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Transport of Pharmaceuticals in Soil

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Abstract

The goal of this project was to examine the sorption characteristics of aqueous ciprofloxacin (CIP) to various soil types. Kaolinite and soils with different amounts of organic carbon (f_{oc}) were synthesized and contacted with CIP to determine their viability for removing CIP from water. UV-spectrophotometer was used to measure CIP concentration. The results showed that both kaolinite and organic carbon efficiently sorbed aqueous CIP. However, kaolinite allowed for greater sorption of CIP in water than soil with the greatest $f_{oc.}$

Acknowledgements

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1 Introduction

Over the past century there has been an ever increasing demand on the world's natural resources and the planet's supply of freshwater is at the center of this issue. Many would say that oil, with its extremely high demand and integral social and economic impacts is our most precious resource. However, the protection and proper management of drinkable water has become our most essential concern with substantial amounts of funding and resources being invested in the protection and upkeep of our freshwater supplies. There is a continuous effort that aims to keep our freshwater sources free from any and all harmful intrusions that may be dangerous to the human population as well as the surrounding environment.

The discharge of antibiotics from wastewater in our septic tanks into the subsurface and drinking water supplies is becoming an increasingly important and complicated issue. The concentrations of these drugs in our wastewater and drinking water have only recently been researched and the effects that they have both on the human population as well as the environment are relatively unknown. Wise (2000), estimated that the total annual worldwide consumption of antibiotics is somewhere between 100,000 and 200,000 tons. Ciprofloxacin (CIP) is one such antibiotic that research has been conducted on to determine how antibiotics move through soils. CIP is one of the most prescribed antibiotics in the world and is one type of Fluoroquinolone (FQ), a wide-ranging class of antibiotics used on both human and animals. Research has shown that up to 75% of CIP and amoxicillin consumed are un-metabolized and have been found to be present in our wastewater. Ultimately the concentrations of these antibiotics both in our environment as well as our drinking water must be reduced.

The approach involves the identification of soil properties and processes such as retardation and distribution coefficients as well as the adaption of isotherm equations. The objective of this report is to describe the interaction between soil and aqueous ciprofloxacin and to design a layer of infiltration based on results. Past research has been done to determine the adsorption and absorption interactions between CIP and various soil types as well as treatment methods for the removal of CIP from drinking water and wastewater.

Although much research and experimentation has been carried out with respect to the treatment and sorption of aqueous CIP, there has been no focus on fractional organic carbon (f_{oc}) or the use of Kaolinite. This project is intended to fill the knowledge gap by developing a methodology and experimental procedure that allows for data to be compiled on the effects of varying f_{oc} and Kaolinite content with respect to the sorption of CIP.

The pinnacle goal of this report is to design and test different soil compositions in order to determine the best technology that allows for effective sequestration of CIP in order to protect against contamination of groundwater. The group accomplished this by determining factors that most affected sorption processes and soil transport by researching previously implemented sequestration techniques. The group then chose to manipulate the fraction of organic carbon in soil samples as well as incorporating activated carbon and previously successful soil types in the sorption of CIP. The team filled the knowledge gaps pertaining to the transport of aqueous CIP in soil through a series of sorption experiments with respect to the alteration of soil fractional organic carbon.

2 Background

The purpose of this chapter is to discuss previous research and key topics about the fate and occurrence of pharmaceuticals the environment, environmental concerns and risks, and effective transport mechanisms used in different studies to treat contaminated water in soils. First we start off by discussing the presence of pharmaceuticals in the environment in order to establish the importance of studies that have been conducted and the risks that pharmaceutically active compounds (PhACs) pose to our environment. This is then followed by the brief history of use of the antibiotic CIP and its chemical structure. Next, infiltration of effluent from WWTP and septic tanks into the soils and groundwater is discussed which is then followed by an overview of groundwater transport mechanisms relevant to our project. Finally, adsorption mechanism in its importance in removal of CIP from water, use of clay mineral (kaolinite) as an adsorbent, relevant physical soil properties and methods used in previous research is discussed.

2.1 Pharmaceuticals in the Environment

Pharmaceuticals have been used in increasing amounts over the recent decades in large quantities and these numbers will continue to rise in the coming years. These antibiotics are neither completely absorbed nor metabolized by humans or animals (Drillia et al., 2005). As a result, the unutilized portion of the pharmaceuticals is discharged into the environment through urine and feces and eventually ends up in raw sewage (Hirsch et al., 1999). In recent years, scientists have detected antibiotics and other pharmaceutical contaminants in treated drinking water. Those contaminants are not removed by modern treatment systems and pass into the environment in many ways, such as through hospital waste water, household waste water and agricultural waste water. Untreated pharmaceuticals affect human health and the ecological system when passing through soil and into ground water. This presence of antibiotics throughout the environment could have important consequences for ecosystems and human health, possibly contributing to the increase of allergies in human and the spread of antibiotic-resistance bacteria (Zuccato et al., 2006). According to the United States Government Accountability Office (USGAO) report, veterinary drugs from the agricultural facilities where large amounts of food-production animals were treated with pharmaceuticals is another potential source for those contaminants in the environment (GAO, 2011). Pharmaceuticals found in drinking water affect human health by creating antibiotic resistance in the human body. According to a study done by University of Insubria in Varese Italy, bacterial resistance to antibiotics has been reported in sewage, surface water, drinking water, farm soil and marine aquaculture sites (Zuccato et al., 2006).

2.2 Ciprofloxacin

The following sections provide an overview of Ciprofloxacin, including history of use, chemical structure, formula, properties, reactions with other compounds, clinical properties and adverse effects.

2.2.1 Brief History of Use

Antibiotics, such as ciprofloxacin and metronidazole are commonly used today for clinical treatment to reduce bacterial growth. Ciprofloxacin is one of the most commonly used and clinically important antibiotics in the world. It has been in use since 1987 for a variety of ailments and is the most-widely used fluoroquinolone in humans and animals worldwide (Clinical Toxicology Review, 1997). According to tests done by Kummerer at University

Hospital Freiburg, it was found that CIP does not biodegrade well and genotoxicity was not eliminated through current treatment methods (Kummerer et al., 2000). Since it's not biodegradable in the environment, aqueous CIP needs to be either sorbed in soil or removed from effluent wastewater using new treatment methods within treatment plants.

2.2.2 Chemical Formula

CIP's systematic name is 1-cyclopropyl-6-fluoro-4-oxo-7(piperazin-1-yl)-quinoline-3-carboxylic acid, which is a second generation fluoroquinolone antibacterial. Its chemical formula is $C_{17}H_{18}FN_3O_3$. As a commonly consumed drug, CIP is marketed in most counties around the world. CIP is a faint to light yellow crystalline powder with a molecular weight of 331.4.

2.2.3 Solubility and pH influence

CIP's solubility in water is approximate 350 mg/L (Roma et al., 2010) and that solubility varied by the pH value of the solution. Avisar's research shows that treatment technology for the removal of antibiotic residues, including CIP, is affected by the solution pH (Avisar et al., 2009). The pH adjustment of the treated water leads to structural modification of the residue's molecule that may enhance direct photolysis by UV light (Avisar et al., 2009). That research also presents that an increase of water pH from 5 to 7 leads to an increase in degradation rate of aqueous CIP (Avisar et, al, 2009). According to the study done by Melo et al., of Universidade de Aveiro, the solubility of CIP in ethanol and 2-propanol is 2 and 3 orders of magnitude lower than its solubility in water (Melo et al., 2005). Figure 1 below shows CIP's solubility featuring various solvents at varying temperatures.

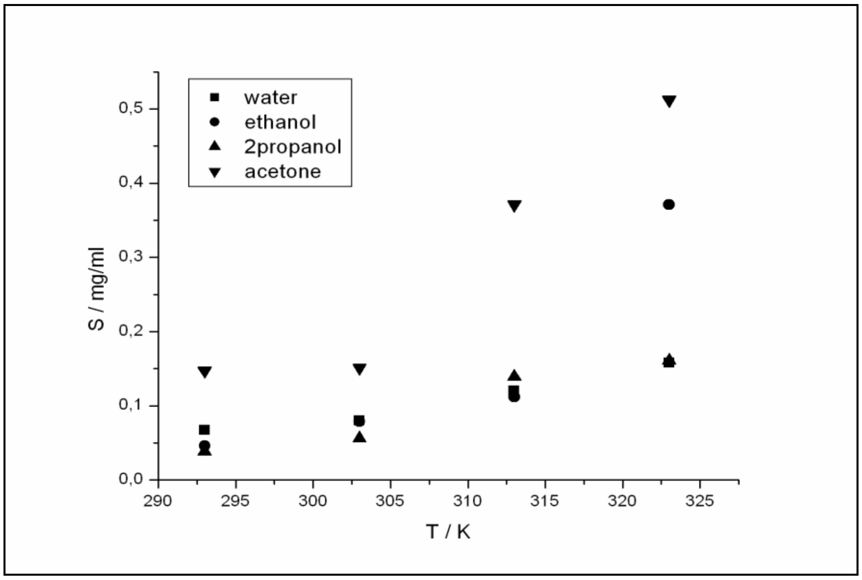

Figure 1: CIP's solubility in different solvents vs. temperature change (Melo et al., 2005)

2.2.4 Chemical Structure

The chemical structure of CIP consists of a bicyclic aromatic ring skeleton with a carboxylic acid group (p*K*a = 5.90 +/-0.15), a keto group and a basic-N moiety group (p*K*a = 8.89 +/- 0.11). It can exist as a cation (CIP^0, +), zwitterion (CIP^-, +) and anion (CIP^-, 0) under typical soil and water pH conditions.

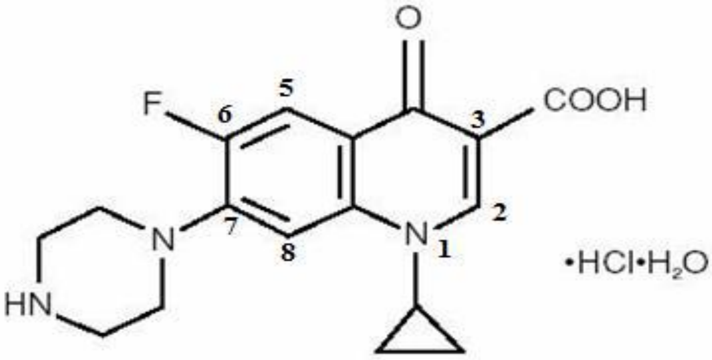

Figure 2: Molecular structure of CIP (DailyMed, 2008)

2.2.5 Toxicity

Like many other antibiotics used in recent years, the major adverse effect of using CIP reported by pharmaceutical manufactories is gastrointestinal irritation. However, fatal liver failure associated with CIP was reported in Lancet in 1994 (Schuld et al., 2010). CIP has been implicated in several cases of acute renal failure and is the most established fluoroquinolone to cause such renal dysfunction (Schuld et al., 2010).

2.2.6 Ionic Components

In general, CIP is a pharmaceutically-active compound which is a complex molecule with different functionalities (Kummerer, 2009). It's frequently called a "micro-pollutant" because it is often found in the μg L^{-1} or ng L^{-1} concentration range in the aquatic environment (Kummerer, 2009).

2.2.7 Pathways of Pharmaceuticals to the Environment

CIP is passed into the environment mainly from human waste and agricultural waste. The pathways are varied by different conditions and locations. CIP can transfer to the soil and ground water through human use (typically hospital waste) and animal use (typically agricultural industry effluent). Beside those two major contributions, there are many other pathways for the CIP to get into the soil and ground water. For example, the CIP may enter the environment directly from water storage structures as a result of accidents or weather conditions, or through the application of manure and liquid waste to croplands (GAO report, 2011). Figure 3 below illustrates many means by which pharmaceuticals can enter water supplies.

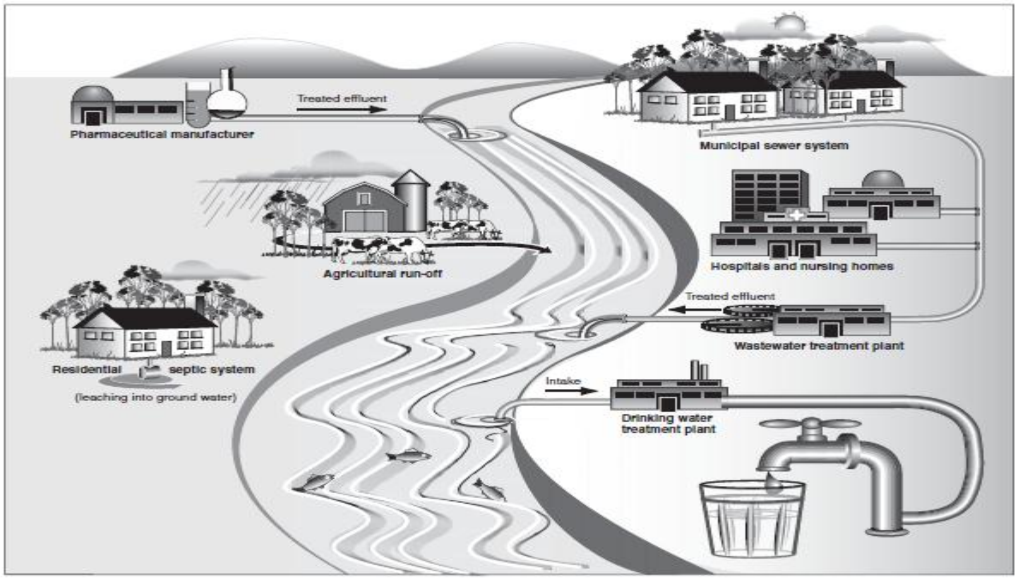

Figure 3: Pathways through which Pharmaceuticals Enter Drinking Water Supplies (GAO report, 2011)

An MQP report by Roma et al. (2011) reported that most of the occurrence studies have been conducted in Italy, Spain, Switzerland, China, USA and Germany, and the studies have identified pharmaceuticals that could cause environmental risks and are not readily degraded in WWTPs. Giger et al. (2003) reported that CIP concentrations in hospital waste water were present above the predicted no-effect concentration (PNEC) of 3-10 µg/L. In another study conducted by Kummerer (2001) it was estimated that the total antibiotic load of municipal wastewater which also contains the contribution of hospitals is 50µg/L, and this concentration takes into account the outdated medicaments and remainders that are disposed of in household drains. Griger et al. (2003) reported that CIP and norfloxacin were found in sewage sludge samples from several wastewater treatment plants at concentrations ranging from 1.4 to 2.4 mg/kg of dry matter and the main concern is that these FQs may reach the terrestrial environment.

According to the research work by Golet et al., the municipal WWTP is acting as the key connection between human pharmaceuticals and the environment. The best way to reduce the environmental impact is through sorption to sewage sludge (Golet et al., 2003). In general, the discharged treated WW is considered as the major entry pathway of pharmaceuticals to the aquatic environment (Golet et al., 2003).

2.2.8 Human Use

According to the GAO study, the main source of human pharmaceuticals in the environment is likely treated wastewater from households, industry, and commercial facilities. Biosolids from waste water treatment plants applied to land as fertilizer may also be a source of human pharmaceuticals in the environment (GAO, 2011). Septic systems may be a source of human pharmaceuticals in ground water also. As to be expected, hospital discharged waste water has a higher pharmaceuticals concentration than municipal sewage (Kummerer, 2009). However, the total substance flow is much lower because of much lower share of effluent from hospitals in municipal effluent in developed countries (Kummerer, 2009). Figure 4 depicts the movement of effluent into below ground water supplies.

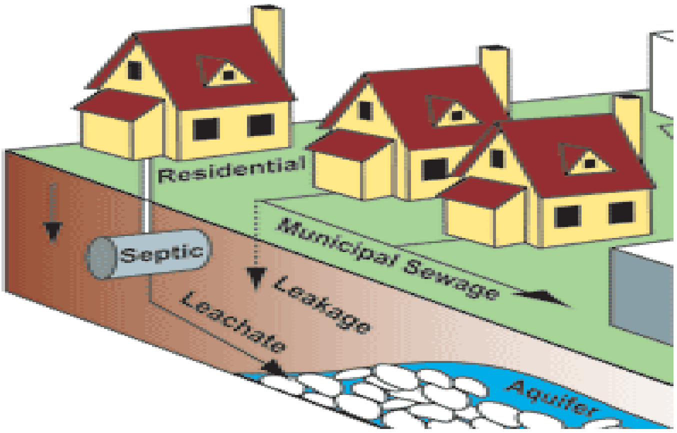

Figure 4: Pathway of PPCP between homes and septic or municipal sewage facilities. (U S EPA)

2.2.9 Veterinary Use

As GAO has reported in 2011, agricultural facilities where large numbers of food-producing animals (such as chickens, cattle, and swine) are treated with pharmaceuticals have become potential sources of veterinary pharmaceuticals in the environment (GAO, report 2011).

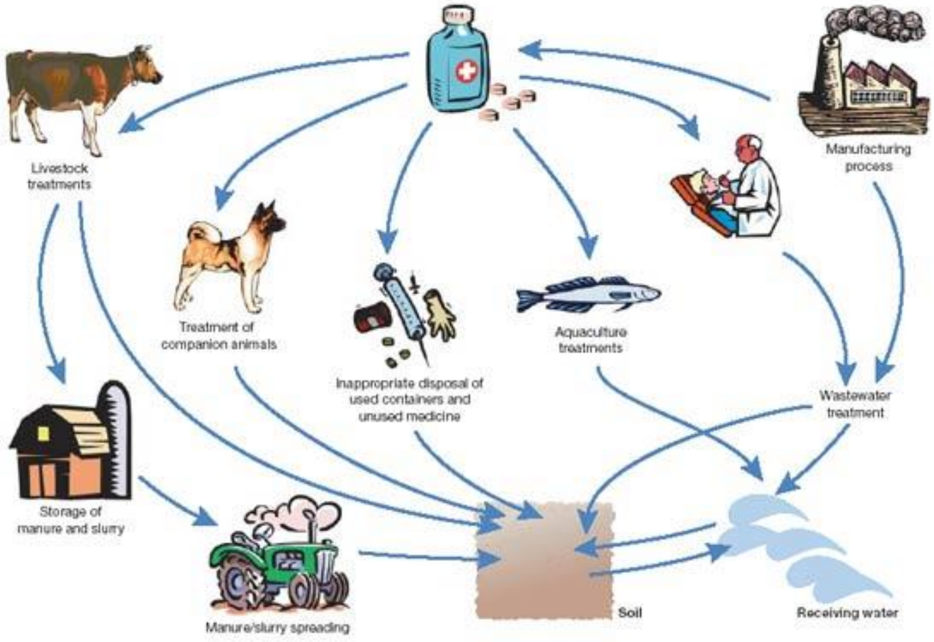

Figure 5: Routes of release of human and veterinary pharmaceuticals to the environment (EMBO report)

Figure 5 above summarizes different uses of pharmaceuticals that are then released to the environment. It also shows the use of pharmaceuticals for treatment of companion animals and aquaculture which also infiltrates in soils and receiving water.

