Feedback mechanisms between precipitation and dissolution reactions across randomly heterogeneous conductivity fields

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Replies to Reviewer #2

We appreciate all efforts invested by the Reviewer in our manuscript and are grateful for the opportunity to resubmit a revised draft for your consideration. We address all comments from the Reviewer in the following itemized list, which we arrange enclosing each answer within corresponding review items. Please, note that Reviewer's comments and our responses are given in black italic and blue fonts, respectively.

Sincerely,

Yaniv Edery, Martin Stolar, Giovanni Porta, Alberto Guadagnini

Reviewer #2

The manuscript, by Edery et al., addresses a significant topic of reactive transport in heterogenous porous media, with precipitation/dissolution scenario. The main contributions of this paper are variation/changes in the spatial-statistical moments of the velocity field during the transport of reactive species, and how different flow zones (i.e., preferential paths and low conductivity zones) are contributing (differently) to precipitation/dissolution.
The manuscript deals with a timely and relevant topic, well-written and presented, and its results have a general contribution for various systems in hydrology and earth science. Therefore, it is suitable for publication in HESS, with a few minor revisions.

We thank the Reviewer for their positive appraisal of our study and the time invested in reviewing our work.

General comments:

- The authors use a Darcy scale model to solve the velocity field, and thus the transport, while the system is "only" 60*24 cm (Lab scale). More important, for Darcy scale, I would expect the use if dispersion coefficient and not diffusion (Eq. 4). Although understanding the authors choice here, in order to use particle tracking approach, they should discuss their choice (i.e, diffusion over dispersion), and emphasis the relevance of their results for larger scale systems (adding references).

We thank the Reviewer for addressing this important point. The scale of the system is indeed intended to mimic a laboratory scale scenario. Our modeling choice is motivated by the reasons detailed in the following. In general, we acknowledge that using a velocity-dependent dispersion would be an option, enabling one to take into account pore-scale processes within a continuum-scale model. It is our view that this would add an additional level of complexity to our numerical simulation without modifying the key elements of our work, which is focused on the interaction between flow patterns and reactive processes. In this context, our choice is to neglect local dispersion while approximating the effect of fluctuations of velocity arising between diverse realizations of the conductivity field. Averaging in a multi-realization context

enables us to represent such effects, which are commonly termed as macrodispersive effects. In line with this reasoning, our choice is to rely on a constant and isotropic diffusion coefficient that can be associated with an advection-dominated transport regime (as quantified in terms of a Péclet number, see below). This choice is also consistent with previous works (e.g., Aquino and Bolster, 2017; Wright et al., 2021)

All of these elements will be included in the revised manuscript

References

E. E. Wright, N. L. Sund, D. H. Richter, G. M. Porta and D. Bolster, Stochastic Environmental Research and Risk Assessment, 1-19 (2021).

T. Aquino and D. Bolster, Transport in Porous Media **119** (2), 391-402 (2017)

- The chemical model (sec. 2.1). I am not sure that "infinite Damkholer number" (line 98) is the correct definition. How much the reaction products are sensitive to the choice of numerical parameters (time interval for reaction), overall particles and the grid size?

We note that the expression infinite (local) Damköhler is related to the observation that reactive processes in our study take place under the assumption of instantaneous local equilibrium. The Da number usually provides an appraisal of the ratio between advective (or diffusive) and reactive time scales. The reactive time scale approaches zero at equilibrium. In this sense, we can state that $Da \rightarrow \infty$. This point will be clarified in the revised manuscript.

Regarding the sensitivity of the results to the numerical parameters, we have run several tests. When considering single realizations, the results showed only minute sensitivity to increasing the number of particles by a factor of 10 (less than 3% difference in the results was observed). Results display a slightly larger sensitivity to the time step, resulting in a difference of less than about 5% in the amount of reaction when decreasing the time interval by an order of magnitude.

We had performed a test to assess possible influences of the grid size on the key results of the study. We did so by considering a numerical grid with elements characterized by half the size of those included in the manuscript. Due to constraints related to computational time, we performed this analysis for 10 random realizations of the heterogeneous conductivity fields associated with the highest initial variance (i.e., variance equal to 5) and comprising 120×120 and 240×240 elements of uniform size $\Delta = 0.1$ and 0.2 cm, respectively (the value $\Delta = 0.2$ cm being then used in the manuscript).

