Parti-Suite UpscaleContinuum

Abstract

Description of ContinuumUpscale Output File and Parameters

William P. Johnson and Eddy F. Pazmino

William.johnson@utah.edu; eddy.pazmino@epn.edu.ec

Parti-Suite UpscaleContinuum Description of Output File and Parameters

Colloid attachment under unfavorable conditions yields profiles of retained colloids with distance from source that deviate from the log-linear decrease from source expected from solution of the advection-dispersion-attachment equation under steady state conditions (e.g., Johnson et al., 2018). Prediction of these deviations in retained profiles requires prediction of colloid attachment under unfavorable conditions, which is provided by inclusion of surface heterogeneity in pore scale simulations (e.g., Ron et al., 2019 and references therein). A novel algorithm for determining fast and slow attachment rate constants (as well as other rate coefficients) via upscaling the pore scale residence times from trajectory simulations was recently described (Johnson et al., 2018).

UpscaleContinuum is the numerical implementation of a standing hypothesis expressed in Johnson et al. (2018); which is that a population of identical colloids effectively yields fast-attaching and slow-attaching sub-populations that appear to be related to their initial colloid locations in the flow field, some of which happen to yield fast attachment. These fast-attaching initial locations are not replenished during transport from pore to pore, yielding an effective separate and rapidly-depleted fast-attaching sub-population. The remaining population is subject to slow attachment that can be simulated via two options to represent the near surface fluid domain. In the implicit option, the near surface fluid domain *is not* explicitly represented, such that simulations *will not* explicitly represent near surface colloids in breakthrough-elution concentration histories or in profiles of retained colloids as a function of distance from source. The implicit option will therefore produce breakthrough-elution concentration histories lacking extended tailing, and profiles ranging from hyper-exponential to log-linear. In the explicit option, the near surface fluid domain *is* explicitly represented, such that simulations **will** explicitly represent near surface colloids in breakthrough-elution concentration histories or profiles of retained colloids as a function of distance from source. The explicit option will therefore produce breakthrough-elution concentration histories with extended tailing, and profiles ranging the entire gamut from hyper-exponential to log-linear to non-monotonic.

The theory underlying the simulations is described further below.

Description of Input
UpscaleContinuum utilizes rate coefficients either calculated from trajectory simulations or input by the user. To calculate the rate coefficients based on pore scale trajectory simulations, the code reads the files output from TRAJ-HAP, the trajectory simulator for the Happel collector, after the user transform those results into an Excel file (e.g., UPFLUX.xls) that is read by UpscaleContinuum using a browse option in the GUI. The user prepares UPFLUX.xls by renaming the summary flux worksheets from the trajectory simulations and copying them into UPFLUX.xls in the following order:

a) FAVATT = favorable attached; b) FAVEX = favorable exited; c) UNFATT = unfavorable attached; and d) UNFEX = unfavorable exited. Example UPFLUX.xls files are provided on the Parti-Suite distribution directory.

The pore scale trajectory codes allow numerical efficiency to be improved by recognizing the practical arrest of very slow moving colloids in contact with the collector surface (using DFACTC and DFACTNS) (further description provided below). This may produce functionally arrested colloids designated with ATTCHK=4 in the summary flux files for "remaining" colloids (HAPHETFLUXREM). The user may wish to append these colloids onto the UNFATT worksheet of UPFLUX.xls since these colloids may also be considered attached depending on the stringency with which DFACT parameters were employed.

UpscaleContinuum uses the user-identified UPFLUX file to determine the following parameters:

Alpha1 and Alpha2 (α_1 and α_2 in Johnson et al., 2018) represent the fraction of near surface colloids that attached fast and slowly, respectively, as determined from the pore scale residence time distributions in trajectory simulations. T

AlphaRFSP (α_{RFSZ} in Johnson et al., 2018) represents the fraction of near surface colloids that reached the RFSZ during the pore scale trajectory simulations. The pore scale trajectory codes discriminate between colloids retained at the rear flow stagnation zone (RFSZ) versus the remaining surface (please see Theory section below for further description).

AlphaREENT (α_{REENT} in Johnson et al., 2018) represents the fraction of bulk fluid colloids that entered the near surface and then exited via reentrainment to bulk solution prior to reaching the RFSZ.

The alpha values (Alpha1, Alpha2, AlphaRFSZ, and AlphaREENT) should total to unity since they are each fractions of the net near surface population.