2.2.10 Environmental risks

The effluent that is released to the environment has a relative low antibiotic concentration compared to other types of contaminants. However, these low concentrations of antibiotics, such as CIP, could be harmful to humans as well as the environment despite discharge rates being within regulatory standards (Avisar et al., 2010). The potential health effects and acute toxicities of those contaminants in the environment are not well known (Avisar et al., 2010). The current major concern of antibiotic pollution would be the development of drug resistant bacteria that may enter our food chain and further affect human health (Avisar et al., 2010).

2.2.11 Raising Concern

In recent years, scientists' attention regarding the presence of pharmaceuticals in the environment has increased significantly. In response to increasing information arising from the scientific community, the news media reported that pharmaceuticals had been detected in drinking water of 24 major metropolitan areas across the United States (GAO report, 2011). However, EPA has not developed specific water quality criteria under the Clean Water Act for most pharmaceuticals. There are no water quality standards or permits that refer to most pharmaceuticals (GAO report, 2011).

There have been many studies investigating the presence of CIP in wastewater effluent with various concentrations being found. According to Fick (2009), a study conducted in Sweden found a concentration of 14 mg/L of CIP in the effluent of some treatment plants. In addition, other pharmaceuticals with lower concentration were also detected in the aquatic environment. Those studies showed that the current treatment methods are insufficient for removing CIP from wastewater. Bhandari et al. (2008) evaluated the occurrence of CIP and other pharmaceuticals in the municipal WWTP in United States. The study showed the average CIP concentration of 1.44µg/L in aqueous phase and 0.59µg/L in waste water treatment system (WWTS) (Roma et al., 2011). Figure 6 shows the occurrence of scholarly works on the concerns of pharmaceuticals in the environment between 1991 and 2008.

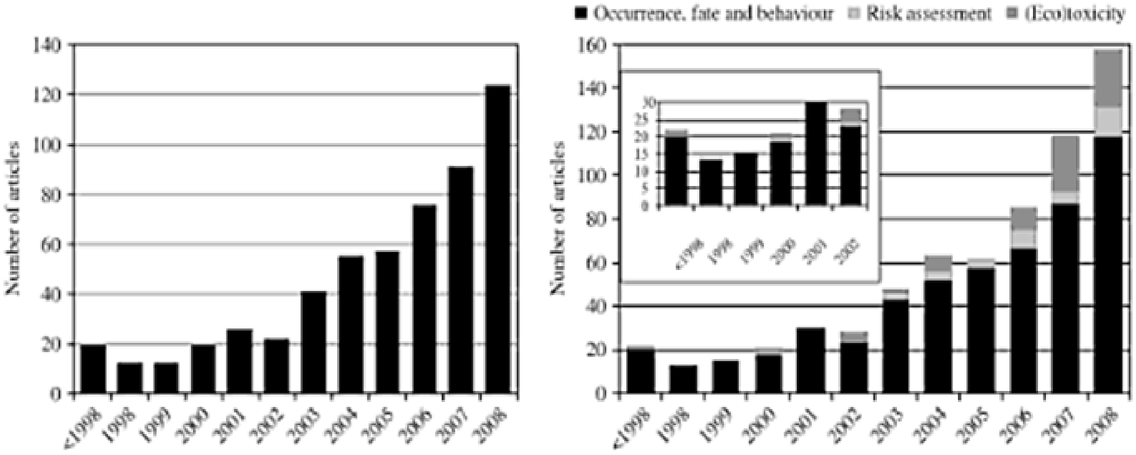

Figure 6: Evaluation of scientific production concerning pharmaceuticals in the environment between 1991 and 2008 (Benoit Roig, 2010)

According to figure 6, the number of scientific research in this area has been increasing throughout the years. The graph on the right also shows the an increase in risk assessment and (eco)toxicity evaluation.

2.2.12 Bacterial Resistance

The development of antibiotics has changed the lives of many. However, the resistance of antibiotics can lead to serious infections which have become an increasingly important issue worldwide. The incidence of resistance to fluoroquinolones has dramatically increased since they were introduced around ten years ago (Acar and Goldstein, 2011). Attention to the regulation of antibiotics in the environment and proper control of pharmaceuticals is needed at this moment.

Wastewater effluent discharged into the environment containing many pharmaceuticals including antibiotics have relatively low concentration which is frequently reported in parts per trillion (GAO report, 2011). The presence of these drugs in soil and ground water can contribute to bacterial resistance which is already a major concern by scientists. Resistant bacteria can cause negative effects on human health due to infection. Accompanied with the development of new antibiotics, there is a need to reduce the spread of pharmaceuticals presented in the environment due to human and veterinary use as well as find practical, efficient and economical ways to treat the wastewater contaminated with various types of pharmaceuticals.

2.2.13 Harmful Concentration Levels

Most pharmaceuticals has been measured in streams and wastewater influents and effluents at concentrations typically less than 1µg/L. Concentrations orders of magnitude higher have been found in the effluents from hospitals (0.7-124.5µg/L) (Kummerer et al., 2000). The majority of pharmaceuticals and personal care products (PPCP) are present in the environment at low concentrations, and these contaminants in the waste water discharged to the environment are not currently regulated under Environmental Protection Agency (EPA) programs (GAO Report, 2011). Under the Safe Drinking Water Act, EPA is responsible for regulating the contaminants in drinking water as well as establishing and revising the national water quality criteria (GAO Report, 2011).

2.3 Infiltration

In many cases treated wastewater is not released as effluent into bodies of water. After treatment, effluent may be released directly into the ground where it infiltrates the soil and groundwater. This occurs through the use of privately owned household septic systems but it can also be the case in areas where recharge of groundwater reserves occurs.

2.3.1 Infiltration on a Large Scale

Through reuse and recycling of treated wastewater, the replenishment of natural water sources such as aquifers can be can be augmented. At the same time we may unknowingly be discharging high concentrations of antibiotics including CIP into the environment. According to the Environmental Protection Agency (EPA), treated water can be spread or injected into aquifers in order to increase water supplies or to prevent the incursion of salt water in areas along the coast (EPA, 2011). For example in Orange County, California, the Water Factory 21 Direct Injection Project has been injecting treated wastewater into the aquifer in order to stave off salt water from the coast as well as boost the present water supply since 1976 (EPA, 2011). Other sources of effluents containing higher concentrations of antibiotics such as CIP may include hospitals. Typically the effluent from hospitals goes to municipal wastewater treatment plants where it is treated before being discharged. Conversely, in some cases, hospitals may treat and discharge their own wastewater. In the instances where hospitals and other sources of wastewater discharge release effluent directly into the ground, higher concentrations of CIP may be found.

2.3.2 Private Household Septic Systems

Many households in the United States utilize septic systems for the treatment of household wastewater. According to the Environmental Protection Agency (EPA), a septic system consists of four main parts: a piping system that carries wastewater from the house to the septic tank, the septic tank itself, a drainage field that treated wastewater is released into, and the soil (EPA, 2005). The septic tank itself is usually a concrete structure with one or more openings and is typically buried in the ground in close proximity to the household. Wastewater is pumped from the home to the septic tank where particles settle to the bottom forming sludge and partially dissolve (EPA, 2005). Before exiting into the drainage field the wastewater passes through screens which remove any remaining solids before the wastewater is released into the drainage field. The partially treated wastewater then flows into the drain-field where it is further treated by the soil. Flooding in the drain-field can occur and in many states a second reserve drainage field is required. After the wastewater is released into the drainage field it is further treated by the soil where harmful bacteria and viruses are removed (EPA, 2005). Figure 7 exhibits a typical household septic system.

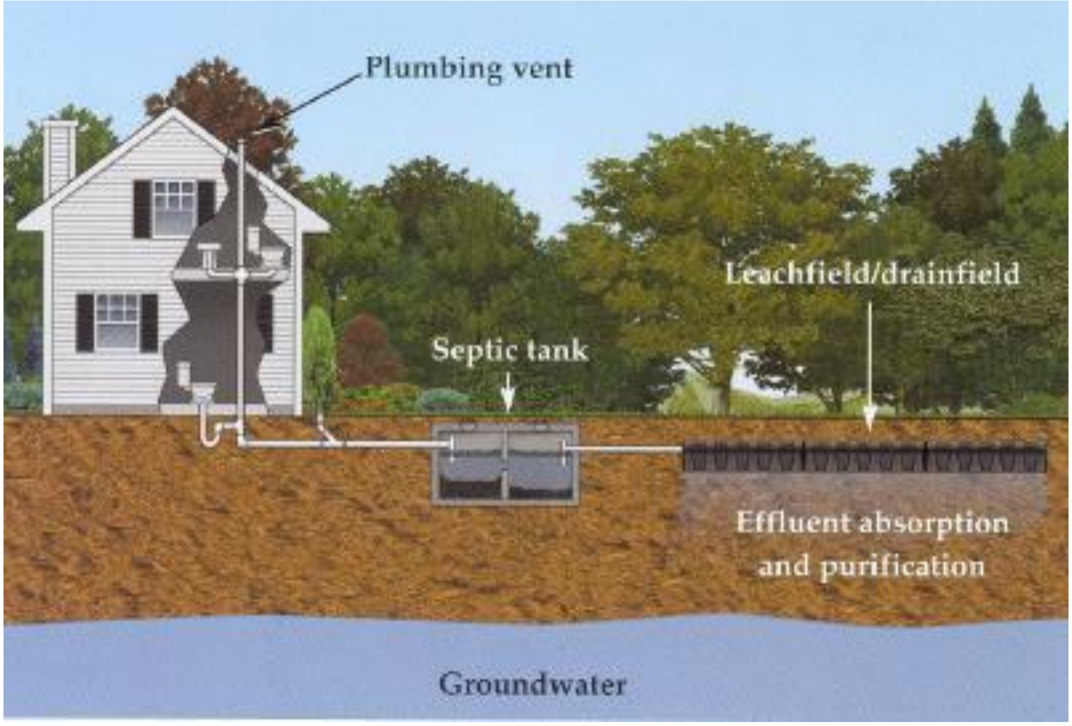

Figure 7: Basic Septic System Configuration

2.4 Groundwater Transport Mechanisms

As has been mentioned earlier, there are many chemicals and pharmaceuticals that are being used and discharged with effluent water from households to the groundwater through septic tanks. However, the effluent from these septic tanks and their operations are not regulated like public waste water treatment facilities (Chalew, 2006). According to a project conducted with EPA and University of North Carolina, it seems that without proper maintenance, septic systems can fail (Chalew, 2006). They have estimated that nearly half the septic systems in North Carolina are no longer effective, which is a scenario likely to be found across the U.S. With such failure, the soil can no longer detoxify the effluent effectively and chemical constituents would have higher potential to reach surface and ground waters. Pharmaceutical contaminants such as CIP can fall under one such category and it becomes necessary to conduct studies and experiments to stop the transport of CIP from septic tank effluent to the groundwater. To hypothesize or come up with any such project it is important to first understand how the contaminated water from septic tank effluents moves through the soil. After a contaminant has entered the ground, it flows from pore to pore through the soil, sometimes traveling several miles and the manner and rate of transport depends on different factors (Coduto, 1999). Some of the factors that play a role in the transport mechanism of CIP in water from septic system effluents will be discussed in upcoming sections. To understand this process better it is necessary to learn about the different pathways and mechanism that the contaminated water goes through into the soil. Some of the mechanisms that can help in this study will be discussed below. In addition, the factors and soil properties that affect the transport of contaminants into the soil will also follow.

2.4.1 Advection

Contaminants travel with moving groundwater through a process called advection. Therefore, advection is the movement of the solute with the bulk water, where the solute could be any contaminant dissolved in the water. Understanding this mechanism helps understand how far the contaminants will travel in a given time and is defined using the seepage velocity equation:

$$V = \frac{Q}{\eta} \qquad (Eqn.\ 1)$$

Where:

V = seepage velocity

Q = specific discharge (L/T)

η = porosity.

2.4.2 Dispersion

When water and contaminants flow through soil, the irregular shape of the pores and the particulate nature of the soil cause some of the contaminants to spread out over a wider area than predicted by advection alone. This spreading process is called dispersion (Coduto, 1999). These two processes dominate contaminant transport in highly permeable soils, such as sands particularly when the hydraulic conductivity gradient is also high (Coduto, 1999). Advection – dispersion analyses are used to assess contamination problems and to assist in the design of remediation methods.

2.4.3 Diffusion

When the concentration of a chemical in a liquid varies from place to place, the chemical naturally moves from the areas of high concentration to areas of low concentration through a process called diffusion (Coduto, 1999). Diffusion is described by Fick's law of diffusion:

$$J = -D\left(\frac{dC}{dx}\right) \qquad (Eqn.\ 2)$$

Where:

J = Flux

D = Diffusivity

C = Concentration

x = Distance

The most important transport mechanism relevant to this study, however, is sorption which is discussed in more details.

2.4.4 Sorption

Sorption is defined as the attraction of an aqueous species to the surface of a solid. In ground water the sorbing species, usually an organic compound, is called the sorbate and the solid media, usually soil, to which the sorbate is attracted, is called sorbent (Ferrante, 1996). This occurs in two different ways. If a molecule, an ion or a particle is attracted and adhered to the outer surface of the sorbent, the processes is called adsorption and if the particle or contaminant is taken up by the sorbent, either liquid or solid, the process is known as absorption. Sorption attenuates the flow of contaminants, thus producing plumes that move more slowly and have lower concentrations than would otherwise occur. The potential for antibiotic sorption and desorption within soil systems plays a key role in their environmental fate and transport (Carrasquillo et al., 2008). It is important to know which soil properties affect the rate of sorption of antibiotics such as CIP from septic system effluent. Our report will focus on the adsorption and absorption processes and their dependence on soil properties.

2.4.5 Adsorption

According to studies conducted, adsorption seems to be one of the mechanisms that can play the most important role on sequestration of contaminates such as CIP from water. Carrasquillo et al., (2008), determined structural criteria responsible for differences in sorption of CIP and Oxtetracyline (OTC) to soils and minerals. Adsorption of a contaminant is generally accomplished using physisorption and chemisorption methods. In physisorption the accumulation occurs in multiple layers which are formed by the weak intermolecular van der Waals forces and can cause a negligible shift in electron density and do not require a specific site on the adsorbent (Roma et al., 2010). This process takes place in four steps. The first one is the bulk solution transport which is the movement of the contaminant from the bulk water solution to the thin layer around the adsorbent particles. When the contaminant contacts with the boundary layer surrounding the adsorbent particle, external resistance to transport occurs while the contaminant is transported by molecular diffusion through the hydrodynamic boundary layer (Letterman, 1999). Pore transport occurs to pass the contaminant from the hydrodynamic boundary layer through the pores to the vacant adsorption sites along the surface at which point intermolecular bonds are rapidly formed between the contaminant and the adsorbate and the contaminant is successfully removed from water. The adsorbent will continue to accumulate on the surface until saturation is reached. According to Letterman (1999), chemisorption can only occur in monolayer because of the necessity for a specific adsorption site for each bond formed. In this process, accumulation occurs through valence bonds which cause a drastic shift of electron density that result in covalent or ionic bonds.

The extent of adsorption is varied by different factors such as pH, temperature, bond types and properties of the sorbate and sorbent. As contaminated water moves through the ground, soil and some of the clay minerals act as sorbents. Some researchers have been using kaolinite to investigate the adsorption behavior of most commonly found metals in ground water and the extent of sorption of CIP and other antibiotics on kaolinite (which will be presented in upcoming section). In order to understand the sorption and desorption mechanisms better, it is helpful to know what makes a good sorbent and to discuss the relevant soil properties that play a major role in sorption process.

2.4.6 Kaolinite

Kaolinite is 1:1 alumina silicate comprising a tetrahedral silica sheet bonded to an octahedral alumina sheet through the sharing of oxygen atoms between silicon and aluminum atoms in adjacent sheet. Successive 1:1 layers are held together by hydrogen bonding of adjacent silica and alumina layers (Pinar Turan et al., 2007). Pure Kaolinite ($AL_2Si_2O_5(OH)_4$) is one of the more weathered clay minerals. It is common in tropical soils and is the second most abundant clay mineral in ocean sediments (Cynthia et al., 2002). Kaolinite is mined as kaolin in different parts of the world such as Brazil, France, United Kingdom, Iran, Germany, India, China, and United States. It is generally found in white, off white or light orange colors. It has a simple structure, is resistant to weathering, and maintains a relatively constant hydraulic conductivity when permeated with contaminants (Cynthia et al., 2002). Kaolinite has a low cation exchange capacity (CEC) of the order of 3 to 15 meq/100g and therefore it is not expected to be an ion-exchanger of high order. The small number of exchange sites is located on the surface of kaolinite and it has no interlayer exchange sites. Nevertheless, the small CEC and adsorption properties may play an effective role in scavenging inorganic and organic pollutants from water (Ghosh et al., 2001). Kaolinite being one of the most common clay mineral found in soils and sediments, could affect the transport of different pollutants in soil or contaminated water travelling through the groundwater. “When different types of pollutants in domestic sewage, industrial effluents, sludge and other solid wastes are dumped on the earth surface, the soil particles including clay minerals can interact with the pollutants. The clay minerals in soil may therefore play a role in scavenging pollutants from the environment (Ghosh et al., 2001).

