

**Response to review comments #1 (RC1)** on Manuscript EGUSPHERE-2025-841 titled  
"Quantifying matrix diffusion effect on solute transport in subsurface fractured media"

**Note: Author's responses are in blue**

We would like to begin with thanking the reviewer for the critical and constructive review. The comments helped improve the quality and clarity of our manuscript. We carefully considered every review comment, and accordingly revised the manuscript.

The manuscript addresses a relevant and interesting question about the role of solute diffusion into the rock matrix during fracture flow. In this work, the authors present a "unified" parameter to assess the relevance of matrix diffusion and a correction term to the analytical solution of solute transport in a single fracture that mimics the effect of matrix diffusion without the need to explicitly model matrix diffusion, thus reducing the computational burden.

Thank you for the overall evaluation of the study.

I have several comments to improve the manuscript:

1) The manuscript remains descriptive in several places where quantitative limits and criteria would benefit the text. These include:

\* I131: "shows extremely small concentrations". I believe values would give the reader a better understanding.

Thanks for the comment. The "extremely small concentrations" here actually means a relative value rather than an absolute value, so we did not specifically provide the value. As we explain in the caption of Fig. 2, under large  $\theta$ ,  $D_m$  and small  $b$ ,  $u$ , matrix diffusion becomes significant and for the fracture-matrix coupled model, the strong matrix diffusion effect greatly retards the transport of solute in the fracture, and therefore within the calculation time window, the solute concentration at the monitoring point is nearly zero (Fig. R1).

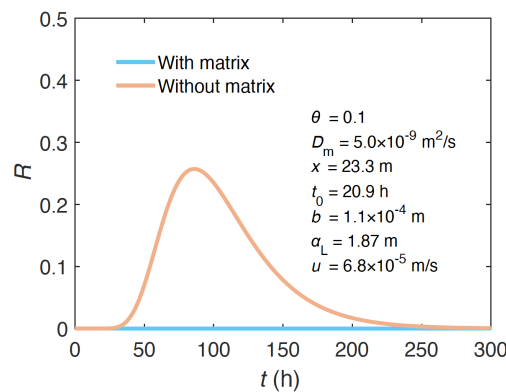


Fig. R1 Comparison of solute breakthrough curves from fracture-matrix coupled and fracture-only models under significant matrix diffusion effect.

Because  $R$  depends on the ratio between solute concentration from fracture-matrix coupled model and that from fracture-only model, we mainly concern about the relative solute concentration rather than the absolute value. According to our simulations, under significant matrix diffusion effect, the solute concentration from the fracture-matrix coupled model is over three magnitudes smaller than that from the fracture-only model. This is the main reason why we use "extremely small concentrations" to describe the solute breakthrough curve from the fracture-matrix coupled model. Based on the reviewer's suggestion, we have removed this qualitative description and added the relative concentration difference in the figure caption, as follows (Lines 147-149 in the updated manuscript).

*"Note that when matrix diffusion effect becomes significant under large  $\theta$ ,  $D_m$  and small  $b$ ,  $u$ , the solute concentration from fracture-matrix coupled model within the calculating window is over four magnitudes smaller than that from fracture-only model"*

\* I132: "R is approaching a maximum value". What specific value? The definition of  $R$  does not seem to approach an analytical limit, since the value depends on the number of data points (see comment below).

Thanks for the comment. This comment is highly relevant to the first comment. As we explained in the answer to the first comment, the reason that  $R$  approaches a maximum value under extremely significant matrix diffusion effect is because the solute concentration from the fracture-matrix coupled model becomes extremely small (Fig. R1). We can take the porosity  $\theta$  as an example for explanation. With the increase of  $\theta$ , the matrix diffusion effect gradually strengthens, and the solute concentration from the fracture-matrix coupled model gradually decreases (within the calculating time window), while the solute concentration from the fracture-only model remains constant (porosity does not affect solute transport in fracture-only model). As a result, the calculated  $R$  gradually increases and approaches to a maximum value.

The reviewer is correct that the definition of  $R$  does not imply any analytical limit, and more data points lead to larger  $R$  values. In this study, we fix the number of data points in breakthrough curves throughout all the calculations in Fig. 2 to ensure a fair comparison. Similar to the "extremely small concentrations" in the first comment, the "maximum" value of  $R$  here also depends on the values of  $\theta$ ,  $D_m$ ,  $b$  and  $u$ , and therefore we do not specifically provide the value.

Note that in a later comment, the reviewer suggests to use integral rather than discrete points to calculate  $R$ . We fully agree with the suggestion and have re-calculated  $R$  for all the cases in the manuscript.

\* I145: "an almost linear relationship". Can a  $R^2$  or any other fit quality parameter be provided to assess the quality of the linear fit? Is there any systematic deviation from the linear trend?

Thanks for the important suggestion. As mentioned by the reviewer, we do observe systematic deviation from the linear trend in the plots for  $\theta$ ,  $D_m$ , and  $b$ . As we can see from the plots for  $\theta$ ,  $D_m$ , and  $b$ , most curves show nearly perfect linear relationship in the log-log coordinate. However, under high  $\theta$ , high  $D_m$ , and small  $b$ , the curves become nonlinear and appear to approaching to an upper limit. The underlying mechanism is that the strong matrix diffusion effect leads to a nearly zero solute concentration for the fracture-matrix coupled model, and therefore the  $R$  gradually approaches to a maximum value, as we have explained in the answers to the previous two comments. Because of the nonlinear relationship under significant matrix diffusion effect, we do not show the  $R^2$  parameter. Nevertheless, from the statistical values (mean and standard deviation) of the slopes annotated in the figure, we can still figure out the strong overall linear relationship from the very small standard deviation values.

\* I171: "shows the largest correlation coefficient". I believe providing Pearson correlation coefficients explicitly in the text would benefit the readers ability to form their own opinion. Thanks for the suggestion and sorry for the confusion. In Fig. 2, we annotated a correlation coefficient ( $r$ ) for each plot. In fact, this correlation coefficient is exactly the Pearson correlation coefficient. We have revised the text as well as the caption of Fig. 2 to clearly demonstrate the results of Pearson correlation coefficient.

\* I184: "has a negligible effect". What do the authors consider negligible? Is it possible to give a quantitative limit.

Thanks for the comment. In this context, the "negligible effect" of matrix diffusion is a conclusion from Raven et al. (1988). Unfortunately, Raven et al. (1988) did not provide a quantitative criterion to determine whether the matrix diffusion is significant or negligible. Later relevant studies, such as Neretnieks (2002) and Reimus and Callahan (2007), did not use any quantitative criterion either.

In the current study, the impact of matrix diffusion on fracture solute transport is quantified by  $R$ , which is defined as the normalized residual sum of squares between the solute concentration from fracture-matrix coupled model and that from fracture-only model. According to the relationship between  $R$  and the newly proposed unified parameter  $\frac{\theta\sqrt{D_m x}}{2bu}$  as well as field data presented in Fig. 3, we identified a threshold of  $5 s^{1/2}$  for  $\frac{\theta\sqrt{D_m x}}{2bu}$  to determine whether matrix diffusion effect is significant or negligible. The threshold roughly corresponds to a  $R$  value of 50. Therefore, we would recommend that  $R < 50$  could be a reasonable quantitative criterion for negligible matrix diffusion effect. We have also added the criterion in the updated manuscript (Lines 214-216):

*"As a result, we recommend a threshold of  $5 \text{ s}^{1/2}$  (corresponding to a  $R$  value of approximately 50) as a reasonable criterion to determine whether matrix diffusion effect is significant or negligible (Fig. 3(f)).*

\* I261: "gives the best result". How was this concluded? Can you provide a quantitative measure from which this statement can be understood?

