

## Answer to Interactive Comment by C. Griebler (Referee)

Dear Christian Griebler,

we would like to thank you for your valuable comments and questions regarding our manuscript, which are all answered below.

### General comments:

*General comments: The paper seeks to model the fate of pesticides and their transformation products in a small catchment as well as their export to a surface water body (river). I highly appreciate that the authors challenge to approach the high complexity of a catchment considering multiple transport pathways in a heterogeneous and dynamic environment. I agree with Nicholas Jarvis that the results appear plausible. However, to my opinion, the final outcome builds on so many assumptions that I would have liked to see a kind of ‘uncertainty propagation’. As a non-expert in modeling I don’t feel fine, if things cannot be tested. I will try to specify this in the specific comments down below.*

**Answer:** Uncertainty propagation in environmental modelling is an important and up-to-date topic. From a practical point of view, the problem with uncertainty estimation is that even with the best methods, a large number of model runs (several thousands) is required. With model run times of 2h these approaches are not applicable using complex distributed models. Therefore, we had to fall back on discussion of possible influences as done in chapter 4.2. Of course, not all possible influences can be discussed in such a manuscript. Still, we recently had a paper accepted for publication in another journal in which a conceptual model for pesticide and TP export was analysed for model uncertainties (Gassmann et al., accepted).

### Specific comments:

*P9853-L6-10: Being a biologist with only general hydrology expertise, I always thought that preferential flow is happening immediately. Here it is stated that first water infiltrates into soil and only the surplus goes into macropore flow.*

**Answer:** For an initiation of preferential flow, saturated areas within the soil or ponding at the soil surface are required. Please see the review by Nicholas Jarvis for further information (Jarvis, 2007). Our assumption that only ponding fills the preferential flow pathways is a simplification owed to the modelling at catchment scale.

*P9856-L14-16: If the mixing layer is a ‘thin soil layer’, how can photooxidation take place there? Is this process relevant here?*

**Answer:** Substances sprayed at the soil surface are generally subject to sunlight decay, as long as they are not transported (by advection or diffusion) into the deeper soil. Thus, photodegradation and microbial degradation may both influence substances in the mixing layer. To which extent photodegradation is relevant depends on many factors including sunshine duration, global radiation intensity and the timespan of the dry period after application.

*P9857-L17 and following: Microbial transformation of pesticides can be very slow in the environment. Still there is Atrazine in groundwater of countries like Germany where it has been banned a decade ago. Moreover, it has been shown that there might be two different degradation rate apply for one*

*and the same compound when being present at high concentrations and at low concentrations (Toräng et al. 2003). I wonder if the factors applied accounting for lower activities (= higher DT50 values) with depth are ok. The authors relate that to gradients of bacterial cell numbers as found in different soils, however, not in the catchment. Furthermore, the fraction of total to active cells is increasing with depth. Consequently, transformation might be considerably slower than assumed.*

**Answer:** We are no microbiologists and thus rely on what information we get from former experimental studies in the catchment and what was done before in modelling studies. The topsoil degradation constants were partially determined in the catchment in former studies or taken from the literature. The exponential increase of first-order half-life times with soil depth was used before as given in the references provided in the text (Jury et al., 1987, Ma et al., 2004). We are not aware of a single modelling study in the literature using actually measured bacterial activity at field or catchment scale. Thus, I think we are approaching a critical point where the hydrologist's knowledge ends and an interdisciplinary cooperation is required. Still, for the aims of this study, we suppose that our assumptions are sufficient since they are in line with former modelling studies.

*P9860-L5: As already mentioned earlier, the outcome of the study builds on many assumptions. One example is the macropores, where the number, the size, and the orientation need to be assumed. Is no empirical data available from other studies in this catchment?*

**Answer:** Unfortunately, there is no information about these parameter values. Therefore, we used values found under similar conditions nearby (Weiler, 2005), as stated in the text (p.9860, L.5-9). As suggested by Reviewer H.H. Gerke, we will refer to these parameters as 'effective' in the revised manuscript, in order to pay respect to the fact that there is a huge heterogeneity in the size and number of macropores.

*P9860-L16: How can the boundaries of a catchment be fixed to have 'no-flow' in the lateral direction. I can also follow the logic to artificially set different vertical boundaries in the southern (impermeable) and eastern sub-basin (permeable) of the catchment according to observations from wells. However any kind of geological records from that site would substantiate these assumptions.*

**Answer:** For overland flow, the no-flow boundary condition is what usually is used to delineate catchment boundaries in hydrology. A simplified assumption for subsurface boundaries is that subsurface water moves under the influence of gravity in the direction of the surface inclination. Although this is a simplification, this assumption is made in most hydrological modelling studies at catchment scale.

