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Hydrology and Earth System Sciences
Discussions

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

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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 stand alone and the reader is 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.

Reply: We thank the reviewer for the appreciation of our work and the useful and valuable comments. We acknowledge that the current layout requires the reader to go forth and back between the SM and the main text. Hence, we will follow the reviewer's

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suggestion by moving the tables S5–7 from the SM to the main text.

Specific comments

1. 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.

Reply: We agree with the reviewer that the mixture of differential and finite difference equations is confusing. We will revise all equations by using the continuous formulation as suggested by the reviewer. Moreover, we will remove "(t)" from all the equations (except for the ones for Csz, Ctz, CET) to improve the readability of the equations.

2. Table S5: Rmax seems like a maximum recharge rate, but please note that the description is missing from Table S7. Moreover, when Qsz > Rmax, where is the remaining flux going? In this equation, I was expecting to see Qsz - OF, to account for the fraction of Qsz not going to recharge the tz. Something is unclear in these equations, please clarify.

Reply: The parameter Rmax is indeed missing in Table S7 as it stems from a former implementation of recharge where the maximum recharge rate was set constant. In the current model formulation, the infiltration capacity of the transport zone is specified by a normal distribution (cf. page 6, lines 14-15 of the main text). Hence, in the revised version, we will change the equation for recharge to the transport zone to Rtz = Qsz – OF to account for overland flow, i.e., the outflow from the source zone that does not flow into the transport zone.

3. Table S6. C0(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.

Reply: C0(t) refers to the average concentration in the sorbed phase of the source zone, which is, indeed, set to the total mass divided by storage. However, the concentration in the source zone outflow does depend on the age distribution of the outflow, which is implemented in the equation of Csz(t) by using pQ,sz(Tsz,t). In other words, the dissolved phase of the source zone does not behave as a well-mixed reactor and thus discharges pesticide molecules with various ages.

4. 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.

Reply: We agree with the reviewer that the calibration procedure should be clarified, which will be added to section 2.8 in the revised manuscript. Briefly, we calibrated the model against the combined objective function NScomb= (1/6*NSQ+NSC+NSδ13C)/(13/6) using the NSQ, NSC, and NSδ13C coefficients as described in the SM. NScomb thus prioritises measured concentrations and δ13C-values over measured discharge (see factor 1/6, which was determined in prior test calibration runs).

We applied the particle swarm optimization algorithm implemented in the open-source R package “HydroPSO” (Zambrano-Bigiarini and Rojas, 2013) and considered parameter sets behavioural if NScomb$\geq$0.7. This criterion was used to determine 10,000 behavioural parameter sets. The NS-efficiency of these behavioural parameter sets ranged between NScomb = 0.7 and NScomb = 0.92 (mean of 0.88), which will be mentioned in section 3.2 in the revised manuscript.

5. 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.

Reply: The parameter identifiability is, indeed, a crucial aspect for conceptual hydrological models such as ours. We will show the distribution of behavioural parameters (see uploaded Fig. 1) together with a discussion on parameter identifiability in the SM and comment on it in section 3.2 in the revised text. Most model parameters show one clear maximum in the frequency distributions, apart from two flow-related and two pesticide model parameters, respectively. The two parameters with a limited identifiability in the flow model are those defining the SAS functions for ET (αET) and old water in discharge from the transport (βQ), respectively. The pesticide model shows a limited identifiability for the parameter determining pesticide transport in ET from the transport zone to the source zone (fex), as well as for the calibration factor of the applied pesticide mass (mIN). Hence, based on the measured data, it was not possible to distinguish the effects of ET from the effects of old water discharge on pesticide concentrations in the study catchment.

Overall, with 14 parameters showing distinct maxima in the histograms, we consider the amount of parameters reasonable in view of the variety of processes described in the model (e.g., time-varying storage selection, and different pesticide degradation and transport processes). Please note that the model did not calibrate well against measured pesticide concentrations without degradation (see Fig. S1 in the SM), which indicates that the concentration reduction at the catchment outlet cannot be ascribed to dilution only.

6. 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.

Reply: As discussed in section 3.4 in the main text (“Insights on pesticide fate and transport from the model”), the alternative model setups did not improve the represen-

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tation of pesticide transport and degradation. Therefore, the original model setup as described in section 2.6 was kept and no model assumptions were relaxed. As this might not have become clear enough, we will specifically state in section 3.4 that the different alternative models tested were not adapted due to lower performance and larger uncertainties compared to the original (i.e., final) model.

Minor comments

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

Reply: According to the reviewer's suggestion, we will move this part to the end of the sentence.

2. 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.

Reply: This type of desorption kinetics has been introduced before in the modelling of nitrate, where a clear dilution effect during storms was found because of nitrate retention in the topsoil (van der Velde, 2010). This reference will be added to the revised version of the manuscript.

As mentioned in section 2.7, we assume that applied pesticides are largely retained in the sorbed phase rather than in the dissolved phase, as farmers will use pesticides preferably during dry periods to prevent losses via fast runoff. Hence, water in the applied spray formulation will quickly evaporate, leaving the pesticide sorbed to the soil and plants.

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

Reply: This is indeed a typographical error, which will be corrected in the revised manuscript.

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

Reply: The reviewer is right. The “coefficient describing pesticide sorption in the source zone” will be referred to with a lowercase l in the revised manuscript.

References van der Velde, Y.; de Rooij, G. H.; Rozemeijer, J. C.; van Geer, F. C.; Broers, H. P., Nitrate response of a lowland catchment: On the relation between stream concentration and travel time distribution dynamics. Water Resour. Res. 2010, 46, W11534, doi:10.1029/2010WR009105.

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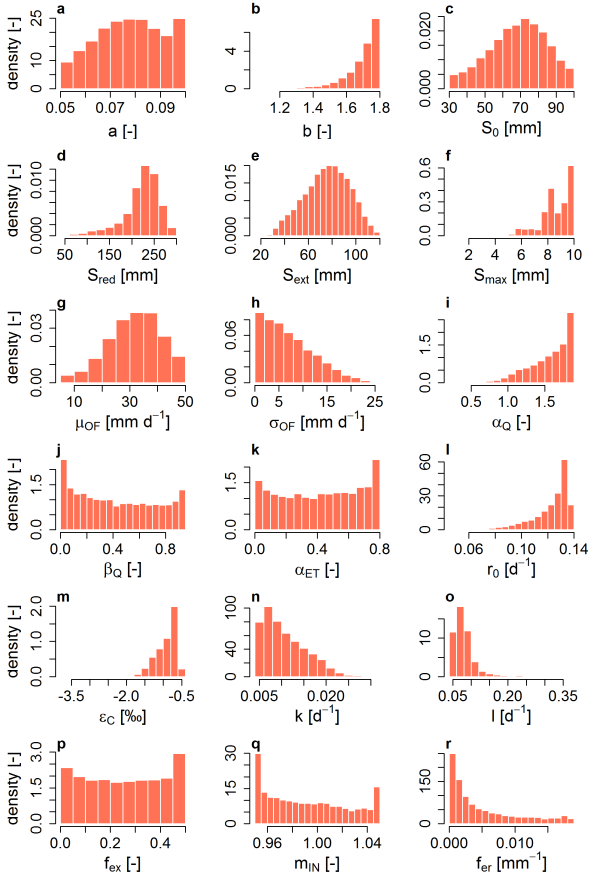

Fig. 1. Histograms (frequency distributions) of the 18 calibrated model parameters from the 10,000 behavioural model simulations.