

Reply to the referee#2' comments:

We acknowledge the comments made by the Referee#2, that we will try to answer and take into account in order to improve our manuscript.

- The first reason we decided to publish this technical note was because we could not find any other published experimental validation of the Gonfiantini (1986) equation where evaporating waters experienced time periods when heavy isotopes were depleted instead of enriched.

Indeed, this was also an opportunity to demonstrate an example of the errors that can be incurred if the meteorological data are just time-averaged, as we did in Figures 4 and A2. However, these graphs show the errors in modelling the isotopy of the evaporating water, but not the errors on the inverse calculation of the volume of evaporated water from its isotopic composition, which is the most frequent target as stated in the introduction.

To this end, we applied an inversion of the equation (1):

$$(1 - x) = \left(\frac{\delta_L - \delta^*}{\delta_o - \delta^*} \right)^{1/m} \quad (R-1)$$

Where δ_o represents the isotopy of the pool water at the beginning of the experiment, i.e. the 'original' water in real applications that can be obtained by the intersection of the LEL and the LMWL (e.g. Benettin et al., 2018), and δ_L represents the isotopy of the water obtained at every visit. The other variables and parameters are the same as for equation (1).

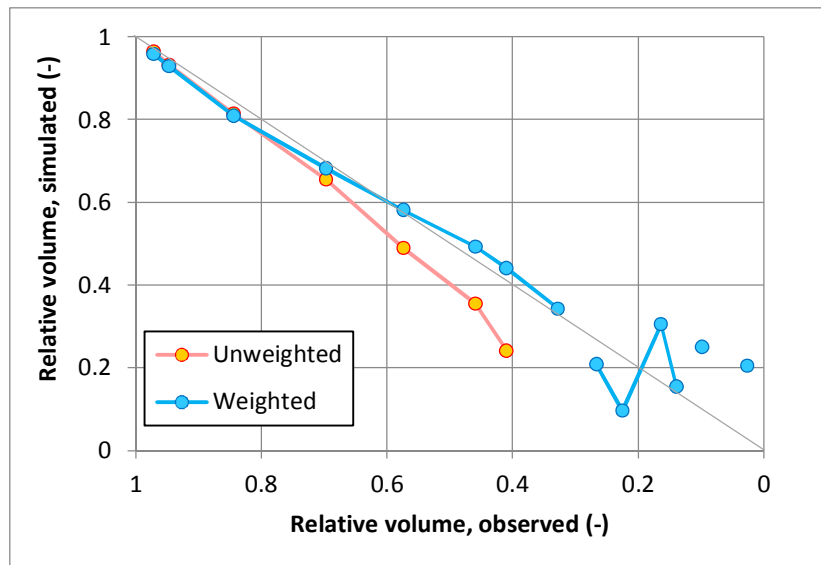


Figure R- 3: Simulation of the relative volumes of evaporating waters applying equation (R-1) and comparing the use of both unweighted and ETP-weighted meteorological parameters. Gaps in the lines correspond to mathematical errors (non-real number results) of equation (R-1).

The application of this equation to ^{18}O is shown in Figure R-3. When time-averaged (unweighted) meteorological data were used, the equation (R-1) predicted slightly smaller residual relative water volumes than observed for the 7 first observations, but it was in mathematical error for the remaining observations. These errors are due to the fact that the limiting water isotopy δ^* had values between the original δ_o and the terminal δ_L ones, an impossible arrangement because, following equation (1), evaporation will approximate the isotopy of water towards δ^* by increasing or decreasing its value, but it cannot modify the

isotopy of water by crossing the δ^* value. Figure 4a shows indeed that (unweighted) δ^* values were smaller than the observed δ_L values for the latter two-thirds of the experiment.

When the equation (R-1) was applied with ETP-weighted meteorological data, the results were much better for most of the observations, although some mathematical errors also occurred (line discontinuities). These errors do occur because the real δ_o of the evaporating process is not the value at the start of the experiment, but the δ_L value of the former step. In Figure 6a, these samples correspond to those that underwent ^{18}O depletion instead of enrichment: the corresponding observed δ values were smaller than the preceding ones but larger than the corresponding limiting δ^* values, so the application of equation (R-1) yields adequate results at the weekly step scale but not at the full experiment scale. The analysis at the weekly step scale are not feasible when time-averaged (unweighted) meteorological data were used, because the limiting δ^* values were strongly underestimated.

