Author's response to Referee Comment RC1 on egusphere-2026-2442

We sincerely thank Referee William Johnson for his careful evaluation of our manuscript and for the constructive comments. Our point-by-point responses are provided below. The referee's comments are reproduced in black italics, our responses are presented in black regular font, and the corresponding revised passages from the manuscript are reproduced in blue.

The manuscript concerns analysis of colloid transport experiments across five flow rates spanning an order of magnitude to discern the relationship of flow rate on the size exclusion effect. The manuscript is well organized and clearly written with effective figures. Before publication however, the reproducibility of the breakthrough curves needs to be addressed, the relevance of the high-porosity media to environmental porous media needs to be addressed, and an apparent misunderstanding among the authors needs to be addressed regarding the sequential steps of colloid interception (entry to the near surface fluid domain, secondary minimum) versus contact (entry to primary minimum) versus attachment (torque balance in contact).

Response: We sincerely thank the reviewer for the careful evaluation and constructive comments. We have revised the manuscript to clarify the experimental velocity range and terminology, distinguish colloid retention from size exclusion, display the variability of the triplicate BTC measurements, and qualify the applicability of the fitted γ values. We also removed the unsupported force/torque interpretation and revised the discussion to remain focused on SEE.

Detailed responses to each comment are provided below. All revised or newly added passages relevant to the reviewer's comments are reproduced in blue so that the changes can be checked directly against the manuscript.

1.Lines 80-81, 85, 323-325. The authors suggest that the torque balance is a primary impact on colloid retention. This is likely not true for the fluid velocities examined here. Under the unfavorable deposition conditions examined here (both colloid and grain surfaces being negatively charged), colloid retention concerns entry to the near surface fluid domain corresponding to the secondary minimum in xDLVO profiles. If nanoscale heterogeneity exists (which it always seems to do) then the electric double layer barrier will be locally eliminated and the colloid may enter the primary minimum (contact). If contact is made, then the colloid may arrest if the torque balance allows, which is the case under the fluid velocities of most colloid transport experiments (see VanNess et al., 2019, Ron et al., 2019). So, depending on the range of fluid velocities in the authors' experiments (the authors should provide these), retention in the experiments is likely far less about torque balance and far more about whether the colloid can come into contact in the first place.

VanNess Kurt, Anna Rasmuson, Cesar A. Ron, William P. Johnson, 2019, A Unified Theory for Colloid Transport: Predicting Attachment and Mobilization under

Favorable and Unfavorable Conditions, Langmuir, 35 (27), 9061-9070, 10.1021/acs.langmuir.9b00911.

Ron Cesar, Kurt VanNess, Anna Rasmuson, William P. Johnson, 2019, How Nanoscale Surface Heterogeneity Impacts Transport of Nano- to Micro-Particles on Surfaces under Unfavorable Attachment Conditions, Environmental Science: Nano, 6, 1921 - 1931, 10.1039/C9EN00306A.

This issue of contact and attachment is actually somewhat problematic for the authors' purposes.

Response: We sincerely thank the reviewer for clarifying the sequential distinction among interception into near-surface fluid domains, contact with a collector surface, and attachment after contact. Our previous explanation compressed these distinct steps and consequently placed excessive emphasis on force and torque balances. This wording could incorrectly imply that torque balance controlled retention throughout the tested velocity range.

Under the unfavorable conditions of our experiments, a colloid must first sample the near-surface fluid domain and establish contact with the collector before any post-contact force or torque balance becomes relevant. Our column experiments were not designed to resolve these individual nanoscale stages. We therefore removed the unsupported force/torque interpretation rather than replacing it with an equally specific attachment or detachment mechanism.

Because the principal objective of this study is SEE, the revised Discussion focuses on the flow dependence of pore accessibility and γ without assigning the retention trend to a single force-, torque-, attachment-, or detachment-controlled process.

We have revised the interpretation of recovery and retention in Section 3.2 (clean version, Pages 17, Lines 338–348):

> "As the flow rate increased, the BTC peaks for silica colloids became sharper, accompanied by an increase in the overall recovery rate (**Table 2**). At lower flow rates (1-4 mL min^{-1}), the peak effluent concentrations were low, with recoveries ranging from 0.5 to 0.9. In contrast, higher flow rates (6-10 mL min^{-1}) yielded elevated recoveries, reaching approximately 0.7-1.0. Similar increases in colloid breakthrough and mobility at higher flow rates have been reported previously (Kretzschmar and Sticher, 1998; Torkzaban et al., 2015). Higher flow rates shortened colloid residence time near collector surfaces and reduced opportunities for colloid-collector contact, thereby decreasing retention under unfavorable conditions (Ron et al., 2019)."