2.5 Physical Soil Properties

Physical soil properties are used to identify soils in a both a qualitative and quantitative manner. There are more than a few characteristics that can be measured and they relate and interact closely with the chemical properties of soils

2.5.1 Porosity

Porosity is one soil transport factor that is important in determining how antibiotics such as CIP move through soils. Porosity is a measurement of space between particles and is a ratio of void space volume to total volume of the solid substance, in this case soil, and the void space (Fechner-Levy and Hemond, 2000). Porosity can be measured by saturating a soil sample, weighing it, and then drying the sample, weighing it again and then dividing this difference in mass by water density. This allows for the determination of void volume which can then be used to find the porosity of the soil through the following equation (Fechner-Levy, Hemond, 2000):

<u>Porosity Equation:</u>

$$\eta = \frac{V_{voids}}{V_{total}} = \frac{V_{voids}}{(V_{solids} + V_{voids})} \qquad (Eqn.\ 3)$$

Where:

V_{voids}= Volume of the voids or spaces between grains (L^3)

V_{solids}= Volume of the grains (L^3)

V_{total}= Total bulk volume of the sample (L^3)

Visual Representation:

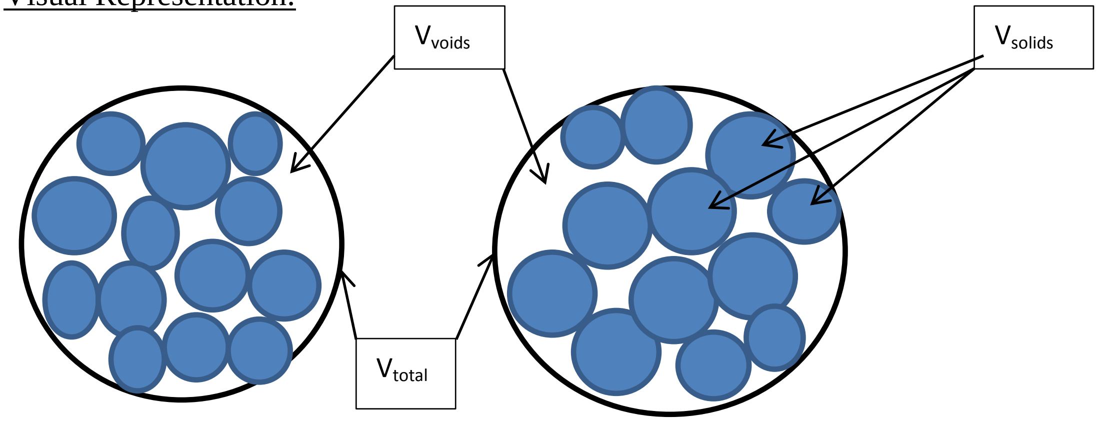

Figure 8: Visual Representation of Porosity

Physical soil characteristics such as particle distribution as well as stacking patterns of the soil grains significantly affect a soil sample's porosity, as can be seen in figure 8 (Portage County, 2008). A soil that has non-uniform particles with a wide range of sizes that allows void spaces between larger grains to be filled with smaller ones results in a low porosity. Similarly effective porosity represents the porosity of soil particles that have the ability to effect the movement of a fluid through that soil.

2.5.2 Bulk Density

Bulk density is the weight of dry soil particles divided by the volume of the sample and can be determined using the following equation (Hemond, Fetchner-Levy 2000):

Bulk Density Equation:

$$\rho_b = (1-\eta) \times \rho_s \qquad (Eqn.\ 4)$$

Where:

ρ_b = Bulk density (M/L^3)

ρ_s= Density of individual soil particles (M/L^3)

η = Soil porosity (L^3/L^3)

According to the U.S. Department of Agriculture (USDA), bulk density indicates the level of compaction of a given soil (2008). Factors that affect bulk density include: soil texture, densities of minerals present in the soil, arrangement of particles in the soil, and land practices.

2.5.3 Soil Content and Texture

Soil content refers to the amount textural classifications present in a given soil. The three main components are sand, silt and clay. By considering the percentages of these three components and by using the U.S. Department of Agriculture Natural Resources Conservation Service (USDA-NRCS) soil texture triangle (shown in figure 9), a soil can be given a classification (2005).

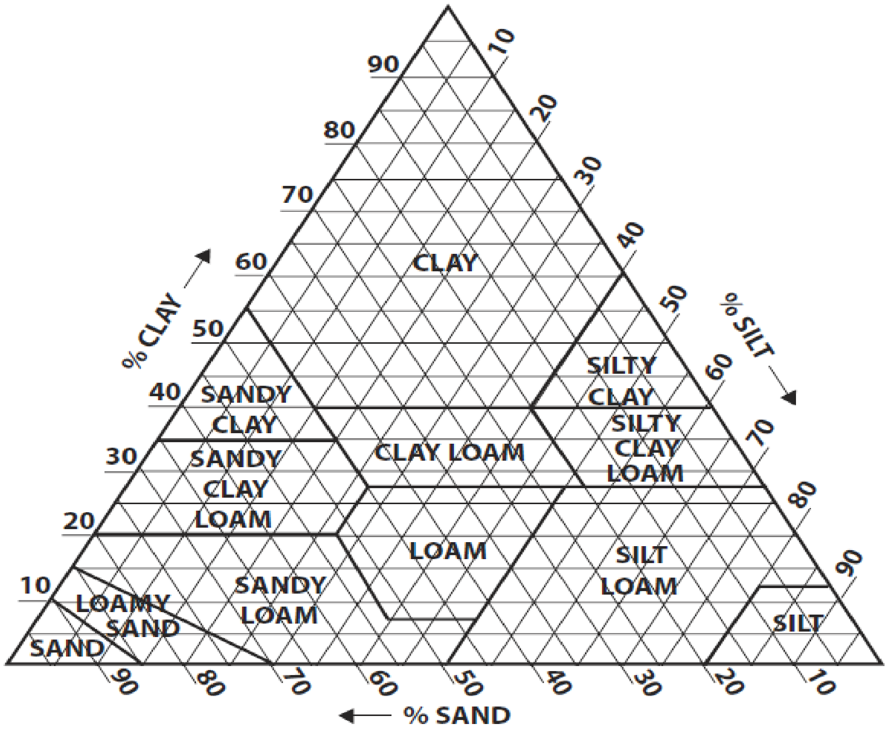

Figure 9: USDA Soil Classification Triangle
(Taken from: http://www.mt.nrcs.usda.gov/about/lessons/Lessons_Soil/)

These materials form the unsaturated and saturated zones of the subsurface area. According to Hemond and Fechner-Levy (2000), the pores of the unsaturated zone contain both air and water conversely the pores of the saturated zone are completely filled by water. In this report the focus will be on saturated soils.

2.5.4 Chemical Soil Partitioning

Chemical partitioning occurs through sorption including both absorption and adsorption. According to Hemond and Fetchner-Levy, (2000) sorption in the environment is difficult because the sorptive solids, or sorbents, differ greatly as do sorption mechanisms. The symbol K_p represents the solid-water partition coefficient whereas K_d represents the distribution coefficient and can be taken as an equivalent representation. Although it is possible to have a linear relationship represented by a constant coefficient in reality this is usually not the case. Instead Hemond and Fetchner-Levy (2000) state; "In actuality, the relationship between dissolved and sorbed chemical concentrations is often nonlinear and may be expressed as a *sorption isotherm"*.

2.5.5 Isotherms

Sorption isotherms are used when the relationship between sorbed chemical concentration and aqueous chemical concentration is nonlinear and temperature remains constant (Hemond, Fetchner- Levy, 2000). The Langmuir isotherm and Freundlich isotherm models most commonly fit data compiled through laboratory testing (Yang, 2003)

Adsorption is often modeled using the empirical two-parameter Freundlich isotherm the Freundlich equation is given below (Cole, Yong, 2006).

$$q_e = K_f \times (C_e)^{\frac{1}{n}} \qquad (Eqn.\ 5)$$

Where:

q_e = concentration of chemical adsorbed per unit weight of adsorbent (mg/g)

K_f = Freundlich constant

C_e= Equilibrium concentration (mg/L)

n = empirical coefficient

K_f and *n* are indicative of the extent of the adsorption and the degree of non-linearity between solution concentration and adsorption, respectively (Turan et al., 2007). This model shows that if empirical coefficient, *n*, is less than one, the sorbed chemical concentration increases with increasing C_e. By the logarithmic linearization of the above equation, the two parameters of the Freundlich equation, K_f and 1/*n* can be estimated. Equation 5 below is obtained by taking the log of each side of the Freundlich equation (equation 4):

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad (Eqn.\ 6)$$

The two parameters are found by plotting lnq_e vs ln C_e where ln C_e is plotted on x-axis and ln q_e is plotted on y-axis. The slope of the graph is 1/*n* and the intercept is ln K_f . The Freundlich isotherm model is considered to be appropriate for describing both multilayer sorption and sorption on heterogeneous surfaces (Coles and Yong, 2006)

The Langmuir isotherm was developed to model monolayer adsorption and represent sorption at distinct adsorption sites assuming the following (Douglas, 1984):

1. The molecules adsorb to defined sites, and the amount of sites is fixed
2. Each of these defined sites can only adsorb one molecule of sorbate
3. Constant temperature throughout the system
4. Adsorption is only present on one layer, no interaction between sites occurs

In order to represent a state of equilibrium the rate of adsorption and desorption can be set equal to each other.

Langmuir Isotherm Equations:

$$Rate\ of\ adsorption = k_a \times C_e(1 - \Theta)$$

$$Rate\ of\ desorption = k_d \times \Theta$$

$$State\ of\ Equilibrium: k_a \times C_e(1 - \Theta) = k_d \times \Theta$$

Where:

k_a= Rate of adsorption

k_d= Rate of desorption

Θ = fraction of covered sorbate surface covered, q/q_m

Rearranging state of equilibrium equation the langmuir isotherm can give:

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{k_a q_m C} \qquad (Eqn.\ 7)$$

Plotting 1/q vs 1/C results in graph of a straight line with a slope of $1/q_m$ and intercept of $1/k_a q_m$ (Douglas, 1985).The Langmuir and Freundlich isotherm equations can be manipulated and these models can then be utilized to plot the relationship between the amount of dissolved chemical and the amount that has been sorbed (Douglas, 1984).

2.5.6 Distribution Coefficient

The distribution coefficient K_d represents the ratio of sorbed chemical concentration to aqueous chemical concentration and is an extremely important factor in the process of sorption (Hemon, Fetchner-Levy 2000). The distribution coefficient is one representation of a partitioning coefficient that contributes to the determination of a retardation factor which can then be used to describe the behavior of a chemical as it sorbs to soil. Numerous sorbing chemicals or sorbates as well as various sorption mechanisms contribute to changing K_d values.

Distribution Coefficient Equation:

$$K_d = \frac{C_s}{C_{aq}} \qquad (Eqn.\ 8)$$

Where:

K_d= Distribution Coefficient

C_s = Sorbed chemical concentration

C_{aq} = Aqueous chemical concentration

This equation relates the sorbed chemical concentration C_s and the aqueous chemical concentration C_{aq} resulting in the distribution coefficient.

2.5.7 Organic Carbon and Chemical Sorption

Many chemical pollutants are hydrophobic, meaning they do not like to be in water, but can associate with other media such as organic carbon in soil. Two partition coefficients are important with respect to organic carbon and the extent of chemical sorption. The first is the octanol-water partition coefficient K_{ow}. This partition coefficient represents the fractional relationship between a chemicals concentration in octanol to its concentration in water. More importantly K_{ow} serves as an indicator of hydrophobicity (Hemond, Fetchner-Levy 2000). According to Hemond and Fechner-Levy,"…smaller molecules and more polar molecules dissolve more readily in water, have lower K_{ow} values, and have less tendency to sorb to solids. Larger molecules and less polar molecules are less soluble, have higher K_{ow} values, and are more likely to sorb to solids (53)." The second partition coefficient is the organic carbon-water coefficient K_{oc}, which can be determined from the octanol-water partition coefficient. The organic carbon-water coefficient can be used in our case to estimate the extent of sorption and is as follows (Hemond, Fechner-Levy, 2000):

Organic Carbon-Water Partition Coefficient Equation:

$$K_{oc} = \frac{Chemical\ Concentration\ Sorbed\ to\ Organic\ Carbon\ \left(\frac{mg}{g}\right)}{Chemical\ Concentration\ in\ Water\ \left(\frac{mg}{ml}\right)} \quad (Eqn.\ 9)$$

The fraction of soil that is organic carbon f_{oc} can be utilized to determine the extent of sorption. According to the Environmental Protection agency (EPA) “Fractional organic carbon (f_{oc}) is a dimensionless, mass measure of the quantity of soil organic carbon relative to soil media. The measure is used to estimate the capacity of a soil to adsorb or bind to certain contaminants (EPA, 2003).” Using the fraction of organic carbon present in the soil we can determine the organic carbon-water coefficient and the distribution coefficient K_d using the following equation:

$$K_d = f_{oc} \times K_{oc} \qquad (Eqn.\ 10)$$

Where:

$K_d =$ = Distribution coeffiecient

f_{oc} = Fraction of soil that is organic carbon

K_{oc} = Organic carbon-water partition coefficient

By using these equations and parameters we can estimate the amount of ciprofloxacin that sorbs to the soil as it is transported.

2.5.8 Dissolved Organic Carbon

Dissolved organic carbon (DOC) is another factor of importance in this study. Antimicrobials are released to the environment through solutions that are rich in dissolved organic carbon (DOC) and association with DOC may facilitate their transport in water… (Carmosini and Lee, 2009). According to the article by Carmosini, reduction in contaminant sorption by soils due to association with DOC can be estimated as follows:

$$\frac{K_d^*}{K_d} = \frac{1}{1 + K_{doc}[DOC]} \qquad (\textit{Eqn. 11})$$

Where:

K_d^* = Apparent soil sorption coefficient in the presence of DOC

K_d = Soil sorption coefficient in the absence of DOC

K_{doc}= Dissolved organic carbon coefficient

$[DOC]$ = Dissolved organic carbon concentration (kg DOC/L).

To determine the effect of DOC using this process, Carmosini and Linda used ciprofloxacin (CIP) as a model amphoteric antimicrobial to investigate sorption by several types of reference and waste derived DOC materials. In their experiment CIP sorption was quantified under several pH and ionic strength conditions using reference fulvic and humic acids with varying chemical properties to evaluate the processes responsible for CIP-DOC interactions. This literature review is helpful in determining the most important factors that will play a major role as well as different conditions e.g. soil pH and its effect on the extent of CIP sorption into the soil.

Soils containing different compounds and minerals or with different properties can also interact with CIP and other chemicals differently which in turn can affect the extent of sorption.

Other studies conducted compare the sorption of CIP and other antibiotics to different soil and soil compositions. “In addition, the extent of fluoroquinolone and tetracycline sorption to soils was found to be strongly influenced by the soils’ cation exchange capacity and to some extent, by the soil’s metal oxide content (Carrasquillo et al., 2008). While the study done by Carrasquillo and his colleagues present some specific cases with specific criteria, it will help us be aware of the different factors that if ignored can result in inaccurate data presentation. One factor that is common in all mechanisms is the hydraulic conductivity which is defined as the rate of movement of water through a porous medium such as soil.

2.5.9 Retardation

Retardation is an important factor that significantly affects the rate of groundwater transport. The retardation factor is used to describe the degree to which advective transport is attenuated (Hemond, Fechner-Levy, 2000). Retardation relates the quantity of chemical sorbed to the soil to the quantity of chemical that remains dissolved in the water. Quantitatively speaking retardation is a fractional measurement of the velocity of chemical that sorbs to the soil compared to the velocity of the water that is infiltrating the soil (Hemond, Fechner-Levy, 2000). The retardation factor is defined with the following general equation (Hemond, Fechner-Levy, 2000):

Retardation Factor:

$$R = 1 + \frac{Sorbed\ Concentration}{Mobile\ Concentration} (Unitless) \qquad (Eqn.\ 12)$$

This relationship can be described with a more explicit equation in terms of the distribution coefficient K_d, sorbed chemical concentration C_s, aqueous chemical concentration C_{aq}, porosity η, and bulk density ρ_b.

Taking this into account, we can develop the retardation expression which will be crucial in quantitatively determining the amount of ciprofloxacin that sorbs to the soil samples we will be testing. The final variable that must be taken into account is bulk density ρ_b. From here we can define the retardation equation (Hemond, Fechner-Levy, 2000):

Retardation Equation:

$$R = 1 + \frac{(C_s \times \rho_b)}{(C_{aq} \times \eta)}\ (unitless) \qquad (\textit{Eqn. 13})$$

Because: $K_d = \frac{C_s}{C_{aq}}$ (Eq. 12), the equation reduces to:

$$\boldsymbol{R = 1 + K_d \times \left(\frac{\rho_b}{\eta}\right)} \qquad (\textit{Eqn. 14})$$

Where:

ρ_b = Bulk density

K_d = Distribution Coeffiecient

η = Porosity

R = Retardation

The use of this expression and its parameters will prove to be vital in our testing process by allowing us to discern the sorption of ciprofloxacin to our soil samples.

2.6 Past Research

Due to the rising concerns about the presence of antibiotics in water systems, many studies and research studies have been and are taking place in order to find a better way to remove these contaminants from water and ensure public health and safety.

Uslu et al. (2007) studied the sorption behavior of fluoroquinolones in different soils using simple analytical methods in which enrofloxacin (ENR) and CIP were the contaminants. Their results showed higher adsorption coefficients for the fluoroquinolones antibiotics for loamy sand soil than the sandy soil and sandy loam soil. Carrasquillo et al. (2008) conducted experiments in which CIP and OTC sorption to montmorillonite, kaolinite, and goethite was measured at pH 7, at which zwitterion concentrations were dominant in the aqueous solutions.

