment, the bottles and the tubing loops were weighed repeatedly (Voyager Pro VP2102C by Ohaus, Pine Brook, USA). Bottles 1 through 5 were disconnected from the distribution unit for this purpose. Samples for isotope analyses (1.6 mL in 2 mL vials) were gathered after 6, 16, and 26 weeks. In case of Bottles 1 to 5, water was withdrawn through the water tube with a syringe. Bottle 6 was sampled through a gas-tight sampling port in its cap (Mininert by VICI Precision Sampling, Baton Rouge, LA, USA) with a syringe. Samples from Bottle 7 were taken with a Pasteur pipette through one of the holes in the cap. To account for these artificial mass losses, the bottles were weighed before and after sampling.

At the end of the test, the obtained water samples were analyzed for their isotopic composition by Laser Cavity Ring-Down Spectroscopy (L2130-i by Picarro, Santa Clara, CA, USA). The results were expressed in per mil (‰) using the conventional delta-notation relative to V-SMOW. The external precisions (±1σ), determined by repeated analyses of a control sample, were ±0.15 ‰ and ±0.6 ‰ (±1σ), for $\delta^{18}O$ and $\delta^{2}H$, respectively.

3.2 Results

3.2.1 Evaporative mass losses

The applied diurnal temperature regime (21-31°C; see Fig. S3) mostly resulted in small but measurable evaporative mass losses that increased over time (Table 1).

After 26 weeks, absolute mass losses ranged between 0.8 and 2.4 g for the bottles connected to the distribution unit (Bottles 1 through 5). Bottle 6 (closed), representing the best case, showed a lower mass loss of 0.24 g and in case of Bottle 7 (open; worst case), a loss of 24.42 g was encountered. The three tubing loops (each 25 cm long) lost about 0.14 g over the same time period (see Table S2).

These data suggest that the diffusive loss through the tubing material of the connected bottles (two tubes per bottle, hence 0.28 g; see tubing loop data) is similar to the flux through the bottle material of Bottle 6 (0.24 g). As all connected bottles exhibited greater absolute mass losses, additional leakages, e.g. at the cable grommets in the bottle caps or at the distribution unit, seem likely. In this context, pressure fluctuations, induced by the diurnal temperature regime, probably play a role. It is also noteworthy that the blocked bottles 4 and 5, containing 300 and 400 mL of water, showed the greatest losses (> 2 g). This observation could point towards an influence of the bottle surface area in contact with liquid water on the diffusive water flux through the plastic. Nevertheless, the overall absolute losses are still rather small, particularly when compared to the worst-case scenario, an unprotected bottle (Bottle 7).

This becomes clearer when the data are put in perspective with the original water amounts. Fractional losses of Bottles 1 through 5 range from 0.40 to 0.94 %-orig, i.e., even after half a year the maximum loss was below 1 %. As expected, these values are somewhat higher than in case of the closed bottle (Bottle 6; 0.24 %-orig), but far below the loss recorded for the open Bottle 7, which lost nearly a quarter of its water (24.42 %-orig).

3.2.2 Isotopic shifts

The bulk of the obtained δ values scatter around the original isotopic signature ($\delta^{18}O$=-8.53 ‰, $\delta^{2}H$=-60.7 ‰; see Table 1). The calculated isotopic shifts, $\Delta\delta^{18}O$ and $\Delta\delta^{2}H$, mostly range between -0.07 and 0.30 ‰ and between -0.2 and 0.7 ‰, respectively (Bottles 1 through 5).

These shifts are rather small. Keeping in mind that the reported external 1σ precisions, ±0.15 ‰ ($\delta^{18}O$) and ±0.6 ‰ ($\delta^{2}H$), apply to the original water and the water after oven exposure, the encountered shifts practically all lie within the analytical error. This also holds true for the shifts of the closed Bottle 6.

The open Bottle 7, by contrast, showed substantial shifts. After 26 weeks, the $\delta^{18}O$ and $\delta^{2}H$ values had increased by about 9.23 and 25.5 ‰, respectively.

4 Discussion

Following a “Keep It Simple” approach, we have designed an elementary and robust sampler, deliberately avoiding complexity such as pumps, solenoid valves, or remote controls (cf. Coplen et al., 2015; Hartmann et al., 2018; Nelke et al., 2018). Avoiding such complexities greatly reduces the failure risk in the field. We also avoided components that permanently consume power (e.g., normally closed solenoid valves during the “open” phase) and complex tubing systems that would possibly require parts of the sampling water to be used for tubing flushes. Hence, our collector is relatively easy to reproduce, although some technical skills are required.

