

## Research papers

# On the reliability of tube-dip-in-water precipitation collectors in isotope hydrology: A field experiment for low rainfall amounts

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## A B S T R A C T

The oxygen and hydrogen stable isotope composition in precipitation serves as a benchmark in most isotope atmospheric, (eco-) hydrological, and paleoclimatological applications. Several rain collectors have been designed for collecting monthly, daily, or event-based precipitations aiming to prevent evaporation and associated isotope fractionation. Oil collectors have been the most widely used for many years and only recently they are being replaced by free-oil Tube-dip-in-water collectors, especially after the production of commercial versions. Although several isotopic studies already adopted this precipitation collector, no field experiments were performed to evaluate the isotopic integrity of low-amount precipitation samples. Field testing of precipitation collectors is therefore encouraged under the same environmental conditions of areas where researchers want to undertake their studies.

In this work, we tested field performances of different Tube-dip-in-water collectors, compared to an Oil collector and a reference collector with no anti-evaporative system, in preventing evaporation during the collection of low-amount monthly precipitation samples. The field experiment was carried out in the city of Pisa (Italy), in the Mediterranean region, over four different periods in spring and summer 2022, when atmospheric conditions were more likely to promote evaporation. Six precipitation collectors were filled at the beginning of each period with distilled water with a known isotope composition. Four collectors (reference, Oil, Palmex Tube-dip-in-water, Home-made Tube-dip-in-water) were filled to less than 2 % of the total volume, and other two Home-made Tube-dip-in collectors were filled to 5 % and 10 %. Evaporative mass losses were determined gravimetrically at the end of each period, and water aliquots were sampled for isotope analyses.

The Oil collector showed the smallest evaporative mass losses and no detectable isotope shifts. The Home-made Tube-dip-in-water collector was also effective in preventing evaporation for low water amounts and it provided acceptable results even for extremely low water volumes, albeit with small isotope shifts. The Palmex collector, by contrast, exhibited worst performance when the collection of very low amount precipitation samples (less than 2 % of the total volume of the bottle) was tested. The isotope shifts were significant and larger than values measured for the Home-made collector filled to same percentage. Among the possible reasons behind the worse performance of this sampler, the outer case material seemed to be the most likely. The Palmex sampler was enclosed in a metal outer case which could have promoted an overheating of the bottle, when exposed to solar radiation, potentially enhancing the day-night temperature fluctuations inside the bottle and between the bottle and the case. This could have led to greater evaporation but potentially also to larger expansion-contraction cycles of the gas inside the bottle, thus promoting vapour exchange with the external atmosphere. However, further experiments will have to be carried out to confirm this hypothesis.

Overall, our results indicated Tube-dip-in-water collectors as a reliable and low-cost alternative to oil models in most studies of isotope hydrology, especially in regions with temperate to semi-arid climate, including Mediterranean areas. However, a prudent approach is recommended at the sampling stage whereby the choice of the collector design should be calibrated according to the climatic features of the area and seasonality.

## 1. Introduction

The stable isotope ratios of oxygen and hydrogen in the water molecule ( $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/^1\text{H}$ ) are widely used as tracers of natural and anthropogenic processes in many scientific disciplines of earth and environmental sciences, including hydrology, meteorology, climatology, ecology, food sciences and forensics (e.g., Bowen et al., 2022;

Carter and Chesson, 2017; Comas-Bru et al., 2016; Gat, 1996; Jasechko, 2019; McCue et al., 2020; Song et al., 2023; Sprenger et al., 2016; Terzer-Wassmuth et al., 2021). Water is involved in all processes occurring in the atmosphere, hydrosphere, and biosphere and is displaced within the hydrological cycle through evaporation, transpiration, condensation, precipitation, infiltration, and runoff (Gleick, 1998). Precipitation represents a key component of the atmospheric processes

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and an integral part of the hydrological cycle, as it is the primary source of surface water and groundwater and the input for all the surface and sub-surface processes. Hence, the isotopic composition of modern precipitation has to be known as the starting point of most isotope applications (IAEA, 2014).

Since 1961, the International Atomic Energy Agency (IAEA) in cooperation with the World Meteorological Organization (WMO) has established the Global Network of Isotopes in Precipitation (GNIP, Dansgaard, 1964; Schotterer et al., 1996), which is a network of monitoring stations for the collection of monthly precipitation samples and the determination of their stable isotope composition of oxygen and hydrogen (IAEA/WMO, 2023). Following the GNIP, national and regional monitoring networks of isotopes in precipitation were established in several countries (e.g., Gibson et al., 2005; Hollins et al., 2018; Longinelli and Selmo, 2003; Stumpp et al., 2014; Vreča et al., 2022), besides a new international database which largely rely on GNIP and other literature data (Waterisotopes, 2023). Detailed collection procedures and sampling technical prescriptions were firstly described by the IAEA in order to obtain reliable isotopic data and to create high quality databases (IAEA, 2014, 1981). Several precipitation collectors have been designed for collecting precipitation (Ankor et al., 2019; Friedman et al., 1992; Gröning et al., 2012; Michelsen et al., 2019, 2018; Prechsl et al., 2014; Scholl, 2006; Stadler, 2003) and most of them, generally referred to as “precipitation totalizers” in the literature, have been assembled to collect an integral monthly sample (IAEA, 2014). In general, the basic elements of a rain collector are a sampling bottle, a funnel, an intake tube and, most importantly, a system to prevent evaporation. Evaporation is accompanied by isotope fractionation (Dansgaard, 1964; Rozanski et al., 1993), which can modify the original isotope composition of precipitation by an increase of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values and a decrease of deuterium excess ( $d$ ) values. Hence, the essential pre-requisite for reliable precipitation sample collection is to avoid, or at least to minimise, water evaporation from the collectors over the sampling periods that results in a net loss of vapour from the detectors and fractionation of the residual water. Evaporation prevention is crucial when monthly precipitation samples are collected, because waters remain in the collection bottles for a long time. Among the various collectors, the oil samplers have been the most widely used for many years due to their reliability in preventing evaporation, low cost, and easy maintenance (Michelsen et al., 2018). A thin layer of paraffin oil floats on top of the water sample and prevents contact between water and air, thus preventing evaporation. However, the main drawback of this collector is the need for removal of paraffin oil before the isotope analysis. Indeed, the presence of oil fractions in the water sample can create various problems for laboratory analysis: for example, it may contaminate the machinery of the mass spectrometer and its periphery or produce spectral interference when using laser spectroscopy (Prechsl et al., 2014; Sánchez-Murillo et al., 2017). A new oil-free collector was pioneered by the IAEA about twenty years ago (IAEA, 2002), in order to avoid the necessity for using of paraffin oil. This device was designed to collect samples on a monthly integrated basis for the GNIP network (IAEA, 2002), but it has been also used for shorter collection periods, such as daily and event sampling (Sánchez-Murillo et al., 2016; Santos et al., 2019). However, only recently this new collector is replacing the old oil collectors, after the formal publication by Gröning et al. (2012) and the production of a commercial version (Palmex Ltd). These collectors consist of a tube leading from the collecting funnel down to the bottom of the bottle, hence the name “Tube-dip-in-water collectors” (Michelsen et al., 2018). In this way, after the first few millimetres of rainfall, the water level begins to rise into the tube thus reducing the water surface exposed to the atmosphere and to evaporation. A pressure equilibration system, made of a long plastic tube, is also required, which allows to adjust the air pressure in the bottle and to avoid the water overflowing from the funnel. Although several isotopic studies readily adopted this new collector for collecting precipitation (e.g., Gospodyn et al., 2023; Hemmerle et al., 2021; Natali et al., 2022; Sánchez-Murillo

