Response to comments 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.

Below is a list of major changes made in the revised manuscript according to the review comments.

1. General revision
    - [1] We have checked the manuscript carefully and several typos have been revised.
2. Introduction section:
    - [1] We have added an explanation (Lines 35-40) to clearly demonstrate parameter uncertainties in the context of subsurface reservoir modeling.
    - [2] We have added an example (Lines 43-45) to further emphasize the computational cost associated with subsurface solute transport modeling. A detailed comparison of the computational cost for 3D fracture-matrix coupled models and 2D fracture-only models is provided (Lines 301-307) to demonstrate the effectiveness of the proposed equivalent solute release function.
    - [3] A further explanation of the unified parameters from the literature in terms of their assumption and physical meaning has been added in the Introduction section (Lines 85-94).
3. Section 2: Matrix diffusion effect on solute transport in fractured media
    - [1] We have revised Equations (2), (6) and (7) and the corresponding descriptions.
    - [2] We have added an explanation for the selection of parameter ranges in Table 1 and also provided relevant references (Lines 134-137).
    - [3] We have provided an explanation for the Latin-hypercube sampling (LHS) method and also added the original reference (Lines 139-141).
    - [4] We have revised Equation (6) from discrete form to integral form and re-calculate the R value for all the cases in the study. Correspondingly, we have also revised Figs. 2, 3, 7, 8, 9, and 10.
    - [5] We have revised the caption of Fig. 2 to avoid any confusion. The qualitative description is removed and a quantitative explanation of the non-linear relationships in the plots is added (Lines 147-149).
    - [6] We have added the results of Pearson correlation coefficient in Figs. 3, 8 and 10.
    - [7] We have provided an explanation for the selection of the threshold for the newly proposed unified parameter (Lines 211-216).

    [8] Figure 3: we have labeled each subplot and cited each subplot separately in the text. The caption is revised accordingly.
    [9] We have further demonstrated the theoretical rationale as well as the physical meaning of the proposed unified parameter (Lines 241-250).
    [10] Figure 4: we have cropped the figure to avoid boundary lines. The caption is also revised to clearly demonstrate the purpose of each plot in the figure. We also remove Fig. 4 to the end of Section 2 to be consistent with the cite of the figure in the text.

4. Section 3: Verification through a 3D numerical model
    [1] We have explained the purpose of the 2D fracture-only model (Lines 268-270).
    [2] We have added a detailed description of the numerical model in terms of governing equations, boundary conditions, initial conditions, as well as numerical methods (Lines 273-279).
    [3] We have added an analysis of the computational cost of the 3D and 2D models (lines 301-307).
5. Section 4: Application to sorptive and degradative solutes
    [1] We add this new section to demonstrate the application of the unified parameter and equivalent solute release function to sorptive and degradative solutes.
    [2] We have provided references for the analytical solutions of sorptive solute (Lines 325-326).
6. Discussion Section:
    [1] We have reorganized the Discussion section. The first half of Section 4.1 is removed to the Introduction section (Lines 60-66), and the second half is incorporated into the Conclusion section (Lines 398-402).
    [2] The results of sorptive solute and degradative solute have been removed from the Discussion section into a new Section 4 (Lines 312-363).
    [3] A parallel discussion of the conservative, sorptive, and degradative solutes have been added in the Discussion section to provide insights of matrix diffusion effect for conservative, sorptive, and degradative solutes (Lines 365-377).
7. Data availability and References
    [1] We have revised the statement of data availability.
    [2] We have added relevant references.
8. Supporting Information
    [1] We have added a figure (Fig. S1) in the Supporting Information to illustrate the matrix diffusion compensation performance of the equivalent solute release function calculated with different average flow velocities.

Our response to each review comment is detailed as follows.

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

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:

* l131: "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 θ, 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).

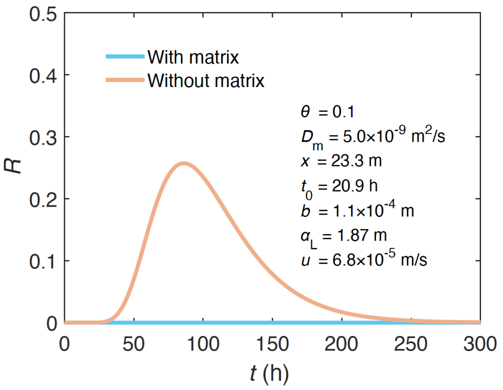

Fig. R1 Comparison of solute breakthrough curves from fracture-matrix coupled and fracture-only models under significant matrix diffusion effect.

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 θ, 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*"

* l132: "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 *θ* as an example for explanation. With the increase of *θ*, 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 *θ*, 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.

* l145: "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 *θ*, D_m, and *b*. As we can see from the plots for *θ*, D_m, and *b*, most curves show nearly perfect linear relationship in the log-log coordinate. However, under high *θ*, 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.

* l171: "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.

* l184: "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 $\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu}$ as well as field data presented in Fig. 3, we identified a threshold of 5 $s^{1/2}$ for $\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu}$ 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 $s^{1/2}$ (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)).

* l261: "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.

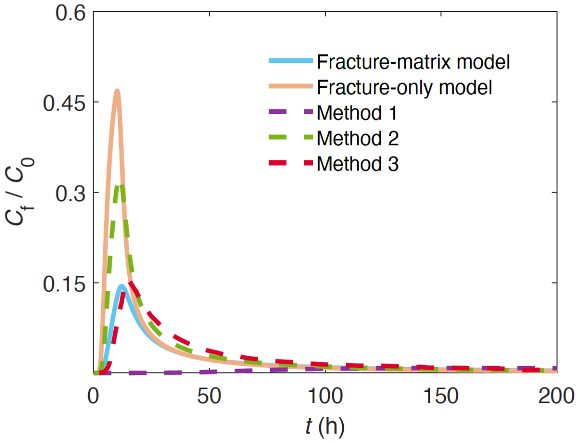

Fig. R2 Comparison of solute breakthrough curves from different models. The solid blue curve is from the fracture-matrix coupled model, and the solid orange curve is from the fracture-only model. The three dashed curves are results from fracture-only model applying the equivalent solute release function. 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)”

* l353: "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 ($\frac{\theta\sqrt{D_\mathrm{m}x}}{2bu}$) 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 $s^{1/2}$) 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.

