## Introduction:

Colloidal suspensions are a mixture of substances in which one phase is suspended in a dispersive medium. The colloid or the dispersion medium can be solid, liquid, or gas and the mixture of the two substances can occupy the same phase with the exception of gasses. Many examples of colloidal suspensions are found in the household, in industrial settings, and are studied across a number of academic disciplines. Products such as whipped cream, a foam created by air suspended in a liquid, and mayonnaise which is a stable emulsion of oil, egg yolk, and vinegar can be found in many households. Geological materials such as pumice and scoria are considered solid foams, gas suspended in a solid, and are used in industrial settings and as building materials for their insulative properties. In the environmental and medical fields aerosols and sols are of notable importance. Aerosols are often described as a solid phase within a gas, such as volcanic ash from an eruption or clouds containing ice particles, but also describe liquids such as fog. Sols describe a solid dispersed phase in a liquid dispersion medium. Red blood cells, white blood cells, platelets, and other dissipated compounds are dispersed in bodily fluids and can be described as a sol. Sols of solid geological material (minerals) and biological matter (bacteria and waste material) dispersed in liquid water are of particular interest to this study. For this study colloid transport and colloidal fluid are defined in reference to sols, although portions of this work could be applied to other dispersed phases and dispersion media.

Much theoretical research has been completed in the field of colloid physiochemical transport. Knowledge of colloid transport and collection efficiency is critical to understanding the transport of emerging contaminants and environmental pathogens. Chemical interactions and the associated interaction energies resulting from interactions between colloid, fluid, and geological materials is central to colloid transport and immobilization. Increased understanding of the physical and chemical transport properties at a sub-micron scale can be used to improve field scale hydrologic models and hydrologic model planning scenarios. Modeling tools exist that can track particles, such as colloids through hydrological systems. Hydrus-1D (*Simunek and others, 2008*) is an unsaturated zone modeling tool which assumes one dimensional flow and can apply the colloid advection-dispersion equation (CDE) with macroscopic parameters describing these processes. A distribution of particles is generated based upon the advection-dispersion parameters and is returned to the user. MODPATH (*Pollack 2016*) is a saturated zone particle tracking software designed to observe particle transport in a three-dimensional hydrological system. This tracking tool is limited to advective flow and saturated systems. No retardation, diffusion, or dispersion is considered. A small number of pore scale models have been developed to track colloid transport in porous media (*Redman and others, 2004, Gao and others, (2010) Qui and others, 2011*). These models either use Lagrangian mechanics which are computationally inefficient for large numbers of colloids, can only be applied to very small fluid domains, have long modeling run times, or operate as novel approaches to modeling micro scale colloid-surface interactions. The limitations of these systems leave the interdisciplinary researcher without a practical option to gain additional insight into controlling factors driving the physiochemical dynamics of colloid transport within their system.

Parameters such as diffusivity and dispersivity are not generally well known for most geological systems and can be time consuming and expensive to collect in the laboratory. A few studies have focused on the hydrologic unit scale description of these parameters (*Zenner and Grub 1973, Stevens and Beyeler 1985*), however these are rare due to limitations presented from cost and extended monitoring. Contaminant transport studies on the basin scale are generally applied to monitoring existing contaminated systems and the associated remediation process. These studies generally have coarse discretization due to a limited number of observation wells, piezometers, and near surface monitoring equipment. Laboratory studies and numerical models are often used to understand the transport, distribution, and immobilization mechanisms in a hydrological system.

Physical forces describing colloid movement and settling in fluid and porous media are integral to colloid transport. Stokes settling can be applied to spherical particles with mass to describe sedimentation in an undisturbed fluid. Gravitational, buoyancy, and viscous drag forces can be used to determine a specific sedimentation velocity for particles of known density and mass. This relationship does not hold in porous media where fluid is rarely static. Drag forces must be extended to account for hydrodynamic and colloid velocity. Non dimensional colloid-surface correction factors presented in *Gao and others (2010)* account for the structure of the porous media in calculating these forces. Fluid velocity vectors must also be included in modeling colloid transport in porous media.

Physical forces alone do not describe colloid-colloid interactions and colloid-surface interactions. Development of colloid-surface interaction theory has been active since Helmholtz identified an interface between ionic solutions and a charged surface in 1853. Surface chemical potentials that define surface charge in colloid-colloid and colloid-surface interactions must be represented in colloid transport models. Significant refinement from Helmholtz’s initial model of surface interactions has provided a base for our modern model of colloid-surface interaction. Electric double layer interaction, Lewis acid-base, and Lifshitz van der Waals forces represent the major contributors to the classical *Derjaguin and Landau (1941)*, *Verwey and Overbeek (1948)````````* (DLVO) interactions. DLVO theory describes the stability of colloids as the balance between electrostatic repulsive forces and attractive van der Waals forces. Inclusion of acid base interactions extends this relationship to account for bonding reactions due to electron acceptor and donor potentials. Representation of these micro-scale forces can provide insight into the dispersivity of colloids in a porous media. The inclusion of Brownian motion defined by a random walk algorithm or defined by a random Gaussian distribution has been used to estimate dispersivity, the random diffusion of particles by heat, solute gradient, and collision.

A fundamental understanding of the basic chemical and physical processes of colloid-surface interaction is necessary to develop accurate prediction models of colloid transport where detailed historical data are not present. *Thomas and others (1993)* performed a basin scale study of radionuclide contamination (Ra, 40K, and U) in the Carson River groundwater basin, Nevada. Their results suggest that sediment transport and a dissolution of U coatings on Fe and Mn oxides is a principal mechanism for groundwater contamination in this watershed. The co-transport of viruses through the soil environment with colloids has also been documented (*Syngouna and others, 2013*). Breakthough curve concentrations suggested that the presence of clay particles influenced the transport of PHI X174 virus. The MS2 virus in this study showed an affinity for attaching to clay particles. Bacterial transport can be modeled to a limited extent using colloid dynamics due to their physical size and chemical properties (*Redman and others, 2004*). Bacterial transport modeling has limitations using current methods, because of their ability to form communities as biofilms and their biological motility. Heavy metals and agricultural nutrients commonly sorb to colloids (*Bradford 2008*). Heavy metals such as As, Ag, and Hg pose an environmental and human health risk if released into surface or groundwater. Colloids provide a vector for cycling of both micro and macro nutrients important for agricultural productivity. Nutrients from Concentrated Agricultural Feeding Operations (CAFO) can be transported in such great concentrations that they pose human health risks (*Bradford 2008*). Elevated nitrate concentrations are associated with the potentially fatal ailment blue baby syndrome (methemoglobinemia) in young children.

While many background studies exist that observe colloid transport as the sum of its parts, colloid transport mechanisms in porous media are still poorly understood, due to the scale of colloid-surface interactions. The driving research question for this study is which physical and physiochemical forces dictate colloid transport and immobilization within a porous media? An understanding of the physical and physiochemical mechanisms driving colloid transport and immobilization at the microscale has applications in column and field scale models. Although laboratory and field scale models can be used to predict colloid transport, microscale insights into macroscopic colloid transport may present an opportunity to refine predictive models and explain unexpected results.

