

Interactive comment on “Sorption and transformation of the reactive tracers resazurin and resorufin in natural river sediments” by D. Lemke et al.

D. Lemke et al.

olaf.cirpka@uni-tuebingen.de

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Response to common Reviewer Comments

We would like to thank all reviewers for their comprehensive and constructive comments on our paper. The major criticism raised by both reviewers is related to the extent of the dataset used in the analysis and interpretation. We agree that the number of column and batch experiments may not be sufficient to determine the dependence of the sorption parameters of resazurin (Raz) and resorufin (Rru) on pH and sediment properties with predictive power. However, that was not the main goal of our study

C7511

and hence any instances that induced this impression by the reader were not intended. Rather, the study aimed at identifying: (1) the key processes controlling sorption of the reactive tracers in streambed sediments, (2) the level of model complexity required to adequately reproduce the measured BTCs, and (3) the experimental setup best suited for determination of the sorption and reaction parameters of Raz and Rru. Accordingly, in the original manuscript the objectives were listed as “(1) assessing the relative importance of kinetic and equilibrium sorption processes of Raz and Rru ..., and (2) assessing whether or not linear sorption models are adequate to describe sorption characteristics of Raz and Rru ...”. The experimental setup described in the paper was chosen in accordance with these objectives and was in our view suitable both in terms of the methodology, as well as the number of experiments to obtain reasonable and significant answers to the posed research questions. The reasoning behind performing the experiments for two different pH values (which represent the typical range of many bicarbonate-buffered natural rivers) and using sediments from two contrasting streams was simply to increase the representativeness of the experiments by not limiting the analysis to a single specific case. But we did not intend to investigate possible interrelations. We believe that the identification of the key processes using suitable lab experiments as provided by this study is a first important step for a better understanding of the sorption properties of the reactive tracers. This is also of major importance for the interpretation of field tracer tests where the respective sorption properties have to be accounted for in the choice of adequate modeling approaches. Therefore, we firmly disagree with the reviewers that the results presented in the manuscript are not useful or do not constitute a significant step forward. We also believe that due to a high natural intra-, as well as inter-stream variability of the sorption properties, a slightly larger number of experiments would not have resulted in a more profound understanding of the sorption properties in general, let alone their prediction based on sediment characteristics. Instead, we strongly suggest adapting the experiments presented in this paper for the sites where readers have performed or are planning field tracer tests of their own. In such a way, the site-specific aspects might be accounted for more

C7512

efficiently and detailed. In addition, more universal information on the variability of the sorption parameters will be provided from a larger range of applications as requested by both reviewers. Such a comprehensive experimental campaign, however, constitutes a tremendous effort (both in terms of finances and time requirements) which goes well beyond the intent and scope of this paper.

In the revised manuscript, we will differentiate the aims of the study more precisely and present the results more clearly by distinguishing between interpretations directly related to the objectives and the more preliminary findings on the dependencies of the sorption properties. We will also add statements on the limitations of the chosen methods and further working steps in the abstract, introduction and conclusion parts of the paper.

Response to Reviewer 2

1. **Comment:** *The overarching aim of the manuscript is to better understand and quantify sorption of Raz-Rru in tracer experiments. The manuscript describes laboratory experiments and aims at "assessing the relative importance of kinetic and equilibrium sorption of Raz-Rru under various physicochemical conditions". And secondly, it aims to "assess whether Raz-Rru can be described under normal field tracer concentration ranges with linear models". The manuscript details on several batch and 4 column experiments (2 sediments and 2 pH). The topic is interesting for the hydrological community and it can contribute to improve the use of Raz-Rru as reactive tracer. The manuscript is very well written and structured. Overall I found the results interesting and trustworthy and the methods are described in a manner the tests can be reproduced.*

Response: The authors thank the reviewer for the positive comments.

2. **Comment:** *Too limited amount of experiments and data. In my opinion the manuscript is promising, important but not finished. How to extrapolate from 2*

C7513

sediments with 2 pH conditions? To make these results really useful for the community, I would like to see a larger range of experiments. I do appreciate the time and energy involved in doing robust lab experiments but at the end of the day, these results are most appreciated by the community if they do not leave too many open questions.

Response: Although the interpretation is based on a dataset from 4 column and 72 batches, we do not agree with the reviewer that the presented manuscript is not finished. This is mainly because the objectives of the paper are quite different from those commented on by the reviewer. For our detailed reasoning, please see our response to the common comments given above. We agree that further work is necessary to investigate the variability of the associated sorption parameters. In the revised manuscript, we will try to emphasize this point by adding statements in the abstract, introduction and conclusions.

3. **Comment:** *I would like to see a writing style that is more specified. Please refrain from using "a series of lab column experiments", "a range of pH", etc. I would rather write: 6 batch experiments, with 2 sediments with different physicochemical characteristics, 2 pH conditions (or pH of 7 and 9). As an example. L5 of abstract could read: "We present 2 lab column and 6 batch experiments on Rza and Rru transport, sorption and transformation within 2 sediments with different physicochemical properties under neutral (pH=7) and alkaline (pH=9) conditions.". The same in the introduction (P12190, L10 – L16). By using words like a series, a range, various, etc., the authors hint on more data rich analysis than the ms is really based on.*

Response: We agree and will change the manuscript accordingly.

