## Colloid model development

### 3.1 LB-Colloid introduction

Colloid transport through the soil environment is of great interest and importance to soil development processes through the aggregation of clays (*Bronick and Lal 2004*), contaminant transport (*Saiers and Hornberger, 1996, Jaisi and others, 2008*), filtration and transport of bio-colloids (*Harter and Wagner, 2000, Redman and others, 2004, Foppen and others, 2005*), and soil nutrient dynamics (*Bradford 2008*). Colloidal influence on the transport of chemical contaminants and soil nutrients should not be understated. Saturated zone contaminant transport models have traditionally been modeled as immobile and mobile phase systems. Translocation and transport of inorganic and organic colloids complicate these models. It has been suggested by multiple researchers that the presence of colloids accelerates the breakthrough of strongly adsorbing contaminants.

Results from column breakthrough studies of 137Cs radionuclide suggests that the first arrival of 137Cs is accelerated by 15 times the rate of first arrival without the inclusion of kaolinite colloids (*Saiers and Hornberger 1996*). *Saiers and Hornberger (1996)* suggest that the accelerated arrival time is due to the presence of kinetic adsorption sites on kaolinite colloids. *Sirivithayapakorn and Keller (2003)* performed micromodel studies with synthetic colloids on differently shaped pore and pore throat sizes; their results suggest that preferential flow, over matrix flow, in porous media drive the early arrival of colloids. Structure, composition, and connectivity are generally considered primary mechanisms that control fluid flow in soils. In both saturated and unsaturated systems macropore flow from earthworm burrows, roots, cracks, and other heterogeneities can be described as preferential flow paths that bypass matrix flow within the subsurface (*Gerke 2006*). Preferential flow has been identified as one of the most significant field-scale mechanisms to determine the pollution potential of chemicals (*Kung and others, 2000*). An increase in the clay content of soil was correlated to the existence of very few, but highly connected, continuous larges pores that drive preferential flow and the acceleration of breakthrough of colloid sorbed contaminants (*Kjaergaard and others, 2004*). Further research into macropores formed as karst conduits shows that higher flow rates in macropores may actually slow the breakthrough of colloids due to increased collisions between colloids and geologic material leading to increased reversible attachment of colloids (*Goppert and Goldscheider, 2008*). Increased shear stresses at interface boundaries led to eventual release of attached colloids in karst conduits experiencing high flow rates (*Goppert and Goldscheider, 2008*) and do not affect long term retention rates.

Bio-colloid transport of Escherichia coli, Total coliforms (*Foppen and others, 2005*), and protozoan oocysts (*Harter and Wagner, 2000*) can contaminant water sources and cause serious health complications. Protozoan oocysts, such as Cryptosporidium parvum and Giardia lamblia can lead to infection with the consumption of as few as ten oocysts (*Harter and Wagner, 2000*). *Sinclair and others (1987)* found evidence of oocysts in shallow, coarse grained, groundwater aquifers in Oklahoma. *Harter and Wagner (2000)* found that depth dependent filtration of C. parvum occurred in clean bed laboratory experiments. Changes in fluid ionic strength, such as a natural rain event, led to the secondary release of attached C. parvum. They conclude that contaminated soil material becomes a significant source of C. parvum due to secondary physiochemical release mechanisms. The transport of fecal coliforms and total coliforms can also be used as indicators of human pathogen transport. In developing countries and impoverished regions of the United States onsite human waste disposal in pit toilets is common. *Lewis and others (1982)* summarize the results of a number of field studies of total and fecal coliform transport. They conclude that bacteria can be transported moderate distances up to several hundreds of meters depending on groundwater flow rates and bacteria survivability in groundwater aquifers. *Foppen and others (2005)* performed laboratory column studies of E. coli bacteria transport; they conclude that, even in sandy soils, straining is a significant immobilization process.

