Response to comments of Anonymous Referee #1

On behalf of all co-authors, I sincerely thank the Anonymous Referee #1 for the thoughtful and detailed assessment of our work.

***R1:** Beyond the various comments I make below about i) the theoretical-methodological background and ii) the model application examples, I believe that the implemented developments, i.e. non-linear sorption and first-order degradation processes, are not substantial enough to warrant a new publication in HESS.*

AS: Thank you for this critical comment. We are not aware of any studies that combine depth-dependent, non-linear sorption and first-order degradation with a particle-based approach for reactive solute transport in the unsaturated zone. Thus, we think that the presented developments of LAST are indeed innovative and relevant. However, we agree that from a mathematical point of view a simulation of reactive transport means just to account for two additional processes represented by quite simple equations for sorption and degradation. However, this does not imply that predictions of reactive transport phenomena are only marginally more complex than simulations of conservative transport. The two additional processes of sorption and degradation increase predictive uncertainty, as reflected in the sensitivity of the simulated Isoproturon profiles to variations of reactive transport parameters (cf. Figure 4b in the manuscript). Moreover, the implementation of sorption into the LAST framework is not straightforward as a retardation factor doesn't help in our approach (cf. comment below). The proposed way to account for sorption is hence pretty novel, and we show that this approach allows feasible predictions of reactive pesticide transport under different, transient flow conditions (well-mixed, preferential flow); also compared to HYDRUS. However, we admit that further testing of this approach is desirable and we look for additional experimental data and we will discuss the novelty of our approach in the revised manuscript more clearly to show the significance to the reader.

Main comments

***R1:** Model equations and simulation algorithm. Missing from the manuscript are the equations of the double-porosity flow and (reactive) transport model which are supposed to be solved (simulated) by the proposed Lagrangian method. While it is clear that the original Lagrangian method by Zehe and Jackisch (2016) was developed to solve the Richards equation, the flow and transport equations equations associated with the extended Lagrangian method are not specified either in the article of Sternagel et al. (2019) or in this manuscript. Without these equations, it is difficult to assess the soundness of the LAST-model framework. What I particularly miss is the mathematical description of water and solute exchanges between the preferential flow domain and the soil matrix domain. The modeling equations for reactive transport processes provided in this manuscript are themselves not self-contained. Let us consider the example of equation (6) which describes the sorption reactions. According to this equation, the mass of reactive solute can only decrease over time. Although it is mentioned that this equation only describes the adsorption process, the equation describing desorption and the coupling between the two equations should also be provided so that the term mrs(t) does not only decrease over time. In addition, I think it would be useful to detail the entire Lagrangian algorithm step by step.*

AS: Thank you for this important comment. Basically, the flow and transport equation of the extended LAST-Model is equal to the Fokker-Planck equation derived by Zehe and Jackisch (2016). The only difference is that we additionally assign a solute mass to each water particle and hence, the solutes are also advectively and diffusively/dispersively displaced (Eq. 5), together with the water particles (cf. comment below). Thus, we do not assume a second particle species representing solutes but tag the water particles by a solute mass and we do not have implemented a new, specific equation for the transport of solutes. Furthermore, in Sternagel et al. (2019) we show in Eq. 6 how the exchange of water particles, and hence solute masses, between matrix and macropores is calculated. In the current manuscript, we explain these points; but in the revision, we will add further (brief) explanation to ensure clarity. We also provide the complete model code on GitHub, if someone is interested in having a closer look at the Lagrangian algorithm and the numeric. We think that presenting and explaining the entire algorithm in detail within the manuscript would exceed the scope of the study. However, we will complement Eq. 6 of the present study with a further equation for desorption to make the implementation of the sorption process clearer.

