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TITLE: **A STUDY OF A FLYASH AMENDED SOIL AND ITS EFFECT ON NITRATE MOVEMENT THROUGH UNSATURATED MEDIA**

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A STUDY OF A FLYASH AMENDED SOIL AND ITS EFFECT ON NITRATE MOVEMENT THROUGH UNSATURATED MEDIA

A Thesis

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ABSTRACT

A Study of a Flyash Amended Soil and its Effect on Nitrate Movement Through Unsaturated Media

By

Ricardo Medina

A sand-clay mixed soil was amended with Class F Flyash (FA) obtained from the coal-fired co-generating power station located near Trona, CA. Flyash was added as an amendment to the soil mixture at four different levels: 0% (no flyash: NFA), 2% (low flyash: LFA), 10% (medium flyash: MFA), and 20% (high flyash: HFA) flyash, by weight. The soil with the FA treatments was packed into a small soil column and placed inside the steady-state centrifuge - unsaturated flow apparatus (UFA). The UFA was used to control the hydraulic properties of the soil, by adjusting the fluid flux and the centripetal acceleration, allowing the soil to be kept at a constant saturation level. Three saturation ranges were maintained: 0.75-0.9, 0.4-0.45, and 0.27-0.29 designated as high-, medium-, and low-saturation, respectively. Deionized (DI) water was used in the soil column until the target saturation level reached steady state, the DI injection line was then replaced with a 7.0 mM ammonium nitrate solution. Leachate from the soil column was collected at predetermined intervals, to a total volume of approximately five pore-volumes. The leachate samples collected were analyzed for nitrate (NO_3) concentration using ion chromatography and the breakthrough curves were constructed. The rate of adsorption and retardation factor of nitrate were calculated from the breakthrough curves for each of the FA treatments at the three saturation levels. The results show that the amount of flyash and saturation level have a significant effect on the nitrate transport. It was shown that adding a FA amendment to the soil will reduce anion exclusion experienced by nitrate and therefore reduce nitrate losses. Additionally, the moisture retention ability of the soil increases with an increase of FA application, however, the LFA sample reduced moisture retention, as compared to the control (NFA). The unsaturated hydraulic conductivity of the soil was also improved by the FA addition, however, it was observed that there is only a small difference between a 10% and a 20% FA amendment to the soil. Soil bulk density increased, while the saturated volumetric water content of the soil decreased, with increasing amount of FA added to the soil. The results indicate that the improved hydraulic properties of the soil, release of sulfate, and reduced anion exclusion of nitrate of a FA amended soil can lead to reduced nitrate losses.

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LIST OF ACRONYMS AND ABBREVIATIONS

ACAA	American Coal Ash Association
As	Arsenic
AWSC	Available water storage capacity
B	Boron
Ba	Barium
Be	Beryllium
Br^-	Bromide
C	Carbon
Ca	Calcium
CaO	Calcium oxide
CCBP	Coal combustion byproduct
CCFA	Class C Flyash
CCP	Coal combustion products
Cd	Cadmium
CFFA	Class F Flyash
Cl^-	Chloride
Co	Cobalt
CO_2	Carbon dioxide
Cr	Chromium
Cu	Copper
DI	Deionized (water)
EIA	U.S. Energy Information Administration

EPA	U.S. Environmental Protection Agency
EPV	Effective pore volume
F^-	Fluoride
FA	Flyash
Fe	Iron
FGD	Flue gas desulfurization
H	Hydrogen
Hb	Hemoglobin
HFA	High flyash (i.e. 20% flyash)
Hg	Mercury
K	Potassium
LFA	Low flyash (i.e. 2% flyash)
MCL	Maximum contaminant level
metHb	Methemoglobin
MFA	Medium flyash (i.e. 10% flyash)
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
N	Nitrogen
NFA	No flyash (i.e. 0% flyash)
NH_3^+	Ammonia
NH_4^+	Ammonium
Ni	Nickel

NO_2^-	Nitrite
NO_3^-	Nitrate
NPK ratio	Ratio (in percent) of nitrogen (N), phosphorous (P) and potassium (K) in a fertilizer
NRC	U.S. National Research Council
O_2	Oxygen
P	Phosphorous
Pb	Lead
PO_4^-	Phosphate
PWP	Permanent wilting point
Rb	Rubidium
S	Sulfur
Sb	Antimony
Se	Selenium
SO_4^-	Sulfate
Sr	Strontium
SSC-UFA	Steady State Centrifuge-Unsaturated Flow Apparatus
V	Vanadium
W	Tungsten
WHO	World Health Organization
WWTP	Waste water treatment plant
Zn	Zinc

LIST OF SYMBOLS

C	Nitrate concentration at any given time
C_e	Equilibrium nitrate concentration
C_0	Initial nitrate concentration
C^*	Mass of solute sorbed per unit weight of solid
K	Hydraulic conductivity
K_d	Adsorption coefficient
P	Matric potential pressure equivalence
p_{max}	Maximum pore volume (in the breakthrough curve)
q	Volumetric flow rate, fluid flux
R_f	Retardation Factor
S	Level of saturation
r	Radial distance from the axis of rotation to the middle of the soil sample
r_1	Radial distance from the axis of rotation to the top of the soil sample
r_2	Radial distance from the axis of rotation to the bottom of the soil sample
θ	Volumetric water content
θ_{AWSC}	Volumetric water content at available water storage capacity
θ_{FC}	Volumetric water content at field capacity
θ_{Sat}	Saturated volumetric water content
θ_{PWP}	Volumetric water content at the permanent wilting point
ρ	Density of fluid (i.e. water)
ρ_b	Bulk density of soil
ψ	Matric potential

ω	Rotation speed

CHAPTER 1

Introduction

Nitrate in drinking water poses an environmental and a potential health risk hazard. Nitrate (NO_3^-) has become one of the most widespread contaminants found in the groundwater in the United States. Nitrate sources can be either anthropogenic or natural and include wastewater treatment facilities, septic tanks, mineral dissolution, inorganic fertilizers, urea, nitrifying bacteria, nitrogen fixing plants, etc. Among these sources, inorganic fertilizers are of most concern because of the large volumes applied in irrigated agriculture. The mechanisms through which nitrate moves in the subsurface are complicated and highly dependent on the hydrogeology of the surrounding region, and other chemical and biological factors that may help reduce or enhance nitrate transport through the subsurface. If nitrate reaches an aquifer, it may pose a potential risk to human health and the environment. When the nitrate concentrations in the aquifers are above the U.S. Environmental Protection Agency's established limit for drinking water, remedial actions must be implemented.

There are currently several techniques to remediate nitrate contaminated groundwater. These techniques include ion-exchange, biological and chemical denitrification, blending (the technique of mixing nitrate-contaminated water with water that has a lower nitrate concentration), and membrane separation. These solutions are designed to deal with the nitrate contamination after it has reached the water body. However, more needs to be done to prevent nitrate from reaching the groundwater in the future.