2.6.1 Previous CIP MQP

A recently completed Major Qualifying Project (MQP) identified the potential negative effects of pharmaceuticals present in discharged effluents from wastewater treatment plants and attempted to identify treatment techniques that would eliminate this threat. The report discussed potential treatment methods that have been studied including adsorption and ultraviolet treatment. The group chose to adjust pH levels of the samples then treated them using UV photolysis and adsorption in order to remove ciprofloxacin from their water samples. First samples were prepared and absorbance was measured then the treatment experiments began. Using a UV lamp and varying the pH levels, the samples were treated with a 75 minute exposure time in order to degrade CIP. Further UV treatment was conducted using hydrogen peroxide to aid in the process of degradation. Finally adsorption experiments were conducted using activated carbon. The report found that all treatment methods were successful. With respect to UV photolysis a wavelength of 254 nm and pH of 3 were found to be most successful. When hydrogen peroxide was added the rate of degradation was doubled but overall ciprofloxacin degradation did not increase at equilibrium. The report also found that one type of activated carbon that was used was more effective. Future research taking into account energy and environmental concerns as well as testing of mixtures of antibiotics was recommended.

3 Methodology

The group developed a methodology once objectives had been determined and hypotheses were formed based on compiled research related to the ultimate goal of the sorption of aqueous CIP. The methodology was created with the intent to provide a procedure by which the group could follow in the lab in order to carry out experiments that aimed at proving the validity of our hypotheses and meeting our objectives.

3.1 Sample Preparation

Solutions containing known initial concentrations of ciprofloxacin (LKT Laboratories) were prepared in Barnstead E Pure water (ROpure ST Reverse Osmosis/tank system). Well mixed solutions were prepared by stirring the solutions with a magnetic stirrer for a minimum of 30 minutes in order for all ciprofloxacin to dissolve. All samples were adjusted to pH 7 by the drop-wise addition of NaOH or HCl and the use of an Accumet Basic AB 15 pH meter (Fisher Scientific).

3.2 Sample Absorbance Measurements

In order to determine the amount of ciprofloxacin sorbed during each trial, ciprofloxacin concentrations were analyzed before and after each experiment. A Varian-Cary 50 Scan UV - visible spectrophotometer was used with Plastibrand UV-cuvette micro (12.4 x 12.5 x 45mm) cuvettes to measure CIP concentrations before and after each trial. First, cuvettes containing water only were analyzed using the UV-scan which was then zeroed before cuvettes containing varying concentrations of ciprofloxacin were scanned. It was found that 270 nm was the optimum wavelength for measuring the absorbance of ciprofloxacin in water. Once a wavelength was determined each concentration of CIP was analyzed at 270 nm and the absorbance was recorded.

3.3 Rotating Mixer Sorption Experiments

Sorption experiments were carried out using fixed sorbent to sorbate ratios at varying concentrations (ranging from 20 mg/L to 200 mg/L) of aqueous ciprofloxacin at pH 7. The trials were carried out to equilibrium to ensure that all possible CIP was absorbed. The fraction of organic carbon (f_{oc}) was then altered and tested at different intervals through the manipulation and mixing of topsoil and sand with known f_{oc}.

3.3.1 Equilibrium Sorption at 0% f_{oc}

In order to obtain sorption equilibrium data with the chosen sorbents, experiments were performed using 42 mL glass vials using a fixed sorbent to liquid ratio and varying concentrations of CIP in the initial solutions. When the rate of sorption and desorption are equal, no further absorption or adsorption occurs to the surface of the chosen media and equilibrium is reached. Prior to mixing both the sand and silica beads were baked at 550^{o}C for 24 hours to remove all organic carbon. Between 1-2 grams of sand or silica beads along with 30 mL of aqueous CIP in water at varying concentrations and pH 7 was pippeted into the vials. The vials were agitated on a fixed speed rotator at room temperature for 48 hours at 15 rpm for sorption equilibrium to be achieved. Control experiments with CIP using blanks containing no adsorbents were performed to ensure that no CIP losses occurred during trial experiments. Once the sorption phase was completed the solutions were centrifuged for 10-20 minutes at 2600 rpm to separate the solids from liquid. CIP in the solutions was quantified using a Varian-Cary 50 Scan UV - visible spectrophotometer with 10mm cuvettes.

3.3.2 Equilibrium Sorption at varying % soil f_{oc}

The same experiments were carried out using the rotating mixer with a range of varying f_{oc}. After obtaining two topsoil samples, one was bought at a commercial store while the second was taken from local soil. f_{oc} was calculated for each sample. Small samples of each were weighed using a Mettler Toledo (AB104-S) scale. The weight of the sample and dish was recorded and then placed in the oven at 105°C for 24 hours to remove all moisture. After the 24 hour period, the sample was removed, reweighed, and the difference was recorded before it was placed back in the oven for additional moisture removal. After several more hours the sample was removed, reweighed and the difference was once again recorded. The process was repeated until the weight difference between two recent time intervals was significantly low. This was done to ensure that all moisture was removed.

The sample was then placed in the muffle furnace at 550°C for 24 hours to remove all organic carbon after which the sample was removed, reweighed and recorded. The process was repeated until the difference in the weight measured at two different time intervals were very low. By subtracting the recorded weight of the sample after it was baked in the muffle furnace from the recorded weigh after moisture was removed, the amount of organic carbon was determined for each soil sample. Once the amount of organic carbon was known this value was divided by the original weight to the sample less the weight of the moisture removed to determine the f_{oc} of each sample. Knowing the f_{oc} of each soil sample, the f_{oc} for each trial could then be changed by determining the correct proportion of soil with a known f_{oc} to sand containing zero f_{oc}. The necessary sand and soil amounts to achieve the desired f_{oc} were placed in the vials along with the 30 mL of varying concentrations of aqueous CIP at pH 7. The vials were agitated on a fixed speed rotator at room temperature for 48 hours at 15 rpm for sorption equilibrium to be achieved. Control experiments with CIP using blanks containing no adsorbents were performed in order to ensure that no CIP losses occurred during trial experiments. Once the sorption phase was completed the solutions were centrifuged for 10-20 minutes at 2600 rpm to separate the solids from liquid. The samples were then filtered using a Millipore Swinnex filter with Glass Microfibre filter papers (GF/F) and 3 mL syringes in order to remove suspended solids. The filtered solution was then placed in a 10mm cuvette and the absorbance was quantified using a Varian-Cary 50 Scan UV - visible spectrophotometer.

3.3.3 Equilibrium Sorption at Varying Proportions of Kaolinite and Sand

The same experiments were carried out using the rotating mixer with a range of varying kaolinite content. After obtaining the kaolinite, the necessary kaolinite and amounts of sand containing zero f_{oc} were weighed and placed in vials to create the desired kaolinite content. Various concentrations of aqueous CIP at a volume of 30 mL and pH 7 were then added to the vials containing both the sand and kaolinite. The vials were agitated on a fixed speed rotator at room temperature for 48 hours at 15 rpm for sorption equilibrium to be achieved. Control experiments with CIP using blanks containing no adsorbents were performed in order to ensure that no CIP losses occurred during trial experiments. Once the sorption phase was completed the solutions were centrifuged for 10-20 minutes at 2600 rpm to separate the solids from liquid. The samples were then filtered using a Millipore Swinnex filter with Glass Microfibre filter papers (GF/F) and 3 mL syringes in order to remove suspended solids. The filtered solution was then placed in a 10mm cuvette and the absorbance was quantified using a Varian-Cary 50 Scan UV - visible spectrophotometer.

4 Results and Discussion

The goal of this report was to determine an effective method for the sequestration of the antibiotic ciprofloxacin using sorption techniques. All trials were carried out at pH 7 and the data was analyzed to determine if by varying the fraction of organic carbon (f_{oc}) in a soil sample the amount of sorbed CIP would change.

4.1 Calibration Curve

A calibration curve was created by using the UV-spectrophotometer to determine the amount of absorbance that occurs at varying concentrations of ciprofloxacin in water. A wavelength of 270 nm was found to be most effective and all aqueous CIP solutions were adjusted to pH 7. Table 3 in appendix C shows the absorbance obtained for different concentrations of CIP in water which was adjusted to pH 7 at ambient temperature.

Adjusting the CIP solution to pH 7 or as close to pH seven was a vital step because CIP can exist in three forms and the difference in pH can result in difference in slope. The difference in slope at each pH can most likely be attributed to the change in speciation after passing through the two pKa values. At pH 3, the cationic form of CIP is dominant due to protonation of the amine group in the piperazine moiety. At pH 7, CIP loses a hydrogen atom off the nitrogen in the peperazine moiety thus establishing a balance of charge on the molecule. This balance is characteristic of the zwitterionic form for CIP. At pH 10, after passing the second pKa, a proton is lost from the carboxylic group and the anionic form of CIP is dominant in solution (Roma et al., 2010).

As can be seen from the reported values as well as the figure 10 below, the absorbance for the lower concentrations are much closer and as the CIP concentrations become higher the difference in absorbance increases as well.

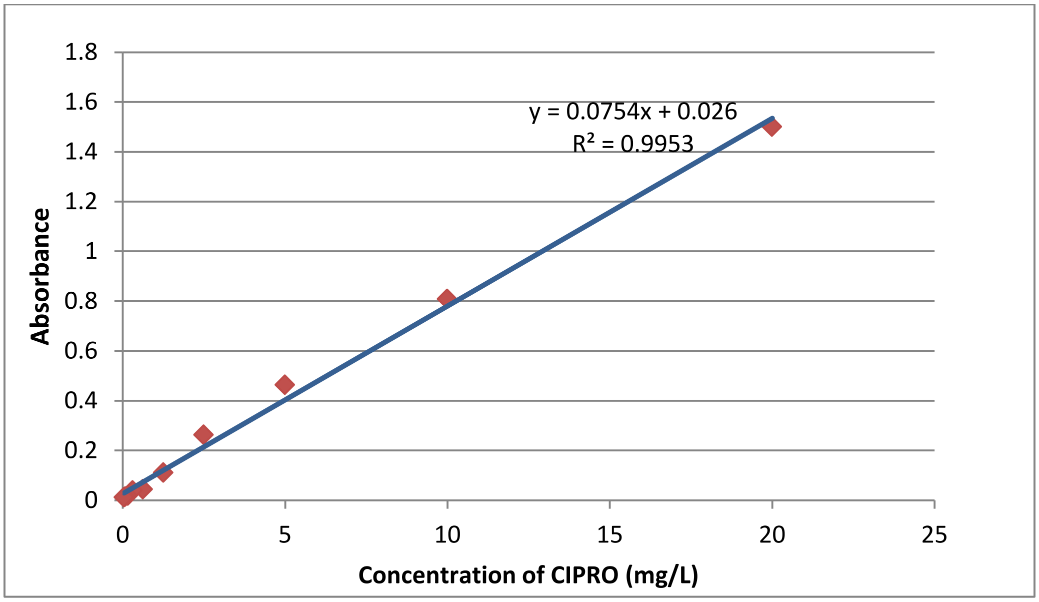

Figure 10: Ciprofloxacin Calibration Curve at wavelength of 270 nm

The accuracy of the calibration curve was considered with the R^2 value that is greater than 0.99. The slope of the line (0.0754) was later used in calculations to determine the equilibrium concentration.

4.2 Absorption Experiments

Absorption experiments were carried out in accordance with our established methodology utilizing multiple soils and sand with known f_{oc} in order to determine if its presence allowed for the absorbance of aqueous CIP.

4.2.1 Distribution Coefficient (K_d) and Organic Carbon – Water Partition Coefficient (K_{oc})

Our trials using soil samples to determine the sorption properties of aqueous ciprofloxacin displayed what we believe to be the characteristics of absorption. The determination of both K_d and K_{oc} were carried out to determine the rate of sorption that CIP had to varying soil samples. The amount of fractional organic carbon (f_{oc}) was manipulated in order to determine if increasing amount of organic carbon in soil would result in a higher rate of sorption and therefore greater K_d and K_{oc}. Once the results from our trials were known they were plotted and a linear trend-line was fitted to the data to first determine the distribution coefficient, K_d.

4.2.2 Distribution Coefficient (K_d) and Organic Carbon-Water Partition Coefficient (K_{oc}) Calculations

Sorption data for soil containing 0.5%, 1.5% and 4.5% organic carbon can be seen below.

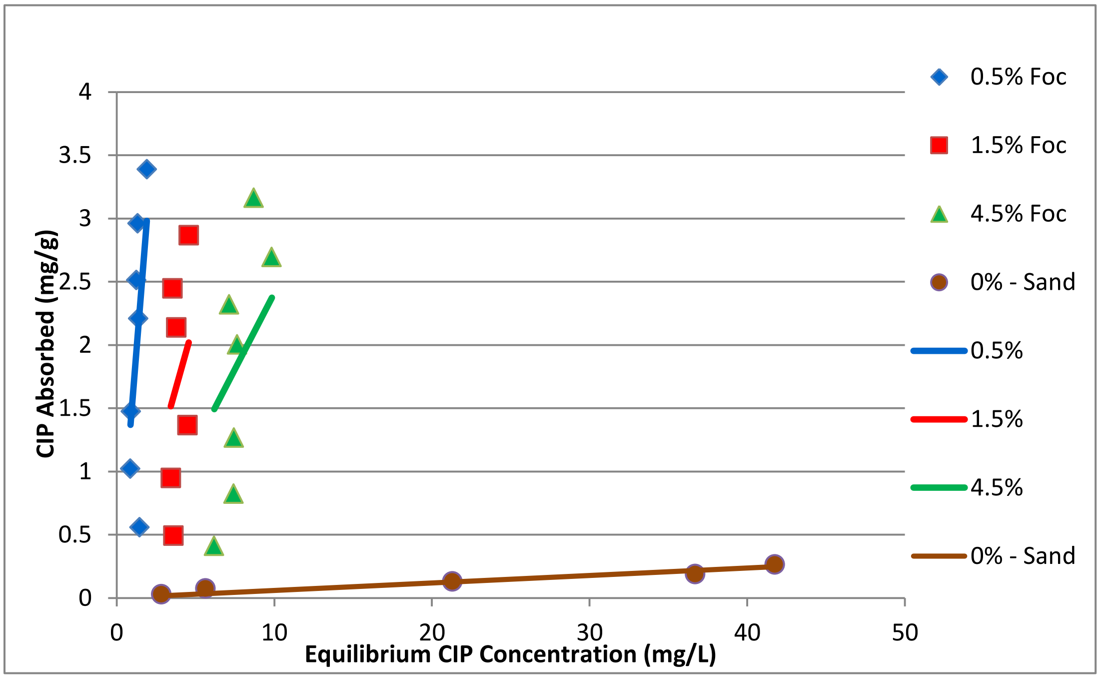

Figure 11: Distribution Coefficient (K_d) Data

The data shown in the graph (figure 11) can be used to determine the K_d and K_{oc} at each fractional amount of organic carbon (f_{oc}). Equations 14 through 17 where formed when a linear fit line was added to each f_{oc}.

$$0.0\%\ f_{oc}:\ y = 0.0059x \quad R^2 = 0.9160 \qquad (Eqn. 15)$$

$$0.5\%\ f_{oc}:\ y = 1.5555x \quad R^2 = 0.3367 \qquad (Eqn. 16)$$

$$1.5\%\ f_{oc}:\ y = 0.4409x \quad R^2 = 0.1446 \qquad (Eqn. 17)$$

$$4.5\%\ f_{oc}:\ y = 0.2413x \quad R^2 = 0.3482 \qquad (Eqn. 18)$$

Recall equation (12) equation (8) from chapter 2:

$$K_d = \frac{C_s}{C_{aq}} \qquad (Eqn. 19)$$

$$K_d = f_{oc} \times K_{oc} \qquad (Eqn. 20)$$

Using these equations, the distribution coefficient K_d and the organic carbon-water partition coefficient K_{oc} can be determined from the linear fit lines at each f_{oc} which is presented in table 1 below.

Table 1: Calculated K_d and K_{oc} Values

f_{oc}	K_d	K_{oc}
0.0%	0.0059	-
0.5%	1.5555	311.1
1.5%	0.4409	29.39
4.5%	0.2413	5.362

The slope of the fitted trend-lines represents the K_d values at each f_{oc}, and by dividing the calculated K_d values by f_{oc} each K_{oc} can be determined. Results in table 1 show that as the percent f_{oc} increases, the distribution coefficient K_d also increases. As previously stated in the methodology, baked sand containing no organic carbon and topsoil containing known fractional amounts of organic carbon were used in our trials to determine whether increasing f_{oc} would result in an increased amount of sorbed CIP. After first considering a K_d value of 0.0059 for 0%

f_{oc} sand and then looking at the rest of the K_d values for the varying amount of fractional organic carbon it is clear that the presence of organic carbon in soil results in an increase of sorption of aqueous CIP. What the data does not show however, is that the amount of sorbed CIP would increase as a result of increased f_{oc}, which was believed to be the case. It is still our belief that by increasing f_{oc} it would directly result in an increase of sorbed CIP and that there are many reasons as to why this was not reflected in our data.

4.2.3 Fractional Organic Carbon (f_{oc}) and Kaolinite Comparison

The graph (figure 12) below compares the sorption data for the varying organic carbon compared with the adsorption data for kaolinite.