To upscale the above efficiencies to rate coefficients, two additional efficiencies (ranging from 0 to 1) are user-specified ($\alpha_{trans-gg}$ and $\alpha_{trans-bg}$) because they concern mass transfer beyond the grain scale. In an actual porous media, RFSZ colloids may either be:

a) translated directly to the near surface of a downgradient grain according to $\alpha_{trans-gg}$; or

b) expelled into the bulk fluid ($1-\alpha_{trans-gg}$)

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Likewise reentrained colloids may

> a) enter the near surface of a downgradient grain according to $\alpha_{trans-bg}$; or

> b) remain in the bulk fluid (1-$\alpha_{trans-gg}$)

The value of these efficiencies depend on whether the grain-grain network is expected to facilitate direct grain-to-grain transfer of RFSZ colloids.

For further explanation of these user-specified efficiencies see the Theory section below.

The user also needs to specify a characteristic velocity for upscaling the efficiencies to a rate coefficient for net colloid transport to the near surface fluid (k_{ns}). Further explanation of which this characteristic velocity (ranging between the near surface and bulk fluid velocities) is provided in the Theory section below.

To allow the user to examine the impacts of their own rate coefficients on colloid breakthrough and retention, and user-defined input box also exists. The user may wish to input their own efficiency values, in which case the code will calculate user-defined rate coefficients from those efficiency values according to the relationships below and in Johnson et al., 2018. Alternatively, the user can input their own rate constants directly in the GUI.

The Continuum Simulation Parameters box on the GUI allows the user to specify continuum parameters needed to predict breakthrough-elution concentration histories and profiles of retained colloids as a function of distance from source.

We have tried to make the GUI flexible for changing input values on the fly between simulations without need for closing the GUI. However, this involves a great deal of error-catching statements. We therefore suggest that if you want to absolutely that ensure your intended values are actually utilized in the simulations, close the GUI between simulations, and work the GUI sequentially from upper to lower sections.

Description of Output
UpscaleContinuum determines (and provides on the GUI) the near surface fluid velocity as approximated by the near surface colloid velocities from the trajectory simulations (in the user-specified UPFLUX.xls). UpscaleContinuum also determines the collector efficiency (η) and attachment rate (k_f) corresponding to favorable conditions (from FAVATT worksheet of user-specified UPFLUX.xls). The other rate coefficients upscaled from pore scale trajectory simulations via the user-specified UPFLUX.xls are described in detail in the Theory section below.

The relationship between pore scale trajectory simulations and continuum scale transport simulations therefore depends primarily on a user-specified spatial density of heterodomains (SCOV) that the user varies to produce the experimentally-observed steady-state breakthrough (C/Co) in unfavorable continuum-scale transport experiments. In order to facilitate this comparison, we also the example calculation in the example UPFLUX.xls spreadsheets (Column AD) to convert attachment obtained from TRAJ-HAP to an attachment rate coefficient ($k_{f,unf}$), and C/C_0. Note that the RSPF colloids are not included in the attachments for this calculation, so this calculated is an approximation of C/C_0 obtained using UpscaleContinuum with $\alpha_{trans\text{-}gg}$ or $\alpha_{trans\text{-}bg} > 0$.

Output files from Upscale-Continuum are provided for retained and exited colloids, and are named accordingly. They also provide rate coefficients and related parameters used in the simulations as well as those upscaled from Traj-Hap simulations.   The output files are located in the program files directory. For example: C:\Program Files\W.P. Johnson Research Group\Jet_Trajectory_GUI0.11\ application\JetWorkdir001, wherein the path above "W.P. Johnson Research Group" will differ with user environment.

Notes for users:
The maximum summary flux file size (number of colloids) for importing into ContinuumUpscale is 50,000.

Theory

Favorable Condition Collector Efficiency and Attachment Rate Coefficient
Upscaling from pore to continuum scale is done to produce rate coefficients for use in continuum scale simulations. This starts with efficiencies that are determined in pore scale trajectory simulations. Under favorable conditions (lacking a repulsive barrier to attachment), the relevant efficiency is the collector efficiency (η) (# attached/# introduced). Upscaling as described in Johnson and Hilpert (2013) yields:
$$k_f = -\left(\frac{N_c}{L}v\right)\text{Ln}(1-\eta)$$
Note that the first term on the r.h.s. is an inverse characteristic residence time from the product of the number of collectors per unit length (N_c/L) and a characteristic velocity (v), which is the average pore water velocity. The second term on the r.h.s. is a probability determined by the collector efficiency. Upscaling thereby produces a rate coefficient ($1/t$) that reflects to ratio of a probability to a characteristic residence time (Johnson et al., 2018). In a Happel sphere-in-cell collector, with diameter d_c and volumetric water content θ, N_c/L is (Nelson and Ginn, 2011):
$$N_c/L = \frac{(1-\theta)^{1/3}}{2d_c}$$

