

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

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Reply to Reviewer 2

General comments

The manuscript “Pesticide fate at catchment scale: conceptual modelling of stream CSIA data” by Lutz et al. presents a combined data-analysis and modelling study, exploring the potential of transit time-based formulations of conceptual hydrological models to reproduce pesticide dynamics on different scales. The experiment is well designed – in particular the comparison of alternative model set-ups is of critical importance (cf. “hypotheses testing”) – and based on sound methods as far as hydrology is concerned (note that I am not an expert in chemistry and I cannot therefore not

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really evaluate the validity of these aspects in the manuscript). The manuscript may be of interest to many in the community as it is a clear demonstration that even relatively parsimonious model frameworks have considerable potential to reproduce and predict non-conservative hydro-geochemical dynamics at the catchment scale. Reply: We thank the reviewer for the appreciation of our work and the useful and valuable comments.

Specific comments

1. P.3, l.7: “confirm” may be too strong a term, perhaps replace by “support”

Reply: In the revised manuscript, we will replace “confirm the occurrence of pesticide degradation” by “provide evidence of pesticide degradation”.

2. P.5, section 2.3/2.4: the number of samples taken is not entirely clear. Maybe I misunderstood something, but in line 6 it is stated that a sample was taken at the catchment outlet every 20m³ between 03 /2012 and 08/2012. In line 18 it is stated that 34 samples were available. 34 samples over a period of 6 months if sampled at 20m³ intervals does not seem a lot, even if it is a very small catchment. Please check and clarify.

Reply: We agree with the reviewer that some information is missing here. Runoff water was sampled every 20 m³ and consecutive samples were then combined to composite samples, leading to a total of 34 samples in six months. During baseflow conditions, samples were merged into weekly composite samples, whereas during runoff events, samples were merged according to the hydrograph components (i.e., baseflow, rising and falling limb) into several composite samples. This information will be added to the revised manuscript.

3. P.6, section 2.5: it is not completely clear how or if pesticide uptake by plants was considered (essentially a loss term). Obviously it is desirable that there is no plant uptake of pesticides in reality. But is it so? Can this assumption be justified? Other

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authors seem to imply otherwise (e.g. Fantke et al., 2011, Chemosphere) and also Figure 2 in the manuscript seems to include a pesticide flux into vegetation. Yet, I could not find this reflected in any of the equations. Please clarify.

Reply: Pesticide uptake by plants was accounted for indirectly, as only a fraction of the pesticide evaporated from the source zone is redirected back into source zone storage (see page 7, lines 20–23). The remainder is thus taken up by plants without re-entering the source zone via plant exudation eventually. The total pesticide mass in ET from the transport zone is determined as $ET_{sz} \cdot CET$. The model parameter f_{ex} (see Table S6, equation for mass flux via plant exudation) gives the fraction of the total mass that will not remain in plants, i.e., the net pesticide transport from the transport zone to the source zone via ET.

4. P.6, section 2.5: please provide more information about the time-variant formulation of the SAS function. How was this done? Which type of distribution was chosen? Which parameter ranges were chosen and thus which shapes were possible?

Reply: The SAS function was approximated by a beta distribution defined by the mixing parameter $m_Q(t)$ (cf. van der Velde et al., 2015). The latter depends on the model parameters α_Q and β_Q . The equation for $m_Q(t)$ is shown in the attached figure, where S_{min} and S_{max} are the minimum and maximum transport zone storage, respectively. The parameter α_Q ranges between 0.2 and 1.9, and β_Q ranges between 0 and 0.95 (see Table S7). Under dry conditions, $m_Q(t)$ approaches α_Q and will primarily lead to old water discharge, whereas, under wet conditions, $m_Q(t)$ approaches $\alpha_Q(1 - \beta_Q)$ and will primarily lead to young water discharge. In other words, the SAS function results in preference for young water if $m_Q(t) < 1$, preference for old water if $m_Q(t) > 1$, and a uniform distribution if $m_Q(t) = 1$ (i.e., “random sampling” of outflow from storage; see Fig. 1 in van der Velde et al., 2015). The equation for $m_Q(t)$ will be added to the SM to provide more information on the SAS approach chosen.

5. P.6, section 2.5, Figure 2: the energy input and/or potential evaporation is missing

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as incoming flux in figure 2

Reply: We will add solar radiation (“IS”) as incoming energy input flux to Fig.1.

