## 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 I define colloid transport and colloidal fluid 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 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. 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 can be extended to account for fluid 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. 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 describe Dispersivity, the random diffusion of particles by heat and solute gradient or 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]. However, bacterial transport modeling is limited 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 predictions 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 farmland in Pennsylvania. Fluid flow was simulated in each soil column using D3Q19 lattice Boltzmann computational fluid dynamics. Simulated hydraulic conductivity was compared to laboratory hydraulic conductivity 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 models are 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. These simulations also acted as a check during 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*), and remediation practices (*Waybrant 1998*). 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 and saturated 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*) using computational models or empirical relationships. Modeling methods applied to CT imagery may be of practical utility in these cases.

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 modeling scheme is one such CFD system, which is applied primarily for its relative ease of programming and its ability to model 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 models. 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 modeled in 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. By considering the fundamentals of information theory (*Shannon 1949*) coarser resolution imagery is more susceptible to partial volume effects and will recover less porosity with certainty than imagery collected using a finer resolution. Given these issues, it is incredible that digital representations has 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; however, a major drawback of the method is the computational time and demand 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* 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 images 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. However, KC methods are not without limitations. The KC model relies on estimation of tortuosity from geometric, hydraulic, diffusive, or electrical relationships within the 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 paper 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. Permeability was measured in the laboratory and was modeled using image analysis data to parameterize the Kozeny-Carman relationship, as well as the numerically intensive lattice Boltzmann scheme. 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.

In this study nine different automated segmentation algorithms are applied to CT images of 4 macropore silt-loam soils. Over one-hundred different segmentation standards currently exist in the literature (*Iassonov 2009*); it is important to have representation from each major class of algorithms, as these can return different representations of pore boundaries and therefore porous media structure. There are a number of CT systems available to the researcher as well; these 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*). 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.

### 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/cm3. An industrial scanner was used to image the soil cores. The scanner used was a HYTEC Flat Panel Amorphous Silicon High-Resolution Computed Tomography (FLASHCTTM) 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 and is detailed in section <>.

#### 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 on each column. was converted to permeability following the relationship

where dynamic viscosity and fluid density where assumed to be at STP 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 columns observed in this study, a soil water characteristic 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 of extreme importance 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 automatically segment images. By selecting these algorithms operator bias in the segmentation step was minimized. Intensity variations due to beam hardening artifacts were corrected 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 the CT data and the column 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*). The following describes each segmentation algorithm using 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 simple 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 digital numbers and a line drawn 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*).

The 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 maximin of entropies 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*]. It is apparent 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.

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.

#### 2.2.4 Kozeny-Carmen methods

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 we define tortuosity according to *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, samples with no effective porosity have been excluded from the results presented in this study.

#### 2.2.5 Lattice Boltzmann methods

Lattice Boltzmann methods (LB) have been shown to simulate a variety of behaviors including unsteady flows, phase separation, evaporation, and interactions with surfaces have been simulated (*Shan 1994, Martys 1996, Chen 1998, Aidun 2010*) # todo: match these references to their behavior #. LB modeling has been developed from the concept of a Boltzmann gas composed of interacting particles. Fluid interactions are described by statistical analysis of individual particles using classical mechanics. LB simplifies this relationship by limiting individual particle movements along a lattice (*Sukop 2007*). LB fluid simulations are relatively easy to program and are not limited to small sample volume, simple physics, or simple geometries (*Chen 1998*). No-slip boundary conditions can handle the complex geometries that are characteristic of natural porous media (*Sukop 2013*).

The single relaxation time method (*Higuera 1989*), which is commonly used with LB models and applied in this study, makes use of a linear collision operator and a relaxation time term . A collision operator known as the Bhatnager-Gross-Krook collision operator is used (*Qian 1992*). The LGBK method allows the operator to control the progression to equilibrium due to the relationship between the relaxation time and the lattice kinematic viscosity. It has been shown that the LGBK approach fully recovers the Navier-Stokes equation at the macroscopic scale (*Qian 1992*).

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. A statistical summation of the motion of all microscopic fluid particles represents a macroscopic velocity for each vector in the system. Common lattices include D2Q9, D3Q15, and D3Q19 where D is the number of dimensions and Q is the number of velocity vectors at each fluid node. Three types of fluid ties exist. Type I has a discrete velocity of 0, type II has a velocity of 1 lu ts-1, and type III has a velocity of lu ts (*Sukop 2007*). The relative values of members of the distribution function can then be thought of as a frequency of occurrence. The total density of particles at an individual lattice node in a D3Q19 grid is:

where is the macroscopic fluid density and is the distribution function. The macroscopic velocity is an average of the microscopic velocities weighted by directional densities (*Sukop 2007*):

The pressure is related to the macroscopic density through the lattice speed of sound which defines the LB equation of state as:

Change this line/////Equations 11-13 allow the equilibrium distribution function to be computed at each time step based on the macroscopic velocity, macroscopic density, and microscopic velocities:

where are weights based on the fluid links. for type I links, for type II links and for type III links (*Qian 1992*) # todo: create a table that shows this #. Finally a streaming and collision operator facilitates replacement of the original distribution function and allows the system to evolve. They are separated in LB code but commonly combined and written as:

Relaxation time controls the evolution to local equilibrium and is commonly set to 1 for numerical efficiency (*Qian 1992, Sukop 2007*).

The single relaxation time approximation allows kinematic viscosity to be estimated though the relationship # todo: <extend this equation to include del x and time> #

The common value of is used, which leads to a kinematic viscosity of lu2ts-1. A single bounce back condition is applied, which means that when a particle distribution moves into a solid node, it is sent back to the node in which it came from (*Chen 1998*). Although relaxation time can be adjusted from , single bounce back boundary conditions are not reliable for (*Pan 2006*). Alteration of the Lattice Boltzmann relaxation time parameter can affect the permeability values reported from the LB models. This step may be appropriate when modeled permeability is within 2x measured permeability. A limitation of the single relaxation time lattice Boltzmann is a viscosity dependence of the boundary conditions (*Pan et al. 2006*).This relationship creates the potential for serious problems, since permeability becomes linked to fluid viscosity instead of being a property that is intrinsic to the porous media. Multiple relaxation time lattice Boltzmann reduces the viscosity dependence of permeability by allowing viscosity independent boundary conditions through an appropriately constructed collision operator (*d’Humeries et al. 2002, Pan 2006*). Improved numerical stability over a wider range of viscosities and Reynolds numbers is observed with multiple relaxation time lattice Boltzmann (*d’Humeries 2002*).

Pressure boundary conditions were applied to initiate the LB models. 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. *Hilpert 2011 and Sukop 2013* outline methods to calculate permeability from single phase, single component lattice Boltzmann models. Darcy’s Law is applied, which states that specific discharge is proportional to the head gradient ## Todo: <change this to darcy’s law representation> ### :

where is the hydraulic conductivity such that flow is in the opposite direction of the head gradient (*Sukop* 2013). Since 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

Solving for permeability yields

where is the dynamic viscosity of water and permeability is in dimensionless lattice units. For both LB and KC models, dimensionless permeability values can be scaled to physical units via:

where is equivalent to the image resolution of the porous media used in the model.

Hydraulic tortuosity can be directly calculated through LB fluid vectors by

where corresponds to the primary macroscopic fluid velocity vector returned from the LB model.

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 study as every 10,000 iterations.

### 2.3 Results

1. Lattice Boltzmann results (No reliable predictions!)
2. Kozeny-Carmen results too (Follow the LB-predictions)

### 2.4 Discussion and conclusions

1. Wrap up the section with analysis of the results and organic matter issues.

## 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’