Review of egusphere-2025-2309 –How combining multi-scale monitoring and compound-specific isotope analysis helps to evaluate degradation of the herbicide S-metolachlor in agro-ecosystems?

The authors present an analysis of multi-scale monitoring in combination with CSIA to assess source apportionment and degradation of the herbicide S-metolachlor in a mesoscale agricultural catchment in France. They calculate that around 98% of S-metolachlor has been degraded over the 5-month growing season based on both their mass balance approach and CSIA. However, CSIA did not give a clear result regarding source apportionment between S-metholachlor from WWTPs and diffuse sources, respectively. The authors show that their CSIA methods can be a time and cost-efficient, yet reliable way to estimate pesticide degradation compared to a mass-balance approach requiring high-frequency measurements at different scales within a catchment.

General and specific comments

The study fits the scope of HESS. It makes a valuable contribution to the field of water quality and shows ways forward in catchment-scale monitoring. It is one of the first studies analysing the use of CSIA for assessing both sources and degradation of a pesticide. The authors present a substantial number of different methods and extensive monitoring data. Overall, the work is clear and described well in the paper. Thank you for the interesting read! See below for some specific comments on the text.

- The title: if you put it as a question, please add “does” or “can” for proper English grammar.
- Lines 76—77: These studies did not use isotope mixing models, at least if you think of the typical use of this term in literature. I'd prefer calling this isotope-fractionation reactive transport modelling, or reactive transport modelling including isotope fractionation or alike.
- Aim (i) of the study: “evaluate the potential of CSIA data collected along the river network as a proxy for evaluating upstream topsoil degradation of S-metolachlor”. Only later in the text it becomes clear to me why you are not looking at CSIA in the topsoil directly, but rather use the in-stream isotope data as a proxy. The reader will only find out in the methods that the latter has not been the original aim, but is a result of the strong matrix effects in the analysis. I would leave this aim more open, as reading this immediately raised questions regarding why you would not go for the isotope data from the topsoil directly. So something along the lines of CSIA data collected at different locations to evaluate topsoil and river degradation of S-metolachlor.
- Figure 1: In this figure, A3 is not the outlet of the catchment. It is obvious that there will be little S-metolachlor added to the stream in the last bit, but I am wondering nonetheless why A3 does not coincide with the actual outlet of the catchment shown here.
- Line 141: could you mention to what extent these three transformation products cover all possible degradation pathways for S-metolachlor? This might be interesting in the comparison of mass balances via CSIA, transformation products, and Eq. 6.
- Lines 161-163: could you mention here what the range of timeframes covered by one composite sample is (roughly)? We can derive this from the data presented later, but it would be good to read about this here already.
- Equation 3: why do you use instantaneous and not average water discharges in period i, similar to what is done for the concentrations?

- Lines 286-287: “2019 for the same month was the five time drier and three times warmer,…”. I do not understand – how did you determine this? What does three times warmer mean to you, for example?
- Lines 327-329: could you explain in more detail why the seasonal ESA to OXA ratio of 3.1”further supports the predominance of subsurface flow in the hydrological functioning of the Souffel catchment”? This is not clear to me.
- Lines 329-331: please correct this sentence.
- Figure 2:
    - Could you add the rainfall in panel (a) also on the right side?
    - What do the colours in d represent?
    - I think in general, the legend could be a bit more clear. It took me some time to understand what I am seeing here. Maybe better to have a small inset in each panel so we know right away what we are looking at?
- Lines 409-410: Could the authors briefly explain how they come to this finding? I assume it is because of the high export combined with low-intensity rainfall, but it would be good to explicitly mention this (briefly) here.
- Lines 443-444: This should be made more clear in the methods (Section 2.5.2). Otherwise it is not clear why d13C values need to be predicted for the topsoil, based on a model that quantifies biodegradation in the topsoil already.
- Lines 267-269: Why could be the main reason(s) that this is consistently lower than the 98% mass balance and CSIA-based estimates? Not all TPs accounted for? Or further breakdown (although they are thought to be persistent)? Not enough measurements?
- Figure 4: Why is there this difference in the predicted soil isotope values between A1 and A2? Metolachlor has not been applied in A1 before June? I am not sure whether this has been mentioned before.
- Lines 502-503: How are these numbers related to line 384 ("ranging from 0 to 100% of the observed mass load at the catchment outlet")?
- Lines 551-553: I am not sure I understand. Larger catchments with longer in-stream transit times or systems with highly reactive hyporheic zones would lead to more degradation and associated isotope fractionation. Would this not support the applicability of C-CSIA?

Supplement

- S1.5.2 Estimation of photodegradation in the Souffel river: I cannot follow the calculations easily, as some equations are not fully explained. What is I0? Is there a word missing in “Then, the depth of the photic zone in the Souffel River and the photic zone is defined as follows:”? What are absorbance and intensity used for? They do not reappear in (S4).
- S1.6 Variation of S-metolachlor concentrations in topsoil: Please clarify why which parameter is estimated. If I understand correctly, the S-metolachlor degradation is calculated to calculate isotope fractionation with (S9). That’s why you get a straight line in Fig. S1. Why don’t you use measured S-metolachlor concentrations in (S9)? Because of the limited number of samples?
- S1.9:
    - good to emphasize here (and also in the main text) that this is about in-stream transit times, not transit times through the subsurface
    - line 195: are you referring to Eq. (6)?

- Caption of Figure S3: “Colours get increasingly red later in the season,”. This is not clear to me – the colour scale has been chosen this way.
- Table S12: Define that column TPS is indeed transformation products.