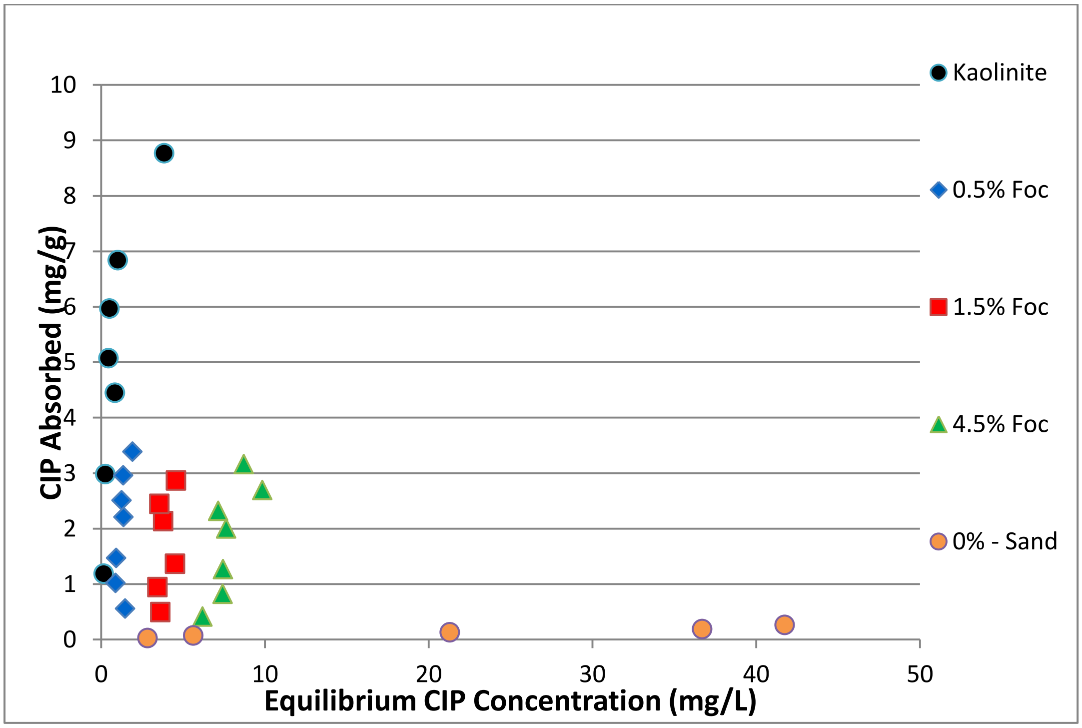

Figure 12: Kaolinite and % f_{oc} Sorption Data Comparison

From this comparative figure it can be inferred from the data that kaolinite was more successful in sorption of aqueous CIP. At a concentration of 100 mg/L of aqueous CIP, almost 6 milligrams of CIP was absorbed per gram of kaolinite. At the same concentration, 0.5% f_{oc} had the highest ratio of sorption among the varying amounts of f_{oc} and yet only 3 milligrams of CIP was sorbed per gram 0.5% f_{oc} sand and soil mixture. This trend proves to be true when comparing the sorbed CIP concentrations in the varying f_{oc} trials to the kaolinite trials at each initial aqueous CIP concentration.   This may suggest that adsorption as opposed to absorption may be the better mechanism for the sequestration of CIP in soils however much more experimentation is needed to prove the validity of this possible scenario. It may also be true that kaolinite is not more efficient in the sorption of aqueous CIP than soils with increased f_{oc} and this too requires more experimentation to better understand the sorption characteristics of CIP.   By analyzing the data and comparing it to that of other published works while also taking into account our hypotheses for the outcomes of our experiments, the group believes that multiple factors and sources of error led to results that did not confirm our original assumptions.

4.3 Kaolinite Trials

In addition to investigating the effect of f_{oc} on CIP sorption to the soil, the effect of kaolinite presence in soil on CIP sorption was also studied to find out different possibilities as well as the difference of CIP sorption to different media. To test the hypothesis that kaolinite could serve as a better adsorbent, trials with pure kaolinite and CIP solution, 50 % kaolinite and 25% kaolinite and sand mix were carried out at around pH 7. The data obtained for the run with kaolinite and CIP solution only is shown in Table 2 below. See appendices C and D for additional kaolinite results.

Table 2: Data for the 100% Kaolinite Trial

Kaolinite (g)	Total Time (hrs)	PH	Con (i) mg/L	Abs (f)	Con(f)	ΔConc (mg/L)	% Decrease	CIP Adsorbed (mg/g)
0.5000	48	7.01	20	0.012	0.163	19.837	99.18%	1.190
0.5000	48	6.99	50	0.020	0.261	49.739	99.48%	2.984
0.5000	48	7.03	75	0.065	0.867	74.133	98.84%	4.448
0.5000	48	7.03	85	0.034	0.452	84.548	99.47%	5.073
0.5000	48	6.98	100	0.039	0.516	99.484	99.48%	5.969
0.5000	48	7.05	115	0.078	1.036	113.964	99.10%	6.838
0.5000	48	7.03	150	0.297	3.944	146.056	97.37%	8.763

Table 2 shows the effectiveness of kaolinite on CIP sorption from water. The CIP concentrations in water were decreased by about 99 % from its original concentrations. For the maximum concentration used in these experiments which is 150 mg/L the percent decrease of CIP concentration in water was about 97%. This trend seemed to repeat itself even when the second set of samples were prepared and run for the same amount of time. Upon observing samples with higher concentrations (150 mg/L) some precipitation of the CIP was noticed in all runs. One of the reasons for this precipitation is the pH dependence of CIP solubility which was also observed several times during the experimental procedures. After preparing the solutions and storing them in the fridge without adjusting the pH to pH 7, no precipitation was observed. However, at pH 7 CIP did precipitate in solutions that's concentrations ranged between (120-150 mg/L). When the CIP precipitated, the centrifuge process should have still separated the particles from the solution but it is possible that some CIP was desorbed which can affect our data.

4.4 Adsorption Isotherms

To investigate the effectiveness of CIP sorption on kaolinite further by establishing equilibrium relationship, the results shown in table 10-12 (see appendix C) were used to generate isotherms for CIP sorption onto kaolinite shown in Figure 13 below with $R^2 = 0.85$.

This was accomplished by plotting the ln CIP Concentration adsorbed (mg/g) vs ln CIP concentration at equilibrium (mg/L). This gives the linear form of the Freundlich isotherm that was shown in equation 5. The plot of the linear Freundlich isotherm is shown in Figure 18 (appendix D) for 100 % kaolinite trial. The parameters 1/n and K_f were determined from the intercept and slope of the line respectively.

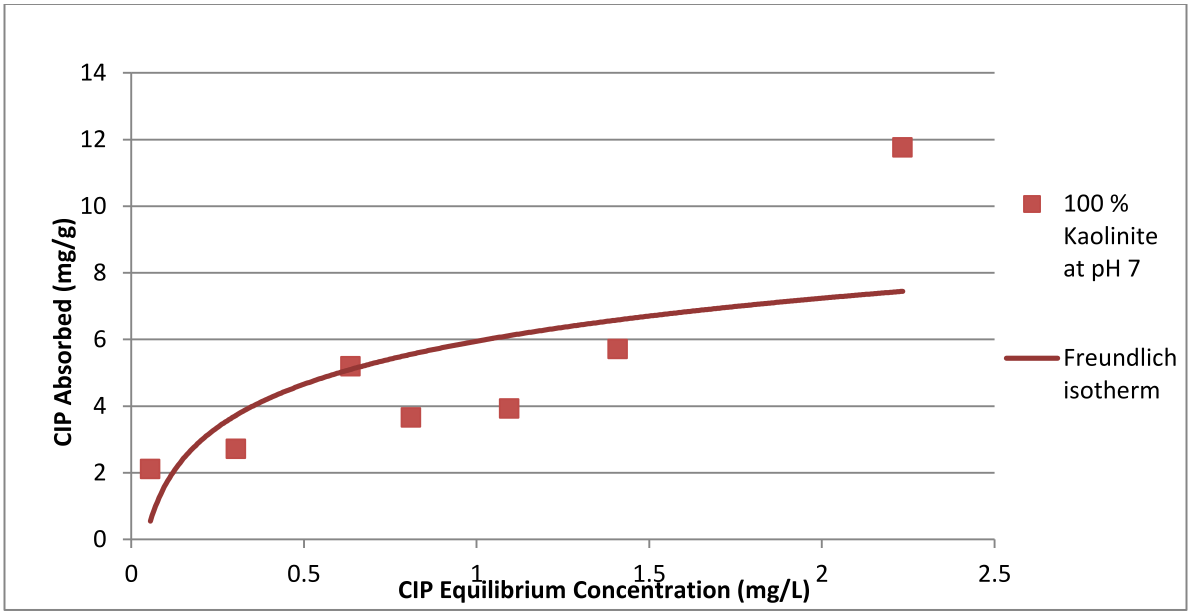

Figure 13: Experimental Freundlich Isotherms for the 100% Kaolinite Trial

In order to find the best fit for the data, both Freundlich and Langmuir isotherms were then modeled using the parameters 1/n and K_f (for Freundlich model), q_m and K_a (for Langmuir model) which were obtained from linear forms. Figure 19 in appendix D compares the Freundlich and Langmuir isotherm. The R^2 for Langmuir isotherm was 0.44 and for Freundlich it was about 0.51. This showed that Freundlich is the better model. Figure 13 is the graph for Freundlich isotherm for 100% kaolinite trial. The trend on the graph shows that as more CIP is adsorbed on kaolinite, the equilibrium concentration also increases which is indicative of sorption capacity of kaolinite. At higher initial concentrations of CIP solution at pH 7 some precipitation was observed during the final CIP concentration determination which was removed after centrifuging the samples. In Figure 13 above this data point is shown with highest CIP concentration that is adsorbed. This will be discussed in upcoming sections discussing sources of error. To determine the extent of CIP sorption onto the kaolinite the following equation was obtained:

$$q_e = 5.68 \times (C_e)^{\frac{1}{1.864}} \qquad (Eqn. 21)$$

To ensure the validity of the above results and to study the CIP sorption in soil with addition of an appropriate adsorbent (in this case kaolinite), trials with combination of different weight percent of kaolinite and sand were also tested. The data for these trials are shown in tables 10-12 of appendix C and tables 15-17 of appendix D. The results were then compared to the pure kaolinite-CIP solutions. This is shown in figure 14 below:

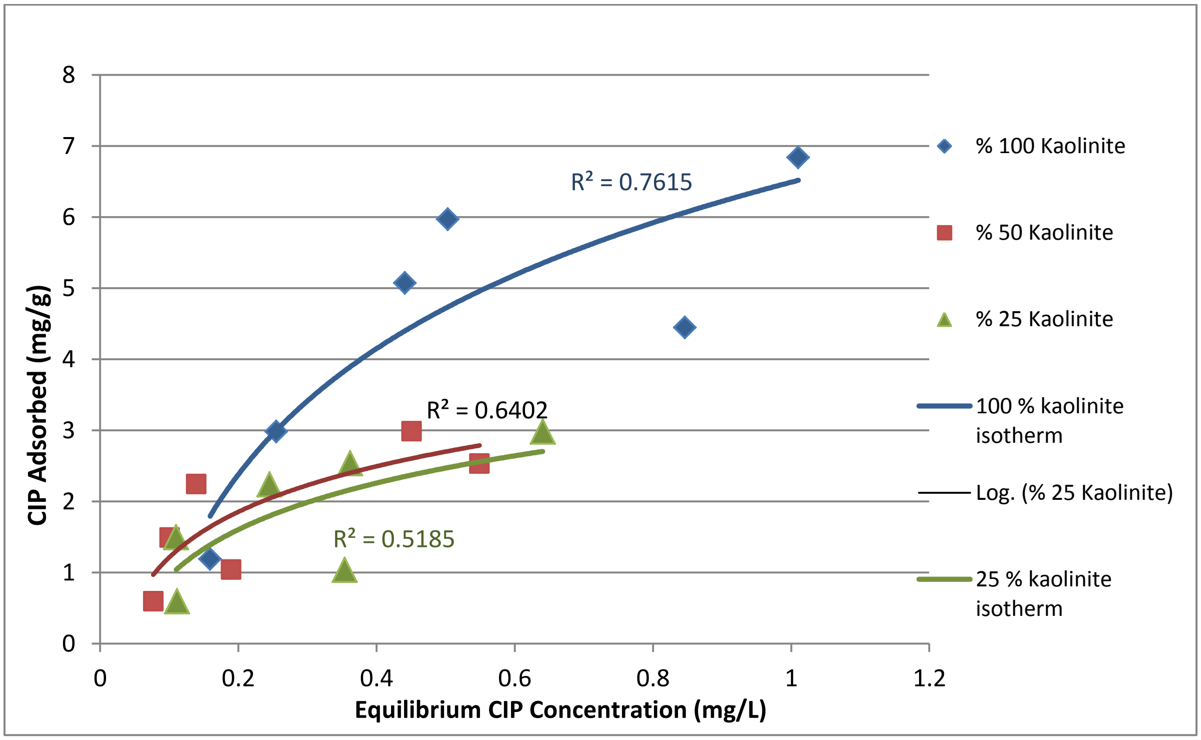

Figure 14: Kaolinite Isotherms

The comparison shown in the figure 14 shows a better correlation and a data fit for sorption of CIP when only kaolinite was used as the medium. This is indicated by the values or R^2 which is highest for 100% kaolinite and lowest for the 25% kaolinite but they all follow the same trend as was expected. Looking at the Freundlich isotherm for each case the extent of adsorption was also compared and is shown in equations (Eq. 19 – 21) below.

$$\text{100\% Kaolinite} \quad q_e = 5.68 \times (C_e)^{\frac{1}{1.86}} \quad R^2 = 0.71 \quad (Eqn. 22)$$

$$\text{50\% Kaolinite} \quad q_e = 4.14 \times (C_e)^{\frac{1}{1.72}} \quad R^2 = 0.58 \quad (Eqn. 23)$$

$$\text{25\% Kaolinite} \quad q_e = 3.57 \times (C_e)^{\frac{1}{1.701}} \quad R^2 = 0.46 \quad (Eqn. 24)$$

The extents of adsorption of CIP on kaolinite is shown by the K_f values in the above equations and are as was expected, presence of more kaolinite did result in removal of more CIP from water at pH 7. These results indicate that kaolinite can serve as one of the adsorbents of choice in removal of CIP from contaminated water.

4.5 Sources of Error and limitations

Errors in determination of f_{oc} may have been introduced due to the soil type used to achieve higher f_{oc} content media. As was mentioned earlier, the higher organic content potting mix obtained from the retail store had vermiculites which are often added to the soil or potting mix for agricultural purposes. However, removing it from the soil samples was not considered and would have been very time consuming. The presence of vermiculites and other significantly small particles in our samples could have interfered with results thus resulting in variance in results for the experiments with varying f_{oc}. Also, determination of percent f_{oc} in the two soil types could be another source of error despite proper calibration of the scales. In that case, the percentage of f_{oc} mixed may not meet our target value. Also, the concentration range of our initial solution is much higher than the CIP detected in natural environment. However, the limitation of available equipment and methods available prompted us to use higher concentrations. In addition, Poor experimental design as well as cross-contamination and not having our desired f_{oc} present in our actual samples are just some of the possible sources of error when considering our organic carbon trials. One of the other main sources of error observed was the solubility of CIP with concentrations higher than 115 mg/L at pH 7. With kaolinite experiments as well as varying soil f_{oc} precipitation of CIP was observed. This resulted in presenting data that did not follow the trend as it showed higher removal rate by sorption while most of the CIP was separated by precipitation and not by sorption on kaolinite or soils. Other overall sources of error included the equipment especially with respect to consistent results and our chosen methods for example the drop-wise method used to attain pH 7 and its potential to create error.

5 Infiltration Bed Design Proposal

Through the use of our experimental data a potential design for an infiltration bed for a septic system for the sorption of aqueous CIP from wastewater effluent was developed. After the analysis of our results it was determined that kaolinite would be used in our design because it showed the greatest success in the sorption of aqueous CIP. For the purposes of this design a four bedroom household will be considered and further adaption of our data could be used in the future to design a layer for an infiltration bed for a larger disposal system such as a wastewater treatment plant.

Assuming the size of the house and following Massachusetts code for residential septic system requirements the amount of necessary kaolinite can first be determined. As mentioned by MassDEP, (2007) in Massachusetts Housing Regulations, a septic system for a four bedroom house is required to handle 440 gallons per day (gpd). The design will allow for a 20 year lifespan and assumes that 1 mg/L of aqueous CIP is released per day. Although this amount of aqueous CIP is higher than what would likely be found in the effluent of a realistic household, for the purposes of our design it works well with our data. This results in a total of 3,212,000 mg of CIP over the aforementioned 20 year period being pumped into the infiltration bed. Our results showed that at an equilibrium CIP concentration of 1 mg/L the resulting sorbed CIP would be about 6.8 mg per 1 mg of Kaolinite. This requires about 472,400 grams of kaolinite for the complete sorption of aqueous CIP over the selected time period. The density of kaolinite is about 1.9 g/cm^3 and with the mass being 472,400 grams the volume can be determined to be 248,700 cm^3. Additional Massachusetts guidelines must be considered to determine the dimensions of our designed infiltration bed. Massachusetts environmental regulations (Title V regulations) call for a maximum length of 100 feet and a maximum of 6 feet between the pipes that release the effluent from the septic system (MassDEP, 2007). Our design will have three pipes with a 1 foot diameter spaced 4.5 feet apart at a length of 80 feet which, according to regulations that state that the pipes must be at least 3 inches in diameter spaced at a maximum of 6 feet apart, is in accordance. Figure 15 below displays the dimensions of our proposed infiltration bed design.