Thanks for the suggestion. To apply the proposed equivalent solute release function to the 3D case, an "average" flow velocity in the fracture needs to be calculated. According to previous studies, here we consider three methods to calculate average fracture flow velocity. The calculated average flow velocity is then used to derive the equivalent solute release function, which is further used in the 2D fracture-only model to simulate fracture solute transport. The effectiveness of the calculated average flow velocity can be evaluated by the matrix diffusion compensation performance of the derived equivalent solute release functions. Fig. R2 shows the comparison of the solute breakthrough curves for fracture-matrix coupled model, fracture-only model, and fracture-only model with equivalent solute release function. The comparison obviously indicates that the third flow velocity calculation method (divide well distance by the time difference between peak concentration time and half of solute injection time to calculate average flow velocity) gives the best compensation result.

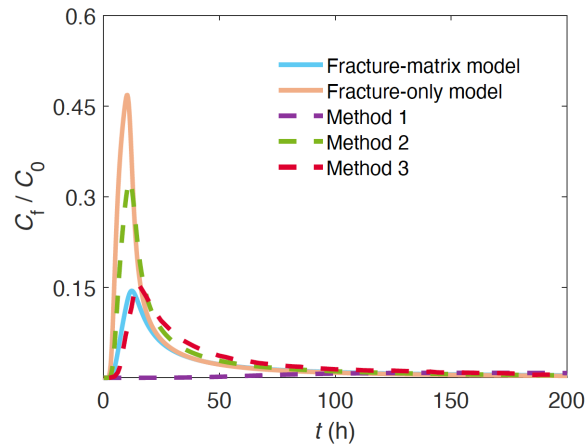


Fig. R2 Comparison of solute breakthrough curves from different models. The solid blue curve is from the fracture-matrix coupled model, and the solid orange curve is from the fracture-only model. The three dashed curves are results from fracture-only model applying the equivalent solute release function. The dashed purple curve uses the first method to calculate fracture average flow velocity and then derive the equivalent solute release function. The dashed green and red curves use the second and third methods to calculate fracture average flow velocity respectively.

To support the conclusion, we have added the comparison plot in the Supporting Information and have revised the manuscript as follows (Lines 290-292):

*"By comparing the matrix diffusion compensation performance of the equivalent solute release functions using the three flow velocities, we find that the flow velocity calculated through the third method exhibits the best result (Fig.S1 in Supporting Information)"*

\* I353: "remains a reasonable criterion". Similar to above: What quantitative measure was used to make this determination?

Thanks for the comment. The effectiveness of the proposed criterion can be assessed by the relationship between the unified parameter ( $\frac{\rho\sqrt{D_m x}}{2bu}$ ) and  $R$ , that a more linear relationship implies a better performance of the unified parameter in characterizing the significance of matrix diffusion effect. Therefore, we can use the Pearson correlation coefficient ( $r$ ) as a quantitative measure of the effectiveness of the criterion. As we can see from Fig. 10, the Pearson correlation coefficient is as high as 0.98, and therefore we make the conclusion that the criterion remains reasonable.

In addition, the rationale of the threshold ( $10 \text{ s}^{1/2}$ ) is supported by the lab and field data on the bottom panel of Fig. 10. The threshold accurately separate data points with significant matrix diffusion effect from that with negligible matrix diffusion effect.

2) The theoretical basis of the paper is sometimes unclear to me, partly because of potentially imprecise formulations

Thanks for pointing out this issue and sorry for the confusion. We have revised the manuscript according to your following detailed comments.

\* I37: "the underlying uncertainties". Uncertainties about what? Which relevant parameters are considered uncertain in which situation and to what degree?

Thanks for the comment. The uncertain parameters that we refer to include reservoir properties (permeability, porosity, diffusion coefficient, etc.), fracture geometry (location, size, orientation) and properties (aperture, permeability). Such uncertainties are widely recognized in many subsurface problems such as nuclear waste disposal, CO<sub>2</sub> sequestration, geothermal exploitation, etc., as we mentioned in the Introduction section. The main reasons of these parameter uncertainties are twofold. First, due to complex subsurface geological conditions, reservoir and fracture properties are normally high heterogeneous. Second, due to the technical and economic difficulties in drilling and subsurface measurements, available geological and geophysical observations/measurements are generally spatially sparse and therefore insufficient to accurately infer the heterogeneous properties.

The degree of parameter uncertainty varies from case to case and largely depends on the inherent complexities of the parameter (such as how heterogeneous the property is) as well as

the amount of data directly or indirectly related to the parameter. For example, Vogt et al. (2012) inferred the permeability of a fractured geothermal reservoir and the result indicated an uncertainty of about one order of magnitude. Wu et al. (2021) inferred fracture aperture from tracer data. Their results showed that the mean aperture was approximately 2.5 mm while the associated uncertainty can be as high as 2 mm. These studies demonstrated that due to the lack of data to accurately constrain reservoir and fracture parameters, the underlying uncertainty could be rather high.

We have also revised the manuscript to clearly demonstrate parameter uncertainties in the context of subsurface reservoir modeling (Lines 35-40):

*"Another challenge of such high-fidelity models is the inevitable uncertainties associated with reservoir and fracture parameters, such as matrix porosity and permeability as well as fracture geometry and aperture, which might be highly heterogeneous under complex geological conditions. Due to the technical and economic difficulties in drilling and directly measuring subsurface reservoirs, available geological and geophysical data are normally spatially scarce and far from adequate to constrain these parameter uncertainties."*

\* Eq. 2: I think the derivation should be in terms of  $z$ , not  $x$  in the diffusion part, to be consistent with the original sources, such as Graf & Simmons (2009). If the authors derive from the original source, this needs considerable attention and explanation.

Thanks for pointing out the error here. We have revised the equation according to the suggestion.

\* Eq. 4: The symbol  $\xi$  is missing an explanation \* l113f: The order for  $C_f$  and  $C_{mf}$  should be "fracture-only and fracture-matrix coupled models, respectively", I guess.

Thanks for the comment. First we want to sincerely thank the reviewer for carefully checking the equations and notations in the manuscript.

The symbol  $\xi$  here is an integral variable and does not have any physical meaning. We have added an explanation for  $\xi$  in the updated manuscript (Lines 116-119):

*"in which  $C_f(x, t)$  is the solute concentration in the fracture at a distance of  $x$  from the solute release point,  $C_0$  is the solute concentration at the release point,  $t_0$  is the solute release duration,  $u$  is fluid velocity in the fracture,  $D_f$  is the fracture hydrodynamic dispersion coefficient,  $\theta$  is the matrix porosity,  $D_m$  is the matrix diffusion coefficient,  $b$  is the half-aperture of the fracture, and  $\xi$  is an integral variable."*

The reviewer is correct that  $C_f$  and  $C_{mf}$  denote solute concentrations calculated from fracture-only and fracture-matrix coupled models respectively. We have revised the manuscript accordingly.

\* Eq. 6: The definition of  $R$  in its discrete form is irritating for me. Should it not follow an integral form related to a tracer recovery form or similar? In its current form,  $R$  seems to depend on the number of data points chosen in the breakthrough curves (BTCs), which could be an arbitrary number or at least depends on the spatial discretization, and makes comparison between BTCs difficult, as I assume the same  $N$  must be used. I think this has a major impact on the analysis presented here. The chosen form, if it remains in the revision, should be justified and critically discussed to improve the readers understanding of this result.