***R1:** Diffusive transport vs. diffusive mixing. As correctly mentioned in P5L1-2 (page 5, lines 1-2), the Lagrangian algorithm described by equation (5) integrates an advective transport term and a diffusive transport term. But the description given P6L8-11 does not seem to be consistent with this equation. The authors discuss the advective displacement of the particles, followed by a redistribution of mass between the different particles that are in the same Eulerian control volume. This mass redistribution is referred to as "diffusive mixing" by the authors. I have two concerns here. On the one hand, the part of the transport described by the second term of equation (5) does not seem to be reflected here, and on the other hand I believe that the expression "diffusive mixing", used at various places in the manuscript, is not appropriate because it could be wrongly confused with diffusive transport. I suggest replacing "diffusive mixing" by "particle mixing" or any other expression that the authors might consider appropriate.*

AS: You have generally recognized our concept of the mass redistribution among water particles. Eq. 5, however, is actually only applied for the displacement of water particles but as the particles carry solute masses, these solutes are also advectively and diffusively/dispersively displaced in each time step, together with the water particles. On page 6, lines 8-11, we no longer refer to Eq. 5, and instead just describe how solute masses are redistributed among the water particles after the advective-dispersive displacement of Eq. 5. We will use a different expression for this “diffusive mixing” of solutes among water particles to avoid confusion.

***R1:** Parameter meaning and values used in the simulations. A number of simulation parameters listed in Tables 1, Table 2, and Table 3 are only very briefly described in the table captions, e.g. alpha, n, and since these parameters do not appear in any of the equations in the manuscript, nor apparently in the equations of the 2009 article, it is difficult to assess the relevance of these parameters. Nor is it specified whether the values indicated in Tables 1-3 correspond to fixed known values, or are empirical (only specified for the Kf and DT50 IPU parameters), or whether these parameters have been estimated through a calibration process to best fit the model against observations. The same question applies for the macropore Ks value (P13L25-26) and for the parameters that control the mass exchanges in the Hydrus dual-domain simulations. It is therefore difficult to assess the comparisons between the LAST and HYDRUS simulations shown in Figure 4c.*

AS: The soil hydraulic parameters (like alpha, n etc.) are the van Genuchten-Mualem parameters, which define the soil hydraulic properties of the soil and can be used to calculate the matric potential of soil at a certain water content, for example. As the van Genuchten-Mualem concept and its parameters are generally well known and established in unsaturated soil physics/hydrology, we do not describe them further. However, we will add a respective citation, when introducing these parameters. Additionally, the residual parameters in Table 1 and 3 are observed, measured data from the described experiments. In Sternagel et al. (2019), we provide a detailed description of how the observed data are processed for use in our model (e.g. macropore data) and how sensitive our model is to the uncertainty range of observed data (e.g. to the saturated hydraulic conductivity *Ks*). However, we will modify the text to improve clarity in the respective passages.

***R1:** Relevance of the simulations provided to illustrate the model's reactive transport simulation capabilities. The yellow profile in Fig. 3a is barely visible. It may be necessary to indicate in figure caption that this yellow profile (simulation taking only sorption into account) and the light blue profile (simulation taking both sorption and degradation into account) overlap. And given this overlap, the statement P15L10 is incorrect: Figure 3a does not show "significant retardation and degradation", as there is no difference between sorption only and sorption associated with degradation. The similarities between figures 4a (sorption only) and 4b (sorption associated to degradation) also suggest a weak influence of degradation, i.e. adding this process in the simulations does not seem to significantly improve the model fit on the observed data. Therefore, the relevance of the data sets used to illustrate the capacity of the LAST model to simulate degradation processes is questionable. I do not question the implementation of degradation in the Lagrangian method, which is actually conventional and straightforward, but the use of this option seems not very relevant with respect to the selected datasets as it does not allow to significantly improve the simulation of real profiles. Similarly, the low sensitivity of the model with respect to the sorption coefficient Kf, as shown in Fig. 4a and acknowledged P21L34-35, also raises questions about the relevance of the data sets used to illustrate the model's reactive transport simulation capabilities. I therefore suggest applying the model to other (more relevant) experimental data to better illustrate the interest of the model add-ons.*

AS: Yes, you are mentioning an important point. However, we think that the current experimental database is suitable to particularly show a noticeable effect of sorption, while the time scale of 2 days may be indeed a little too short to explore the role of degradation in its entirety. We will examine another dataset of a breakthrough experiment and check the possibility to adapt the model setup to simulate the solute concentration time series of the breakthrough.

