1. Introduction:

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

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

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

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

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

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

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

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

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

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