The purpose of this study is to examine the physical and chemical forces of colloid transport on the micro-scale and determine controlling factors of colloid transport using computational fluid dynamics. The study begins by examining a series of nine segmentation algorithms applied to four X-ray micro computed tomographic representations of soil columns. These soil columns were collected from a floodplain grazing site in Pennsylvania. Permeability was simulated in each soil column using D3Q19 lattice Boltzmann computational fluid dynamics and estimated using the Kozeny-Carman equation. Simulated permeability was compared to laboratory permeability measurements for validation. Results from this initial study inform decisions in the development of a computational fluid dynamic system to simulate colloid transport.

In the second section of this study the framework for a computational fluid dynamic system that is able to simulate colloid transport at pore scale is presented. Colloid transport simulations are performed with modeling software developed from a D2Q9 lattice Boltzmann computational fluid dynamic system. Steady state colloid transport was simulated in a series of computer generated synthetic porous media. Each porous media was simulated under a variety of initial conditions to isolate the driving factors of kaolinite colloid transport in synthetic glass bead media. Sensitivity analysis was performed for multiple computer generated glass bead simulation domains. These simulations served as a check throughout the development process to ensure boundary conditions were properly represented.

The final section of this study focuses on titanium dioxide nanoparticle transport through porous media. Breakthrough concentrations of titanium dioxide nanoparticles collected by (*Wang and Brusseau; written communication, 2017*) were examined with colloid transport simulations. Pore scale colloid transport simulations were performed on synthetically generated porous media, roughly matching the physical properties of the laboratory soil columns that colloid transport studies were performed on. Results from colloid transport simulations were compared to laboratory results. Calibration of computational fluid dynamic simulations were performed during the validation process and results from calibration runs are reported.

## Analysis of segmentation methods using lattice Boltzmann and Kozeny-Carmen equations on four macropore soil cores

### 2.1 Introduction

Quantifying permeability, an intrinsic property of porous media, has widespread application in industrial settings such as oil and gas production (*Stone 1973*), water treatment and membrane design (*Pendergast and Hoek, 2011*), contaminant transport (*Mulligan and others, 2001, Berkowitz 2002*), remediation practices (*Waybrant and others, 1998*), and aquifer characterization. Permeability is typically measured in laboratory settings using fluids (*Fetter, 2001*) or gases (*Ferreira and others, 2010*) which can be expensive, laborious, and challenging for macropore soils (*Sukop and others, 2013*). Standard petrophysical methods such as air permeability, constant head and falling head hydraulic conductivity methods have limitations on the maximum rates they can accurately determine (*Sukop and others, 2013*).With these limitations in mind, it is beneficial to investigate whether permeability can be derived from segmentations of CT-scanned porous media (*Spanne and others, 1994, Hilpert 2011, Sukop and others, 2013*) or thin sections (*Schaap and Lebron, 2001, Oren and Bakke 2003*) using computational fluid dynamics or empirical relationships. Modeling methods applied to CT imagery may be of practical utility if permeability can be accurately estimated using computational fluid dynamics or empirical relationships.

High computational overhead and large amounts of storage have historically, and continue to be, limiting factors for computational fluid dynamics. With advancing computer technology and an ever reducing cost of storage devices, CFD continues to become more attractive. The lattice Boltzmann equation is one such CFD system, which is applied primarily for its relative ease of programming and its ability to simulate fluid flow in complex geometries such as those found in natural porous media. Although computationally intensive, the single relaxation time lattice Boltzmann equation has been shown to fully recover the Navier-Stokes equation (*Qian and others, 1992*). Because of this ability, lattice Boltzmann computational fluid models are able to quantify permeability and saturated hydraulic conductivity of porous media (*Martys and Chen, 1996, Keehm and others, 2004, Zhang and others, 2005, Carmago and others, 2011, Hilpert 2011, Sukop and others, 2013*), gain insights into multiphase and multiple component flow (*Shan and Chen, 1993, Martys and Chen, 1996, Schaap and others, 2007*), and represent enhanced colloidal transport (*Laad and Verberg, 2001*).

X-ray computed tomography (CT) has made it possible to simulate flow in natural porous media using CFD. CT images can be digitally reconstructed into a three-dimensional representation of the original porous media. Before CT imagery can be utilized for fluid modeling purposes, soil structure must be separated into distinct phases through segmentation. Segmentation schemes are susceptible to image artifacts present in the CT collection and reconstruction process (*Ketcham and Carlson, 2001*). Current CT resolutions are on the order of one micron (*Wildenschild and others, 2002*). Since pores can be much smaller than this, CT may not be able to fully recover porosity. There are a number of CT systems available to the researcher. CT systems differ in x-ray source and intensity, detector geometry, and resolution scale. Common systems include synchrotron systems, which provide high intensity monochromatic x-rays and can resolve to the micron scale; medical systems which have been developed for use with soft tissue and have mm scale resolution; and industrial (benchtop) systems which utilize a broad-spectrum x-ray source and have the potential to provide easy access to the researcher for experimental set up (*Ketcham and Carlson, 2001, Wildenschild and others, 2002*). By considering the fundamentals of information theory (*Shannon 1949*) coarser resolution imagery is more susceptible to partial volume effects and is subject to more uncertainty than imagery collected using a finer resolution. Further complicating CT image analysis, over one-hundred different segmentation standards currently exist in the literature (*Iassonov and others, 2009*). Each method can return different representations of pore boundaries and therefore porous media structure. Given these issues digital representations of geologic materials have been used to gain insight about connectivity (*Vogel 2002*), spatial correlation and tortuosity (*Coles and others, 1998*), volumetric water content (*Hopmans and others, 1992*), contaminant transport (*Clausnitzer and Hopmans, 2000*), colloidal transport (*Gaillard and others, 2007*), and fluid modeling using lattice Boltzmann (*Chen and Doolen, 1998*).

Models such as lattice Boltzmann have been used to recover the permeability of porous media. A major limitation is the computational time and resources required to return results. Semi-empirical models such as the well-known Kozeny-Carman relationship (*Carman 1937, 1939*) are of value because they require very little computational power to return the permeability of porous media. *Schaap and Lebron (2001)* used this relationship to calculate the permeability of porous media thin sections. By applying the KC relationship to three-dimensional CT imagery it may be possible to estimate permeability and hydraulic conductivity from digital representations of natural porous media. All that needs to be known is the porosity, hydraulic radius, and tortuosity to predict permeability. These parameters can be derived from CT imagery using simple image processing techniques, which require less computational power than standard CFD models. KC methods are not without its own limitations. The KC model relies on the estimation of tortuosity from geometric, hydraulic, diffusive, or electrical relationships within a sample. These relationships are generally derived from idealized data sets such as glass beads or artificially generated media that does not represent the complex heterogeneity and structure of natural porous media. As a result, these relationships may not correlate across data sets consisting of different soil textures and structures. Even more problematic for soil physics, the KC relationship is based off of the false assumption of soil pore structure as a bundle of capillaries (*Hunt and others, 2013*).