The population growth at an exponential rate has placed an additional burden on societies: they must be able to provide enough food and clean drinking and potable water, while also providing enough habitable space for its people. Urbanization, the transformation of a virgin landscape into an urban, industrial, and/or residential area, is considered by many to be a threat to the environment. The urbanization of an area leads to an increased amount of pollution generated within a small region. Though the contamination is generated from a reduced space, such as a small city, it can have a broader impact if the pollutants reach a greater common area, such as an aquifer.

The higher demand for food has inadvertently given rise to large agro-businesses and the agricultural practice known as intensive agriculture. Intensive agriculture is the practice of using a low fallow ratio and heavy use of pesticides and fertilizers. The goal of intensive agriculture is to produce as much food as possible in the shortest amount of time, thus, the high reliance on fertilizers. Fertilizers provide essential plant nutrients such as Potassium (K), Phosphorous (P), and Nitrogen (N). There are natural sources for these nutrients, such as cow manure and urea, however, agriculturalists often rely on synthetic fertilizers as a source for the nutrients. Abundance of nitrogen will allow the plant to grow faster and larger, thus, many of the synthetic fertilizers use high nitrogen fertilizers. One such fertilizer is ammonium nitrate fertilizer (NH_4NO_3), which provides the greatest amount of nitrogen. When the ammonium nitrate is dissolved in water it is separated into two different ions, ammonium and nitrate, both of these ions contain nitrogen and both are easily taken up by plants. Though plants can take up many different forms of nitrogen, including organic and inorganic forms, the readily availability and cheap price-tag of nitrogenous inorganic fertilizers have made them the most widely used form of nitrogen applied to the crops (Mosier, et al., 2012)

In a national study conducted by the U.S. Environmental Protection Agency (EPA) surveying the integrity of groundwater aquifers throughout the U.S., it was reported that volatile organic compounds and nitrate are, currently, the contaminants of greater concern threatening groundwater aquifers (U.S. EPA, 2012). The report also highlighted that septic tank systems, fertilizer application, animal feedlots, and pesticides were reported as a major source of contamination in 31, 23, 17 and 15 different states, respectively. These four potential contaminant sources are also associated with the leaching of nutrients, i.e. N, P, K, to the groundwater. In 2008, the California State Water Resources Control Board (State Water Board), in consultation with other agencies, conducted a study on nitrate contamination in five counties in the Northern California Region (Viers, et al., 2012). Land use in these five counties is largely agricultural, with some residential use as well. The five counties in the study are some of the highest producers of fruits and vegetables in the U.S. and have a combined population of about 250,000. Most of the population relies on groundwater as a drinking source, and some people in the rural areas have groundwater as their sole source for drinking water (Viers, et al., 2012). The report concluded that many of the inhabitants of this region are at a significant risk of drinking nitrate contaminated water and families in the lower income strata are more likely to have a higher risk for exposure to nitrate contaminated drinking water. More importantly, the report highlights that the source of the nitrate contamination observed today was applied at the surface years or decades ago and predicts that the nitrate problem will only get increasingly worse, as farmers apply more fertilizers now than they did decades ago.

The findings by the State Water Board are significant because: (a) longer drought periods cause lower precipitation, may increase dependence on groundwater for irrigation and drinking water. Increased dependence on groundwater for irrigation and as a drinking water source means that the nitrate contaminated water will be increasingly recycled and groundwater aquifers may decrease their storage capacity which makes any further addition of nitrate even more significant. (b) nitrate contamination in the region is a widespread problem; though nitrate fertilizers may only be applied at a localized farming region, the interconnectedness of groundwater aquifers and complex pathways through which nitrate moves will increase the impact area of contamination. (c) lower income families have a higher potential for drinking nitrate contaminated water as groundwater might be the only source for drinking water; and (d) nitrate is being considered a legacy contaminant, which means that the nitrate concentrations being observed today were applied years before even, decades. With the growing reliance on synthetic fertilizers for agricultural practices, it is speculated that any nitrate leaching from the surface into the groundwater will not be detected until years later. This fact calls for researchers, scientists, and agriculturists to better manage application of nitrate to the soil and more importantly to reduce or prevent, whenever possible, the leaching of nitrate into the groundwater.

This study focuses on using soil amendments to slow down the movement of nitrate in the subsurface. A material that has gained some attention by researchers as a soil amendment is flyash. Flyash is a coal combustion byproduct (CCB), and is generally disposed of, or re-used as a concrete additive for its binding properties. The use of flyash as a liming agent, replacing lime and gypsum, in acidic soils has been documented by Yunusa et al. (2006). Researchers have also reported a significant increase in crop production of several products such as rice, wheat, maize, grass, mustard (Kalra, et al., 1998; Sarangi, et al., 2001; Basu, et al., 2009) when flyash was added as a soil amendment. However, most of these investigations combined flyash with some form of organic matter and could not conclusively say that the increased crop yield was directly correlated to flyash addition. Though flyash has been shown to increase crop yield in some instances (Kalra, et al., 1998; Sarangi, et al., 2001; Basu, et al., 2009), researchers are still very cautious about recommending flyash as a soil amendment for concerns over the possibility of heavy metals leaching out of the flyash. Trace metal leaching from flyash is highly dependent on the type of flyash, the source of the parent coal, treatment and storage of flyash, whether flyash has been weathered or not, and amount of flyash.

Both, positive and negative, effects of flyash when used as soil amendment must be well understood before a recommendation can be made. Much research has been done to study the potential for trace elements leaching from flyash. Results from the various investigations indicate that trace element leaching from flyash is highly dependent on the alkalinity of flyash, chemical properties and pH of the leachant solution, distribution of elements, and the chemical composition and source of the parent coal (Ghodrati, et al., 1995; Iyer, et al., 2001; Iyer, 2002; Kim, 2002). Kim (2002) concluded that cations in flyash (including trace elements) are only slightly soluble and thus are not too prong to leaching. Kim (2002) also showed that elements tend to be more soluble when an acid solution is passed through the flyash, with arsenic being the only exception. Ghodrati et al. (1995) demonstrated that heavy metal concentrations in the leachate from flyash decreased rapidly as the leachate solution was passed through. This indicates that any soluble metals will be leached rapidly out of the flyash. Ghodrati et al. (1995) suggest that the harmful heavy metals leach out of the FA rapidly. If the heavy metals are leached out rapidly, it can be expected that the harmful trace elements might be washed out of the FA after being weathered; this weathering process can take place naturally while the FA is stored. Sarangi et al. (2001) showed that the flyash amended soil increased plant biomass and grain yield of rice; however they also noted that flyash retarded belowground biomass production. Though researchers have shown that flyash amended soil improves crop yield, they have not been able to attribute the increased crop yield entirely on flyash, instead it was attributed to various combinations of flyash, organic matter, and nutrients (via sludge or fertilizers). The inconsistencies and conflicting results of flyash incorporated to an agricultural system indicate that there is much room for further investigation, and a study on the effect of flyash on nitrate movement is lacking.