Compared to other devices (Coplen et al., 2008; Hartmann et al., 2018), it has fewer but bigger bottles. The latter aspect implies that analyses do not have to be restricted to $\delta^{18}O$ and $\delta^{2}H$, but other parameters such as ^{3}H, major ions (incl. bicarbonate by titration), etc. could in principle be studied as well.

Most importantly, our device gathers integral samples over freely selectable collection periods (minutes to weeks) and effectively reduces post-sampling evaporation. In combination with the low power consumption, these features render it a potential candidate for autonomous rain sampling at remote, unmanned sites. Traditionally, precipitation samples for isotope analyses are mostly collected on a monthly integral basis (e.g., in the Global Network of Isotopes in Precipitation, GNIP; IAEA/WMO, 2019). Yet, due the advent of laser-based isotope analyzers and the associated decreasing costs for analyses (Berman et al., 2009; Herbstritt et al., 2012; Wassenaar et al., 2018), shorter collection periods (e.g., weekly integral samples) have become more popular (e.g., Otte et al., 2017). An important advantage of sampling schemes with a higher temporal resolution is the gain in flexibility. They allow, for example, a correlation between isotope signature and meteorological variables (Akers et al., 2017; Hughes and Crawford 2013; Rao et al., 2008), but data can still be aggregated to precipitation-weighted monthly values for seamless comparison with other monthly data sets (e.g., GNIP).

Due to the relatively low costs (parts <600 €), several automatic collectors can be deployed simultaneously to address spatial variability. A number of researchers reported pronounced spatial variability of the isotopic composition of rain in small catchments (Fischer et al., 2017; Kato et al., 2013) or at the city scale (Chen et al., 2017). In these studies, $\delta^{18}O$ values partly varied by several ‰ within short distances (a few hundred meters to a few kilometers). In case of throughfall, $\delta^{18}O$ values can even differ significantly on the plot scale, i.e., within meters, and differences of more than 1 ‰ (Allen et al., 2014, 2015; Kato et al., 2013) or even several ‰ (Hsueh et al., 2016) have been observed. Further, it has been shown that ignoring the spatial variability impairs isotope-based hydrograph separations (Cayuela et al., 2019; Fischer et al., 2017). These findings highlight the need for collector arrays or networks (cf. Lutz et al., 2018; Scholl et al., 1995, 1996). Using expensive, commercial equipment in such networks might be prohibitively expensive for many researchers. Rodgers et al. (2005), for instance, report resource constraints preventing the installation of a second sampler in their catchment to capture the local altitude effect. In such cases, an affordable custom-made alternative is extremely useful. This also applies to study areas in which vandalism or theft of monitoring equipment might be an issue (cf. Kongo et al., 2010; Otte et al., 2017; Pramana and Ertsen, 2016). In such settings, researchers on a limited budget would possibly hesitate to leave expensive equipment unattended at a remote site for longer time periods and a low-cost alternative would be appreciated.

Although this work focused on the isotopes ^{18}O and ^{2}H, gathered samples could also be analyzed for other isotopes or their hydrochemistry. Since the funnel is permanently exposed, the sampler would act as a bulk sampler (collecting wet and dry deposition). Hydrochemical analyses could, for instance, include chloride for recharge estimations via the Chloride Mass Balance method (e.g., Eriksson and Khunakasem, 1969; Guan et al., 2010).

5 Potential modifications

While the presented sampler suits our purposes, we acknowledge that other researchers might have different expectations towards such a collector. Thus, we explicitly encourage others to modify our design and tailor it to their specific needs.

Potential modifications might address the number of bottles and their size. In addition, the tubing can be changed, but we suggest the use of opaque tubing for the exposed section from the funnel to the sampler itself to reduce the risk of algae growth, which has occasionally caused problems in rain collectors (Scholl et al., 1995). Although it might be tempting to replace the push-in ports by ordinary barbed hose fittings, we suggest not to do so for the following reasons: 1) Given the potential risk of disconnection of tubing, the used ports are deemed a safe option. 2) Their handling is easier, particularly when dealing with tens of connections in a confined space. 3) They do not introduce an additional constriction.