We have also refocused the Discussion on the hydrodynamic meaning of γ rather than force- or torque-controlled retention (clean version, Pages 23-24, Lines 434–436, and Lines 452–454):

> "Consequently, γ inferred from BTC fitting reflects a hydrodynamically effective parameter rather than a fixed geometric fraction independent of flow."

> "Therefore, the decrease in γ likely reflects greater utilization of existing

low-flux pore domains within the experimental timescale, rather than a change in the geometry of the pore space."

2.The authors need to be clearer about the conditions under which deposition versus SEE impacts the early breakthrough. It should be noted that irreversible deposition (which colloid deposition almost always is in the absence of perturbations in flow or chemistry) does not impact timing of breakthrough.

Response: We thank the reviewer for emphasizing this important distinction. Irreversible deposition or retention primarily affects the recovered colloid mass and BTC magnitude rather than the timing of breakthrough relative to a conservative tracer. Our previous presentation discussed recovery and early breakthrough too closely together, which could create the impression that reduced retention was being used as evidence of SEE.

We have therefore separated these two processes conceptually and structurally. In the model formulation, colloid retention is represented by the retention coefficient K_r, whereas SEE is represented by the inaccessible pore-space fraction γ together with the breakthrough-time metrics ΔT_b and ΔT_{peak}. In Section 3.2, changes in BTC peak magnitude and recovery are discussed first as retention-related behavior. A separate paragraph then identifies SEE from the earlier arrival of the colloids relative to $NaNO_3$ and evaluates its velocity dependence using ΔT_b and ΔT_{peak}. Section 3.3 is now reserved for the quantitative analysis of SEE using γ.

We have explicitly distinguished retention from SEE in the model formulation in Section 2.4 (clean version, Pages 11-12, Lines 231–239):

“where ρ is soil bulk density (g cm^{-3}), K_r is the colloid retention rate (s^{-1}), and S is the solid phase colloid concentration (mg g^{-1}). To account for size exclusion, the accessible porosity for mobile colloids is expressed as (Bradford et al., 2003; Chrysikopoulos and Katzourakis, 2015; Wang et al., 2024):

$$\theta_p = \theta - \gamma\theta \quad (4)$$

where γ represents the fraction of pore space inaccessible to colloids (Bradford et al., 2003; Wang et al., 2025; Wang et al., 2024). Accordingly, colloid retention is characterized by K_r, whereas the size exclusion effect is evaluated using γ together with the breakthrough timing metrics. ”

We have described BTC magnitude and recovery separately as retention-related behavior in Section 3.2 (clean version, Page 17, Lines 338–347):

“As the flow rate increased, the BTC peaks for silica colloids became sharper, accompanied by an increase in the overall recovery rate (**Table 2**). At lower flow rates (1-4 mL min^{-1}), the peak effluent concentrations were low, with recoveries ranging from 0.5 to 0.9. In contrast, higher flow rates (6-10 mL min^{-1}) yielded elevated recoveries, reaching approximately 0.7-1.0. Similar increases in colloid breakthrough and mobility at higher flow rates have been reported previously (Kretzschmar and Sticher, 1998; Torkzaban et al., 2015). Higher flow rates shortened colloid residence time near collector surfaces and reduced opportunities for colloid-collector contact, thereby decreasing retention under unfavorable conditions (Ron et al., 2019).”

We have then identified early colloid arrival relative to the tracer as SEE in a separate paragraph (clean version, Page 20, Lines 366–374):

> "Meanwhile, the colloids consistently broke through earlier than the conservative tracer, indicating SEE. To further analyze the size exclusion behavior, the relationships between Darcy velocity and two characteristic parameters of early breakthrough were examined (**Figure 5**). These parameters were ΔT_b (the difference in normalized breakthrough time at C/C_0=0.05) and ΔT_{peak} (the difference in normalized peak arrival time) between the colloids and the conservative tracer. Both parameters were expressed in pore volumes (PV), thereby minimizing the direct influence of differences in hydraulic residence time among flow conditions. Larger ΔT values (for both ΔT_b and ΔT_{peak}) indicate more pronounced early breakthrough and a size exclusion effect."

We have reserved Section 3.3 for the quantitative evaluation of SEE using γ (clean version, Pages 20-21, Lines 383–387):

> "Given that analyzing the SEE of colloids based on ΔT values provides a relatively macroscopic perspective, HYDRUS-1D modeling was employed to quantify SEE using the fitted parameter γ (Bradford et al., 2003; Wang et al., 2025; Wang et al., 2024). In this numerical framework, γ represents the fraction of water saturation that is inaccessible to mobile colloids."