Increased production of nanomaterials and the ensuing effects on environmental health presents many research challenges and needs to be addressed (*Klaine and others, 2008*). Nanomaterials such as TiO2 are produced in a variety of sizes and included in many consumer goods for its preservative, coloration, and photoreactive qualities. High concentrations of TiO2 nanomaterials are commonly found in commercial sunblock, lotions, toothpaste, and can also be found in some prepared foods (*Weir and others, 2012*). Although municipal wastewater treatment systems are able to remove a large proportion of these particles, application of biosolids removed from wastewater treatment provide a vector for the release and transport of nanomaterials through the soil environment (*Weir and others, 2012*). Nanomaterials behave as colloids within the soil environment and have been shown to aid in the transport of heavy metals (*Hassellӧv and others, 2008*). Nanoparticles have also been shown to cross the placental barrier and display negative effects on embryo development (Ou and others, 2016). Pore-scale simulations may be able to illustrate mechanisms and thresholds for physical and chemical transport bounds on nanomaterials, since field scale testing has been limited to the use of conservative and non-conservative tracers, which are not subject to the same suite of forces as colloids.

Many field studies apply inverse modeling of the advection dispersion equation (ADE) updated for colloid transport (CDE). Application of mobile-immobile and mobile-immobile-mobile region refinement of CDE have also been applied in the literature. *Bradford and others (2003)* present an inverse modeling solution implemented with HYDRUS-1D (*Simunek and others, 2005*) that utilizes non-linear least squares optimization. Inverse modeling, however still requires laborious and often expensive laboratory or field methods to collect colloid transport data and recover CDE parameters. *Torkzaban and others (2005)* indicate that their columns were excavated at 1 cm intervals and concentrations of retained colloids were measured in centrifuge tubes. The attachment of colloids to geological materials and straining by constricting pores and immobile regions is heavily influenced by the physical and chemical characteristics of the hydrological system. Changes in physical characteristics (fluid velocity, reduced porosity due to compaction) and chemical characteristics (slight changes in fluid ionic strength from a rainfall event or mixing) can alter the distribution of colloids by altering the balance of chemical and hydrodynamic forces. Most laboratory studies focus on recovering macroscale parameters of colloid transport via laboratory analysis (*Saiers and Hornberger, 1996, Kretzchmar and others 1997, Harter and Wagner, 2000, Sirivithayapakorn and Keller, 2003, Kjaergaard and others, 2004*) and field scale modeling. Processes such as colloid straining in pore throats or immobilization due to fluid stagnation zones are not visible at the field scale and play an important role in colloid retention (*Torkzaban and others, 2008*).

Physiochemical forward modeling of colloid transport has the potential to return similar colloid transport results, significantly reducing research time and cost when used in conjunction with laboratory or field studies. Understanding the pore scale mechanics of colloidal transport is essential for elucidating the controlling factors of colloidal transport and for making more accurate predictions of colloidal deposition and transport on the field scale. Micro-scale analysis of fluid flow domains can provide a means of identifying controlling factors for colloid-surface interactions and illustrate mechanisms of colloid retention that are not obvious in column or field scale studies.

Pore scale colloid transport modeling may be able to bridge a gap in the understanding and analysis of colloid transport studies. Previous colloid modeling systems have not been released as open source tools, and as a result become limited as novel approaches. The development of an open source colloid tracking software allows for greater reproducibility of scientific studies and encourages collaboration among scientists to improve upon the existing code base using shared knowledge. Collaboration between scientists becomes extremely important as academic funding becomes more limited.

In this study the development of a colloid particle tracking system is prioritized. An object oriented D2Q9 lattice Boltzmann simulation framework is developed for colloid particle tracking. This framework allows for simplified code maintainability and future extension to include more complex boundary conditions, three dimensional simulations, multiphase simulations, and heterogeneous geology. A colloid particle tracking system is presented with regard to the basic researcher and the advanced user. Synthetically generated glass bead thin sections are used in the development and sensitivity analysis of the colloid particle tracking system to avoid issues with pore space representation due to image collection and segmentation methods.

### 3.2 LB-Colloid methods

#### 3.2.1 Synthetic porous media generation

#### 3.2.2 Lattice Boltzmann methods

Two-dimensional, nine fluid node (D2Q9) lattice Boltzmann was chosen for the development of a simplified pore scale colloid tracking system. Differences between D3Q19 lattice Boltzmann and the D2Q9 lattice Boltzmann simulations include the number of dimensions, fluid node numbers, non-dimensional fluid velocity along a link, the eigenvector array, and the applied weights associated with each fluid node link. A listing of these values is presented in Table xxx. Even with these changes, the lattice Boltzmann equation remains as described in section 2.2.5.