As an example of the type of results we obtain, Figure R2.1 depicts the average across the considered 10 realizations of the temporal evolution of the sum of all conductivity changes $|\Delta K|$ in the domain taking place, values of conductivity changes being evaluated across temporal windows of width equal to 1 minute (see Figure 4b in the manuscript). These results show that the overall trend is not significantly affected by the grid size. Results of similar quality are obtained also for the remaining values of initial log-conductivity variance examined. This analysis imbued us with confidence about the quality of the results obtained with the grid size employed in the manuscript, which we selected as good compromise between computational accuracy and execution time constraints, in light of the objectives of the study.

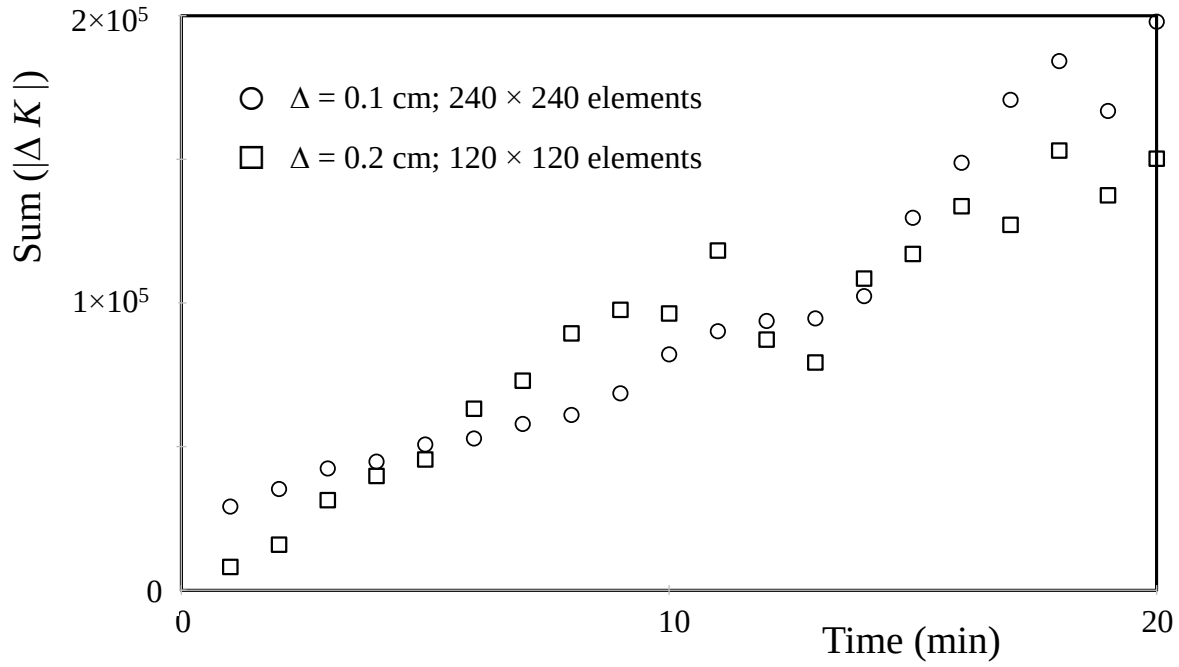

Figure R2.1. Temporal evolution of the sum of all conductivity changes |ΔK| (averaged across 10 realization) for the setting corresponding to initial log-conductivity variance $\sigma_0^2 = 5$. Values of conductivity changes are evaluated across temporal windows of width equal to 1 minute, as in Figure 4b in the manuscript. Results are depicted for grids comprising 120×120 and 240×240 elements of uniform size Δ = 0.1 and 0.2 cm, respectively (the value Δ = 0.2 cm being then used in the manuscript)

- The relation between the non-Fickian transport behavior and the CTRW pdf TPL. Although the fits of psi(t) are reasonable (Fig. 2), the authors might add a fit to the breakthrough curve, for a selected realization, to show that the transport in a non-reactive system follows the ctrw model (TPL). Also, how the authors find the TPL parameters (table. 1)? Are they related to the statistical moments (i.e., particle mean velocity and variance)?