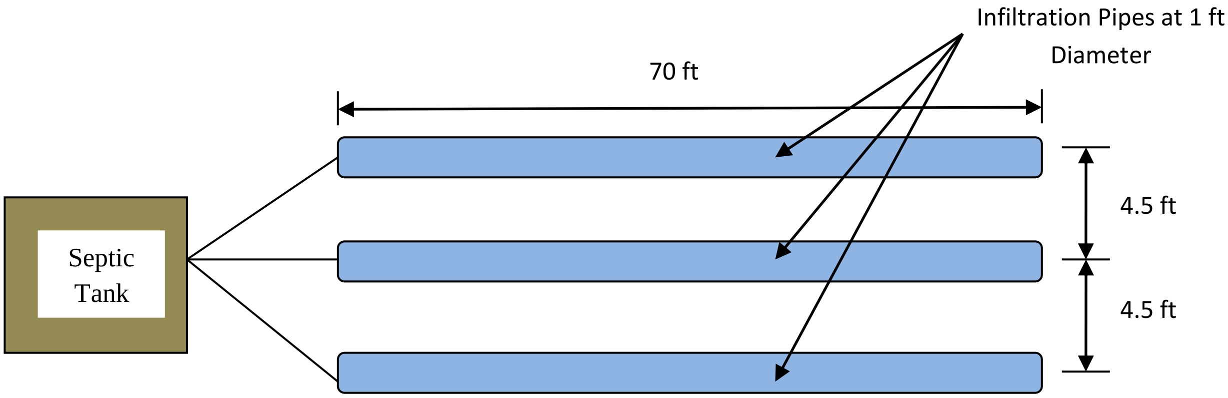

Figure 15: Infiltration Bed Design Dimensions

Once the dimensions for the design were determined the infiltration bed could be designed in accordance with the determined amount of necessary kaolinite. Allowing for an additional foot to taking into account dispersion, the total length comes to 72 feet while the total width comes to 12 feet. This design will have a loading rate of about 0.51 GPD/ft^2, which is within the range of requirements stated within Massachusetts environmental Regulations. With these dimensions and a volume of 248,700 cm^3 (8.78 ft^3) of kaolinite, we can propose our design for a kaolinite layer. The layer will consist of a mix of kaolinite and crushed stone gravel that will be 0.5 inches thick and have a volume of 36 ft^3. The layer will consist of 8.78 ft^3 of kaolinite and 27.22 ft^3 of crushed stone gravel. The infiltration bed for our design will consist of one foot of stone gravel held in place by a geotextile, upon which the infiltration pipes will rest, followed by the layer of kaolinite and then the natural soil. Figure 16 displays a cross section of the proposed infiltration bed design.

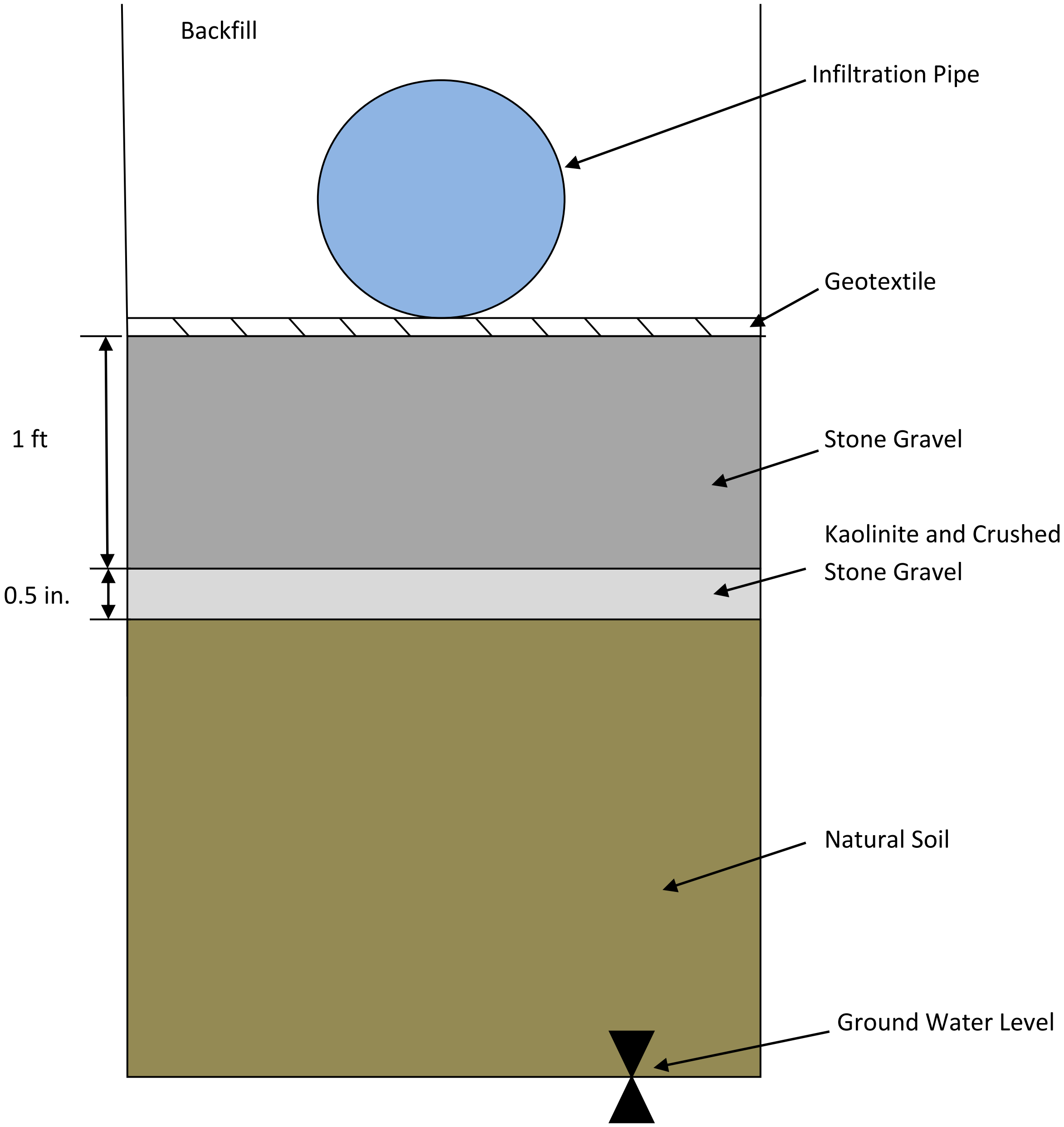

Figure 16: Cross Section of Proposed Infiltration Bed Design

There are many things to consider for the further development of our proposed design. The first is cost, this is a large amount of kaolinite and it is unknown whether it makes sense to use this much economically for either a household septic system or a larger system. Also, methods for the removal and or replacement of the kaolinite layer must be determined. Finally the amount of aqueous CIP and consequently the amount of kaolinite necessary for its complete sorption will require re-evaluation when applying this design on different scales for both smaller septic systems and larger wastewater treatment where bed infiltration is utilized.

It is our hope that this design will provide a means to remove aqueous CIP found in wastewater effluent and future development of such design may be employed in order to determine its effectiveness and economic feasibility.

6 Conclusions and Recommendations

All methods for the sequestration of aqueous ciprofloxacin in soil examined in this report proved to be successful, yet there is much more future research and experimentation needed to prove that these methods are viable. Kaolinite proved to be the most successful of all the trials with sorbed CIP concentrations that more than doubled that of any f_{oc} sample at any given initial aqueous CIP concentration. Kaolinite fit to the Freundlich isotherm model but did not fit well to the Langmuir isotherm model, yet the data had a large variance and therefore did not have strong correlation in any of three trials. Future experimentation should be undertaken at other ratios of kaolinite to sand to further confirm the ability of kaolinite to adsorb CIP. It is also recommended to undertake studies to compare sorption of CIP on kaolinite with other clay minerals such as montmorillonite. If other clay minerals can be found in effectively removing of CIP from water, tit may present an efficient and cost effective alternative.

Our data showed that of all the fractional amounts of organic carbon 0.5% f_{oc} proved to be the most successful in the adsorption of CIP and three trials confirmed the initial hypothesis that the presence of f_{oc} increases sorption of aqueous CIP. Although the data does not confirm the validity of our other initial proposition that increasing f_{oc} would result in an increase in the amount of sorbed CIP, we believe this to be the case.

Since CIP can exist as cation, zwitterion, and anion, further studies with cation and anion form is also suggested. This could reveal more information on how much CIP (in different) could be adsorbed on kaolinite. Also, investigation of CIP sorption on kaolinite at different pH levels is highly suggested as some research has shown a change in sorption mechanism of CIP and kaolinite. In addition, further studies that would include time trials could be more beneficial as it can help determine the minimum time required for CIP concentration to reach equilibrium concentration which in turn is needed to better understand and design a full functional process or system for removal of CIP from contaminated waters.

Further research is needed to confirm whether or not the implementation of kaolinite or increased f_{oc} in soil is a plausible method for the sorption of CIP. A better method for the determination and implementation of f_{oc} in each sample must be developed to ensure that the desired f_{oc} is present in each sample. One possible method for ensuring that this is the case would be to bake off all the f_{oc} in a soil sample then add the desired amount of f_{oc}. To confirm this potential method the soil could be weighed once the f_{oc} has been added and then baked again then the f_{oc} could be calculated to determine if the desired f_{oc} was actually present in the sample. It is also possible that a pre-treatment may be necessary to remove particles or elements present in wastewater that may also sorb to kaolinite or organic carbon and prohibit the additional sorption of CIP. Also, use of humic and fulvic acid for f_{oc} experimentation should be considered in future studies as their use might eliminate some of the sources of error that are associated with drying, baking and weight measurements that can fluctuate based on humidity and moisture level in the lab.

A complement to this report that would also require additional research and experimentation would be a cost-benefit analysis of designing and implementing these measures. In addition any environmental affects that increased f_{oc} or the presence of increased amounts of Kaolinite in soil might cause, need to be investigated. Research should also be carried out to determine when a layer of kaolinite or high f_{oc} soil may have to be removed from an infiltration bed or filtration system once the maximum CIP has been sorbed and how the disposal will be carried out.

Our research and experimentation proved that there is at least some validity to the presumption that the presence of organic carbon and kaolinite in soil aides in the sequestration of CIP, nevertheless further inquiry must be made to prove its validity.

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Appendix A: Nomenclature

C	Chemical concentration
C_{aq}	Aqueous chemical concentration
C_e	Sorbed Chemical concentration at equilibrium (mg/L)
C_o	Initial CIP concentration
D	Diffusivity
$[DOC]$	Dissolved organic carbon concentration (kg DOC/L).
f_{oc}	Fraction of soil that is organic carbon
J	Flux
$\mathrm{k_a}$	Rate of adsorption
K_a	Langmuir constant
K_d	Distribution Coefficient
K_d^*	Apparent soil sorption coefficient in the presence of DOC
K_{doc}	Dissolved organic carbon coefficient
K_{oc}	Organic carbon-water partition coefficient
$\mathrm{K_{ow}}$	Octanol-water partition coefficient
K_f	Freundlich constant
n	Empirical constant of freundlich model
m	Mass
Q	Specific discharge (L/T)
q_e	Concentration of chemical adsorbed per unit weight of adsorbent (mg/g)
R	Retardation factor
V	Seepage velocity
V_{voids}	Volume of the voids or spaces between grains (L^3)
V_{total}	Total bulk volume of the sample (L^3)
x	Distance
η	Porosity
ρb	Bulk density
Θ	Fraction of covered adsorbate surface

Appendix B: Glossary of Terms

CEC	Cation Exchange Capacity
CIP	Ciprofloxacin
DOC	Dissolved organic carbon
EPA	Environmental Protection Agency
FQ	Fluoroquinolone
GAO	Government Accountability Office
MQP	Major Qualifying Project
OTC	Oxtetracyline
PNEC	Predicted No-Effect Concentration
PPCP	Pharmaceuticals and Personal Care Products
USDA	U.S. Department of Agriculture
USDA-NRCS	U.S. Department of Agriculture Natural Resources Conservation Service
USGAO	United States Government Accountability Office
WWTP	Waste Water Treatment Plant
WWTS	Waste Water Treatment System

Appendix C- Raw Data

Calibration Curve

Table 3: CIP Absorbance data from UV spectroscopy

Concentration of CIPRO Solution (mg/L)	pH	Absorbance
20.000	7.03	1.5003
10.000	7.01	0.8088
5.000	6.99	0.4640
2.500	6.98	0.2626
1.250	6.98	0.1105
0.625	7.05	0.0439
0.313	7.02	0.0394
0.156	6.97	0.0184
0.078	7.01	0.0141
0.039	7.01	0.0114

Fraction of Organic Carbon (% f_{oc})

Table 4: Zero percent f_{oc} Sand

Mass of 0% f_{OC} Sand (g)	$Conc_i$ (mg/L)	Volume (mL)	pH	$Absorb_f$	% Difference	$Conc_f$ (mg/L)	ΔCIP Conc (mg/L)	CIP Adsorbed (mg/g)
6	200	10	7.02	3.1925	4.88%	42.341	157.659	0.263
6	150	10	7.00	2.8515	18.40%	37.818	112.182	0.187
6	100	10	7.02	2.0522	41.85%	27.218	72.782	0.121
6	20	10	6.97	0.2193	87.74%	2.908	17.092	0.028
6	50	10	7.01	0.4355	86.28%	5.776	44.224	0.074
6	100	10	7.03	1.6457	50.01%	21.826	78.174	0.130
6	150	10	7.02	2.837	16.60%	37.626	112.374	0.187
6	200	10	7.01	3.2272	7.30%	42.801	157.199	0.262

Table 5: Zero percent f_{oc} Silica Beads

0 % f_{OC} Silica Beads (g)	Conc$_i$ (mg/L)	Volume (mL)	pH	Absorb$_f$	% Difference	Conc$_f$ (mg/L)	ΔCIP Conc (mg/L)	CIP Adsorbed (mg/g)
1.0000	20	30	7.01	1.184	33.30%	15.703	4.297	0.129
1.0006	50	30	7.01	3.2285	1.48%	42.818	7.1817	0.215
1.0041	75	30	6.99	3.6025	-13.98%	47.779	27.221	0.813
1.0000	100	30	7.01	3.3994	-1.20%	45.606	54.394	1.632
1.0065	125	30	6.97	3.4387	-5.12%	46.521	78.4788	2.339
1.0046	150	30	7.02	3.5077				
1.0092	175	30	7.01	-				

Table 6: 0.5% f_{oc} Sand and Soil

CIP Conc$_i$ (mg/L)	Mass of Sand (g)	Mass of Soil (g)	Total Weight (g)	pH	Volume of CIP (mL)	Absorb$_f$	Conc$_f$ (mg/L)	ΔCIP Conc (mg/L)	CIP Adsorbed (mg/g)
20	0.9408	0.0567	0.9975	7.02	30	0.1127	1.495	18.505	0.557
35	0.9453	0.0563	1.0016	6.99	30	0.0680	0.880	34.120	1.022
50	0.9434	0.0559	0.9993	7.01	30	0.0707	0.938	49.062	1.473
75	0.9445	0.0561	1.0006	6.99	30	0.1061	1.407	73.593	2.206
85	0.9434	0.0567	1.0001	7.02	30	0.0971	1.288	83.712	2.511
100	0.9439	0.0563	1.0002	7.02	30	0.1038	1.377	98.623	2.958
115	0.9440	0.0572	1.0012	7.00	30	0.1481	1.964	113.036	3.387

Table 7: 1.0% f_{oc} Sand and Soil

CIP Conc$_i$ (mg/L)	Mass of Sand (g)	Mass of Soil (g)	Total Weight (g)	pH	Volume of CIP (mL)	Absorb$_f$	CIP Conc$_f$ (mg/L)	ΔCIP Conc. (mg/L)	CIP Adsorbed (mg/g)
20	0.8877	0.1120	0.9997	7.02	30	0.229	3.037	16.963	0.509
35	0.8881	0.1136	1.0017	6.99	30	0.342	4.532	30.468	0.912
50	0.8877	0.1118	0.9995	7.01	30	0.275	3.643	46.357	1.391
75	0.8877	0.1122	0.9999	6.99	30	0.258	3.419	71.581	2.148
85	0.8878	0.1123	1.0001	7.02	30	0.118	1.558	83.442	2.503
100	0.8875	0.1123	0.9998	7.02	30	0.236	3.129	96.871	2.907
115	0.8874	0.1117	0.9991	7.00	30	0.177	2.350	112.650	3.383

Table 8: 1.5% f_{oc} Sand and Soil

CIP Conc$_i$ (mg/L)	Mass of Sand (g)	Mass of Soil (g)	Total Weight (g)	pH	Volume of CIP (mL)	Absorb$_f$	CIP Conc$_f$ (mg/L)	ΔCIP Conc	CIP Adsorbed (mg/g)
20	0.8328	0.1679	1.0007	7.03	30	0.2349	3.1154	16.8846	0.5062
35	0.8309	0.1692	1.0001	6.97	30.000	0.2724	3.6127	31.3873	0.9415
50	0.8317	0.1682	0.9999	7.02	30.000	0.2331	3.0915	46.9085	1.4074
75	0.8311	0.1690	1.0001	7.02	30.000	0.3223	4.2745	70.7255	2.1216
85	0.8312	0.1681	0.9993	7.03	30.000	0.2700	3.5809	81.4191	2.4443
100	0.8316	0.1685	1.0001	6.99	30.000	0.1802	2.3899	97.6101	2.9280
115	0.8312	0.1693	1.0005	7.02	30.000	0.2084	2.7639	112.2361	3.3654

Table 9: 4.5% f_{oc} Sand and Soil

CIP Conc$_i$ (mg/L)	Mass of Sand (g)	Mass of Soil (g)	Total Weight (g)	pH	Volume of CIP (mL)	Absorb$_f$	CIP Conc$_f$ (mg/L)	ΔCIP Conc (mg/L)	CIP Adsorbed (mg/g)
20	0.5040	0.5020	1.0060	6.99	30	0.4664	6.1857	13.8143	0.4120
35	0.5055	0.5002	1.0057	6.99	30	0.5601	7.4284	27.5716	0.8225
50	0.5042	0.5035	1.0077	7.01	30	0.5615	7.4469	42.5531	1.2668
75	0.5058	0.5035	1.0093	7.02	30	0.5766	7.6472	67.3528	2.0020
85	0.5017	0.5053	1.0070	6.98	30	0.5387	7.1446	77.8554	2.3194
100	0.5025	0.5015	1.0040	7.02	30	0.7420	9.8408	90.1592	2.6940
115	0.5041	0.5044	1.0085	7.01	30	0.6566	8.7082	106.2918	3.1619