Unfavorable Condition Efficiencies

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Under unfavorable conditions, wherein a repulsive barrier to attachment exists, colloids translate across collector grain in the near-surface fluid domain since repulsion from the bulk surface prevents their attachment except where nanoscale zones of attraction (heterodomains) exist (Pazmino et al., 2014; Ron et al., 2019). The delivery of colloids to the near-surface fluid domain is η; however, repulsion restricts attachment. The relevant pore scale near-surface efficiencies under unfavorable conditions are (Johnson et al., 2018):

   a) Fast attachment efficiency (α_1), which is the fraction of all colloids that enter the near surface and that attach with residence times prior to attachment that fall within the distribution that occurs under favorable conditions.
   b) Slow attachment efficiency (α_2), which is the fraction of all colloids that enter the near surface and that attach with residence times prior to attachment that exceed the distribution that occurs under favorable conditions.
   c) RFSZ efficiency (α_{RFSZ}) which is the fraction of all colloids that enter the near surface and which do not attach until they reach a heterodomain at the RFSZ (within one colloid radius of the rear flow stagnation point, RFSP).
   d) Some colloids that enter the near surface will reentrain (α_{reent}) prior to reaching the RFSZ.
   e) The above pore scale efficiencies are fractions of the net near surface population, and so should total to unity:

$$1 = \alpha_1 + \alpha_2 + \alpha_{RFSZ} + \alpha_{reent}$$

Because the Happel sphere-in-cell collector is nonphysical, it does not represent potential mass transfer between upstream and downstream grains; i.e.:

   f) efficiency of transfer of near-surface micro-scale colloids (low diffusion) at the grain RFSZ to the near-surface the downstream grain ($\alpha_{trans-gg}$), which is the fraction of RFSZ colloids that transfer to the near surface of a downstream grain rather than expel back to the bulk fluid upon reaching the RFSZ; and
   g) efficiency of transfer of reentrained nano-scale colloids to the near-surface the downstream grain ($\alpha_{trans-bg}$).

Only recently has the relationship between $\alpha_{trans-gg}/\alpha_{trans-bg}$ and pore/grain network structure begun to be explored and related (e.g., Johnson et al., 2018). The parameter α_{trans} is currently empirical, but can potentially be characterized in direct observation experiments, and predicted in multigrain mechanistic simulations (e.g., Long and Hilpert, 2009; Johnson et al., 2007). A continuum scale simulation approach incorporating binary decisions for near-surface colloids was recently developed that complements the approach described below for UpscaleContinuum (Hilpert et al., 2017; Hilpert and Johnson, 2017).

Unfavorable Condition Rate Coefficients Implicit Near Surface
Under unfavorable conditions, observed profiles of retained colloids as a function of transport distance are often hyper-exponential, indicating that the fraction of fraction of fast-attaching

colloids rapidly depletes with increasing transport distance (Johnson et al., 2018). We represent this by applying k_f only to the α_1 fraction of the population, wherein residence time prior to attachment reflected favorable conditions absent a repulsive barrier.   The remainder of the population $(1-\alpha_1)$ is subject to the unfavorable condition efficiencies (α_2, α_{RFSZ}, $\alpha_{trans-gg}$) described above. Note that all efficiencies except $\alpha_{trans-gg}$ are defined by the mechanistic pore-scale simulations, allowing the user to gain insight regarding how those two efficiencies influence breakthrough-elution concentration histories and distributions of retained colloids with distance from source.

The above efficiencies are upscaled to produce continuum scale rate coefficients, which can be used to simulate transport for conditions where the near surface fluid domain is simulated implicitly or explicitly. In simulations with an implicit near surface, mass transfer is considered direct from the bulk fluid to the collector grain surface, with the complexity of near surface transport subsumed into the rate coefficients. Implicit simulations therefore involve fast (k_f) and slow (k_{f2}) attachment rate coefficients:

    a) $k_f = - \left(\frac{N_c}{L}v\right) \mathrm{Ln}(1-\eta)$

           applied to the α_1 subfraction of the population

The remainder of the population is subject to a slower attachment rate coefficient upscaled from the efficiencies corresponding to the slow attached fraction plus the fraction transferred to the near surface of down-gradient grains, and residence time scaled to the near-surface fluid velocity (v_2) (Johnson et al., 2018):

    b) $k_{f2} = - \left(\frac{N_c}{L}v_2\right) \mathrm{Ln}\left(1-\eta\left(\alpha_2 + \alpha_{RFSZ}\alpha_{trans-gg} + \alpha_{Reentrain}\alpha_{trans-bg}\right)\right)$

           applied to the $(1-\alpha_1)$ subfraction

The rationale for using v versus v_2 in upscaling to k_f versus k_{f2} is that whereas the simulation treats the near-surface fluid domain as implicit, the greater residence times prior to attachment associated with the slow-attaching subpopulation reflect longer residence in the near surface fluid via: i) transport to RFSZ for micro-scale (low diffusion) colloids; and ii) transport repeatedly between bulk and near-surface fluid via reentrainment for nano-scale (high diffusion) colloids. Furthermore, practically speaking, scaling residence time to v_2 ensures that if α_2 were to approach unity, k_{f2} would remain below k_f.

