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Hydrology and Earth System Sciences Discussions

Interactive comment on "Spatial variability of herbicide mobilisation and transport at catchment scale: insights from a field experiment" *by* T. Doppler et al.

Anonymous Referee #2

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The authors have carried out a comprehensive study on water flow and pesticide fate in a small catchment in Switzerland. They have worked in the area for many years and know the catchment very well. The design of the study is impressive. The result is, in short, that, at least under the weather conditions of the study period, pesticide transport to surface water occurs mainly with surface runoff (infiltration excess overland flow).

General comments

The study is undoubtedly suited for publication in HESS, but I have a few major concerns that should be resolved before publication.

First, the Results and Discussion section should be restructured. The authors have a clear viewpoint on the processes going on in their catchment and I really appreciate their detailed knowledge of the catchment. However, their paper does not leave sufficient room for alternative interpretations (to theirs). The current style of the paper does not always follow the well-established rules of publication. The authors should first present their data, step by step (Results section), and then discuss them (Discussion section). By way of example, see the second paragraph of 3.1.1 (Overland flow and erosion). In this paragraph, the authors draw their most important conclusion regarding the herbicide transport process (it is actually the main result of their study), before having shown the herbicide results.

The restructuring should be carried out by the authors, not the reviewers, but I roughly recommend the following sequence: 1. Connectivity analysis with field observations, 2. hydrographs including electrical conductivities, 3. chemical concentrations in the discharge water (present the earlier hydrographs first), 4. overland flow, 5. sorption and dissipation. Move interpretations and speculations to the Discussion section.

Second, the authors seem to be only partly familiar with the state of knowledge in sorption kinetics. With triazine herbicides, kinetic sorption is to be considered the rule, not the exception. As shown many years ago kinetic sorption of organic chemicals in soil is mainly due to diffusion into organic matter (Brusseau and Rao, CS, 1989; Brusseau et al., EST,1991). The reference cited in the text (Villaverde et al., EST, 2009) addresses a physical non-equilibrium process that may play an additional role in some soils (Brusseau et al., WRR, 1991). With the pesticides under study, it was shown that the usual 24 or 48 hours are not sufficient to attain equilibrium (simazine: Streck et al., WRR, 1995; terbuthylazine: Zander et al., Streck and Richter, JEQ, 1999). Instead, equilibration rather takes weeks if not months. A consequence is that the authors' kD is only apparent, as already conceded by the authors. Further, equation 3 will not hold (there are more reasons why this equation can only be considered a crude approximation). Yet, the most important consequence is that the 24-hr equilibration

period after the addition of water before centrifugation is too short to reach equilibrium. The addition of water is necessary for practical reasons, but the 24-hr period makes the measured "pore water concentrations" a function of the deviation from the "water holding capacity". In other words, the method produces artifacts. This may explain the missing relationship between M ratio and kD ratio in figure 6. I do not plead for skipping this part, but the issue should be thoroughly discussed in the discussion section.

Third, although the paper is in general well written, it would benefit from a cross-reading by a native speaker. Formulations are sometimes unnecessarily laborious. The excessive use of the word "for" is annoying.

Detailed comments

2358-25 How can a storage volume such as a catch basin be a short-cut?

2364-5 define soil thickness

2364-12 artificially appears to be pleonastic

2364-19 hydrological variables

2365-4 add ...and alpha, beta, gamma are parameters

2367-4 The experimental setup cannot be verified because Figure 1 does not contain the runoff sensors.

2367-6 Which events?

2367-21 Ambiguous. Make clear if Mix A contains atrazine or not. Specify the (Give the range of) application rates in terms of a.i.

2367-25 better: Moreover, we recorded the substance amounts and . . ..

2370-4 Unclear. Do you mean that 20 topsoil samples were taken at seven dates? Rephrase.

2370-17 The procedure outlined below does not yield the pore water concentration.

Rephrase: the concentration measured in the centrifuged solution was used as a proxy for the pore water concentration.

2371-10 Define water holding capacity. How was it measured and was it measured in each of the soils? Give the details of centrifugation, in particular acceleration and duration.

2372-9 this part should be shifted to the Results section (Connectivity subsection).

2372-11 Give the accuracy of the DEM.

2372-21 Why were 15 m chosen? Shouldn't the buffer zone depend on soil texture?

2372-24 artifacts

2373-10 Explain "appropriate".

2373-14 Really? According to Figure 3 there was at least one major rainfall of 5-10 mm. It appears that there was as much rainfall as between about day 10 and 40 after application.

2373-18 In the graphs, the discharge events, not the rain events are marked - rephrase.

2374-14 explain what hanging water tables are

2375-22 explain solid manure

2375-4 Which herbicides? This phrase comes too early and it is a conclusion. This indicates that the structure of the paper needs to be improved.

2375-7 observations of

2375-24 How was this area mapped? Probably as indicated in the GIS analysis subsection. These two subsections should be combined.

2376-18 How can you or the reader know that there is a shortcut and that the shortcut is active?

2376-19 This paragraph comes too early. This indicates again that the structure must be improved.

2377-14 I find the excessive use of the word "for" annoying, not only in this paragraph. You may want to let a native speaker check the language of the paper.

2377-20 The term aging was introduced in times when the kinetic nature of the sorption of organic chemicals was widely neglected. Unless it can really be shown that sorption is irreversible, e.g. by a change of conformation of soil organic matter, it should be avoided.

2378-9 Mobilisation or mobility? Which macropores?

2380 Subsection 3.3 comes too late, it should be the first subsection in 3.

2381-27 An interpretation belongs into the discussion section.

2383-2 Subsection 4.0 is unnecessary. It should be deleted.

2386-11 explain the connection to ponding - no ponding.

2387-17 Regarding sorption kinetics, the paper is not up to date.

Equations Always state the units with the definitions.

Figure 1 "Well-drained soils" does not define a soil type. Are these the cambisols? The symbol of overland flow should not have the same color as that of the technosol.

Figure 2 Wouldn't it make things clearer to directly compare the rain intensities after application?

Figure 3 Repeat the (calendar) date of application in the figure caption.

Figure 9 This map is reader-unfriendly. The shading is bad. Improve or delete it.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 9, 2357, 2012.