Kaolinite

Table 10:100% Kaolinite

Kaolinite (g)	Total Time (h)	pH	Conc$_i$ (mg/L)	Abs$_f$	Conc$_f$	ΔConc (mg/L)	% Decrease	CIP Adsorbed (mg/g)
0.5000	48	7.01	20	0.012	0.163	19.837	99.18%	1.190
0.5000	48	6.99	50	0.020	0.261	49.739	99.48%	2.984
0.5000	48	7.03	75	0.065	0.867	74.133	98.84%	4.448
0.5000	48	7.03	85	0.034	0.452	84.548	99.47%	5.073
0.5000	48	6.98	100	0.039	0.516	99.484	99.48%	5.969
0.5000	48	7.05	115	0.078	1.036	113.964	99.10%	6.838
0.5000	48	7.03	150	0.297	3.944	146.056	97.37%	8.763

Table 11: 50% Kaolinite

CIP Conc$_i$ (mg/L)	Mass of Sand (g)	Mass of Kaolinite (g)	Total Weight (g)	pH	Volume of CIP (mL)	Absorb$_f$	CIP Conc$_f$	ΔCIP Conc (mg/L)	CIP Adsorbed (mg/g)
20	0.4991	0.5001	0.9992	7.02	30	0.0058	0.0769	19.9231	0.5982
35	0.5001	0.4999	1.0000	7.03	30	0.0143	0.1897	34.8103	1.0443
50	0.5018	0.4996	1.0014	6.99	30	0.0076	0.1008	49.8992	1.4949
75	0.5001	0.4996	0.9997	7.00	30	0.0105	0.1393	74.8607	2.2465
85	0.4996	0.5000	0.9996	7.00	30	0.0414	0.5491	84.4509	2.5345
100	0.4998	0.4997	0.9995	6.99	30	0.0340	0.4509	99.5491	2.9880

Table 12: 25% Kaolinite

CIP Conc$_i$ (mg/L)	Mass of Sand (g)	Mass of Kaolinite (g)	Total Weight (g)	pH	Volume of CIP (mL)	Absorb$_f$	CIP Conc$_f$	ΔCIP Conc (mg/L)	CIP Adsorbed (mg/g)
20	0.7501	0.2494	0.9995	7.02	30	0.0084	0.1114	19.8886	0.5970
35	0.7500	0.2494	0.9994	7.03	30	0.0267	0.3541	34.6459	1.0400
50	0.7497	0.2494	0.9991	6.99	30	0.0083	0.1101	49.8899	1.4980
75	0.7508	0.2498	1.0006	7.00	30	0.0185	0.2454	74.7546	2.2413
85	0.7510	0.2496	1.0006	7.00	30	0.0273	0.3621	84.6379	2.5376
100	0.7496	0.2491	0.9987	6.99	30	0.0483	0.6406	99.3594	2.9847

Appendix D: Sample-Calculations

Determination of f_{oc}

Table 13: Calculations to Determine f_{oc} in Soil Sample

Mass of Soil Initial (g)	Mass of Dish (g)	Mass of Soil + dish Initial (g)	Mass Soil after Drying	Mass Soil after Muffle Furnace	Moisture weight (g)	Remaining Soil + Organic Carbon Total Weight (g)	Mass of Organic Carbon (g)	% f_{oc}
15.0336	83.3366	98.3702	91.851	91.0936	6.5192	8.5144	0.7574	8.90%

Table 14: Calculation of Masses of Sand/Soil at Necessary f_{oc}

Ult. %f_{oc}	%f_{oc} of Soil	% f_{oc} of Sand	Ult % f_{oc}/Soil	Total Mass (g)	Mass of Soil (g)	Mass of Sand (g)
0.50%	8.90%	0.00%	17.80	1.00	0.0562	0.9438
1.00%	8.90%	0.00%	8.90	1.00	0.1124	0.8876
1.50%	8.90%	0.00%	5.93	1.00	0.1685	0.8315
2.00%	8.90%	0.00%	4.45	1.00	0.2247	0.7753
2.50%	8.90%	0.00%	3.56	1.00	0.2809	0.7191
3.00%	8.90%	0.00%	2.97	1.00	0.3371	0.6629
4.45%	8.90%	0.00%	2.00	1.00	0.5000	0.5000

Kaolinite Isotherm Data

Table 15: 100% Kaolinite Data and Variables Calculations

Freundlich Isotherm		Langmuir Isotherm		Freundlich Isotherm Variables					
ln CIP Conc_f (mg/L)	ln CIP Adsorbed (mg/g)	1/CIP Conc_f (mg/L)	1/CIP Adsorbed (mg/g)	$\ln(k_f)$	K_f	1/n	n	C	q
-1.838	0.174	6.285	0.840	1.738	5.684	0.539	1.854	0.0551	2.109
-1.367	1.094	3.924	0.335	1.738	5.684	0.539	1.854	0.3029	2.7191
-0.167	1.493	1.182	0.225	1.738	5.684	0.539	1.854	0.635	5.1941
-0.818	1.624	2.267	0.197	1.738	5.684	0.539	1.854	0.81	3.6556
-0.687	1.787	1.987	0.168	1.738	5.684	0.539	1.854	1.0954	3.9247
0.010	1.923	0.990	0.146	1.738	5.684	0.539	1.854	1.409	5.7159
1.347	2.171	0.260	0.114	1.738	5.684	0.539	1.854	2.2339	11.757

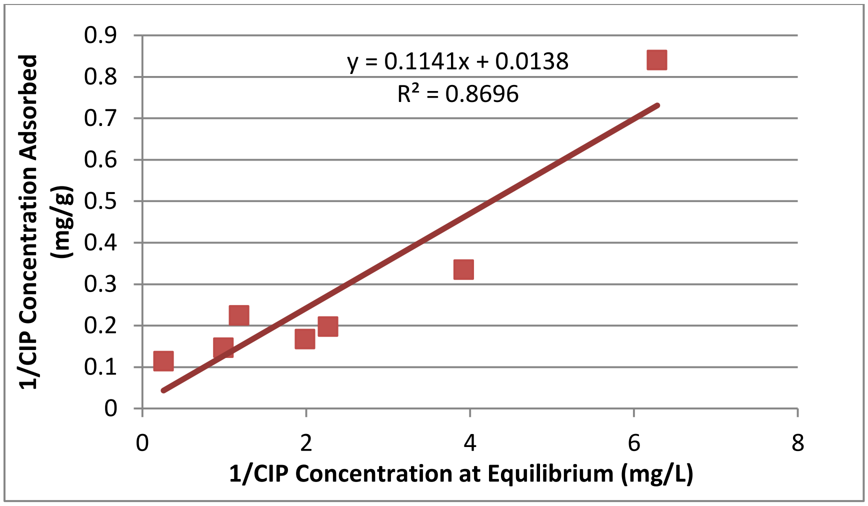

Figure 17: 100% Kaolinite – Langmuir Isotherm Data

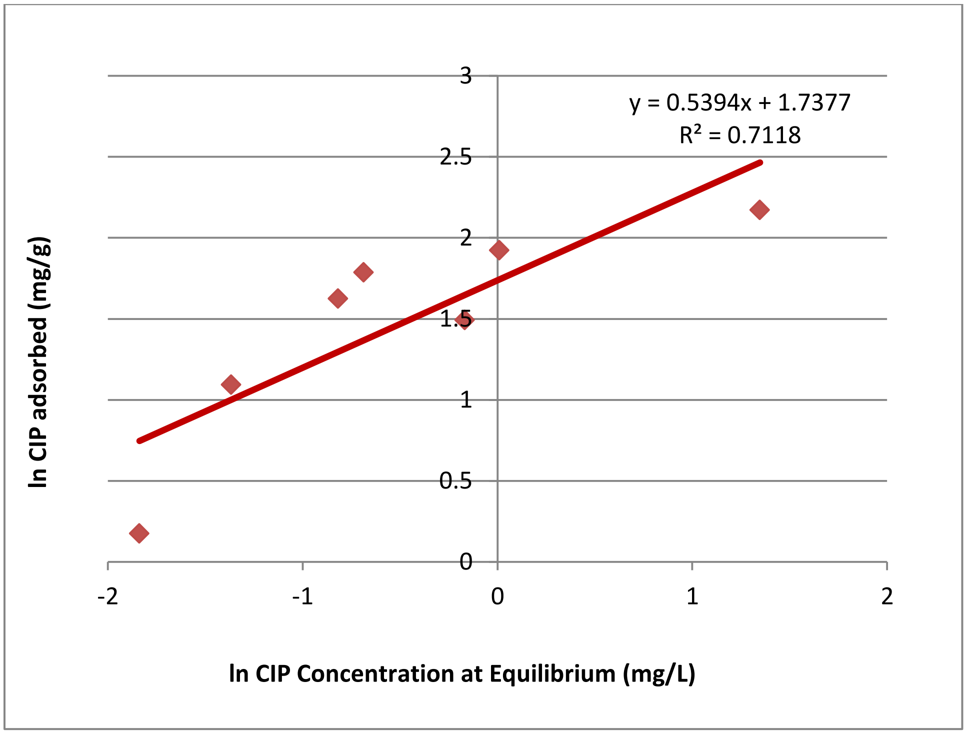

Figure 18: 100% Kaolinite - Freundlich Isotherm Data

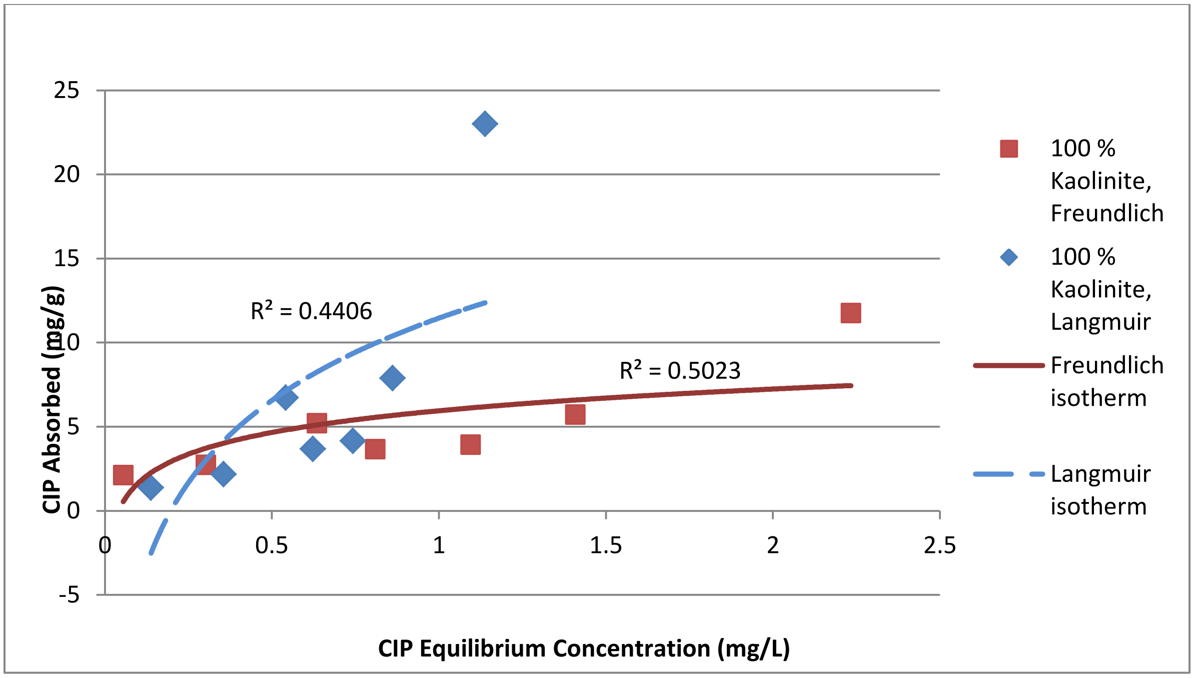

Figure 19: Comparison of Freundlich & Langmuir Isotherm for 100 % kaolinite

Table 16: 50% Kaolinite Data and Variables Calculations

Freundlich Isotherm		**Langmuir Isotherm**		**Freundlich Isotherm Variables**					
ln CIP $Conc_f$	**ln CIP Adsorbed**	**1/CIP $Conc_f$**	**1/CIP Adsorbed**	**$\ln(k_f)$**	**K_f**	**1/n**	**n**	**C**	**q**
-2.565	-0.514	13.000	1.672	1.421	4.140	0.582	1.717	0.036	0.930
-1.663	0.043	5.273	0.958	1.421	4.140	0.582	1.717	0.094	1.572
-2.295	0.402	9.921	0.669	1.421	4.140	0.582	1.717	0.174	1.088
-1.971	0.809	7.181	0.445	1.421	4.140	0.582	1.717	0.350	1.313
-0.600	0.930	1.821	0.395	1.421	4.140	0.582	1.717	0.431	2.920
-0.796	1.095	2.218	0.335	1.421	4.140	0.582	1.717	0.571	2.604

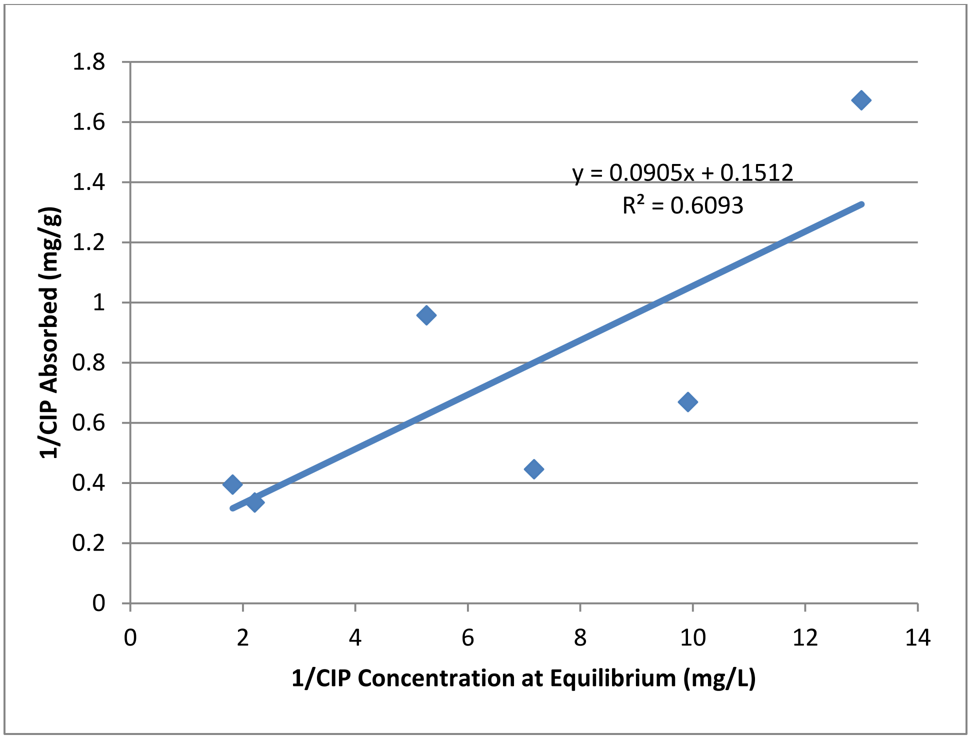

Figure 20: 50% Kaolinite – Langmuir Isotherm Data

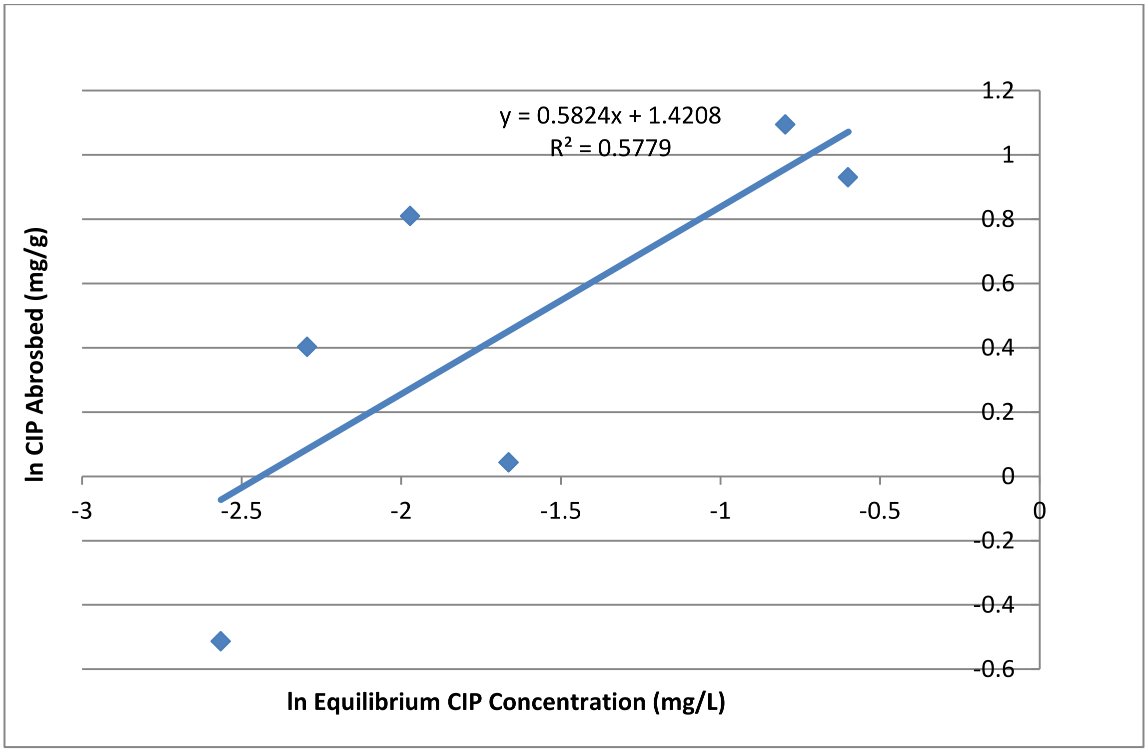

Figure 21: 50% Kaolinite – Freundlich Isotherm Data

Table 17: 25% Kaolinite Data and Variable Calculations

Freundlich Isotherm		Langmuir Isotherm		Freundlich Isotherm Variables					
ln CIP Conc$_f$	ln CIP Adsorbed	1/CIP Conc$_f$	1/CIP Adsorbed	ln(k_f)	K_f	1/n	n	C	q
-2.195	-0.516	8.976	1.675	1.274	3.574	0.588	1.701	0.048	0.984
-1.038	0.039	2.824	0.962	1.274	3.574	0.588	1.701	0.122	1.941
-2.207	0.404	9.084	0.668	1.274	3.574	0.588	1.701	0.228	0.977
-1.405	0.807	4.076	0.446	1.274	3.574	0.588	1.701	0.452	1.565
-1.016	0.931	2.762	0.394	1.274	3.574	0.588	1.701	0.558	1.967
-0.445	1.093	1.561	0.335	1.274	3.574	0.588	1.701	0.736	2.751