Because implicit simulations lack explicit treatment of near-surface colloids, they lack elution of near surface colloids, which eliminates extended tailing in breakthrough-elution concentration histories as well as non-monotonic profiles of retained colloids as a function of transport distance). To predict these features based on pore scale trajectory simulations, we explicitly simulate the near surface fluid domain in continuum scale simulations.

Unfavorable Condition Rate Coefficients Explicit Near Surface

The explicit approach replaces k_{f2} with k_{ns}, the latter representing the rate coefficient for **net** transfer to the near surface: Net transfer means that k_{ns} does not include colloids that enter the near surface and then reentrain without return ($\alpha_{\text{reent}}[1-\alpha_{\text{trans-bg}}]$) nor RFSZ colloids that expel back to bulk fluid ($\alpha_{\text{RFSZ}}[1-\alpha_{\text{trans-gg}}]$).

   a) $k_{ns} = -\left(\dfrac{N_c}{L}v^*\right)\mathrm{Ln}\left(1 - \eta\left(\alpha_2 + \alpha_{RFSZ}\alpha_{trans-gg} + \alpha_{Reentrain}\alpha_{trans-bg}\right)\right)$
   where v^* is a characteristic velocity described below

In Johnson et al. (2018), the **characteristic velocity** used for k_{ns} was the average pore water velocity (v), although it can be argued that the characteristic velocity should reflect v_2 because k_{ns} reflects (is reduced by) processes operating in the near surface, such as reentrainment back to bulk fluid, and expulsion to bulk fluid at the RFSZ. Using v_2 as the characteristic velocity would make the formula for k_{ns} equivalent to the formula for k_{f2}. k_{ns} therefore is less defined with respect to characteristic velocity, but the characteristic velocity range is between v_2 and v, with the geometric mean of v and v_2: $(vv_2)^{1/2}$, being an option.

Near-surface colloids are explicitly tracked and translated according to v_2, and may become attached via rate coefficient k_{f2}^*, wherein the probability of attachment is set by $Ln(1-\eta\alpha_2)$, and the characteristic residence time is set by v_2 and the grain half circumference (πa_c) where a_c is collector radius:

   b) $k_{f2}^* = -\left(\dfrac{v_2}{\pi a_c}\right)\mathrm{Ln}(1 - \eta\alpha_2)$

The example results below demonstrate the influence of implicit versus explicit simulations, as well as the impacts of $\alpha_{\text{trans-gg}}$, as well as the impact of using v_2 versus the geometric mean of v and v_2 as the characteristic velocity for k_{ns}.

The upshot is that retained profiles shift from hyper-exponential to non-monotonic based on the mechanistics efficiencies, as well as the user-defined values for $\alpha_{trans-gg}$, and v^*. Ongoing work will constrain these parameters and their relationships to to pore/grain network characteristics.

Example Results for Micro-Scale Colloids

Example parameter values and corresponding breakthrough-elution concentration histories and profiles of retained colloids are provided below. Both implicit and explicit approaches yield hyperexponential profiles under conditions corresponding to experimentally-observed hyperexponential profiles (i.e., for glass beads and CML) (Johnson et al., 2018). Non-monotonic profiles were achieved for conditions corresponding to quartz sand and CML using the explicit approach (Johnson et al., 2018).

The results below were obtained by feeding UPFLUX files output by TRAJ-HAP corresponding to 1 μm carboxylate-modified microspheres (CML) in 510 μm glass beads and quartz sand at 4 m/day average pore water velocity, pH 6.7 and 6 mM NaCl. These UPFLUX files are provided as example files for user orientation. The distributions of residence time prior to attachment show limited overlap between unfavorable and favorable conditions, reflecting the longer residence time in the near surface under unfavorable conditions.
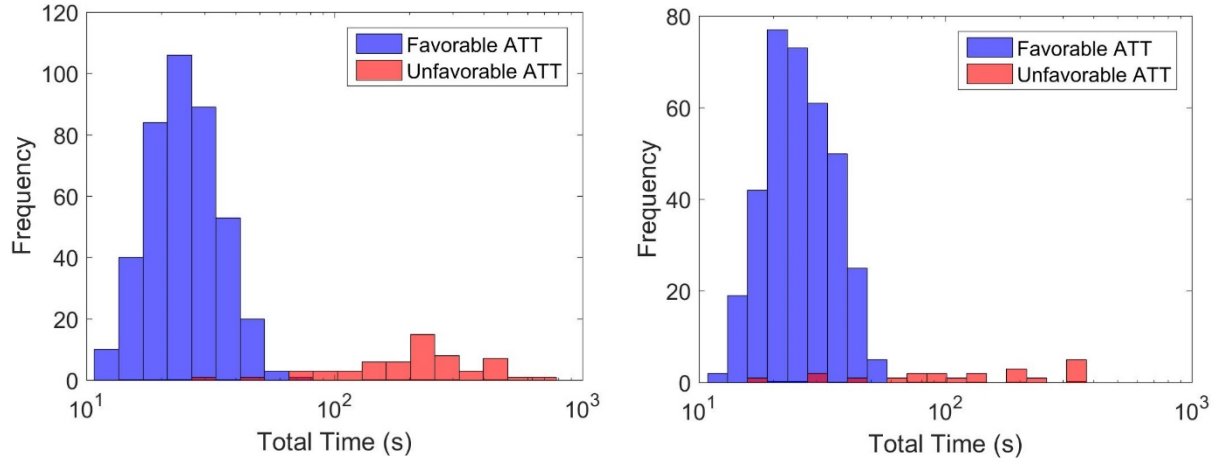
Figure 1: Residence time distributions determined by UpscaleContinuum using output from Traj-Hap trajectory simulations. Glass bead media (left) and quartz sand media (right)

