

This is a review of “Nitrate and Water Isotopes as Tools to Resolve Nitrate Transit Times in a Mixed and Use Catchment” by Radtke et al.

The manuscript proposes a model that combines isotopic signature of  $^{18}\text{O}$  in stream water in both water and nitrate to understand the relation between water and nitrate transit times and the impact of denitrification processes.

The approach is innovative and original and could represent a significant advancement in the use of transit time distributions and isotope as tracers. The contribution can thus potentially be of interest for HESS and its readership. There are however some unclear parts and missing details that prevent me to fully evaluate the content at this stage. They are detailed below.

### **Model formulation**

I appreciate that the authors decided to summarize the SAS model here in order for the paper to be self-contained, however, few more lines are needed to define variables and explain all the model details. Please add the definitions of the age ranked storage, the normalized age-ranked storage, and of the age “ $T$ ”. I guess parameters  $KQ1$  and  $KQ2$  (and  $KL1$  and  $KL2$ ) are the parameters of a (linear ?) relation between  $k$  and the wetness index, but which one is which?

The model mentions evapotranspiration fluxes from the upper and lower storages, but I do not see how fractionation due to evaporation is addressed. I assume the authors assumed that evaporation is negligible with respect to transpiration. If so, please say this explicitly. (I also note that line 179 mentions only evaporation). However, on average stream water seems heavier than precipitation (Figure 8) in the data and in the model as well, pointing to some evaporation. Was this addressed somehow in the model?

If I understand correctly line 205, discharge used in the SAS calculation is the output of the mHM-Nitrate model, not the measured one. This choice has its benefit as it is important to have consistent leaching and discharge fluxes. However a reader is curious to see how well the model is reproducing the observed discharge to fully evaluate the results. Please add a comparison between the two (for instance in Figure 3).

Equations 2-5 use the symbol  $T$  for the age (although not defined), while equation 9 uses  $\tau$ . Is this used to make a distinction between age and transit time? Most papers on the topic use the same symbol, indeed they are both ages evaluated for different samples. I think using two different symbols could be confusing.

Overall, I suggest the author to review with care the symbology used. For instance symbol  $k$  is used for both the SAS parameter and the denitrification rate. “1” and “2” refer to the two parameter relation for  $kQ$  and  $KL$ , but to the storages for parameter  $K_{ET}$ . Also the use of superscripts and subscripts is not consistent across the manuscript and the symbol  $\delta$  is not rendered in the pdf of the manuscript in a couple of places. Having a clear, intuitive and consistent symbology is crucial for the readability of the manuscript.

## Parameter estimation

I do not follow how parameter estimation was performed. The model can produce as output  $C_{NO_3}(t)$ ,  $\delta^{18}O - NO_3$ , and  $\delta^{18}O - H_2O$ , and all three variables can be compared with the observations in order to estimate parameters. However, from line 262 it seems that only the isotopic signatures were used. Why was nitrate concentration excluded? It does contain crucial information to constrain the denitrification rate.

Moreover, how was the metrics of KGE of water and nitrate  $\delta^{18}O$  combined to select parameters? It is not possible to consider  $\delta^{18}O - NO_3$  and  $\delta^{18}O - H_2O$  together (i.e. compute a unique KGE) because they have a completely different mean and standard deviation.

Line 267, caption of table 1 and line 370 mention the KGE of only water and not nitrate, which is confusing. How was the nitrate isotopic signature used? Finally, if the 10% best KGE simulations of 10000 parameter sets was retained, why table 1 reports 212 simulations instead of 1000? Overall, the parameter estimation procedure needs much more details to be understood and reproduced.

Please in Table 1 report also the lower and upper bounds of the range from which parameters were randomly extracted. Also please report, maybe as supplementary material, the classical GLUE plot with the scatter of each parameter value against the performance metric used, highlighting the behavioral sets.

## Model results

Figure 8. Please report the range of the behavioral simulations in the modeled isotopic signature of water in discharge.

I do not follow lines 396-398 as they seem to contradict the caption of figure 9. In the caption the orange range is described as the 10% best simulations, while in the text the authors refer to a range of possible parameters taken from the literature, and not the results of the GLUE approach. Please clarify (this is related to the confusion about the performance metric used in the GLUE). Also the statement "Most of the measured values plot within that simulated range" is clearly not in agreement with the results reported in Figure 9 where just few points are within the orange range.

Line 440. I do not understand the sentence: "Orange area= 10% best simulation according to a small bias between observed and simulated nitrate  $\delta^{18}O-NO_3$  in stream." What do the authors mean by "according to a small bias"?

Figure 9A. I am curious about the difference between the nitrate concentration simulated by the two models. Does the mHM model include a more complex set of processes? But most importantly, **how do the two models compare with the data?** The comparison must be reported to interpret and fully evaluate model results. Maybe the authors can add a different panel with the comparison because the concentration in the leaching is off scale for a visual comparison.