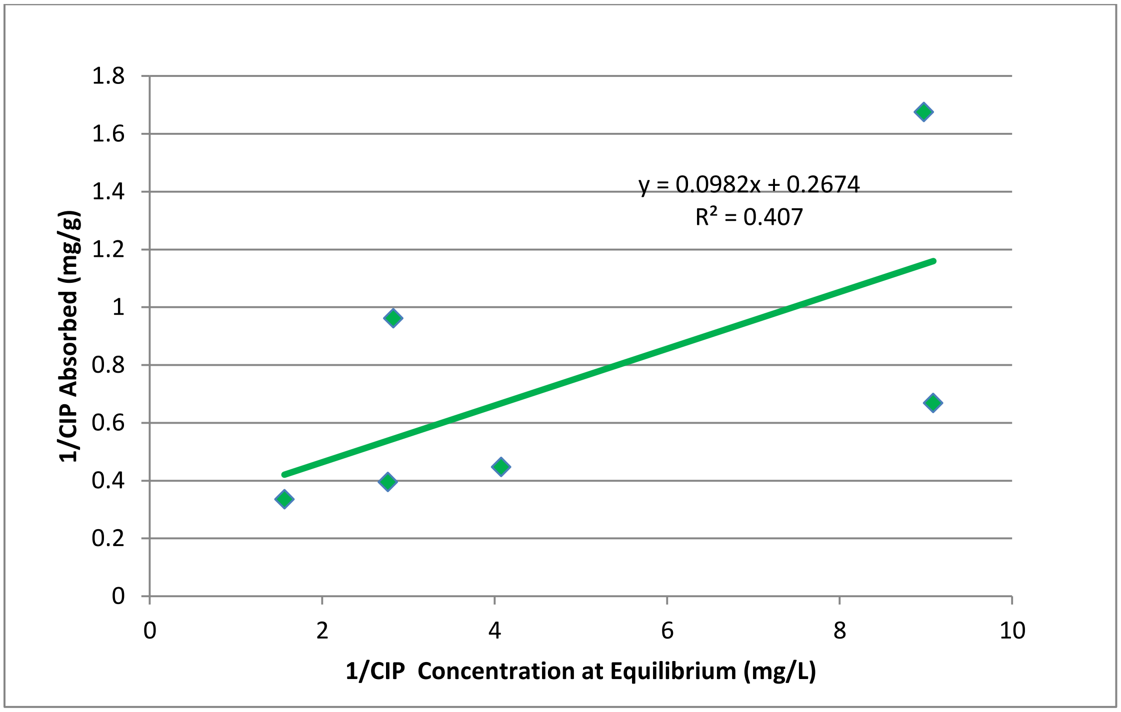

Figure 22: 25% Kaolinite – Langmuir Isotherm Data

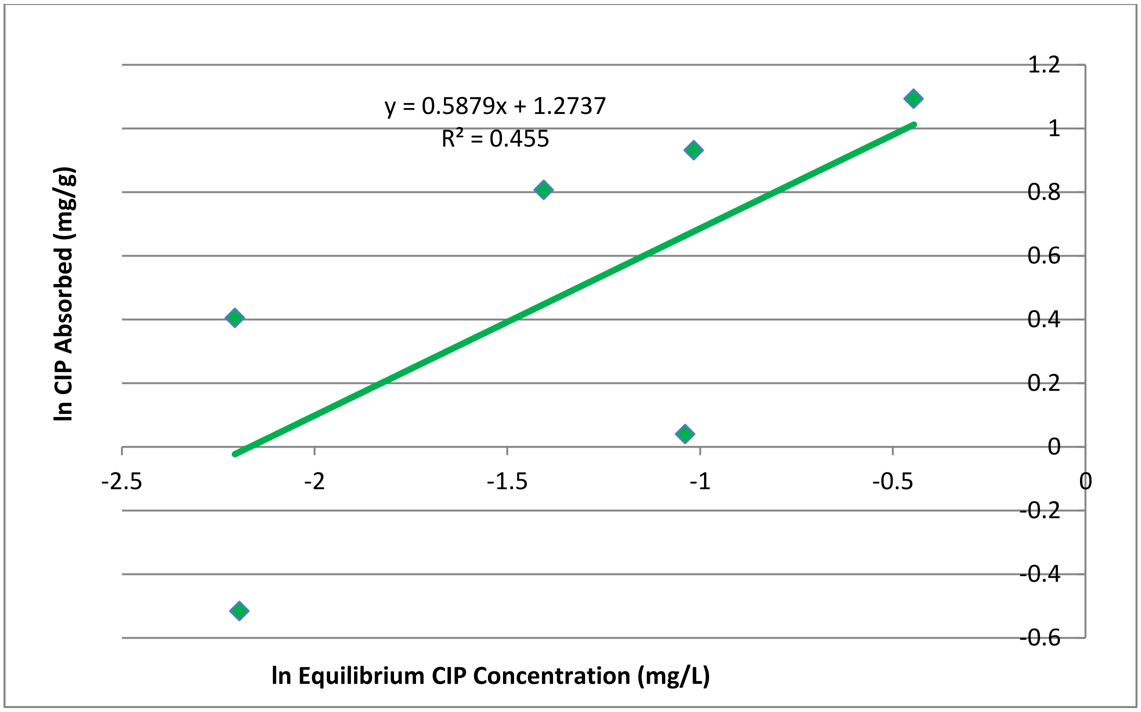

Figure 22: 25% Kaolinite – Freundlich Isotherm Data

Fractional Organic Carbon (f_{oc}) K_d and K_{oc} Data

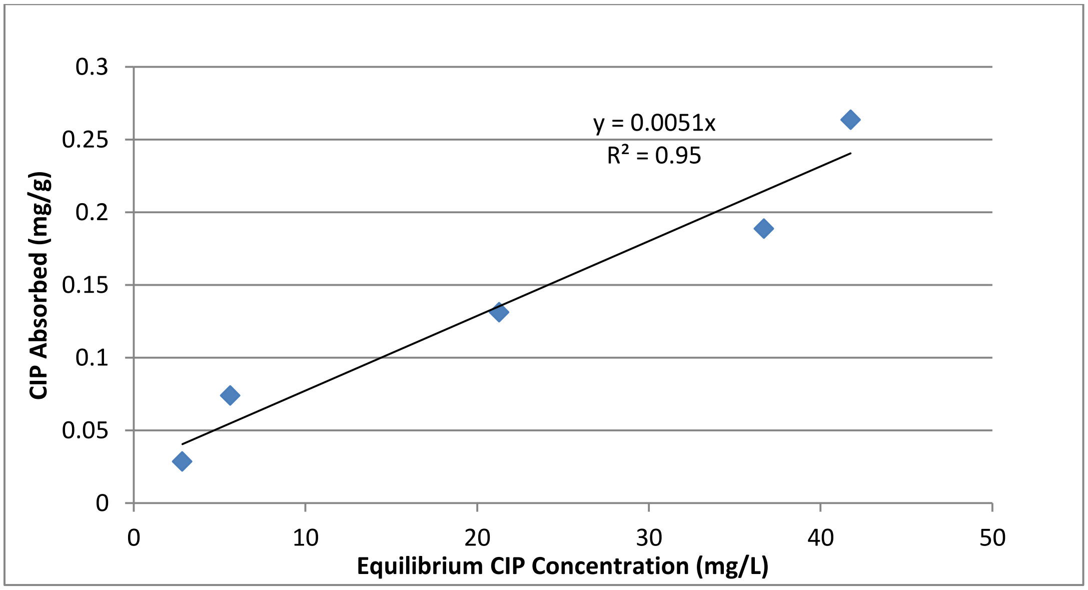

Figure 23: Zero percent f_{oc} Sand Data

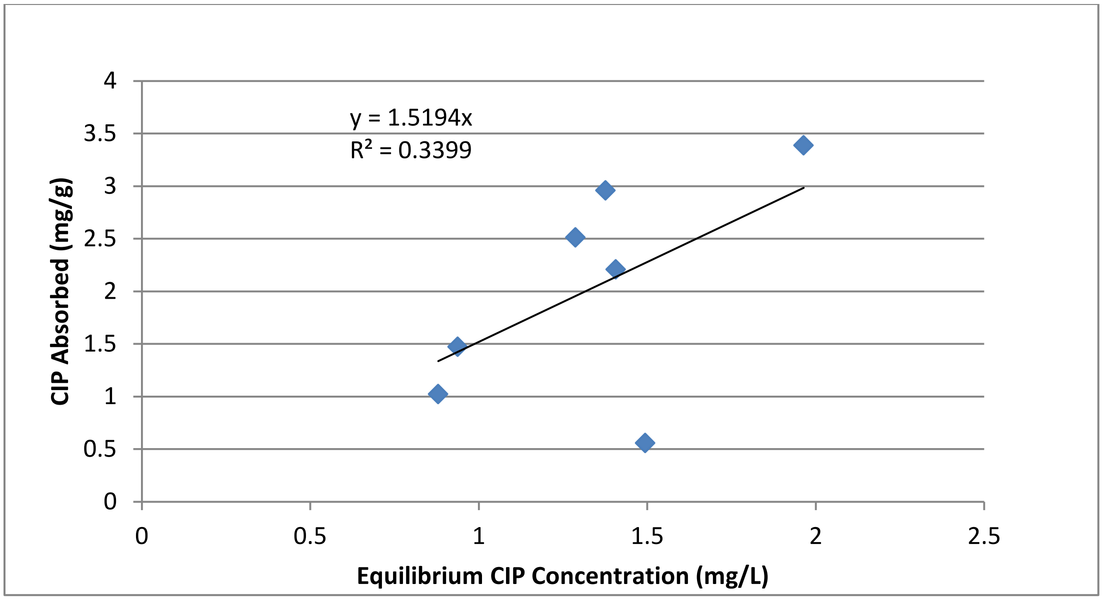

Figure 24: 0.5% f_{oc} Data

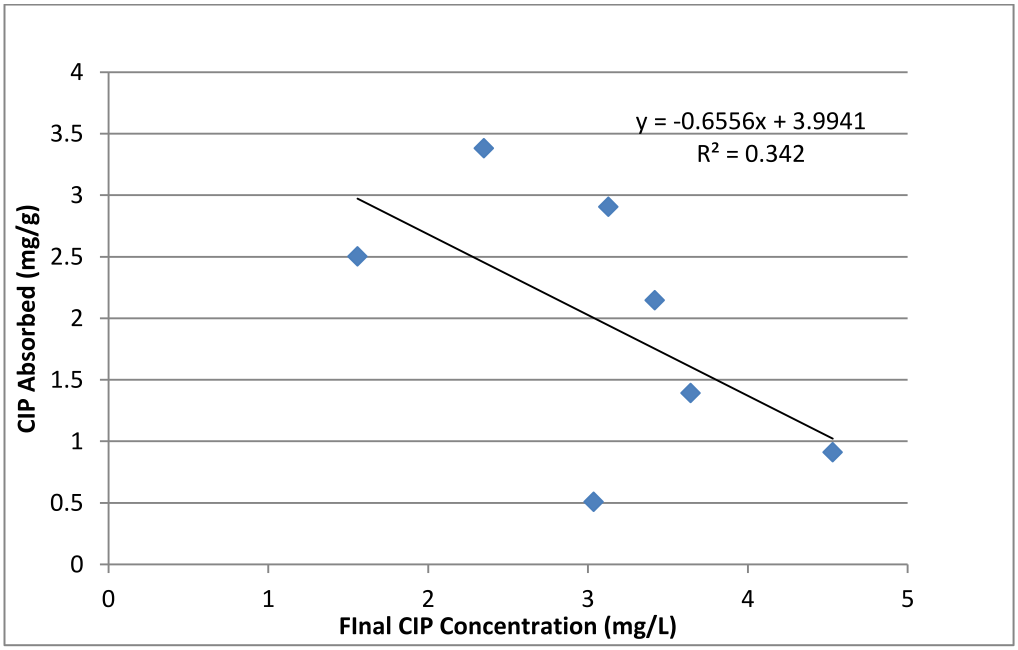

Figure 25: 1.0% f_{oc} Data

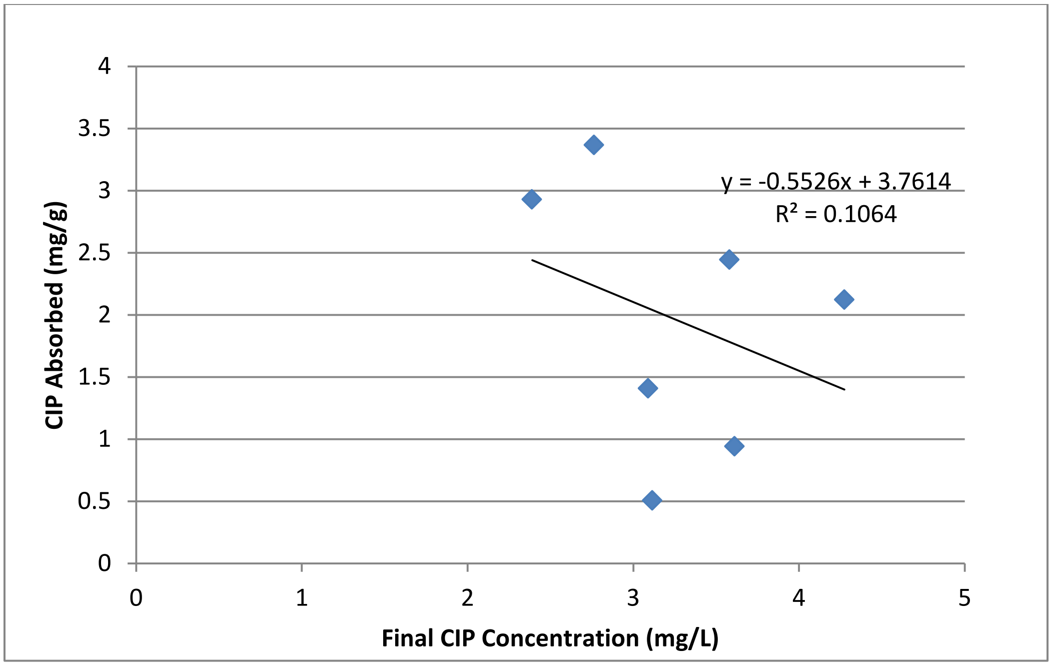

Figure 23: 1.5% f_{oc} Data

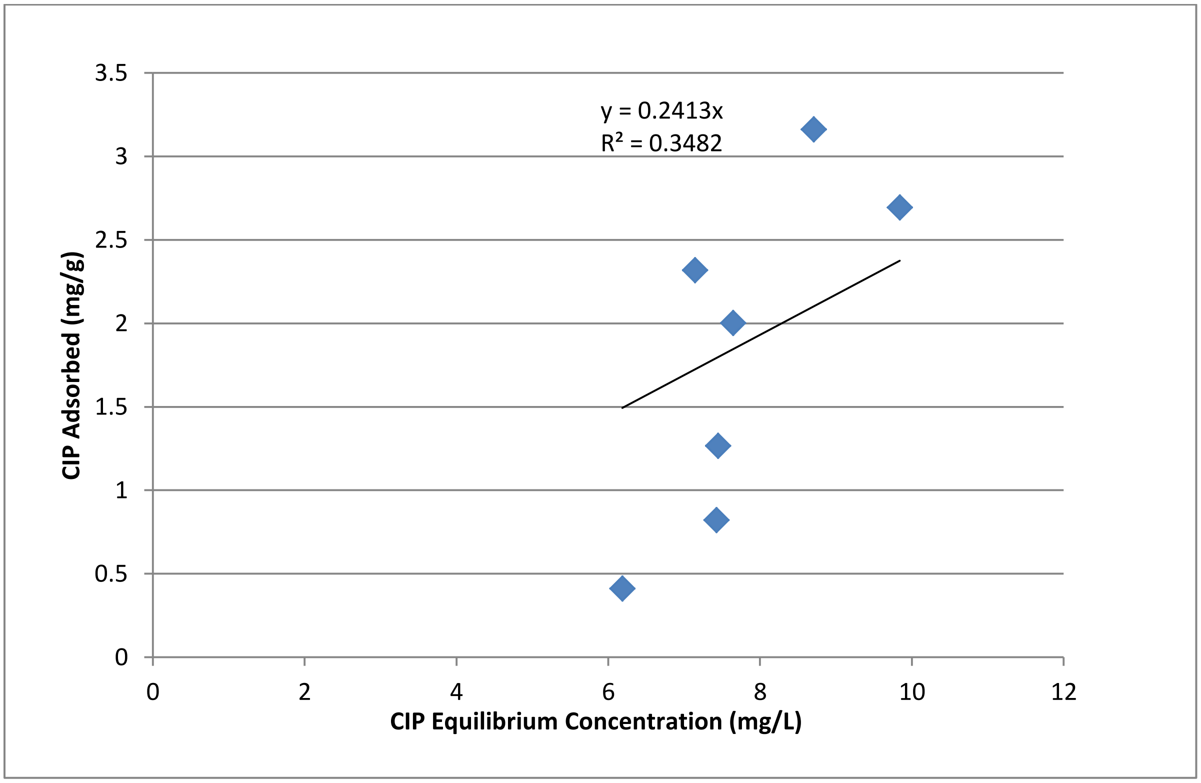

Figure 24: 4.5% f_{oc} Data