The present research will investigate the effect of flyash on the transport of nitrate through unsaturated media. Previous researchers (Ghodrati, et al., 1995; Van der Hoek & Comans, 1996) demonstrated that iron (Fe) has the possibility of slowing down nitrate transport, however, it was also shown that the nitrate concentration in an iron-rich soil was much higher at very low saturation level as compared to high saturation levels. These results are significant because flyash is, by nature, a ferro-alumino-silicate material and the iron contained in flyash may have a significant role in the transport of nitrate through the flyash-amended soil at different saturation levels. As such, the first part of this study will look at the effect that the amount of flyash added to the soil has on the transport of nitrate at different saturation levels. The latter part of the study will look at the effect that the amount of added flyash has on the hydraulic properties of the soils.

CHAPTER 2

Background

There are sixteen different nutrient elements essential for plant growth, which are divided into essential, primary, secondary, and micro nutrients. There are three essential nutrients, carbon (C), hydrogen (H), and oxygen (O_2), these essential nutrients are taken from atmospheric carbon dioxide and water and are usually abundant, thus are not of great concern (Tucker, 1999; Mosier, et al., 2004; Addiscott, 2005). The primary nutrients, nitrogen (N), phosphorous (P), and potassium (K), are usually applied in mixed fertilizers. Mixed fertilizers include one or more of the primary nutrients; the grade of a specific fertilizer is designated based on the percentage (as a ratio) of each nutrient, i.e. a 10-10-10 grade fertilizer provides equal amounts (10%) of N, P, K nutrients. The secondary nutrients, calcium (Ca), magnesium (Mg), and sulfur (S), are required in smaller amounts than primary nutrients. Micronutrients include, iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), chlorine (Cl), boron (B), and molybdenum (Mo). Micronutrients are those required in even smaller amounts (Tucker, 1999).

Of the primary nutrients, nitrogen is required by the plants in the largest amount. Nitrogen promotes rapid growth, increases quality and size of leafs, accelerates crop maturity, and promotes fruit and seed development (Tucker,1999). Additionally, nitrogen plays an important role in almost all plant metabolic processes because nitrogen is a constituent in amino acids, which are required to synthesize proteins and other compounds (Tucker, 1999; Mosier, et al., 2004). It is nitrogen's essential role in the rapid growth of the plants, quality sought by farmers, which makes it the most used nutrient in fertilizers. Fertilizers that contain high nitrogen percent, as compared to the other two major nutrients, or fertilizer that contain only nitrogen are commonly used. The latter are known as nitrogenous fertilizers, most commonly used in large quantities to increase crop yields and shorten growth time. Common nitrogenous fertilizers include ammonium nitrate (34-0-0), urea nitrogen (46-0-0), sodium nitrogen (16-0-0), and liquid nitrogen (30-0-0). Of the four nitrogenous fertilizers (N-fertilizers) the most common is ammonium nitrate. Ammonium nitrate (NH_4NO_3) is used globally because it is easy to manufacture, it is relatively cheap and highly available, and it is in a form most favorable for plant uptake (Addiscott, 2005; Viers, et al., 2012). Even after ammonium nitrate is dissolved in water, its dissociated form leaves two ions: nitrate and ammonium. The plants can take up nitrate quite easily; ammonium can be readily converted to nitrate by soil microbes through a process known as nitrification making ammonium nitrate a preferred fertilizer.

It is believed that the first non-organic nitrogen fertilizer used was gas liquor from coal gas production (Addiscott, 2005). Early sources of nitrogen fertilizers include (i) ammonium sulfate, produced by heating coal in coking ovens to produce coke for industrial purposes; (ii) Peruvian guano, bird excrement deposited over thousands of years in the Chincha Islands off the coast of Peru, this guano contained about 15% nitrogen; and (iii) Chilean nitrate, this nitrate source was variable in nitrogen amount 10-70% (Smil, 2001; Addiscott, 2005). The widespread use of inorganic fertilizers would not have been possible without the work done by Fritz Haber and Carl Bosch, from Germany in the early 1900's. Haber and Bosch developed the process by which ammonium is synthesized at high pressures and temperature (Smil, 2001; Addiscott, 2005). The synthesizing process known as the Haber-Bosch Process, have led to the development of virtually all synthetic fertilizers. Though the Haber-Bosch process was developed in the early 1900's, widespread use of nitrogen fertilizer by farmers only started in the mid-twentieth century. Figure 2.1 shows the progression of nitrogen fertilizer use throughout the past century. It is undoubtedly evident that our dependence on nitrogen fertilizer has been in direct response to the increased world population. As Smil (2001) points out, we would only be able to feed about 40% of today's world population without the use of nitrogen fertilizers. Furthermore, Smil (2001) argues that the world has not only become dependent on nitrogen fertilizers, but we have become increasingly dependent on Haber-Bosch process derived fertilizers, as seen on Figure 2.2.

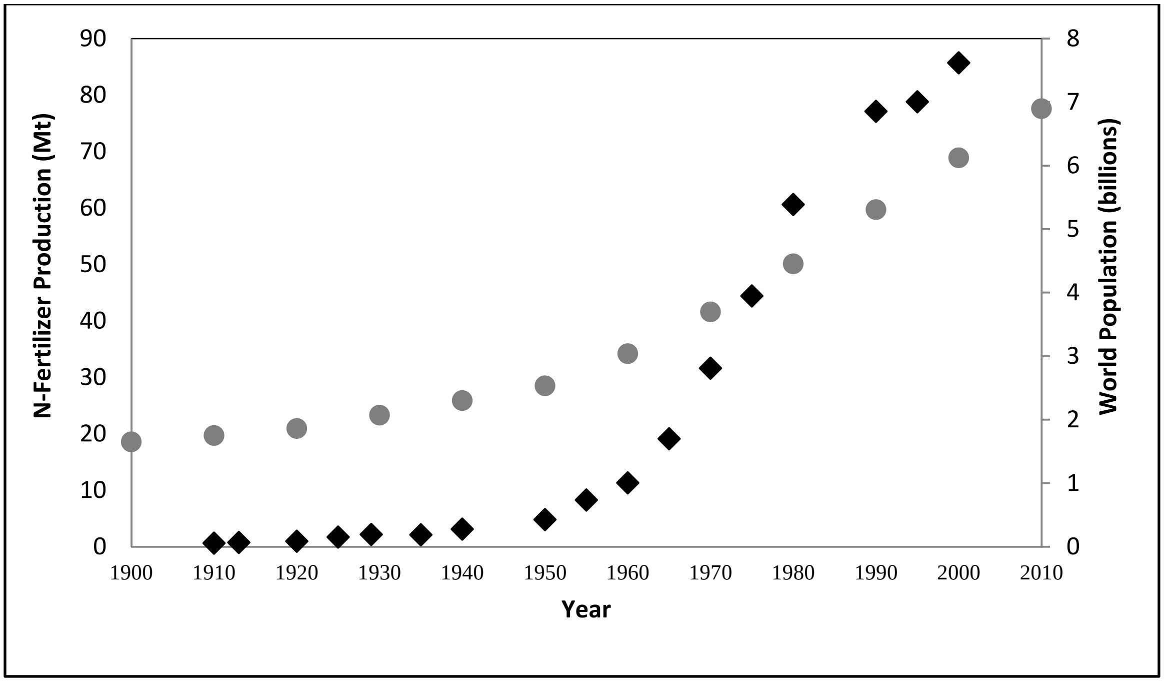

Figure 2.1. World fertilizer production (black diamond) & World population (grey circle) between 1900 and 2010. (Based on Appendix L of Smil, 2001 and United Nations, 2011)

