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Interactive comment on "Pesticide peak concentration reduction in a small vegetated treatment system controlled by chemograph shape" *by* Jan Greiwe et al.

Anonymous Referee #1

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The authors present an interesting study design with almost experimental character. Based on Fig. 1, one can conclude that there is a spatial separation between different crops in the catchment (arable crops versus vineyards). Because these crops receive different pesticide treatments (with regard to timing, compounds) one gets a signal in the outlet of the catchment that is related to a certain spatial unit. This design has the potential for learning how spatial aspects, physico-chemical properties of pesticides and agricultural practices influence pesticide losses (dynamics, loss rates). This could also be relevant for better understand the functioning of the wetland as is the main purpose of this manuscript.

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The manuscript analyses the effect of a wetland at the outlet of this agricultural catchment on pesticide transfer further downstream. Based on samples taken during 10 events and five baseflow periods, the retention capacity is studied for four active ingredients and two metabolites regarding the relative reduction of peak concentrations and pesticide mass transported downstream. Specifically, the authors investigated the effect of the shape of the chemograph at the inlet and a few compound properties and explain the differences in the chemograph shapes of different compounds by being applied to different parts of the catchment.

Monitoring pesticide dynamics in natural systems is demanding and requires substantial efforts in the lab and in the field. The observed pesticide behaviour in the environment is complex and often influenced by specific conditions at the local scale. Therefore it is valuable for science and practice if such observations get published from different locations and catchments because it broadens our understanding of the environmental fate of pesticides under different conditions.

Unfortunately, there a number of issues that limit the value of the manuscript in its current status. I describe my main concerns below and add some further details at the end.

Scientific quality:
The data analysis is rather superficial and several of important conclusions are not strongly backed up with data. This holds true for example for the interpretation of the different dynamic patterns identified (L. 210 - 221). For example, the authors hypothesise that fungicides from the upstream vineyards are more quickly transported to the stream than the herbicides applied closer to the creek in the valley bottom (L. 210 - 213). Why this should be the case remains unclear. Checking a previous publication on the catchments (Gassmann et al., 2012) reveals that there is a dense road network connected to the pipe drains. These structures are made explicit in the earlier publication but no linear structures are indicated in the catchment map of this manuscript. Given the fact that pesticide drift to non-target surfaces such as roads may be impor-

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tant for pesticide transport in vineyards (Lefrancq et al., 2013) important aspects of the catchment are neglected and not included into the discussion of the results.

Also temporal aspects are only treated superficially. The shape of the chemograph of a pesticide is strongly influenced by the rainfall dynamics. Because the authors compare the dynamic of different pesticides across different events (this is not really evident from the main text, but see the SI), differences in concentration dynamics could also be strongly influenced by rainfall patterns and discharge behaviour. Unfortunately, no respective data is shown or discussed.

This holds also true for the timing between the last application of a pesticide and the rainfall event. The authors do not discuss this aspect and treat all compounds and all events the same (except for two events for flufenacet where too many samples $<$ LOQ). However, inspection of the actual concentration data reveal strong differences in the concentration levels of the different compounds across all events. High concentrations of several hundred to thousands of ng L^{-1} were found for boscalid for all events, while flufenacet was only found in one event above 1600 ng L^{-1} but otherwise never above 40 ng L^{-1} . Obviously, the history of the compounds since the last application was very different. Neglecting such aspects but interpreting the different relative concentration dynamics with respect to transport differences from different parts of the catchments is not very solid.

This also limits the value of the cluster analysis. The results in Fig. 3 show that a given compound appears in different clusters. However, this aspect is not properly discussed and no explanation is provided why this was the case nor what this implies for interpretation of these clusters. Additionally, it is not clear to which degree these results reflect the full spectrum of observed pesticide dynamics. The authors mention in the Method section (L. 190) that they have removed outliers based on purely statistical analyses. I don't think the procedure is sound (see below) and may bias the findings by excluding unusual - or simply rare - dynamics.

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Finally, the calculation retention rates raises a number of question marks, which may further impact the subsequent linear model for describing the retention efficiency of the wetland. First, given the measured concentrations (see SI, but also Fig. 3) it is evident that in many cases the last data point does not reflect baseflow concentrations after the event. Accordingly, the mass loss during the events may have been substantially larger in some cases. The extent of this effect depends on the unobserved concentration dynamics but also on the discharge. Unfortunately, no discharge data is provided that illustrate which part of the event hydrographs have actually be covered by the sampling. Second, the observed concentration levels demonstrate that for compounds such as flufenacet most events reflect conditions long after the last application. Accordingly, the concentration signal is rather weak and calculated retention is laced with considerable uncertainty. This aspect is not mentioned.

Scientific significance:

The issues listed above reduce the scientific significance of the manuscript. Additionally, there are questions about the scientific insight conveyed by the manuscript. There are two major issues:

Relevance of the shape of the chemograph The effect of the chemograph is almost a trivial finding. Given the short residence time in the wetland (about 1 h; see L. 81) degradation processes will be very limited and the main effect on peak concentrations in the outlet is expected by dispersion (as expected by the authors, see below), i.e. mixing water of different concentrations at the inlet. Obviously, the more variable the input, the larger the relative effect of mixing on the relative maximum concentrations. Actually, the authors have stated this outcome already in the Introduction as fact: "'*Peak concentration reduction will be stronger for a signal with pronounced peak and low background than for a signal with small peak and high background if both signals are exposed to the same dispersion.*"' (L. 54 - 55).