* l37: "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_2 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. There 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 ξ here is an integral variable and does not have any physical meaning. We have added an explanation for ξ 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, θ is the matrix porosity, D_m is the matrix diffusion coefficient, b is the half-aperture of the fracture, and ξ 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):

$$R = \int_0^{T_0} (\frac{C_\mathrm{f} - C_\mathrm{mf}}{C_\mathrm{fmax}})^2 dt \qquad \text{(R1)}$$

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	$2b$ µm	α_L m	θ	D_m m^2/s	
Lenda and Zuber (1970)	Tritium	22	0.0024		590	7.4	0.064	1.0×10^{-10}	S
Kreft et al. (1974)	Tritium	21.3	0.0012		400	0.96	0.064	1.0×10^{-10}	S
Ivanovich and Smith (1978)	Tritium	8	0.001		150	0.64	0.275	1.0×10^{-10}	S
Grisak et al. (1981)	Chloride	0.76	3.4×10^{-4}	345600	40	0.04	0.35	5.0×10^{-11}	S
Novakowski et al. (1985)	^{82}Br	10.6	4.7×10^{-4}	600	510	1.4	0.003	4.8×10^{-12}	N
Raven et al. (1988)	^{82}Br	12.7	6.3×10^{-4}	15	135	0.95	0.003	1.0×10^{-10}	N
Shapiro and Nicholas (1989)	Sodium chloride	19.8	0.0119	60	5340	0.538	0.135	5.7×10^{-8}	S
	Sodium chloride	17.2	0.0177	60	4160	0.161	0.12	3.4×10^{-8}	
Maloszewski et al. (1990)	Deuterium	10.2	0.0044		250	0.2	0.4	1.0×10^{-10}	S
Andersson et al. (1993)	^{131}I	168	0.0016		1000	5.5	0.002	1.0×10^{-10}	N
	^{82}Br	223	0.0027		1000	13.5	0.002	1.0×10^{-10}	
McKay et al. (1993)	Bromide	4	1.2×10^{-7}	21600	11	0.1	0.0001	5.8×10^{-10}	S
	^{18}O	6	8.1×10^{-7}	432000	21	0	0.0001	5.5×10^{-10}	
Novakowski and Lapcevic (1994)	Lissa mine FF	5.21	4.0×10^{-6}	642	282	0.06	0.009	4.5×10^{-10}	S
		5.22	4.0×10^{-6}	642	57	0.04	0.028	4.5×10^{-10}	
		11.64	4.0×10^{-6}	642	248	0.4	0.013	4.5×10^{-10}	
		11.78	4.0×10^{-6}	642	154	0.3	0.008	4.5×10^{-10}	
		14.94	4.0×10^{-6}	642	235	0.25	0.012	4.5×10^{-10}	
		16.58	4.0×10^{-6}	642	126	0.3	0.024	4.5×10^{-10}	
		19.18	4.0×10^{-6}	642	241	0.4	0.011	4.5×10^{-10}	
		26.61	4.0×10^{-6}	642	243	0.3	0.008	4.5×10^{-10}	
Hadermann and Heer (1996)	Uranine	4.9	6.9×10^{-5}		930	0.25	0.15	5.5×10^{-11}	S
	Eosine	346	2.2×10^{-4}		434	3.46	0.03	4.5×10^{-10}	S

Himmelsbach et al. (1998)	Uranine	235	4.0×10^{-4}		444	3.91	0.049	4.5×10^{-10}	
	Pyranine	48	0.0027		576	2.45	0.061	1.5×10^{-9}	
	Pyranine	11.2	0.0016		110	2.14	0.035	1.5×10^{-9}	
	Pyranine	21.4	4.3×10^{-4}		256	0.3	0.053	1.5×10^{-9}	
	Pyranine	11.2	0.0015		265	0.3	0.054	1.5×10^{-9}	
	D_2O	11.2	0.0015		107	0.17	0.048	2.5×10^{-9}	
	Eosine	11.2	0.0044		117	0.17	0.035	4.5×10^{-10}	
	Uranine	11.2	0.0026		268	0.25	0.03	4.5×10^{-10}	
Maloszewski et al. (1999)	bromide	11	1.5×10^{-4}		232	1.64	0.023	4.7×10^{-11}	S
		225	0.0027		232	2.25	0.023	4.7×10^{-11}	
		330	0.004		232	6.6	0.023	4.7×10^{-11}	
Jardine et al. (1999)	He	6	0.0012	15552000	84	0.1	0.2	6.9×10^{-9}	S
		9.2	0.0012	15552000	84	0.1	0.2	6.9×10^{-9}	
		16.8	0.0012	15552000	84	0.1	0.2	6.9×10^{-9}	
	Ne	6	0.0012	15552000	84	0.1	0.2	4.0×10^{-9}	S
		9.2	0.0012	15552000	84	0.1	0.2	4.0×10^{-9}	
		16.8	0.0012	15552000	84	0.1	0.2	4.0×10^{-9}	
	Br	6	0.0012	15552000	84	0.1	0.2	2.3×10^{-9}	S
		9.2	0.0012	15552000	84	0.1	0.2	2.3×10^{-9}	
		16.8	0.0012	15552000	84	0.1	0.2	2.3×10^{-9}	
Lapcevic et al. (1999)	Fluorescent dye Lissamine FF	10.8	5.6×10^{-5}	396	98	0.1	0.015	1.8×10^{-10}	S
		11.8	5.6×10^{-5}	396	248	0.1	0.012	1.8×10^{-10}	
		15.9	6.7×10^{-5}	396	282	0.1	0.015	1.8×10^{-10}	
		19.1	5.6×10^{-5}	396	154	0.1	0.019	1.8×10^{-10}	
		23.7	5.6×10^{-5}	396	85	0.1	0.01	1.8×10^{-10}	
		34.8	7.8×10^{-5}	396	125	0.1	0.026	1.8×10^{-10}	
		41.2	7.5×10^{-5}	396	230	0.1	0.027	1.8×10^{-10}	
Becker and Shapiro (2000, 2003)	HDO	36	3.7×10^{-4}		400	1.8	0.015	6.0×10^{-13}	N