Thanks for this important point. We agree with the reviewer that the integral form instead of the discrete form should be used to calculate  $R$ . According to the suggestion, we have used a new definition for  $R$  and re-calculate all the cases in the study. The new equation for  $R$  is as follows (Equation (6) in the updated manuscript):

$$R = \int_0^{T_0} \left( \frac{C_f - C_{mf}}{C_{fmax}} \right)^2 dt \quad (R1)$$

in which  $C_f$  and  $C_{mf}$  denote solute concentrations calculated from fracture-only and fracture-matrix coupled models respectively,  $C_{fmax}$  is the peak solute concentration from the fracture-only model, and  $T_0$  is the simulation time.

In the original manuscript, the number of data points in each BTCs is quite dense. The total number of data points is  $N = 181$ , meaning that the interval between data points is 1000 s (the whole simulation time is 50 hours). We re-calculate  $R$  using the new equation and compare the  $R$  values with that calculated through the old discrete form equation. It turns out that the new  $R$  is 1000 times of the old  $R$  because the data interval is 1000 s in the old discrete form equation. In other words, changing the  $R$  equation from the discrete form to integral form changes the absolute values of  $R$  but does not affect the data trends and patterns in Figs. 2, 3, 7, 8, 9 and 10. In the updated manuscript, we have revised Figs. 2, 3, 7, 8, 9 and 10 according to the new  $R$  equation results.

\* Table 1: The given values are not justified. Why were these values chosen? What kind of host rock/fracture system and application do the authors have in mind for their analysis?

Thanks for the comment. The value ranges used in Table 1 are mostly from previous tracer transport studies, including both laboratory/field tests and numerical modeling. We do not target a specific rock type or fracture system, as the purpose of this study is to analyze the general effect of matrix diffusion on solute transport in fractures. Note that we consider a relatively wide value range to cover most typical reported parameter values in the literature, and we have added relevant references in the updated manuscript (Lines 134-137):

*"We consider a relatively wide parameter range to include both lab and field scale scenarios (Table 1) according to previous studies in the literature (Grisak et al., 1981; Novakowski et al., 1985; Shapiro and Nicholas, 1989; Himmelsbach et al., 1998; Jardine et al., 1999; Maloszewski et al., 1999; Reimus, 2003, 2007; Zhou et al., 2006)."*

The table below shows parameters reported in previous laboratory/field tracer tests, and we also include the table in the Supporting Information (Table S1 in Supporting Information).

Table R1. Laboratory and field experiments on conservative solute transport in fractured media from the literature. In the last column, S means significant matrix diffusion effect, and N means negligible matrix diffusion effect.

Reference	Solute	Parameters							Matrix diffusion effect
		$x$ m	$u$ m/s	$t_0$ s	$2b$ $\mu\text{m}$	$\alpha_L$ m	$\theta$	$D_m$ $\text{m}^2/\text{s}$	
Lenda and Zuber (1970)	Tritium	22	0.0024		590	7.4	0.064	$1.0 \times 10^{-10}$	S
Kreft et al. (1974)	Tritium	21.3	0.0012		400	0.96	0.064	$1.0 \times 10^{-10}$	S
Ivanovich and Smith (1978)	Tritium	8	0.001		150	0.64	0.275	$1.0 \times 10^{-10}$	S
Grisak et al. (1981)	Chloride	0.76	$3.4 \times 10^{-4}$	345 600	40	0.04	0.35	$5.0 \times 10^{-11}$	S
Novakowski et al. (1985)	$^{82}\text{Br}$	10.6	$4.7 \times 10^{-4}$	600	510	1.4	0.003	$4.8 \times 10^{-12}$	N
Raven et al. (1988)	$^{82}\text{Br}$	12.7	$6.3 \times 10^{-4}$	15	135	0.95	0.003	$1.0 \times 10^{-10}$	N
Shapiro and Nicholas (1989)	Sodium chloride	19.8	0.0119	60	5340	0.53 8	0.135	$5.7 \times 10^{-8}$	S
	Sodium chloride	17.2	0.0177	60	4160	0.16 1	0.12	$3.4 \times 10^{-8}$	
Maloszewski et al. (1990)	Deuterium	10.2	0.0044		250	0.2	0.4	$1.0 \times 10^{-10}$	S
Andersson et al. (1993)	$^{131}\text{I}$	168	0.0016		1000	5.5	0.002	$1.0 \times 10^{-10}$	N
	$^{82}\text{Br}$	223	0.0027		1000	13.5	0.002	$1.0 \times 10^{-10}$	
McKay et al. (1993)	Bromide	4	$1.2 \times 10^{-7}$	216 00	11	0.1	0.000 1	$5.8 \times 10^{-10}$	S
	$^{18}\text{O}$	6	$8.1 \times 10^{-7}$	432 000	21	0	0.000 1	$5.5 \times 10^{-10}$	
Novakowski and Lapcevic (1994)	Lissamine FF	5.21	$4.0 \times 10^{-6}$	642	282	0.06	0.009	$4.5 \times 10^{-10}$	S
		5.22	$4.0 \times 10^{-6}$	642	57	0.04	0.028	$4.5 \times 10^{-10}$	
		11.64	$4.0 \times 10^{-6}$	642	248	0.4	0.013	$4.5 \times 10^{-10}$	
		11.78	$4.0 \times 10^{-6}$	642	154	0.3	0.008	$4.5 \times 10^{-10}$	
		14.94	$4.0 \times 10^{-6}$	642	235	0.25	0.012	$4.5 \times 10^{-10}$	
		16.58	$4.0 \times 10^{-6}$	642	126	0.3	0.024	$4.5 \times 10^{-10}$	



