## Introduction:

1. Describe what a colloid is:

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 its 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 media. 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 matter) 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.

1. History of colloid research (brief relevant):
2. Describe why we care about them environmentally (colloids sorb chemicals, viruses, bacteria and can increase transport rates):

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 et. al. 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 to observe particle transport in a three dimensional hydrological systems. 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 et. al. 2004, Gao et. al. 2010, Qui et. al. 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, and operate as novel approaches to modeling micro scale colloid-surface interactions or have not been released into the public domain. 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 are 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 et. al. 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 or 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 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, Verwey and Overbeek (DLVO) interactions. <todo: history> Representation of these micro-scale forces can provide insight into the dispersivity of colloids in a porous media. The inclusion of random motion defined by a random walk algorithm or Brownian motion described 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 accurately develop prediction models of colloid transport where detailed historical data are not present. *Thomas et al. 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 has also been documented due to colloid transport (*Syngouna et. al. 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 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 Arsenic, Silver, and Mercury 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 is associated with the potentially fatal ailment blue baby syndrome (methemoglobinemia) in young children.

1. Briefly describe the approach that was taken for performing research:
2. Define the structure of the paper (in the approach?):

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 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 graphene colloid transport through porous media. Breakthrough concentrations of graphene colloids collected by (*Wang and Brusseau 201x*) 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 2011*), contaminant transport (*Mulligan 2001, Berkowitz 2002*), remediation practices (*Waybrant 1998*), and aquifer characterization. Permeability is typically measured in laboratory settings using fluids (*Fetter 2001*) or gases (*Ferreira 2010*) which can be expensive, laborious, and challenging for macropore soils (*Sukop 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 2013*).With these limitations in mind, it is beneficial to investigate whether permeability can be derived from segmentations of CT-scanned porous media (*Spanne 1994, Hilpert 2011, Sukop 2013*) or thin sections (*Schaap 2001, add refs*) 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.

TODO: REDO Computational fluid dynamic (CFD) modeling systems have gained popularity in the literature over recent years. Development of more efficient computational systems and easier access to systems with relatively fast processing speeds, large amounts of random access memory, and decreasing storage cost has made it easier to create complex fluid models using real porous media. 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 1992). Because of this ability, lattice Boltzmann computational fluid models are able to quantify permeability and saturated hydraulic conductivity of porous media (*Ferreol 1994, Martys 1996, Keehm 2004, Zhang 2005, Carmago 2011, Hilpert 2011, Sukop 2013*), gain insights into multiphase and multiple component flow (*Shan 1993, Martys 1996, Schaap 2007*), and represent enhanced colloidal transport (*Laad 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 (*Ketchum 2001*). Current CT resolutions are on the order of one micron (*Wildenschild 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 (*Ketchum 2001, Wildenschild 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 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 2000*), spatial correlation and tortuosity (*Coles et. al. 1998*), volumetric water content (*Hopmans et. al. 1992*), contaminant transport (*Clausnitzer 2000*), colloidal transport (*Gaillard et. al. 2007*), and fluid modeling using lattice Boltzmann (*Chen 1998*).

Models such as lattice Boltzmann have been used to recover the permeability of porous media (refs!). 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 2001* (other refs) 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 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 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 both 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 et. al. 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 et. al. 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 et. al. 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 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 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 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 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, 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 1990*). A short description of each segmentation algorithm is provided. Algorithms are grouped together following the scheme outlined in *Iassonov 2009*.

Global thresholding is the most commonly applied approach to image segmentation (*Iassonov 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 segmentation algorithm Yet Another Segmentation Algorithm (YASA) was applied with three different treatments to the raw CT data. YASA is a histogram based method? Summarize Marcel’s work with YASA.

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 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 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 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 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 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 2000, Doube 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 et. al. 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 we present only the tortuosity relationship that returns the lowest RMSE in permeability for the greatest number of segmentation algorithms tested in this study. Table 2 presents 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 et. al. 1986*). The discretization processes and application of simple bounce back rules enables the representation of complex geological structures. Application of either body force of 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 et. al. 1992*). Lattice Boltzmann CFD models have been successfully used to represent fluid flow in saturated systems (*Blunt et. al 2013*), unsaturated systems (*Porter 2009*), heat transport (*He et. al 1998*), and macropore fluid flow (*Sukop et. al 2013*). Colloid transport has been simulated using lattice Boltzmann as a computational base for simulating colloid distribution in porous media (*Redman 2004, Gao 2010, Qui 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 1>. 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 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 2006, Pan et. al. 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 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 2002, 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 et. al 2006*).

Streaming and collision in the model domain is achieved using the BGK (*Qian 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. ### TODO: describe the pressure boundary condition (ZHO HE) approach to LB ###. The pressure distribution allows the LB model to compute an initial macroscopic velocity using ### Equations 11-13 ###. 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 ### (Eq. 14) ### (*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 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.

Hydraulic tortuosity can be directly calculated using the primary macroscopic fluid velocity vectors recovered through the momentum density calculation outlined in the equation of state.

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 1). 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 serious 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 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). Percent 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

*Schaap and Lebron 2001* show that the Kozeny-Carman predictive model applied to digital images yielded permeability results with an R2=0.91. 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 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 results display variation in harmonic mean porosity from 0.1% to 20%. *Iassonov 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 2013*). Options for measuring samples characterized by high flow rates include mega air permeameters (*Ferreira 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. It is shown that pore deformation and/or destruction may have occurred during the cutting process for column 7 and column 8. Laboratory results show slightly less than a 1:1 ratio between harmonic mean permeability and the permeability of the intact soil columns (Table 1).

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 et. al.* *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 be 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 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 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* 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 2001*). Misclassification of boundary voxels could significantly affect modeled permeability results. Visual inspection of three dimensional imagery of model pore networks—such as seen in Figure 8—support the possibility of voxel misclassification in some models. Column 3, section 2 is used as an example, because lattice Boltzmann simulations returned permeability values that are comparable to laboratory values. Differences in permeability values between models could be influenced by partial boundary effects.

#### 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

1. Describe the importance of colloid transport
2. Brief history of relevant of colloid research
3. Describe the problem with regard to previous research (long model run time, closed source simulation software, overly complex, etc…)
4. Brief overview of the project approach

### 3.2 LB-Colloid methods

1. Describe the relevant mathematics used within the LB-Colloids simulation software
2. Brief background on the equations, and meaning of each term (what it is, where its from, what it calculates)

### 3.3 Initial results

1. Display sensitivity analysis results from initial runs of colloids models

### 3.4 Discussion

1. Interpretation of the initial results with regard to principal components of the colloid equation

### 3.5 Outcomes/Deliverables

1. Reference the LB-Colloids user manual (Appendix #{}) and describe the functionality and extensibility of the software

## LB-Colloids validation

### 4.1 Introduction to graphene simulation

1. Describe the importance of graphene transport
2. Describe background research on graphene transport
3. Describe the research problem
4. Brief overview of the project approach

### 4.2 Simulation initial conditions/methods

1. Describe the initial conditions for simulating colloid transport
2. Describe the laboratory setup for colloid breakthrough experiments

### 4.3 Results

1. Show initial results for LB-Colloid simulations
2. Identify limitations with the results

### 4.4 Calibration

1. Describe the model calibration process
2. Display the calibrated simulation results

### 4.5 Discussion

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)

### 4.6 Conclusions

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

## References

## 6.0 Appendicies