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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.

Anonymous Referee #2

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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 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. I only

have a few minor remarks and I would thus be glad to eventually see this manuscript published.

(1) P.3,l.7: "confirm" may be too strong a term, perhaps replace by "support"

(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.

(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 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.

(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?

(5) P.6, section 2.5, Figure 2: the energy input and/or potential evaporation is missing as incoming flux in figure 2

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

(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.

(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: phiex(t)=fex*phiet(t)

(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 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 ETtz and the associated phiet 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).

(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 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 $\sim$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).

(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.

(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.

(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.

(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.

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