We thank reviewer 1 for the useful comments. We address each of these comments below:

1. "In contrast, I found some difficulty to follow the logic from the simulation results to conclude "CSIA is a feasible and expedient technique for the analysis of transport pathways and the assessment of the extent of degradation of diffusive pollutants". To make this main conclusion statement clear, the authors should primarily state what parameters (e.g. degradation rate, proportion of surface/subsurface flow pathways, contribution of aerobic and anaerobic reactions etc.) are expected to be quantified (or qualitatively described) in what conditions."

Reply:

Concentration data do not provide clear evidence of degradation processes, since lower concentrations might result from enhanced degradation or dilution. In contrast, isotope data can serve as an indicator of contaminant transformation (see P8792-L23), and allow for the quantification of the extent of degradation. In this study, the simulated isotope ratios were used to determine the extent of pesticide degradation, and the relative importance of the aerobic and anaerobic reaction pathways to overall degradation (see P8818-L9 and P8821-L1).We did not attempt to estimate degradation rates from the extent of degradation. The Rayleigh-equation based estimates of the extent of degradation matched very well with the known model results. The simulation results also showed that CSIA data have potential to assess transport routes under favourable conditions: isotope ratios equal to those of the emission source indicate fast and shallow transport routes, whereas enriched isotope ratios are associated with deeper and slower transport pathways. Similarly, the simulation results suggest that isotope data of two elements can, under favourable conditions, allow for the distinction between two reaction mechanisms.

- In scenario 1, the relative contribution of dilution and degradation to the overall concentration reduction could not be inferred from the concentration data alone. The isotope data, in contrast, allowed for the quantification of pesticide degradation, and comparison of the magnitude of concentration reduction by dilution and degradation (see P8806-L23). We therefore suggest that isotope ratios during baseflow conditions

indicate the maximum potential of natural attenuation, as they are not influenced by fast pesticide transport routes such as surface runoff (see scenario 2).

- In scenario 2, the maximum concentration in response to the rainfall event indicated enhanced pesticide transport to the hillslope outlet. However, the concentration and mass flux data did not allow for the identification of the main transport route (see P8813-L11). This could only be derived from the isotope data, which indicated that pesticide transport to the hillslope outlet following the rainfall event occurred predominantly via surface runoff. It was, however, not possible to directly quantify the proportion of surface and subsurface flow pathways based on the simulated isotope ratios. In reality, the detection of surface runoff by CSIA would require high temporal resolution sampling, comparable to the temporal resolution needed for concentration measurements during rainfall events (see P8818-L1). Moreover, a distinction between transport via surface runoff and other flow pathways is only possible if the isotopic signature of the diffuse pollution source is known and distinguishable from isotope ratios that are associated with pesticide discharge via subsurface flow pathways.
- In scenario 3, the interplay of transient hydrological conditions and temporally varying pesticide input complicated the identification of the main drivers of concentration changes. In contrast, the analysis of the extent of degradation, which was calculated from the isotope data, gave insight into the dynamics of pesticide transport in the hillslope system. First, it showed that the dry season was associated with the discharge of more degraded pesticide compared to wet conditions (see P8813-L1). Second, it indicated that large rainfall events did not only result in dilution of pesticide concentrations, but also in the discharge of less degraded pesticide (see P8815-L22). In addition, the analysis of the relative contribution of aerobic and anaerobic reaction pathway to overall degradation (parameter F), which was derived from the two-dimensional isotope data, revealed an increasing importance of deeper flow pathways for pesticide transport during dry conditions (see P8812-L14 to P8813-L1). A qualitative analysis of the interplay between different flow pathways based on F would be feasible for systems such as the modelled hillslope where different mechanisms of pesticide degradation can be attributed to

spatially distinct areas, and are associated with known and distinct enrichment factors.

We will revise the text and mention more explicitly and more clearly which processes can be quantified with CSIA in the revised manuscript. We will also add a new discussion section ("4.2 Validity of model assumptions") that addresses possible deviations in the model results due to volatilization and sorption processes, and preferential flow pathways (see also comment 2 from reviewer 2).

