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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.

T. Doppler et al.

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We appreciate the detailed and constructive reviews. We agree with the reviewers in most points and adapted the manuscript according to the suggestions. The answers to the comments can be found below. We restructured the manuscript to achieve a clear separation of methods, results and discussion, since this was a main criticism of both reviewers and the editor. We also extended the discussion on sorption kinetics and added relevant references.

Review 1

The authors observed pesticide transport behavior in an agricultural catchment over a period of approx. two months and several storm events with different precipitation characteristics. They controlled the pesticide application in the catchment, sampled the pesticide transport along the flow paths (soil, surface runoff, surface depressions, tile drains, stream) and observed hydrological processes and hydrological connectivity during the study period. They linked pesticide transport with catchment behavior, underlined the importance of field-stream connectivity, and found that pesticide mobilization was independent of the chemical properties. The study and the results are definitely of interest to the reader of HESS and contribute to process understanding in agriculture hydrology. The scientific approach is appropriate and the data set is very valuable and comprises a big and rare effort. Nevertheless the manuscript needs several improvements before it can be published in HESS. The necessary improvements are related to clear objectives/hypotheses, needed citations, structure, and language/style. I highly recommend that a native speaker improves the language throughout the manuscript. A serious problem in the manuscript is the structure of the different sections. E.g. methods are reoccurring in the result section while discussion is occurring in both, the results and the conclusion. A more consistent structure with a more precise story line linked to clear expressed objectives will significantly improve the readability and impact of the work.

Answer:

We reformulated the objectives and hypothesis to make the goals of the study clearer. We also make a clearer link to the conclusions. We restructured the manuscript to achieve a clear separation of methods, results and discussion. The language of the revised manuscript was corrected by a native speaker.

Additional the discussion section is mainly based on work of the EAWAG group itself. I imagine that, at least for pesticide transport in infiltration excess overland flow, more work exists.

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Answer: We do not know of catchment scale studies with controlled herbicide applications and spatially resolved sampling other than the Eawag studies cited. There are, however, studies on certain aspects that we cite where appropriate.

I think these improvements are achievable. If they are included I see no obstacle for publication. In the following I present some suggestions for improvements, and (if necessary) outline scientific concerns.

Detailed comments Abstract

The abstract is clear, well-structured, and summarizes the paper well. But it is clearly to long (ca. 400 words) and should be shorten by 100-150 words.

A: We think that an abstract should be as stated above: “clear, well-structured, and summarizes the paper well”. With the proposed substantial shortening this would not be the case anymore. We do not see shortening potential without losing significant information.

Introduction p.2359,L.21: “: : :of little importance for most pesticides.” Citation needed.

A: Citation added, p3L14

p.2359.L22/23: “large differences of pesticide losses” In what: amount? What is large (too subjective)?

A: agree, sentence reformulated, p3L16

p.2359,L25: add: “of a catchment can cause the”

A: sentence changed, p3L18-20

p2360L5 “or contributin areas” (Citation needed)

A: Citation added, p4L1

p2361/2362 L25-L2: PrefFlow is linked to surface runoff, but it can also occur and various other boundary conditions. E.g. Jarvis (2007) showed that PF can start with

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precipitation intensities as low as 1mm/h.

A: We agree. But here we only focus on pref flow fed by surface runoff. To carry substantial amounts of herbicides, the pref flowpath requires the lateral inflow of large water volumes with high pesticide concentrations. Soil concentrations are high at the surface, so pref flow has to be initiated close to the surface or at the surface to have high pesticide concentrations. We extended the explanation on which processes we focus and why. p5L15-25

p2363/L1-L19: in the objectives you missed that you also linked the chemical properties of the herbicides to behavior. A large part of results/discussion consist of that. Also you writing the objective in the past: "..procedure allowed us: : :". You take the results ahead of the story (in parts). I think the last part of the introduction need to be reworked. The objectives/hypothesis must be defined more clear at the end of the section. Right now you give a vague formulation of the objective (L5-7), then you present another problem (L8ff) and give there another objective (transferability), that is not even handeled in the following. The objectives have to be the end of the introduction, clearly formulated, and completely addressed in the manuscript.