		19.18	$4.0 \times 10^{-6}$	642	241	0.4	0.011	$4.5 \times 10^{-10}$	
		26.61	$4.0 \times 10^{-6}$	642	243	0.3	0.008	$4.5 \times 10^{-10}$	
Hadermann and Heer (1996)	Uranine	4.9	$6.9 \times 10^{-5}$		930	0.25	0.15	$5.5 \times 10^{-11}$	S
	Eosine	346	$2.2 \times 10^{-4}$		434	3.46	0.03	$4.5 \times 10^{-10}$	
	Uranine	235	$4.0 \times 10^{-4}$		444	3.91	0.049	$4.5 \times 10^{-10}$	
	Pyranine	48	0.0027		576	2.45	0.061	$1.5 \times 10^{-9}$	
	Pyranine	11.2	0.0016		110	2.14	0.035	$1.5 \times 10^{-9}$	
Himmelsbach et al. (1998)	Pyranine	21.4	$4.3 \times 10^{-4}$		256	0.3	0.053	$1.5 \times 10^{-9}$	S
	Pyranine	11.2	0.0015		265	0.3	0.054	$1.5 \times 10^{-9}$	
	D <sub>2</sub> O	11.2	0.0015		107	0.17	0.048	$2.5 \times 10^{-9}$	
	Eosine	11.2	0.0044		117	0.17	0.035	$4.5 \times 10^{-10}$	
	Uranine	11.2	0.0026		268	0.25	0.03	$4.5 \times 10^{-10}$	
Maloszewski et al. (1999)	bromide	11	$1.5 \times 10^{-4}$		232	1.64	0.023	$4.7 \times 10^{-11}$	
		225	0.0027		232	2.25	0.023	$4.7 \times 10^{-11}$	S
		330	0.004		232	6.6	0.023	$4.7 \times 10^{-11}$	
		6	0.0012	155 520 00	84	0.1	0.2	$6.9 \times 10^{-9}$	
	He	9.2	0.0012	155 520 00	84	0.1	0.2	$6.9 \times 10^{-9}$	S
		16.8	0.0012	155 520 00	84	0.1	0.2	$6.9 \times 10^{-9}$	
Jardine et al. (1999)		6	0.0012	155 520 00	84	0.1	0.2	$4.0 \times 10^{-9}$	
	Ne	9.2	0.0012	155 520 00	84	0.1	0.2	$4.0 \times 10^{-9}$	S
		16.8	0.0012	155 520 00	84	0.1	0.2	$4.0 \times 10^{-9}$	
		6	0.0012	155 520 00	84	0.1	0.2	$2.3 \times 10^{-9}$	
	Br	9.2	0.0012	155 520 00	84	0.1	0.2	$2.3 \times 10^{-9}$	S
		16.8	0.0012	155 520 00	84	0.1	0.2	$2.3 \times 10^{-9}$	
Lapcevic et al. (1999)	Fluorescent dye	10.8	$5.6 \times 10^{-5}$	396	98	0.1	0.015	$1.8 \times 10^{-10}$	
		11.8	$5.6 \times 10^{-5}$	396	248	0.1	0.012	$1.8 \times 10^{-10}$	
		15.9	$6.7 \times 10^{-5}$	396	282	0.1	0.015	$1.8 \times 10^{-10}$	S
	Lissamine FF	19.1	$5.6 \times 10^{-5}$	396	154	0.1	0.019	$1.8 \times 10^{-10}$	
		23.7	$5.6 \times 10^{-5}$	396	85	0.1	0.01	$1.8 \times 10^{-10}$	

		34.8	$7.8 \times 10^{-5}$	396	125	0.1	0.026	$1.8 \times 10^{-10}$	
		41.2	$7.5 \times 10^{-5}$	396	230	0.1	0.027	$1.8 \times 10^{-10}$	
Becker and Shapiro (2000, 2003)	HDO	36	$3.7 \times 10^{-4}$		400	1.8	0.015	$6.0 \times 10^{-13}$	N
Callahan et al (2000)	Iodide	0.16	$8.4 \times 10^{-6}$	115 200	700	0.01 04	0.27	$3.7 \times 10^{-10}$	
	Iodide	0.16	$8.4 \times 10^{-5}$	104 40	700	0.01 04	0.27	$3.7 \times 10^{-10}$	
	Iodide	0.16	$3.4 \times 10^{-5}$	273 60	700	0.01 04	0.27	$3.7 \times 10^{-10}$	S
	Bromide	0.16	$1.6 \times 10^{-5}$	415 08	1160	0.05 37	0.27	$1.3 \times 10^{-9}$	
	PFBA	0.16	$1.6 \times 10^{-5}$	415 08	1160	0.05 35	0.27	$4.3 \times 10^{-10}$	
Reimus (2003)	PFBA	30	$7.0 \times 10^{-7}$		7190	44	0.12	$7.2 \times 10^{-10}$	
	Bromide	30	$7.0 \times 10^{-7}$		7190	44	0.12	$2.1 \times 10^{-9}$	S
	Lithium	30	$7.0 \times 10^{-7}$		7190	44	0.12	$1.0 \times 10^{-9}$	
Witthüser et al. (2003)	Uranine	10	$9.6 \times 10^{-4}$		397	0.11	0.51	$1.5 \times 10^{-11}$	
	Lithium	10	$1.0 \times 10^{-3}$		405	0.11	0.51	$2.6 \times 10^{-11}$	S
Liu et al. (2004)	Bromide and PFBA	20	$5.8 \times 10^{-6}$		740		0.11	$2.1 \times 10^{-9}$	S
Novakowski et al. (2004)	KBr	9.5	$3.5 \times 10^{-4}$	50	697	0.18	0.11	$1.9 \times 10^{-9}$	
	Lissamine FF	9.5	$3.5 \times 10^{-4}$	50	697	0.18	0.11	$4.5 \times 10^{-10}$	
	KBr	9.5	$3.5 \times 10^{-4}$	50	918	0.31	0.18	$1.9 \times 10^{-9}$	S
	Lissamine FF	9.5	$3.5 \times 10^{-4}$	50	918	0.31	0.18	$4.5 \times 10^{-10}$	
Reimus (2007)	Bromide	0.16	$5.9 \times 10^{-6}$		970		0.272	$6.2 \times 10^{-10}$	
		0.17	$3.4 \times 10^{-5}$		250		0.138	$3.8 \times 10^{-11}$	
		0.12	$6.4 \times 10^{-5}$		260		0.288	$3.0 \times 10^{-10}$	
		0.22	$1.5 \times 10^{-5}$		490		0.298	$1.0 \times 10^{-10}$	
		0.25	$1.5 \times 10^{-5}$		650		0.297	$2.0 \times 10^{-11}$	
		0.24	$5.0 \times 10^{-5}$		230		0.369	$2.5 \times 10^{-10}$	S
		0.23	$6.0 \times 10^{-6}$		380		0.303	$4.3 \times 10^{-10}$	
		0.15	$3.5 \times 10^{-5}$		270		0.111	$3.3 \times 10^{-11}$	
		30	$2.5 \times 10^{-4}$		1800	6.3	0.064	$4.5 \times 10^{-11}$	
		30	$1.0 \times 10^{-5}$		1800	6.3	0.02	$4.5 \times 10^{-11}$	
		30	$9.2 \times 10^{-6}$		850	3.2	0.019	$4.5 \times 10^{-11}$	
Zhou et al. (2006)	Iodide	30	$4.0 \times 10^{-4}$		534	0.59	0.049	$6.1 \times 10^{-11}$	S

\* Section 2.2: Why do the authors focus on the linear part of the relationships? Isn't the nonlinear part the much more interesting relationship?

Thanks for the comment. In Section 2.2, we aim to comprehensively investigate how different parameters affect the strength of matrix diffusion effect (represented by  $R$ ). Fig. 2 shows that  $\theta$ ,

$D_m$  and  $x$  exhibit a positive relationship with  $R$ , while  $b$  and  $u$  exhibit a negative relationship with  $R$ . Fig. 2 also indicates that for most parameter sets tested in this study, there exists a strong linear relationship between reservoir/fracture parameters and  $R$  in a log-log coordinate. Such a linear relationship is the primary result from Fig. 2, and is further used to derive the unified parameter in subsequent sections.

We also notice that some curves show a non-linear relationship in the plots for  $\theta$ ,  $D_m$ ,  $b$  and  $u$ . As we explained earlier, the main reason is that under large  $\theta$ ,  $D_m$  and small  $b$ ,  $u$  conditions, matrix diffusion becomes significant and for the fracture-matrix coupled model, the strong matrix diffusion effect greatly retards the transport of solute in the fracture, and therefore within the calculating time window, the solute concentration at the monitoring point is nearly zero (Fig. R1), and the calculated  $R$  reaches a maximum value. Further increasing  $\theta$ ,  $D_m$  or decreasing  $b$ ,  $u$  does not change  $R$ . We agree with the reviewer that this is an interesting finding but since the purpose of Fig. 2 is to reveal the sensitivity of matrix diffusion effect to reservoir/fracture parameters, we only focus on the majority linear curves. Nevertheless, we provide an explanation for the nonlinear relationship in the caption of Fig. 2 (Lines 147-150 in the updated manuscript).