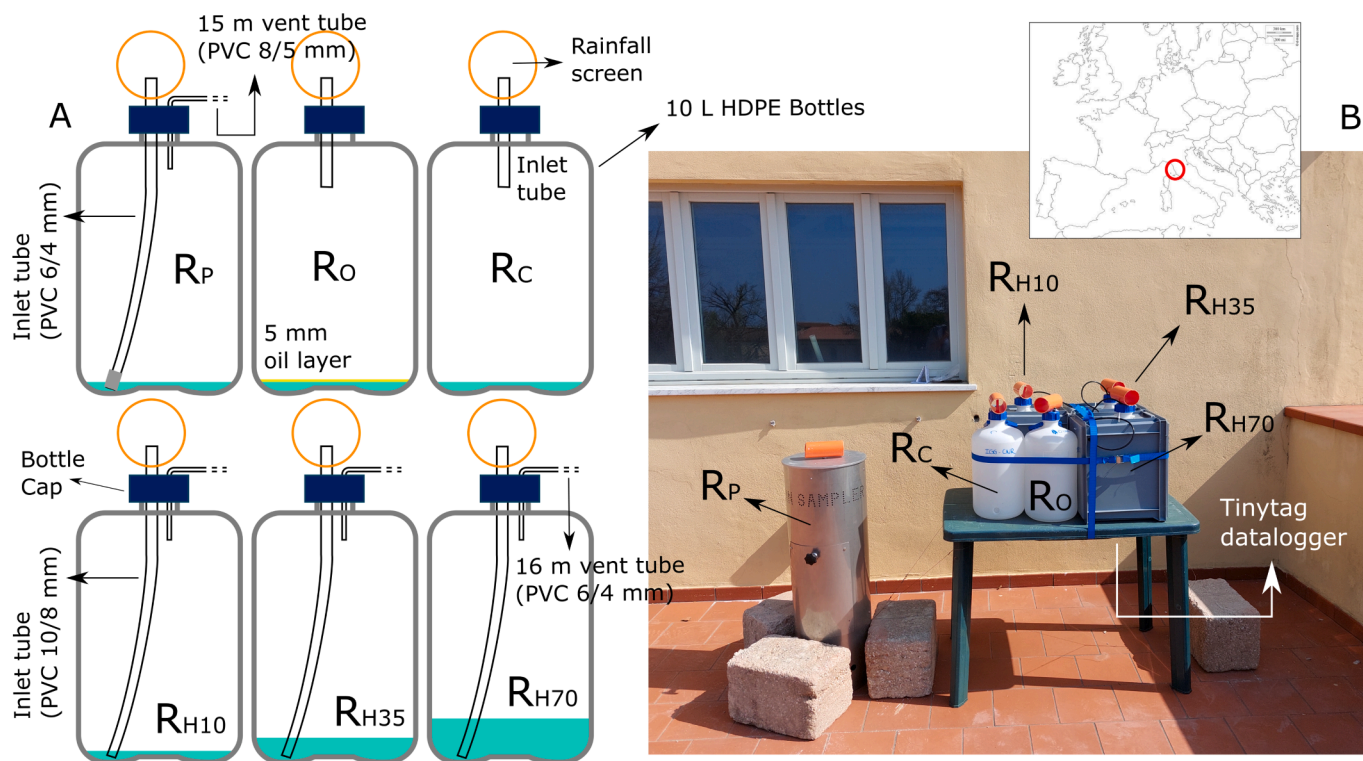
et al., 2017, 2016; Wanner et al., 2023), many doubts remain about the correct functioning of the Tube-dip-in-water anti-evaporative system when dealing with low precipitation amounts. For example, Michelsen et al. (2018) performed a laboratory experiment under extreme conditions of temperature and relative humidity, using bottles filled to 20 % with water of known isotope composition. They observed a shift in  $\delta^{18}\text{O}$  higher than the analytical error and higher than the shift observed for the oil collector. Since under natural conditions a sample may represent significantly less than 20 % of the bottle filled, as the funnel size and bottle volume are generally optimized to ensure sufficient sample for analysis but minimizing the risk of overflow for large events, results from Michelsen et al. (2018) suggest that the Tube-dip-in collector may fail to prevent evaporation and isotope fractionation when low precipitation amounts are collected. Moreover, few field experiments have been carried out (or published) aimed at evaluating the isotopic integrity of precipitation samples collected using Tube-dip-in-water collectors (Ankor et al., 2019; Gröning et al., 2012; Terzer et al., 2016). Field testing of these samplers is therefore encouraged, which should be carried out under the same environmental conditions of areas where researchers want to undertake their studies.

In this work, we tested field performances of different Tube-dip-in-water collectors in preventing evaporation and isotope fractionation during the collection of low precipitation samples. We simulated the collection of low-amount monthly precipitation samples in spring and summer, when atmospheric conditions are more conducive to evaporation. An Oil sampler was also tested for comparison. Two main goals were behind this study: i) to evaluate the reliability of precipitation samplers equipped with a Tube-dip-in-water anti-evaporative system in preventing isotope fractionation in extreme/harsh conditions (sampling of very low precipitation amounts); ii) to test the performance of a Home-made Tube-dip-in collector for different water amounts, including very low ones.