A: This part of the introduction was reformulated. We added an introduction part on herbicide sorption (p5L26-p6L14) and formulate our objectives and the corresponding hypothesis at the end of the introduction. p7L12 - p7L27

Methods and material Please describe/mention the calculation of the runoff ratio

A: We added a description of runoff ratio calculation and adapted fig 3 to also show the chosen time interval for runoff ratio calculation. p9L21 and Fig 3.

P2364, please add the percentage of paved area. Also are all roads paved?

A: We added a more detailed description of the paved area. p8 L19-20, p9L2-3

P2364, L24, rewrite: "Discharge was measured at five locations" (Try to bring verbs in front of your sentences)

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A: sentence changed, p9L9

P2364, L26, change “Isco” to “ISCO”

A: changed

P2365, L25/26: I haven’t found that you used the temperature data in this paper, so don’t describe that they were measured in the method section.

A: we deleted the description of data that we do not use in this paper.

P2366/2367 L22-L2, please rewrite point two.

A: reformulated, p11L4-6

P2367L3: exchange position of “16 overland flow detectors” and “eleven runoff sensors”, point 1 before point 2. I can not see the locations that were equped with both sensors in figure 1. Do they have different marker?

A: No they did not have a different marker. For the revised version we used different markers for the different devices. The map is more crowded now but the experimental setup can be verified. Fig. 1

P2367L7. “Figure 4” Here you haven’t introduced figure 2 and 3, yet. The introduction of the figures has to be in order.

A: Figure numbering changed

P2367L7-10. You could formulate that section more positive.

A: section reformulated, p11L7-14

P2367L12, delete the comma

A: deleted.

P2368L14. Change “In the 13 rain: : :” to “during the 13 rain: : :”

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A: changed

P2368L17: “PP”=Polypropylene? Full word. Issues with sorption in those bottles?

A: we added the full word and a sentence to the sorption issue that was investigated in a previous study. P13L12 and p12L23

P2369L14: delete “which was also: : :” Citation is not necessary here.

A: deleted

P2372L21: Based on what assumption the 15 m drainage width was chosen? Some knowledge about catchment processes, data from other studies? Work about drainage e.g.: Shipitalo&Gibbs (2000, Soil Science Society Am. Jour.), Klaus&Zehe (2010, Hydrol. Proc.)

A: This sentence was reformulated. This calculation was only used for the calculation of the percentage of drained land and to show the drained area on the map. We do not use that area to calculate catchments of tile drains or similar. p18L3-5

Result section: The results section is a mixture between results and discussion. Usually the results section should only include a description of the results without any discussion. In my opinion the discussion part in the result section should be moved to the discussion section. That would increase readability of the section. Of course it is also possible to join section 3 and 4 together and rename them as “results and discussion”.

A: We restructured the manuscript

Further section 3.1 should also include the runoff ratio that are presented in Table 2, but remain unmentioned throughout the manuscript. Is there a correlation between runoff coefficient and processes? A link to pesticide transport in mass and timing? I guess they will also allow a better interpretation if used in the discussion.

A: We agree. We included more discussion related to the runoff ratio. Results: p19L9-

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12, Discussion p24L27 - 29. However, some of the points raised go beyond the purpose of this paper.

P2373L14: “The period: : : was very dry”. How many mm? What was the water deficit evap. versus precip.?

A: We added the rain sum of the 50 days before application. Hydrograph and rain intensities can be seen in figure 3. p19 L3-4

P2373L18-20. Rewritte: “Four of the five largest events: : :”

A: rewritten

P2378L22. “The human: : :” to “Human modification: : :”

A: 2373, changed

P2378L26: Change “Very peaky” suggestions: “sharp”, “pronounced” etc.