1. Table of lattice Boltzmann fluid velocities and eigenvectors

Dimesionalization of velocity vectors is accomplished by using the Reynolds number calculation described in section 2.2.5. A velocity dimensionalization factor is used to convert non-dimensional fluid velocity to physical fluid velocity by rearranging the equation and setting lattice Boltzmann fluid velocity equal to 1

#### 3.2.3 Colloid particle tracking methods

Pore-scale modeling has the potential to elucidate colloid retention mechanisms (attachment, straining, and exchange with immobile regions) and provide not only breakthrough concentrations of colloids, but also the colloid immobilization distribution. A small number of pore scale models have been developed to model colloid transport at the pore scale. *Gao and others (2010)* presents a colloid modeling approach which was updated by *Qiu and others (2011)* to include more detailed solutions of van der Waals and Lewis acid base forces based on lattice Boltzmann computational fluid dynamics. *Qui and others (2011)* model colloids using a Lagrangian trajectory over a unit cell. This model examined effects of ionic strength on colloid attachment in a glass bead micro-model.

A colloid equation of motion is outlined by *Qui and others (2011)* and has been updated to include gravitational and buoyancy forces which were not present in their approach:

where are the mass of colloid and change in colloid velocity with change in time.

Colloid drag forces describe fluid resistance acting in the opposite direction to the apparent velocity of a colloid with fluid velocity as a reference. Colloid drag forces can be calculated in normal and tangential directions as particles move through the fluid domain

*Gao and others (2010)* define a set of hydrodynamic correction factors for colloid transport in porous media as

The non-dimensional gap distance describes the distance between colloid and surface normalized by a colloid’s radius. Fluid velocity along with complete the drag force calculation where is the fluid viscosity and is the colloid’s radius.

Gravity and buoyancy forces are calculated to account for the upward force exerted by the simulation fluid on a colloid as a result of displacement. Gravity and buoyancy are often combined into one equation, but are presented here as individual components of the colloid particle tracking equation

where are colloid and water density respectively and is the gravitational constant.

Dispersive processes can be represented through Brownian motion. Brownian motion describes the random movement of an object due to collision and bombardment from fast moving atoms in a gas or liquid (*Qui and others, 2011*). In the instance of colloid transport Brownian motion describes random motion due to the random collision of fluid molecules with dispersed colloids. Brownian motion is estimated by

where is the product of the Boltzmann constant and temperature (Kelvin). represents a random Gaussian distribution whose mean is zero and standard deviation is one.

Chemical forces are split into three terms representing the three major components of DLVO theory, electric double layer repulsion (EDL), Lifshitz-van der Waals (VDW), and Lewis acid-base (LAB) interactions. The chemical force term for colloid-surface interaction is (*Qui and others, 2011*).

Electrostatic double layer repulsion describes interactions between surfaces based upon structural and pH dependent surface charge. PH dependent surface change is sensitive to changes in ionic strength and composition. Surface-colloid electrostatic double layer interaction energy is taken from *Hogg and others (1996)* and represented by:

where is the dielectric permittivity of a vacuum, is the dielectric permittivity of water, , are the surface potential of the porous media and the colloid which are calculated from their respective zeta potential . Zeta potential is defined as the electrostatic potential at the slipping plane interface. This interface separates the mobile fluid phase from tightly bound fluids. Surface potential is calculated from zeta potential by:

We assume that the thickness of the Stern layer meters (*van Oss 2008*). The Debye length, which represents the thickness of the diffuse double layer, is then calculated as

The Boltzmann constant , Avogadro’s number , and electron charge are used to parameterize to Debye length calculation leaving the solution temperature and two times the solution ionic strength to be supplied or calculated.

Ionic strength is calculated from the cation charge and molarity of each ionic constituent.