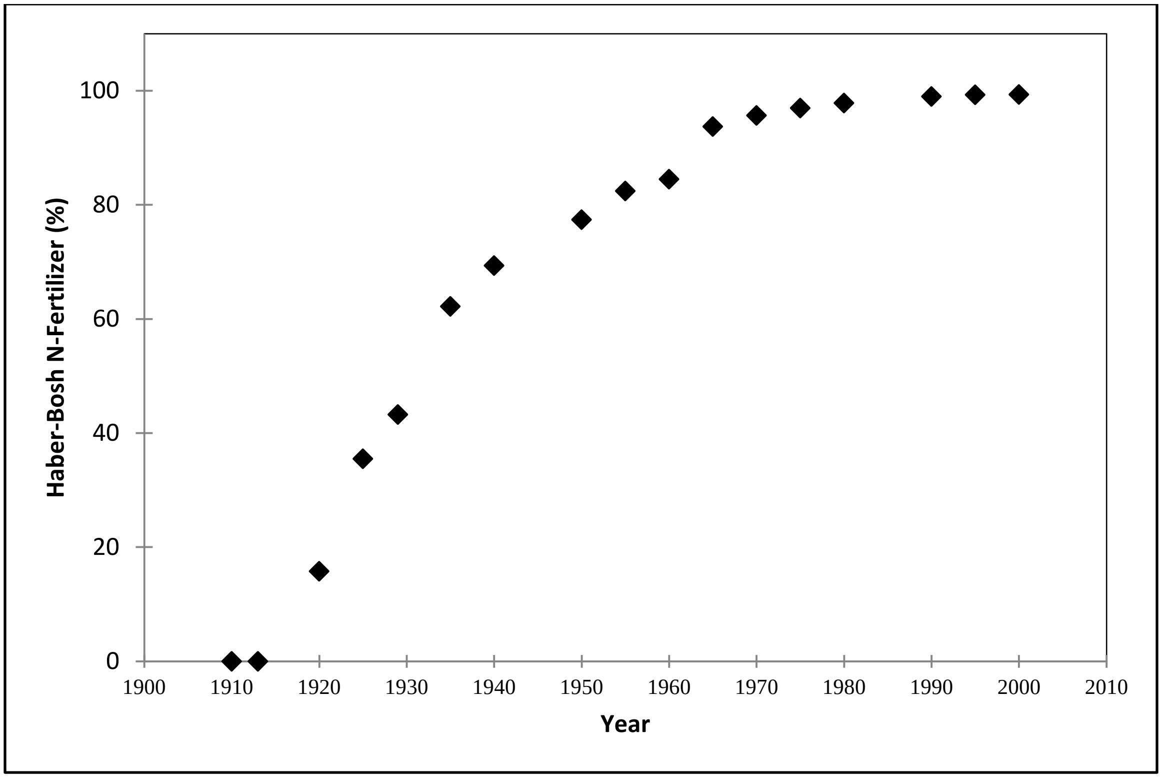

Figure 2.2. Percentage of global nitrogen fertilizer produced by the Haber-Bosch process, 1910-2000. (Data from appendix L of Smil, 2001)

The global agriculture's dependence on nitrogen fertilizers means that we cannot simply stop using fertilizers and still expect to feed the growing population. New agricultural methods and practices must be explored in order to grow enough food while reducing use of fertilizers. The problem with the dependence on nitrogen fertilizers is that farmers must apply large quantities of the fertilizer to make nitrogen available to the plants. The over-application of nitrogenous fertilizers means that a large amount of nitrogen (in the form of nitrate) is made available to leach into the groundwater causing a potential threat to human health and the environment. The mechanism through which nitrate is transported from the surface to the groundwater is complex and depends on various factors. Nitrate transport depends on the soil pH, amount of nitrifying bacteria, rates of nitrification, amount and type of mineralizing bacteria, rate of mineralization, soil properties such as hydraulic conductivity and saturation level and other factors. Because the transport mechanism is so complex, it is difficult to determine the amount and rate of nitrate leaching into the groundwater. However, it is widely known that a large percentage, up to 70 percent, of the nitrate applied at the ground surface will be leached out into the groundwater (Mosier, et al., 2004; Addiscott, 2005)

Nitrate's high susceptibility to leaching, the over application of nitrogen fertilizers, and the global agriculture's dependence on fertilizers have led scientists to search for ways to reduce the nitrate loading or improve the nitrate use efficiency of plants or farming systems as a whole. Some scientists, most notably in Europe, have looked at the possibility of using flyash as a soil amendment, as a possible source of plant nutrients (Mittra, et al., 2005; Pandley, et al., 2009; Basu, et al., 2009; 21 163). These scientists proposing incorporation of flyash into the agriculture claim that it may increase nutrient loading to the plants in hopes of increasing crop yield or reduce fertilizer application. These researchers, however, point out that flyash lacks any significant amount organic carbon or nitrogen; this lack of nitrogen would have to be compensated through the application of fertilizers. The author could not find any research that has looked at the relationship between the direct application of flyash and fertilizer savings. Flyash, a coal combustion byproduct (CCBP), is the mineral residue consisting of small particles carried up and out of the boiler in the flow of exhaust gases (Jala & Goyal, 2006). Flyash (FA) incorporation into the agricultural practices would have large implications because it reuses a byproduct of another necessary process and gives it a beneficial use, thus creating a cradle-to grave- to cradle scenario for the FA which would otherwise be sent to the landfill. However, the implications of FA use in agriculture must be well understood so that it can be safely and efficiently implemented. The present work will examine the effect of different flyash levels added to a loamy sand on nitrate transport under three soil saturation levels.

2.1 Nitrate

As discussed before, nitrogen is the most important essential nutrient for the plant growth. If organic nitrogen is not found naturally in the soil or if organic nitrogen has been depleted from the soil through agricultural practices, then nitrogen is provided through fertilizer application. There are two forms of nitrogen fertilizers: organic (e.g. poultry litter, animal manure, urea (from manure), compost, seaweed, etc.) and inorganic, also known as synthetic (e.g. ammonium nitrate, liquid nitrogen, urea, ammonium sulfate, anhydrous ammonia, etc.). From this point on, inorganic, synthetic and non-organic fertilizers are used interchangeably and are used to refer to synthetically produced fertilizers. Nearly all of the nitrogen used by plants is in the form of nitrate and to a lesser amount ammonium, however, ammonium tends to be readily converted to nitrate. Because of this, ammonium nitrate is the commercial fertilizer most widely used in agriculture. Ammonium nitrate (NH_4NO_3) provides a significantly large amount of nitrogen, 50% percent of the nitrogen is provided by the nitrate and 50% by ammonium; this fertilizer has a NPK ratio of 34-0-0. The nitrogen cycle must be reviewed and understood in order to understand the pathways for nitrate leaching into the groundwater and its implications to human health and environmental impacts.

