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Discussions
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Interactive comment on "Pesticide fate at catchment scale: conceptual modelling of stream CSIA data" *by* Stefanie R. Lutz et al.

Anonymous Referee #1

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This manuscript combines field measurements (pesticide concentration and isotopic composition) with modeling to investigate the fate of pesticides in the hydrological cycle. The modeling part uses a state-of-the-art approach that features description of water ages using state-dependent SAS functions.

Overall, the MS makes a significant contribution to the literature on this topic by extending current models to the analysis of compound specific stable isotopes (CSIA). Moreover, it represents a good example of how data and models should be combined to gain the maximum knowledge of the underlying processes. There are however some issues that need to be addressed before publication.

The authors decided to put most of the model technical details in the supplementary material, which is a viable option. However, the description in the main text does not

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stand alone and the reader if forced to go back and forth between the text and the Supplementary Tables. So I suggest to either put an even more concise version of the methods in the text (and develop a more detailed version in the SM), or put the equation and parameter description in the main text.

I had a hard time following the equations in Table S5 because there is a mixture of continuous (differential equations) and finite difference equations. The author should decide one way to present the model and stick with it. I would suggest to use a continuous formulation. How this is then discretized into a finite difference equation for the numerical evaluation is quite trivial. For instance, ET_{sz} should be

$$ET_{sz}(t) = ET_{pot}(t)\ if\ S_{sz} > 0$$

and

$$ET_{sz}(t) = 0$$

otherwise. Or, using the the Heaviside function

$$ET_{sz}(t) = ET_{pot}(t)H(S_{sz})$$

Discharge then reads:

$$Q_{sz}(t) = (P(t) - ET_{sz}(t))H(S_{sz} - S_{max})$$

and so on for the other equations. Otherwise the authors could write all difference equations, including the two storage balance equations. Also in this case there are some typos in the remaining equations. For instance in the equation for discharge from the sz, the symbol d should not appear in the numerator. The same applies to the ET_{tz} equation.

Table S5. R_{max} seems like a maximum recharge rate, but please note that the description is missing from Table S7. Moreover, when $Q_{sz} > R_{max}$, where is the remaining flux going? In this equation, I was expecting to see $Q_{sz} - OF$, to account for the fraction

of Q_{sz} not going to recharge the tz. Something is unclear in these equations, please clarify.

Table S6. $C_0(t)$ is computed assuming a well mixed reactor (i.e. total mass divided by storage). However, this seems to contradict the model formulation which assumes that every parcel of water has a certain pesticide concentration that depends on the age, and the age distribution differs from the well mixed one. The rational for this choice must be explained.

Page 9, lines 6-9. I read these lines a couple of time but I could not figure out exactly what was actually done. Which algorithm did you use for calibration. How large was the NS-efficiency? And the NS-efficiency range? Please expand and clarify on this. With 18 free parameters, the calibration is always going to be a critical point.

The authors should show the distribution of the "behavioral parameters". Were the parameters identifiable? With such a high parameter vs data ratio, I am expecting a quite broad distribution. This should help explaining why the model could be calibrated reasonably well also without degradation.

I would anticipate in the model description that some assumptions will be relaxed later, as shown in the result section. Otherwise the reader would continue reading wondering whether all the complexity is really necessary.

MINOR COMMENTS

Page 2. Line 22: I would move "provided that ... non-toxic" at the end of the sentence.

Page 7. Line 13. Is this type of modeling of desorption introduced here for the first time? If so, please expand a little the description. Otherwise refer to other publications.

Page 7. Line 20. Do you rather mean "evapotranspiration".

Table S7. If I understand correctly "L" should read "l".

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