Callahan et al (2000)	Iodide	0.16	8.4×10^{-6}	115200	700	0.0104	0.27	3.7×10^{-10}	S
	Iodide	0.16	8.4×10^{-5}	10440	700	0.0104	0.27	3.7×10^{-10}	
	Iodide	0.16	3.4×10^{-5}	27360	700	0.0104	0.27	3.7×10^{-10}	
	Bromide	0.16	1.6×10^{-5}	41508	1160	0.0537	0.27	1.3×10^{-9}	
	PFBA	0.16	1.6×10^{-5}	41508	1160	0.0535	0.27	4.3×10^{-10}	
Reimus (2003)	PFBA	30	7.0×10^{-7}		7190	44	0.12	7.2×10^{-10}	S
	Bromide	30	7.0×10^{-7}		7190	44	0.12	2.1×10^{-9}	
	Lithium	30	7.0×10^{-7}		7190	44	0.12	1.0×10^{-9}	
Witthüser et al. (2003)	Uranine	10	9.6×10^{-4}		397	0.11	0.51	1.5×10^{-11}	S
	Lithium	10	1.0×10^{-3}		405	0.11	0.51	2.6×10^{-11}	
Liu et al. (2004)	Bromide and PFBA	20	5.8×10^{-6}		740		0.11	2.1×10^{-9}	S
Novakowski et al. (2004)	KBr	9.5	3.5×10^{-4}	50	697	0.18	0.11	1.9×10^{-9}	S
	Lissamine FF	9.5	3.5×10^{-4}	50	697	0.18	0.11	4.5×10^{-10}	
	KBr	9.5	3.5×10^{-4}	50	918	0.31	0.18	1.9×10^{-9}	
	Lissamine FF	9.5	3.5×10^{-4}	50	918	0.31	0.18	4.5×10^{-10}	
Reimus (2007)	Bromide	0.16	5.9×10^{-6}		970		0.272	6.2×10^{-10}	S
		0.17	3.4×10^{-5}		250		0.138	3.8×10^{-11}	
		0.12	6.4×10^{-5}		260		0.288	3.0×10^{-10}	
		0.22	1.5×10^{-5}		490		0.298	1.0×10^{-10}	
		0.25	1.5×10^{-5}		650		0.297	2.0×10^{-11}	
		0.24	5.0×10^{-5}		230		0.369	2.5×10^{-10}	
		0.23	6.0×10^{-6}		380		0.303	4.3×10^{-10}	
		0.15	3.5×10^{-5}		270		0.111	3.3×10^{-11}	
		30	2.5×10^{-4}		1800	6.3	0.064	4.5×10^{-11}	
		30	1.0×10^{-5}		1800	6.3	0.02	4.5×10^{-11}	
		30	9.2×10^{-6}		850	3.2	0.019	4.5×10^{-11}	
Zhou et al. (2006)	Iodide	30	4.0×10^{-4}		534	0.59	0.049	6.1×10^{-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 θ, 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 united parameter in subsequent sections.

We also notice that some curves show a non-linear relationship in the plots for θ, D_m, b and u. As we explained earlier, the main reason is that under large θ, 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 θ, 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 θ, 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."

* l175: 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 l194 and l220f, 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 θ 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 θ, 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., $\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu}$. 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 $\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu}$*, 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),

$$\frac{C(t)}{C_0}=\begin{cases} erfc(\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu\sqrt{t}}), 0\le t\le t_0 \\ erfc(\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu\sqrt{t}})-erfc(\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu\sqrt{t-t_0}}), t>t_0 \end{cases} \tag{R2}$$

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 (θ, 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 $\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu}$, 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 $\frac{\theta\sqrt{D_\mathrm{m}x}}{2bu}$ and gradually diminishes with time. In other words, the unified parameter $\frac{\theta\sqrt{D_\mathrm{m}x}}{2bu}$ quantitatively determines the strength of matrix diffusion effect.

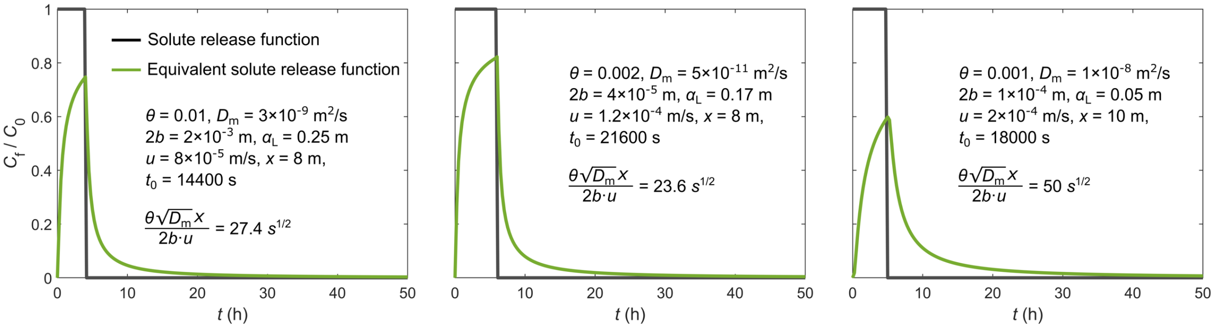

Fig. R3 Comparison between original and equivalent solute release curves under various parameters.

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 ofequivalent solute release function C(t) from C0 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.”

* l265: "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 $\theta = 0.0026$, $D_m = 3\times10^{-9}$ m^2/s, $2b = 2\times10^{-4}$ m, $\alpha_L = 1.63$ m, $u = 4.4\times10^{-4}$ m/s, $t_0 = 97492$ s (also annotated in the caption of Fig. 6). The unified parameter is therefore 80.9 $s^{1/2}$, much higher than the previously recommended threshold of 5 $s^{1/2}$. 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 $s^{1/2}$ (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."

* l67: 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.

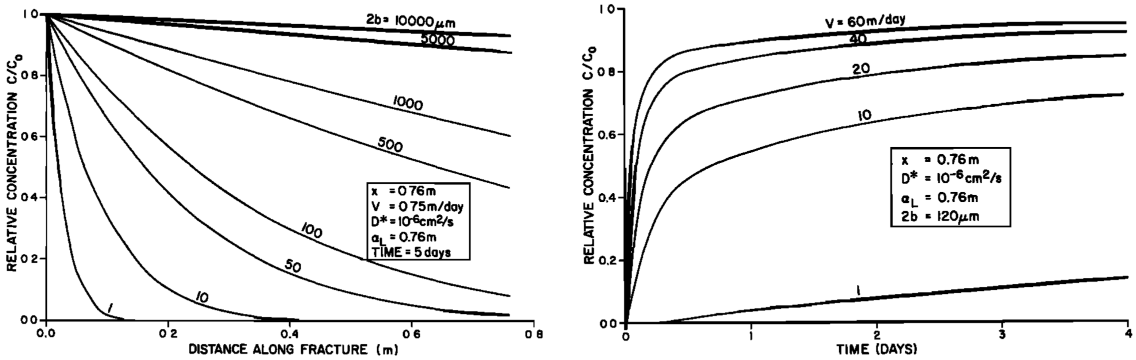

Fig. R4 Effect of fracture aperture (left) and flow velocity (right) on solute concentration profiles in a fracture (Grisak and Pickens, 1980).