## 2. Methods and materials

### 2.1. Tested precipitation collectors

The field experiment comprised three different precipitation collector models equipped with anti-evaporative system, namely the Oil collector ( $R_O$ ), the Palmex Tube-dip-in collector (type RS-2i, Palmex Ltd., Zagreb, Croatia,  $R_P$ ), and the Home-made Tube-dip-in collector ( $R_H$ ) (Fig. 1). 10 L high-density polyethylene (HDPE) bottles (ca. 2 mm wall thickness) were used for all collectors with a cylindrical section and an inner diameter of 210 mm, except for the bottles used for the Palmex collector. These bottles (ca. 3 mm wall thickness) had a square section with a side of 190 mm, and they are specific for the Palmex model. The Oil collector was assembled by adding a thin layer of paraffin oil (ca. 0.5 cm) to the collecting bottle. The Palmex RS-2i collector was equipped with an intake plastic tube (PVC 6/4 mm, where 6 mm is the outer diameter and 4 mm the inner diameter) and a ca. 15 m long vent tube (PVC 8/5 mm). The collecting bottle, along with the intake and vent tube, were enclosed in a metal outer case that ensured air circulation through small holes on the bottom. Three Home-made collectors were assembled by one of the authors of this work (M. Nigro), following the prescriptions recommended in Gröning et al. (2012) and by IAEA (2014). A schematic of the Home-made Tube-dip-in-water samplers and other collectors is reported in Fig. 1. These were composed of a 10 L HDPE bottle with an intake tube (rigid PVC 10/8 mm) and a 16 m long compensating tube (flexible PVC 6/4 mm) and enclosed in a plastic box with some holes that provided air circulation and protecting for thermal insulation. The bottles' caps were drilled to insert the inlet and vent tubes. The drilled holes had a 9.5 and 5.5 mm diameter, respectively for the inlet and vent tube, to ensure a tight contact with the hole walls. We also included a Control collector ( $R_C$ ), as a reference, with no system to prevent sample evaporation. The inlet tube was the same for the Home-made collectors, but it was shorter and suspended in the air in the upper



**Fig. 1.** Experimental design. A) Schematic of the experimental setup reporting all the key design information for each sampler; B) Photograph of the experimental site with six precipitation collectors tested in this experiment. The orange plastic tubes were used as rainfall screen to prevent precipitation from getting inside the bottles with water of known isotope composition. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

part of the bottle. No vent tube was adopted for the Control and Oil collectors. No funnels were installed on the rain samplers, unlike in real precipitation sampling, because we were not interested in sampling rainfall. However, all the collectors were kept open to the atmosphere through their intake tube and covered with a plastic tube to prevent rainfall from getting inside the bottles with water of known isotope composition (Fig. 1).

## 2.2. Experiment

The experiment was carried out on the rooftop of the Earth Science Department of the University of Pisa (Tuscany, Italy) over four different periods from March 2022 to July 2022 (Table 1). These periods had a duration of about a month, except for the last one, in order to reproduce the collection of monthly precipitation samples. The aim was to test the field performance of two models of Tube-dip-in-water collectors (the Palmex and the Home-made), compared to the well-established Oil collector, in preventing evaporation when weak precipitation occurs and the water amount inside the collectors is particularly low. Our intention was to simulate the collection of small amounts of total monthly precipitation using a collector model typically used in areas with a marked climatic seasonality (e.g., Mediterranean region): 10 L bottles and funnels with a diameter of 13.5 cm. This configuration is optimized to ensure sufficient sample for analysis but minimizing the

**Table 1**  
Experimental periods.

Period	Date	n (days)
1	28/03/22–26/04/22	29
2	27/04/22–30/05/22	33
3	01/06/22–28/06/22	27
4	11/07/22–27/07/22	16

risk of overflow for large precipitation samples without the need to change the funnel throughout the year or to use bottles of different volumes. Nevertheless, low precipitation may occur during drier months and in these cases the water volume collected within the sampling bottle may be very low, thus potentially compromising the proper functioning of the anti-evaporative system of a Tube-dip-in-water collector. In the Mediterranean area, drier and warmer months are between late spring and early autumn, when lower relative humidity and higher temperatures cause atmospheric conditions that are more favourable to water evaporation inside the bottles (Gröning et al., 2012). For these reasons we decided to test a monthly precipitation sample of about 10 mm, which is a rather frequent amount for summer months, and sporadic in spring, in the Mediterranean area where the city of Pisa is placed.

The experimental setup consisted of six precipitation collectors that were filled at the beginning of each period with distilled water with a known isotope composition ( $\delta^{18}\text{O} = -7.12\text{‰} \pm 0.02\text{‰}$ ,  $\delta^2\text{H} = -40.6\text{‰} \pm 0.2\text{‰}$ ,  $d = 16.4 \pm 0.3$  VSMOW). Four collectors (Control collector, Oil collector, Palmex Tube-dip-in collector, Home-made Tube-dip-in collector, hereafter  $R_C$ ,  $R_O$ ,  $R_P$  and  $R_{H10}$ , respectively) were tested for a monthly precipitation amount of about 10 mm. Using sampler models equipped with 10 L bottles and 13.5 cm funnels, 10 mm of precipitation corresponded to a filling volume of  $\sim 0.14$  L and a filling percentage lower than 2 % of the total volume (Table 2). Moreover, the other two Home-made Tube-dip-in-water collectors (hereafter  $R_{H35}$  and  $R_{H70}$ ), designed as the 10 mm one, were tested for monthly precipitation amounts of about 35 mm and 70 mm (corresponding to filling percentages of about 5 % and 10 %, respectively, Table 2), in order to evaluate the reliability of these low-cost models also for higher precipitation amounts. Therefore, all six collectors were filled at the beginning of each period and placed on the rooftop of the Earth Science Department of the University of Pisa exposed to the atmosphere and solar radiation (exactly as it happens in a real monitoring). The water depth (mm) was measured within each sampler at the beginning of each



**Table 2**

Types of precipitation collector tested in the experiment ( $R_C$  – Control,  $R_O$  – Oil,  $R_P$  – Palmex,  $R_{H10}$  – Home-made 10 mm,  $R_{H35}$  – Home-made 35 mm,  $R_{H70}$  – Home-made 70 mm) and relative amount of simulated rainfall in mm, in g, in L for a funnel of 13.5 cm in diameter, in mm of water depth, and in percentage of the bottle filling. The water depth was measured on a corner of bottles.

Collector	Amount (mm)	Weight (g)	Volume (L)	Depth (mm)	Filling %
$R_C$	10	143.1	0.143	10	1.4
$R_O$	10	143.1	0.143	10	1.4
$R_P$	10	143.1	0.143	11	1.4
$R_{H10}$	10	143.1	0.143	10	1.4
$R_{H35}$	35	501.0	0.501	23	5.0
$R_{H70}$	70	1002.0	1.002	37	10.0

experimental period. Bottles were weighed at the beginning and at the end of each period under the same laboratory conditions, making sure to clean any dust particles and to dry any rain drops on the external walls of the bottles. The evaporative mass losses ( $\Delta w$ ) were then determined gravimetrically (Kern KFB, Arroweld Italia S.p.A., precision:  $\pm 0.2$  g). After weighing, water aliquots were sampled from each collector for isotope analysis, transferred in 12-mL glass vials and stored at a temperature of about  $+4$  °C before the analysis. Water samples from the Oil collector were accurately separated by using separatory funnels (IAEA, 2014), to avoid the presence of oil fractions. The atmospheric temperature and relative humidity were also monitored throughout the experiment by using a Tinytag Plus 2 Logger (Gemini Data Loggers) which was placed in the shade. Moreover, daily records of precipitation, relative humidity, and temperature were derived from the meteorological station of Pisa (code: TOS01000544) of the Tuscany Region Hydrologic Service (SIR, <https://www.sir.toscana.it/>).

