

Interactive comment on “Modelling biocide and herbicide concentrations in catchments of the Rhine basin” by Andreas Moser et al.

Anonymous Referee #1

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General comments

Developing and testing the limits of a parsimonious model of micropollutants transport from catchment to river at various scales is relevant both for stakeholders and for the scientific community to address the degree of simplification required/able to capture the micropollutants patterns. The key concept of this approach (link the load of micropollutants to the discharge and/or the rain) is not new but the approach to validate at small scale with European databases the load then upscaling the approach at larger scale reaching the main part of the Rhine catchment is new. The spatial pre-processing of existing European data to improve the information for the subcatchment can also be underlined. The state of the art on the different components covered by the work is well presented with relevant references. The model development, main hy-

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potheses and calibration/validation/transposition steps are clearly presented. However, a scheme summarizing spatial and temporal discretization with associated processes across scale (calibration then validation catchments and full Rhine scale) is clearly missing in the main text. A very simple scheme (focused on subcatchment delineation) is presented in SI but can't play this summary goal.

The results are clearer for herbicides than for biocides. The reader discovered different hypotheses that reduce progressively the extent of the biocides loads and transport modelling at larger scale. I wonder if a focus on herbicides only, should not be better and stronger. I detailed below specific comments and corrections

P1 L30: check homogeneity (S-metolachlor and metolachlor are used in the text)

P2 L28: Missing dot at the end of a sentence “2013) One”

P3 L13-14: original aspect of this work +add that it's a daily or hourly time step

P3 L23: all the basin? just after it's mentioned that only the basin upstream of the station Emmerich am Rhein is covered by this study, precise

P4 L6: general comment: An overall scheme of the model should be relevant to improve understanding of the spatial links between objects, considered processes and links between AWAQa and AQUASIM (what's happened in the sub-catchment scale and then in the river, degradation, . . .) The appendix A2 is one aspect of the discussion but it not covers the processes.

P5 L8 and L9: in the equations 2 and 3 Kdeg has to be used instead of Kd to be homogeneous with the rest of the paper

P5 L11: not clear at this stage how the available fraction is link to rainfall

P5 L21: interesting but why 1/14? Expert panel, reasonable fractionation? Sensitivity of the model to this fraction?

Does it means that 14 days are required to consider 100% of application? Can this

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hypothesis impact peak modelling due to dilution of input signal?

P6 L23: no rainfall dependency?

P6 L34-35: not clear for me, does it mean that any transformation is considered in the river routing model?

P7 L8: should be interesting to mention in the abstract and in the introduction...

P7 L11-12: is it possible to mention an unpublished paper in HESS?

P7 L17: I think it is the table S2 (in the appendix A4) and not the table S4.

P7 L20: not easy to understand even if it's describe below... a scheme should be relevant to improve understanding.

P7 L25: what % considered considering strahler order less than five?

P7 27: Explain briefly the area ratio method to help the reader at this stage

P7 31: Same comment, explain briefly the map-correlation method to help the reader at this stage

P8 L16-18: not clear for me! -6.5° per km (in z?)

P8 L21: Expected evolution if 2000 is the reference? Impact of rotation of crops (spatial difference between years)?

P9 L17: Diuron was also used in vineyard still 2008 in France. Is it the same in Germany and Switzerland? Expected impact of missing the agricultural uses in this analysis?

P9 L24-29: not clear for me: range of available data? 2008-2012 so 5 years for all the study site excepted for Lorraine? Right? You have to mention the Appendix A5 (figure S3 and S4) to visualize the spatial variability. The reader discovers in the caption of the figure S4 (appendix A5) that the Diuron pattern was just a copy of the carbendazim map. Is it correct? I do not find any discussion on that in the text.

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P9 L34: does any other sources can (even partially) validate this hypothesis?

P10 L22: "application season" Perhaps explain why... to take into account the fact that during application period difference can occur between real applications (unknown) and modelled application (splitted with 1/14 depending of weather windows).

P10 L22: "error-scaling function" try to better introduce this function, why and how, it's not very clear for the reader.

P10 L30: the text and the equation 13 are not supported by any reference

P11 L10: studies are mentioned to assess the prior distribution of $\tilde{\mu}$, which one? Wittmer et al (2010) mentioned in L26?

P11 L28: I suggest to mention the table S4 and S5 (Appendix A8) after "of the priors for $\tilde{\mu}$ and $\tilde{\sigma}$ "

P12 L28: "larger rivers" (Rhine, Aare;" I suggest to mention all main tributaries or use "such as"

P12 L31: The fact that biocide was finally not modelled at the Rhine scale (due to lack of biocides export coefficient in France and Germany) should be precise clearly in the abstract and introduction by differencing the two scales (calibration/validation in the Switzerland scale of herbicides and biocides, and only extrapolation of herbicides at the Rhine scale).