A: 2373, changed, p19L17

P2374L4-L22: This paragraph has to be restructured and rewritten. There is no clear story line, it is too much of a mixture between results, a rudimental discussion, and methods (the description of mixing). Line 17ff is similar to hydrograph separation or a mixing of two end-member with a tracer. The mixing proportions can be quantified be calculations resulting in 52%-84% if rain water in surface runoff (when assuming that EC is conservative and that rain and groundwater are the only endmember). Might help to give a more quantitative description, although problems with nutrients at the soil surface will exist.

A: We reformulated this section, and shifted it into the discussion. We mention the measurement of electrical conductivities in overland flow in the method part. However, the section stays qualitative. We did calculate mixing ratios, which are not mentioned in the paper because they are not meaningful due to the following reasons (some are already mentioned in the comment above): 1) Soil pore water is another end-member

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where EC is unknown 2) EC of exfiltrating groundwater does not need to correspond to baseflow EC 3) EC is not conservative, due to ions that are easily dissolved. Pure infiltration excess runoff has higher conductivities than rain, even though soil contact is short. The interpretation of these results stays semi-quantitative. It is not possible to give meaningful numbers, neither with respect to mixing ratios nor is it possible to give area percentages where which process occurred. However, we think that the average EC values in the overland flow deserve being mentioned because they do contain additional (more spatially distributed) information on the occurring processes. On catchment scale the distinction between sat.excess and inf. excess is not easily possible and therefore we think that the additional information that supports the information gained by the measured groundwater levels is important enough to be mentioned even as a semi-quantitative statement. Method: p11L15-20, Results: p20L5-7, Discussion: p24L9-27

P2374L15; “regional” is too coarse description. Regional groundwater usually describes a way larger scale then in this study.

A: We reformulated. “regional” was used as distinction from perched water tables produced by low conductivity layers within the soil profile. We changed the term “hanging watertabels” to “perched watertabels” p20L2-4

P2374L17 change “as measured in the” to “of”

A: changed

P2374L18 “main effect”, calculations would help here

A: See answer to comment on P2374L4-L22 above

P2375L1, Repetition: it is already stated that infiltration excess overland flow is the main process

A: section reformulated, p24L3 - p25L4

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P2375: Does saturation excess overland flow has a different chemical/isotopic composition than infiltration excess overland flow so that EC can distinguish them? Please give citation for that. It could be that mixing during sat. over. Flow is limited and thus rain is also the main source of overland flow.

A: We argue that saturation excess OF consists of a mixture of exfiltrating groundwater, porewater and rain, while infiltration excess OF mainly consists of rain (no GW, limited mixing with pore water). We added a citation where EC of OF is used in a similar way. We hope the argumentation is clearer in the reformulated section. p24L9-27

P2376L4: Explain the process via catch basins better, I have difficulties with the understanding of how that works.

A: Sorry, catch basin is the wrong term here, we changed it. What we mean are storm drains for road and farmyard runoff.

P2376L6/7: "The connectivity analysis" better: "GIS analysis"

A: We added subsection titles in the GIS analysis method section and still call it connectivity analysis which is the more specific term. P17 and p18 section structure.

P2376L8-10: "This connectivity analysis: : :worst-case assumption" That is method, no point to describe it in the result section P2376L10-18: Discussion, not results

A: manuscript restructured. the possible limitations of the method are now discussed in the discussion. p30L8-15

P2377L5-25: Please shorten. Not so much method detail. Maybe present data in table?

A: We moved the description of half life calculation to the method part. (p16, sect. 2.7.4) We think that presenting the data in a table would give too much weight to these results. They are interesting and important results and they need to be mentioned in the context of the paper, but they are not the main focus of the work.

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P2378L2: ": : :decresed with time(.)" P2378L3: "while the absolute: : :" to "The absolute: : :", delete: "at the stations"

A: changed

P2378L4-5: "depended on the proportions of the sample water: : :" Can you quantifiy that, do you have numbers? Otherwise it is discussion not results.

A: We reformulated the section (p22, sect 3.2.2). We can not quantify mixing ratios, see above.

P2378L11-P2379L5: This section belongs to the method section. Considering the citation of Neitsch et al. (2005). Is there also a journal article that you could cite?