The residence time distributions were utilized in UpscaleContinuum to obtain the above-described efficiencies and rate constants. These rate constants were then utilized in continuum scale Lagrangian simulations to predict breakthrough-concentration histories and profiles of retained colloids with distance from source (shown below), as described above.

Glass Beads

These results set k_{ns} characteristic velocity to v_2

Alpha 1	Alpha 2	Alpha RFSP	Alpha reentrain	Alpha trans	v2	kf	kf2/kns	kf2star
0.00215	0.00914	0.0360	0.9527	0.0	0.004	7.59	0.00329	0.0462

Implicit

Explicit

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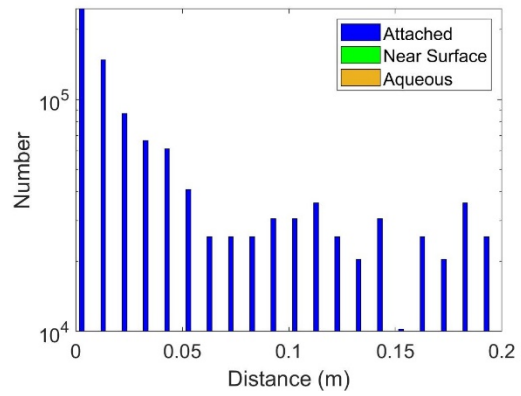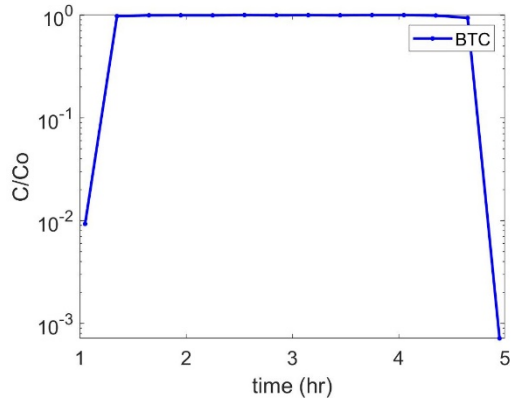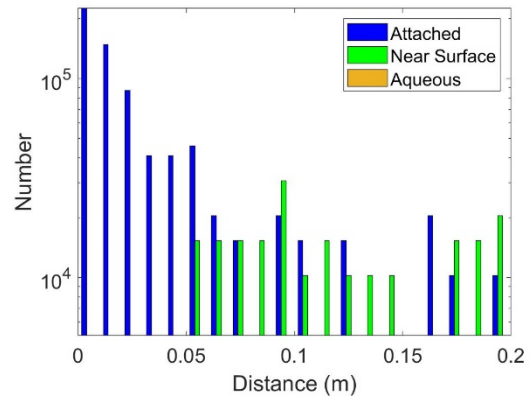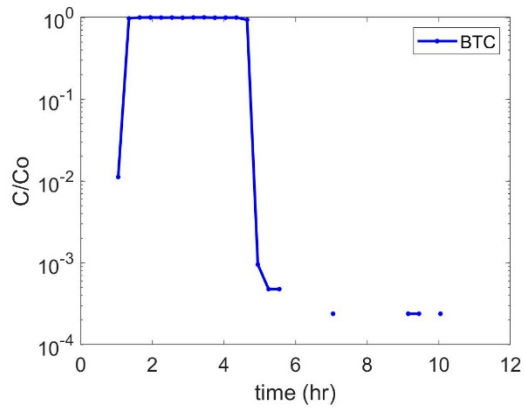
Glass Beads Continued