2.1.1 Nitrogen Cycle

It is taken as a fact that: without the use of fertilizers, global agriculture would not be able to provide enough food for the world's population. If agricultural practices would have remained as those used in the early 1900s we would only be able to feed nearly 40-50 % of the population and with a smaller diet. It is argued by some, that the discovery of inorganic fertilizers (or the process of ammonia synthesis, known as the Haber-Bosch process) is one of the most important discoveries for mankind. It is undoubtedly one important discovery which allows us to produce enough food (and even more) than our bodies and current diets require; however, this discovery has also brought about unintended consequences which we have to deal with. Most notably the excess use of these inorganic fertilizers (from this point on, the author makes reference to N-fertilizers unless otherwise stated) may lead to environmental impacts and pose potential human health risks. It is therefore important to understand how these fertilizers move from the farm into the potential receptors and how these receptors may be connected to human health and the environment.

As previously noted, nitrogen is an essential element for all living organisms. Nitrogen is transported, used, converted and cycle through the atmosphere, hydrosphere and biosphere. There are many different processes through which nitrogen may be chemically or biologically converted in form. The main processes are nitrogen fixation, mineralization, immobilization, nitrification, and denitrification. These processes are shown in Figure 2.3. and are discussed next.

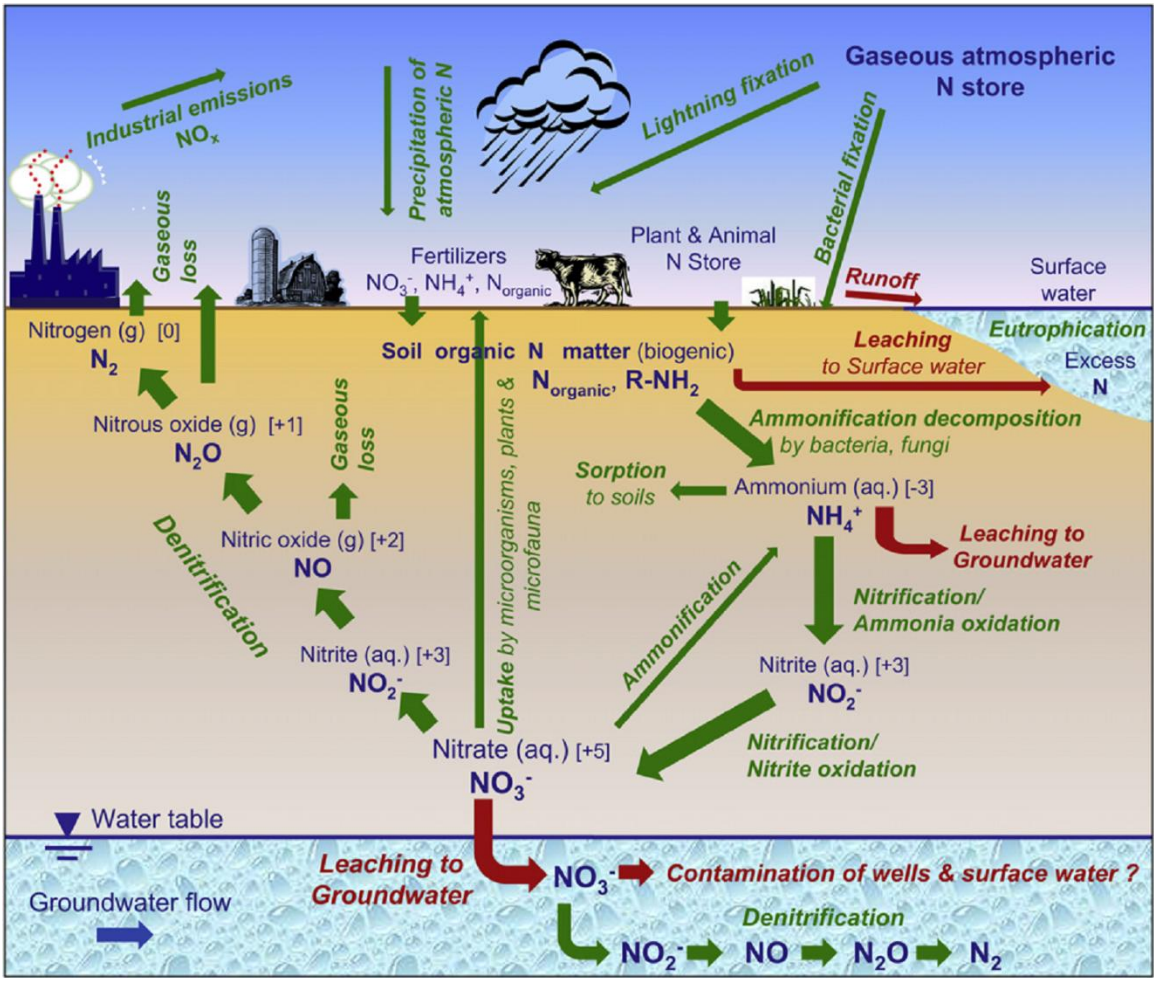

Figure 2.3. The nitrogen cycle (from Rivett et al., 2008)

Nitrogen is found in the atmosphere in the stable form of inert N_2 gas. Nitrogen is taken up from the atmosphere and it is biologically fixated, by specific microorganisms; this fixation converts N_2 to a nitrogen form which is favorable for plant use, i.e. ammonia, which in turn can be easily converted to nitrate or ammonium. Nitrogen fixation occurs at the ground surface. Not all plants can fixate atmospheric nitrogen, instead, they rely on soil organic matter accumulated, such as remains of plants, animals and microbial communities for nitrogen. Mineralization is a combination of processes by which soil microbes convert organic nitrogen, in the form of amino acid R-NH_2 from manure, organic matter and crop residue to inorganic nitrogen forms, mainly ammonium (Viers, et al., 2012). The rate of mineralization depends on the type of organic matter available and environmental factors, such as pH, temperature, available oxygen, and moisture. The first product of the mineralization is ammonia (NH_3) which is easily converted to ammonium (NH_4^+), however, under anaerobic conditions microbes can convert ammonium (NH_4^+) first to nitrite (NO_2^-) and then to nitrate (NO_3^-).

$$R - NH_{2\,(organic\ N)} \rightarrow NH_{3\,(ammonia)} \rightarrow NH^{+}_{4\,(ammonium)} \tag{2.1}$$

Immobilization is the opposite of mineralization; soil organisms take ammonium and nitrate and convert it to soil organic nitrogen, making it unavailable to crops. However, the lock-up of N by immobilization is only temporary, as the organic N contained in the cells will be converted by mineralization or nitrification to plant available nitrate as the microorganisms die off (Viers, et al., 2012).

$$NH^{+}_{4\,(ammonium)}\ and/or\ NO^{-}_{3\,(nitrate)} \rightarrow R - NH_{2\,(organic\ N)} \tag{2.2}$$

Nitrification is the process (chemical or biological) by which ammonium is oxidized and converted to nitrite; further oxidation converts nitrite to nitrate.