* l86: 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 $\frac{\theta\sqrt{D_\mathrm{m}}}{2b}$, 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 $\frac{\theta\sqrt{D_\mathrm{m}}}{2b}$. 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 $\sqrt{2D_\mathrm{m}\cdot t^*}$ 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 ($\frac{\theta\sqrt{D_\mathrm{m}\cdot t^*}}{2b}$) and the fourth unified parameter ($\frac{\theta\sqrt{D_\mathrm{m}\cdot t^*}}{b}$) 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 $G = LW\theta D_\mathrm{m}^{1/2}$, 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 $\frac{\theta\sqrt{D_\mathrm{m}\cdot t^*}}{b}$. 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 $\frac{1}{b}\sqrt{\frac{D_\mathrm{m}}{R\lambda}}$ 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.

To address the concern, we have removed Fig. 4 to the end of Section 2.

* 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_2), 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 $s^{1/2}$ 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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Response to review comments #2 (RC2) on Manuscript EGUSPHERE-2025-841 titled "Quantifying matrix diffusion effect on solute transport in subsurface fractured media"

 # Reviewer 2 comments

General Comments

The authors propose a new unified parameter for quantifying matrix diffusion effects, which is incorporated into an analytical fracture-only model to effectively reduce computational cost. Overall, the manuscript presents a solid discussion with a clearly defined research objective. The comparison between the proposed model and the fracture–matrix model, as shown in Figure 4a, further supports the credibility of the approach. However, the manuscript does not quantitatively address how the proposed model improves computational efficiency and predictive accuracy compared to existing methods. Additionally, some explanations are unclear, and it is difficult to correlate them with the referenced figures. Addressing these issues would significantly strengthen the overall contribution of the study.

Thank you for the overall evaluation of the study. We have revised the manuscript according to the suggestion to improve the quality and clearance of the study. Below we provide a point-to-point response to the specific comments.

Specific Comments

Line 121. Please provide citations and justify the wide range of each parameter, demonstrating that these values fall within realistic and commonly observed limits in relevant experimental or field studies.

Thanks for this important suggestion. The parameter ranges in Table 1 are mostly from tracer testing studies reported in the literature, including both laboratory/field tests and numerical modeling. The detailed parameters from these studies are provided in Table S1 in Supporting Information. According to the suggestion, we have added relevant references in the main text (Lines 134-137 in the updated manuscript):

"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)."

Line 123. Please explain the Latin hypercube sampling (LHS) approach and provide the original citation where the method was first introduced.

Thanks for the suggestion. Latin hypercube sampling (LHS) is a statistical method for generating a random sample of parameter values from a multidimensional probability distribution. It is an effective stratified sampling approach that ensures all portions of a given partition can be sampled. We have provided an explanation for LHS and also added the original reference in the updated manuscript (Lines 139-141):

"LHS is originally proposed by McKay et al. (1979) and has been widely used for sampling high-dimensional parameter spaces as it effectively ensures that all portions of the parameter space are sampled."

Figure 3. Please add panel labels such as (a), (b), and (c), and refer to these labels when discussing specific parts of the figure in the text.

Thanks for the suggestion. We have revised the figure according to the suggestion as follows.

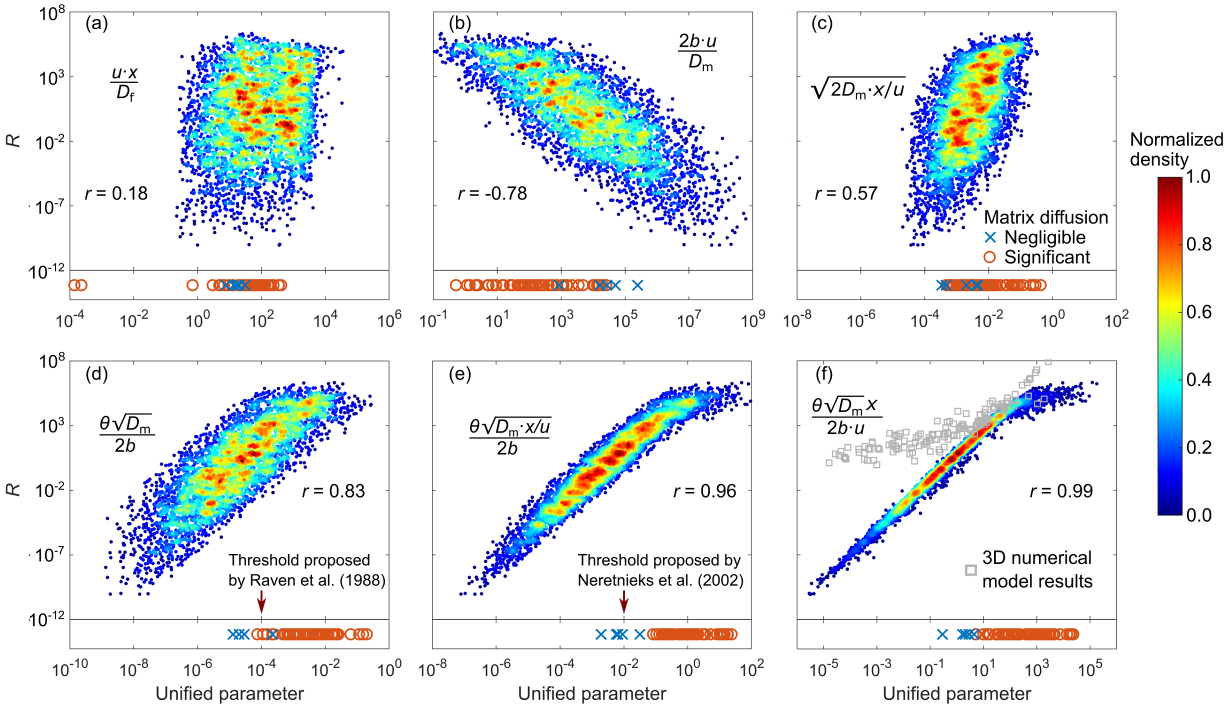

Figure R1 Relationship between matrix diffusion effect and unified parameters. All the 5,000 data points are shown, with the color denoting the normalized density of data points. The Pearson correlation coefficients (r) are also annotated. In the bottom panel of each plot, we show 78 cases from the literature. For each case, the unified parameter is calculated and marked as a blue cross if matrix diffusion is identified as negligible in the literature, and a red circle if matrix diffusion is identified as significant. (a) Peclet number $u\cdot x/D_\mathrm{f}$. (b) Peclet number $u\cdot 2b/D_\mathrm{m}$. (c) Diffusion distance $\sqrt{2D_\mathrm{m}\cdot x/u}$. (d) Diffusion parameter $\frac{\theta\sqrt{D_\mathrm{m}}}{2b}$. Threshold proposed by Raven et al. (1988) is annotated. (e) Strength of matrix diffusion $\frac{\theta\sqrt{D_\mathrm{m}\cdot x/u}}{2b}$. Threshold proposed by Neretnieks et al. (2002) is annotated. (f) The newly proposed unified parameter $\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu}$. We also show the results (gray squares) from 3D numerical models with a point source for solute release.

