

Referee#1:

We thank the reviewer for his comments, which show us some aspects of our note that we did not explain well enough.

- The intended more original aspect of the note is not the role of diurnal variations, but the evidence of periods of heavy isotope depletion during water evaporation, along with the adequate prediction of these periods using customary fractionation equations parameterized with air conditions.

In the recent literature, heavy isotope depletion of water is usually attributed to exchange with atmospheric moisture in equilibrium conditions, whereas our results show that it can happen during evaporation when relative humidity is still far from saturation. The early definitions of δ^* concentrations are not only the "isotopic composition which a water reaches in its final evaporation stages", but also "If $h > 50\%$ the isotopic composition rapidly approaches the limiting value A/B (δ^*) and then remains practically constant, simulating the occurrence of an isotopic steady state in the final evaporation stage" (Gonfiantini, 1986).

Indeed, Craig et al. (1963) already stated that "The deuterium and oxygen 18 concentrations of water evaporating into air of nonzero humidity do not follow the simple batch distillation equation but increase asymptotically to a stationary isotopic state as the mass of water decreases to zero".

These concepts are very relevant, because if the δ^* concentrations are understood as only reached in the "final evaporation stages" (as reiterated in several recent articles) there is no way to understand how evaporation can result in depletion of heavy isotopes. Conversely, if these δ^* concentrations are understood as "a stationary isotopic state" that is rapidly approached when the relative humidity of the air is rather high, it is easy to understand that changes in atmospheric conditions can induce the decrease of δ^* concentrations below the concentrations already reached in the pan water, and determine the depletion of heavy isotopes during evaporation.

Several authors recommended the use of evaporation flux-weighted atmospheric conditions for isotopic fractionation studies, but we found no evaluation of the errors that can be incurred if these recommendations are not followed.

-The sentence "rapid molecular exchange of isotopes between the water body and the atmospheric vapour, which predominates over the net isotopic effect of a simple evaporation process" is not ours, but quoted from Craig et al., 1963. We acknowledge the proposal of more updated citations, but we try to show that our findings can be explained by the early developments made many years ago on the isotopy of evaporating open water bodies.

-We did not explain well ourselves with our sentence "In drier conditions, these δ^* rapidly increase with decreasing air humidity and become detached from precipitation and atmospheric moisture isotopic content". We wanted to remark that, following eq. (2) and the resulting Fig (3), when the air is dry, the δ^* values sharply increase to an

extent that the variations of atmospheric moisture isotope become poorly relevant. Indeed, the results in our experiment show that the observed temporal changes in air relative humidity become much more important than those in air moisture isotope, as estimated from precipitation isotope. The new figure 6 shows the dependence of weekly $\delta^{*18}\text{O}$ and air moisture $\delta^{18}\text{O}$ estimates on relative humidity along the experiment. Air relative humidity explains 92% of $\delta^{*18}\text{O}$ variance while moisture isotope explains only 25%.

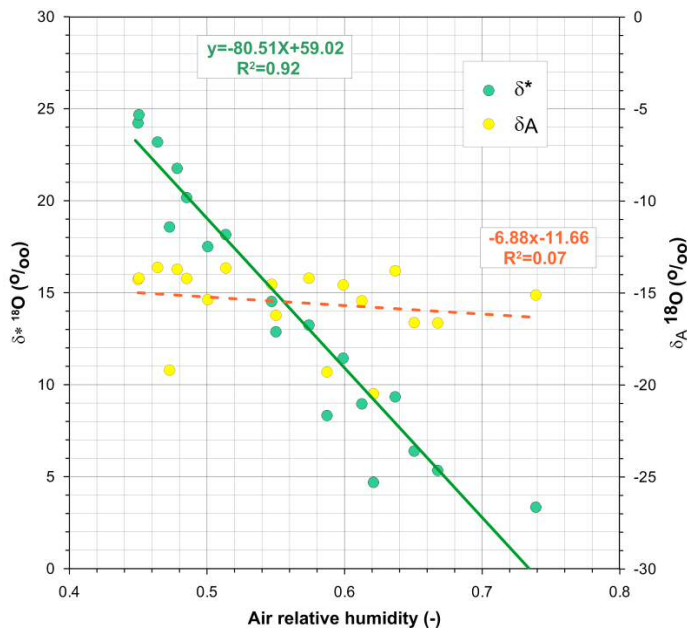


Figure 1: Weekly estimates of ^{18}O isotopic composition, limiting (δ^*) and in air moisture (δ_A), in relation to relative humidity. Vertical scales are offset 30‰ from each other.