### 2.3. Isotope analysis

Water samples were analyzed for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  at the laboratory of Stable Isotope Geochemistry of Institute of Geosciences and Earth Resources of National Research Council (IGG-CNR) in Pisa. The concentration of water isotopologues was determined using a Picarro L2140-i analyzer based on cavity ring-down spectroscopy (CRDS). Samples were analyzed by the “High Precision N2” analysis mode with nitrogen gas purging, sample volume injected of 1.8  $\mu\text{L}$  and each injection cycle lasting 9 min. To reduce memory effects the number of injections per sample was set as 9. The first 6 injections were then discarded whereas the mean value of the last 3 ones was calculated. For drift monitoring, an in-house quality control (QC) sample with an isotope value in the range of the analyzed samples (DIp:  $\delta^{18}\text{O} = -6.75$  ‰  $\pm 0.04$ ,  $\delta^2\text{H} = -39.7$  ‰  $\pm 0.4$ ) was re-analyzed in the sequence. Finally, the data set was normalized to the VSMOW/SLAP scale by using three in-house reference waters (calibrated directly against VSMOW2 and SLAP2) that were distributed regularly over the sequence (SSW:  $\delta^{18}\text{O} = -0.49$  ‰  $\pm 0.03$ ,  $\delta^2\text{H} = -1.62$  ‰  $\pm 0.4$ ; ORMEA:  $\delta^{18}\text{O} = -11.57$  ‰  $\pm 0.02$ ,  $\delta^2\text{H} = -78.4$  ‰  $\pm 0.4$ ; NIVOLET:  $\delta^{18}\text{O} = -22.48$  ‰  $\pm 0.1$ ,  $\delta^2\text{H} = -172.45$  ‰  $\pm 0.4$ ). All data are reported in the standard  $\delta$ -notation in per mil (‰) compared to the international reference standard V-SMOW. The uncertainty propagation calculated on the precision of measurements (standard deviation between injections) and normalization procedure resulted in an error of  $\pm 0.05$  ‰ for  $\delta^{18}\text{O}$  and  $\pm 0.5$  ‰ for  $\delta^2\text{H}$ .  $d$  was calculated by Dansgaard’s equation (Dansgaard, 1964) using the relationship  $d\text{-excess} = \delta^2\text{H} - 8*\delta^{18}\text{O}$ . Error propagation for  $d$  resulted in a value of about  $\pm 1.1$  ‰. The deviations from the original isotope composition, i.e., isotopic shifts ( $\Delta\delta^{18}\text{O}$ ,  $\Delta\delta^2\text{H}$ ,  $\Delta d$ ), were calculated as differences between the final isotope composition and the initial isotope composition of waters. The propagated error for isotope shifts was  $\pm 0.07$  ‰ for  $\Delta\delta^{18}\text{O}$ ,  $\pm 0.7$  ‰ for  $\Delta\delta^2\text{H}$ ,  $\pm 1.6$  ‰ for  $\Delta d$ .

## 3. Results

### 3.1. Atmospheric conditions

The environmental atmospheric conditions during the experiment became more conducive to evaporation as the season proceeded (Fig. 2). *In-situ* measurements were only available from the end of April 2022, therefore data from the SIR station were used for the first experimental period (1). However, *in-situ* and SIR data showed a very similar pattern. The temperature ranged from a minimum of 13.1 °C in the first period (April 2022) to a maximum of 29.5 °C in the last period (July 2022). Conversely, the relative humidity was higher in period 1 (mean value of 70 %) and lower in periods 3–4 (mean value of 58 %). Humidity was also much more variable than temperature during each experimental period, with decreases up to values of about 30 %.

### 3.2. Water depth and evaporative mass losses

The water depth measured within bottles of each rain sampler is reported in Table 2. We checked that the inlet tube touched the bottom of each bottle at one of its corners, to ensure that the end of the tube was submerged at that water depth. Since the centre of the bottles’ bottom was slightly raised, water tended to accumulate in the corners for the first few millimetres and only after reaching a certain thickness it formed a homogeneous surface. The collectors filled to  $<2$  % ( $R_O$ ,  $R_C$ ,  $R_P$ ,  $R_{H10}$ ) had a slightly higher water depth than this surface, but the end of the inlet tube was submerged in all cases (Fig. 1).

The calculation of evaporative mass losses was useful for identifying two cases when the experiment failed (Table 3). The first one was for the Oil collector during the experimental period 3, when we measured a slightly higher final mass than the initial one. This was likely due to the entry of humidity and/or precipitation from the outside into the bottle, which is due to an incorrect positioning of the tube protecting the cap from water inflow. The second case of experiment failure was for the Home-made Tube-dip-in-water collector filled to 5 % during period 4, when an evaporative mass loss of 40 % was measured with respect to the initial mass. This value was much higher than mass losses measured in other tests for all tested collectors, which may not be only attributed to poor performances of the anti-evaporative system. It may be due to incorrect positioning of the cap of the collecting bottle, thus exposing a larger water surface to the atmosphere, or to an accidental loss of water resulting in incorrect weighing. Therefore, these two cases were considered failed tests, and these data were not used for further consideration. The climatic conditions over the experimental periods caused rather low evaporative mass losses for all precipitation collectors (Table 3). Among collectors filled with a precipitation amount of about 10 mm (filling percentage  $<2$  %), the Oil collector experienced the smallest losses, always lower than 0.2 % of the original mass, followed by the Control collector and the  $R_{H10}$  (mass losses lower than 0.4 %). Conversely, the Palmex collector showed the largest losses that ranged in the interval 0.5–1.0 %. The two Home-made Tube-dip-in-water collectors  $R_{H35}$  and  $R_{H70}$  exhibited very low mass losses that were lower than 0.2 %.

### 3.3. Isotope shifts

The isotope composition of water from collectors at the end of each experiment is reported in Table 3, along with isotope shifts relative to the original isotope composition ( $\Delta\delta^{18}\text{O}$ ,  $\Delta\delta^2\text{H}$ ,  $\Delta d$ ). The deviations from the original isotope composition for each collector are shown in dual-isotope plots ( $\Delta\delta^2\text{H}$  vs.  $\Delta\delta^{18}\text{O}$ , Fig. 3). The area indicated by the grey box is defined by propagated errors associated with the  $\Delta\delta^2\text{H}$  and  $\Delta\delta^{18}\text{O}$ , such that only the points lying outside the box can be considered as shifted with respect to the original isotope composition, net of their relative error. Among collectors filled to  $<2$  %, the Oil collector exhibited the smallest isotope alterations that were within (or at limit)