$$NH^{+}_{4\,(ammonium)} \rightarrow NO^{-}_{2\,(nitrite)} \rightarrow NO^{-}_{3\,(nitrate)} \tag{2.3}$$

Denitrification is the nitrogen reducing process which converts nitrate (NO_3^-) to a reduced form, the ultimate goal of denitrification is to convert nitrate to dinitrogen gas (N_2), however it is also possible that denitrification release nitrogen oxides (NO_x) gases as a byproduct. This process can be described as:

$$\mathrm{NO_3^-}_{\text{(nitrate)}} \rightarrow \mathrm{NO_2^-}_{\text{(nitrite)}} \rightarrow \mathrm{NO}_{\text{(nitric oxide)}} \rightarrow \mathrm{N_2O}_{\text{(nitrous oxide)}} \rightarrow \mathrm{N}_{2\,\text{(dinitrogen gas)}} \tag{2.4}$$

The rate of the aforementioned processes controls the nitrogen cycle and amount of nitrogen found in each of its available forms. Groundwater aquifers have become an important part of the nitrogen cycle because of nitrate's high susceptibility to leaching. Nitrate does not adhere to or react with most geologic materials, making it easy to leach down to the groundwater, once nitrate reaches the aquifer it moves with the groundwater flow. The amount, concentration, and form of nitrogen entering the groundwater aquifer varies and is dependent on the source as well as some environmental factors, i.e. pH, temperature, moisture, etc. Nitrate sources may be industrial, urban, agricultural and natural. The main sources of natural nitrate include bedrock nitrogen and nitrogen leached from natural soils (Viers, et al., 2012). Additionally, the conversion of arid and semi-arid landscape to irrigated agricultural area created an additional source of nitrate by mobilizing the previously accumulated organic nitrate in the soil (Viers, et al., 2012). Anthropogenic sources of nitrate in the groundwater include agricultural cropland, animal manure, waste water treatment plants (WWTP), food processors, septic drainage systems, animal corrals, parks, defective urban sewer lines, lawns, dry wells, storm water recharge, industrial nitrous-oxide emissions (Addiscott, 2005; Viers, et al., 2012).

The focus of this study is on nitrate derived from fertilizer application at the farm scale. The upper portion of Fig. 2.4. depicting the nitrogen cycle at a farm scale, shows the soil surface-atmosphere interface; this interface receives direct application of most of the nitrate inputs, i.e., runoff, fertilizer application, and nitrogen fixation by plants and microorganisms. The middle section represents the top soil; this section is the region where most of the activity (i.e. nitrogen transformation) takes place. Typically, the top soil consists of the upper 6 inches of soil, but can reach depth of 25 inches. The third region is the subsoil. This last region is of little importance because it is typically unavailable to the roots, any nitrogen accumulated in this region is prone to leaching to the underlying groundwater.

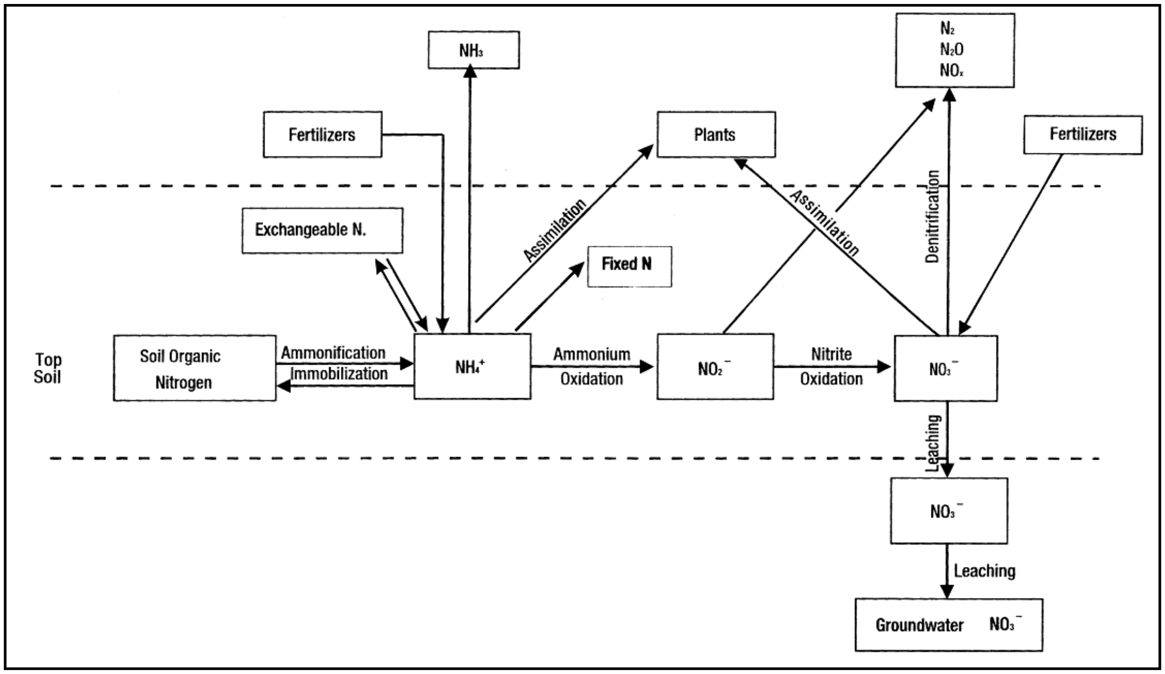

Figure 2.4. Localized nitrogen transformation at the farm scale (from Rao and Puttanna, 2000)

2.1.2 Nitrate and Human Health

Nitrate has long been associated with methemoglobinemia, an impairment of oxygen transport in the blood commonly known as "blue baby syndrome", in infants - generally three months old or younger. In 1945 Hunter H. Comly (1945) published a paper linking infantile cyanosis and nitrate from drinking water pulled from a well. Comly described two specific cases and cited three additional cases where infants expressed symptoms of cyanosis. Comly (1945) noted that these infants' families all lived in rural areas and obtained their drinking water from privately owned dug-wells which was also used to prepare milk formula for the infants. Chemical analysis from these wells revealed that they all had elevated concentrations of nitrate, as high as 140 mg L^{-1} (nitrate-N). Comly and other researchers (Comly, 1945; Downs, 1950; Campbell, 1952; Knobeloch, et al., 2000; Ward, et al., 2005) maintain that ingested nitrate (NO_3^-) from drinking water can be reduced to nitrite (NO_2^-) in the infant's gastrointestinal tract. Though nitrate itself is mostly harmless, as it can be easily absorbed and excreted, the potential for its reduction to nitrite persists. If nitrite reaches the bloodstream it can react with hemoglobin (Hb), which is a metalloproteinase in red blood cells in charge of transporting oxygen. The hemoglobin contains iron (Fe^{2+}) which can react with the nitrite; the product of this reaction is an oxidized form of hemoglobin known as methemoglobin (metHb, now containing Fe^{3+}) which leads to the impaired delivery of oxygen to vital organs (Schmidt, 1956; U.S. NRC, 1972; Avery, 1999; Knobeloch, et al., 2000), this reaction is represented by Equation 2.5:

$$NO_2^- + oxyHb(Fe^{2+}) \rightarrow metHb(Fe^{3+}) + NO_3^- \qquad (2.5)$$

The lack of oxygen produces symptoms of cyanosis, causing the infants' skin to become blue-gray or purple in color. Methemoglobin is normally found at levels of 1-2 percent of the total hemoglobin in blood; clinical symptoms (cyanosis) are only expressed once the levels reach 10-15 percent and death may occur if the level of methemoglobin reaches 50-75 percent (U.S. NRC, 1972).