*"Note that when matrix diffusion effect becomes significant under large  $\theta$ ,  $D_m$  and small  $b$ ,  $u$ , the solute concentration from fracture-matrix coupled model within the calculating window is over three magnitudes smaller than that from fracture-only model, and the calculated  $R$  approaches to a maximum value, resulting in the non-linear relationship between the parameter and  $R$ ."*

\* I175: The proposed unified parameter is never derived or motivated. Its physical interpretation is not given. This makes it very difficult for the reader to assess its full potential as the parameter seems rather arbitrary in its present form. How did the authors arrive at this parameter? Especially with the results in I194 and I220f, an interpretation of the unified parameter would be very helpful for the reader.

Thanks for this important comment about the theoretical basis of the unified parameter. We fully agree with the reviewer that a theoretical derivation and physical interpretation of the unified parameter is important. We want to clarify that the unified parameter is not arbitrarily determined but derived from the parameter sensitivity analyses in Fig. 2. Moreover, we also prove that the unified parameter can be theoretically derived from analytical solutions in Section 2.4.

In Section 2.2, we perform a comprehensive analysis on the effect of various reservoir/fracture parameters on matrix diffusion strength. The results in Fig. 2 clearly demonstrate that the matrix diffusion effect increases with the increase of  $\theta$  and  $D_m$ , and decreases with the increase of  $b$ ,  $u$ , and  $x$ . The relative dominance of these parameters on matrix diffusion can be roughly estimated from the slope of the almost linear curves in Fig. 2. According to the statistics of curve slopes summarized in the embedded table in Fig. 2, we find that the slopes for  $\theta$ ,  $D_m$ ,  $b$ ,  $u$  and  $x$  are

approximately 2, 1, -2, -2 and 2 respectively. It is therefore straightforward to propose a lumped parameter by using the slopes of parameters as their exponents, i.e.,  $\frac{\theta\sqrt{D_m x}}{2bu}$ . We have also revised the manuscript to explicitly explain that the unified parameter is first derived from the sensitivity analyses (Lines 192-194 in the updated manuscript):

*“Following the sensitivities in Fig. 2, we propose a new unified parameter according to the curve slopes of different parameters, which turns out to have a form of  $\frac{\theta\sqrt{D_m x}}{2bu}$ , and then analyze its capability in quantifying matrix diffusion effect (Fig. 3).”*

We understand that although the above derivation uses the quantitative sensitivity results to determine the exponents of different parameters, it still remains qualitative or empirical, as there lacks a solid theoretical base, and the physical meaning of the unified parameter is unclear. Nevertheless, the derivation of the equivalent solute release function in Section 2.4 provides a rigorous theoretical base for the unified parameter. As we explained in Section 2.4, the equivalent solute release function aims to compensate for the matrix diffusion effect in fracture-only models by tailoring solute release function. In other words, the equivalent solute release function actually represents matrix diffusion effect on fracture solute transport. By comparing the equivalent and original solute release function, we can quantitatively assess the strength of matrix diffusion effect.

The detailed derivation of the equivalent solute release function is provided in Text S1 in the Supporting Information. We use the method from Liu et al. (2018) to decouple the effect of fracture advection-dispersion and the effect of matrix diffusion in the classical ADE analytical solution in Laplace domain, and then incorporate the term representing matrix diffusion effect into the injection term to get an equivalent injection term (i.e., the equivalent solute release function). The ratio between the equivalent and original solute release functions can be derived as follows (Eq. (7) in the manuscript),

$$\frac{C(t)}{C_0} = \begin{cases} \operatorname{erfc}\left(\frac{\theta\sqrt{D_m x}}{2bu\sqrt{t}}\right), & 0 \leq t \leq t_0 \\ \operatorname{erfc}\left(\frac{\theta\sqrt{D_m x}}{2bu\sqrt{t}}\right) - \operatorname{erfc}\left(\frac{\theta\sqrt{D_m x}}{2bu\sqrt{t-t_0}}\right), & t > t_0 \end{cases} \quad (R2)$$

Where  $C(t)$  and  $C_0$  represent the equivalent and original solute release functions respectively. The right side of the equation contains complementary error functions, which are functions of time and depend on five reservoir/fracture parameters ( $\theta$ ,  $D_m$ ,  $b$ ,  $u$  and  $x$ ). A striking finding is that the coefficient within the complementary error functions is exactly identical to the proposed unified parameter  $\frac{\theta\sqrt{D_m x}}{2bu}$ , indicating that the equivalent solute release function can be uniquely determined by the unified parameter. Because the equivalent solute release function is

theoretically derived, this finding provides a solid theoretical base for the rationale of the unified parameter.

With the equivalent solute release function, we can further analyze the physical meaning of the unified parameter. Fig. R3 below compares the original and equivalent solute release curves to demonstrate how the solute release curve is tailored to account for matrix diffusion. In general, solute concentration is reduced during the release period and increased after solute release stops. This means that the matrix diffusion effect can be modeled as a sink during the release period, and a source after solute release stops. The strength of the “source/sink” is determined by the unified parameter  $\frac{\theta\sqrt{D_m x}}{2bu}$  and gradually diminishes with time. In other words, the unified parameter  $\frac{\theta\sqrt{D_m x}}{2bu}$  quantitatively determines the strength of matrix diffusion effect.

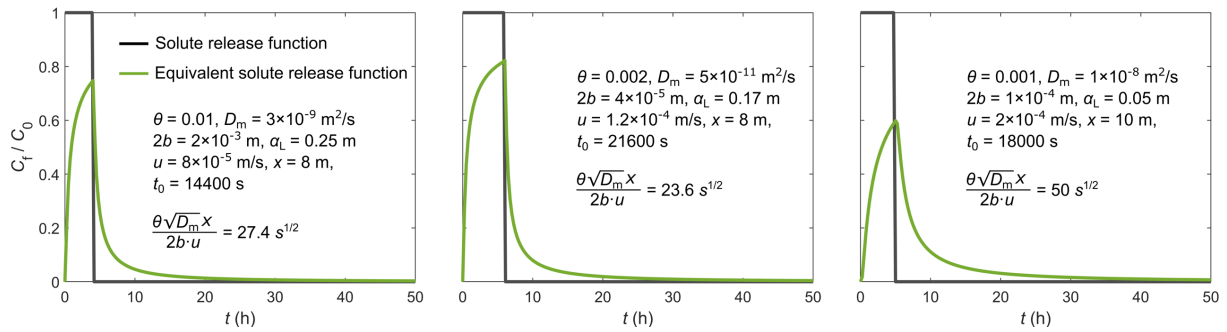


Fig. R3 Comparison between original and equivalent solute release curves under various parameters.