Line 176-178. The previously reported correlation coefficient of 0.96 already indicates a strong relationship. Please clarify whether the 0.03 improvement represents a meaningful difference that justifies the claim that the newly proposed method is better.

Thanks for this interesting point. The enhancement of the correlation coefficient from 0.96 to 0.99 seems insignificant, but if we compare the distribution of data points for $\frac{\theta\sqrt{D_\mathrm{m}\cdot x/u}}{2b}$ and $\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu}$ in Fig. 3, we find that the scattering of data points for $\frac{\theta\sqrt{D_\mathrm{m}\cdot x/u}}{2b}$ and $\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu}$ actually show remarkable difference. Data points for $\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu}$ exhibits a considerable narrower band than that for $\frac{\theta\sqrt{D_\mathrm{m}\cdot x/u}}{2b}$, indicating that $\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu}$ has a stronger linear relationship with matrix diffusion effect (represented by *R*) than $\frac{\theta\sqrt{D_\mathrm{m}\cdot x/u}}{2b}$. Therefore, although the Pearson correlation coefficient is slightly enhanced, the linear relationship actually improves remarkably.

More importantly, as we explained in the derivation of the equivalent solute release function in Subsequent Section 2.4, $\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu}$ has a theoretical base while $\frac{\theta\sqrt{D_\mathrm{m}\cdot x/u}}{2b}$ does not. 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. From the analytical solutions of solute transport in a single fracture-matrix system, we derived the equivalent solute release function as follows,

$$\frac{C(t)}{C_0}=\begin{cases} erfc(\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu\sqrt{t}}),0\le t\le t_0 \\ erfc(\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu\sqrt{t}})-erfc(\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu\sqrt{t-t_0}}),t>t_0 \end{cases} \quad \text{(R1)}$$

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 (θ, D_m, b, u and x). As we can see from the equation, the coefficient within the complementary error functions is exactly identical to the proposed unified parameter $\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu}$, 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 $\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu}$. Therefore, from the theoretical perspective, proposing this new unified parameter ($\frac{\theta\sqrt{D_\mathrm{m}}x}{2bu}$) is important and necessary.

Line 193-195 & 288-289. Please provide a detailed explanation for why cases with values beyond 0.01 are identified as having negligible matrix diffusion, and why a threshold of 5 $s^{1/2}$ is considered a reasonable criterion.

Thanks for this important suggestion. Fig. 3 presents two thresholds from the literature, one for the unified parameter $\frac{\theta\sqrt{D_\mathrm{m}}}{2b}$ and the other for the unified parameter $\frac{\theta\sqrt{D_\mathrm{m}\cdot x/u}}{2b}$. The two thresholds, however, are somewhat subjectively determined rather than theoretically derived. This is expectable as the identification of significant or negligible matrix diffusion is itself subjective and may vary from case to case.

The threshold of 0.01 for parameter $\frac{\theta\sqrt{D_{\mathrm{m}} \cdot x/u}}{2b}$ is proposed by Neretnieks (2002). Neretnieks (2002) used a qualitative criterion to derive the threshold, i.e., if the time needed to reach 95% solute concentration at the monitoring point does not exceed the mean residence time (x/u) by more than 5%, then matrix diffusion could be neglected. With this criterion, they reached a threshold of 0.01 for $\frac{\theta\sqrt{D_{\mathrm{m}} \cdot x/u}}{2b}$. They also mentioned that a relatively less strict criterion could be that 50% solute concentration is reached at twice the mean residence time. This would give a threshold of 0.48 for $\frac{\theta\sqrt{D_{\mathrm{m}} \cdot x/u}}{2b}$. The selection of the 0.01 threshold is therefore subjective, and we tend to not specifically mention how the threshold is determined but directly use the 0.01 threshold in Fig. 3.

As for the newly proposed unified parameter $\frac{\theta\sqrt{D_{\mathrm{m}}}x}{2bu}$, we recommend a threshold of 5 $s^{1/2}$ to determine the significance of matrix diffusion effect. The threshold is determined through a comprehensive investigation of lab and field solute transport data. As we explained in the manuscript as well as the caption of Fig. 3, we comprehensively analyzed solute transport data from lab and field experiments reported in previous studies. Some of these studies reported rock and fracture parameters, and explicitly discussed whether matrix diffusion was significant or negligible based on measured solute concentration data. For each of such cases, we first calculate $\frac{\theta\sqrt{D_{\mathrm{m}}}x}{2bu}$ values according to the reported rock/fracture parameters, and then plot them in the bottom panel of Fig. R2 (Fig. 3(f) in the manuscript). Cases that have been reported to have significant matrix diffusion are marked as red circles, and those reported to have negligible matrix diffusion are marked as blue crosses. Obviously, if the red circles and blue crosses can be separated in the plot, we can identify a threshold of $\frac{\theta\sqrt{D_{\mathrm{m}}}x}{2bu}$ to determine whether matrix diffusion is significant or negligible. Fortunately, according to Fig. R2, the blue crosses and red circles are successfully separated. The largest $\frac{\theta\sqrt{D_{\mathrm{m}}}x}{2bu}$ for the blue crosses and the smallest $\frac{\theta\sqrt{D_{\mathrm{m}}}x}{2bu}$ for the red circles are quite close to 5 $s^{1/2}$, and therefore we recommend a threshold of 5 $s^{1/2}$ as a criterion for $\frac{\theta\sqrt{D_{\mathrm{m}}}x}{2bu}$.