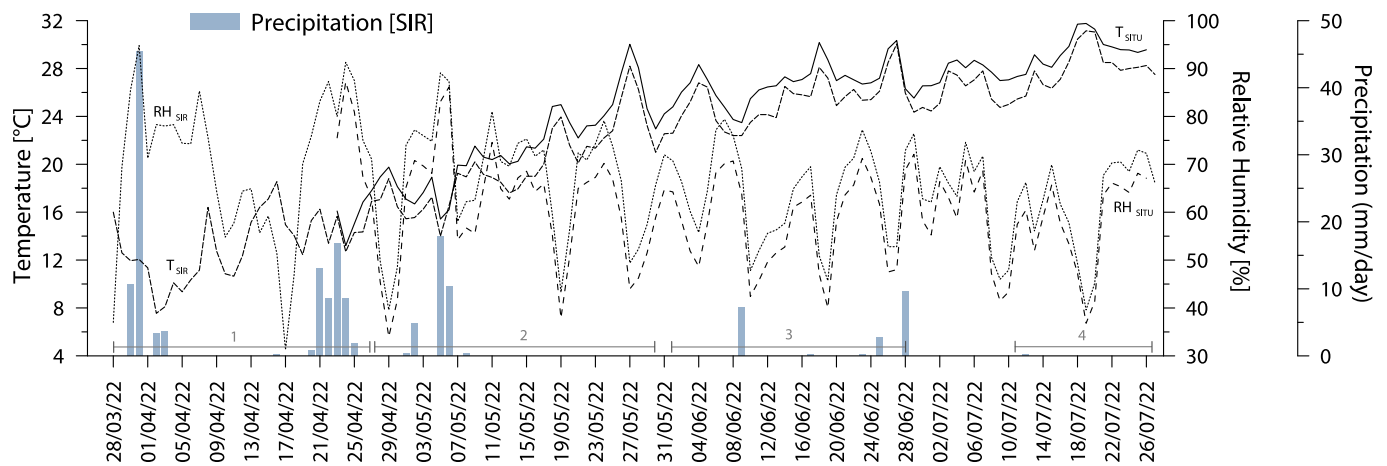


Fig. 2. Environmental conditions of daily mean atmospheric temperature (T), relative humidity (RH), and daily precipitation during the experiment. The four experimental periods are indicated by the grey horizontal bars along the time axis and labelled as period 1, 2, 3 and 4.

Table 3

Experimental data for each precipitation collector ( $R_C$  – Control,  $R_O$  – Oil,  $R_P$  – Palmex,  $R_{H10}$  – Home-made 10 mm,  $R_{H35}$  – Home-made 35 mm,  $R_{H70}$  – Home-made 70 mm) over the four experimental periods. Evaporative mass losses ( $\Delta w$ ) and isotope shifts ( $\Delta\delta$ ) are reported. The mass losses are expressed as absolute mass losses [g], and as percentages of the original water masses [%]. The underlined values indicate isotope shifts larger than analytical errors. Two cases when the experiment failed are indicated in blue and they were excluded from the discussion.