A: Manuscript restructured. We moved the section to introduction (p6L7-14) and methods (p17 sect 2.8) . We use an equation that is part of a simulation program. We think it is appropriate to cite the report where the program is described.

P2379L14: Retardation is used in the title while retention is used in the text. I think Retardation is already defined by the difference in travel times/travel distances of 2 solutes (e.g. Jury&Horton, 2004 Soil Physics).

A: The process we observed is sorption of dissolved chemicals to a porous medium. This is the same process that leads to retardation. However, the coefficient we calculate is not the retardation coefficient (as used e.g. in groundwater modeling), therefore we call it retention coefficient to prevent confusion. We will only use retention in the revised version.

P2379L15-P2380L6: It is very difficult to follow this section. It is again mixing of methods and results, this hides the important findings within this section. Separating them will lead to a better and clearer message. Can you give a process explanation how this retention process works in detailed? (or discuss possibilities in the discussion section, would be very interesting)

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A: We moved the description of the calculation of M and R to the method part (p17 sect2.9). The explanation of the results is sorption (see above).

P2380L7ff. Can you give an example of the correlation factors between the different pesticides, to have a value of similarity? Also correlation coefficient for similarity between chemograph and hydrograph.

A: We calculated correlation coefficients between different substances and between substances and discharge. They support the described correlation that is visible in the figures. P23 sect 3.3

P2380L19. Is that a singular pattern for one solute and one event, or is that more frequent?

A: Terbuthylazine and mesotrione show good correlations with discharge in all the events and at most of the stations (which is what we expected). We decided not to show this figure (Fig 8 in the discussion paper) anymore, it does not contain important additional information.

P2380L28: "observations" What observations do you mean?

A: we added citations p32L1

P2382L2: "On the other hand", Language problem, you have to use "On the hand" before. A singular use of "... other hand" is not possible. Occurs several time in the manuscript.

A: Thank you for the hint, we reformulated

P2382L5-7: What do you exactly mean with higher? Please give number. Can this higher EC derive from solutes that are dissolved from the surface?

A: This section was shifted to the discussion (sect 4.4, p31-34). We can not give numbers of the pure end-members. We only have measurements of the drainage water that consists of all the 3 flow components. We think that the EC in macropore flow

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(flow component 2) is higher than EC of shortcut runoff (flow component 1) because macropore flow is not pure overland flow but also contains pore water. Pore water has higher EC because of solutes.

P2382L8/9: change “where the situation : : : only one experiment” to “with less complexity”

A: sentence reformulated p33,L9

P2382L20 “dominated by road runoff”. On what measurement is this conclusion based?

A: There is no single measurement that this can be based on. Two observations allow that conclusion: 1) The hydrograph follows the precipitation intensity very closely (see fig 11 in the discussion paper). 2) A large part of the road runoff from the main road in the west of the catchment is connected to that sampling station. We added an explaining sentence. p33,L19

P2382L24: “the two (add: possible) flow paths”, delte: “that the water from the fields could take”. How does the concentration dynamic reflect the possible flow paths. Explain.

A: we added an explaining sentence p33 L24-29

P2383L1-6: Repetition, not necessary

A: section deleted

P2383L11-12. Is it surprising that infiltration excess overland flow is an important transport process. I think that previous studies just didn’t observed rain with the intensities of this study.

A: It is not per se surprising that inf. excess OF can be an important transport process. In dryer climate, inf.excess is often the main driver for herbicide transport. The particularity of this study is that it could show the importance of infiltration excess over-

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land flow for the transport of herbicides to the stream at catchment scale under climate conditions that were characterised by considerable amounts of rain during the application period. The occurrence of infiltration excess OF alone is not sufficient to make it an important transport process. The link between the observed hydrological process and the observed herbicide transport is necessary. We extended the discussion in this paragraph. p26L13-21

P2383/84L25-5 I think citations are needed in this section.

A: Citations added. p25L23

P2384L7: This equation does not consider preferential flow that is generated without surface runoff. I think that is ok so for, but has to be mentioned in the discussion.