4. **Comment:** *P12204, L1. Raz-RRu behaves non-conservative. This implies we need batch and column experiments adjacent to field experiments to be able to model and interpret field experiments in order not to have "erroneous charac-*

C7514

terization of hyporheic exchange". - The column experiments have a duration of 15 minutes. Is this also the time scale of field hyporheic exchange? Would longer duration lab column experiments give different results? - Is the 2.5 cm radius of the column not allowing for too much preferential flow to the side walls of the cylinder? Do we get same results if upscaled to 10 cm radius? - Along the same line, would a longer cylinder / lower flow velocity to increase residence time influence the results?

Response: The column experiments take considerably longer than 15 minutes. In fact, the total time for these experiments was determined by the time until the system reached steady-state conditions (indicated by the plateau conditions) plus the time needed until tracer concentrations at the outlet fell under the limit of quantitation (i.e., the time until most of the tracers were desorbed from the sediment). Prolonging the experimental time would only prolong the time when the system is at steady-state. At steady-state, only information about the reaction mechanisms of the tracers can be obtained, but none regarding their sorption characteristics, because in this case the respective terms drop out of the model equations. Since plateau conditions were clearly reached in all experiments, longer experiment times would not have led to other or even more accurate results. We agree that preferential flows, especially at the walls of the columns, can hardly be entirely excluded. However, our columns were specifically built for this purpose and the whole setup met official national standards (e.g., LANUV, 2000). Thus, we are confident that if these preferential flows existed, they would have had a negligible effect on the experimental results. Consequently, the use of columns with other dimensions would not have led to different or more accurate results. The general findings will also be valid for different flow velocities, although changing the flow velocity would result in different contributions of kinetic sorption (the faster the flow through the columns, the lower the contribution of equilibrium sorption) and in the associated parameter values. The flow velocity chosen in the presented column experiments with a mean travel time of the

C7515

tracers through the column of 15 minutes corresponds well with mean hyporheic travel times derived from field tracer tests using Raz reported in literature.

5. **Comment:** P12204, L15. "However, we could not identify clear relations of physicochemical properties ... with sorption characteristics." You only have two sediments, how would this result in reliable relationships between physicochemical conditions and Raz-Rru behaviour? More, different sediments are needed.

Response: We agree (see also our response to the common comments given above). However, we think it is still worth noticing that in our cases the sorption and decay characteristics did not correlate with the organic carbon content as it has been shown in numerous previous studies. We thus suggest to rephrase the sentence to: "However, we could not identify clear relations of the organic carbon content of the sediments with the sorption and decay characteristics of Raz and Rru."

6. **Comment:** P12204, L20: OK not to study the relations between reaction rate and pH for Raz to Rru, as it is about interaction with sediments and OM you are interested in. But you see pH dependence. Would it not be robust to extend the experiments with pH = 6, 8, 10 and have some information about the influence of pH on reaction rate / decay rate?

Response: Again, please see our response to the common comments given above. The question about the influence of the pH on the reaction and decay mechanisms of Raz and Rru, as it is already briefly mentioned on p.12203, line 15-28, definitely requires closer attention in the future in order to gain a better understanding of Raz and Rru as hydrological tracers. We agree that a broader range of pH conditions would be needed to solidly characterize this relation. However, tackling or even answering this question was beyond the scope of this paper. One has to bear in mind that performing the experiments at other pH values most probably will require further experimental work and/or corrections of measured

C7516

values as the fluorescence strongly depends on pH outside the pH range investigated here. The choice of the pH values of 7 and 9 was guided by the assumption that the majority of natural streams will exhibit pH values that lie within this range.

7. **Comment:** *P12204, L20: How well was the sterilization of the sediments? Did you test different intensities or duration of sterilization?*

Response: The sterilization of the sediments was conducted by an external company because highly-specialized instruments are needed to perform this γ -radiation treatment. Testing different radiation intensities would have been very cost-intensive, because fixed minimum prices become due with every individual process, regardless of the number of samples. Thus, we did not test different intensities of radiation and chose the dose of 10 kGy because this intensity has been recommended by previous studies (see p.12191, line 26).

8. **Comment:** *P12205, L 7. "we highly advice independent column studies ..." What I was probably looking for, based on a wider palette of experiments, was some kind of recipe for 'standardized' batch and lab experiments to run alongside a tracer field experiment for 'optimal' interpretation. Although maybe a step too far at this stage, it seems to me it would be beneficial if the authors summarize their experience in specific column / batch experiment 'guidelines'.*

Response: We agree with the reviewer that this is a good point to further improve the manuscript. Although we believe that the manuscript contains most information that is necessary to reproduce the described batch and column experiments, we will add a section highlighting the important requirements to run lab experiments alongside a field tracer experiment for 'optimal' interpretation. Such a guideline may also be most beneficial for the necessary assessment of the influence of pH and sediment properties on the reactive transport parameters, as outlined in the response to the common reviewer comments.

9. **Comment:** *It could be beneficial to add a flow direction arrow in the column (Fig C7517*

1) as the flow direction arrow in the resolution reservoir in the right upper part is not that clear.

Response: Done.

Reference LANUV, (2000) Empfehlung für die Durchführung und Auswertung von Säulenversuchen gemäß Bundes Bodenschutz- und Altlastenverordnung (BBodSchV), Merkblatt Nr. 20, Essen, Germany.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 10, 12187, 2013.