- We thought that showing the temporal variation of δ^* values was sufficient to explain why we have decreasing isotopic composition at the late intervals. The comment leads us to add a new figure 7, following the one proposed by A. Rhode (cited by Saxena, 1986), which can help to understand the behaviour of our pan water.

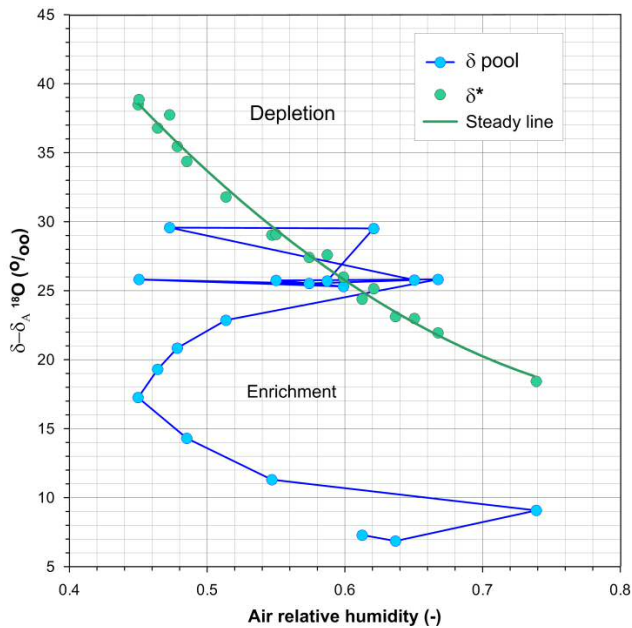


Figure 2: Evolution of the weekly differences between the isotope of water and air, plotted in relation to air relative humidity (from bottom to top). The green line that connects the $\delta^* - \delta_A$ points is a second order polynomial, shown only as visual reference.

In this figure, the differences in $\delta^{18}\text{O}$ between water and air moisture are plotted against air relative humidity, and the differences respect to δ^* values split the plot into a lower part where the differences in water isotope are lower than that of δ^* and an upper part where these are higher. According to equation (1), water conditions located on the δ^* curve undergo evaporation without any isotopic change (steady state or dynamic equilibrium), while evaporating waters located outside this curve tend to move towards it, becoming enriched (upward) or depleted (downward). Minor vertical displacements of the points may be due to changes in the isotope of the air moisture.

The isotopically depleted initial conditions (lower points) of the pan water determined its progressive enrichment during evaporation in spite of wide changes in air relative humidity. But by the ninth week of the experiment, pan water was already so enriched that a relevant increase in air relative humidity caused a strong decrease of δ^* and moved the situation of the pan water point to the 'depletion' area of the graph. Since this event, successive alternations in relative humidity determined isotopic enrichment and depletion periods, as already shown in Figures 2 and 6. We hope that these two new figures will help to show the changing environmental conditions along the experiment.

- We used air relative humidity because this is requested in the equations we used. Before using reference evapotranspiration for weighting relative humidity we tested several simpler options such as global radiation, vapour pressure deficit, as well as the combination of mean, minimum and maximum daily relative humidity. We agree that Penman formulation would be more adequate than Penman-Monteith reference formulation, but parameterisation of Penman-Monteith equation to 5-minute steps is

more physically sound and, although we did not use it for estimating pan evaporation, it predicted the decrease of its level with a determination coefficient of $r^2=0.994$.