We have revised the manuscript to further demonstrate the theoretical rationale as well as the physical meaning of the proposed unified parameter (Lines 241-250 in the updated manuscript):

*“Interestingly, the coefficient within the complementary error functions in equation (7) is exactly identical to the newly proposed unified parameter  $\frac{\theta\sqrt{D_m x}}{2bu}$ , indicating that the deviation of equivalent solute release function  $C(t)$  from  $C_0$  directly depends solely on  $\frac{\theta\sqrt{D_m x}}{2bu}$ . Although the unified parameter is first empirically proposed based on the sensitivity analyses in Fig. 1, Eq. (7) provides a strong corroboration for the theoretical rationality of the unified parameter in quantifying matrix diffusion effect is further corroborated by the derivation of the equivalent solute release function  $C(t)$ . The underlying logic of the equivalent solute release function is to consider matrix diffusion as a source/sink for fracture solute transport. when solute concentration in fracture is larger than that in matrix (during solute injection period), solute will diffuse into the matrix (matrix as a sink term), while when solute concentration in fracture is smaller than that in matrix (after solute injection), solute in the matrix gradually diffuses into the fracture (matrix as a source term). Essentially, the equivalent solute release function accurately compensates for matrix*

diffusion by delicately capture the source/sink effect of matrix on fracture solute transport processes."

\* Section 3: The numerical model lacks a detailed methodological description. What equations have been solved? With which software? Has the code been benchmarked? Initial conditions? Boundary conditions? Compared to other models? ...

Thanks for the comment. The numerical model solves the advection-dispersion equation to simulate solute transport in the fracture-matrix model. Because the advection-dispersion equation has been widely reported in the literature, we do not specifically provide the equation in the manuscript. Instead, we have provided relevant references about advection-dispersion equation in the manuscript in case readers are curious on the underlying equation (Lines 270-272 in the updated manuscript).

*"We first simulate fracture flow field and then solve the advection-dispersion equation to simulate solute transport process (Grisak and Pickens, 1980; Tang et al., 1981; Wu et al., 2019)."*

The equation is solved using COMSOL Multiphysics, a widely used commercial software for multi-physics coupled simulations in subsurface reservoirs. Many previous studies have used COMSOL Multiphysics to simulate solute transport in fracture-matrix systems, thoroughly demonstrating the feasibility of the software in solute transport modeling. Therefore, we do not include extra benchmark studies to verify the capability of the software. Again, we provide references that use COMSOL Multiphysics for solute transport modeling in the updated manuscript (Lines 277-279):

"The advection-dispersion equation with the specified boundary and initial conditions are numerically solved using the finite element method implemented in COMSOL Multiphysics (Hu et al., 2020; Want et al., 2023)."

As we mentioned in the manuscript, we first simulate fracture flow field and then solve the advection-dispersion equation to simulate solute transport process. Therefore, the initial and boundary conditions need to be specified for both the flow and transport processes. For the flow modeling, we assume a hydrostatic initial pressure and the lateral model boundaries are assumed impermeable. Fluid is injected into the fracture through the injection point annotated in Fig. 5 with a flow rate of  $q$  (randomly generated as mentioned earlier), and the production point is an open boundary with the pressure fixed at its initial value. For the solute transport modeling, the solute is injected with a constant concentration of  $C_0$  for a period of  $t_0$  (randomly generated as mentioned earlier). The production point is an open boundary for solute and the lateral model boundaries are assumed impermeable for solute. To more clearly illustrate the initial and boundary conditions, we have revised the manuscript as below (Lines 273-277 in the updated manuscript):

*"A hydrostatic initial pressure is assumed in the model, and the pressure at the production well is fixed at its initial pressure. Fluid is injected into the fracture through the injection well with a flow rate of  $q$ , and solute is injected with a constant concentration of  $C_0$  for a time period of  $t_0$ . Note that the production well acts as an open boundary for both fluid and solute, and the lateral boundaries of the 3D and 2D models are assumed impermeable for both fluid and solute."*

\* I265: "the fracture-only model overestimates solute transport". What is the result for the unified parameter derived earlier? Does this parameter also indicate that matrix diffusion is relevant? Thanks for the comment. The case analyzed in Fig. 6 is the third case illustrated in Fig. 4(b). The parameters for this case, as annotated in Fig. 4(b), are  $\theta = 0.0026$ ,  $D_m = 3 \times 10^{-9} \text{ m}^2/\text{s}$ ,  $2b = 2 \times 10^{-4} \text{ m}$ ,  $\alpha_L = 1.63 \text{ m}$ ,  $u = 4.4 \times 10^{-4} \text{ m/s}$ ,  $t_0 = 97492 \text{ s}$  (also annotated in the caption of Fig. 6). The unified parameter is therefore  $80.9 \text{ s}^{1/2}$ , much higher than the previously recommended threshold of  $5 \text{ s}^{1/2}$ . Therefore, the reviewer is correct that the unified parameter also indicates a significant matrix diffusion effect. In the updated manuscript, we have specifically mentioned the value of the unified parameter for this case (Lines 295-296):

*"We select the third case in Fig. 4(b) with a unified parameter of  $80.9 \text{ s}^{1/2}$  (i.e., significant matrix diffusion effect) to further compare the distribution of solute concentration from fracture-matrix coupled and fracture-only models."*

3) The structure of the manuscript needs to be improved.

\* The introduction could more clearly state the computational burden. Currently it only seems to be an additional parameter to be guessed with a simple diffusion equation, which seems not very computationally cumbersome these days. Especially as the authors focus on a solution for a single fracture and not fracture networks.

Thanks for the suggestion. The reviewer is correct that reducing computational burden is one of the main motivations for this study and needs to be further illustrated in the Introduction section. We agree with the reviewer that modeling solute transport in a fracture-matrix system with only one single fracture is not very computationally cumbersome, even with a very fine mesh. However, the problems that we considered in this study, such as solute transport prediction and solute data (such as tracer data) interpretation, may require tens or hundreds of thousands of such solute transport modeling trials. The computational burden is not from a single simulation, but from numerous simulations.

As we explained in the manuscript, subsurface reservoir and fracture parameters generally face significant uncertainties, meaning that a reliable solute transport prediction requires numerous solute transport simulations under various reservoir and fracture parameters to accommodate parameter uncertainties. Solute data interpretation, such as tracer data inversion for reservoir

characterization, is generally performed in an iterative way and also involves tremendous solute transport simulations. We can use our previous work on field tracer data inversion to characterize fracture aperture as an example to further illustrate the computational burden associated with subsurface solute transport analysis. Details can be found in Wu et al. (2021). In this work, we aimed to use tracer recovery data collected at the EGS Collab testbed (a meso-scale field testbed for enhanced geothermal system in South Dakota, USA) to infer fracture aperture distribution. We used a stochastic inversion framework, i.e., generating numerous fracture aperture models and running tracer transport simulations to obtain tracer breakthrough curves. The obtained tracer data were then compared with field tracer data to identify fracture aperture models that could reproduce field tracer data. To obtain satisfactory fitting results, we run 50,000 tracer transport simulations. If we use a 3D matrix-fracture coupled model, each simulation costs approximately 0.5 hour to 10 hours on a single core, while if we use a 2D fracture-only model, each simulation costs approximately 14 s to 2 hours. To run the 50,000 simulations, using 3D matrix-fracture coupled model requires extremely huge computational resources (25000 ~ 500,000 core hours) that are almost unrealistic for most research organizations. We therefore chosen the 2D fracture-only model to run tracer transport simulations and totally 40,000 core-hours were used. We believe this case strongly demonstrates the necessity of simplifying 3D matrix-fracture coupled models to 2D fracture-only models from a computational feasibility perspective. Of course, some advanced tracer data inversion algorithms can effectively reduce the total simulations required to fit tracer data, but using 2D models can still substantially reduce the overall computational burden.

To address the concern of the reviewer, we have added the example of Wu et al. (2021) in the updated manuscript (Lines 43-45) to further emphasize the computational issue. However, we tend to not include the specific core-hour numbers, as they are specifically for the case in EGS Collab testbed.