In fact, Figures 2a and R-3 demonstrate the limitations of the isotopic method for assessing the residual volume of water in a pool. This method would require a monotonic change in the isotopy for a decreasing volume of water, but this requirement fails when the isotopy of the pool water comes close to the steady ratio δ^* . When this occurs, evaporation may continue with either sustained or decreasing concentrations of heavy isotopes.

- Although we have 5-minute weather data, our data on water level and rain and pool water isotopy were obtained at the weekly step. Therefore, although we recognise its possible interest, we discarded doing any simulation with a smaller time step, because we could not validate the results, losing the main purposes of our work. We acknowledge the suggestion and retain it for further investigations on the subject.

L28 the cited papers did not all use weekly-monthly means.

- We are amending this mistake in the revised version

L35 bidirectional exchange is ubiquitous, not just when humidity is high.

- We will modify this sentence following the writing of the cited authors and taking into account this recommendation.

L45 isotope equilibration field studies have been conducted across a range of climates. The novelty of a subhumid climate is not great; e.g., the cited works by Gonfiantini include field data from Italy.

- Yes. This is right, we are changing the sentence adequately.

*L67 it is a fine distinction, but the *expected* isotopic composition was modeled as Eq 1.*

- Modeled instead of calculated is being stated

L69 Eq 1 is explicitly derived "assuming that the evaporation conditions remain unchanged" (Gonfiantini 1986, eq 7), so it is no surprise that it does not perform well at weekly timescales.

- The results show that the equation works reasonably well at weekly timescales when parameterized with ETP-weighted air temperature and relative humidity, as shown in Figures 6 and A4.

Fig 3 d-precipitation does not appear in Eq 2; I assume this should be d-A?

- In equation (2), δ^* are indeed calculated from δ_A (atmospheric moisture), which is derived from δ_p (precipitation) using equation (4). The value of both δ_p were set at =0 for designing the graph in order to obtain both $\delta^* = 0$ when air is at saturation.

L100, L124-126, L129, L132 text duplicates figure captions with no additional information.

- More explanations will be added to the text.

L105 apply how? weekly means?

- At any time step. This was written in order to show that equation (1) can simulate both depletion and enrichment. We can change the sentence into: "In fact, when equation (1) is applied to changes in pan water volume, the isotopic composition of the residual water (δ_L) can approach δ^* either following trends of both enrichment and depletion of heavy isotopes".

L106 but there is a 4-week period when d18O was increasing in the pan while d was less than the pan.*

-This behaviour is shown in Figure 4a, where δ^* values were underestimated because time-averaged temperature and humidity were used, but not in Figure (6a) obtained with ETP-weighted parameters. We will warn in the caption of the Figure (4) that these results are inadequate.

L108 because d is completely theoretical and not a measured quantity, it is not clear why something "might" cause a decrease in d*. Why is there any question? Similarly, L109-110 is simply restating the theory being applied, with no original content being contributed by the experiment.*

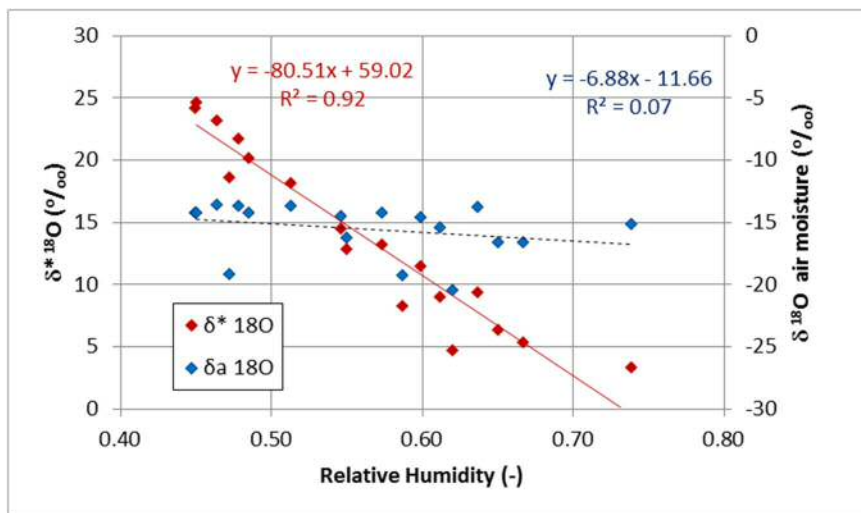


Figure R 1: weekly estimates of ^{18}O concentrations; steady (δ^*) and in air moisture (δ_a), in relation to relative humidity. Vertical scales are offset $30 \text{ } ^\circ\text{‰}$ from each other.

