

Interactive comment on “Controls of fluorescent tracer retention by soils and sediments” by Marcus Bork et al.

Marcus Bork et al.

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We thank the reviewer for spending his time to review our manuscript. We appreciate his detailed suggestions that definitely helped us to improve our manuscript. Below, we described point by point how we will address the comments (in italics) in the revised paper. Additional and improved tables and figures can be found in the supplement to this responses.

General comments

Comment 1: *Fluorescent dyes are highly important tracers for many different applications because of their ease of use, highly sensitive and selective detection methods,*

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benign environmental and toxicological behaviour, and a large dataset of specific properties. Applications range from simple water transport studies, the visualization of flow patterns and accumulation sites to contaminant transport studies, where the tracers are used as a proxy for pollutants with similar transport behaviour. This submission aims to extend the characterisation of the sorption behaviour of two tracers, Na-fluorescein and sulforhodamine B, to some soil components. The sorption properties are tested as a function of the pH-value, content of organic matter, and clay content. Unfortunately, there are too many open questions with regard to the experimental setup and the data evaluation, as well as inconsistencies in text and tables.

Response 1: We are grateful for the honest comment. We will thoroughly improve the description of our experimental setup and the data evaluation and will conscientiously consider the referees remarks. We apologize for possible ambiguities and will do our best to remove inconsistencies in the manuscript.

Comment 2: *Eg. it is written, that SRB does not sorb to Clay0 (p10 l8) but a K_D of 1.3 is given in table 4.*

Response 2: The referee is right to point out that inaccuracy. At this point we were imprecise. We changed the statement on p.10,l.8 to: "SRB only slightly adsorbed to the sediment without clay addition (Clay0)".

Comment 3: *The mineralogical composition of the sediment is missing.*

Response 3: We thank the referee for this comment. In table 2 we gave the texture of the sediment (sand, silt, clay), the OC-content, the oxalate and dithionite extractable metals (Fe, Al and Mn) and the SSA. Additionally to this information, we will add information of the mineralogical composition (quartz sand with a carbonate content of 1.13%).

Comment 4: *The effect of the SSA on the sorption parameters should be included as a figure.*

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Response 4: We thank the referee for this suggestion. It will certainly improve the understanding of the influence of SSA on tracer adsorption. We will include Fig. 1 and Fig. 2 as new figures to the supplement of the manuscript.

Comment 5: *None of the results are given with quantitative prediction intervals or confidence intervals.*

Response 5: This is a very important suggestion. We will add confidence intervals for the Kd-values (see Tab. 1 in the supplement to this response which is the updated Table 4 of the original manuscript). Moreover, we will add a paragraph in the material and methods sections to specify how confidence intervals were calculated and we will insert the values at the appropriate places in the results and discussion section. Additionally, we will add standard deviations from three measurements for metal concentrations and range of two single measurements for DOC and SSA in an updated version of table 2 (see Tab. 2 in the supplement to this response which is updated Table 2 of the original manuscript). Additionally, we will add confidence intervals to figure 2 - 5 (see 3, 4, 5 and 6 in the supplement to this response).

Comment 6: *Since the experimental setup with a complex matrix leads to ambiguous results, the derived conclusions have to remain vague. This issue is intrinsic to a majority of experiments with natural sediments. One potential way to overcome this issue would be to do a multicomponent analyses of the sorption behaviour and a forward calculation of the sorption parameters based on the sorption parameters of the individual components. This way, parameters which are not easily accessible in experiments, like the effect of multilayered surfaces, show up at least semi-quantitatively.*

Response 6: We agree that this is an important point and will discuss this problem in a new paragraph in the results and discussion section. Based on relevant literature we will highlight the challenges of experiments with complex matrices (that show the net effect of naturally occurring systems) compared to multicomponent approaches. Here we see our experiments as a compromise: We did not just compare different natural

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substrates, but rather manipulated natural substrates in a controlled way by e.g. adding clay minerals or controlling pH-values.

Some specific remarks

Comment 7: *p4 l21: Our own studies did show that SRB and UR do compete for sorption places on carbonates. The reason why you might not have seen this behaviour is that the K_D values in carbonates in our studies are on the order of 0.02-0.3 for UR and 3-30 for SRB, whereas the K_D values in this study, especially for UR are higher.*

Response 7: We thank the referee for raising this important issue. We wrote at p.4,l.21 that "we assumed that the tracers did not interact in solution and did not compete for sorption places". We found this assumption feasible since we worked at a low concentration range to observe linear sorption. In this concentration range we can assume that sorption places are in excess and UR and SRB do not have to compete for sorption places. We will add this justification for the assumption in the material and methods section. Furthermore, we would like to ask the referee for a literature reference of his values because we would love to compare our results with his findings. For this comparison it would be helpful to know the exact conditions under which the referee determined the Kd-values for UR and SRB. We really think that our manuscript will benefit from this comparison. In our study, the only sample containing carbonates is the sediment. Here, the Kd-value of UR is 0.2 and that of SRB 1.3 which is, especially for UR and nearly for SRB in the range of the values cited by the referee.

