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Comment on hess-2022-258

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Referee comment on "Estimation of groundwater age distributions from hydrochemistry: comparison of two metamodelling algorithms in the Heretaunga Plains aquifer system, New Zealand" by Conny Tschritter et al., Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2022-258-RC2, 2023

This work explores the use of metamodelling techniques to predict groundwater age distributions from hydrochemistry. It is a novel and interesting contribution aiming at increasing the availability of groundwater age information from easily available hydrochemical data in catchments. The knowledge gap is convincing and the paper is nicely written. However, I have some comments that should be addressed before publication.

My main concern comes from considering the LPM-derived age distributions as the true representation of groundwater age distribution, which is later used as the metamodel prediction target. I understand the interest of this choice, but I think it is a strong assumption that should be further discussed in the paper. In particular, the following points are missing:

- Where are the age tracer data? They are not in the Supplementary Material as indicated l. 219, and I could not easily find them in Morgenstern et al. 2018. There is an extensive description of how these data where acquired (l. 228-238) and how they are used to fit LPM (l. 238-264) but results are never presented in the paper while they are very important. Age tracer data fitted by the LPM must appear in Supplementary Material, to evaluate the confidence in the LPM predictions later used.
- Without this, it is hard to evaluate uncertainties associated with the LPM-derived age distributions. Would it be possible to estimate the uncertainties? How much are the trained models sensitive to the LPM? Could uncertainties in LPMs explain part of the errors?

My second main concern comes from the relationships obtained between hydrochemical data and groundwater age distribution and the processes that could explain them.

- Based on which argument and figure can you tell that "NH3-N, Fe and Mn all tend to increase with groundwater age, whereas concentrations of DO and NO3-N tend to decrease" (l. 424)? This affirmation does not appear clearly on Figure 8 and it does not appear clearly either in the correlation matrix Figure 2.
- I found interesting to try to quantify the consumption of DO in the catchment, by assuming that the organic matter oxidation is only related to DO. However, no explanations are given on how the average rate constant was derived and additional information are required. A first-order kinetics on the DOM concentration was considered, therefore not accounting for the DO concentrations (if I understood correctly from the reference given). Is it correct? It should be specified. Which groundwater age percentile was considered for the calculation? How were the DOM concentrations averaged?
- The inverse relationship between age and temperature is not expected as we would expect that older groundwater shows higher temperature. But this relationship is really strong and I think this paper would highly benefit from a close look at this relationship and clarifications in the explanations given. I do not understand the calculation of the activation energy made and I doubt the interpretation that is made from it. First, it somehow considers an aggregation of all reaction types. Secondly, where does the k1/k2=0.8 come from? Here, the age ratio is 0.8. But why would the kinetic rate ratio be equal to the age ratio? I agree that an increase in T would increase the reaction rates. However, how do you relate this to the effect of T on modelled age? Please clarify the process that is presented here to explain the inverse relationship between age and temperature. I would be more convinced by a hydrological explanation. The paper would benefit from a more convincing explanation of the relationship obtained between temperature and age.
- Relationships between Ca, Mg, Na, K and SiO2 and age would highly depend on the aquifer lithology. Would these elements be better predictors of groundwater age if an *a priori* classification based on the rock lithology was made?

Minor comments :

Fig.1: What are the red lines?

l. 136: it would be interesting to give the value of the recharge rate of the area

l. 140: what is the confined aquifer zone near the coast? Maybe worth showing on the map?

l. 195: there is a confusion between the text and Fig. 3, one refer to mean residence time and the other to the 50^{th} percentile, please correct.

Figure 6: At least for the example given in Figure 6, the lumped parameter model should be described in the main text (singular or binary EPMs? Which values of the parameters?)

l. 337 : MAE : Mean Absolute Error?

Figure 8: change DRP for PO4-P as this is how it is referred to in the main text

l. 540 I wonder of the generalization of the approach and on the application of the trained model elsewhere. The obtained hydrochemistry-age relationships are not easy to explain (at least for temperature), and therefore it is difficult to tell if they are applicable elsewhere or if they are only related to some local effects. Would other predictive parameters such as depth, distance to the river, or elevation inform on water age predictions?

The authors acknowledge that the work might be only applicable to the selected catchment. Is there another similar catchment, where age data are available and where the models could be applied to determine groundwater age distributions from hydrochemistry, in order to validate the method?