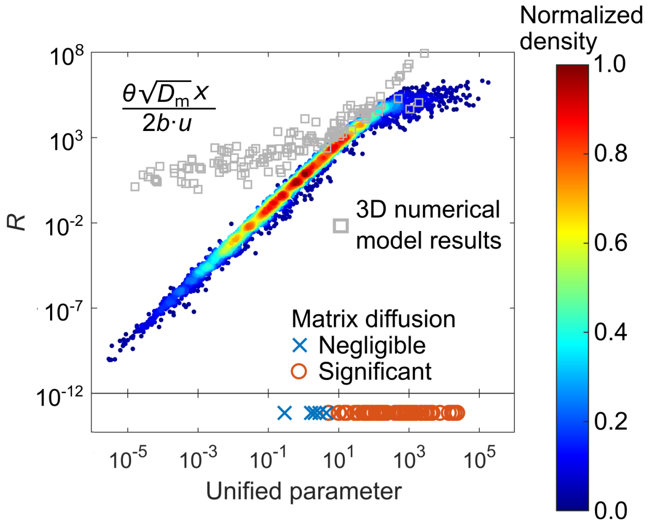

Figure R2 Relationship between matrix diffusion effect and the unified parameter $\frac{\theta\sqrt{D_m}x}{2bu}$. The bottom panel shows lab and field data from the literature. The blue crosses are cases with negligible matrix diffusion, and the red circles are cases with significant matrix diffusion.

We have also revised the manuscript to provide an explanation for the selection of the threshold for the newly proposed unified parameter (Lines 211-216):

"For $\frac{\theta\sqrt{D_m\cdot x/u}}{2b}$, the threshold of 0.01 from Neretnieks (2002) turns out to be relatively conservative as a case beyond 0.01 is identified as having negligible matrix diffusion (Fig. 3(e)). For the newly proposed $\frac{\theta\sqrt{D_m}x}{2bu}$, we find that the largest $\frac{\theta\sqrt{D_m}x}{2bu}$ value for the blue crosses (negligible matrix diffusion) and the smallest $\frac{\theta\sqrt{D_m}x}{2bu}$ value for the red circles (significant matrix diffusion) are both close to 5 $s^{1/2}$. As a result, we recommend a threshold of 5 $s^{1/2}$ (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))."

Line 204-206. Could you quantify the additional computational cost associated with using a fracture–matrix model relative to a fracture-only model that approximates matrix diffusion?

Thanks for the suggestion. Reducing computational burden is one of the main motivations for this study. In Section 3, we developed a 3D fracture-matrix coupled model and a corresponding 2D fracture-only model to demonstrate the feasibility of the proposed unified parameter and equivalent solute release function. We randomly generated 150 parameter sets (porosity θ, diffusion coefficient D_m, fracture aperture 2b, dispersivity α_L, injection duration t_0, and flow rate q) and performed 3D and 2D numerical simulations for each parameter set. We can use the computational costs of these 3D and 2D simulations to illustrate the additional computational cost associated with using a fracture–matrix model relative to a fracture-only model that approximates matrix diffusion.

According to the 150 simulations, the computational cost of 3D fracture-matrix coupled models is approximately 0.5 ~ 1 core hour, while 2D fracture-only models can be completed within ten seconds on a single core. The computational cost of 2D fracture-only models is therefore 0.28% - 0.56% of 3D fracture-matrix coupled models. To address the reviewer's concern, we have added an explanation of computational costs associated with the 3D and 2D numerical simulations in Section 3 (Lines 301-307 in the updated manuscript):

"As aforementioned, the main purpose of simplifying the 3D fracture-matrix coupled model to 2D fracture-only model by applying the equivalent solute release function is to reduce the computational cost associated with solute transport modelling in subsurface fractured media. According to the above 150 3D and 2D simulations, the computational cost of 3D fracture-matrix coupled models is approximately 0.5 ~ 1 core hour, while 2D fracture-only models are generally completed within ten seconds on a single core. The computational cost of the 2D fracture-only models is therefore only 0.28% - 0.56% of the 3D fracture-matrix coupled models, corroborating the effectiveness of the equivalent solute release function in improving computational efficiency."

Lines 242 and 255: What is the rationale for introducing the 2D fracture-only model? Please clarify its purpose and how it contributes to the overall analysis.

Thanks for the comment. The main purpose of this study is to provide a unified parameter to quantify the strength of matrix diffusion on solute transport in subsurface fracture-matrix systems. For cases that matrix diffusion only has a minor effect on fracture solute transport, we could use a fracture-only model to analyze solute transport processes in fractures. However, for cases that matrix diffusion has a significant effect on fracture solute transport, we have to include both fracture and the surrounding matrix in the model. As we mentioned in the response to the last comment, the fracture-matrix coupled model is much more computational intense than a fracture-only model. To alleviate the computational burden, we also developed an equivalent solute release function, which can be used to correctly compensate for matrix diffusion effect in a fracture-only model, thus one can still use the fracture-only model to analyze fracture solute transport even for cases with significant matrix diffusion.

In Section 3, we developed a 3D fracture-matrix coupled model to test the effectiveness of the unified parameter and the equivalent solute release function. We want to demonstrate that with the equivalent solute release function, we can simplify the 3D fracture-matrix coupled model to a 2D fracture-only model to reduce computational burden. Therefore, we also developed the 2D fracture-only model. By comparing the solute breakthrough curves from the 3D fracture-matrix coupled model and that from the 2D fracture-only model applying the equivalent solute release function, we proved that the equivalent solute release function successfully compensates for matrix diffusion effect in the 2D fracture-only model.

We have revised the manuscript accordingly as follows to further explain the purpose of the 2D fracture-only model (Lines 268-270):

"To examine the applicability of the derived equivalent solute release function, we also develop a 2D fracture-only model and then apply the equivalent solute release function (Fig. 5(b)). Solute transport simulations are then performed to obtain solute breakthrough curves for both the 3D and 2D models."

Line 251-253. Please explain what causes the discrepancy between the 3D model and the proposed unified term shown in the sixth panel of Figure 3.
Thanks for the comment. The unified term is proposed based on analytical solutions for a 2D fracture-matrix model with uniform flow field. In the 3D model, as we use a point injection and production scenario, and the flow field in the fracture is not uniform. Therefore, the analytical solutions are actually not applicable to the 3D model, and the unified term cannot quantify matrix diffusion effect in the 3D model as good as that in the 2D model, manifesting as the discrepancy between the 3D model results sand 2D model results in Fig. 3(f).

However, as we can see from Fig. 3(f), the unified term still exhibits a strong relationship with *R*, meaning that it can still quantify matrix diffusion satisfactorily.