Lifshitz-van der Walls interaction energy accounts for London dispersion forces, dipole interactions (Keesom forces), and induction forces. Lewis acid base forces account for acid-base bonding interactions. *Qui and others (2011)* calculate these as separate force terms based on *Van Oss (1994).* The primary disadvantage of this approach is that it relies on van der Waals surface tension measurement values based on wicking studies and electron acceptor parameters that may not be readily available to the researcher

A more flexible option is to combine the attractive interaction energy calculations and estimate the attractive contribution from Lifshitz-van der Walls and Lewis acid base interactions based on *Liang and others (2007).*

The Hamaker constant provides a means to estimate the van der Walls potential between two objects. A combined Hamaker constant can be calculated for colloid-surface interactions using surface potentials (*Israelachvili 1991)*

Taken as a universal constant, , returns values in good agreement to those that are measured, even for very different liquids and solids (*Israelachvili 1991*).

Colloid-colloid chemical interaction energies can be calculated using similar DLVO formulations. The electrostatic repulsion between two colloids is computed by *Elimelech and others (1995), Qui and others (2011)*

This method is limited however by user specifying the valance of all ionic components in the system, some of which may be unknown in a soil solution without additional laboratory analysis. *Hogg and others (1965)* derive repulsive interaction energies between two identical spheres. Their simplified formulation matches identically to that derived by *Derjaguin (1939)* for spherical particles.

This approximation is limited to surface potentials less than 60 mV. Changes in net repulsive interaction due to fluid ionic strength are wrapped into the surface potential calculation and the calculation of the Debye length for this approach, making it an attractive method for use in colloid simulations.

Colloid-colloid attractive interaction energies, Lifshitz van der Waals and Lewis Acid Base, can be calculated as a bulk term similarly to colloid-surface interactions (*Liang and others, 2007*)

In a finite element grid the spherical nature of the colloid shell can be accounted for in each principal direction by the formulation

where is the colloid-colloid chemical interaction energy in a finite element grid space and are grid distances normal and tangential with regard to the colloid center.

Using the simplified approach taken in this study the colloid chemical force calculation becomes

for both colloid-surface and colloid-colloid interactions, respectively.

With the emergence of new materials such as single walled carbon nanotubes, graphene and industrial nanoparticles, van der Waals and Lewis Acid Base parameters may be extremely difficult to find in the current bank of scientific literature. For this reason, a simplified simulation backend was developed. This approach to colloid transport has the potential to evolve and include increased complexity based on advances in colloidal science.

### 3.3 Initial results

#### 3.3.1 Simulation parameterization

Synthetic porous media was generated using PSPHERE software as described in section 3.2.1. An initial synthetically generated porous media, *Synthetic\_256* was used for code development. *Synthetic\_256* is a simulation domain primary used for testing boundary conditions. No colloid simulations were performed in this domain although lattice Boltzmann fluid simulations were performed to acquire fluid flow velocity vectors for input into the colloid particle tracking software. A bi-linear interpolation scheme was developed to allow grid refinement from lattice Boltzmann to colloid simulations. This step has been deemed appropriate due to the difference in scale from CT imagery of natural porous media (μm) to colloid chemical interaction scale (nm). The bilinear interpolation scheme is applied to both the fluid velocity vectors and model pore boundaries to preserve surface area of the porous media.

Colloid simulations were performed on a series of five synthetically generated porous media. Each simulation domain is 100 x 100 pixels and was discretized at 1 µm/px. Model domains range in porosity from 0.36 to 0.54 (Table xxx).

1. Physical properties of five synthetically generated porous media used for development and testing purposes with the LB-Colloids simulation system.

Development models are assumed to be packed glass bead porous media. Lattice Boltzmann computational fluid dynamics were performed on each of the five porous media. Models were run until equilibrium conditions were present. Mean fluid velocity in each porous media ranged from 1.73e-6 m/s to 2.28e-4 m/s after dimensionalization. The average pore diameter of each domain ranges from 8.3e-6 m to 1.94e-5 m.

Colloid simulation domains were simulated at 0.1 μm discretization. Zeta potential for sodium kaolinite colloids and glass bead porous media was modeled based on values reported in academic literature. Glass bead porous media zeta potential was calculated from surface potential measurements reported by *Decker and others (1992).* A logarithmic regression (R2 = 0.99) of laboratory collected zeta potentials against solution ionic strength was performed for simulation parameterization (Figure xxx). Sodium Kaolinite zeta potentials were calculated from zeta potential measurements reported by *Chorom and Rengasamy (1995)*. Logarithmic regression with regard to fluid ionic strength was performed (R2=0.91) for colloid simulation parameterization (Figure xxx).

