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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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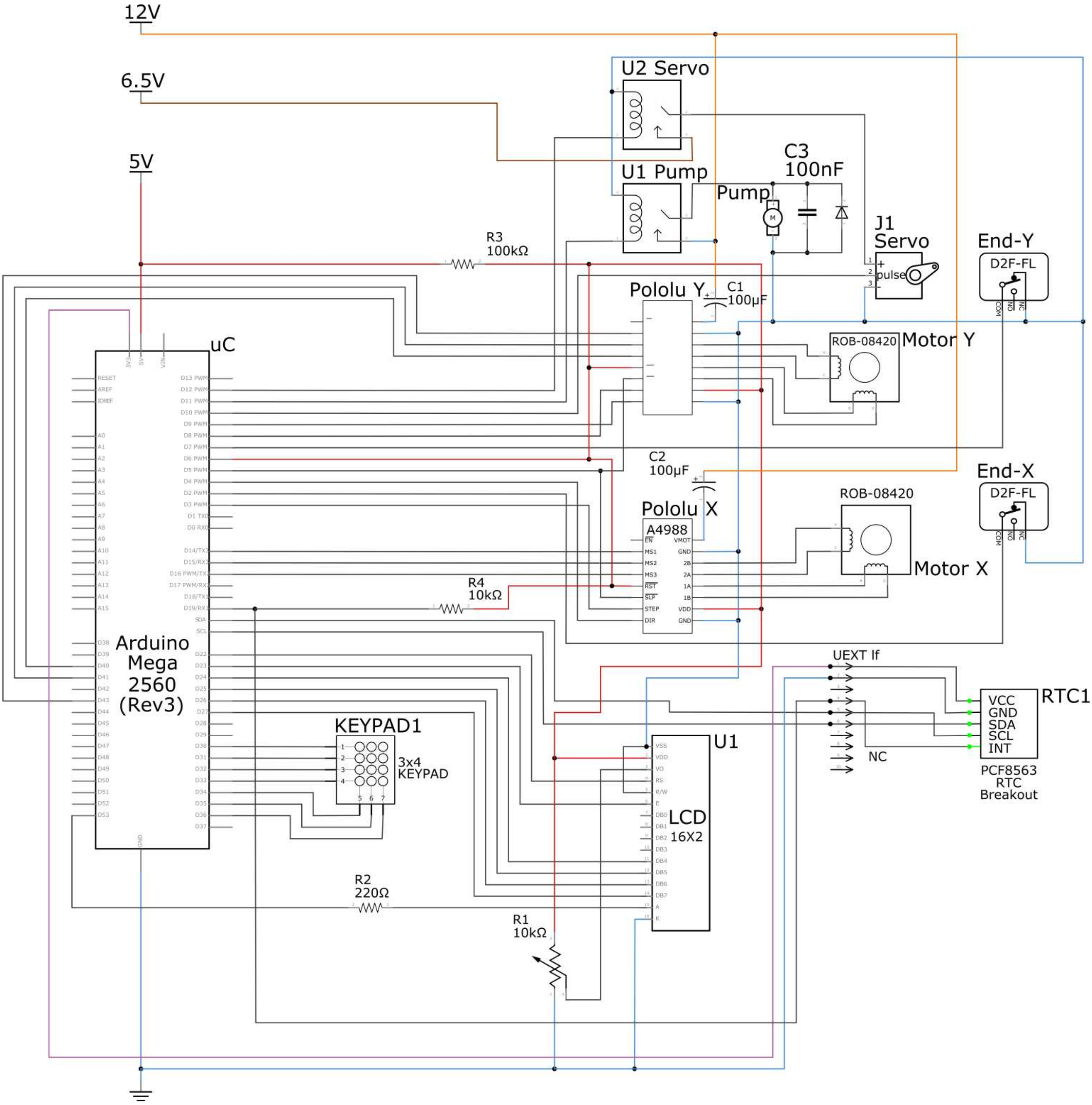
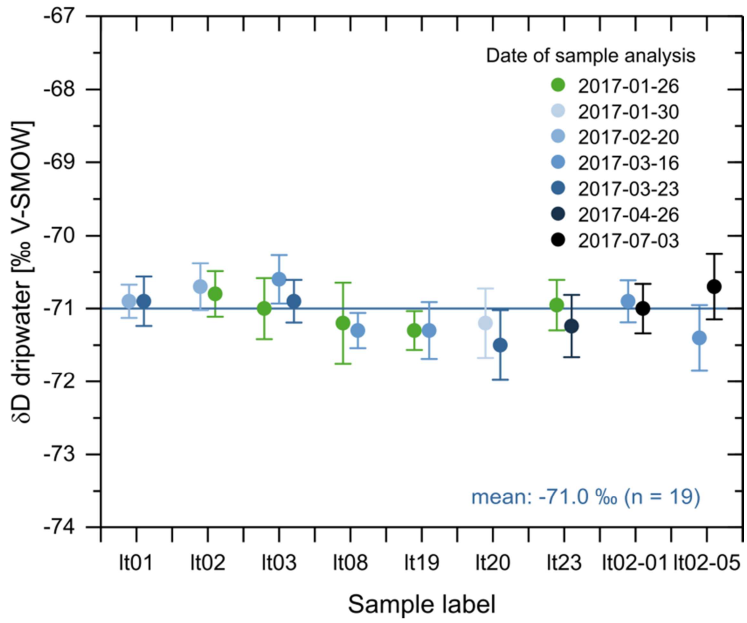
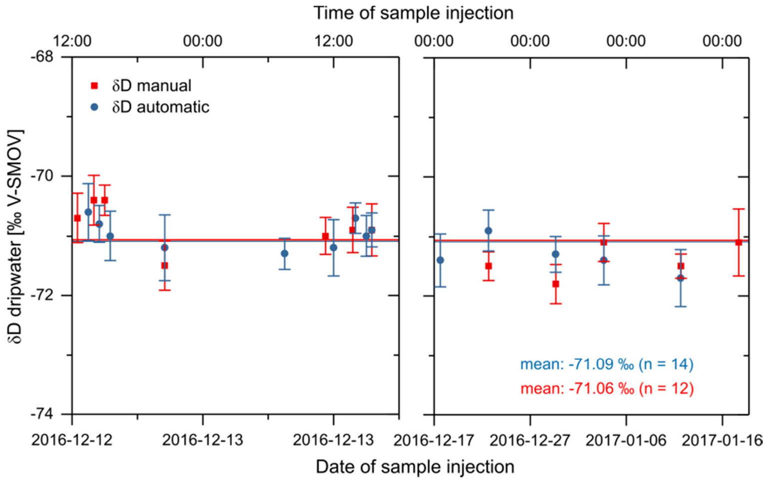