6. P.6, section 2.5, l.23: Hrachowitz et al. (2015, Hydrological Processes) would fit better here.

Reply: We will replace the reference to Hrachowitz et al. (2016, Water) by Hrachowitz et al. (2015, Hydrological Processes).

7. P.7, section 2.6 and 2.7: it is stated that pesticides are mostly applied during dry periods and that drying leads to particle adsorption to soil particles. The study site description suggests that the soils are mostly silty-clay. While in section 2.7 volatilization and deposition is mentioned, I can imagine that in addition wind induced migration of soil particles will lead to some degree of pesticide redistribution (i.e. deposition minus erosion), in particular on arable land. This is obviously difficult to quantify, but may warrant some discussion.

Reply: Pesticide redistribution by wind-induced erosion might be a significant process, which is, indeed, difficult to quantify. However, the role of this process in the study catchment is assumed minor relative to erosion via overland flow, which is accounted for in the pesticide model. This aspect will be added to the revised version of the manuscript at the end of section 2.7. Moreover, we will mention wind-induced erosion as potential reason for the detection of acetochlor in the plot samples, in addition to drift and applications in previous years.

8. P.7, section 2.6, Table S6: I think it may be clearer to provide the equation for plant exudation in the following form to avoid confusion: $\phi_{ex}(t) = f_{ex} \cdot \phi_{in}(t)$.

Reply: We will change the expression for $\phi_{ex}(t)$ accordingly in order to avoid confusion.

9. P.7, l.20ff: I am not entirely convinced that this reasoning makes sense. What is the source zone? In most “conceptual” hydrological models it is the part of unsaturated zone that contributes to the non-linear response of hydrological systems. Roughly

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speaking, this is due to the fact that storage capacities below field capacity are generated by (1) soil evaporation and more importantly by (2) plants extracting water with their roots for transpiration. This essentially implies that the source zone encompasses the unsaturated root zone. As in deeper layers (i.e. “transport zone”), direct soil evaporation becomes of less importance and, by definition, no roots are present anymore (as it is not the root zone anymore) and thus the water content is always close to field capacity (except for the moments when a wetting front passes), the presence of a significant upward flux caused by evaporation or transpiration is rather unlikely. I believe that the conceptualization of ET_{tz} and the associated ϕ_{het} should be reconsidered. Although it is, of course, clearly possible (if not even likely) that there is an upward flux, I think it will be, given the fine grained soils, either be linked to capillary rise, or, what I find most plausible given my limited knowledge of the study site, is that these upward water and pesticide fluxes are linked to fluctuations in the groundwater table (i.e. the changing depth of the source and transport zones, respectively), reflecting a bit what was reported by Rouxel et al. (2011, Hydrological Processes).

Reply: In our model, the source zone is a shallow layer at the ground surface, where the applied pesticide is initially sorbed and flushed out by infiltrating water (cf. Bertuzzo et al., 2013). Hence, the term “source zone” refers to the source of pesticide rather than the source of water. The transport zone comprises the entire subsurface below this shallow layer, i.e., the unsaturated zone including the root zone, and the aquifer. Hence, evapotranspiration from the transport zone needs to be simulated. Instead of further compartmentalising the subsurface, we opted for a single control volume and implemented time-varying storage selection to produce “non-random” sampling from storage (cf. the “direct SAS approach” in Benettin et al., 2017).

We will remove the plant symbols in Fig. 2, as they might erroneously suggest that the root zone does not extend to the transport zone.

10. P.8, section 2.8: the calibration and model evaluation procedure would benefit from some more detail. Was the model *simultaneously* calibrated with respect to the

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three objective function, or only with respect to one of them, or individually one after the other? If simultaneously, how were the individual objective functions weighted? Which model performance was accepted as behavioural? What was used as likelihood weight for the uncertainty estimation? In addition, please do not only provide the prior parameter distributions (Table S7) but also the posterior distributions. Also, given that the source zone storage capacity essentially reflects the storage capacity in the unsaturated root zone, a value between 0.1 and 10mm (Table S7) seems to be excessively low for this not very humid environment (i.e. aridity index ~ 1.2). For such an environment this storage capacity is more likely to be in the range of about 50-250mm as recently suggested by Gao et al. (2014, Geophysical Research Letters).