1. Regression model of reported values of zeta potential with ionic strength for glass bead porous media.
2. Regression model of reported values of zeta potential with ionic strength for sodium kaolinite colloids.

#### 3.3.2 Initial colloid simulation run

An initial colloid simulation was performed with the *Synthetic2* simulation domain. A fluid ionic strength equivalent to 0.001 M NaCl was used to represent an ionic strength found in natural soils. Colloid zeta potential (-49.47 mV) and glass bead surface zeta potential (-61.2 mV) were calculated from logarithmic regression models (Figures <xxx, xxx>). Two-thousand colloids were released into the inlet of the domain at the beginning of the simulation as a pulse. Colloid particle transport was simulated for 0.03 seconds (30,000 timesteps) or approximately 2.5 pore volumes of fluid flow. All colloids released into the model domain flowed entirely through the column. No colloids displayed immobilization in this simulation. The colloid breakthrough curve (figure xxx) shows that approximately 80% of colloids were transported through the flow domain at 0.5 pore volumes.

1. Simulated colloid breakthrough profile for a pulse of Na-kaolinite colloids, ionic strength = 1e-03 M

This suggests that the presence of immobile regions is reducing the mean flow path, effectively creating a preferential flow path for colloids. From 0.5 pore volumes to 1.5 pore volumes the slope of the breakthrough curve becomes shallow and suggests temporary immobilization and remobilization of colloids within the simulation domain. The DVLO force profile <figure xxx> displays a strong repulsive barrier to colloid-surface attachment extending to approximately 0.4 μm.

1. Simulated colloid-surface DLVO force profile for Na-Kaolinite colloids, ionic strength = 1e-03 M

At very close distances, if colloids are able to break through the repulsive energy barrier, permanent attachment is possible.

The breakthrough velocity analysis of colloids shows that the range of colloid velocities are 0.1 m/s to 5e-3 m/s. The range of fluid velocity suggests that advective flow drives colloid transport in this simulation. Further analysis shows that approximately 50% of colloids in the system display a breakthrough velocity of 5e-2 m/s (Figure xxx). Colloids displaying slower breakthrough velocity likely follow a more tortuous path and may display temporary immobilization followed by remobilization.

1. Simulated mean colloid velocity for Na-Kaolinite colloids, ionic strength = 1e-03 M, Synthetic2 model domain.

#### 3.3.3 Colloid simulation chemical parameter sensitivity analysis

Colloid simulations were performed on four synthetic simulation domains (*Synthetic2, Synthetic3, Synthetic4, and Synthetic 5)* where the fluid ionic strength was varied from 1e-5 M to 1 M NaCl. Colloid zeta potential and glass bead surface zeta potential was calculated for each simulation from logarithmic regression relationships to ionic strength (Figure logarithmic regression of zeta potentials). Two thousand colloids were released into the inlet of the domain as a pulse at the beginning of each simulation. Colloid transport was simulated for approximately two pore volumes of fluid drainage.

Electric double layer repulsive force profiles, attractive force profiles, and DLVO force profiles were generated for each of the simulation ionic strengths. The chemical force profiles are consistent across simulation domains because the colloid and surface material did not vary between domains. The electric double layer profiles show that as ionic strength increases, the magnitude of double layer repulsion decreases. A collapse of the double layer repulsive distance is also observed with increased ionic strength. The attractive force profiles display similar results for all ionic strengths tested. At 1 nm distance the difference in force profile is most pronounced. DLVO force profiles (combination of EDL and attractive forces) shows the collapse of a repulsive energy barrier with increased ionic strength (Figure xxx). At 1e-3 M NaCl solution the maximum repulsive force observed is approximately -4e-9 N. When ionic strength is increased to 0.1 M NaCl the repulsive energy barrier has a maximum of approximately -1.5e-9 N. The decrease in magnitude of this energy barrier may allow colloids to overcome it and fall into the attachment zone at approximately 1 nm distance.