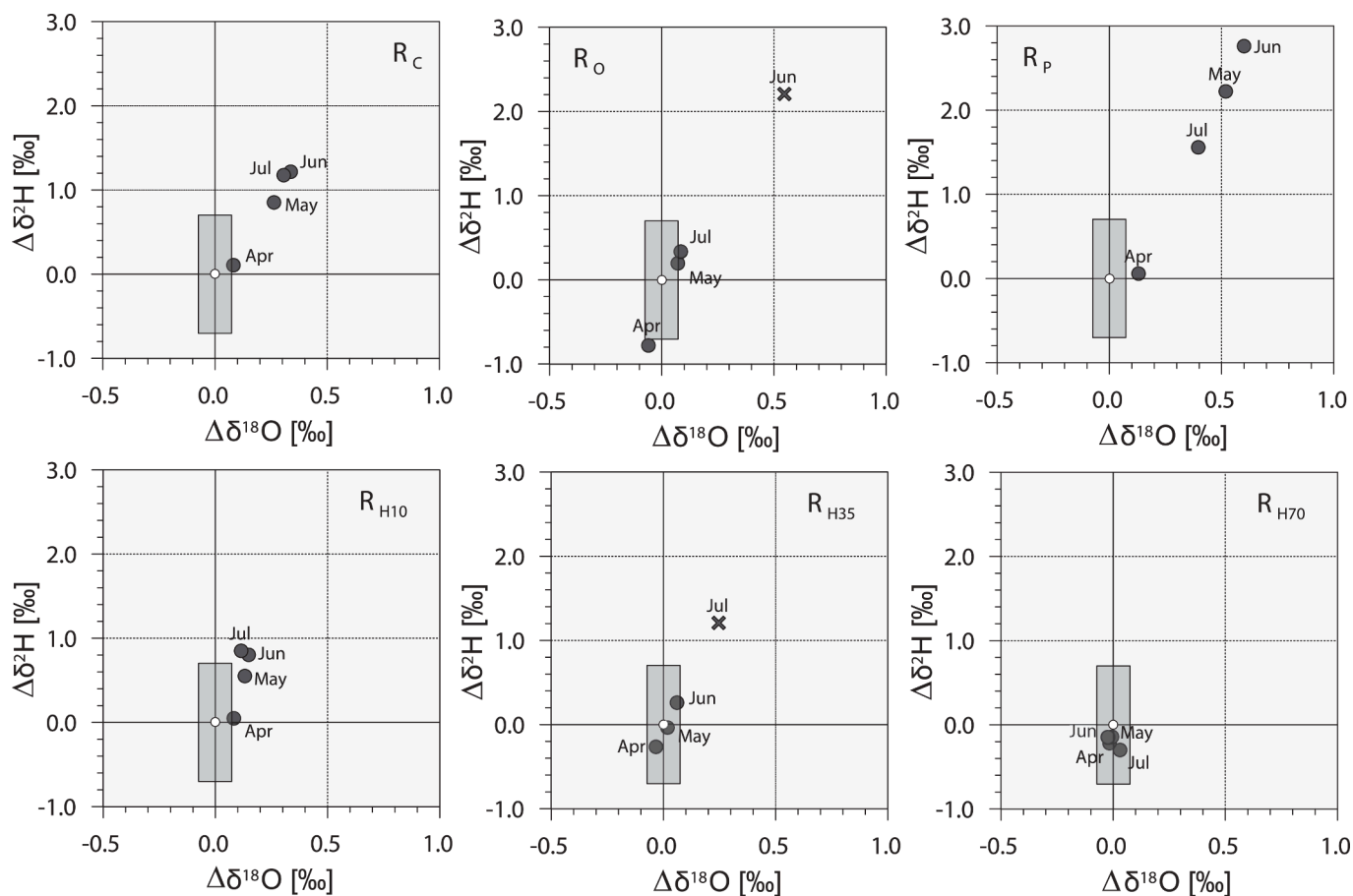
Code	Period	$w_{in} H_2O$ [g]	$w_{fin} H_2O$ [g]	$\delta^{18}O$ [‰]	$\delta^2H$ [‰]	$d$ [‰]	$\Delta w$ [g]	$\Delta w$ [%]	$\Delta\delta^{18}O$ [‰]	$\Delta\delta^2H$ [‰]	$\Delta d$ [‰]
$R_C$	1	143.1	142.6	-7.04	-40.4	15.9	-0.5	0.1	<u>0.08</u>	0.1	-0.5
	2	143.1	142.1	-6.86	-39.7	15.2	-1.0	0.1	<u>0.26</u>	<u>0.9</u>	-1.2
	3	143.1	141.1	-6.79	-39.3	15.0	-2.0	0.3	<u>0.34</u>	<u>1.2</u>	-1.5
	4	143.1	140.6	-6.82	-39.4	15.2	-2.5	0.4	<u>0.31</u>	<u>1.2</u>	-1.3
					<b>mean</b>	<b>-1.5</b>	<b>0.2</b>	<b>0.25</b>	<b>0.9</b>	<b>-1.1</b>	
$R_O$	1	143.1	143.1	-7.18	-41.3	16.1	0.0	0.0	-0.06	<u>-0.8</u>	-0.3
	2	143.1	142.6	-7.05	-40.4	16.1	-0.5	0.1	0.07	0.2	-0.4
	3	143.1	146.1	-6.58	-38.3	14.3	3.0	0.4	<u>0.54</u>	<u>2.3</u>	<u>-2.1</u>
	4	143.1	141.1	-7.04	-40.2	16.1	-2.0	0.2	<u>0.08</u>	0.3	-0.3
					<b>mean</b>	<b>-0.8</b>	<b>0.1</b>	<b>0.03</b>	<b>-0.1</b>	<b>-0.3</b>	
$R_P$	1	143.1	140.1	-6.99	-40.5	15.5	-3.0	0.5	<u>0.13</u>	0.1	-1.0
	2	143.1	138.6	-6.61	-38.3	14.5	-4.5	0.8	<u>0.52</u>	<u>2.2</u>	<u>-1.9</u>
	3	143.1	137.6	-6.52	-37.8	14.4	-5.5	1.0	<u>0.60</u>	<u>2.8</u>	<u>-2.0</u>
	4	143.1	140.1	-6.73	-39.0	14.8	-3.0	0.5	<u>0.40</u>	<u>1.6</u>	-1.6
					<b>mean</b>	<b>-4.0</b>	<b>0.7</b>	<b>0.41</b>	<b>1.7</b>	<b>-1.6</b>	
$R_{H10}$	1	143.1	141.6	-7.04	-40.5	15.8	-1.5	0.2	<u>0.08</u>	0.0	-0.6
	2	143.1	140.6	-6.99	-40.0	15.9	-2.5	0.4	<u>0.13</u>	0.6	-0.5
	3	143.1	141.6	-6.98	-39.8	16.1	-1.5	0.2	<u>0.15</u>	<u>0.8</u>	-0.4
	4	143.1	140.1	-7.01	-39.7	16.4	-3.0	0.4	<u>0.11</u>	<u>0.9</u>	-0.1
					<b>mean</b>	<b>-2.1</b>	<b>0.3</b>	<b>0.12</b>	<b>0.6</b>	<b>-0.4</b>	
$R_{H35}$	1	501.0	499.0	-7.16	-40.8	16.4	-2.0	0.2	-0.03	-0.3	-0.1
	2	501.0	499.0	-7.11	-40.6	16.3	-2.0	0.2	0.02	-0.1	-0.3
	3	501.0	498.5	-7.06	-40.3	16.2	-2.5	0.2	0.06	0.2	-0.3
	4	501.0	81.0	-6.88	-39.3	15.7	-420	40	<u>0.24</u>	<u>1.3</u>	-0.7
					<b>mean</b>	<b>-2.2</b>	<b>0.2</b>	<b>0.00</b>	<b>-0.1</b>	<b>-0.2</b>	
$R_{H70}$	1	1002	999.0	-7.14	-40.8	16.3	-3.0	0.2	-0.02	-0.2	-0.1
	2	1002	1001	-7.13	-40.7	16.3	-1.0	0.1	-0.01	-0.1	-0.1
	3	1002	998.5	-7.15	-40.7	16.5	-3.5	0.2	-0.02	-0.1	0.0
	4	1002	999.5	-7.09	-40.9	15.9	-2.5	0.2	0.03	-0.3	-0.5
					<b>mean</b>	<b>-2.5</b>	<b>0.2</b>	<b>-0.01</b>	<b>-0.2</b>	<b>-0.2</b>	

Note: Tab. Change to Table globally kindly check.

the error for both  $\delta^{18}O$  and  $\delta^2H$ . The Home-made Tube-dip-in collector  $R_{H10}$  also showed satisfactory results, with isotope shifts just over the precision for  $\delta^{18}O$ , but within the  $2\sigma$  interval for  $\delta^2H$  in two of the four cases. For the Palmex collector, we found considerable isotope enrichments reaching values of 0.60 ‰ for  $\Delta\delta^{18}O$  and 2.8 ‰ for  $\Delta\delta^2H$ . The isotope shifts were even worse than those observed for reference collector with no system to prevent sample evaporation. The isotope shifts were lower in period 1 (April 2022) for both Palmex and Control collectors, when environmental conditions were less prone to evaporation, and they increased as the experiment progressed through warmer and drier conditions. The two Home-made Tube-dip-in-water collectors  $R_{H35}$

and  $R_{H70}$ , that were filled with higher water volumes, exhibited the lowest isotope modifications and the corresponding data points scatter around the original isotope composition.

To include the gravimetric data, we also plotted the  $\Delta\delta^{18}O$  values of each test against the corresponding mass losses (Fig. 4). As expected, the smallest isotope shifts are accompanied by low mass losses, whereas higher mass losses were associated to large isotope changes for the Palmex and Control collector. Shifts in the deuterium excess were also observed (Table 3), but they were significant and larger than the error associated to this parameter only in two cases for the Palmex collector.  $\Delta d$  was rather low in the Oil and Home-made collectors.

