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

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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 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 intent 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 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 1

1. **Comment**: *The manuscript "Sorption and transformation of the reactive tracers resazurin and resorufin in natural river sediments" is about the popular tracers resazurin and resofurin. Although they are increasingly used a lot of basic questions about their environmental fate and characteristics are still unclear. Thus, interpretation of resazurin and resorufin tracer tests is difficult and based on speculations and inappropriate simplifications. Having said this, the present manuscript could be a valuable contribution to clarify some basics such as sorption behavior in aquatic sediments.*

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

2. **Comment**: *The dataset on which the manuscript and all interpretations are based is extremely small (1 experiment with 4 columns and 1 experiment with 72 batches). Experiments, manuscript, conceptual model, writing and everything else are really good. But with such an insufficient dataset Lemke and coworkers cannot make the required step forward. With only two different pH values, the interpretation of pH effects remains pure speculation. With only two sediment types*

it is not plausible to draw conclusions about the impact of the sediment type on the sorption characteristics. I suppose that the experiments could easily and without much effort be repeated with other sediments and other pH values. According to the material and methods section this would require one or two weeks with additional experiments. If the results confirm the previous results no rewriting of the manuscript would be necessary. Simply adding those data to the manuscript will significantly increase the worth of the interpretations and make the manuscript a relevant contribution to the scientific discussion. However, if the experiments won't confirm the previous interpretation a rewriting of the manuscript will need some additional effort but with that an incorrect paper would have been avoided. I know that scientists are forced to publish their results in smaller and smaller pieces but with the present manuscript the border of usefulness is not reached at all.

Response: Although the interpretation is based on a dataset from "only" 4 column and 72 batches, we do not agree with the reviewer that the results presented in the manuscript are not useful or do not constitute a step forward. 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 above. Furthermore, we would like to point out that the time frame for additional experiments, as estimated by the reviewer, is unrealistically low and will more likely be in the range of several months, if the time for setup, preparation, tests, and mathematical modelling is included. Additionally, performing the experiments at other pH values most probably will require further experimental work and/or corrections of measured values as the fluorescence strongly depends on pH outside the pH range investigated here. One might even question whether experiments with the chosen fluorescent tracers should be performed at all at pH 6 or lower because: (i) fluorescence of all three compounds is quenched, (ii) fluorescein sorbs so that it cannot be considered an ideal tracer anymore, and (iii) such pH conditions are uncommon in natural streams.

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Discussion Paper

We agree that further work would be useful to investigate the variability of the associated sorption parameters with pH or relevant sediment properties such as grain size, pore geometry, or organic matter content. However, this is beyond the scope of this paper. A quite likely outcome could be that sorption parameters need to be identified at each site of investigation specifically. In the revised manuscript, we will try to emphasize the objectives of the study and the obtained results by adding statements in the abstract, introduction and conclusion.

3. **Comment**: *As far as I understand the biogeochemistry of resazurin the redox potential is an important variable. It might have been good to measure oxygen or redox at the beginning and the end of the columns and at the start and end of the batch experiments.*

   Response: In the column experiments, we indeed measured dissolved oxygen concentrations in the reservoir solutions and also logged this parameter at the outlet of the columns. From this data we hoped to confirm or refine the findings from previously published studies where the reaction of Raz to Rru was suggested as a proxy of metabolic activity. Unfortunately, measurements of oxygen at the column inflows were incomplete because of technical reasons. As a consequence, the oxygen concentrations at the outlet were difficult to interpret and, therefore, we did not include these data in the manuscript. We agree with the reviewer that oxygen is an important variable. Therefore, after careful reevaluation of the measured oxygen concentrations, we may use the data in the revised manuscript to relate the reaction of Raz to Rru to the oxygen consumption during the column experiments, at least on a qualitative level. For the batch experiments, oxygen concentrations were not measured because the γ-treatment of all batch samples resulted in close to sterile sediments, and we did not expect any changes of oxygen concentrations and/or redox conditions in the batch reactors as a result of biogeochemical processes. Performing a mass balance of oxygen in batch reactors with head space is of course a challenge by itself, as

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the expected turnover is not very large.

4. **Comment**: *You mention that the sorption of resazurin onto natural, metabolic active sediments is difficult to determine due to the rapid transformation of resazurin to resorufin in metabolic active sediments. Having said that, is it really necessary to know the desorption characteristics of resazurin? Or is most of the sorbed resazurin transformed to resorufin. Then desorption characteristics of resofurin would be sufficient.*

   Response: We agree that desorption of Raz would be negligible if this process was considerably slower compared to the reaction of Raz to Rru. This point has also been made by Argerich et al. (2011), where the same explanation was given. However, in the analysis of kinetic sorption in our experiments we found that typical kinetic timescales are on the order of 15 minutes (p.12204, line 10). When comparing this to the reaction rates $\lambda12$ (Tab. 2) we find that they are roughly in the same order of magnitude, so that desorption of Raz may actually be relevant and should not be neglected in this set of experiments. We will address this in the revised manuscript.

5. **Comment**: *P12192 L6: I would assume that discarding the finest fraction (< 0.08 mm) causes severe artifacts since that small fraction has probably a large highly reactive surface area.*

   Response: We agree that the small fractions may have an impact on reaction rates and also sorption mechanisms. However, we had at least two reasons for such pre-treatment of the sediments before using them in the experiments: (1) as explained on p.12191, line 5-10, the fractions < 0.08 mm would considerably influence the fluorescence measurements by decreasing the quality of the measurements of Raz and Rru so that large parts of the BTCs shown in Fig. 3 would fall below the limit of quantitation; (2) not sieving the samples would have resulted in an incomparability of the different column experiments, because we would not have known the exact grain size distribution in the individual columns. Thus, we accept that the loss of finest fraction might introduce a bias to the reaction and/or sorption behavior derived from the experiments. However, we believe that without sieving the sediments we would not have achieved the excellent data quality that is vital for the presented analysis of the dominant sorption and transformation mechanisms. In the revised manuscript, we will add statements on the possible bias to the methods as well as to the results sections.