*"For example, Wu et al. (2021b) used a stochastic inversion framework to interpret tracer recovery data from the EGS Collab testbed and infer fracture aperture distribution. A total of 50,000 tracer transport simulations were performed to obtain satisfactory fitting results, requiring substantial computational resources."*

\* I67: smaller apertures lead to higher flow velocities. Hence, it remains unclear how "smaller fracture apertures and flow velocities" should result in the same effect regarding matrix diffusion. Thanks for the comment. We understand the reviewer's concern of the "conflict" here. The premise of "smaller aperture leads to higher flow velocity" is that fracture flow rate remains constant. If we fix the injection flow rate into a fracture, then aperture and flow velocity are mutually dependent on each other. A smaller aperture means a higher flow velocity. However, if we fix the injection pressure instead of injection rate, then a smaller aperture will cause a lower



flow velocity because fracture permeability decreases with the decrease of aperture. In previous studies on the impact of different parameters on matrix diffusion, aperture and velocity are treated as two independent parameters, and therefore they reached the conclusion that smaller fracture aperture and flow velocity lead to more significant matrix diffusion. Fig. R4 shows the parameter sensitivity studies from Grisak and Pickens (1980). For the analysis of fracture aperture, flow velocity is fixed, while for the analysis of flow velocity, fracture aperture is fixed.

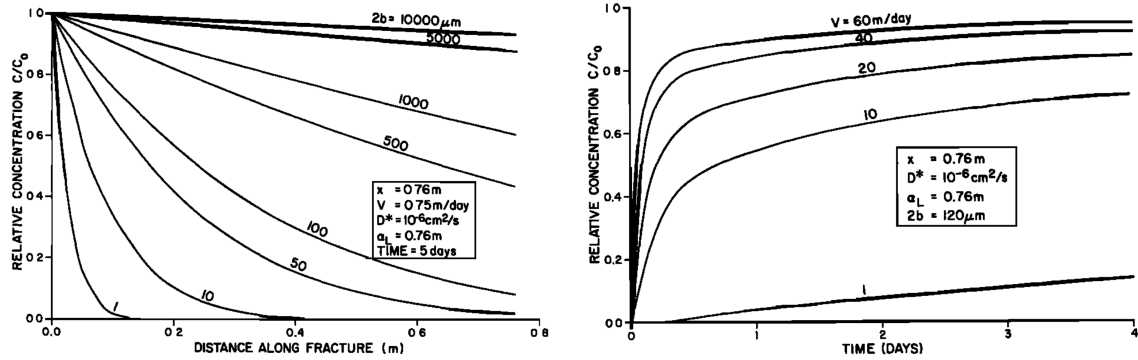


Fig. R4 Effect of fracture aperture (left) and flow velocity (right) on solute concentration profiles in a fracture (Grisak and Pickens, 1980).

\* I86: The introduction would benefit from a concise discussion of the other five unified and dimensionless parameters from literature, their underlying assumptions and derivations. Thanks for the suggestion. Table 2 in the manuscript lists the expressions of the five unified parameters from the literature that have been used as quantitative measures of matrix diffusion strength. Below we first introduce each unified parameter in terms of their derivation and then describe how we revise the manuscript to address this comment.

The first unified parameter is called diffusion parameter with an expression of  $\frac{\theta\sqrt{D_m}}{2b}$ , which is originally from Maloszewski and Zuber (1985). Note that this unified parameter is not dimensionless but has a unit of  $s^{-1/2}$ . Maloszewski and Zuber (1985) developed a single fracture model for tracer transport in fractured media and derived the analytical solution for tracer concentrations in the fracture. The analytical solution contains three lumped parameters, i.e., mean travel time  $x/u$ , Peclet number  $ux/D_m$ , and diffusion parameter  $\frac{\theta\sqrt{D_m}}{2b}$ . Many studies then used the diffusion parameter to quantify matrix diffusion rates (Liou, 2007; Reimus and Callahan, 2007; Zhou et al., 2007). The diffusion parameter considers the effects of porosity, diffusion coefficient and fracture aperture on matrix diffusion, but other relevant parameters such as the mean travel time are not incorporated.

The second unified parameter is named diffusion distance with an expression of  $\sqrt{2D_m \cdot t^*}$  and a unit of m (Callahan et al., 2000). This parameter is proposed to estimate the penetration depth of solute from fracture into the surrounding matrix. Obviously, the more significant the matrix

diffusion effect, the larger the penetration depth. Nevertheless, Callahan et al. (2000) did not provide the derivation of the unified parameter.

The third unified parameter ( $\frac{\theta\sqrt{D_m\cdot t^*}}{2b}$ ) and the fourth unified parameter ( $\frac{\theta\sqrt{D_m\cdot t^*}}{b}$ ) have the same parameter combination and are both dimensionless. Neretnieks (2002) used a single fracture model with matrix diffusion to describe tracer transport in fractured rocks, and derived the analytical solution for tracer concentration in the fracture. Based on the analytical solution, Neretnieks (2002) defined a material and flow path property group  $G = LW\theta D_m^{1/2}$ , where  $L$  and  $W$  are fracture length and width respectively. The analytical solution mainly depends on  $G$ . In the following analysis, Neretnieks (2002) used the term  $G/(q(t^*)^{1/2})$  to determine whether matrix diffusion has a significant effect on fracture tracer transport. The term  $G/(qt^{1/2})$  actually equals to the fourth unified parameter  $\frac{\theta\sqrt{D_m\cdot t^*}}{b}$ . Hyman et al. (2019) further used the term to quantify the strength of matrix diffusion for solute transport in fracture networks. Unfortunately, Neretnieks (2002) did not provide theoretical explanation for this unified parameter either.

The fifth unified parameter  $\frac{1}{b}\sqrt{\frac{D_m}{R\lambda}}$  is from Zhu and Zhan (2018), which is also defined according to the analytical solution of solute transport in a single fracture-matrix system. Although the unified parameter is also directly defined by the authors, Zhu and Zhan (2018) provided an explanation of the physical meaning of the unified parameter, that it is essentially a ratio of a characteristic diffusive length into the matrix over the fracture aperture.

As we can see from the above summary, these unified parameters are mostly proposed based on analytical solutions for a single fracture-matrix system, and do not really have a solid theoretical derivation process. The underlying assumptions are therefore similar to that in this study, i.e., single fracture system, uniform aperture and flow field, low matrix permeability so advection in matrix can be ignored, etc.

We agree with the reviewer that a further explanation of the unified parameters in terms of their assumption and physical meaning is necessary. In the Introduction section, we have added more descriptions of these unified parameters (Lines 85-94 in the updated manuscript):

*“Most of such unified terms were proposed based on analytical solutions for solute transport in a single fracture-matrix system with ideal conditions such as uniform aperture and fracture flow field, as well as negligible solute advection process in rock matrix. Unfortunately, these unified terms generally lack a rigorous theoretical derivation and exhibit different forms in terms of the combination of fracture and matrix parameters. For example, Maloszewski and Zuber (1985) proposed a diffusion parameter to quantify matrix diffusion rate, considering the effect of rock porosity, matrix diffusion coefficient and fracture aperture. Neretnieks (2002) further*

*incorporated mean residence time and defined a new matrix diffusion factor to quantify the strength of matrix diffusion. Another unified parameter from Zhu and Zhan (2018) mainly considered the effect of matrix diffusion coefficient and fracture aperture, and the parameter was used to characterize the diffusive length of solute into matrix. There is still a lack of consensus on such a unified term for matrix diffusion effect quantification.*

\* Fig4: Based on the occurrence in the text, the placement and order of Figs 4 & 5 should be reconsidered.