These results set k_{ns} characteristic velocity to $(v_{pore}*v_2)^{(1/2)}$

Alpha 1	Alpha 2	Alpha RFSP	Alpha reentrain	Alpha trans	v2	kf	kf2	kns	kf2star
0.00215	0.00914	0.0360	0.9527	0.0	0.004	7.59	0.00166	0.0168	0.0462

Implicit
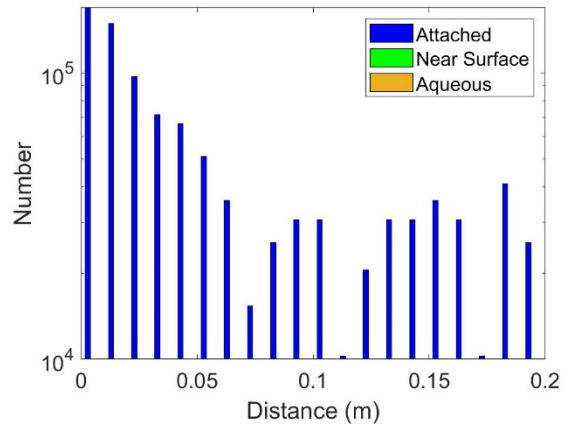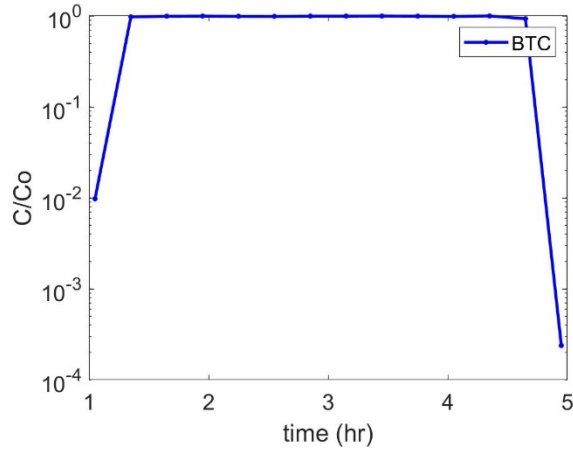
Explicit
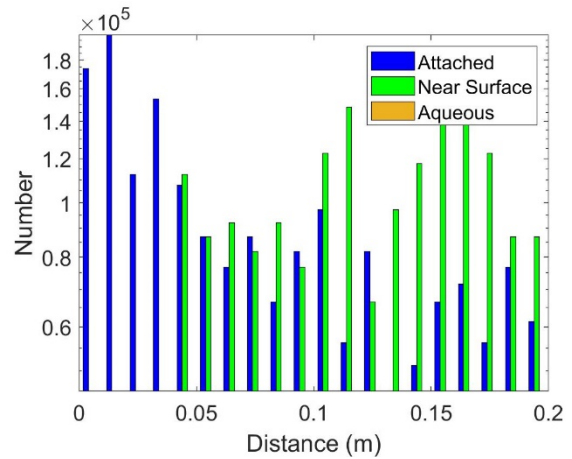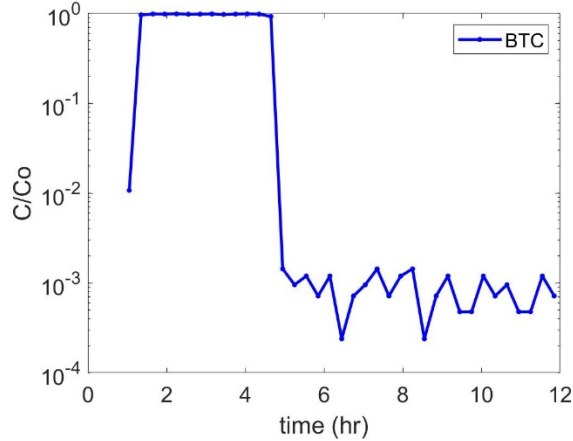
An obvious difference between implicit and explicit approaches is the absence versus presence of near surface colloids (in extended tailing portion of breakthrough-elution concentration history and retained profile), although the results are qualitatively equivalent.

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Quartz Sand

Explicit yields nonmonotonic profiles for conditions that produce them (quartz sand and CML) (Johnson et al., 2018, *Environ. Sci. Technol.*, 2018, 52 (13), pp 7230–7239, DOI: 10.1021/acs.est.8b00811).