Following Comly's findings, various researchers started reporting similar cases of infants afflicted by cyanosis, though at varying degrees. Most of the reported cases were in rural areas, mainly in the mid-western U.S. and some cases in Europe. By 1965 there were 350 and 1,000 cases reported in the U.S. and Europe respectively, with 41 deaths in the U.S. and 80 deaths in Europe (U.S. NRC, 1972). Most of the reported cases of cyanosis were attributed to nitrate from drinking water with just a few related to nitrates in food. It is also important to note that only infants are susceptible to methemoglobinemia, older babies and adults are more tolerant to nitrate contaminated water. The indirect link between nitrate in drinking water and levels of methemoglobin in the infants' blood, led the U.S. Public Health Service to establish a strict limit on the permissible concentration of nitrate in drinking water. This limit was set at 44 mg of nitrate L^{-1} (equivalent to 10 mg of nitrate-N L^{-1}). The World Health Organization (WHO) also set the limit of 45 mg of nitrate L^{-1} (equivalent to 11 mg of nitrate-N L^{-1}) (WHO, 2011). In 1971 with the establishment of the U.S. EPA and the passage of the Safe Drinking Water Act of 1974 the Maximum Contaminant Level (MCL) for nitrate in drinking water supplied by any public agency was established by a federal agency.

Though the link between nitrate in drinking water and human health has been established for over sixty years, this view has been challenged in recent years. Strong evidence now exists that endogenous nitric oxide/nitrite production, triggered by intestinal infection rather than exogenous dietary nitrate intake, is responsible for the symptoms described as being that of cyanosis (McKnight, et al., 1999). Recent research shows that methemoglobinemia may be caused by genetic deficiencies in key methemoglobin-reducing enzymes, exposure to oxidant drugs and chemicals (including nitrite), and genetic abnormalities in hemoglobin that make the protein more susceptible to oxidation (Avery, 1999). However, the possibility of nitrate being reduced to nitrite persists. The debate on whether the MCL for nitrate is too strict remains, however, all researchers still agree that the MCL for nitrite is appropriate (1 mg L^{-1} NO_3-N). Whether nitrate, directly or indirectly, causes methemoglobinemia is a question that remains to be answered, however that discussion is beyond the scope of this study.

2.1.3 Nitrate and the Environment

The over-application of nitrogen fertilizers can be extremely detrimental to the environment, especially because N-losses are a function of the amount of application, rather than the source of the nitrogen (Di & Cameron, 2002; Peoples, et al., 2004). The leaching of nutrients applied at an agricultural site can reach groundwater aquifers and may be carried on to other fresh water bodies such as lakes and rivers. It is well known that fertilizer derived nutrients directly contribute to nutrient loading in water which may lead to the deterioration of aquatic and terrestrial ecosystems.

This nutrient unbalance may lead to eutrophication , especially if there is an excessive amount of nitrogen or phosphorous, two of the major nutrients required by plants and the ones most used in fertilizers. Here, in discussing eutrophication, the author refers to the anthropogenic or "artificial" addition of nutrients to a water body. Though nutrients (i.e., nitrogen (N) and phosphorous (P)) occur in natural environments, they do not usually exceed the established MCLs and are known as limiting nutrients. Winneberger (1982) points out that a lake may become eutrophic, naturally, in geologic time, however, this process is slow and could take decades. The problem with eutrophication of lakes is the increased rates at which they receive leaching nutrients, essentially speeding up a process which would otherwise be naturally slow. Anthropogenic sources provide nutrients at rates and concentrations much higher than any natural geologic process could potentially provide.

Eutrophication is one of the most pronounced manifestations of increased contamination of a water body. Though there are many sources of the anthropogenic nutrients, cropland is by far the largest source of nitrate, contributing up to 90 percent of all nitrate leached to groundwater in some regions (Harter, et al., 2012). The increased input of nutrients stimulates the growth of algae and phytoplankton; slimes and the growth of blanket weed (Cladophora) may reduce the visual appeal of the lake and may lead to changes in the dominant fish species present or the death of all fish (Sawyer, 1966; Lund, 1972). When the algae or plankton dies off, it is deposited at the bottom of the lake. Once the dead algae have settled at the bottom, they are digested by bacteria such as protozoa and worms (Sawyer, 1966), this requires oxygen to be consumed. This process leads to the depletion of oxygen near the bottom surface of the lake creating an anoxic condition which is unfavorable to some fish species. Additionally, the algal blooms or blanket weeds reduce sunlight infiltration creating a stratified lake with a warm layer of water overlying a cooler anoxic layer. Whether eutrophication is good or bad for a lake is a question that has been debated in the past, however, in recent years it has been established that the rates at which nutrients are being supplied to the various water bodies are more detrimental than beneficial for these water bodies.

Though research in soil science, crop science, aquatic environments and environmental engineering have significantly contributed to the understanding of the fate of nitrate in the groundwater and other natural water bodies, there is still opportunity to reduce the nutrient loading to natural water bodies derived from anthropogenic agricultural sources. In the next 50 years, the growing demand for food to feed the growing population will create a greater stress on a fragile environment. This greater demand of food may lead to an increasing intensive farming system and the widespread use of N-fertilizers, and if not managed properly, may exacerbate and accelerate nitrate contamination and subsequent degradation of groundwater aquifers and other fresh drinking water resources.

2.2 Flyash

One of the ways in which nitrate losses can be minimized is by incorporating better fertilizer-crop management practices. Among these management practices, researches have studied the use of N_2-fixing plants, N-fixing bacterium, early soil tillage, crop rotation, and various soil amendments. Of the proposed soil amendments, flyash seems to have caught the interests of scientists. Flyash (FA) is produced as a byproduct of coal combustion power plants. FA is described as a heterogeneous mixture of amorphous and crystalline phases and is generally a fine powdered ferroaluminosilicate material with Al, Ca, Fe, Na, and Si as the predominant elements. Certain elements like

B, Mo, S, Se are characteristically enriched in FA particles as well (Lokeshappa & Dikshit, 2011). The attractive aspect of using FA as a soil amendment is that by definition, it is a coal combustion byproduct (CCBP), making FA inexpensive and readily available. Furthermore, it is currently being investigated for its potential to provide additional nutrients (from the secondary and micronutrient classes discussed in Chapter 2) that are essential for plant growth.