2. P8790-L16: "These results suggest that CSIA can help to determine whether pesticides enter the stream via groundwater exfiltration or via surface runoff." In the actual condition, the streamflow is typically originated through both flow pathways. Does the author intend to say the proportion can be quantified by CSIA?

Reply:

CSIA does not allow for a direct quantification of the proportion of groundwater exfiltration, flow through the shallow soil layers and surface runoff. Regarding the modelled system, CSIA helped in the qualitative interpretation of scenario 2, as it clearly indicates a significant contribution of surface runoff to pesticide transport to the stream in response to the extreme rainfall event.

We will change the wording of this sentence in the abstract to make this clearer.

3. P8790-L24: "The analysis of simulated isotope ratios also allowed quantifying the contribution of two different reaction pathways to the overall degradation." Does "two different reaction pathways" mean aerobic and anaerobic? If so, what is the effect of the assumption of "aerobic reaction in the topsoil and anaerobic reaction in the subsoil and bedrock"? In other words, if the proportion of aerobic and anaerobic reactions are quantified based on the assumption of enrichment factors, how certainly can we relate this to the different flow paths (i.e. topsoil and subsoil-bedrock)?

Reply:

The two different reaction pathways are indeed aerobic and anaerobic degradation. We will clarify this in the revised manuscript.

We assumed that the anaerobic reaction pathway can be attributed to the hillslope subsoil and bedrock zones, whereas the aerobic reaction pathway occurred in the topsoil zone. This enabled us to relate the contribution of these two reactions (i.e. parameter *F*) to different flow pathways. It was thus possible to qualitatively describe the importance of shallow versus deep groundwater exfiltration for the overall pesticide flux to the stream, and identify changes in their relative importance to the overall flux under transient hydrological conditions (see scenario 3). Even though it is reasonable to expect that aerobic degradation occurs in the surface soil layers and anaerobic degradation in saturated deeper layers, different reaction mechanisms might not be spatially exclusive, or their spatial distribution might be unknown. Hence, the parameter *F* may not necessarily allow for the determination of prevailing transport routes. Nonetheless, if different reaction pathways are active only under certain conditions and the spatial distribution of these conditions is known (as it is the case for the assumed redox conditions of the hillslope system), the occurrence and relative contribution of these reaction pathways can be related to different zones and thus indicate different flow pathways (see above).

We will clarify in the revised manuscript that the interplay between shallow and deep groundwater exfiltration could be inferred from the parameter *F* because it was assumed that the two reaction mechanisms occurred in spatially distinct and clearly defined subsurface zones. We will also point out that we may not always be able to know the spatial distribution of the different reactions.

4. P8822-L1: In conclusion, "CSIA thus offers a unique tool for the assessment of pesticide transformation, and even for the analysis of the interplay between different transport routes". This sentence needs to be more precise. I could not understand how the authors quantified the interplay between different transport routes in the simulation, and which extent they expected to do so under various uncertainties in the actual fields.

Reply:

In the revised manuscript, this sentence will be changed to “CSIA thus offers a unique tool for the assessment of pesticide transformation, and even for a qualitative description of the interplay between transport via shallow and deep flow pathways”. CSIA did not allow for a

direct quantification of the contribution of different transport routes to pesticide transport (see comments 1 and 2). The qualitative description of transport routes is based on the parameter *F* and depends on the assumed enrichment factors. It is only possible to draw conclusions about the interplay between different transport pathways from *F* if the active reaction pathways and their spatial distribution (e.g., anaerobic beneath the aerobic zone) are known, and if they lead to a different extent of isotope fractionation (see above). The latter will be added to the revised manuscript to clarify the conclusion.

5. P8802-L9: "Two conservative tracers with $C_0 = 1.0$ were applied ... across the entire surface of the model domain and at the application area". The statement of "entire surface" and "the application area" seem to be in conflict.

Reply:

This sentence is indeed not clear. In the revised manuscript, the sentence will be changed to "In addition, one conservative tracer with $C_0 = 1.0$ was applied across the entire surface of the model domain and another tracer (also with $C_0 = 1.0$) at the application area only, to allow for the calculation of the mean travel time of groundwater".