These results set k_{ns} characteristic velocity to v_2

Explicit

Alpha 1	Alpha 2	Alpha RFSP	Alpha reentrain	Alpha TRANS	v2	kf	kf2	kns	kf2star
0.0042	0.0449	0.933	0.0178	0.50	0.0019	8.715	0.0527	0.0527	0.1139
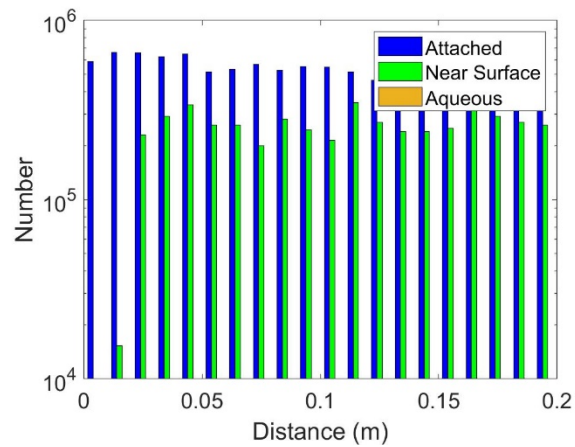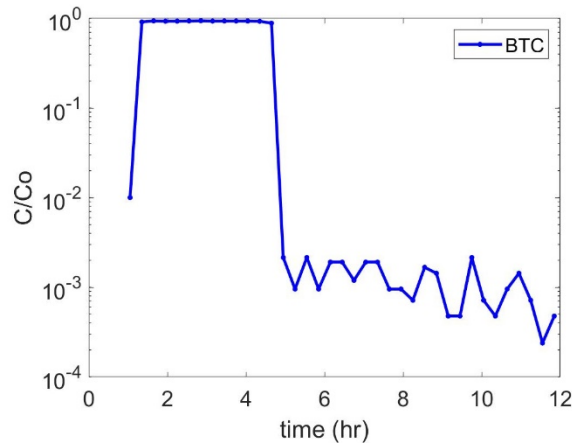
These results set k_{ns} characteristic velocity to $(vpor*v_2)^\wedge(1/2)$

Explicit

Alpha 1	Alpha 2	Alpha RFSP	Alpha reentrain	Alpha TRANS	v2	kf	kf2	kns	kf2star
0.0042	0.0449	0.933	0.0178	0.50	0.0019	8.715	0.0527	0.4838	0.1139
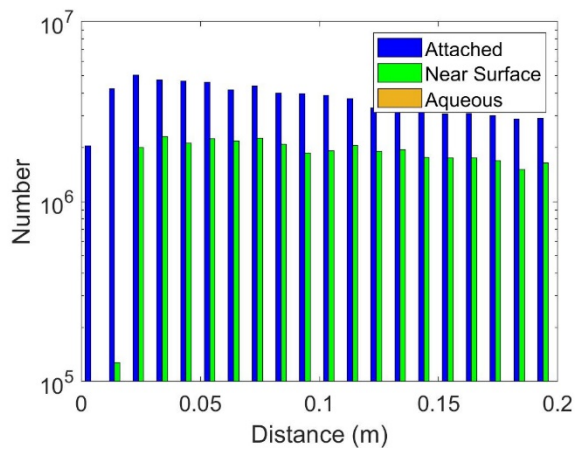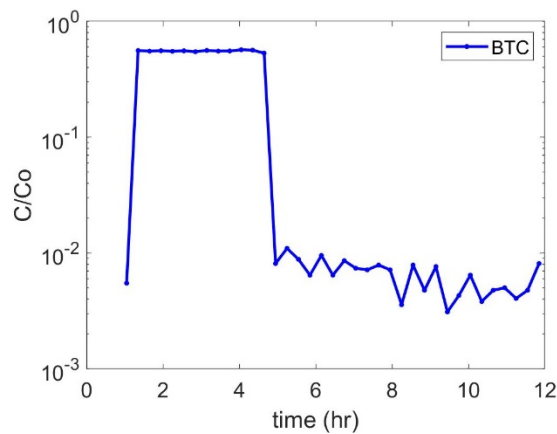
Example Results for Nano-Scale Colloids

Whereas micro-scale colloids tend to experience longer residence times and accumulate at the RFSP due to their stronger secondary minimum interactions and lesser diffusion, nano-scale colloids experience total residence times similar to favorable conditions, and diffuse out of the near-surface before reaching the RFSP. It is also possible for these colloids to diffuse back into the near-surface from the bulk pore water (α_{trans} bg) at downstream grains.