1. Simulated colloid-surface DLVO force profiles for Na-kaolinite colloids and glass bead porous media, multiple ionic strengths

Sensitivity analysis results for the *Synthetic2* model domain show that all colloids break through the domain by 1.5 pore volumes, with the exception of the 1.0 M simulation. One percent of dispersed kaolinite colloids were immobilized either through adsorption, straining, or immobilization in fluid stagnation zones. Breakthrough profiles returned expected results based upon DLVO theory and calculated DLVO interaction profiles (Figure xxx). 1e-4 M NaCl solution provided the earliest arrival of the breakthrough profile, with 100% of all colloids exiting the system within 1 pore volume elution. This suggests that advective forces funneled through a preferential flow path dominated the transport of colloids throughout the system. Surface exclusion effects due to a large repulsive energy barrier contribute to the dominance of advective flow.

1. Breakthrough profiles for pulse flow of Na-kaolinite colloids, multiple ionic strengths, Synthetic2

*Synthetic3* sensitivity analysis results returned an unexpected pattern. A minimum (79%) of colloids were transported entirely through the system with the 1e-3 M NaCl simulation. The 1e-4 M ionic strength simulation produced a cumulative breakthrough of 84% colloids, which was also lower than the higher ionic strength simulations. The remaining three simulations produced similar results showing that approximately 10% of simulated colloids were immobilized within the domain. The *Sythetic3* simulation domain displays the smallest mean pore diameter and the lowest mean fluid velocity of all of the tested simulation domains. Because of the small pore to colloid ratio, repulsive effects of colloid-colloid interactions likely play a large role in the overall distribution of colloids within the system. Figures xxx and xxx show colloid distribution plotted every 100 time steps for 1 M NaCl and 1e-3 M NaCl solutions. It appears that colloids display increased dispersion due to colloid-colloid double layer repulsive effects in the 1e-3M solution simulation. This dispersion affected colloid travel paths causing immobilization and attachment in zones where colloids did not stream to in the 1 M NaCl simulations.

1. Simulated Na-kaolinite colloid timeseries distribution for 2000 colloids released, 1 M NaCl, Synthetic3
2. Simulated Na-kaolinite colloid timeseries distribution for 2000 colloids released, 1e-03 M NaCl, Synthetic3

Sensitivity analysis results from *Sythetic4* show purely advective flow through a macropore. Preferential transport through this single pore dominated the system. For all ionic strengths simulated, 100% of colloids released exited the system by 0.5 pore volumes of elution (Figure xxx). Physical properties of the *Synthetic4* domain, reported in table <xxx>, show that the mean pore diameter is 1.94e-5 m and the ratio of pore diameter to colloid radius is 19.4. This is the highest reported pore to colloid ratio radius of all simulation domains. Due to the large macropore the mean fluid velocity of *Sythetic4* was up to 3 orders of magnitude larger than the other reported simulation domains.

1. Breakthrough profiles for pulse flow of Na-kaolinite colloids, multiple ionic strengths, Synthetic4

Sensitivity analysis results from *Synthetic5* return results consistent with DLVO theory, with the exception of the 1M NaCl simulation. The 1e-4 M simulation shows that all colloids break through the simulation domain by 0.5 pore volumes of elution. A limited number of colloids were immobilized for simulations with ionic strengths of 1e-3 M to 0.1 M NaCl. Less than 10% of kaolinite colloids were retained in these simulations. Simulation results for 1.0 M NaCl returned complete breakthrough of all colloids by 2 pore volumes of elution. This result was not expected because of the repulsive energy barrier between solid and colloid is lowest for this simulation ionic strength. Colloid-colloid attractive interaction may have contributed to the complete breakthrough of all colloids. Additionally, Brownian motion can affect colloid immobilization. Brownian motion has the potential to overcome attractive surface interactions, causing colloids to move from immobile fluid zones or attachment sites back into mobile fluid regions of porous media.

1. Table of colloid breakthrough

#### 3.3.4 Colloid simulation sensitivity to Brownian motion

A series of xx simulations were set up with *Synthetic2, Synthetic3,* and *Synthetic5* to identify variability and sensitivity of colloid transport to Brownian motion. *Synthetic4* was not simulated due to the dominance of advection observed in previous colloid transport simulations. For each simulation fluid ionic strength was held constant at 1e-3 M NaCl. All other input parameters were also held constant. Any variability observed in simulated breakthrough profiles can be primarily attributed to effects of Brownian motion.