- Pan level and the isotopy of both pan and precipitation waters were observed at weekly intervals, so it was necessary to aggregate air temperature and relative humidity to these periods for applying equations. The values of δ^* were obtained for every weekly step using equation (2). Pan evaporation x was obtained from observed water level changes in the pan and the simulated isotopy δ_L of pan water was calculated using equation (1). For the first step, the original isotopy of the pan water was used as the initial isotopy δ_0 , and for the subsequent time steps, the isotopy δ_L obtained in the former step was used as the initial isotopy δ_0 for the new step.

Citation:

Saxena RK. Estimation of canopy reservoir capacity and oxygen-18 fractionation in throughfall in a pine forest. Nord Hydrol 1986, 17:251–260.

Referee #2:

We acknowledge the comments made by the Referee#2, that we took 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):

$$(1 - x) = \left(\frac{\delta_L - \delta^*}{\delta_O - \delta^*} \right)^{1/m} \tag{11}$$

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).

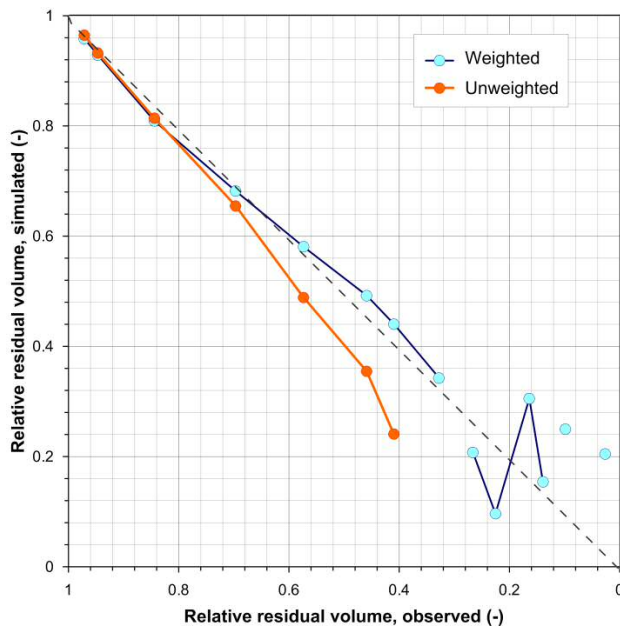


Figure 3: Simulated versus observed residual volumes of evaporating water applying equation (11) and comparing the use of both unweighted and PET-weighted meteorological parameters. Gaps in the lines correspond to lacking points due to mathematical errors (non-real number results) of equation (11).

The application of this equation to ^{18}O is shown in the new figure (11). 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 (11) 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 8 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 amended this mistake in the revised version

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

- We modify this sentence into: "Isotopic exchange that induces the depletion rather than enrichment in heavy isotopes of the evaporating water has been identified..."

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, but not to complete dryness; we changed the sentence into: "an artificial pan was set up and subjected to evaporation to complete dryness in a location with a sub-humid climate, as a counterweight to the more frequent studies in dry climates".

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

- Modeled instead of calculated is now 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 5 and A5.

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 are now 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. This sentence has been deleted and the fact that equation (1) may predict both enrichment and depletion is stated when the equation is explained: "It is worth emphasizing that this equation does not determine that evaporation induces an increase of δ_L with respect to δ_0 (enrichment) but that δ_L approaches δ^* in either direction (enrichment or depletion)."

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 2a, where δ^* values were underestimated because time-averaged temperature and humidity were used, but not in Figure (5a) obtained with ETP-weighted parameters. We warn now in the caption of the Figure (5) 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.*

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 figures 6 and 7. This explains most of the temporal variation in δ^* shown in Figure 5a. We could delete the citation to Craig et al. (1963), but the original outcome of the experiment is to show (Figure 5a) 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.