Lines 264–267: Figure 4b presents results from the 3D case, while Figures 6b and 6c correspond to 2D cases. It is unclear why the 3D case is being compared with 2D cases, which may be confusing for readers. Additionally, the explanation of the 3D case shown in Figure 6a appears to be missing or unclear.
Thanks for the comment and sorry for the confusion. We compare the results of the 3D fracture-matrix coupled model with the results of the 2D fracture-only model to demonstrate the effectiveness of the equivalent solute release function. In Fig. 6(a), we show fracture solute concentration profiles in the 3D fracture-matrix coupled model, and in Fig. 6(b), we show the results from the 2D fracture-only model. The comparison of Fig. 6(a) and (b) shows that ignoring matrix diffusion (2D fracture-only model) significantly impacts solute transport in the fracture. Fig. 6(c) further shows the results from the 2D fracture-only model applying the equivalent solute release function, and we can see that fracture solute concentration resembles that in Fig. 6(a), meaning that the equivalent solute release function is able to largely compensate for matrix diffusion effect. We further compare the solute breakthrough curves at the production well for the three cases in Fig. 4(b) to corroborate the effectiveness of the equivalent solute release function.

To address the reviewer's concern of the confusion, we have revised the caption of Fig. 4 (Lines 260-265), and also added an explanation of Fig. 6(a) (Lines 296-299):

"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 from the 2D 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 from the 3D numerical model with point injection/production for conservative solute. (c) Results from the 2D analytical model for sorptive solute."*

"Compared with the results from the 3D fracture-matrix coupled model (Fig. 6(a)), the fracture-only model overestimates solute concentration in the fracture due to the neglect of matrix diffusion (Fig. 6(b)), and such an overestimation is largely corrected with the application of the equivalent solute release function (Fig. 6(c))."

Figure 6: Why does the concentration around the well become fainter over time? Please clarify the physical or modeling reasons behind this trend.
Thanks for the comment. I suppose the reviewer refers to the solute concentration around the injection well. This is because we only inject the solute into the fracture for a relatively short period of time (much shorter than the whole simulation time window). After solute injection, the solute gradually transports towards the production well under the advection and diffusion processes, and the concentration around the injection gradually reduces to zero. For the case in Fig. 6, the solute injection time is 97492 s (as explained in the caption of Fig. 6), while the simulation time is 298000 s.

Line 318-319. Does the sorptive solute model only account for retardation, without considering the potential release (desorption) of sorbed solutes back into the fracture?
Thanks for the comment. For the sorptive solute, we consider both the sorption and desorption processes. During the derivation of the equivalent solute release function for sorptive solute, we used analytical solutions for 2D fracture-matrix models assuming an equilibrium sorption model, which means that the sorption and desorption processes achieves equilibrium in a very short time. This is a common assumption in many previous studies, such as Tang et al. (1981) and Dai et al. (2012). For the detailed explanation of the equilibrium sorption model, we refer to the two references.

We have also added the two references in the manuscript in case readers are interested (Lines 325-326):

"The equivalent solute release function for sorptive solute is derived based on analytical solutions for 2D fracture-matrix models (Tang et al., 1981; Dai et al., 2012), and can be expressed as"

Line 345-346. Could you please explain the role of the degradation coefficient in solute transport, and clarify the basis on which the range of this parameter was selected?
Thanks for the comment. Degradative solutes are a common concern in subsurface, such as nuclear waste and degradative tracers (for example, butyramide and uranine) used for subsurface characterization. The degradation coefficient describes the rate of solute degradation in the first-order degradation process. The role of degradation process in solute transport processes has been widely discussed in the literature and we cite the governing equation from Zhu and Zhan (2018) to demonstrate the role of degradation coefficient:

$$R_f \frac{\partial C_f}{\partial t} = -V \frac{\partial C_f}{\partial x} - \lambda_f R_f C_f - \frac{q_1}{b} - \frac{q_2}{b}$$

Where λ_f is the degradation coefficient for solute in the fracture.

The range of the degradation coefficient in this study is from 10^{-10} to 10^{-5} s^{-1}, which is mainly determined according to the data reported in the literature. We provided the detailed data for degradation coefficient in Table S3 in the Supporting Information.

Rearranging the figures and paragraphs could improve the clarity and readability of the manuscript.
Thanks for the comment. We understand the concern of the reviewer. The main source of such confusion might come from the cross citation of figures throughout the manuscript. To avoid such confusion, we have improved the manuscript through the following revisions:

1) We have reorganized the Discussion section. The results for sorptive and degradative solute have been moved forward to form an independent section.
2) We have revised the captions of Figs. 3 and 4 to clearly explain each subplot.

It may be clearer to switch the order of Figures 4 and 5. Alternatively, relocating Figure 5 and the corresponding first paragraph to the methodology section could improve the logical flow of the manuscript.
Thanks for the suggestion. Fig. 4 shows how matrix diffusion effect could be compensated for 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.

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. In the following Section 3, we demonstrate the results for 3D model, and Fig. 4(b) is cited here. From the occurrence of Figs. 4 and 5, the current order is correct.

We understand the reviewer's concern that Fig. 4(b) is the results of the 3D model presented in Fig. 5, thus showing Fig. 5 ahead of Fig. 4(b) might be more logical. However, as Fig. 4(a) is first cited in Section 2.4, switching the order of Figs. 4 and 5 will cause other conflicts. We have been thinking about splitting Fig. 4 into three figures. Nevertheless, we finally decide to keep it in the current form because the three subfigures in Fig. 4 share the same purpose and plotting style.

The reviewer's second suggestion is to move the first paragraph which describes the 3D numerical model to the methodology section. However, the current manuscript does not have a methodology section. Our logic is to present the 2D analytical model and describe how we propose the unified parameter and equivalent solute release function based on 2D analytical solutions in Section 2, and then further extends to 3D scenario in Section 3. To address the concern, we have removed Fig. 4 to the end of Section 2.

Sections 4.1 and 4.2 contain overlapping content. It would be more concise and effective to combine these sections into a single, streamlined discussion.
Thanks for this important suggestion. We have reorganized the Discussion section. As Section 4.1 is a summary rather than a discussion, we have removed the first half of Section 4.1 into the Introduction section, and incorporated the second half of Section 4.1 into the Conclusion section. Section 4.2 now remains in the Discussion Section 5.2 as a single, streamlined discussion on the limitation of the unified parameter and equivalent solute release function.