A: We do not consider this process, as we state in the introduction of the revised paper. See answer to p2361/2362 L25-L2

P2384L12-15 Maybe a own section on management implications, or in conclusion?

A: We did not write a separate section for management implications. They stay within the discussion and the conclusion sections. See also answer to the comments on the conclusion section.

P2384L15-22: Please shorten this section, especially on precip variability, maybe just state that precip variability causes variability in Ainf_ex

A: Section shortened, p26L1-12

P2385L2-5. It is nice that this work confirmed previous work, but where does it go beyond? Here is the change to make an important statement that can show why this study should be cited.

P2385L6/7 delete: “-which is: : : areas-“

A: Since the pesticide problem only affects crop production regions we think that this

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statement is important. It shows that the observations in this study might, at least partly, be true for other agricultural catchments. p29L21

P2385L21 ": : :risk for herbicide transport (add: to streams) can : : :"

A: changed

P2385L24 "On the other hand: : :", missing "on the one hand", see above

A: agree, see above

P2386L1 change "fields: : :network" to: "fields showed no surface connectivity"

A: changed

P2386L4-5. "In this context: : : " clarify sentence

A: sentence changed, p31,L9-11

P2386L7 rewrite and clarify "miss the inlet to the shortcut"

A: sentence rewritten, p30L8-17

P2386L9-11: rewrite "In addition: : : water."

A: sentence reformulated

P2386L13-14. "It has already: : : van Beinum, 2009)" Why? Give explanation?

A: This is a statement from the cited review, it's an empirical finding. Many reasons are possible (dilution, sorption, time delay,...).

P2386L19-21 Suggestion, change: "had shown" to "showed", "that the loss rates" to "the loss rates", "depended to depend", "substances" to "chemicals". P2386L21. Citation needed for Previous observations, for both the loss rates and the sorption effect

A: Sentence rewritten and citations added. p26 L23-27

P2386L24-25. What about the strong effect of the macropore coating on sorption?

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A: The sentence describes conclusions from other studies, we can not change them. It is however possible that macropore coating is responsible for the observed retention.

P2386L25 Delete “interestingly”

A: deleted

P2386L26: here you mentioned what you expected in the work. It would be great using this in the introduction to formulate objectives/hypotheses

A: We added our expectations in the introduction. see above

P2386L27: When you write about mobilization you are referring to the timing of the mobilization? Because to overall recovery might me reduce compared to non reactive chemicals. Please clarify what you mean with “mobilization” in the manuscript. Is there an effect of sorption on pesticide recovery? High sorptivity leads to lower recovery during events with same chemograph dynamics?

A: We clarified the sentence that was obviously misunderstood (P27L4). We refer to mobilisation as the defined coefficient M. This has nothing to do with timing, reactivity and recovery. See also answer below.

P2387L6: Retardation, I think you mean your defined retention? Retardation is measured by the travel time of the center of mass (Jury&Horton, 2004)

A: Sentence reformulated, see also answer to comment P2379 L14

P2387/88L15-L2: In my opinion that does is a little bit contradicting the finding that herbicides applied at the same field have the same temporal dynamics in concentration. If some solutes will enter the aggregate and some stay at the surface of the aggregate the temporal dynamics of pesticides applied in the same field should be different (different time to get in the mobile phase. But it is not.

A: We do not have time resolved samples of overland flow and no exact timing information on when the overland flow sample bottle was filled. We can therefore not address

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the topic of timing in mobilisation. However, in figs 10 and11 (of discussion paper) it is visible that in the beginning of the event atrazine has higher concentrations than sulcotrione, while at the end of the events the concentrations are similar. The overall dynamics are however very similar. sulcotrione as the less sorbing substance could potentially take longer to move out of the soil aggregates and therefore increase its concentration in comparison to atrazine during the event. We added a Figure in SI that shows the increase of the ratio Sulcotrione/Atrazine during one event. This increase does support our interpretation of the mobilisation.