However, the question remains of how to define a significant difference between results. We think that there are indeed at least noticeable differences between, especially, the results of the conservative, reference simulation runs and the simulations performed with full reactive transport, particularly with respect to the spatially small and temporarily short scale.

Regarding the results of the well-mixed simulations presented in Figure 3, we refer here especially to the difference between the conservative, reference simulation and the simulations performed with full reactive transport, which is clearly visible (RMSE difference of 7.3 %). Of course, the influence of degradation is relatively small but still detectable due to the quite high *DT50* value of 23 days and the short time scale. We will rephrase this passage to make it clearer.

Regarding the results of the preferential flow dominated simulations presented in Figure 4, we think that, in particular, the blue highlighted area in Figure 4b indeed shows clear differences in the final mass profiles, when varying the *DT50* value in observed ranges. Thus, the mass profile simulated with a high *DT50* value exhibits the strongest difference to the mass profiles simulated only with retardation in Figure 4a (with a total mass loss of around 0.131 g IPU for an input of 1 g in just two days, which we think is significant).

To summarize, we of course admit that further simulations with long-term datasets would be desirable but the availability of suitable data is scarce. However, we also think that the presented results provide scientifically significant insights and demonstrate the feasibility of the implementation of depth-dependent sorption and degradation into a Lagrangian framework. To the best of our knowledge, there are no other studies implementing depth-dependent, non-linear sorption and first-order degradation into a particle-based Lagrangian approach to simulate reactive solute transport in the unsaturated soil zone.

R1: *Long-term simulations. As stated in the introduction, P3L18-21, one of the main objectives of this work is to assess the ability of the LAST model to perform long-term simulations. It is later clarified that "long term" refers to a period of 7 days, where short term refers to a period of two days (P10L25-27). Beyond the questions that could be raised about whether or not the difference in duration between these periods is significant, I wonder more generally about the capacity of such a model to simulate flow and transport over longer durations involving a modification of the soil structure over time. I think it would be interesting to add a few lines on this topic in the manuscript.*

AS: We agree that the expression “long-term” might be misleading and we will change the expression in the revised manuscript. Yet, we think that there are indeed remarkable differences between a simulation period of 2 and 7 days. In particular, the drainage phase after irrigation is longer, which implies that water and dissolved bromide have more time to redistribute and diffuse through the soil. This is reflected in the accumulation above the gley horizon observed in the experiments. Further, as we have discussed in the manuscript, the reactive substance IPU can indeed exhibit DT50 values of just a couple of days in natural soils, which is surely relevant when comparing periods of 2 and 7 days (cf. Fig. 4b and 5b of the manuscript). We will add these clarifications to the revised manuscript to justify the difference between the 2 and 7 days simulations.

However, the soil structure may of course change on larger time scales. In our application cases, this might have no significant influence as we work on quite small spatial scales of around 1 m³ on artificially shaped, agricultural fields. The soils on these fields may have a more persistent structure than natural soils because conditions are better controllable. Up to now, our LAST-Model has not been accounting for a changing soil structure but we think, this could be straightforward to implement, e.g. by just changing the soil hydraulic parameters and macropore data after certain phases in long-term simulations.

R1: *Over-Mixing. The authors mention possible over-mixing artefacts in their simulations at long times (one week duration), but this hypothesis is described as uncertain, e.g. P20L18-19, P22L18-19, P22L35-36. Yet this type of problem is supposed to be easily identifiable. Simulations should be repeated using a more refined spatial (Eulerian grid) discretization and the results compared. Why has this not been done? I believe it is important to fix this question, and not to relegate it to a future study as suggested in the concluding remarks (P24L6).*

AS: Thanks for this interesting point. We repeated the long-term simulation using a finer soil domain discretization *dz* of 0.05 m. The results show that the solute over-mixing is indeed slightly mitigated but a too strong displacement below 1 m is still clearly visible (Fig. 1), which we attribute to over-mixing. However, an even finer discretization would lead to huge, excessive simulation times because the finer soil discretization has the consequence that also the time steps become smaller to fulfil the Courant criterion and a much higher amount of particles would be needed. Without a higher particle amount, in the single soil layers would be too little particles to distribute them to the bins properly and to ensure a numerically and statistically valid random walk. We will add a respective passage to this issue in the revised manuscript and show the simulations results for a finer discretization for comparison.