A parallel discussion of the conservative, sorptive (Section 4.3), and degradative (Section 4.4) solutes in the results section would benefit readers. Currently, Figure 4c presents the sorptive case, but this case is not discussed earlier in the text, which may cause confusion.
Thanks for the comment and sorry for the confusion. We also realize that Section 4.3 (sorptive solute) and Section 4.4 (degradative solute) are results rather than discussions. This might be the main reason of the confusion. In the updated manuscript, we have added a new Section 4 and move the original Sections 4.3 and 4.4 into this new Section to specifically demonstrate the application of the unified parameter and the equivalent solute release function to sorptive and degradative solutes (Line 312):

"***4 Application to sorptive and degradative solutes***"

We agree with the reviewer that a parallel discussion of the conservative, sorptive, and degradative solutes is beneficial. We have added a subsection in the Discussion section to provide insights of matrix diffusion effect for conservative, sorptive, and degradative solutes (Lines 365-377):

*"**5.1 Matrix diffusion effect for conservative, sorptive and degradative solutes***

Conservative, sorptive and degradative solutes are three commonly encountered solute types in most subsurface reservoir applications. According to the above analyses on matrix diffusion for the three solute types, we find that matrix diffusion for conservative solute is mainly controlled by rock porosity (θ), rock diffusion coefficient (D_m), fracture aperture (2b) and mean residence time (x/u). For sorptive solute, retardation coefficient in matrix (R_m) is also an important controlling parameter, and its impact on matrix diffusion is similar to that of rock diffusion coefficient. A larger retardation coefficient leads to more significant matrix diffusion effect. For degradative solute, an interesting finding is that the degradation coefficient (λ) does not show significant impact on matrix diffusion. The proposed unified parameter is therefore the same for sorptive and degradative solutes. The relative strength of the effect of these parameters on matrix diffusion can be discussed based on the unified parameter. Rock porosity, mean residence time and fracture aperture exhibit stronger impact on matrix diffusion than rock diffusion coefficient and retardation coefficient. Although rock diffusion coefficient directly describes the diffusion rate of solute from fracture into matrix, its effect on the overall matrix diffusion effect is smaller than that of rock porosity, fracture aperture and solute mean residence time in fracture. "

Figure 4 contains boundary lines. Please remove them if they are unnecessary.

Thanks for pointing out the issue. We did not see the boundary lines in Fig. 4, which might be a result of Mac/Windows system. To avoid such issues, we have cropped Fig. 4 and regenerated a new version in the updated manuscript (also attached below).

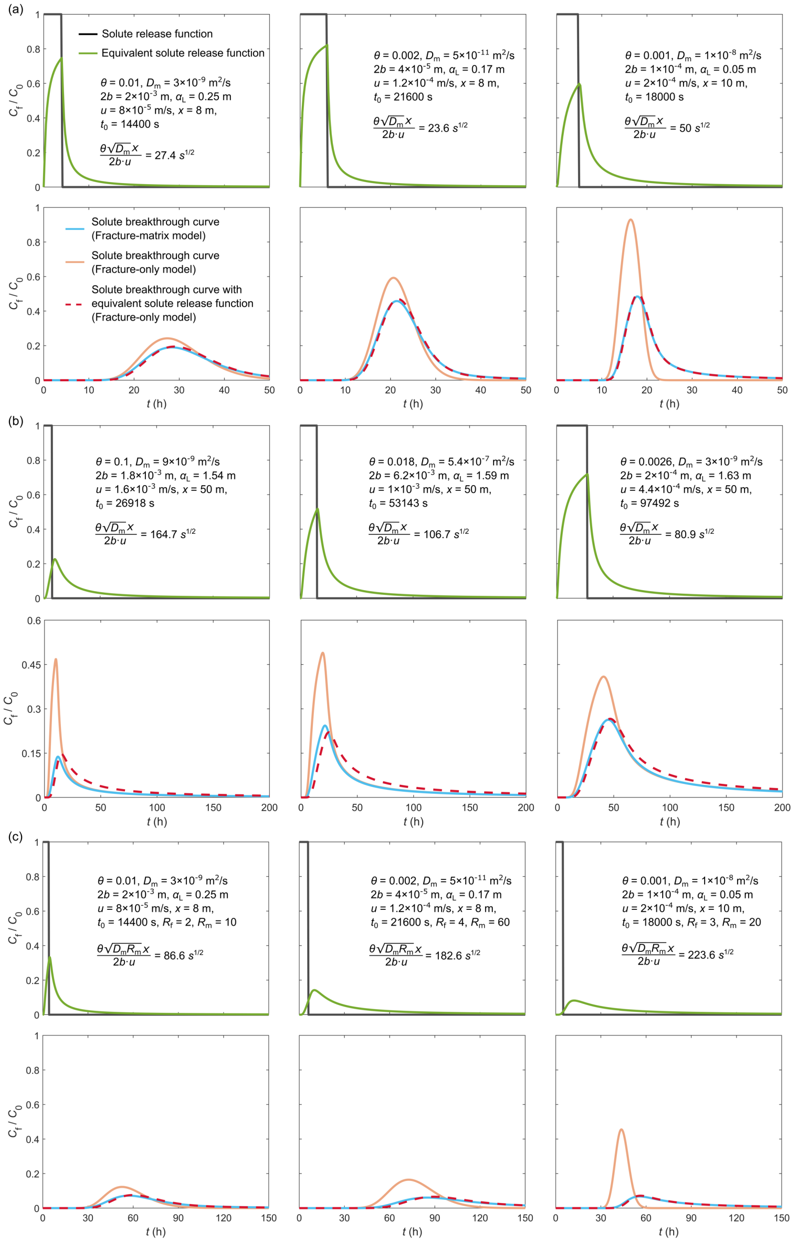

Figure R3 Compensation of matrix diffusion effect through the use of equivalent solute release function in fracture-only models.

References

Dai, Z., Wolfsberg, A., Reimus, P., Deng, H., Kwicklis, E., Ding, M., Ware, D., Ye, M. (2012). Identification of sorption processes and parameters for radionuclide transport in fractured rock. Journal of Hydrology, 414-415: 516-526.

Neretnieks, I. (2002). A stochastic multi-channel model for solute transport-analysis of tracer tests in fractured rock. Journal of Contaminant Hydrology, 55: 175-211.

Tang, D. H., Frind, E. O., Sudicky, E. A. (1981). Contaminant transport in fractured porous media: Analytical solution for a single fracture. Water Resources Research, 17(3): 555-564.

Zhu, Y., Zhan, H. (2018). Quantification of solute penetration in an asymmetric fracture-matrix system. Journal of Hydrology, 563: 586-598.