Thanks for the comment. Fig. 4 shows how matrix diffusion effect could be compensated in a fracture-only model through the proposed equivalent solute release function for three different models, i.e., (a) 2D ideal analytical model, (b) 3D numerical model, and (c) 2D ideal analytical model with sorptive solute. We combine the three comparisons into one figure because they share the same purpose and plotting style. Section 2.4 discusses the compensation effect of the equivalent solute release function for 2D ideal analytical model, and therefore Fig. 4(a) is first cited in Section 2.4. Section 3 extends to 3D model and cites Fig. 4(b). As we further discuss the application of the equivalent solute release function to sorptive solute, Fig. 4(c) is cited in Section 4. The order of Figs. 4 and 5 is consistent with their occurrence in the text.

\* Section 4.1 reads very much like a repetition from the introduction and a summary of previous results but does not present a critical discussion of the obtained results.

Thanks for pointing out the concern. We agree with the reviewer that Section 4.1 is a summary rather than a discussion. The first half of Section 4.1 emphasizes the importance of quantifying matrix diffusion, and the section half summarizes the main results of this study. To address this concern, we have incorporated the first half of Section 4.1 into the Introduction section, and the second half into the Conclusion section (Lines 60-66 and lines 398-402 in the updated manuscript).

*"For contaminant remediation, understanding matrix diffusion-induced contaminant spread and persistence is essential for the design of long-term remediation strategy. For geological storage (nuclear waste, CO<sub>2</sub>), matrix diffusion on one hand is an important retaining mechanism and on the other hand may lead to unexpected leakage pathways. Quantifying the long-term effects of matrix diffusion is critical for the optimization of containment systems and risk management. From the computational perspective, correctly assessing matrix diffusion effect could provide useful insights for the simplification of solute transport model for prediction and data interpretation."*

*"In the present study, we provide a convenient and practical method to quantify matrix diffusion effect on solute transport in subsurface fractured media. We propose a unified parameter that incorporates matrix/fracture properties as well as spatial-temporal scales and demonstrate that*

*the unified parameter shows better prediction capability of matrix diffusion effect than previously proposed unified parameters. Through a comprehensive analysis with lab and field data, we find that a threshold of  $5\text{ s}^{1/2}$  of the unified parameter appears appropriate to evaluate whether matrix diffusion effect is significant or negligible.*

\* Sections 4.3 and 4.4 seem to be rather results than a discussion.

Thanks for pointing out the concern. In the original manuscript, we want to focus on the derivation and verification of the unified parameter and the equivalent solute release function. Therefore, we only consider the inert solute in Sections 2 and 3, and put the extension to sorptive and degradative solutes in the Discussion section. However, as the reviewer pointed out the concern, we decide to follow the reviewer's suggestion and move Sections 4.3 and 4.4 into the Results section. In the updated manuscript, we add a new Section 4 to specifically demonstrate the application of the unified parameter and the equivalent solute release function to sorptive and degradative solutes.

\* A critical discussion of the results, especially addressing limitations of the unified number and the correction term are needed to provide the reader with a critical assessment of the accomplishments achieved by the authors.

Thanks for the comment. In the current study, we use the analytical solutions for a 2D single fracture model to investigate the impacts of matrix/fracture parameters on matrix diffusion, and the derivation of the unified parameter as well as the equivalent solute release function is also based on the analytical solutions. Although we demonstrate that the unified parameter and the equivalent solute release function are also applicable to 3D models, the main limitation is that we only consider single fracture systems, and the applicability of the unified parameter and the equivalent solute release function to more complex situations such as multiple parallel fractures, heterogeneous fracture aperture distribution, and discrete fracture networks needs further investigations. Regarding the limitation, we have provided detailed discussion in Section 5 (Lines 379-396 in the updated manuscript):

*"The current study uses a single-fracture model to derive the unified parameter and equivalent solute release function, which have relatively simple expressions and can be easily applied for matrix diffusion effect analysis. However, in real-world field applications, subsurface fractured media normally involve complex fracture characteristics such as multiple parallel fractures, heterogeneous fracture aperture distribution, discrete fracture networks, etc. For solute transport in such complex fracture scenarios, the application of the unified parameter and equivalent solute release function needs careful considerations. In cases with multiple parallel fractures, matrix diffusion around one fracture may affect matrix diffusion in adjacent fractures, and the interaction strength between two fractures depends on the distance between them. If the fracture distance is sufficiently large that the solute transport process in one fracture is*

*independent of that in other fractures, then the unified parameter and equivalent solute release function are applicable for matrix diffusion analysis. On the contrary, if the fracture distance is relatively small, then it should be considered as an additional parameter that affects matrix diffusion, and future work is necessary to investigate how the distance could be incorporated in the unified parameter and equivalent solute release function.*

*In cases with heterogeneous fracture aperture or discrete fracture networks, flow and transport paths between solute release and monitoring points are normally highly channelized. The applicability of the unified parameter and equivalent solute release function is therefore compromised as they assume a uniform flow field, represented as  $u$  in Eq. (7). Nevertheless, the proposed unified parameter, as a practically convenient method, can still provide fast and quantitative estimations of matrix diffusion effect in complex field environments. The equivalent function should be able to at least partially offset the impact of ignoring matrix diffusion, but further investigations are required to improve its accuracy and applicability to such complex fracture characteristics."*

4) The data availability statement seems incomplete and partly imprecise.

Thanks for the comment. We have revised the data availability statement to avoid any confusion (Lines 408-410):

*"The fracture and matrix parameters used in the present study are randomly generated according to the presented method. The solute breakthrough curves are calculated through the analytical solutions demonstrated in the main text, and can be reproduced with the analytical solutions. Field and lab experimental data are provided in the Supporting Information."*

Which BTCs are calculated with analytical solutions? I assume section 3 is not based on analytical solutions but computer models/codes are not mentioned in the statement. It should be more clearly stated that the field and lab data is a summary of literature results to avoid confusion.

Thanks for the comment. The BTCs in Fig. 4(a) and Fig. 4(c) are calculated with analytical solutions, while those in Fig. 4(b) are calculated through numerical models. We have revised the caption of Fig. 4 to avoid any misunderstanding (Lines 260-265):

*"Figure 4 Compensation of matrix diffusion effect through the use of equivalent solute release function in fracture-only models. We randomly select three cases with relatively large  $\frac{\theta\sqrt{D_m x}}{2bu}$  (as annotated) for analysis. (a) Results for from the 2D the analytical model for conservative solute. The upper row compares the original solute release function and the equivalent solute release function. The lower row compares solute breakthrough curves from three models, i.e., fracture-matrix and fracture-only models with the original solute release function, and fracture-only model with the equivalent solute release function. (b) Results for from the 3D numerical model*

with point injection/production for conservative solute. (c) Results from the 2D analytical model for sorptive solute."

The lab and field data are a summary of literature results. We have also further emphasized this in the updated manuscript (Lines 203-206):

*"To validate the unified parameters as well as the corresponding thresholds, we analyze and compile solute transport data from lab and field tests in fractured media reported in the literature, and select cases for which matrix diffusion effect (significant or negligible) has been explicitly discussed."*

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