Conclusion: Overall the conclusion need to be clearly shortened. You have to link it directly to the objectives and hypothesis and present the novelty of this study. In this manuscript the conclusion is an extension of the discussion. P2388L14-19 p2389L1-5 are discussion and should not be a part of the conclusions.

A: We agree on linking the conclusions to the objectives and hypothesis, which we do more explicit now in the beginning of the conclusion section. We think that the conclusions should not be a repetition of the abstract but should go further and also explore what implications the results of the study have. In our case these are management implications. We did, however, shorten the discussion on management within the conclusion section. P34-34, sect 5

P2388L20-21. Is that really a new finding? No other study found pesticide transport in inf.ex. surface runoff? I doubt that this was unknown that this is new, since we know that surface runoff will transport pesticides, and we also know that infil.excess surface runoff can occur in humid (agricultural) catchments.

A: see answer to comment P2383L11-12

References: After the year of the publications there are often a bunch of numbers. That seems to be strange to me. E.g. P2390L24 “J. Hydrol., 365, 23-36, 2009. 2362, 2386”; P2390L32/33, etc.

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A: this is HESSD style, these are the page numbers on which the reference is cited

Figures: The font size might be too small in the final version of the paper, in both the maps and the figures. Please have a look at that in the final version before publication Using solid lines for the pesticide concentration (Fig.8, 9, 10) is not accurate, since there is no information between the sampling points. Using data points without lines is more appropriate to the sampling conditions. With the (low) sampling frequency your sampled peak concentrations cannot be assumed to be the real concentration peak.

A: We increased the font size in the figures and maps of the revised version. We agree that the connecting lines do not contain information, but they are needed to read the figures. The dynamics of the different substances would be hard to see without connecting lines. We agree that our sampled peak concentrations do not represent the real peak concentrations.

Figures 1, 2, 4, 9 add coordinates. Also in the text figure 4 follows figure 1. Need to be corrected

A: done, now figures 1,2,4 and 11

Figure 3. y-captions, Unit (L s-1), l think HESS uses small l symbol for liters (but check again), if so please change, letters might be too small in the publication

A: done, Fig 3

Figure 6 and 7, add unit to Kd, also needed throughout the manuscript

A: The figures (now 8 and 9) show ratios of Kd which are unitless. We added units in the text where missing

Figure 8. l instead of L

A: done

Figure10. Maybe avoid overlapping of the discharge and precipitation peak. Use l for

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liter instead of L.

A: The overlap is between terbuthylazine concentration and precipitation. avoiding the overlap creates to much white space in the figure without information.

Review 2

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.

A: We restructured the manuscript to achieve a clear division between results, discus-

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sion and conclusions. We also added a sentence on the manuscript structure at the end of the introduction (P8 L2-5)

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.

A: We are aware that non-equilibrium sorption is the rule for the herbicides studied with soils and soil organic matter, which we expressed by using the term "apparent Kd values". However, we agree with the reviewer that this issue requires some further discussion in the manuscript and expanded it accordingly (p27L13-p29L7). We think that within the study period right after application liquid and solid phase concentrations are at no time at equilibrium for relatively rapidly dissipating compounds such as the studied herbicides. In addition to dissipation, changing soil moisture conditions pre-

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vent equilibration. Thus, even if we determine the (near-)equilibrium Kd after several weeks it will be of little practical relevance, and such a determination would by hardly possible for rapidly degrading compounds without sterilization of the soils, which itself affects the sorption process. Thus, our approach of a 24 h equilibrium is based on practical issues, but also mimics a saturation of soil and the displacement of the non-equilibrium porewater into overland flow under standardized conditions. Thus, we would not consider this as artifacts but as a measure to understand the processes in the field. Conceptually, a mobilization of compounds from the soil into overland flow can be considered as consisting of at least two processes: A displacement of pore water with a certain herbicide concentration at near-equilibrium with the solid phase, and a kinetic desorption of herbicides into infiltrating water at lower concentrations following a chemical potential gradient.

We agree that equation 3 can only be considered a crude approximation and our data support this statement.