Reply: We agree with the reviewer that the calibration and model evaluation should be clarified, which we will do in section 2.8 in the revised manuscript. Briefly, we calibrated the model simultaneously against the NSQ, NSC, and NS $\delta^{13}C$ coefficients by using the combined objective function $NS_{comb} = (1/6 * NSQ + NSC + NS\delta^{13}C) / (13/6)$. The factor 1/6, which was determined via prior test calibration runs, ensures that all three terms contribute approximately evenly during the optimization process. The equation for NS_{comb} will be added to the SM.

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 $NS_{comb} \geq 0.7$. This criterion was used to determine 10,000 behavioural parameter sets. The NS-efficiency of these behavioural parameter sets ranged between $NS_{comb} = 0.7$ and $NS_{comb} = 0.92$ (mean of 0.88), which will be mentioned in section 3.2 in the revised manuscript. The posterior parameter distributions will be shown and briefly discussed in an additional figure in the revised SM.

As the source zone represents the upmost soil layer at the ground surface where the pesticide is applied, we assume that a maximum storage capacity of 10 mm is sufficient. If the source zone represented the entire root zone, this value would, indeed, be too small. As explained above, we tried to minimize the compartmentalisation of catch-

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ment storage, which also avoids additional parameters to define the storage capacity of each catchment compartment.

11. P.9, section 3.1, Figure 3: please add flow and/or precipitation to Figure 3 to allow the reader to make the link between water and pesticide dynamics.

Reply: Precipitation and discharge time series will be added at the top of both columns of Figure 3 in the revised manuscript.

12. P.12, section 3.3: although nicely discussed and presented in Table 1, it may be interesting to see how/if the individual relative contributions change over time. I would be glad to see a figure showing that.

Reply: A figure showing the contribution of the mass-balance terms in 2012 will be added and referred to in the revised version of the manuscript.

13. P.13, section 3.4, l.12-15: please provide a bit more detail here. How was this assessment made? On basis of the model performance for the calibration period? Or post-calibration in a validation period? This is a crucial difference: if the assessment was done based on the calibration period, it is not at all surprising that a model with more calibration parameters (and thus more degrees of freedom) provides a better performance. It is almost (accounting for the uncertainties in the low number of Monte Carlo realizations used in the model) a mathematical necessity and thus provides only limited information about the model improvement. This can only be done in a meaningful way if compared for an independent test period (i.e. "validation period"). Please clarify.

Reply: Unfortunately, due to the limited amount of measured data, the comparison of the different model setups was not possible for a validation period. We fully agree with the reviewer that a more detailed model should always improve the model results during calibration. Therefore, indeed, the observation that the model improves by itself is not that valuable. However, because we implemented several small model adjustments,

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we can compare the relative change in NSE between the alternative model setups. Furthermore, we compared the model results range outside the calibration period. We argue that if the more detailed model yields a smaller range in model results outside the calibration period compared to the range of the simpler model during the same period, the more detailed model is actually an improved model that is better able to grasp the flow and transport processes. In contrast, if the result range had been larger for the more detailed model, this would have indicated that the extra parameters mostly led to an increased model equifinality and thus did not really improve the model.

14. A more general remark: the similarity check indicated a relatively high overlap with previously published material (PhD-thesis?). You may want to reformulate the relevant parts of the manuscript to avoid complications.

Reply: The reviewer is right that parts of the manuscript are based on a chapter of the PhD-thesis by the main author. Despite the high overlap indicated by the similarity check, the manuscript has been considerably changed and improved with respect to the thesis chapter. We were in the understanding that self-plagiarism is not applicable in the case of material transferred between a PhD-thesis and respective journal papers of the same author. We checked with the editorial office of HESS, which confirmed that using parts of a PhD-thesis text without rephrasing is permitted. The thesis chapter has been published on the university's website as part of a PhD-thesis, but not in a scientific journal. Given the answer of the editorial office, we thus refrain from rephrasing the similar parts in the manuscript.

References

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van der Velde, Y.; Heidbüchel, I.; Lyon, S. W.; Nyberg, L.; Rodhe, A.; Bishop, K.; Troch, P. A., Consequences of mixing assumptions for time-variable travel time distributions. *Hydrological Processes* 2015, 29, (16), 1099-1085, doi:10.1002/hyp.10372.

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$$m_Q(t) = \alpha_Q \left(1 - \beta_Q \frac{S(t) - S_{\min}}{S_{\max} - S_{\min}} \right)$$

Fig. 1.

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