The objective of this chapter is to identify potential limitations and assumptions made in the digital modeling process of four natural porous media samples collected from a floodplain grazing site in southern Pennsylvania. Because macropore soils are generally characterized by high flow rates through comparatively large pores, CT imagery in this study was collected with a coarse resolution industrial scanner. Nine different automated segmentation algorithms are applied to CT images of 4 macropore silt-loam soils. Permeability was measured in the laboratory and was modeled using image analysis data to parameterize the Kozeny-Carman relationship, as well as the lattice Boltzmann equation. Lattice Boltzmann methods have the ability to simulate fluid flow processes whereas the Kozeny-Carman approach is purely empirical, based on image analysis, and can return non-zero permeability when a pore network does not percolate. Lattice Boltzmann methods were expected to provide better estimates of permeability than the Kozeny-Carman approach. Apparent failure of both methodologies is observed in this study while using automated approaches to segmentation. User defined optimization procedures were foregone because they would introduce additional operator biases to the data.

### 2.2 Methods

Cylindrical soil columns of 7.5 cm diameter and 20 cm height were collected from a floodplain grazing site in Franklin County Pennsylvania, USA. The soils were collected from the A horizon of a fine-silty, mixed, mesic, Aeric Fragiaquults (*soil survey staff, 1999*). Site soil texture was noted as 28% sand, 46% silt, and 26% clay with 3.3% organic matter present at the site (*Martinez and others, 2010*). Bulk density was recorded as 1.43 g cm-3. An industrial CT scanner was used to image the soil cores. The scanner used was a HYTEC Flat Panel Amorphous Silicon High-Resolution Computed Tomography (FLASHCT) system at Washington State University. *Martinez and others, (2010)* noted that the samples slightly detached from the polycarbonate cylinders prior to mounting the columns on the CT rotation stage. The columns were scanned at 380 keV and 1.7mA current. Copper filters were used between the X-Ray source and the soil columns to pre-harden the beam. The resulting CT radiographs were reconstructed to volumes of 820 x 820 x 1480 voxels (*Martinez and others, 2010*). These volumes were cropped to 680 x 680 x 1480 voxels to remove unused negative space for modeling purposes. A wall correction of 15 voxels was applied around the circumference of the soil columns and is detailed in section 2.3.1.

#### 2.2.1 Laboratory methods

Soil columns were saturated and placed on a perforated disk inside of a funnel. Water head of 25 mm was kept constant on soil surface, and outflow was measured for each soil column over a 10 minute period with 1 minute sample intervals. Constant water level was maintained manually with an accuracy of 2 mm in this study. This procedure was repeated 3 times and linear parts of the cumulative outflow curves were used to calculate the saturated hydraulic conductivity.

Saturated hydraulic conductivity () measurements were completed for each macropore soil column. Measurements were made for the full soil column (16.28cm), followed by cutting and measuring for eight, 2-cm sections of each column. was converted to permeability following the relationship

where dynamic viscosity and fluid density where assumed to be at standard temperature and pressure during laboratory procedures.

The harmonic mean permeability of the eight, 2-cm section was compared to the full permeability by calculating (*Prakash and Sridharan, 2013*).

The size of each column segment is and is the permeability for each corresponding column section. Table 1 shows the comparison between for the harmonic mean of the 2-cm sections and the calculated permeability value for the intact column. This metric provides insight into possible damage to the pore structure during the cutting process.

Although no soil water retention curves were measured for the CT imaged soil columns observed in this study, a soil water retention curve was collected for Column 01. This soil column was collected from the same floodplain grazing site and is considered representative of the four macropore soil columns studied in this paper. A pore size distribution was calculated for Column 01 using the relationship

where describes the matric potential component of the soil water characteristic at the corresponding pore diameter (*Schjønning* *2009*).

#### 2.2.2 Segmentation Methods

Standardization of segmentation methods is critical to the field of pore scale modeling (*Marcelino and others, 2007*). For this reason, each segmentation method chosen was selected for the ability of the algorithm to be automated. By selecting these algorithms, operator bias in the segmentation step was minimized. Intensity variations due to beam hardening artifacts were corrected before segmentation with the Intensity Correction Procedure described in *Iassonov and Tuller (2010)*. The ICP combines both the thresholding and correction step. Only high intensity correction in the solid phase is achieved since this method filters in the solid phase after a threshold has been drawn. Iteration of this method has been shown to remove beam hardening effects in the solid phase (*Iassonov and Tuller, 2010*). ICP was applied to the CT data in conjunction with each of the six segmentation methods used in this study. In addition to ICP, a radially weighted local regression model was applied to reduce beam hardening effects on each of the columns. Finally, median filtering was applied to soil CT data in an attempt to fully remove image artifacts. Median filters utilize a median value as output from each particular view taken by the algorithm. This effectively removes outliers, and is robust at smoothing image data when noise characteristics are not known (*Astola and others, 1990*). A short description of each segmentation algorithm is provided. Algorithms are grouped together following the scheme outlined in *Iassonov and others, (2009)*.

Global thresholding is the most commonly applied approach to image segmentation (*Iassonov and others, 2009*). Histogram based methods collect a global distribution for all grayscale values and a threshold can be selected by the user to binarize the data. Problems arise when image grayscale distributions are not bimodal, and each image of a three-dimensional volume must be segmented separately or a representative distribution must be selected for the entire volume (*Rosin 2001*). HS-Rosin is suitable for thresholding images with a unimodal distribution unlike many other histogram-based approaches (*Rosin 2001*). It assumes that there is one dominant peak relative to the rest of the population of intensity values. The method attempts to maximize the distance between a single point on the histogram of grey scale values and a line is calculated from peak (mode of DN) to corner of the intensity value distribution to determine a threshold. Errors may be introduced by strongly peaked histograms (*Rosin 2001*).

A novel series of segmentation algorithms, Yet Another Segmentation Algorithm (YASA), was applied with three different treatments to the raw CT data. YASA uses the grey scale histogram and two probability distribution functions, one for pore space and one for solid space, to estimate the probability of a voxel being a pore. YASA1 segmentation assumes that the number of misclassified pore voxels is equal to the number of misclassified solid voxels during segmentation. The YASA2 technique assumes that if the probability of a pore voxel is greater than 0.5 it will be segmented as pore space. YASA3 applies stochastic modeling using uniform random numbers. If a random seed is less than probability of a pore voxel, it will be segmented as a pore voxel.

The second global thresholding category uses clustering to maximize the mean of each voxel class and determine a threshold from a statistical distribution of the classes (*Iassonov and others, 2009*). From this information a global threshold can be selected automatically or by the user to binarize the data. CL-Otsu uses probability distributions between foreground and background voxels to maximize ‘the measure of separability’ between each voxel class (*Otsu 1979*). An automatic threshold is then applied. As the numbers of classes increase the credibility of class separation decreases (*Otsu 1979*).

A third category of global thresholding methods uses signal entropy to separate the background and foreground classes (*Iassonov and others, 200*9). EN-Brink evaluates two-dimensional entropies by using both global and local grey level information. A two-dimensional scatter plot is created that maximizes the entropies for the foreground and background class. A threshold is automatically selected by finding the largest series of minimum values of entropy by iteration (*Brink 1992*). EN-Yen follows the maximum entropy criterion which is to choose a threshold so the total amount of information in the background and foreground is maximized. Automatic thresholding is applied by the use of a cost function (*Yen and others, 1995*).