S1: Electrical circuit diagram of the GUARD autosampler.

The δD results (S2) 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 (S2).



S2: 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.



S3: First field testing of the GUARD autosampler: Hydrogen isotope values (indicated as δD 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.

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}:

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

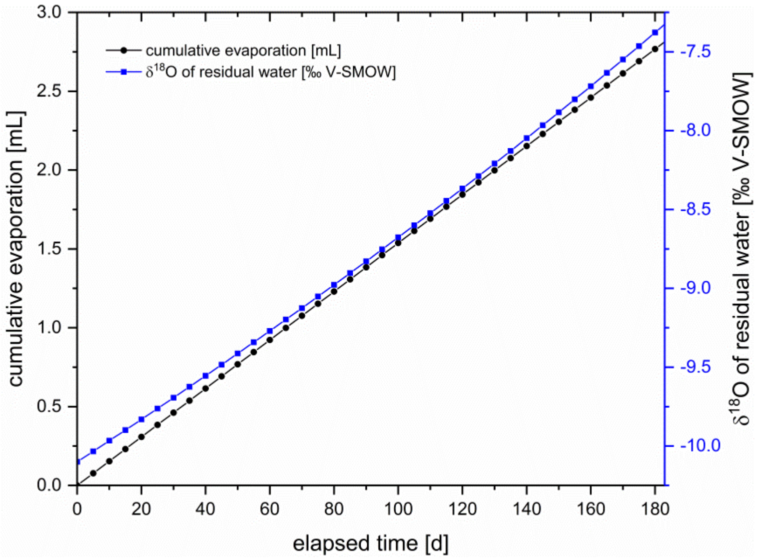
where $\dot{m}$/A is the evaporation rate [kg $(m^2\ hr)^{-1}$], v_w is the air velocity over the water surface [m s^{-1}],
P_w is the saturation vapour pressure at the water temperature [mm Hg], P_a is the saturation vapour pressure at the air dew point [mm Hg] and ΔH_v is the latent heat of water at 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):

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

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 (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 $\delta^{18}O$ 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.



S4: 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 %.

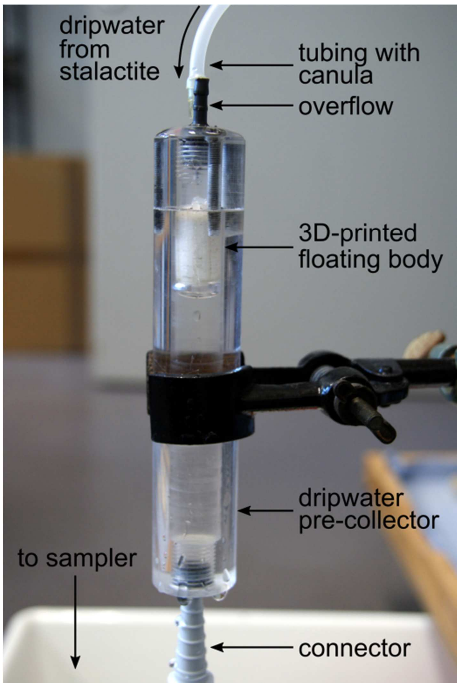
S5: Integral components of the GUARD autosampler of relevant size

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° $step^{-1}$, 0.265Nm, 4 wires	42x42x24 mm
Pump	Peristaltic (flexible-tube) pump, model AP-40; operating voltage 12 V	55x50x42 mm

S6: Bill of Materials

Components	Description	quantity	cost/unit	cost	company	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	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^2C 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	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 €**		

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 (S6).



S7: Pre-collector used during the case studies.

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