3.Line 114: The 0.434 porosity is very high, suggesting a very open structure *presumably because the grains are angular and uniform. Most uniform sands have a porosity of 0.35-ish. The porosity of non-uniform sands trends toward 0.3. The authors should address the relationship of the authors' media to environmental porous media, and how the breakthrough (SEE) results shown for the authors' media might relate to colloid breakthrough in environmental porous media.*

Response: We appreciate the reviewer's concern regarding the relatively high measured porosity of 0.434. This value is higher than that commonly reported for many compact or poorly sorted natural sediments, but it is comparable to values reported for uniformly packed quartz-sand columns. It primarily reflects the narrowly graded quartz sands and the controlled saturated-packing procedure used to construct the columns. We added Wang et al. (2019) and Yan et al. (2019), who reported porosities of approximately 0.44 and 0.47, respectively, for comparable uniformly packed quartz-sand columns, demonstrating that the measured value is reasonable for this type of laboratory system. Moreover, similar porosities may occur in loose, well-sorted, unconsolidated sandy sediments. We have therefore clarified that the tested columns represent the relatively open and homogeneous end of natural subsurface sandy media rather than an environmentally unrealistic structure.

We have added the porosity context and a limitation on extrapolation to natural sediments in Section 2.2 (clean version, Page 7, Lines 129–131) and Section 4 (clean version, Page 26, Lines 474–479):

> "The porosity of the packed columns was approximately 0.434, which is within the range reported for uniformly packed quartz-sand columns used in laboratory

colloid-transport studies (Wang et al., 2019; Yan et al., 2019)."

"The porosity of the packed columns was approximately 0.434, which is comparable to values that may occur in loose, well-sorted, unconsolidated sandy sediments. The tested columns therefore represent the relatively open and homogeneous end of natural subsurface porous media. Although greater structural heterogeneity in natural sediments may alter the absolute γ values, the observed dependence of γ on hydrodynamic conditions is expected to remain relevant to natural sandy environments."

4.Lines 126-128: UV absorbance quantification is typically coarse. I've never before seen (Figure 4) such fine-scale changes in breakthrough using UV absorbance. The authors should demonstrate that the range across triplicate experiments under a single condition is significantly smaller than the range associated with changing the flow rate.

Response: We thank the reviewer for raising this important point. The UV absorbance measurements were not performed using intermittently collected effluent samples. Instead, the column effluent was continuously passed through a flow-through UV detection cell, allowing absorbance to be recorded continuously at a high sampling frequency. Therefore, the fine temporal resolution of the breakthrough curves in Figure 4 primarily reflects the continuous-flow measurement configuration rather than the unusually high analytical resolution of conventional discrete UV measurements.

To demonstrate experimental reproducibility, each condition was independently repeated three times, and Figure 4 has been revised to present the mean breakthrough curves together with the variability among the triplicate experiments.

We have added the number of replicates and the definition of the error bars in Section 2.2 (clean version, Pages 7-8, Lines 145–147):

> "All colloid transport experiments were conducted in triplicate under each condition. The BTC data are presented as mean values, and the error bars represent standard deviation."

We have also revised the Figure 4 caption to report the replicate mean and standard deviation explicitly (clean version, Page 18, Lines 350–355):

> "Figure 4. The observed and fitted breakthrough curves of $NaNO_3$ and silica colloids in saturated porous media at different flow rates: in fine sand with column lengths of 10 cm (a) and 30 cm (b), medium sand with column lengths of 10 cm (c) and 30 cm (d), and coarse sand with column lengths of 10 cm (e) and 30 cm (f). A small inset image in the upper right corner of each figure displays a magnified view of the highlighted yellow region. Symbols represent the mean values of three replicate experiments, and error bars represent one standard deviation."

5.Line 303: The authors state that the BTC shapes "are strongly dependent on flow velocity". The fact is that the apparent dependence is not strong, the breakthrough *curves only modestly change with flow rate (or fluid velocity). But the curves show a surprising implied reproducibility via consistent minor changes in the timing and magnitude of breakthrough with changes in velocity. I've already brought up the need to demonstrate reproducibility of the trend.*

Response: We thank the reviewer for this careful assessment of the BTC results. The differences among the BTCs at different flow rates are modest, and the terms "strongly dependent" and "strong dependence" overstated the magnitude of the changes visible in Figure 4. We have therefore removed these expressions and the redundant statement from the revised manuscript.