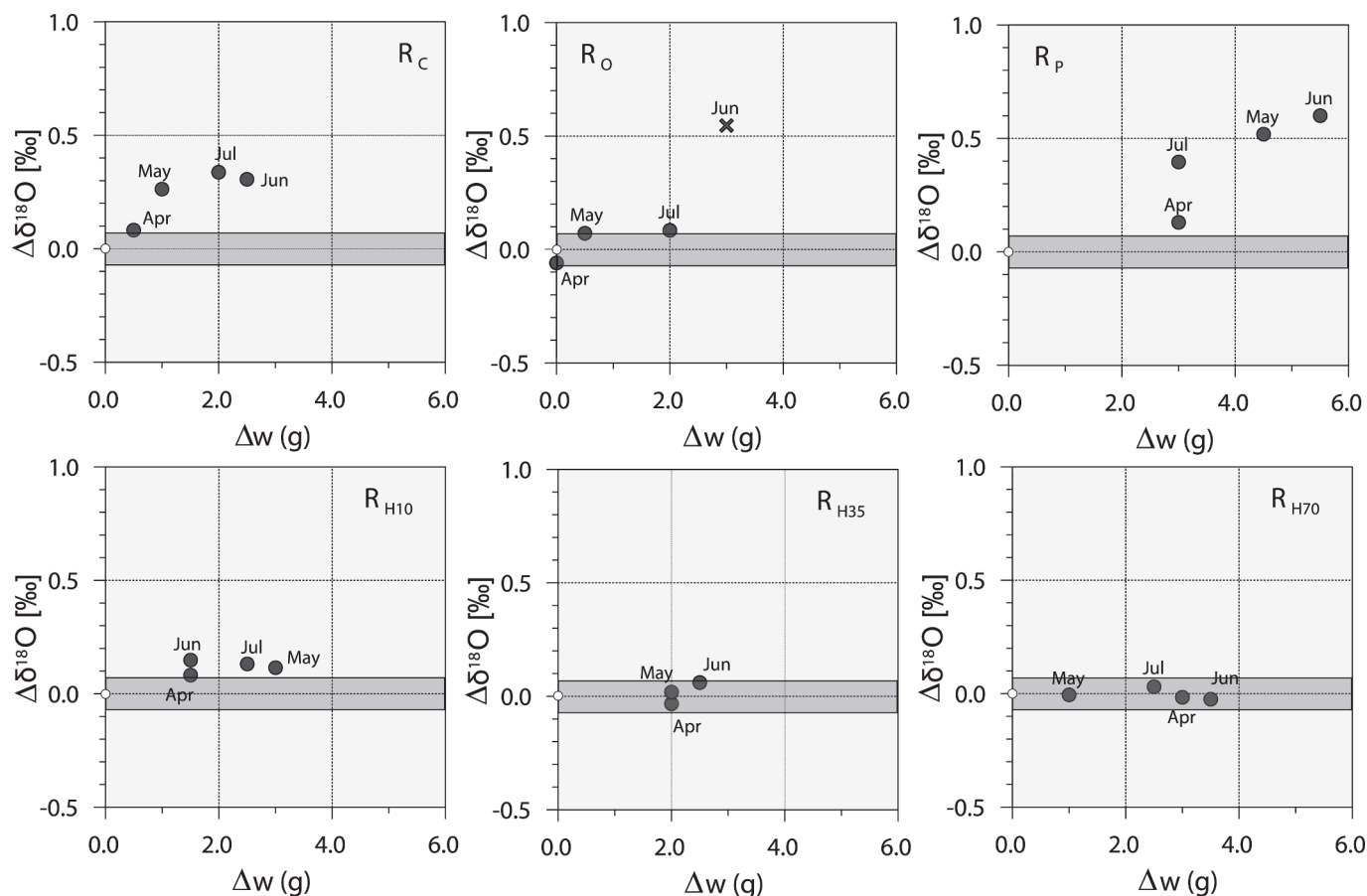


**Fig. 3.** Dual-isotope plots ( $\Delta\delta^2\text{H}$  vs.  $\Delta\delta^{18}\text{O}$ ) reporting the isotope shifts from the original isotope composition for each collector ( $R_C$  – Control,  $R_O$  – Oil,  $R_P$  – Palmex,  $R_{H10}$  – Home-made 10 mm,  $R_{H35}$  – Home-made 35 mm,  $R_{H70}$  – Home-made 70 mm) and each experimental period. The small white dots represent a null isotope shift, whereas the grey boxes represent the propagated errors associated with the  $\Delta\delta^2\text{H}$  and  $\Delta\delta^{18}\text{O}$ . Two “failure” periods of the experiment are indicated with a cross symbol, and they were excluded from the discussion.

#### 4. Discussion

Results from the experiment carried out in this study demonstrated the reliability of oil as an efficient method to prevent water evaporation within collecting bottles, also when very low amounts of total monthly precipitation were tested. This outcome is congruent with results from the laboratory experiment by Michelsen et al. (2018) and it explains the popularity of this collector in isotope hydrology studies on monthly precipitation. Tube-dip-in-water collectors, by contrast, exhibited worse performance in preventing evaporation of very low amount precipitation samples, albeit with different results. The Home-made sampler ( $R_{H10}$ ) showed rather low isotope shifts that were significantly lesser than those observed for the Control collector (with no system to prevent evaporation) and close the analytic uncertainties for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ . Moreover, this sampler model provided excellent results when bottles were to 5% ( $R_{H35}$ ) and 10% ( $R_{H70}$ ) of the total volume, as evidenced by very low mass losses and not significant isotope shifts (Figs. 3, 4). This proved the Tube-dip-in-water design as effective in preventing evaporation for low-amount precipitation samples and indicated acceptable performance of this anti-evaporative system also for very low water volumes. Unexpectedly, the Palmex collector showed significantly larger isotope shifts than values measured for the Control and  $R_{H10}$ , and also than results from the laboratory experiment performed by Michelsen et al. (2018). The isotope modifications were even greater than the shifts measured in the field experiment carried out by Gröning et al. (2012). However, larger water volumes were used by these authors with bottles filled to higher percentage compared to our experiment, although their test was performed under more extreme environmental

conditions. Therefore, while the anti-evaporative system was rather effective in the Home-made collector ( $R_{H10}$ ), albeit with small isotope shifts, large isotopic fractionation occurred inside the Palmex bottle. Since this outcome was fairly unexpected, we tried to explore the possible reasons behind the worse performance of this Tube-dip-in-water collector. Firstly, we ensured that the end of the inlet tube was submerged for each sampler, including Palmex, thus excluding the possibility of vapour exchange through an open inlet tube. However, the water depth tested for  $R_P$  and  $R_{H10}$  (the same for  $R_C$  and  $R_O$ ) was extremely low (<2%) and it may not have been enough to correctly fill the inlet tube, thus limiting the effectiveness of the system. Possible cycles of evaporation and condensation into the headspace of the bottles with a very high vapour/water ratio might have also represented the main cause of isotope modification (as also suggested by Michelsen et al. 2018). The Palmex square-section bottle was also 15 cm<sup>2</sup> larger than the cylindrical bottles used for the other samplers, and this factor may also have influenced in some way the correct functioning of the anti-evaporation system. Results from Spangenberg (2012) proved that HDPE bottles were effective in preventing water evaporation due to vapour diffusion through bottle walls. The caps of each sampler were tightly closed and the pressure inside of bottles were the same as the external one; therefore, vapour diffusion through the walls and/or lid seal may be reasonably excluded. Also, differences in the inlet and vent tubes used for the Home-made and Palmex collectors were too small to justify different vapour diffusion. Considering the short-term variations of local temperature and pressure, the vent tubes used for both samplers were enough for accommodating the air displacement due to the internal air expansion. The main difference between the Palmex collector and