Most of the timeseries of Kd (one substance, one field) show a steady increase with time (over the 2 month) without large fluctuations because of soil wetness or the addition of water. We added a figure in the SI to show that steady increase. It can be seen as indication that the measured values are not too much influenced by artifacts. (Fig SI 1)

We also added a part on sorption in the introduction. P5L26-p6L14

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.

A: The revised manuscript was corrected by a native English speaker.

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

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A: Sorry, catch basin is the wrong term here, we changed it. What we mean are storm drains for road and farmyard runoff.

2364-5 define soil thickness

A: definition added, its the thickness between soil surface and C horizon, P8L17

2364-12 artificially appears to be pleonastic

A: agree

2364-19 hydrological variables

A: changed

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

A: changed, P9L15

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

A: we use separate symbols for the two types of overland flow measurement devices in the revised version. Fig 1

2367-6 Which events?

A: The details given in the caption of fig 4 were copied to the text. p11L9-10

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.

A: We reformulated to make the applied substances clear. We added the application rates in g/ha. p12L3-7

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

A: agree, we reformulated, p12L7-8

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

A: we rephrased the soil sampling procedure. p14 sect 2.6.

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.

A: agree, we rephrased p14L17-19

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.

A: Centrifugation details and description of the WHC measurement added. p15 sect2.7.2

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

A: We don't agree. This is a method description and does not contain any results. It describes how we did the GIS analysis.

2372-11 Give the accuracy of the DEM.

A: done, p8L11

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

A: we reformulated. This buffer calculation was only used for the calculation of the percentage of drained land and to show the drained area on the map. We do not use that area to calculate catchments of tile drains or similar. p18 sect 2.10.2

2372-24 artifacts

A: changed

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2373-10 Explain "appropriate".

A: We explain the procedure in more detail in the revised version. p18L19-20

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.

A: We reformulated this section and give more details. What is important here is that none of the rain events had a significant reaction in the hydrograph. p19L3-4

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

A: We now mark both, rain and discharge, in the graph and call them events. Fig 3

2374-14 explain what hanging water tables are

A: we change the word, what we mean are perched water tables

2375-22 explain solid manure

A: solid manure is cattle dung mixed with straw. We think that this is a well known term and do not explain it in the manuscript.

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.

A: manuscript restructured

2375-7 observations of

A: agree

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

A: Yes this is how the area was mapped. we made this clearer in the revised manuscript (p20,L24). But we will not combine the two sections (Method and Results), see above

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

A: We know because of field observations that there is a drainage system manhole and we observed overland flow entering that manhole during event E2 (when the picture was taken).

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

A: manuscript restructured

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.

A: The revised manuscript was corrected by a native English speaker.

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.

A: We reformulated the section on sorption and avoided the term aging.

2378-9 Mobilisation or mobility? Which macropores?

A: Mobilisation. We don't find the word macropores in that section.

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

A: We restructured the manuscript, but we did not put the concentration dynamics at the beginning of the results. We think that it is better to first understand the hydrology of the catchment and the substance property related processes before the concentration dynamics can be understood.

2381-27 An interpretation belongs into the discussion section.

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A: manuscript restructured

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

A: agree, we deleted

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

A: we added an explaining sentence P31L14-19

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

A: Sorption part reformulated and citations added. mainly p27L13-p29L7

Equations Always state the units with the definitions.

A: agree, units added where missing.

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.

A: We agree that well-draind soils are not a soil type. We combined different types of cambisols and luvisols (Braunerde, Kalkbraunerde and Parabraunerde in the Swiss soil classification) into that group. For our purpose the water regime of the different soils is the important property. We added details in the figure caption. We changed the colors. Fig. 1

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

A: This comment probably refers to Fig 12 of the discussion paper. Yes, the direct comparison of rain intensities of the main loss event would be easier and is important. We do this comparison in the text (P25L6-9). However, Fig 12 (of the discussion paper) contains additional information on rain intensity distributions. To judge how important the two processes (infiltration excess OF and sat. excess OF) are, the frequency distribution of rain intensities during the period is necessary.

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

A: done, Fig 3

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

A: We changed the shading color. Fig. 11

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