Nanoparticles experience higher v_2 compared to micro-scale colloids as their enhanced diffusion causes them to experience a broader range of fluid velocities. In contrast, larger colloids experience lesser diffusion and stronger secondary minimum interactions, which hold them in closer to the surface and decrease their average v_2. For example, average v_2 for 0.1 μm and 1.0 μm colloids were 0.083 m/hr and 7E-3 m/h, respectively. Higher v_2 serves to increase k_{f2} and k_{f2}^*, resulting in greater retention for nanoparticles.
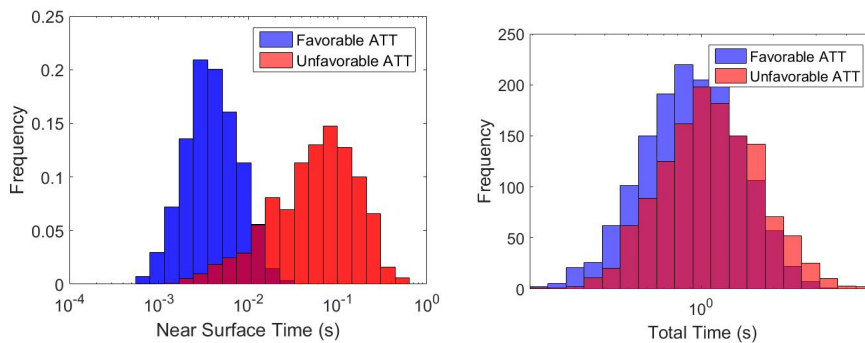
Additionally, it's possible for colloids that spend little time in the near-surface to skew the average v_2. For example, in the plot below the average v_2 falls above the peak in the data (dashed black line). The user is encouraged to plot NSVEL versus NSVISIT from the Happel output to identify such a skew in the data. To correct for skew, the average was calculated from colloids that had > 1000 NS visits (dotted line black line).
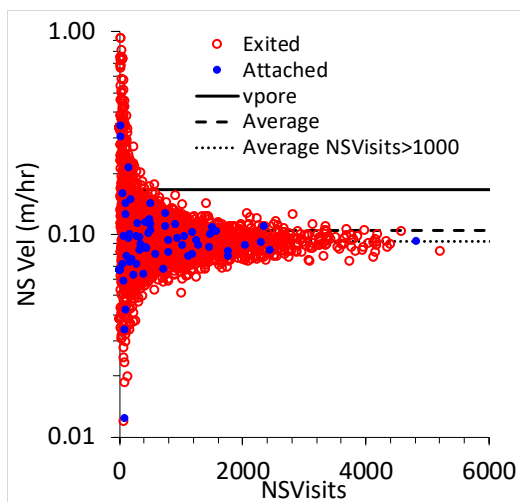
The results below show the sensitivity of α_{trans} bg. They were obtained from HAPPEL UPFLUX files for 100 nm colloids and a 100 µm collector and a surface coverage of 1E-2. Surface coverage and collector radius each influence retention and breakthrough.

The figures below show simulated results compared with experimental values. Note that the last five segments in the experimental retained profile were assigned lesser confidence due to high background signal in flow cell cytometry analyses.

The Continuum Upscale implicit and explicit modes yield hyperexponential profiles that capture the sharp decrease in retention between the first and second segments. For both implicit and explicit modes, increasing $\alpha_{trans\text{-}bg}$ decreased breakthrough and steepened the profile. These effects were less sensitive under the explicit compared to implicit mode.

Implicit

Alpha 1	Alpha 2	Alpha RFSP	Alpha reentrain	Alpha TRANS gg	v2	kf	kf2	kns
8.1E-1	3.1E-3	0.0	1.8E-1	0.0	0.09	800.7	1.13	1.54

Explicit

Alpha 1	Alpha 2	Alpha RFSP	Alpha reentrain	Alpha TRANS gg	v2	kf	kf2	kns
8.1E-1	3.1E-3	0.0	1.8E-1	0.0	0.09	800.7	1.13	1.54
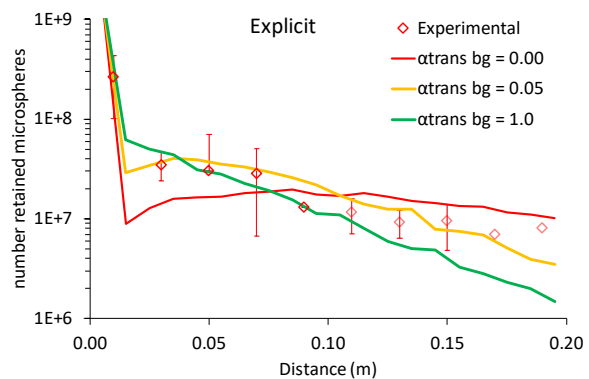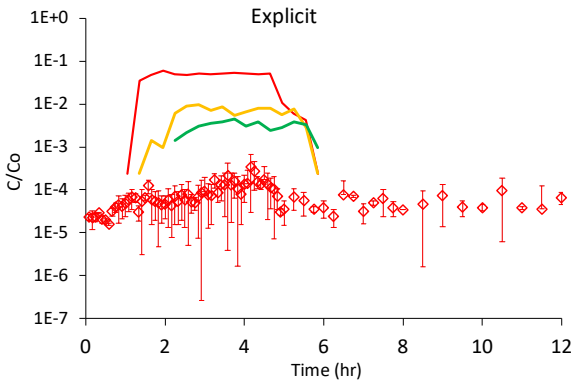
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