

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 rather 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 sometimes 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).

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 “an isotopic steady state” or dynamic equilibrium that can be 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), as the air becomes drier, the δ^* values sharply increase to an extent that the variations of atmospheric moisture isotopy 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 isotopy, as estimated from precipitation isotopy. Figure R 1 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 isotopy explains only 25% (not shown in this graph).

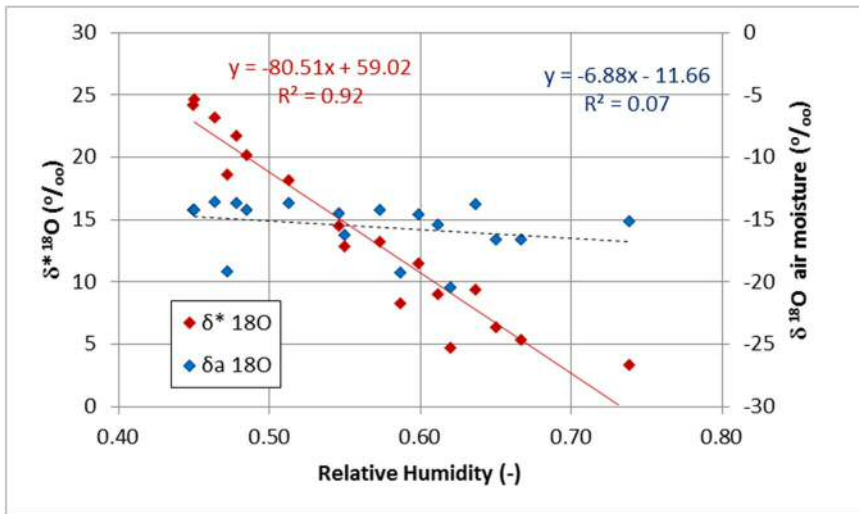


Figure R 1: weekly estimates of ^{18}O concentrations; steady (δ^*) and in air moisture (δa), in relation to relative humidity. Vertical scales are offset $30 \text{ }^{\circ}/_{\text{oo}}$ from each other.

- 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 reviewer's comment leads us to add a new Figure R 2, similar to the one proposed by A. Rhode (cited by Saxena, 1986), which can help to understand the behaviour of our pan water.

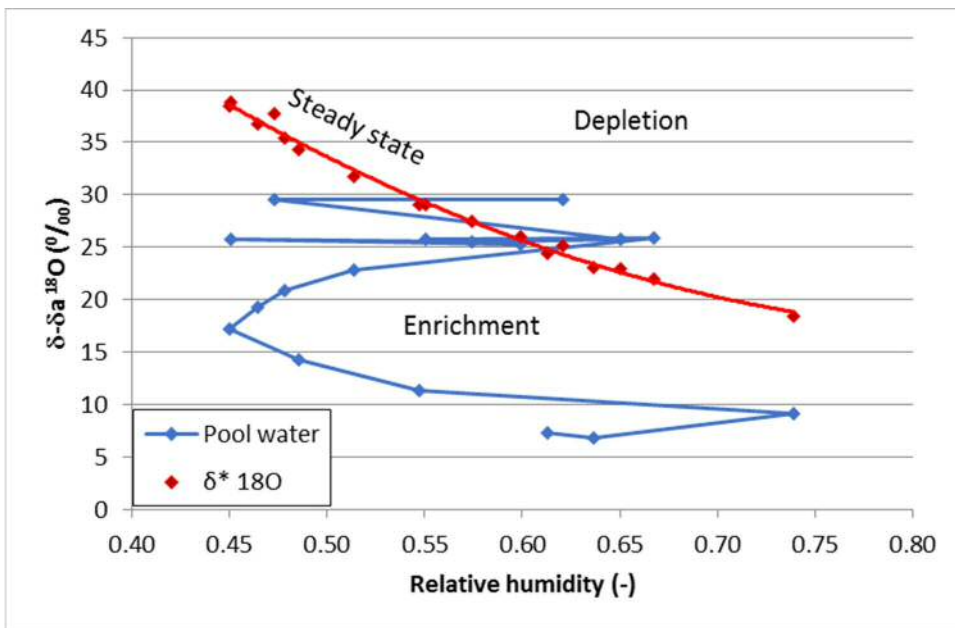


Figure R 2: Evolution of the weekly differences between the moisture isotopy of water and air, plotted in relation to relative humidity (from bottom to top).

In this figure, the differences in $\delta^{18}\text{O}$ between water and air moisture are plotted against air relative humidity. The differences between δ^* and air moisture δ values split the plot into a lower part where the differences in pan water isotopy 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 isotopy 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 measured at weekly intervals, so it was necessary to aggregate air temperature and relative humidity data 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 isotopic composition 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.

We hope these explanations will help readers better understand our note. Any other comments or recommendations are welcome.

Citation:

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