The vertical boundary conditions will be justified in the revisions by adding information about the bedrock in the catchment: "The catchment is underlain by tertiary alluvium in the Northeastern part and the rest of the catchment by moraine material (Leu et al., 2004a)."

*P9862-L19-21: Does this mean, that in the catchment modeled there is no recharge of the aquifer? The model says 40% of precipitation is evapotranspiration, 58% is discharge (surface runoff and drainage?), but only 1% subsurface (underground) flow.*

**Answer:** The question of actual aquifer recharge is not easy. In the model, a shallow aquifer provides baseflow. The recharge to this shallow aquifer is not listed explicitly, but is included in the storage change and the discharge (which is all water leaving the catchment). What we called 'underground

outflow' may be interpreted as deeper aquifer recharge (12 mm). We will clarify this in the revised manuscript.

*P9863-L19: I strongly doubt that 89-99% of the different pesticide compounds have been mineralized with the short time span. This is a point which, to my opinion needs to be evaluated. How big is the chance that PCs are still in the soil at higher concentrations or have left the system by other pathways (into the aquifer)?*

**Answer:** We agree with the reviewer, that the parent compound is most likely not mineralized to 89-99%. What we call 'mineralized' is only what is not available in the model as parent compound or the considered TP. TPs which were NOT considered in this study are included in the 89-99% of 'mineralization'. We will clarify this part in the revisions.

*The authors conclude that the major export pathway was overland flow. Does this mean that the degradation of the PCs took place during overland transport? Neglecting sorption and taking into account the applied DT50 values 10 to 20 for the parent compounds, then did the major export events (23d after application and 60-71d after application) allow sufficient decay before the PCs should have ended up in the river?*

**Answer:** We assume that most of the transformation takes place in the mixing layer (largest decay rates). Overland flow is in exchange with the mixing layer, depending on the sorption strength and sorption kinetics. Thus, the time for degradation in the mixing layer for the two main events is 23d and 60-71d, but the export takes place by overland flow (where, given the short residence time, hardly any degradation occurs).

*P9867-L1-2 & L12-14: I don't agree. To support such a comprehensive and complex modelling approach hopefully leading to progress in future research, sampling and longer computation times are acceptable.*

**Answer:** We agree that it would be interesting to do so. Still, analytical costs for pesticides and TPs are huge. According to our analytical chemistry department, each sample may be assigned a cost of about 50 EURO. With about 50 sampling points in the catchment in order to get a sufficient spatial resolution and sampling in three soil layers and at the soil surface, the total analytical costs for six substances (3 parents, 3 TPs) would be around 60000 EURO, only to get the initial condition. This would be hard to justify in a research project for such a small catchment. It certainly would not be applicable for consulting projects.

Regarding computational time: As written in the manuscript, the differences between Freundlich isotherm and linear isotherm were supposed to be small, at least for atrazine (Stamm et al., 2004). Thus, we don't expect big differences in the outcomes and the much lower calculation times (orders of magnitude) facilitate work largely.

#### **References cited in answer to reviewer comment**

Gassmann, M., Khodorkovsky, M., Friedler, E., Dubowski, Y. , & Olsson, O. Uncertainty in the river export modelling of pesticides and transformation products. Accepted for publication in Environmental Modelling & Software, doi: 10.1016/j.envsoft.2013.09.021

- Jarvis, N.J., 2007. A review of non-equilibrium water flow and solute transport in soil macropores: principles, controlling factors and consequences for water quality. *Eur. J. Soil Sci.* 58 (3), 523–546.
- Jury, W.A., Focht, D.D., Farmer, W.J., 1987. Evaluation of Pesticide Groundwater Pollution Potential from Standard Indices of Soil-Chemical Adsorption and Biodegradation. *J. Environ. Qual.* 16 (4), 422–428.
- Ma, Q., Wauchope, R.D., Ma, L., Rojas, K.W., Malone, R.W., Ahuja, L.R., 2004. Test of the Root Zone Water Quality Model (RZWQM) for predicting runoff of atrazine, alachlor and fenamiphos species from conventional-tillage corn mesoplots. *Pest Manag. Sci.* 60 (3), 267–276.
- Stamm, C., Waul, C., Leu, C., Freitas, L.G., Popow, G., Singer, H., Muller, S., 2004. Sorption effects on herbicide losses to surface waters in a small catchment of the Swiss Plateau. *Zeitschrift für Pflanzenkrankheiten und Pflanzenschutz – Journal of Plant Diseases and Protection* 19, 951–958.
- Weiler, M., 2005. An infiltration model based on flow variability in macropores: Development, sensitivity analysis and applications. *J. Hydrol.* 310 (1-4), 294–315.