6. **Comment**: *P12197L8: Raz or Rru?*

   Response: σ_{Rru} is 2.23 mol m^{-3} and σ_{Raz} is 0.12 mol m^{-3}, typo will be corrected.

7. **Comment**: *P12198L23: ratios*

   Response: Will be corrected in the revised manuscript.

8. **Comment**: *P12199L27: The sediment was dried prior to the experiments? Why is that not mentioned in the material and methods section. There you note that experiments were conducted 5 h after sampling. Please explain this discrepancy.*

   Response: On p.12191, line 9 it should say ”...collection of the sediment and the start of the column experiments...” and on p. 12191, line 21 ”...water and 35 g sediment that has previously been dried in order to be able to adjust an exact solid-to-liquid ratio in the batch reactors.” This will be changed in the revised manuscript.

9. **Comment**: *P12200L8: I do not really agree that a pH change of 0.8 is fairly small. That is nearly one order of magnitude. It might have been better to use higher buffer concentrations in the experiments. However, I would not argue to repeat the experiments.*

   Response: We agree that this may be misleading. In the revised manuscript, the statement on p.12200 ”these alterations are fairly small” will be changed. It

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is indeed unfortunate that the buffer capacity of the used sediments was that high. However, we believe that the pH difference between the samples that were initially adjusted to pH 9 and pH 7 are still big enough that they represent distinct settings. This noticeable alteration of pH has also not been observed in the column experiments, so that the changes in pH are most likely caused by the comparably long experimental times of the batch experiments.

10. **Comment**: *P12200L20: I think all Raz fits are bad (see insets) and not the one mentioned here in the manuscript! I wonder whether a much more simple fitting would not result in similar poor fittings and cannot see the advantage of the highly sophisticated fitting applied by you.*

    Response: The statement on p.12200, line 20 is based on the calculated RMSE value between simulated and measured curves, which indeed is significantly higher for Raz in the experiment with the Steinlach sediment at pH 7, as compared to the other column experiments. Using the RMSE allows to evaluate the quality of a simulation, but it has a subjective judgment to a certain extent, as the performance at high concentrations dominates the RMSE value. This is probably the reason for the discrepancy of our statement in the manuscript, which is related to the RMSE and therefore the performance at high concentrations, and the reviewers comment, which as we understand it, is related to the deviations between simulations and measured Raz curves in the tails of the BTCs.

    We agree, that in this part the simulated Raz concentrations show deviations from the measured curves (a potential reason is given below). However, we do not agree that ”all Raz fits are bad” (especially when looking at the Goldersbach pH 9 results), because one has to keep in mind that the deviations as well as the absolute concentrations are in general very small and the former only become visible when using a log scale shown in the insets. To make these points more clear, we will reformulate the corresponding section in the revised manuscript. Concerning the use (or not use) of simpler model approaches, we know from previous studies (Lemke et al. 2013; Liao et al. 2013; and unpublished data) that applying simpler models (e.g., one that neglects kinetic sorption) will most likely result in worse agreement with measured data, particularly at the beginning of the plateau phase at relatively high concentrations. The importance of kinetic effects is most likely also indicated by the deviations between simulated and measured tracer tails in Fig. 3, producing extended tailings of the BTCs. Accounting for these long-term processes might be possible by including intra-particle diffusion in the modeling approach. However, this would result in a further increase in model complexity and in the number of parameters. Overall, we have sufficient evidence that all sorption and reaction/decay mechanisms that our model accounts for do apply when Raz and Rru come into contact with natural sediments. These issues will also be discussed in more detail in the revised manuscript.

11. **Comment**: *P12201L12: charged, too.*

    Response: Will be corrected in the revised manuscript.

12. **Comment**: *Fig.2: According to the description of the experiment (mm) there should be six different concentrations in each batch experiment. However, the figure shows only results of 4 or 5 different concentrations. Furthermore, you have conducted three replicates. It might be a good idea to present the results of the three replicates.*

    Response: When determining the sorption isotherms there were sporadic outliers that were removed from the figure. We tried adding all replicates to the figure and also to use error bars instead, but actually in both cases the figure becomes confusing. The information regarding the replicates are available in the supplementary Excel-file. However, we agree that it would be worth to point that out in the manuscript and will add on p.12198, line 15: ”...equilibration. The complete data set of all replicates is available in the supplementary information. The dashed...”.

13. **Comment**: *Fig. 3: Correct the spelling of Resazurin. For some insets the modelled curves do not cover the whole length of the inset? Why are the modelled data missing?*

    Response: Spelling will be corrected. The simulated data has been cut-off as soon as the concentrations fall below the limits of quantification of the respective fluorescence tracers. A corresponding statement will be added to the figure caption in the revised manuscript. To avoid confusion, we will also cut-off the measured data accordingly.

References Argerich, A., et al. (2011). Quantification of metabolically active transient storage (MATS) in two reaches with contrasting transient storage and ecosystem respiration. J. Geophys. Res. 116(G3), 2005-2012.

Lemke, D., et al. (2013). Concurrent conservative and reactive tracer tests in a stream undergoing hyporheic exchange. Water Resour. Res. 49(5), 3024-3037.

Liao, Z., et al. (2013). Modeling and inverting reactive stream tracers undergoing twoâĂŘsite sorption and decay in the hyporheic zone. Water Resour. Res. 49(6), 3406-3422.

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