A major finding of this study is documenting that spatial heterogeneity of reaction leads to (*a*) the emergence of non-Fickian transport in settings where a Fickian model can be used to characterize non-reactive solute migration prior to reaction (i.e., the scenario corresponding to a unit log-conductivity variance of the original system); or (*b*) enhancing the non-Fickian pattern associated with non-reactive solute migration prior to reaction (i.e., the scenarios corresponding to the high log-conductivity variances of the original system).

Quantification of departure from a Fickian pattern is here addressed through the tail of the probability density function (PDF) of particle waiting times for a tracer test performed on the conductivty field prior and after reaction has taken place.

In this context, we do not explore the skill of a model such as, e.g., the CTRW (mentioned by the Reviewer), to interpret non-reactive transport across the conductivity fields prior and/or after reaction is documented. We note that some of the parameters of a CTRW model can be estimated directly from the above mentioned PDF. Namely, the slope of the tail of the PDF and the values of t_1 and t_2 can be estimated through a log-log representation of the type depicted in Figure 2 of the original manuscript. We will add this clarification in the revised manuscript.

Given our objective, we did not fit breakthrough curves (BTCs) associated with the non-reactive transport simulations in our study, a feature which is then out of the scope of our study.

We note that fitting a BTC with a CTRW model formulation would require estimating the dispersion coefficient, while relying on the parameters estimated through the above mentioned PDF and the arithmetic mean velocity in the domain. This would render an effective one-dimensional CTRW-based representation of the BTC of the kind that is typically presented.

Following the request the Reviewer, we employ a one-dimensional CTRW model to interpret BTCs associated with non-reactive transport taking place in the original conductivity fields and at various times after reaction takes place while (*a*) accounting for the parameters of the PDF of the of particle waiting times and mean velocity and (*b*) fitting dispersion.

Table R.2.1 lists the values of the parameters obtained from the PDF of the of particle waiting times (i.e., $\boldsymbol{\beta}$, t_1, and t_2) evaluated as described above, of the mean velocity ($\boldsymbol{v_T}$), and of the dispersion coefficient ($\boldsymbol{D}$), the latter being obtained through a least-square fit of a one-dimensional CTRW model against numerical BTCs, for selected single realizations of log-conductivity fields with initial variance σ_0^2 = 1 and 5 and some observation times (t = 0 corresponding to the conductivity distribution prior to reaction).

One can clearly note the increasingly non-Fickian nature of transport from the values of the parameters obtained from the PDF of the of particle waiting times (i.e., $\boldsymbol{\beta}$, t_1, and t_2). This corresponds to the major finding associated with our study and does not require relying on a CTRW transport formulation.

	$\boldsymbol{\sigma_0^2 = 1}$			$\boldsymbol{\sigma_0^2 = 5}$		
t [min]	0	10	20	0	10	20
$\boldsymbol{D}$	0.007	0.085	0.91	0.27	0.345	0.372
$\overline{\boldsymbol{v_T}}$	0.36	0.37	0.38	0.45	0.46	0.47
$\boldsymbol{\beta}$	2	1.4	1.05	1.4	0.8	0.6
$\boldsymbol{t_1}$	0.1	0.09	0.06	0.08	0.03	0.01
$\boldsymbol{\mathrm{Log}_{10}(t_2)}$	1	2.5	2.8	1.6	2.5	3

Table R.2.1. Values of the parameters obtained from the PDF of the of particle waiting times (i.e., $\boldsymbol{\beta}$, t_1, and t_2), of the mean velocity ($\boldsymbol{v_T}$), and of the dispersion coefficient ($\boldsymbol{D}$), the latter being obtained through a least-square fit of a one-dimensional CTRW model against numerical BTCs, for selected single realizations of log-conductivity fields with initial variance σ_0^2 = 1 and 5. Results corresponding to some selected observation times (prior and after the reaction takes place) are listed.

Otherwise, Figure R2.2 depicts the results obtained through the one-dimensional CTRW formulation associated with the parameters listed in Table R.2.1 and the BTCs evaluated in our numerical analyses. We stress that, as stated above, these are obtained upon estimating dispersion through a CTRW fit.