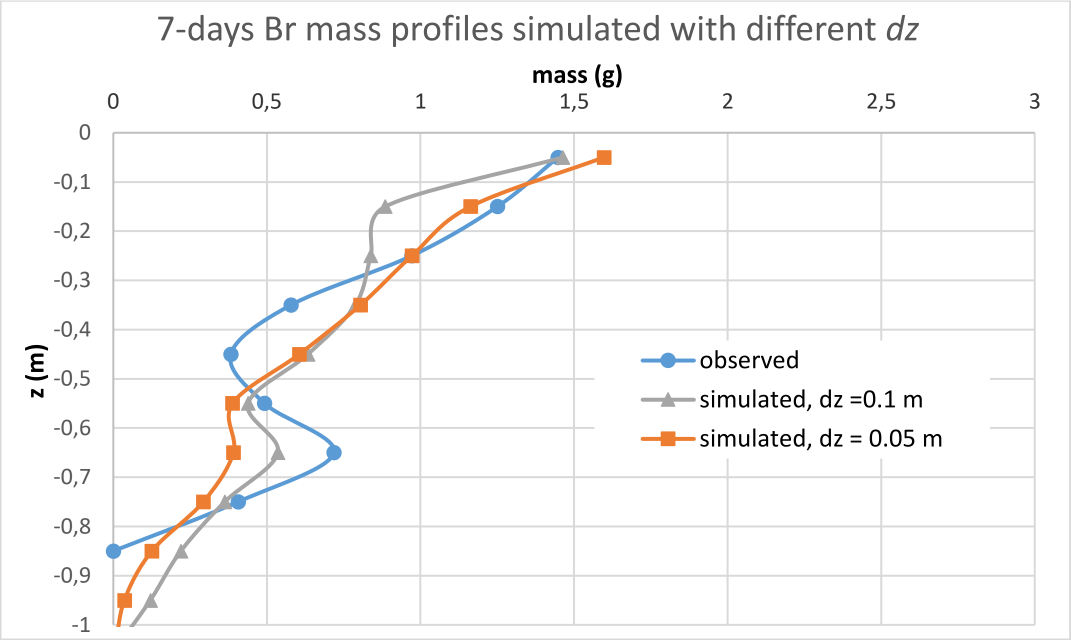

Figure 1. Bromide (Br) mass profiles of 7-days simulation using different soil discretizations *dz* and compared to observed mass profile.

Other specific comments

***R1:** P2L15-17. It should be acknowledged that the laminar flow assumption applies equally to the LAST model.*

AS: In general, you are right for flow in the matrix domain because the theoretical starting point of the displacement equation (Eq. 5) of LAST is the Richards equation (Eq. 1), as we describe in section 2. Further, we use an adaptive time stepping to fulfil the Courant criterion and to ensure that the particles do not travel further than the length of a grid element *dz* in a time step. We will discuss this issue in the revised manuscript.

***R1:** Something is missing to understand the transition from equation (3) to equation (5). On the one hand it is expected, according to the classical formalism of RW, to have theta(t) instead of theta_r+i*delta_theta, and on the other hand the term Theta_r is not described in the following lines P5L2-4. One must wait for line 13.*

AS: Yes, you are generally right. With our expression $\theta_r + i \cdot \Delta\theta$ in Eq. 5, we mean the soil moisture of the current bin in a grid element and time step. This is formally equivalent to $\theta(t)$ but a speciality of our binning-approach, which is then described in the subsequent passage (page 5). We will revise and already introduce this formal equivalence of expressions as well as θ_r directly after Eq. 5.

