

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 #2

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The authors present an interesting and well written paper on transport and dissipation processes of different substances in a constructed wetland at the lab scale. This is a highly relevant topic that is within the scope of HESS and of interest for a broader audience. The experiments and results are highly interesting and are largely presented clearly. A few points in the analysis and interpretation, however, should be revised to be less speculative and more supported by the results. This requires mainly further elaboration of the discussion, as detailed in the specific comments below.

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1 General comments

1. Recovery

A main concern is the low recovery of most of the substances. Except for bromide and SRB, less than a third of the applied masses were detected in the investigated compartments (the data on SRB suggests a recovery between 48 and 105 % - Fig. 8). Because it is ambiguous to judge the parts that have not been observed, care needs to be taken in drawing conclusions on transport and dissipation from the data. The authors often did well in this regard, and addressed possible pathways of the substances' fates by deduction and use of available literature. Sometimes they overachieved a bit, and some aspects deserve further clarification.

I would appreciate if the authors discussed possible reasons for low recovery in more detail. What about the formation of other transformation products – is this likely, are other TP known that might be formed under the given circumstances? If sorption is a major pathway, why have the substances not been detected in sediment/plants? Which other pathways are possible, especially for the substances that are not likely to be adsorbed or degraded? Can the expected degradation/mineralisation be quantified using literature values, and contrasted with the measurements?

With regard to the transformation/degradation of UR: How much of the degradation was possibly due to photolysis in the inlet container or at the system's surface? Could you estimate photolysis rates quantitatively? Microbial degradation of UR seems not to be enhanced after the first application, as illustrated by the similar recovery rate in the second part. If the system has not been exposed to UR before, and microbial decay was a major pathway, the first application of tracer probably would have fostered the microbial community capable of degrading the dye (Käss 1998), which would have enhanced microbial decay in the sec-

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ond run. Can alteration of fluorescent properties be a reason for apparent loss of UR (pH values are given in Table 2, but apparently only one measurement)?

The different substances were mixed in one solution for application, but possible interactions of the applied substances are not discussed. Can interactions of the different organic compounds be ruled out? Testing a reference sample of the injection solution repeatedly over time could give further hints on interactions or degradation rates of the mixture.

2. Flow paths and preferential flow

The flow paths during the tracer application are not completely clear to me. From Fig. 3 it appears as if the tracer solution was applied to the surface near the inlet container by letting the inlet container overflow. The arrows indicate vertical movement downwards near the inlet, and vertical movement upwards elsewhere. Is the ponding on the surface from surface flow from the inlet, or from upward flow through the soil? In case of the former: Has air been entrapped in the system?

A great part of the transport in the experiment has been attributed to preferential flow in the upper and lowermost layer. Given the coarse texture of the soil, hydraulic conductivity will be high and lead to fast regular flow rates already. Is the observed breakthrough still considered preferential when compared with expected flow rates using conductivity and hydraulic gradient? If preferential flow is an issue, how would that influence the spatial distribution of substances in the sediment, and in turn the recovery of substances from sampling sediment?

3. Correlation analysis

Much of the interpretation is based on a correlation analysis. Please describe in bit more detail what was correlated – I expect you used measured concentration time series? Sorption is significant for some of the substances. How would retardation affect the results of the correlation analysis?

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2 Specific comments

P6, LL 33-35: This part is unclear. How does the design of the inlet cause preferential flow towards the bottom? And what is meant with “plants channel flow to the surface” – flow from lower layer to the soil surface? Or do you mean enhanced infiltration from the surface?

P6, LL39-40: Consider rewriting sentence. Br^- had almost complete recovery and was found in plants and roots, so you may delete “possibly”, and refer to Fig. 8 and not only the lack of measured Br^- in pore water.

P7, L4: “Early Breakthrough” – compare with expected flow velocity (see comment above)

P7 L12: “absence of BTC in middle layer” and “early BTC in uppermost layer” “confirmed the influence of plants” is too strong as a statement. Other explanations are possible for these observations – preferential flow without the influence of plants (fingering), bias in the observations, etc.

P7 L 14 “evidenced” – too strong as well. It might be a hint, but could also be that the degradation is just a function of time, and transport over that time ended in the vegetated part, opposite from the inlet.

P7 LL23-27/Table 4: How significant are the differences in recovery of Br^- given in Table 4, which is the basis for your argumentation here? The differences do not appear large enough to justify the conclusion.

P8, L 36: Please explain “low leaching potential” as a property of a substance – does that mean high sorption?

P9, L 38: “could be identified” – an unambiguous identification was unfortunately not possible in the experiment, but valuable hints / indications were collected

P10, L 5: “biochemical transformation had a major contribution” – only <10 % of the parent substance were found as TP, so it is not possible to say which was a

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major contribution

Fig 4: How do you explain the obvious differences in Br^- breakthrough between the first and second run? Fig 7: Recovery of TP in % - how can the total amount be known?

Fig. 8: Please comment on the large error bar for SRB, which indicates recovery to be between 48 and 105 %. Would more sediment samples have reduced this uncertainty? How does this uncertainty influence your interpretation?

3 Technical comments

P2, L32: $100 \text{ mg L} \rightarrow 100 \text{ mg L}^{-1}$

P2, L35: Please give the dimensions of the constructed wetland system also without inlet/outlet.

P5, L11: resulted curves \rightarrow resulting curves

P5, L13, and elsewhere throughout the text: $\text{Br} \rightarrow \text{Br}^-$

P7, L26: “was most likely” \rightarrow “were most likely”

P8, L28: “were classified”: classified for what (recovery rate, I presume?)

Fig 4: Consider duplicating the figure and display vegetated and non-vegetated parts separately, which would make distinguishing these parts a lot easier

4 References

Käss, W. (1998): Tracing technique in geohydrology, 581 pp., Balkema, Rotterdam, The Netherlands.

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