Although we used a Texas Instruments microcontroller, we can imagine that the functionality of the sampler could also be achieved with parts from the popular Arduino ecosystem, though probably at the cost of greater power consumption.

Moreover, one could transform the timer-actuated into a volume-controlled rain sampler, for instance by means of a microcontroller-based tipping bucket system. The latter would calculate the filling status of a sampling bottle based on the

recorded number of tips and automatically direct the water into the next bottle when the first one is full (cf. Muller et al., 2015).

Also, a transformation into a surface water sampler is feasible. To this end, one could combine the current device with a timer-triggered peristaltic or submersible pump. The microcontroller provides several unused input/output and communication pins and further unutilized resources to allow for such customizations.

6 Summary and conclusions

Our microcontroller-based automatic rain sampler enables timer-actuated integral rain sampling. The simple, low-cost device is robust and effectively minimizes post-sampling evaporation from the collection bottles and the associated isotope fractionation. The excellent performance of the device during an extensive evaporation experiment in a laboratory oven (26 weeks; 21-31°C) suggests that even multi-week field deployments in warm climates are feasible. In the spirit of Open Science, we share all relevant details on our sampler and encourage others to adapt it to their specific needs.

Data availability

All details needed to copy our sampler are freely available (supplement and https://www.ufz.de/index.php?en=44048, section Documentation). Data on the evaporation experiment, enabling a performance evaluation, are given in the main article and the supplement.

Author contribution

NM, GL, and TM conceptualized the sampler. GL was responsible for the detailed sampler design and programmed the microcontroller. GL, JF, ABABS, and TM conducted initial tests. NM carried out the evaporation experiment. SMW performed isotope and data analyses. NM wrote the manuscript with contributions from all co-authors.

Competing interests

The authors declare that they have no conflict of interest.

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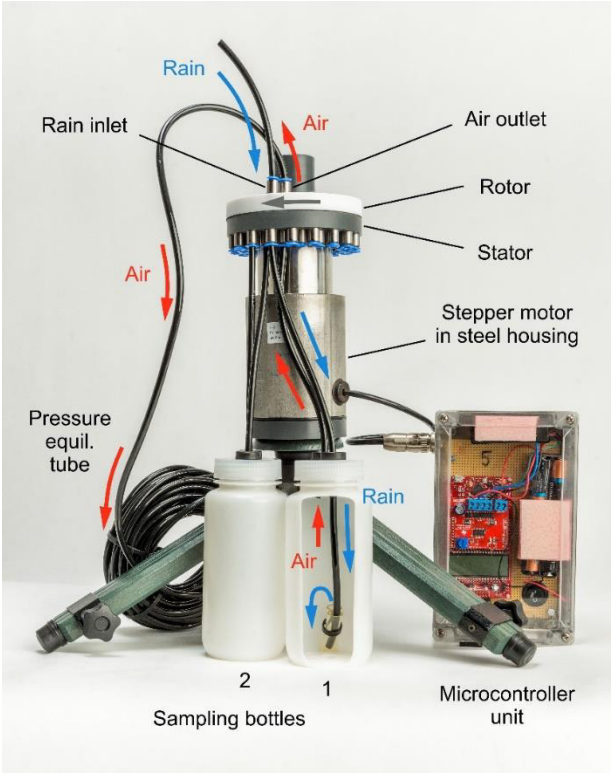

Figure 1: Overview of the automatic sampler principle (Photo by André Künzelmann, UFZ). Water (blue arrows) flows from the rain inlet through the distribution unit and into the first bottle (cutaway view). Displaced air (red arrows) leaves the bottle and flows through the distribution unit and the air outlet into a 15 m long pressure equilibration tube. At the end of the sampling interval, the rotor is turned (grey arrow), leading the rain into the second bottle.