***R1:** P5L5-6. According to the way equation (5) is written, the random number Z should not be drawn from a uniform distribution between -1 and 1 but from a standard normal distribution.*

AS: Thank you. You are of course right; it should be a random number from a standard normal distribution. We will revise this.

***R1:** P7L12-13. This sentence suggests that retardation coefficients are only used with Eulerian models whereas their use is also common with Lagrangian methods.*

AS: This sentence specifically refers to our Lagrangian approach. In LAST, there are not two separated particle species for water and solute but we only assume one species of particles/parcels, which represent water and can carry a solute mass. Thus, the travel distance of water particles and solutes cannot be uncoupled, which means that the use of a retardation coefficient is not meaningful in our approach. However, you are right by stating that indeed other Lagrangian approaches use such a retardation coefficient because they may employ two distinct particle species for water and solutes, which is commonly applied in modelling water flow and solute transport in groundwater. We will revise and clarify this passage.

***R1:** Much of section 6.3 "General reflections on Lagrangian models for solute transport" would be better placed in the introduction.*

AS: Of course, some general aspects of this section could also be mentioned in the introduction but we think that they better fit into the discussion, as the reader knows all the details of LAST after reading the entire manuscript and can better compare it to the other new particle-based models, which are described in section 6.3.

***R1:** P23L15-18. The fact that with the miRPT method the degradation reactions are restricted to immobile particles is presented as a drawback... but I do not see the difference with the authors' Lagrangian method. If I understand correctly what is written in P6L36, P8L19, and in chapter 3.2, the degradation reactions are also restricted to the adsorbed phase... Please clarify.*

AS: Sorry for the misunderstanding. The drawback is not related to the restriction of degradation to immobile particles but to the transfer process of solute masses as described on page 23, lines 15 ff.: *"However, this approach also has drawbacks. For example, the miRPT algorithm of Schmidt et al. (2019) transfers all solute masses from mobile particles (= water phase) to immobile particles (= soil solid phase) for reaction and subsequently back to the mobile particles for further transport."*

What we mean here is the fact that in the miRPT model all solute masses must be ultimately transferred from the water phase to the solid phase to calculate degradation in each time step. Subsequently, the residual, not degraded masses are again transferred back to the water phase. This approach is quite consuming because most masses are moved there and back between the phases without being subject to degradation or adsorption. In LAST, we use specific calculations for the transfer of masses from water particles to adsorbing phase, whereby just a part of solute masses is transferred (= adsorbed). Only these adsorbed masses are then subject to degradation and the residual, not degraded masses stay in the adsorbing phase until the concentration gradient between water and adsorbing phase may turn and desorption occurs. Further, you are of course right by arguing that LAST also calculates degradation only in the adsorbing phase. We will revise this passage to make this point clearer.

***R1:** Appendix. I do not think this Appendix is useful. What is reported here corresponds to results already published, i.e. the reader can find the figures A1 and A2 with the related information in the articles of Zehe and Jackisch (2016) and Sternagel et al. (2019). I suggest deleting the Appendix and referring directly to the articles in question.*

AS: Yes, this could be one option but we think that the Appendix might be useful for some readers to conveniently access and compare the main findings of the previous LAST studies.

Minor comments

AS: Thank you for the further minor comments. Most of them seem clear and constructive. We will check and consider changing the manuscript, accordingly.

***R1:** P13L19-20. Remove the quotes from the ref. Gerke and van Genuchten 1993.*

AS: Please note that this is not a reference but the actual name of the selected dual-permeability approach in HYDRUS.

R1: P25L6 and Fig. A1. Please consider changing the term "naive" to "classical" or "standard" (more neutral) when referring to the RW method.

AS: Here, we just use the same formulation as Zehe and Jackisch (2016) to be consistent.

Thank you very much,

Alexander Sternagel on behalf of all authors

References

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Sternagel, A., Loritz, R., Wilcke, W., and Zehe, E.: Simulating preferential soil water flow and tracer transport using the Lagrangian Soil Water and Solute Transport Model, Hydrology And Earth System Sciences, 23, 4249-4267, 10.5194/hess-23-4249-2019, 2019.