This can also be easily shown with the following example: Let's assume that two compounds have the same background concentration (C_{min}) but during a discharge event the concentration of compound B reaches higher values than compound A with the same relative dynamics during the event:

$$C^B = C_{min} + \alpha \, (C^A - C_{min}) \tag{1}$$

Assuming only mixing to occur, it is evident that the maximum outflow concentration ranges between C_{min} and $C_{min} + \Delta C_{max}$ for compound A (indicated by the fraction β of the maximum possible value):

$$C^A_{out} = C_{min} + \beta \, \Delta C_{max} \tag{2}$$

$$C^B_{out} = C_{min} + \alpha \, \beta \, \Delta C_{max} \tag{3}$$

Accordingly, the relative peak concentrations in outflow compared to inflow is given as follows:

$$R^A = \frac{C_{min} + \beta \, \Delta C_{max}}{C_{min} + \Delta C_{max}} \tag{4}$$

$$R^B = \frac{C_{min} + \alpha \, \beta \, \Delta C_{max}}{C_{min} + \alpha \, \Delta C_{max}} \tag{5}$$

Taking the ratio of the relative peak concentrations shows that the relative concentration for the compound with the more pronounced peak is more strongly reduced: $R^A > R^B$:

$$\frac{R^A}{R^B} = \frac{C_{min} + \beta \, \Delta C_{max}}{C_{min} + \Delta C_{max}} \, \frac{C_{min} + \alpha \, \Delta C_{max}}{C_{min} + \alpha \, \beta \, \Delta C_{max}} = \tag{6}$$

$$= \frac{C_{min}^2 + (\alpha+\beta)C_{min}\Delta C_{max} + \alpha\beta(\Delta C_{max})^2}{C_{min}^2 + (1+\alpha\beta)C_{min}\Delta C_{max} + \alpha\beta(\Delta C_{max})^2} \quad (7)$$

This ratio is always ≥ 1 because $\alpha + \beta \geq 1 + \alpha\beta$ (for $\alpha \geq 1, 0 \leq \beta \geq 1$) [1].

In this context I am furthermore surprised that the authors did not use the model that was developed for the study wetland for evaluating the effect of different chemograph shapes (Schuetz et al., 2012). Although the wetland may have undergone changes since the last tracer experiments, it would be a useful null model for testing how different input signals influence the reduction in peak concentrations.

How to generalise the findings? It is difficult to generalise any of the findings reported in the manuscript because they are very context dependent and results such as the cluster analysis are very phenomenological. The aspect that the shape of the chemograph has an influence on the relative degree by which peak concentrations are reduced is quite evident for the type of system under investigation.

Detailed comments:

L. 30: The phrase "'*... which may be equally or more mobile, persistent and toxic than their PC ...*"' is misleading because it does not mention the general case that transformation products are less toxic.

L. 93: How often were grab samples taken?

L. 123: How adequate is it to only take one single isotope-labelled internal standard not corresponding to the target compounds? Checking these compounds in one of our current analytical methods, retention times vary between 16.7 (metazachlor-ESA) and 21.0 min (penconazole). Also the K_{OC} values vary by a factor of 400

[1] with $\alpha = 1 + \delta$: $\alpha + \beta \geq 1 + \alpha\beta \Rightarrow 1 + \delta + \beta \geq 1 + \delta\beta + \beta$

between these two compounds. Please provide additional information supporting the assumption that terbutryn as an adequate internal standard (e.g., recoveries).

L. 129 - 130: Please check the correct number of significant digits (can you measure with a precision of tens of picograms per litre?).

L. 142: Please provide the version of R. I assume that you did not implement the algorithm but used `kmeans()` implemented in standard R.

L. 174 - 176: Why did you include DT_{50} a priori? I'd recommend to leave it in. The subsequent analysis would reveal whether or not is had any statistical relevance.

L. 179: How did you quantify the water balance error? Please explain.

L. 190: The definition of outliers and their handling is not sound. Cook's distance is simply a mean of identifying data points that deviate in a statistical sense from the rest of the data population and have a strong influence on a derived regression model. This does not imply that the data point corresponds to an outlier that can be discarded from the analysis! It may be that the outlier reflects reality as well as all other data. They may simply reflect rare events. Of course it is important to assess the influence of statistical outliers on model performance and predictions. However, unless there are sound reasons to exclude data as outliers because these reasons indicate the outliers to be wrong, outliers have to be included in the analysis. For example, it can be made transparent that some data (explicitly shown) deviate from the others in a specific way and discuss possible reasons. Hiding them to the scientific community introduces bias.

References

Gassmann, Matthias, Jens Lange, and Tobias Schuetz. 2012. 'Erosion modelling designed for water quality simulation', Ecohydrology, 5: 269-78.

Lefrancq, M., G. Imfeld, S. Payraudeau, and M. Millet. 2013. 'Kresoxim methyl deposition, drift and runoff in a vineyard catchment', Science of the Total Environment, 442: 503-08
Schuetz, T., M. Weiler, and J. Lange. 2012. 'Multitracer assessment of wetland succession: Effects on conservative and nonconservative transport processes', Water Resources Research, 48: W06538

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