Locally adaptive methods use image information to make a segmentation decision for each voxel. Local information can provide better segmentation quality and account for some image artifacts (*Iassonov and others, 2009*). LA-Indicator Kriging (IK) uses a histogram to create two global thresholds that separate the background and foreground phase of the image. Voxels that fall between the two thresholds are assigned by utilizing estimates of short scale indicator covariance functions (*Oh and Lindquist, 1999*). LA-K-means Markov Random Field (KMMRF) segments image sequences in three dimensions based on neighboring voxel interactions. Seed voxels are required to provide a mean and standard deviation of each voxel class before segmentation can be performed (*Kulkarni and others, 2012*). K-means clustering algorithm is applied to automatically seed each voxel class and eliminate operator bias.

#### 2.2.3 Image analysis methods

Specific Euler number, a metric of soil pore structure is defined by:

where is the number of isolated pore voxels, is the number of connections between pore voxels, describes the number of voxels in completely enclosed cavities, and is the total number of voxels in the volume (*Vogel and Roth, 2001, Doube and others, 2010*). The specific Euler number calculation shows that as the connectivity of a sample increases will become more negative.

CT porosity was calculated using the standard volume-based definition of porosity

Radial porosity at a Euclidean distance along the XY plane from the center of each segmented column was calculated as a check for CT processing artifacts such as beam hardening and wall separation by

where is the number of pore voxels at a specific Euclidean distance from the XY plane center of a soil sample and the number of solid voxels at the same Euclidean distance. Localized discontinuities in radial porosity are indicative of image artifacts.

Hydraulic radius is a commonly used hydrological metric that describes the ratio of the cross-sectional area of a channel divided by the wetted perimeter of that channel. This description of provides a two-dimensional relationship. This relationship is extended to represent a three-dimensional system by the equation:

where refers to the number of pore voxels and is the total number of pore to solid contacts. Theoretically, is equivalent to exactly half of the radius for a cylindrical pore. In natural porous media, decreased porosity and increased tortuosity equates to an increase in .

#### 2.2.4 Kozeny-Carmen methods

Unlike hydraulic conductivity, permeability is a function of only the porous media, and for straight pores can be described by Torsional rigidity theory as:

where describes the pore radius and is a shape factor where for cylindrical pores and varies for different pore geometries (*Schlueter* *1995*). This relationship is only valid for uniform pore shapes and cannot account for the interconnected, tortuous, and non-uniform nature of natural porous media. Refinements to this relationship have been made through the Kozeny-Carman relationship:

From this relationship it is apparent that permeability is directly proportional to porosity . The hydraulic radius and tortuosity represent frictional forces in this empirical relationship. Since tortuosity encompasses broad definitions in the literature—diffusive, geometric, hydraulic, and electrical tortuosity (*Ghanbarian and others, 2013*)—multiple tortuosity models have been evaluated. Tortuosity relationships were selected on the basis of having no adjustable parameters and to represent each definition with the exception of electrical tortuosity which is not represented in this study.

Although multiple tortuosity methods were evaluated in the parameterization of the Kozeny-Carman relationship, the tortuosity relationship that returned the lowest RMSE in permeability for the greatest number of segmentation algorithms tested in this study is presented. Table <xxx> displays RMSE results from the methods applied and RMSE for each method with regard to segmentation algorithm. For this paper tortuosity is calculated following *Li and Yu (2011).* They derive the relationship

from a Sierpinski carpet pore fractal model.

An apparent limitation of the KC relationship is that a non-percolating soil sample can return , as long as a non-zero porosity is used in the model. Because of this limitation, segmented cores with no effective porosity have been excluded from the results presented in this study.

#### 2.2.5 Lattice Boltzmann methods

Lattice Boltzmann computational fluid dynamics is a refinement of lattice gas automata (*Frish and others, 1986*). The discretization processes and application of simple bounce back rules enables the representation of complex geological structures. Application of either body force or pressure boundary conditions (*Zou and He, 1997*) drives flow within the system. Fluid flow is slightly compressible, and has been shown to return an approximation of the Navier-Stokes equation (*Benzi and others, 1992*). Lattice Boltzmann CFD models have been successfully used to represent fluid flow in saturated systems (*Blunt and others, 2013*), unsaturated systems (*Porter and others, 2009*), heat transport (*He and others, 1998*), and macropore fluid flow (*Sukop and others, 2013*). Colloid transport has been simulated using lattice Boltzmann as a computational base for simulating colloid distribution in porous media (*Redman and others, 2004, Gao and others, 2010, Qui and others, 2011*). Three-dimensional, nineteen fluid node lattice Boltzmann fluid CFD was selected for this portion of the study.

Fluid is represented as a particle distribution of a numerical density following traditional Boltzmann gas dynamics. Particles can interact and collide with one another, can collide with the solid phase and be reflected, and can stream according to a number of velocities associated with the specific direction and alignment of fluid nodes. In single phase, single component models, distributions of real-valued particle numbers are represented on a discrete lattice and are restricted in movement to adjacent nodes at each time step. Each fluid node is tied to neighboring nodes on a regular lattice and therefore each tie represents a discreet distance and velocity. D3Q19 lattice Boltzmann fluid velocities and eigenvectors are defined in <Table xxx>. The eigenvector distribution preserves physical fluid vectors in a Newtonian system. An applied weight is given to each link type for streaming purposes and to preserve a mass balance in the system.

Non-dimensional particle density is calculated from the equilibrium distribution function and defines one of three base equations that form the equation of state. Non-dimensional fluid density is simply the summation of the particle distribution function with regard to each macroscopic fluid node.

Momentum density and non-dimensional fluid velocity may also be calculated similarly by extending the previous equation to include the representative eigenvectors of the distribution function.

Fluid pressure is related to the macroscopic density through the lattice speed of sound . This relationship closes the equations of state for the lattice Boltzmann equation.

Non-dimensional fluid viscosity is calculated through the parametrization of a relaxation time . The single relaxation time method (*Higuera and others, 1989*) makes use of a linear collision operator and a relaxation time term . Adjustments to the relaxation time parameter effectively alters the shear viscosity and controls the progression of the model to equilibrium (*Sukop and Thorne, 2006, Pan and others, 2006*). Non-dimensional time step and node separation are both commonly set to 1 and drop out of the equation.

Although relaxation time can be adjusted from , single bounce back boundary conditions can be unreliable for (*Pan and others, 2006*). Alteration of the Lattice Boltzmann relaxation time parameter can affect the permeability values reported from the LB simulations due to a viscosity dependence in the dimensionalization process. Multiple relaxation time lattice Boltzmann implementations have been presented by *d’Humeries and others (2002)* and *Hilpert (2011)*. These methods account for instability in boundary conditions from relaxation times that diverge significantly from 1. Alternative boundary conditions have been developed and can extend the stable range of the relaxation time parameter for fluids (*Pan and others, 2006*).

Streaming and collision in the model domain is achieved using the BGK (*Qian and others, 1992*) solution to the lattice Boltzmann equation. These functions are often separated in calculation, but represented as a single equation in the literature

A general form of the equilibrium distribution function closes the single relaxation time lattice Boltzmann CFD equation.

Node weights are applied as outlined in table 1.

Pressure boundary conditions were applied to initiate D3Q19 LB simulations. A partial period boundary condition is set up at the inlet and outlet allowing densities from the outlet to stream into the inlet, but not in reverse. The pressure distribution allows the LB model to compute an initial macroscopic velocity. The initial macroscopic velocity and density distribution allows for the initiation of the LB model by calculating the unknown members of the distribution through the equilibrium distribution function along the partial periodic boundary (*Zou and He, 1997*). Fluid models are evolved to equilibrium over a series of time steps. Permeability models return fluid velocity in the x, y, and z direction as well as porosity and fluid density.