6. P8802-L17: What is the "coupling length"?

Reply:

The coupling length determines the degree of continuity in pressure heads between the surface and the subsurface domain, and thus affects the generation of overland flow in the model (Verbist et al., 2012). A lower coupling length results in increased coupling of the overland flow domain to the subsurface domain. The coupling length was briefly explained at P8796-16. We will further clarify the meaning of the coupling length in the revised manuscript.

7. P8807-L18 and Fig.4(b) Why are the simulated isotopic ratios of $\delta^{13}C$ and $\delta^{2}H$ constant during rainfall event and change rapidly after the cease of rainfall? Is there any interpretation presented in the main text?

Reply:

The isotope ratios remained at a constant pre-event level during the rainfall event as surface runoff reaching the hillslope outlet during rainfall did not contain any pesticide (i.e. it originated from the lower hillslope; see P8813-L22). Contaminated surface runoff arrived at the hillslope outlet later, which occurred, by coincidence, at the end of rainfall. It caused the rapid change (drop) of the isotope ratios to the source values, because the short travel time of the pesticide in surface runoff did not allow for degradation-induced isotope fractionation, and transport via surface runoff dominated the overall pesticide fluxes to the stream at that time. Hence, the isotope ratios decreased to the values of non-degraded pesticide (i.e. to the source values). This was explained in Section 4.1.3. and will be further clarified in the revised manuscript.

8. P8817-L14: Describe the authors' perspective with respect to preferential flow representation of the applied model either implicitly represented or excluded from the simulation. If it is excluded, it needs to describe the effects of preferential flow on the obtained conclusions.

Reply:

While we agree that preferential flow pathways are important, we did not explicitly include them in the simulations because it would make the simulations more complex and the results more difficult to interpret. Other 'virtual experiments' using physically-based (Richards-equation based) models have excluded preferential flow for the same reasons (e.g. Hopp and McDonnell, 2009; Mirus et al., 2011; Mirus and Loague, 2013; Hopp and McDonnell, 2011; James et al., 2010).

We agree that it would be useful to discuss the expected effects of preferential flow on the simulated results and will therefore include this in the revised version of the manuscript. We anticipate that vertical preferential flow leads to a faster transition of water through the soil layers, and thus decreases the extent of degradation in the soil layers due to a shorter residence time of water in these layers. Overall, this will lead to a faster transport of water through the hillslope and therefore less degradation and thus less isotope fractionation. This will increase pesticide concentrations and decrease the isotope ratios at the hillslope outlet. We also expect that the incorporation of vertical preferential flow into the simulation would

result in a lower contribution of the aerobic reaction pathway to overall degradation, and a more pronounced decrease in $\delta^{13}C$- than in $\delta^{2}H$-values, as carbon isotope fractionation is stronger in the topsoil than in the underlying layers and hydrogen isotope fractionation is stronger in the subsoil and (always saturated) bedrock. Nonetheless, the residence time of water in the unsaturated zone is already relatively short compared to the total travel time to the hillslope outlet when preferential flow pathways are not included. This suggests that the overall impact of vertical preferential flow pathways on concentrations and isotope ratios at the hillslope outlet may be secondary.

Lateral preferential flow in the soil layers will decrease flow through the bedrock, and thus result in a faster subsurface flow response to rainfall. This would, similar to vertical preferential flow, lead to less degradation and isotopic enrichment. However, the effect of lateral preferential flow pathways on the relative contribution of aerobic and anaerobic degradation to overall degradation, and thus on carbon and hydrogen isotope ratios at the hillslope outlet, depends on their spatial distribution in the soil.

Whereas the influence of preferential flow on concentrations and isotope fractionation might be small, it may affect the accuracy of the CSIA method, as it would cause enhanced mixing between recently applied and partially degraded pesticide in the soil matrix. This might result in a stronger attenuation of apparent isotopic enrichment, and thus amplify the underestimation of degradation by the Rayleigh equation approach.

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