P13 L20: I suggest to link here the table S6 and S7 no called in the main text.

P13 L27-28: this sentence needs to be followed by some hypotheses for this bi-modal pattern, especially if physical explanations can help to improve the model for biocides release.

P13 L 32: I can't see how two clusters can be derived from the figure 4. Could you clarify this point?

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P13 L39: because the GRI is probably less known compared to the NSE criteria, it could be relevant to provide quality thresholds to consider poor, acceptable, good and very good capabilities of the model.

P14 L3: could you provide in SI Table S9 the unit of RRMSE (%)? Its not clear in SI if it's really in % (very low value if in %). The table S9 is not used to support quality of the model in the main text.

P14 L2: what could be the interest to reproduce the cumulative concentration (observed and simulated sorted) if the dynamic (timing) is not correctly capture?

P14 L16: how the reader can derive this information? Which tables or figures supports this statement?

P14 L24-25: If I well understand, you observed more dissipation than prior estimation. Does it mean that missing dissipation pathways (leaching to deeper groundwater) could be counterbalance in the model by more sorption (model structure error)?

P15 L2-3: do you mean cumulative distribution or chemogram (dynamic evolution of concentration)?

P15 L4: Could you provide hypothesis or compare this behaviour with other similar approach (calibration in small scale and validation at large range of scale)?

P15 L15: do you have hypothesis for this over-estimation? Could this overestimation in the validation sites be due to an overestimation of the diuron release in the calibration sites owing to agricultural use neglecting?

P15 L26: Could you provide figures or tables (in the main text or SI) to help the reader to understand the differences between the 2 routing methods?

Perhaps it could be relevant to sort the results depending of the catchment area to underline the threshold from which the full routing model improve the concentration prediction.

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P15 L39-40: you mentioned previously that you did not simulate the biocide due to a lack of the input database for Germany and France.

P15 L2: missing figure number! Figure 8, I guess

P15 L4: why applications during fall were not considered? Isoproturon is usually applied in October on winter wheat

P16 L16: Probably not at the larger scale! It's probably a strong hypothesis for which scenarios with and without river processes (degradation and sorption) could be tested with available dataset (DT50 water...)

P16 L15: same comment as previously for unpublished paper (possible in HEES?)

P22 L6: Figure 1 : I suggest a modification of the titre: the study area covered the Rhine river upstream the Emmerich discharge gauge (red circle)

I suggest also to delineate more clearly the Rhine basin with bold line

P24 L3: Figure 3: I suggest to express concentration in $\mu\text{g/L}$ to be able to better link them to EU drinkable threshold ($0.1 \mu\text{g/L}$)

I also suggest to add application dates to see interplay between application and rainfall calendars

For biocides, P/Q is not easily understandable, is it a ratio? The sentence (Line 26-27, page 13) that biocide concentration follows rainfall patterns can not easily be derived from this figure), especially at the end because legend hides the rainfall/discharge dynamic (probably high)

Finally, on the left you have to remove one ng/L (two times in the figure)

P16 L25: I agree for herbicides, but it could be remembered that seasonal peaks of biocides were not well represented. This weakness seems not to be discussed in the paper. Which types of processes can explain a seasonal variation of biocides exports

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from roofs and walls?

P16 L27: the authors argue that iWaQa can help to identify potential hotspots in river network. I'm not convince according the way that herbicides loads is calculated. Could the authors more clearly underline the strengths and weaknesses of this model to identify hotspot according conceptual structure and processes taken into account? If I well understand, the inputs are derived from administrative data and can not explain extreme applications and associated peak of concentration at small scale.

P16 L35: missing number of figure Table 5 and Figure ...?

P17 L5: modify the way that the reference is called. I suggest "as discussed in Honti et al. (2017)

P17 L21 to27: I suggest to order the different elements (1) too high herbicide. . . , (2) seasonal biocide . . . and (3) the lack of an isoproturon application. . . In the following sentences, I only see discussion on the points 3 and 2 and not for the point 1. Reorganize this section.

P17 L29: "This agrees with the findings from the error models", I suggest to link here the tables in SI providing range of error.

P17 L37: missing number for the figure mentioned

P25 Figure 4: even if the calculation is remembered in the caption, it could be relevant to add in the different box of this figure, arrows and captions underlining that if residual > 0 the model underestimated concentration and the opposite if < 0 .

I also suggest to move this figure in the SI.

P26 L2: I suggest to explain that the catchments are sorted by size (with an arrow and associated surface to better support the sentence (Line 4-5, page 15)

P28 Figure 7: move to SI

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P30 Figure 9: move to SI

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