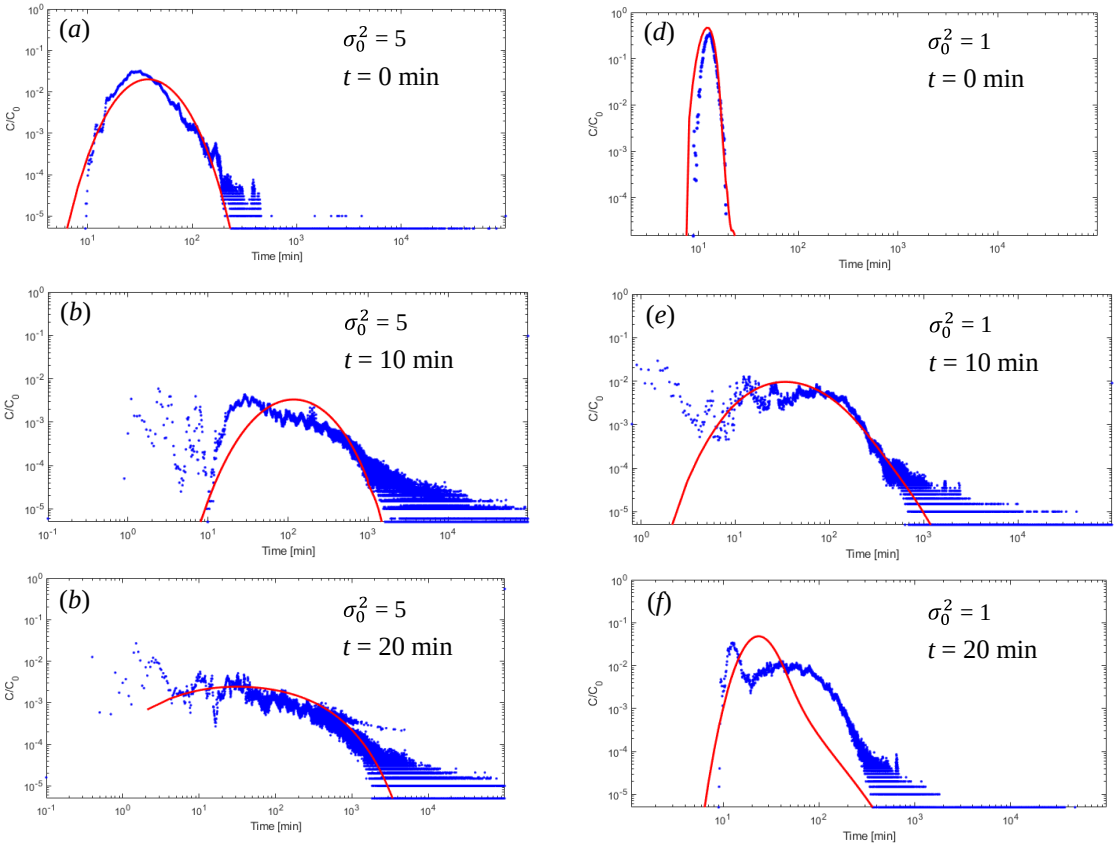

Figure R2.2. Results obtained through the one-dimensional CTRW formulation associated with the parameters listed in Table R.2.1 and the BTCs evaluated in our numerical analyses.

These latter results clearly show that the non-Fickian nature of transport, as embedded in the parameters characterizing the PDF of the of particle waiting times (i.e., $\boldsymbol{\beta}$, t_1, and t_2), is not captured entirely by the 1D solution of the CTRW transport formulation when considering the log-conductivity fields resulting from reaction. As we state above, our study is not aimed at exploring the skill of a model such as, e.g., the CTRW, to interpret non-reactive transport across the conductivity fields prior and/or after reaction takes place and we will defer this particular analysis to a subsequent study.

We will further clarify this element in our revised Conclusions.

In this context, maybe to add the mean velocity value to table. 1.

Values of mean velocity and of the weighted velocity for the tracer test are now included in the revised Table1.

- What is the magnitude of Pe. Seems that the transport is at (relatively) high Pe (advactive dominant), and thus the occurence of preferential paths is more relevant. However, many water resources are usually under low Pe value.