Dimensionalization of lattice Boltzmann fluid domains has been covered in some detail by (*Hilpert 2011, Sukop and others, 2013*). The relationship between non-dimensional lattice Boltzmann and model dimensions can be derived through the non-dimensional Reynolds number:

where represents the mean pore radius of a geological media and is the porosity of the media. The non-dimensional Reynolds number is assumed to be constant between lattice units and physical units, therefore we can equate a lattice calculation and physical calculation of Reynolds number and solve for the unknown fluid velocity in physical units.

An alternative method of dimensionalization can be used to recover permeability from lattice Boltzmann simulations through Darcy’s law.

represents the saturated hydraulic conductivity and is a property of both the simulated fluid and porous media. Since simulated flow is driven by a pressure gradient , can be represented as follows:

where is the force of acceleration due to gravity and is the domain length in voxels. From this equation permeability can replace by the relationship.

Substitution of the preceding equation for hydraulic conductivity and rearrangement yields an expression for lattice permeability.

Lattice dynamic viscosity must be calculated from shear viscosity to return a non-dimensional lattice permeability. For both LB and KC models, dimensionless permeability values can be scaled to physical units using the image resolution of the porous media used for CFD simulation.

Lattice Boltzmann permeability simulations were performed under saturated conditions for each of the soil columns studied. Each modeled section has a domain size of 185 x 680 x 680 voxels. Image resolution was 110 . Models were run for up to 400,000 iterations to reach equilibrium. We define equilibrium flow for this chapter as .

### 2.3 Results

Eighth sections of column 3 and column 9 display a larger harmonic mean permeability than the intact soil column (Table xxx). It is possible that isolated or non-percolating pores which were present in the intact columns are able to percolate in the eighth sized sections after cutting. Higher harmonic mean permeability is expected if this is the case and was observed. Sections 7 and 8 of column 3 display a much lower permeability, 0.04 and 0.07 respectively, than the upper 6 sections which have measured permeability values ranging from approximately 1 to 30 . This suggests that the bottom two layers create a “bottleneck” which contributes to the lower measured permeability of the intact soil column. A similar pattern is observed in column 9. Measured permeability in section 8 (0.57 ) is much lower than measured permeability in sections 1-7 (approximately 2.5 to 11 ). Laboratory results from column 7 and column 8 show slightly less than a 1:1 ratio between harmonic mean permeability and the permeability of the intact soil columns (Table 1). A lower harmonic mean permeability suggests that during the cutting process, some previously undisturbed pores may have been deformed or even destroyed. This would subsequently reduce the overall permeability of the cut sections. Smearing and destruction of the original pore structure in the laboratory measurements is a concern for all soil cores presented in this study.

#### 2.3.1 Image wall corrections

Separation of the soil samples from their polycarbonate cylinders was observed prior to CT scanning (*Martinez and others, 2010*). It was noted that slow saturation of the samples from the bottom was performed to minimize this issue. Radial porosity plots display a distinct increase in the mean porosity at an euclidean distance of approximately 325 vx from the center of the soil column (Figure xxxx). The discontinuity in mean porosity suggests that wall separation was present in portions of Column 3 when CT scanning occurred. A wall correction of 15 vx was applied to the each of the columns. The sharp increase in porosity near the polycarbonate cylinder wall is minimized for Column 3 with this correction (Figure xxxx). RMSE permeability decreases significantly with wall correction for both LB and KC methods (Table xxx, Table xxx). The number of percolating simulations also decreases when wall corrections are applied for Brink, Rosin, YASA, and Yen segmentation algorithms. A heat map distribution of mean porosity in the z-direction shows that when wall correction is applied, separation effects that were observed through radial porosity plots (Figure xxx) are not present around the column edges (Figure xxx).

#### 2.3.2 Lattice Boltzmann permeability models

Permeability results from the LB models varied for each segmentation algorithm. Column 3 lattice Boltzmann results show that of the six segmentation algorithms, EN-Brink, HS-Rosin, LA-IK, and LA-KMMRF follow a similar trend across all simulated soil core sections (Figure 3). The YASA 2 model for column 3, section 2 returned a permeability value of 6.78 as compared to measured permeability of 3.19 . The YASA 1 model returned a permeability value of 12.97 (laboratory 31.93 ) for section 3. Yen returned 28.91 and 2.67 for sections 5 and 6 which show the least error from laboratory measured permeability (19.82 and 2.92 ). All simulations for percolating segmentations predict permeability values that are 1-4(O) higher than laboratory values for the remaining cut sections. Variability in permeability values exists between each of the modeled algorithms as a direct result of the mathematical models use to binarize data. Extremely high permeability is reported for KM-MRF and CL-Otsu. However no other models produced percolating results for sections 7 and 8. IK did not return viable data once the wall correction was in place.

Simulation results for columns 7-9 follow similar trends as Column 3. Although high in total porosity, the IK method did not produce viable results for any of the soil columns. Instead it was characterized by unsteady flow when parameterized uniformly with the other LB models. The majority of LB models estimate permeability values of 1-4(O) higher than laboratory measurements (Figure 4). Few instances of percolating models return permeability values of less than 3 are observed. EN-Yen and YASA segmentation data return data points below the 3 threshold. Most models return permeability values between 101 and 104 , where laboratory permeability ranges from 10-2 to 101 . RMSE permeability of YASA 3 was the lowest of all segmentations at 10.19. However, 28% of the simulated soil column sections did not percolate with this method. KM-MRF and CL-Otsu were the only two segmentation methods that produced percolating models in all instances tested. RMSE of these methods was much larger than any other tested segmentation algorithm (KM-MRF: 915.41 , CL-Otsu: 853.78 ).

#### 2.3.3 Kozeny-Carman permeability models

In this study the Kozeny-Carman equation is used independently of LB to assess the CT data by predicting permeability directly from the segmented images rather than simulating fluid flow with computational fluid dynamics. A geometric mean tortuosity is used, which differs from *Shaap and Lebron (2001)*, because it displays a lower RMSE as compared to hydraulic tortuosity. KC permeability estimates cluster into two distinct groups (Figure xxx). A high group is present that includes KM-MRF, CL-Otsu, and LA-IK. The lower group and includes EN-Brink, HS-Rosin, HS-YASA methods, and EN-Yen. The high group over predicted permeability by up to 3(O) in for all sections. Column 3, sections 1,2 and 6 returned model results that fall within the same order of magnitude as experimental results. YASA 2 segmentation returned a permeability value of 0.47 compared to the laboratory value of 0.99 for section 1. EN-Brink returned a value of 3.54 for section 2 which is within one standard deviation of the laboratory value 3.19 0.36 . HS-Rosin returned a value of 1.48 compared to a value of 2.92 measured in the laboratory. In sections 3-6 the lower group under predicted permeability by up to 2(O). No segmentation method belonging to the lower group produced a percolating model for sections 7 and 8. KC permeability results from non-percolating sections have been excluded because KC will erroneously return for non-percolating sections with .