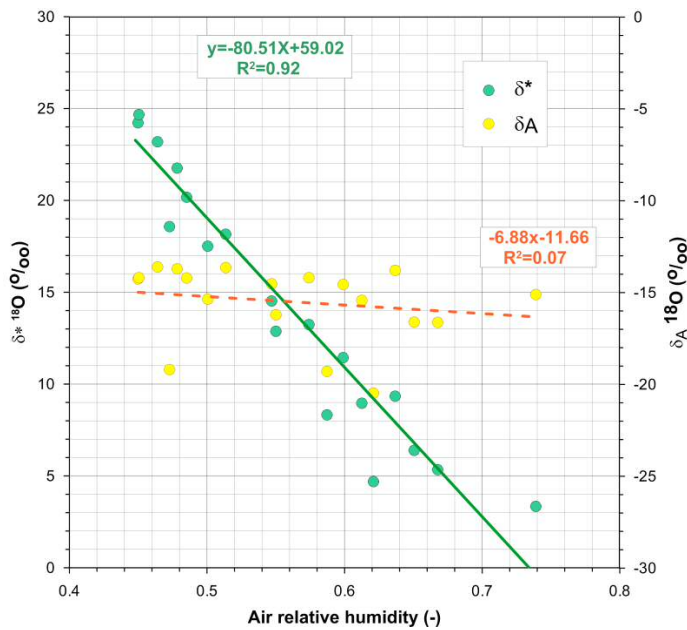


Figure 4: Weekly estimates of ^{18}O isotopic composition, limiting (δ^*) and in air moisture (δ_A), in relation to relative humidity. Vertical scales are offset 30‰ from each other.

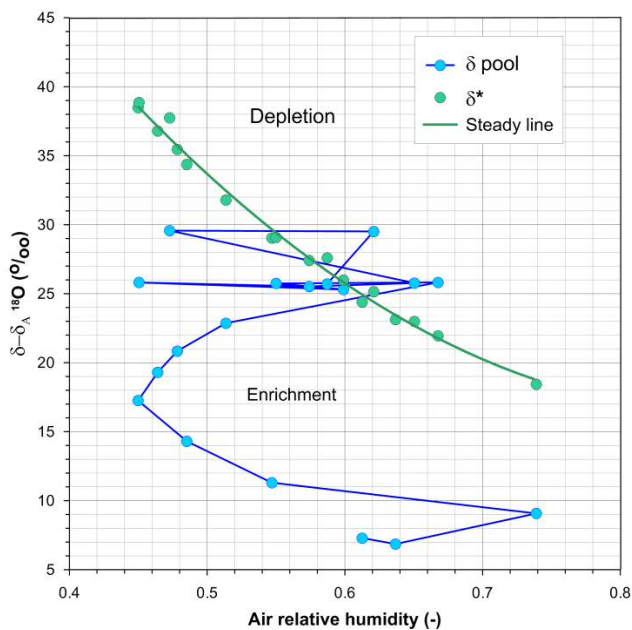


Figure 5: Evolution of the weekly differences between the isotopy of water and air, plotted in relation to air relative humidity (from bottom to top). The green line that connects the $\delta^* - \delta_A$ points is a second order polynomial, shown only as visual reference.

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 ^{16}O 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:

$$R_{sa} = (\delta/1000 + 1) \cdot R_{st} \quad (9)$$

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:

$$M_l = M_w \cdot na / (1 + R_{sa}) \quad (10)$$

Where na 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 now use "h" for relative humidity.

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

-Yes, we now 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 are now shown in the final graphs.

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

- We state in the methods 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 6 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 or rainfall isotopies become marginal.

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 $d18O$ in the pan become more negative?"

- We deleted this sentence and wrote the following one: "Evaporation of water does not always induce heavy isotope enrichment, but may progress without isotopic change in a steady state process when the composition of evaporating water is equal to the limiting δ^* value, or it can lead to isotopic depletion when it exceeds this value.

In this experiment, we observed several alternating weeks of heavy isotope enrichment and depletion during evaporation of pan water. These events were successfully simulated using classical equations and attributed to temporal increases of air relative humidity and corresponding decreases of the limiting δ^* values, below the composition reached by the evaporating water."

List of relevant changes

Many changes have been made to the wording of the manuscript according to the referees' comments, without changing its structure or meaning.

Three new equations (9, 10 and 11) were added.

The old Figure 1 was deleted.

Four new figures (6, 7, 8 and A4) were added