This refers to a time sequence: for the same isotopy of the atmospheric moisture, a temporal increase in relative humidity will determine (equation 2) a decrease in δ^* , as shown in Figure 3, and also in the enclosed figure R1. This explains most of the temporal variation in δ^* shown in Figure 6a. We can delete the citation to Craig et al. (1963), but the original outcome of the experiment is to show (Figure 6a) that the water in the pan was depleted in heavy isotopes during several fragmented weeks during evaporation, and that these depletion events were adequately simulated by the Gonfiantini (1986) equation because an increase in air relative humidity determined a decrease of the δ^* value below the antecedent δ_0 value in the pan

water. In other words, we observed and simulated using well known methods that water evaporation may cause weekly events of depletion in heavy isotopes of the evaporating water without the need of a high salinity of the water that would induce its progressive depletion instead of an irregular one.

L111 there are no methods presented that would allow these mass balance estimates. Was the mass or volume of water in the pan measured each time? If so, please consider presenting those data instead of the calculated 16O mass. L114 suggests volume data are available.

- Yes, we missed to explain in the methods section that the water volume was measured at every weekly visit, as shown in figures 4a and 6a.

We deemed that it was not necessary to describe how the amounts of light isotopes were calculated for the balance, but this was made as it follows:

First, the mass of water in moles M_w was obtained for every visit from its volume using a density of 0.9976 kilograms per litre and a molar mass of 18.015 grams per mole. Small changes in these values due to the variation in heavy isotope concentrations were not taken into account because they are mutually cancelled out.

Then, R_{sa} sample isotope ratios were obtained for each of the two heavy isotopes from the corresponding δ values:

$$R_{sa} = (\delta/1000 + 1) \cdot R_{st} \quad (R2)$$

Where R_{st} are the isotopic ratios of the VSMOW standards which were taken as 1/6420 for ^2H and 1/498.7 for ^{18}O .

Finally, the mass in moles of the light isotopes M_l were obtained for every sample and isotope using:

$$M_l = M_w \cdot n / (1 + R_{sa}) \quad (R3)$$

Where n is the number of atoms in each water molecule: 1 for oxygen and 2 for hydrogen.

L118 I suggest not using "RH" because "h" is already defined as the same thing.

-Yes, we will use "h" for relative humidity.

*L124 "d*18O" is not a concentration, it is a deviation.*

-Yes, we will use only the term 'value' for the denomination of δ , as done in most publications

Fig A2 the meaning of the solid lines is not specified.

- These are respectively a linear and a second order polynomial without any modelling purpose that are shown only as visual references. The equations will be shown in the final graphs.

L125, Fig 5, Fig A2 details of the methods to estimate PET are needed.

- We will state in the figure captions that PET was estimated using the Allen (1998) method. The estimation of PET were made as operationally recommended by the FAO in Allen et al (1998); we did not describe it the methods section because we did not introduce any

modification in the method, this is a well-known procedure and its description would need a much longer extension of the technical note.

L136 relevant to what?

- Relevant to the difference between isotope fractionation by a distillation process and by evaporation in a natural environment. We will try to improve the clarity of the sentence.

L138-140 I do not understand the point being made about rainfall and humidity and d^ . It appears the sentence assumes something about the relationship between rainfall and isotopic composition of atmospheric water vapor, but their relationship is irrelevant to d^* and only the vapor matters. It is of no importance to this statement that the isotopic composition of rainfall was used as a surrogate for the isotopic composition of vapor in this experiment.*

- There are several publications that claim that the isotopic composition of the air moisture is very relevant to the fractionation of evaporating waters, but equation (2), used to design the standard Figure 3 and the above Figure R1 showing experiment outcomes demonstrate that this is only true when relative humidity is high, but the values of δ^* rapidly increase when relative humidity decreases, to an extent that the variations of atmospheric moisture isotopy become marginal (may explain up to 8% of the δ^* variance in Figure R1).

We will try to explain this better.

L142 what is a "heavy isotope depletion period"? It is not clear which of the three nouns are being modified by "heavy." It is also not clear what a "depletion period" is L143. Are these referring to periods when d_{18O} in the pan become more negative?"

- We wanted to state "the susceptibility of the occurrence of periods in which water evaporation causes isotope depletion instead of enrichment must be taken into account." Yes, these refer to the samples (weeks) when the δ values decrease instead of increase respect to the preceding ones. We will modify these final remarks using the results corresponding to the new Figure R3 above.