Figure 10B. Please report also the isotopic signature in the leaching flux. I think it is crucial to understand the dampening and fractionation that occur in the routing storage.

Line 435. This seems to indicate that the denitrification rate and fractionation factor were assumed, not calibrated, as Table 1 suggests. The treatment of the nitrate model parameters need to be clarify because it is very unclear at the moment.

Figure 10. Please report also the variability of  $TT_{50}$  related to the different behavioral parameter sets .

To summarize, it is unclear how nitrate data (concentration and isotopic signature) were used in parameter estimation. At points it seems that they were not used at all, which would represent a weak point of the manuscript that, in my view, must be revised for further consideration.

### Nitrate Transit Time

The focus variable of the manuscript (starting from the title) is the nitrate transit time. However, details about its calculation are not provided. From the definition “time from its formation during nitrification in the soil until nitrate release to the stream” (line 50), I would proceed to the calculation of the transit time distribution of nitrate in the discharge ( $p_{NO_3,Q}$ ) as follows:

$$p_{NO_3,Q}(\tau, t) = \frac{[C_{S,^{18}O}(t - \tau)e^{-k^{18}O\tau} + C_{S,^{16}O}(t - \tau)e^{-k^{16}O\tau}]p_Q(\tau, t)}{C_{NO_3}(t)}$$

It this correct? I think it is not such a straightforward detail that can be omitted from the text. Also it is important to add the detailed calculation for the results to be reproducible.

Moreover, the analytical expression of  $p_{NO_3,Q}(\tau, t)$  helps in understanding the factors controlling the difference between  $p_{NO_3,Q}(\tau, t)$  and  $p_Q(\tau, t)$ . As the isotopic ratio of oxygen in nitrate in the soil is around  $2 \cdot 10^{-3}$ , for the purpose of calculating  $p_{NO_3,Q}(\tau, t)$ ,  $C_{S,^{18}O}$  is negligible with respect to  $C_{S,^{16}O}$ , and therefore the above equation can be approximated as:

$$p_{NO_3,Q}(\tau, t) \approx \frac{C_{S,^{16}O}(t - \tau)e^{-k^{16}O\tau}p_Q(\tau, t)}{C_{NO_3}(t)}$$

It is interesting to note that if  $C_{S,^{16}O}$  is fairly constant in time, or fluctuates around a mean value, the difference between nitrate and water transit time is driven by the denitrification rate  $k$ , and mathematically, the median nitrate transit time is lower than the water travel time for any  $k > 0$ , and the difference increases with  $k$ . However, also in the absence of denitrification  $k = 0$ , differences between nitrate and water transit time could arise because of temporal fluctuations of  $C_{S,^{16}O}$ . I think this preliminary considerations are useful to guide the reader in interpreting the results.

Line 442: “Once mobilized, the transport of nitrate within the catchment is expected to be closely linked to the transport pathways of water (Maher, 2010; Maher, 2011). Therefore, the TTDs of nitrate should display a similar behavior as the TTDs of water.” Please note that the expectation in the second sentence is incorrect, even for a passive solute. As highlighted in the equation above, even for  $k = 0$  (passive solute) difference between TTDs of water and TTDs of solutes arise because of

temporal variation in the solute input concentration. Think at this simple counterexample: a system with continuous input of water but just an impulse of solute at time  $t_0$ . At any time  $t > t_0$ , the TTD of water is potentially greater than 0 for any TT, but only solute with  $TT = t - t_0$  can be found in the sample.

This set up a false premise for the following discussion (line 444-455) where differences between TT50 of water and nitrate are discussed only in terms of denitrification, while the seasonal fluctuations of the nitrate concentration in the leakage (Figure 9A) can partially explain such differences.

Line 456: “most likely caused” sounds strange as the authors are commenting model results, not observations, so they can reconstruct exactly what is driving the observed pattern.

Line 461-462. Similarly to the comment before, the offset is produced by a model that has a constant denitrification rate, how can thus such difference be assumed to be caused by lower denitrification rates?

Line 480-486. Shouldn't farmers be interested in the nitrate transit time in the upper soil layer, rather than in the lower soil layer. Also, the farmer perspective should employ a forward transit time approach, not a backward one like in this case.

Overall, in my view, the authors fail to make a strong case for the use of nitrate transit time as a useful metric. As discussed above, nitrate TTD depends on nitrification (leaching concentration), denitrification in the deep layer and water TTD. I think that classical mass balance metrics about these fluxes are more informative than the summary metric of the TT50 of nitrate (or its difference with TT50 of water), which blends together information about the underlying processes and provides overall less information.

### **Minor comments**

Line 382: “felt” should read “fell”