As described in our response to Comment 4, Figure 4 now presents the mean BTCs and standard deviations from three independent experiments. The error bars demonstrate the within-condition variability and allow it to be compared directly with the changes observed across flow rates. Although the changes in the raw BTCs are modest, their direction is consistent across the three porous media and two column lengths. We therefore describe the BTC changes cautiously and evaluate the velocity dependence of SEE primarily using ΔT_{b}, ΔT_{peak}, and the fitted γ values rather than the visual differences among the BTCs alone.

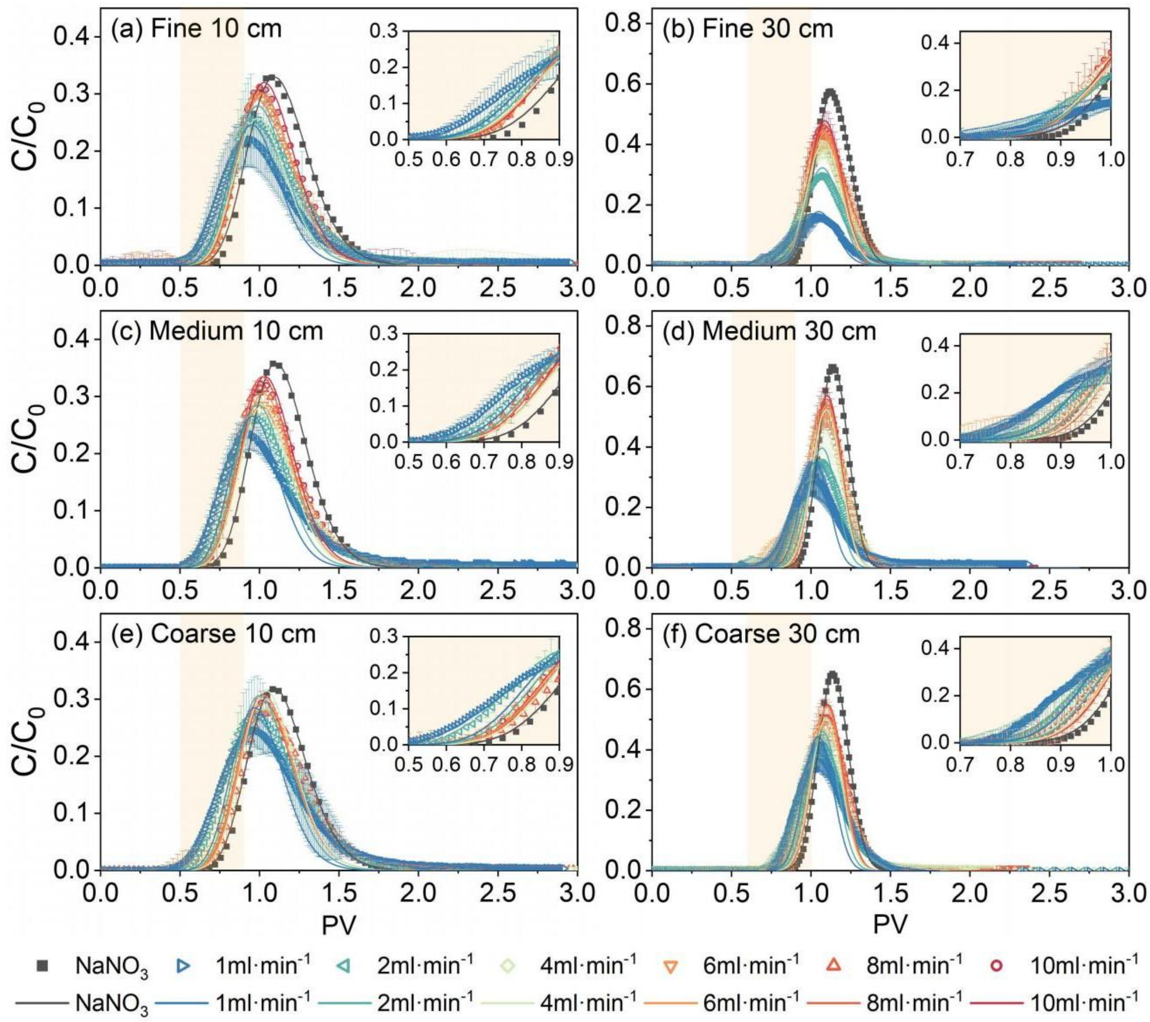
We have revised the description of the BTC changes and removed the earlier claim of a strong dependence (clean version, Pages 17, Lines 338–343):

> "As the flow rate increased, the BTC peaks for silica colloids became sharper, accompanied by an increase in the overall recovery rate (**Table 2**). At lower flow rates (1-4 mL min^{-1}), the peak effluent concentrations were low, with recoveries

ranging from 0.5 to 0.9. In contrast, higher flow rates (6-10 mL min^{-1}) yielded elevated recoveries, reaching approximately 0.7-1.0."