**Fig. 4.** Dual plots ( $\Delta\delta^{18}\text{O}$  vs.  $\Delta w$ ) reporting the  $\delta^{18}\text{O}$  deviations from the original isotopic value for each collector ( $R_C$  – Control,  $R_O$  – Oil,  $R_P$  – Palmex,  $R_{H10}$  – Home-made 10 mm,  $R_{H35}$  – Home-made 35 mm,  $R_{H70}$  – Home-made 70 mm) and each experimental period with respect to mass losses. The small white dots represent a null isotope shift, whereas the grey boxes represents the propagated error associated with the  $\Delta\delta^{18}\text{O}$ . The “failure” period of the experiment for the Oil collector is indicated with a cross symbol, whereas the one for  $R_{H35}$  is not reported because it was out of scale. Both these isotope shifts were excluded from the discussion.

the Home-made Tube-dip-in-water models was the outer case material. The Palmex sampler was enclosed in a metal outer case, whereas a plastic box was used for the Home-made collectors. Metal is a strong heat conductor, and this could have promoted an overheating of the Palmex bottle, when exposed to solar radiation, potentially enhancing the day-night temperature fluctuations inside the bottle and between the bottle and the case. This could have led to greater evaporation but potentially also to larger expansion–contraction cycles of the gas inside the bottle, thus promoting vapour exchange with the external atmosphere. Conversely, the plastic box had lower thermal conductivity than the metal case, and this could have significantly reduced the temperature fluctuations. However, we would like to stress that this is just a hypothesis, and further tests will have to be carried out also by measuring the temperature fluctuations outside and inside the bottle.

Overall, results from our experiment suggest that isotope fractionation may occur for water depth of about 1 cm both for the Palmex and Home-made Tube-dip-in-water collectors, whereas no significant isotope shifts were measured for water depth of about 2.3 cm for the Home-made sampler. Hence, we cannot exclude isotope fractionation for precipitation samples corresponding to water depth lower than about 2 cm using samplers equipped with this anti-evaporative system. Therefore, using this model of precipitation sampler may be risky when precipitation samples are very low, especially in arid and semi-arid climates, and in warm dry seasons. On the other side, the excellent results achieved with the Home-made collectors tested for higher water volumes confirmed the effectiveness of Tube-dip-in-water collectors in preventing post-sampling evaporation (Gröning et al., 2012; Michelsen et al., 2018), and proved, for the first time, their reliability in a

Mediterranean area, such as the city of Pisa (*Csa* according to Köppen’s classification system, Köppen, 1931) where this field experiment was carried out. Hence, we feel that the Tube-dip-in-water model may be reliably used in most isotope hydrology studies, especially in regions with temperate to semi-arid climates, including Mediterranean areas. However, the choice of the optimal configuration (e.g., funnel size, bottle volume and section, vent tube diameter and length, etc.) may be complicated in areas characterized by a marked climatic seasonality, such as the Mediterranean region. In these cases, researchers should perform an accurate climatic analysis of the studied area, for instance by evaluating the trend of mean monthly rainfall over a sufficiently representative time interval, in order to properly size all the components of the rain sampler. In the event that the selected configuration leads to the collection of too small water volumes (i.e., water depth  $<2$  cm) in some periods, the researchers should adjust the design of their precipitation collectors throughout the year depending on climate conditions: smaller funnels and/or larger bottles in rainier seasons; larger funnels and smaller bottles in drier periods. Moreover, the vent tube inner diameter and length should be sized accordingly to the maximum expected pressure and temperature variations inside the sample bottle, as well as the ambient conditions at the installation site.

With regard to the worst performances achieved by the Palmex collector, it is worth highlighting that no evidence emerged from this study about the inaccuracy of this sampler in preventing evaporation and isotope fractionation for higher volumes of precipitation samples than those tested in this experiment. We only tested an extremely low water depth ( $<2$  %) with this collector, and therefore we cannot exclude better performance for higher volumes. Further investigations would be



necessary to test the effectiveness of this collector model for higher water amounts and to better constrain the reasons behind the worse performance of this Palmex sampler and to suggest possible solutions for this device. The experiment should be repeated by testing multiple water levels and accurately monitoring the temperature and pressure fluctuations within and around the collector.

Finally, valuable implications of this work are that data for low-amount monthly precipitation samples collected with Tube-dip-in-water samplers, including where these have been deployed in global networks such as the GNIP, may be prone to a somewhat systematic error, particularly in the warmest and driest climates. This may have an impact where these data are used in local–global scale climate or hydrology applications. However, for hydrology, low rainfall months are somewhat irrelevant since they represent a negligible component of the total annual precipitation which contributes to recharge within the hydrological cycle.

## 5. Conclusions

We tested field performance of different Tube-dip-in-water collectors in preventing evaporation and isotope fractionation during the collection of low-amount monthly precipitation samples, through a field experiment carried out in the city of Pisa (Tuscany, Italy), in the Mediterranean region. The survey allowed for an evaluation of the reliability of precipitation samplers in areas with a Mediterranean climate during warmer and drier seasons, when weak precipitation more frequently occur.

The Oil collector is confirmed as the most reliable model to collect precipitation, also for very low water amounts, as indicated by the smallest evaporative mass losses and lowest isotope shifts. Particular attention should be paid during isotope analysis by laser spectroscopy (Prechsl et al., 2014; Sánchez-Murillo et al., 2017) and oil should be accurately removed before the analysis. Oil-free Tube-dip-in-water collectors represent a reliable alternative in most studies of isotope hydrology, but a more prudent approach is strongly recommended at the sampling stage. Researchers should carefully calibrate the choice of the size of the funnel and the volume of the bottle to use according to the climatic features of the area and seasonality. The choice should be aimed at minimizing the air/water ratio inside bottles in all seasons, also resorting to modifications of design during monitoring and adopting different solutions for different seasons.

Results from our tests performed on the Palmex collector suggest the need of further field experiments for this collector model, aimed to evaluate its reliability in warmer and drier environments (i.e., semi-arid and arid regions) where the atmospheric conditions are more conducive to evaporation and weak precipitation generally occurs. As previously suggested by Michelsen et al. (2018), we encourage researchers to conduct their own field experiments in areas where they carried out their investigations.

The Home-made Tube-dip-in-water collector tested in this work proved to be reliable, thus representing a viable low-cost alternative to more expensive commercially available models.

## CRedit authorship contribution statement

**Stefano Natali:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Matteo Nigro:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Iliaria Baneschi:** Writing – review & editing, Validation, Resources, Data curation. **Roberto Giannecchini:** Writing – review & editing, Resources. **Marco Doveri:** Writing – review & editing, Resources. **Giovanni Zanchetta:** Writing – review & editing, Resources.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data are included in the manuscript (Table 3)

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