KC Model results follow similar trends for column 7, column 8, and column 9. YASA 2 and YASA 3 results return the lowest RMSE values of the tested segmentation algorithms with values of 5.12 and 2.31. YASA 2 and YASA 3 only returned percolating volumes for 72% of the tested soil sections. LA-IK, KM-MRF, and CL-Otsu returned percolating models for all tested soil sections. Of these three methods CL-Otsu returned displays the smallest RMSE in permeability at 357.07. Variation of up to 3(O) of magnitude is observed in either direction from laboratory methods (Figure 6). In most cases these permeability values are much less or much greater than laboratory measured values which fall into the range of 102 to 10-2. These results suggest that image derived model data is not representing the same pore structure as was measured in the laboratory.

### 2.4 Discussion

#### 2.4.1 Variability in returned permeability values between segmentation algorithms

The importance of the variability between automated segmentation algorithms cannot be overstated at this juncture. Column 03 image analysis results for segmented simulation domains display variation in harmonic mean porosity from 0.1% to 20%. *Iassonov and others (2009)* identified these wide-ranging variations in porosity based solely on segmentation algorithm selection. Although porosity is not a main predictor of permeability, this variability also scales with large differences in connectivity as observed through specific Euler number (Table 5). A more negative specific Euler number is indicative of higher connectivity within the sample (Equation 4). It is also apparent that the tortuosity is inversely proportional to the porosity.

Modeled permeability results display the impact of this variability between segmentation practices commonly used in digital soil physics. The cases displayed in this study show variation of up to four orders-of-magnitude difference in permeability for LB models (Figure 4). LB models seem to follow a similar trend as laboratory data although the few matches in permeability seem to be more of a coincidence than model rigor. LB model permeability do not appear to scale directly with porosity or modeled tortuosity. Instead LB models are influenced directly by pore connectivity and a combination of factors including but not limited to porosity and tortuosity.

KC model tortuosity is directly calculated from porosity via equation 10. Two distinct groups of data are observed within the KC results. Higher porosity segmentation methods are defined as algorithms that returned mean porosity of greater than 5% porosity. These high porosity models return high permeability values and seem to follow a similar trend as each other. The lower porosity group of segmentation methods, return permeability values that are more similar to laboratory values and also follow a similar trend as one another. These methods still show significant variability between returned permeability values. It is obvious that the low permeability methods do not return trends that are consistent with the general trend displayed by the laboratory data (Figure 5). Extremely high tortuosity values in this group, 8.77 – 20.59, highly influence the results since permeability scales with . It is apparent that CT porosity is the controlling factor in the KC model because geometric tortuosity approaches infinity as porosity approaches but does not equal 0. The variability observed here illustrates the direct influence to modeled permeability of variations in modeled porosity and connectivity returned to the researcher by applying different segmentation algorithms.

#### 2.4.2 Potential sources of uncertainty between modeled and measured permeability

Analysis of the data reveals that none of the models from the six segmentation algorithms provide a reliable representation of the original pore structure when considering the full soil columns. With the exception of a limited set of KC and LB models, the segmentation algorithms created digital pore structures that return modeled permeability values that spanned a range of 3 orders-of-magnitude less to 4 orders-of-magnitude larger than those measured in the laboratory. Many potential sources of error come into play when discussing these results.

Common petrophysical laboratory methods such as gas permeameters are limited to making measurements of up to 10 um2; these methods cannot produce representative permeability for macropore samples which are characterized by much higher flow rates (*Sukop and others, 2013*). Options for measuring samples characterized by high flow rates include mega air permeameters (*Ferreira and others, 2010*) and measuring outflow from constant head fluid methods (*Fetter 2001*) as in this study. Considering the relatively small amount of variation in the standard deviation (Table 2) of the laboratory measurements taken, it is unrealistic to assume that the differences in modeled permeability and laboratory measurements can be explained by standard laboratory error.

A soil water characteristic curve was taken for a representative soil core from the same floodplain grazing site as columns 3, 7, 8, and 9. Pore-size distribution was modeled using equation 3 (Figure 7a). Over 98% of the porosity is present in pores smaller than the image resolution (Figure 7b) and can be classified as unresolvable micro-porosity. This suggests that macropores should be responsible for transmitting the majority of fluid through the simulations. However, laboratory permeability results returned values ranging from 0.02 to 32 . These are equivalent to hydraulic conductivity values ranging from a minimum of approximately 2.07E-5 cm/s to a maximum of approximately 0.04 cm/s. The lower permeability values are consistent with those belonging to clay loams and silty clay loam textured soils. Permeability values above approximately 7 seem to be consistent with macropore flow based upon UNSODA and Soil Survey textural tables reported in *Leij and others* *(1999)* assuming macropores percolate faster than sand. Only 14 sections in total of all 32 measured eighth sized soil sections reported laboratory permeability results greater than 7 . Each soil column reports at minimum one measured eighth size soil section that is less than 1 which is inconsistent with macropore flow being main conduit for fluid flow through these tested soil column sections. The assumption that macropore conduits are continuous from top to bottom of the entire intact soil columns may have been erroneous. Instead the data suggests that macropore conduits occupy specific portions the intact soil columns but are not continuous throughout the entire soil column. Organic material present in the original sample may not be resolved in the CT samples since, single energy CT scanning, without the use of specific dopants creates challenges in resolving differences between materials (*Wildenschild and others, 2002*). Due to the challenges associated with resolving organic materials some of the CT images represent a separate system than what was measured in the laboratory.

CT collection and image data are rarely perfect representations of the physical world, since they are disturbed by optical transfer functions, scattering, and noise (*Kaestner and others, 2008*). Operator bias such as image resolution choice, exposure settings, beam energy, and flux may result in systematic errors in subsequent imaging processing steps (*Houston and others,* 2013). Due to averaging of the attenuation of multiple materials or phases in a single voxel, partial volume effects may be present, and boundary voxels may be misclassified (*Ketcham and Carlson, 2001*). Misclassification of boundary voxels could significantly affect modeled permeability results.

#### 2.4.3 Observed relationships between lattice Boltzmann and Kozeny-Carman models

It is apparent that both KC and LB models tend to predict permeability within a similar range of variation from the laboratory data (Figure 4, Figure 6). Kozeny-Carman predictions, do not match 1:1 with lattice Boltzmann results. Instead KC models produce results that display a much smaller RMSE permeability than LB (Table 6). By using the assumption of , KC models assume perfectly cylindrical pores (*Carman 1927*). KC models predict permeability values that regularly 1-2 orders of magnitude less than lattice Boltzmann permeability results across all model results (Figure 9). At very low porosity, both LB and KC display significant changes in permeability values with small changes in porosity. The KC equation displays this trend more strongly due to the large influence of the geometric tortuosity at low porosity values (Figure 10).

KC model permeability values are highly correlated with porosity (r2=0.59) (Figure 10). In the KC model porosity is included directly in the numerator, in the calculation of Tortuosity, and indirectly in the hydraulic radius calculation. LB model values correlate less strongly with porosity (r2=0.39). At permeability changes dramatically with very small changes in . The data supports that macropores are the primary path of fluid transmission in these CT models. For both modeling equations, small increases in porosity yields a smaller density of fluid particles contacting frictional surfaces (Figure 10). These types of increases may not generally be observed in natural systems, due to organic matter such as hummus and root mass providing additional friction surfaces in macropores. The models in this study behave more ‘pipe-like’, due to the inability of the collected CT data to represent organic material. Although no optimization between LB and KC model results is applied, a strong correlation is observed in the permeability data (Figure 8). Power regression analysis of LB and KC results yields a relationship of . This is a notable relationship given the underlying assumption that all pores in the KC model are cylindrical. From this observation, it may be prudent to consider LB models for fine resolution numerical analysis. However, for a quick estimation of CFD modeled permeability, the relationship presented here supports that KC may be a practical alternative to more numerically intensive models such as lattice Boltzmann.