Results from *Synthetic2, Synthetic3,* and *Synthetic5* show differing amounts of variability in the total relative number density of colloids that are immobilized within the system when input parameters are held constant (Figures xxx).

1. Simulated Na-kaolinite breakthrough profiles characterizing the effects of Brownian motion, 1e-03 M NaCl, Synthetic2.
2. Simulated Na-kaolinite breakthrough profiles characterizing the effects of Brownian motion, 1e-03 M NaCl, Synthetic3.
3. Simulated Na-kaolinite breakthrough profiles characterizing the effects of Brownian motion, 1e-03 M NaCl, Synthetic5.

Results from *Synthtic2* indicate that Brownian motion is not a significant source of variability. Immobilized colloids ranged from 0-1% of all colloids released into the system. Advective flow is shown to be the primary driver of colloid transport within this simulation domain. *Synthetic3* displays the greatest range in the percentage of colloids immobilized during simulation runs. Colloid immobilization ranges from 15-25% of all colloids released. This simulation domain also has the lowest mean velocity of the three simulation domains tested. Results from *Synthetic5* show a range of 3-7% of colloids are immobilized during model runs.

1. Table of breakthrough results for Brownian motion tests?

These results show that Brownian forces are a significant contributor to colloid transport within the simulation algorithm. Variability from Brownian motion, is minimized when advective forces dominate colloid transport. In simulation domains with the lowest mean fluid velocities (*Synthetic3* and *Synthetic5*) random interactions create significant differences in the returned results. Multiple model runs are therefore necessary to bound the effects of Brownian motion within a simulation domain.

### 3.4 Summary and deliverables from colloid model development

A D2Q9 lattice Boltzmann computational fluid dynamic system for simulating colloid transport through artificially generated porous media was presented. This method can be applied to digitized and binarized thin sections of natural porous media to simulate colloid transport and immobilization. This methodology can also be extended to D3Q15 and D3Q19 lattice Boltzmann computational fluid dynamic domains by using the existing equation presented and adding one additional dimension to the colloid particle tracking algorithm. The base algorithm can also be expanded to represent heterogeneous geologic materials by applying a multicomponent segmentation algorithm to the simulation layering colloid-surface force profiles based on solid phase components. Unsaturated flow could also be simulated, however feedback mechanisms to the lattice Boltzmann equation as well as air-water interfacial forces would have to be added to the current code.

Chemical parameter sensitivity analysis was performed on the code to investigate colloid-surface interaction and colloid-colloid interaction during simulation. Results from sensitivity analysis indicate that as ionic strength increases the repulsive energy barrier of the DLVO profile decreases in force and extent within the simulation domain. Due to this change in repulsive energy more colloids are generally immobilized, and a greater proportion of colloids are retarded in comparison to simulations run with a lower ionic strength. Some exceptions to this statement were observed. In both *Synthetic3* and *Synthetic5* colloid-colloid repulsive interactions at low ionic strength caused greater dispersion of colloids. Colloids were pushed into immobile regions of the simulation domain and attached to surfaces. This observation gives insight into unexpected colloid transport results where colloids break through at a lesser quantity under more favorable depositional conditions.

Sensitivity analysis was performed with regard to Brownian motion. Results indicate that fluid domains dominated by advective flow are insensitive to variability caused due to Brownian forces. In the fluid domains that displayed the lowest fluid velocities, *Sythetic2* and *Synthetic3*, Brownian motion caused up to 10% variability in the number of colloids that were immobilized between simulation runs. These results illustrate the importance of performing multiple simulation runs to bound the effects of Brownian motion for reported results when performing prediction simulations.

User documentation is provided for the *LB-Colloids* package in Appendix <xxx>. The user documentation includes basic background to the D2Q9 lattice Boltzmann equation and the colloid particle tracking system. Instructions for parameterization through the use of formatted text files is provided to the user in this document. An example problem is also shown for clarity. Application program interface (API) documentation is provided for the super user and developer. The API documentation provides explanation of inputs and outputs to all modules and classes within the *LB-Colloids* package. *LB-Colloids* source code is available at <>.