We consider the following formulation for the Pe number (see, e.g., Huysmans and Dassargues, 2005):

$$Pe = \frac{V_d\sqrt{k}}{n_e D_d} = \frac{V_d\sqrt{K\frac{\mu}{\rho g}}}{n_e D_d} = \frac{5\cdot\sqrt{1\cdot\frac{0.0105}{10^5}}}{0.3\cdot 10^{-5}} = 540$$

where V_d is Darcy velocity; k is the intrinsic permeability; n_e is effective porosity; K is (arithmetic) average; μ and ρ are dynamic viscosity and density of water, respectively; g is gravity; and D_d is diffusion. The ensuing value of Pe is indeed indicative of an advection-dominated transport setup. An additional study on the sensitivity of the results to the magnitude of Pe for a completely uniform conductivity field is currently under completion and preliminary results confirm that the same feedback mechanism between reaction and evolution of preferential pathways is observed . We do agree that results might be different in a diffusion-dominated system and would require additional analyses. We are planning of tackling these in a separate study because the simulations will require a more efficient computational methods for the implementation of the reaction and transport.

References.

M. Huysmans and A. Dassargues, Hydrogeology Journal **13** (5-6), 895-904 (2005)

- The system seems to be sensitive to the choice of the boundary conditions, where the low velocity sampling (which contributes most to the non-Fickian behavior) is only around the inlet boundary. The authors should discuss that in more details and add more references (e.g., Kang et al., 2020 https://doi.org/10.1029/2020WR027378)

We start by thanking the Reviewer because their comment enabled us to clarify that the original manuscript included an inappropriate description of the meaning of the diverse colors employed to illustrate the results depicted in Figure 3g&h. The green color in Figures 3 g&h marks the **decrease** in conductivity (and not the **increase** in conductivity as written in the original version of the manuscript), this being also consistent with the color palette in Figure 3e&f. The red color in Figures 3 g&h marks the **increase** in conductivity and not the **decrease** in conductivity, this being also consistent with the color palette in Figure 3c&d. These elements are now fixed in the revised manuscript.

The documented conductivity increase near the inlet is consistent with the constant low pH value introduced by the step function of particles injected in the system which leads to a high dissolution rate and therefore higher conductivity near the inlet, an effect evidenced in several studies (Fredd and Fogler, 1998; Nogues et al., 2013; Kang et al., 2013; Molins et al., 2014; Jung and Navarre-Stichler, 2018). The study suggested by the Reviewer (Kang et al., 2020) deals with fractured rocks and the inlet effect therein is regarded to be the result of dead-end fractures, which is not the case in our study. We agree that the initial/boundary conditions can affect non-Fickian transport features, as it has been demonstrated in a number of works also referring to flow in porous media simulated via Darcy scale models. The injection mode will certainly affect solute transport close to the inlet boundary, which will then be reflected in the recorded residence times and the related statistics. We prefer to adhere here to the investigated set of boundary conditions (flux-weighted injection, mean uniform flow), which are representative of a well-studied framework and not to delve into a discussion on this point. We feel the latter would only distract the reader from the key messages of the study. The point is mentioned in the Conclusions as a possible extension of the proposed analysis.

References.

C. N. Fredd and H. S. Fogler, AIChE journal **44** (9), 1933-1949 (1998).

Q. Kang, D. Zhang and S. Chen, Journal of Geophysical Research: Solid Earth **108** (B10) (2003).
J. P. Nogues, J. P. Fitts, M. A. Celia and C. A. Peters, Water Resources Research **49** (9), 6006-6021 (2013).
S. Molins, D. Trebotich, L. Yang, J. B. Ajo-Franklin, T. J. Ligocki, C. Shen and C. I. Steefel, Environmental science & technology **48** (13), 7453-7460 (2014).
H. Jung and A. Navarre-Sitchler, Geochimica et Cosmochimica Acta **234**, 70-83 (2018).

Specific comments:

- In the Kozeny-Carmen model, the authors might add the formula for the porosity evolution.

Done.

- Lines 171-172: what will be the effect of different boundary constrains?

These constraints are set for consistency with our assumptions, i.e., to consider Darcy flow across the porous domain. A complete clogging (or opening) of a void space would require a different mathematical and conceptual treatment, which is beyond the scope of our study. We clarify this point in the revised manuscript.

- Are 20 realizations being significant for a robust statistic? What is the variability within realizations?