### 2.5 Summary and Conclusions from the analysis of segmentation methods

The objective of this chapter was to identify limitations of modeling permeability from CT data of natural porous media using KC and LB methods. Simulation domains were generated from nine different automated segmentation algorithms and compared to laboratory measurements in an effort to validate each model and gain insight into relationships between KC and LB models. Four macropore soil columns composed of 8 sections each were modeled using both KC and LB methods. Results were compared with laboratory measurements. Both KC and LB models returned permeability values that ranged from 2 orders of magnitude less than laboratory measured permeability values to 3 orders of magnitude greater than laboratory collected permeability values. Models that returned permeability values that were comparable to a discrete section of a soil column, rarely returned comparable values in an adjacent section. KC models returned permeability values that were closer in value to laboratory collected values, but did not seem to follow a similar trend as the laboratory data when comparing measurements for adjacent soil core sections. LB models returned values that followed the same general trend as laboratory methods, but consistently returned values up to 2 orders-of-magnitude greater than the laboratory methods. Neither, modeling approach was able to be validated using this data set.

Partial volume effects may contribute to some of the variability in returned permeability values when comparing models of the same soil column and section that were prepared with different segmentation algorithms. The variability between automated segmentations of the same soil column supports the notion that segmentation methods need to be standardized. Detachment of portions of the soil column from the polycarbonate cylinder was corrected using a wall correction factor. The single energy CT scan used in this study is unable to represent organic material that is present in the soil columns. Frictional surfaces that organic material likely provides in the original soil columns are not captured in the CT imagery. Due to these challenges, it would be incredible if KC or LB models were able to be validated against laboratory measurements. The assumption that—for most models—CT images are representing a separate percolation structure from the original samples that were processed in the laboratory is appropriate.

Tortuosity were not a practical metric for independent analysis of Column 3. Tortuosity was modeled directly from porosity to parameterize the KC equation and could not be used as an independent variable. The geometric tortuosity relationship presented here approaches infinity as porosity approaches zero. As a result, the low porosity group of models (Table 5), displayed unrealistically high mean tortuosity values. Specific Euler number, which represents connectivity, correlated moderately with permeability in Column 3 with the exception of the EN-Brink models. LB boundary conditions may influence these observed relationships at low porosity. This metric may be useful in determining the relationship of relative permeability for multiple soil columns without simulating actual permeability. The KC and LB equation are used to estimate the actual permeability represented by the segmented images they receive.

KC and LB models predicted permeability values with KC models returning results 1-2 orders-of-magnitude less than LB using the assumption that KC models are represented by cylindrical pores. Both KC and LB permeability models are shown to correlate with porosity. KC permeability models correlate strongly with porosity, because is directly included in the calculation, and was modeled from porosity. At values of permeability changes are exaggerated with respect to changes in porosity. Power regression analysis of the KC equation produced a relationship of (r2=0.78) to the LB models. LB models may be suited for fine numerical resolution, but this relationship suggests that KC models can be used as an economical alternative to more computationally intensive fluid models when working with three-dimensional CT data. Verifying that the segmented porous media percolates is necessary when applying the KC relationship.

## 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 int 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.

Increasing 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 1cm 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.

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 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 in 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 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). 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 ranges 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.

#### 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. 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. 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.

#### 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 xxx, xxx). 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.

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. 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.

*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 1M 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 1M NaCl simulations.

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.

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.

#### 3.3.4 Colloid simulation sensitivity to Brownian motion

A series of 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). 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.

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 <>.

## Titanium dioxide nanoparticle simulation with LB-Colloids

### 4.1 Introduction to titanium dioxide simulation

1. Describe the importance of titanium transport
2. Describe background research on titanium transport (expand on these parts!)

Titanium dioxide nanoparticles are commonly used in consumer products such as toothpaste, sunblock, lotions, and house paints. Titanium dioxide based sunscreens can enter the environment directly by being washed off during swimming or other outdoor activities. Weathering of house paints and industrial materials creates another non-point source release mechanism for TiO2 into the environment. A case study of municipal wastewater treatment systems shows a large proportion of these particles are removed in the treatment process. The same study points out that a significant concentration of TiO2 nanoparticles are released through point source wastewater releases from tertiary treatment systems (*Kiser and others, 2009*). Further complicating the matter, application of bio-solids removed from wastewater treatment provides a non-point source vector for the release and transport of nanomaterials in much greater concentration through the soil environment (*Weir and others, 2012*).

A challenge for modeling nanoparticle transport is uniquely manufactured shapes such as rods and pyramids. Traditional colloid transport equations may not be able to adequately represent nanoparticle stability, transport and immobilization. Pore scale modeling however, may be able to bridge gaps in our knowledge of nanomaterial transport and allow for more accurate forecasting and prediction. Due to potential transformations, irregular shapes, and hetero-aggregation with other microscale particles calibration of nanomaterial transport may be necessary to model transport through the pore scale environment.

1. Describe the research problem
2. Brief overview of the project approach

Titanium nanoparticle transport is investigated with this study using D2Q9 lattice Boltzmann based colloid particle tracking code called LB-Colloids. Two-dimensional, nine fluid node lattice Boltzmann was used for computational efficiency and to develop a practical methodology for pore scale colloid transport modeling. Titanium dioxide nanoparticle breakthrough studies were performed by *Wang and Brusseau (written communication, 2017)* through packed sand beds. Pore scale modeling attempts to simulate the macroscopic breakthrough profiles of TiO2 nanoparticles in an effort to gain insight into transport, immobilization mechanisms, and provide a tool for making predictions with changes in environmental conditions. Results from forward models and calibrated models are presented in this chapter.

### 4.2 Laboratory methods

Laboratory nanoparticle breakthrough profiles were taken using a 5.08 cm long packed quartz sand bed. Quartz sand particles displayed a median grain diameter of 0.7 mm. Quartz sand was packed to 1.66 g/cm3 bulk density. Porosity was estimated as 0.375 based on a particle density of 2.65 g/cm3. The packed bed transport study was performed using a 0.3 mM phosphate-buffered saline with a constant outflow rate of 0.6 mL/min, which corresponded to a Darcy velocity of 1.83e-05 m/s. Titanium dioxide colloids were introduced into the system continuously at a concentration of 100 mg/L for approximately 13 pore volumes of elution. The experiment continued to run for approximately 31 pore volumes of elution to generate a titanium nanoparticle break though profile (Figure xxx).