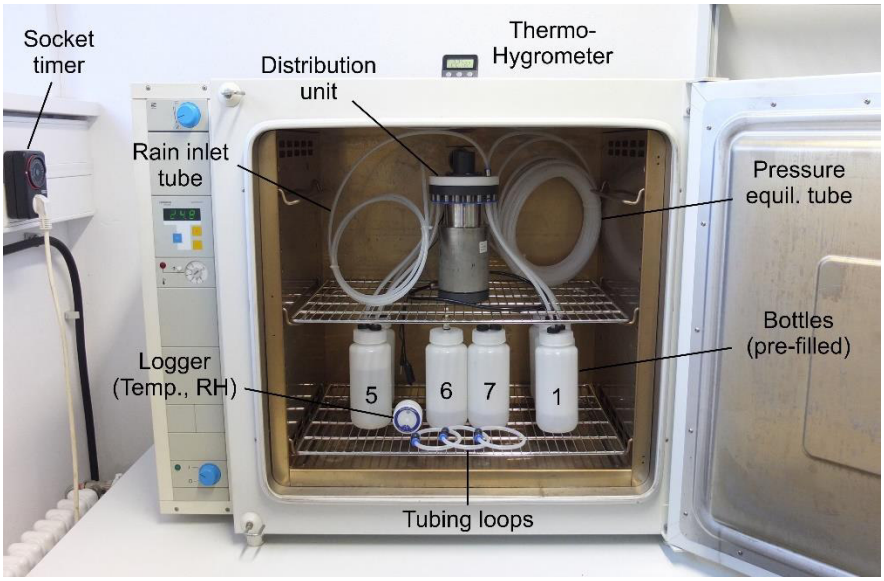

Figure 2: Photograph of the evaporation experiment setup. Note that the bottles were pre-filled with water of known isotopic composition, i.e., no water flowed through the tubing, and the distribution unit did not rotate during the test.

Table 1: Overview of collected samples and associated water losses and isotopic shifts. Water losses Δm are given as absolute mass losses [g] and as percentages of the original water amount [%-orig]. Isotopic signatures ($\delta^{18}O$ and $\delta^{2}H$) and isotopic shifts away from the original composition ($\Delta\delta^{18}O$ and $\Delta\delta^{2}H$) are given in ‰ V-SMOW. Note that the analytical precisions for $\delta^{18}O$ and $\delta^{2}H$ account for ±0.15 ‰ and ±0.6 ‰ (±1σ), respectively.

ID	Description	t [weeks]	Δm [g]	Δm [%-orig]	$\delta^{18}O$ [‰]	$\delta^{2}H$ [‰]	$\Delta\delta^{18}O$ [‰]	$\Delta\delta^{2}H$ [‰]
Orig.	Original water	0	n.a.	n.a.	-8.53	-60.7	n.a.	n.a.
Bottle 1	exposed, 100 mL	6	0.17	0.17	-8.32	-60.2	0.21*	0.5*
		16	0.56	0.56	-8.50	-60.6	0.03*	0.1*
		26	0.94	0.94	-8.44	-60.2	0.09*	0.5*
Bottle 2	blocked, 100 mL	6	0.20	0.20	-8.42	-60.4	0.11*	0.3*
		16	0.56	0.56	-8.23	-60.0	0.30*	0.7*
		26	0.93	0.93	-8.46	-60.2	0.07*	0.5*
Bottle 3	blocked, 200 mL	6	0.16	0.08	-8.49	-60.7	0.04*	0.0*
		16	0.46	0.23	-8.49	-60.6	0.04*	0.1*
		26	0.81	0.40	-8.59	-60.9	-0.06*	-0.2*
Bottle 4	blocked, 300 mL	6	0.43	0.14	-8.53	-60.8	0.00*	-0.1*
		16	1.16	0.39	-8.50	-60.5	0.03*	0.2*
		26	2.04	0.68	-8.57	-60.7	-0.04*	0.0*
Bottle 5	blocked, 400 mL	6	0.53	0.13	-8.53	-60.8	0.00*	-0.1*
		16	1.47	0.37	-8.55	-60.7	-0.02*	0.0*
		26	2.41	0.60	-8.60	-60.6	-0.07*	0.1*
Bottle 6	closed, 100 mL	6	0.05	0.05	-8.60	-60.9	-0.07*	-0.2*
		16	0.14	0.14	-8.65	-60.9	-0.12*	-0.2*
		26	0.24	0.24	-8.66	-60.9	-0.13*	-0.2*
Bottle 7	open, 100 mL	6	5.27	5.27	-6.85	-56.1	1.68	4.6
		16	14.18	14.18	-3.70	-46.9	4.83	13.8
		26	24.42	24.42	0.70	-35.2	9.23	25.5

n.a.: not applicable; *: Δδ within analytical precision ($|\pm 1\sigma| = 2\sigma$)