We have analyzed convergence of the results with respect to the number of realizations. As an example of the type of results we obtain, Figure R2.3 depicts the average of the temporal evolution of the sum of all conductivity changes $|\Delta K|$ in the domain as a function of the number of realizations considered for the most heterogeneous setting (values of conductivity changes being evaluated across temporal windows of width equal to 1 minute, as in Figure 4b in the manuscript). These results show that the number of realizations we employ is sufficient to characterize the reactive process, as quantified through the metric depicted. Results of similar quality are obtained also for the remaining values of initial log-conductivity variance examined.

While we think including Figure R2.3 in the revised manuscript will not bring additional value to the study, we will explicitly refer to such a preliminary analysis in our revised text.

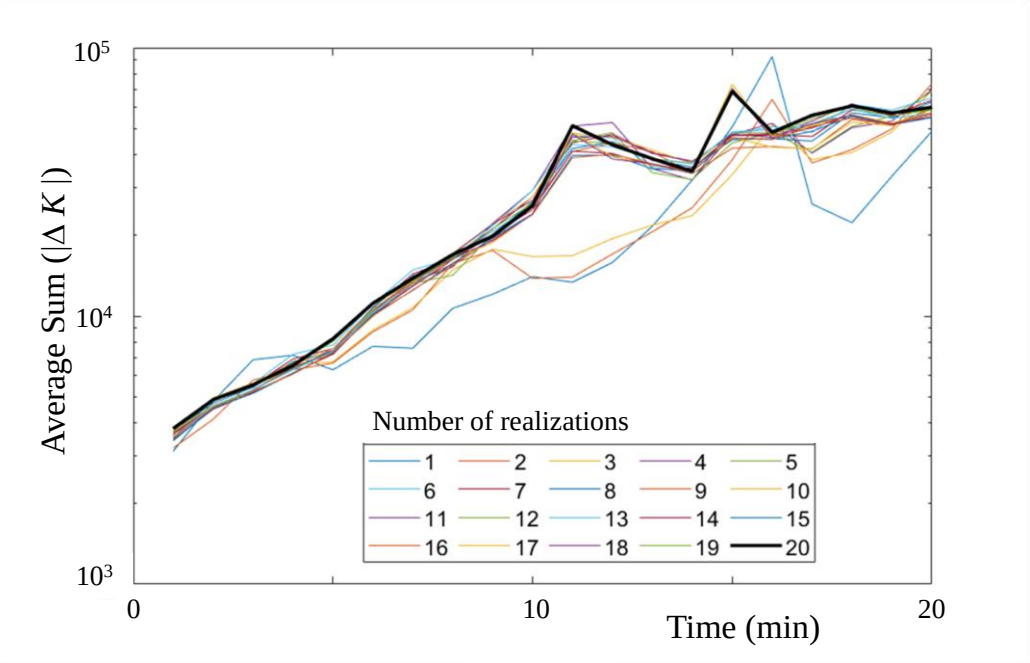

Figure R2.3. Temporal evolution of the sum of all conductivity changes $|\Delta K|$ averaged according to an increasing number of Monte Carlo realizations for the setting associated with initial log-conductivity variance $\sigma_0^2 = 5$. Values of conductivity changes are evaluated across temporal windows of width equal to 1 minute, as in Figure 4b in the manuscript.

- How the pore volume is defined? By the initial condition? As the overall flux is evolving during the simulations.

Yes, the pore volume is calculated using the initial condition, i.e., before porosity and permeability are altered by the reactive processes. This is now clarified in the revised manuscript.

- For larger pore volumes, are the monotonic behavior in Fig. 4 might shifts? And therefore, precipitation becomes more dominant.

As pore volume increases we can obtain a higher amount of available carbonic acid due to the dissolution near the inlet, which can then be followed by precipitation downstream and hence can alter the overall conductivity and flow field. As the current study focuses on the dynamics of the first pore volume we did not address this option. Otherwise, we acknowledge the possibility to observe the result mentioned by the Reviewer. As our numerical results do not enable us to document these features, we prefer to avoid a discussion of this point in the revised manuscript.

- Line 153, please check the random walk formula for 2D

Thanks, we corrected a typo.

Technical corrections:

- Figure 3. Missing space “d and f Panels….”

Done.