6. The figure would be clearer if the authors used a consistent color ramp, e.g., cool to warm colors across lower to higher flow rates.

Response: We thank the reviewer for this practical suggestion. We revised Figure 4 so that all six panels use the same cool-to-warm progression: cooler colors consistently denote lower flow rates, and warmer colors denote higher flow rates. The symbols and fitted curves follow the same color assignment in every medium and column length, which makes comparisons among panels more direct and reduces the possibility of confusing the flow-rate order. The revised figure is reproduced below (clean version, Page 18).



(a) Fine 10 cm
(b) Fine 30 cm
(c) Medium 10 cm
(d) Medium 30 cm
(e) Coarse 10 cm
(f) Coarse 30 cm
C/C$_0$
PV
NaNO$_3$
1ml·min^{-1}
2ml·min^{-1}
4ml·min^{-1}
6ml·min^{-1}
8ml·min^{-1}
10ml·min^{-1}

7.BTW, "flow velocity" is an oxymoron. It's either flow rate or fluid velocity. The authors create redundant and misstated observations by also stating on line 315: "Additionally, the BTCs of the colloids exhibit a strong dependence on the flow rate".

Response: We thank the reviewer for identifying this terminology problem. The term "flow velocity" did not clearly distinguish between volumetric flow rate and velocity normalized by the column cross-sectional area. We now use flow rate exclusively for the imposed volumetric rate Q (mL min^{-1}), Darcy velocity U for the volumetric flux normalized by the column cross-sectional area (cm s^{-1}), and pore-water velocity v for U/θ.

We reviewed the Abstract, Methods, Results, figure captions, table captions, and Conclusions to apply these definitions consistently. The experimental pump settings are therefore reported as flow rates, whereas the analysis of SEE, γ, and Péclet number is expressed using Darcy velocity or pore-water velocity as appropriate. The definition used in the Péclet-number calculation has also been stated explicitly.

In addition, we removed the redundant sentence stating that the BTCs exhibited a strong dependence on flow rate. The revised manuscript instead describes the modest changes in the BTCs and evaluates the hydrodynamic dependence of SEE using the timing metrics and fitted γ values.

We have revised the terminology in the Abstract (clean version, Page 1, Lines 14–23):

> "Despite extensive studies on colloid transport in porous media, the influence of Darcy velocity on the size exclusion effect (SEE) remains poorly understood. In

this study, nuclear magnetic resonance (NMR) and micro-computed tomography (μ-CT) were employed to characterize the pore structures, and column experiments combined with HYDRUS-1D modeling were conducted to quantitatively analyze colloid transport under varying Darcy velocities."

"Both the relative breakthrough time difference (ΔT_b) and the relative peak arrival time difference (ΔT_{peak}) consistently indicated the occurrence of the size exclusion effect."

We have distinguished flow rate, Darcy velocity, and pore-water velocity in Section 2.2 (clean version, Page 7, Lines 132–135):

"To investigate the effect of flow rate on colloid transport, experiments were performed at flow rates of 10, 8, 6, 4, 2, and 1 mL min^{-1}. These flow rates corresponded to Darcy velocities of approximately 0.004-0.032 cm s^{-1}. Based on the measured column porosity of 0.434, the corresponding pore-water velocities were approximately 0.009-0.074 cm s^{-1}."

We have also used Darcy velocity in the revised Conclusions (clean version, Page 27, Lines 490–492):

"By integrating NMR, μ-CT, column experiments, and HYDRUS-1D modeling, this study systematically quantified the influence of Darcy velocity on the size exclusion transport of colloids in saturated porous media."

8. Line 99: Is particle "size" the diameter or radius?

Response: We thank the reviewer for pointing out this ambiguity. The reported particle size of 0.5 μm refers to the particle diameter. We have revised the corresponding description to state this explicitly.

We have revised the description of the silica colloids in Section 2.1 (clean version, Page 6, Lines 112–113:

"Silica colloids were used as the model particles in this study, characterized by a particle diameter of 0.5 μm and a zeta potential of -39.1 mV."

Reference

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