### 4.2 LB-Colloid simulations

LB-Colloids, a simulation software that applies lattice Boltzmann computational fluid dynamics to a binarized dataset and includes additional colloid transport equations to simulate the transport and immobilization of colloid sized particles, was used for this study. A complete LB-Colloids simulation consists of two steps – 1) A lattice Boltzmann model is run until steady-steady state has been achieved 2) outputs from the steady-state lattice Boltzmann simulation are used as the input fluid domain and a colloid model is run. The benefit of the modular, two-step approach, is that transient state simulations can be added to this framework with the extension of the base LB-Colloid code and a method to save transient fluid domains from computational fluid dynamic models. The colloid particle tracking code base is also not limited to using lattice Boltzmann fluid domains. The only requirements needed are a fluid domain of velocity vectors and a binarized model domain.

“Virtual” TiO2 nanoparticles were simulated in this study. Nanoparticles are represented by their zeta potential, bulk density, and radius; nanoparticles are assumed to be spherical in these simulations, however in the natural environment nanomaterials and colloids encompass many shapes (both natural and engineered). Adjustments to the defining physical and chemical parameters of a colloid during calibration can assist in simulating non-spherical shapes.

#### 4.2.1 Spatial and Temporal Discretization

Synthetic porous media were generated using PSHPERE (discussed previously) at 200 pixels by 200 pixels which corresponds to 40,000 nodes. A discretization of 1 micron per pixel was used which corresponds to a domain size of 0.20 mm by 0.20 mm. Each porous media was generated to 0.37 +- 0.01 porosity. A grid refinement factor of 10 was applied to each porous media, for colloid simulations, bringing the total number of nodes to 4,000,000. A final discretization of 0.1 micron per pixel was used to simulate colloid transport within the fluid domain. The finer discretization allows for a more accurate representation of colloid-surface interactions than using the 1-micron lattice Boltzmann discretization.

For all simulations 1,000 non-dimensional time steps were performed to reach steady state with lattice Boltzmann. Dimensionalization of each set of simulation results through the non-dimensional Reynolds number allows for the time discretization between lattice Boltzmann computational fluid dynamics and the colloid transport equations. Each secondary colloid simulation was simulated for 22,000,000 time steps at a time discretization of 1e-6 seconds per time step for a total of 22 seconds. 22 seconds corresponds to approximately 2 pore volumes of elution from these porous media. Two pore volumes of elution was chosen to capture the breakthrough profile of TiO2 nanoparticles recorded in the laboratory. Longer simulations to match the complete laboratory profile are possible, however the computational time would be much longer and better suited for prediction modeling instead of the inverse modeling approach taken in this study.

#### 4.2.2 Porous Medium Boundary conditions

Porous media was randomly generated as a binary array in which each value (0, 1) represents a distinct phase (solid, pore space). Porosity for each porous media was specified to be 0.37 +- 0.01 to correspond with laboratory reported porosity. The specific grain radius for each simulation was specified as 1.7e-5 m. This grain radius, is 0.1 times the laboratory grain radius. However, due to the two-dimensional assumption of the lattice Boltzmann colloid models, the smaller grain radius produced surface areas that are similar to those reported from the laboratory study (table of porous media properties).

#### 4.2.3 Lattice Boltzmann Boundary conditions

Lattice Boltzmann simulations were performed on each randomly generated porous media. No flow boundary conditions were added to the fluid domain boundaries in the x-principal direction. A periodic boundary condition was applied to the fluid domain boundaries in the y-principal direction. Five fluid boundary layers were applied to the top and bottom of the lattice Boltzmann simulation. Addition of these boundary layers prevents localized velocity maximums from occurring at the inflow boundary of the porous media due to the velocity distribution of outflow. No slip and bounce back boundary conditions were applied at pore-solid interfaces within the fluid domain as described in previous sections.

Each lattice Boltzmann fluid simulation was parameterized with a number of constants. A non-dimensional fluid density of 1.0 was held constant as an initial condition for all simulations. The relaxation time parameter (non-dimensional) was also held constant at 1.0 for all simulations. As stated previously, relaxation time values which deviate from 1.0 can cause numeric instability due to simple bounce back boundary conditions. A body force was applied to each simulation, with an initial estimate of 0.001, and calibrated until the simulation darcy velocity was within a specified tolerance of laboratory conditions. More discussion on this process is covered in the section titled Calibration.

#### 4.2.4 Colloid transport Boundary conditions

Titanium nanoparticle, porous media, and fluid physical and chemical properties were specified for each simulation. Nanoparticle simulations were parameterized using laboratory data and assumptions from literature. Simulated zeta potentials for quartz sand and titanium dioxide nanoparticles were taken from laboratory measurements (-51.2 and -42 mV respectively). Fluid ionic strength was simulated with the laboratory supplied value of 0.3 mM NaCl. Titanium dioxide nanoparticles were assumed to have a bulk density of 3800 Kg/m3 (reference) which equates to a colloid mass of 2.8e-10 mg at a measured diameter of 260 nm. Initial parameterization of fluid ionic strength was specified at 3.0e-4 to match the laboratory experiment. Colloids were released in the first fluid layer of the domain at the rate of 2 colloids per 0.1 second for the duration of the simulation. This value was chosen to match the fluid concentration of colloids released into the experimental setup.

### 4.3 Calibration

A three-step inverse modeling approach was taken for TiO2 nanoparticle simulations. Porous media, lattice Boltzmann, colloid simulations were calibrated in series. Each calibration will be described in the following sections. An unweighted PHI of 1.0 was specified as the limit of acceptable error during calibration. If the calibration criteria failed at any point, calibration was restarted from the beginning.

#### 4.3.1 Porous media calibration

Porous media model domains were generated by applying a random Gaussian approach using PSHPERE. Porosity and grain size were specified as inputs and held constant. The Gaussian approach, however does not produce a domain that is consistent with the specified porosity. A simple algorithm was applied to regenerate the porous media if the domain is not within a specified tolerance (0.01 for this study). A secondary sweep line algorithm was applied to all model domains to ensure percolation. The third porous media calibration criteria was a mean pore diameter to colloid radius ratio greater than 70 (dimensionless).

#### 4.3.2 Lattice Boltzmann calibration

Steady state lattice Boltzmann simulations were performed on each of the synthetic porous media. Steady state simulations were calibrated to laboratory column darcy velocity by altering the applied simulation gradient. A gradient upgrade factor for calibration was calculated by

where was the target velocity and was the simulation’s darcy velocity. Application of this upgrade factor led to rapid convergence toward the target, often yielding a solution within three iterations. Simulation velocities were calibrated within a tolerance of +- 1.0e-06 m/s. (Add table of name, gravity, and darcy velocity).

#### 4.3.3 Colloid simulation calibration

Colloid particle tracking outputs were used to calculate the residual (PHI) and determine if a simulation was within the limit of acceptable error. Secondary calibration of colloid simulation ionic strength was performed using a random perturbation method. The slope of the phi was then calculated to determine the direction of ionic strength adjustment during calibration update iterations. XX simulations met the residual criteria and were used in this study (table of residuals, figure of 1:1 simulated vs. laboratory? With regression talk about these calibration results?). If the simulation did not meet residual criteria (PHI < 1.), it was automatically restarted from the beginning of the calibration process, by generating a new simulation domain.

### 4.3 Calibration Results

### 4.4 Discussion/Limitations

1. Talk about the limitations/advantages of this approach
2. Link CDE to a field-based approach if possible (maybe show a Hydrus1d run of colloid transport)

### 4.5 Conclusions

1. Conclude research with ‘Life’s a happy song’

## References

## Appendices