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Interactive comment on "Hydrological tracers for assessing transport and dissipation processes of pesticides in a model constructed wetland system" *by* Elena Fernández-Pascual et al.

Anonymous Referee #1

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Scientific significance:

The manuscript aims at improving the understanding of the fate of pesticides in constructed wetlands, which are implemented to mitigate pesticide pollution of surface water bodies. To that end, the authors describe in quite some detail findings from a complex laboratory experiment simulating the fate of different (organic) chemicals and Br^- as a conservative tracer (except for plant uptake) in a constructed wetland. To improve with regard to previous studies, the authors have put a lot of effort in obtaining spatial and temporal resolution of the concentrations of their model compounds in the experimental wetland.

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Discussion paper

Despite the fact that constructed wetlands have some practical relevance as mitigation measures, the scientific relevance of the manuscript seems to be limited. On p. 2, L. 5 – 9, the authors describe their objectives. However, in the current form they are very specific to the experimental design and it remains unclear (also subsequently in the manuscript, see also comments below) how answers to the posed question can be generalised:

- How to gain general insights if one knows in detail the spatial and temporal patterns of pesticide fate processes in this particular wetland at the lab scale (refers to objective i))?
- How to generalise the findings related to the different behaviour of the model compounds (refers to objective ii))?
- How to generalise the results regarding vegetation and hydrologic conditions (refers to objective iii))?

My statement does not imply that no such general insight could be gained from the experiment. However, in order to do so, one would need to ask first general scientific questions and subsequently demonstrate how the experiment can provide such generalizable answers. Such questions however are missing. The sentence on p. 2, L. 3 – 4, is too vague in this respect. This limitation is subsequently reflected in the Conclusion section. There is a lack of novelty and the statements are either very general or too speculative.

One way how the generality could be improved would for example be to put the characteristics of the study wetland (texture, organic carbon content, water residence time, redox conditions etc.) into the context of real-world wetlands, to reflect – based on scientific theory – what follows for pesticide retention in such wetland and to demonstrate respective insights that go beyond prior knowledge. I missed such information in the manuscript.

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Scientific quality:

Overall, the manuscript indicates that the experiments were carefully planned and executed. There are few technical questions that are listed below.

However, there are conceptual limitations that also relate to the comments on the scientific significance above. A major issue is the lack of replication. There is only one vegetated and one non-vegetated chamber of the experimental tank. I am aware of the effort needed to carry out such experiments and to build such experimental facilities. Nevertheless, the results and conclusions hinge solely on single realisations of two experimental treatments. Especially in the context of preferential flow phenomena, this may be very critical because a single connected flow paths may exert a strong effect on the overall outcome. Without replication, it is very difficult to judge the robustness of the differences observed between the two treatments.

Another limitation is the lack of quantitative analyses that could link the different pieces of information. The authors report for example K_{oc}-values for the different compounds from the literature but do not provide quantitative analyses how transport and concentrations levels were expected based on this information. I also missed key features such as expected hydraulic residence time in the system etc. One could probably calculate such things from the information in the text and Tab. 2 but it would be useful for readers to directly get such information.

Presentation quality:

In general, the paper is clearly written and the findings are carefully presented in the figures and tables.

Detailed comments:

Title: Use of tracers: Why do you distinguish between tracers and pesticides? Uranine and sulforhodamine B are organic chemicals as are the three pesticides used in the study. Of course, there is a difference in the use of the compounds, but why is this

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distinction relevant for elucidating the fate of the pesticides (given the fact that also these tracers undergo sorption plant uptake and degradation)?

Abstract:

p. 1, L. 10: What are spatial and temporal mechanisms? p. 1, L. 13: What was the rationale behind the selection of these compounds? p. 1, L. 16 – 17: What do you mean by the statement that transport dominated for some compounds? p. 1, L. 17 – 18: What other dissipation processes could be expected? This statement is not very informative.

Introduction:

p. 1, L. 27: The reference is not very recent. Many others are available representing more current findings. p. 1, L. 28 – 29: Generally, transformation products are less toxic. There are exceptions but the wording may be misleading. p. 1, L. 40: This is an important aspect. Unfortunately, this manuscript does not really elaborate any further on this topic. It would be interesting to learn how the results reported here relate to other studies and what the results imply for mitigation capacities. p. 2, L. 13 – 18: The critical question about the compound selection is what insight can be gained. In the result section (p. 9, L. 1 – 20), the results about the compound-specific differences are summarised. The reported findings basically reflect the knowledge already used for making the compound selection. Hence, the authors miss to derive more general insight that goes beyond the prior knowledge.

Methods:

p. 2, L. 28: How reliable is terbutryn as an internal standard for the other pesticides? p. 4, L. 8: Generally, glass bottles are used for storing pesticide samples. p. 4, L. 30: What about possible inferences with the fluorescence of the background matrix? p. 5., L. 4: Where are LOQ/LOD provided? p. 5, L. 12: How can an independent background be determined? p. 5, L. 35 – 36: This sentence sounds strange because transport

processes affect all compounds irrespective whether or not they are sorbed or not (or degraded or not).

Results and discussion:

p. 6, L.10: What means an early breakthrough? Early compared to what? p. 6, L.10 – 30: These paragraphs list different findings without a clear structure and logic. p. 6, L. 37: Where can one see these redox conditions? p. 7, L. 6: I assume that sorption takes place all the time and not only during the initial phase. p. 7, L. 18: Where can one see this correlation? p. 7, L. 20 – 30: These sentences are confusing. p. 7, L. 30 – 33: This paragraph is not well linked into the structure. p. 8, L. 11 – 13: Please be aware that different transformation products may have different source terms because they are generally formed at different rates and possibly in different parts of the subsurface. p. 8, L. 22 – 24: This is very qualitative. What were the expected compound-specific differences solely based on the K_{oc}-values? p. 8, L. 25 – 26: Again, this statement appears rather isolated in the text. p. 9, L. 31: Here you contradict yourself: above you have argued that SRB is expected to be strongly sorbed because of its K_{oc}-value (p. 8, L. 23)

Figures: Fig. 4: - It is difficult to distinguish all the different lines. - What were the hypotheses how the breakthrough would differ between the different depths and the different compounds? Fig. 7: Is there no differentiation between vegetated and non-vegetated treatments? Fig. 8: You might consider comparing the two treatment with separate bars. Fig. 9: Is the sorption consistent with K_{oc}-values known for SRP?

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