Comment 8: *p4 l23: please state the $\Delta\lambda$ and the wavelength range used for the synchron scan (or did you just measure at 488 and 560 nm?).*

Response 8: We thank the referee for this important comment. We will add the missing data to the material and methods section. We used a synchron scan at a wavelength range of 250-650 nm; $\Delta\lambda$ was 25 nm and the maxima of UR was 488.01 nm and that of SRB was 560.60 nm.

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Comment 9: p4 l24: at pH 7 UR shows 80% of the fluorescence intensity (Käss, 2004) which is why usually 3 drops of KOH are added to the solution to ensure a pH above 10! This might explain, why the K_D values for UR are so high. Did you measure the pH value after addition of EDTA?

Response 9: The referee is right to point out that pH 7 is not enough to ensure 100% fluorescence intensity. Indeed, we were inaccurate at this point, as we raised the pH to 9-10 by the addition of one drop 1.5 M EDTA and controlled it by measurement of pH. Therefore, 100% fluorescence intensity was ensured during measurement of UR and SRB and K_D -values were not biased by fluorescence measurement. We will specify this in the material and methods section.

Comment 10: p5 l5: the simplification should be supported by data, not by words, as small is not defined anywhere.

Response 10: We thank the referee for this important remark. The mean of relative standard deviation of triplicates was 6.2 % +/- 4.5 %. In the new Fig. 7 the concentrations in solution of UR and SRB are shown as bar plots with the standard deviation as error bars. We will add this figure to supplement of the revised manuscript.

Comment 11: p5 l27: how was the pH measured and kept constant during shaking?

Response 11: Before shaking, the pH was measured using a pH-Meter (Metrohm, Germany) and was adjusted to the respective pH (5.5, 6.5 and 7.5) by adding HCl and NaOH. During shaking the pH was measured two times (after approx. 16 - 24 h) and was, if necessary, corrected again by adding HCl and NaOH.

Comment 12: p5 l32: why are you going for linear sorption isotherms? Freundlich is also an option and would be much better to describe the overall behaviour at a wider range of concentrations. At the moment the use of the presented data is strictly limited to the concentration range tested.

Response 12: We agree with the referee that freundlich or langmuir isotherms would

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also be an option and would increase the range of validity of the sorption constants. However, we designed the experiment to explicitly stay in the linear sorption range because K_d -values, which describe linear sorption, are used and published by most researchers (as one can see in table 1). Furthermore, in field experiments many researchers work in low concentrations ranges (despite the concentration directly after injection) where the assumption of linear sorption is justified. For comparing the sorption of UR and SRB between our treatments, we concentrate on relative differences and therefore, the interpretation of the data does not depend on the concentration range. For example, we found a decrease of K_d with increasing OC-content. This result would not change if we would have used freundlich or langmuir coefficients. We will clarify the selection of the sorption model in the updated manuscript.

Comment 13: *p6: which type of fit did you apply in R (lm/lqs/nls)? Please give the prediction intervals for each fitted parameter (predict function in R).*

Response 13: We used the lm-function. As we answered to comment 5 we will give the confidence intervals in a table, describe them in the material and methods section and will show and discuss them in the results and discussion section.

Comment 14: *p9 l29: the unit for the SSA (%) is wrong.*

Response 14: We are sorry for this mistake. Of course, the unit of SSA must be m^2/g and will be corrected in the paper.

Comment 15: *The discussion should focus on the accessibility of the surfaces, which is clearly different for pure montmorillonite added to the sediment and clay minerals coated with eg. OC in the topsoil.*

Response 15: We thank the referee for suggesting this. In our original manuscript (p.10,l.5/6) we had written that "the clay fraction of the pure clay mineral montmorillonite potentially possessed more or easier accessible sorption sites than the clay fraction of the topsoil." In the updated manuscript we will adopt the statement of the referee which

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is more precise.

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Comment 16: *p10 l8 and table 4: if no SRB is sorbed to the sediment, which we never observed in any of our experiments, how is the K_D value of 1.3 in table 4 justified?*

Response 16: We again apologize for this confusion. We will correct this (see response 2).

Comment 17: *Table 1 should include the ranges of the presented study (excerpt from table 4)*

Response 17: In accordance with the referees' wishes, we will include the range of our data in an updated version of table 1.

Please also note the supplement to this comment:

<https://www.hydrol-earth-syst-sci-discuss.net/hess-2018-549/hess-2018-549-AC2-supplement.pdf>

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., <https://doi.org/10.5194/hess-2018-549>, 2018.

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