Fossil fuel-burning power plants (i.e. coal, natural gas (dry), crude oil, and natural gas plant liquids) have been a dominant force of the energy sector in the U.S. for a long time. In 2012, coal accounted for 33.23 percent of the energy produced by all fossil fuels and 26.12 percent of the total energy produced by all sources (fossil fuel, nuclear, and renewable) in the U.S (U.S. EIA, n.d.; ACAA, 2011). Providing over one-quarter of the total U.S. energy requires a copious amounts of raw coal, which subsequently translates to considerable amounts of byproducts: CO_2 and other gases, flyash, boiler slag, bottom ash, flue gas desulfurization (FGD) gypsum, and other byproducts associated with coal combustion power plants. The latest figures indicate that in 2011, there were approximately 60 million tons of flyash produced and only 22.9 million tons were used, approximately 38.2% of FA produced (ACAA, 2011), leaving close to 60% of the FA unused. The majority of this flyash was utilized in civil and construction materials and/or projects with a small fraction applied to agriculture related activities: 567,476 tons used for soil modification or stabilization and 13,627 tons used for agriculture (ACAA, 2011). This underutilization creates an opportunity to increase the use of FA in agricultural applications. Flyash is a byproduct of a service which is essential, i.e., coal fired power, and will continue to be for decades, creating an abundant source of the resource which has to be utilized otherwise it will be stored and eventually disposed of, i.e. sent to landfill.

Flyash is classified, based on the percentage of calcium oxide (CaO also known as burnt lime) and the type of coal used for burning, as Class C flyash (CCFA) containing more than 20% CaO and Class F flyash (CFFA) containing less than 20% CaO. In addition to CaO, the major chemical components of flyash include SiO_2, Al_2O_3, and Fe_2O_3; the percent content of each component vary widely. The physical properties of flyash depend on the parent-coal type, boiler type, and collector setup, the ash content of the coal used, and the combustion method. Flyash generally has a silt loam texture with 65-90% of the particles having a diameter of less than 0.010 mm (Basu, et al., 2009). Ash particles are empty spheres (cenospheres) filled with smaller amorphous particles and crystals (plerospheres); the cenosphere fraction constitutes as much as 1% of the total mass and gets easily airborne (Jala & Goyal, 2006; Basu, et al., 2009; Pandey, et al., 2009; Pandey & Singh, 2010). Flyash is also characterized by its low bulk density, hydraulic conductivity and specific gravity. One of the concerns with FA is that it has been noted that the aluminum and iron oxides are situated at the surface of the FA particles and can attract toxic trace elements, such as Sb, As, Be, Cd, Pb, Hg, Se, and V, which tend to concentrate on the surface (Pandey, et al., 2009; Basu, et al., 2009; Pandey & Singh, 2010)

The chemical composition and concentrations in FA are influenced by the chemical content of the parent coal burned (i.e. lignite, anthracite, and bituminous). Several studies (Theis & Wirth, 1977; Kim, 2002; Basu, et al., 2009) found that the main components of flyash are Al, Fe, and Si, with smaller amounts of Ca, K, Na, Ti, and S.

The major elements Al, Fe, and Si are found in the forms of common minerals constituting FA including quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), hematite (Fe_2O_3) and magnetite (Fe_3O_4) (Petrik, et al., 2009). They also found some trace metals in varying amounts. Some of the trace metals found in FA may be essential to plants and animals, but they may be toxic at higher concentrations. Flyash contains essential macronutrients including P,K, Ca, Mg, and S, and micronutrients like Fe, Mn, Zn, Cu, Co, B, and Mo (Basu, et al., 2009). The potential for plants to absorb and use the nutrients found in FA make it an appealing material to be used as an amendment to the soil. However, all nitrogen and carbon is depleted during the burning process, thus FA lacks any significant amount of organic carbon and nitrogen. Even if FA is used as a soil amendment and source of nutrients, N will remain scarce, and needs to be provided through external application, i.e., with the use of fertilizers.

2.2.1 Flyash Application in Agriculture

The overproduction as a CCBP, the underutilization, its chemical composition, physical properties, the silt-sized particles, and the calcium oxide content make flyash an attractive soil amendment. Flyash contain a significant amount of calcium oxide (CaO) which can be used to replace agricultural lime used to regulate soil pH, though the CaO content depends on the type of coal used during combustion, both CCFA and CFFA have been used for its lime content. Flyash has also been proven to reclaim previously unusable mine soils. Fail and Wochok (1977) proved that the addition of FA was effective as an acid soil neutralizer and enhanced the growth and development of plants. They tested the growth of several plants (i.e. bentgrass, Sericea lespedeza, Kentucky 31 fescue, and soybeans) and found that FA amended soil increased growth and total yield as compared to the non-amended soil. Furthermore, Petrik et al. (2003) showed that FA incorporated to acid mine drainage may be able to neutralize these hazardous waste streams. FA has also been proposed as an amendment for pyritic mine tailings. Pyrite (FeS_2) in wastes and mine spoils is oxidized to form sulfuric acid, resulting in a highly acidic soil; FA may help suppress the pyrite oxidation (Pandey, et al., 2009). The incorporation of FA to acid mine soils and tailings seems to be promising, however, it seems that this application can only support a minimum amount of FA and still leaves the opportunity for a large-scale application for the re-use of FA.

A possible large-scale application for FA can be found in agriculture. Several works have proposed the use of FA as part of a nutrient management system, relying on the fact that many of the essential macro- and micronutrients are found in FA, though at varying concentrations. In addition to its chemical properties, FA has gained attention because of its physical properties, i.e., low bulk density, small particles (silt sized), and high surface area. FA added to an agricultural soil results in overall lower bulk density of the soil, increased pore space, and increased available water (Fail & Wochok, 1977; Pandey, et al., 2009; Pandey & Singh, 2010). This properties are favorable for plant growth because lower soil bulk density and increased pore space allows a greater plant growth by reducing the burden of soil on the plant root. The increased available water and reduced hydraulic conductivity of the soil (Schumann & Sumner, 2000) means the water drainage is slowed down, which allows the plant root enough time to absorb additional water which would otherwise have drained out and lost. Several workers (Schumann & Sumner, 2000; Adriano, et al., 2002; Pathan, et al., 2003) used FA as a soil amendment for turf growth. Adriano et al. (2002) applied high amounts of FA, as high as

1120 tones ha^{-1}, and saw no significant difference in dry plant mass; however, they revealed that turf grass, and other non-food plants similar to the one studied, can tolerate high levels of FA without showing a toxic effect and does not threaten the groundwater via chemical leaching. Pathan et al. (2003) showed that FA amended soils yielded increased root mass and concluded FA to be suitable for turf culture on sandy soils without adverse effects on plant chemical composition.

Utilization of FA was shown to be beneficial for non-food agriculture and yielded positive results for the production of turf grass. However, if FA is to find increased use in agriculture it should also be able to be used for agronomic-crops. Workers have found that FA addition generally increases crop yield and nutrient uptake. It has been demonstrated to improve yields of wheat (Triticum aestivum L.), mustard (Brassica juncea L.), rice (Oryza sativa L.), and maize (Zea mays L.), alfalfa (Medicago sativa), barley (Hordeum vulgare), Bermuda grass (Cynodon dactylon), bentgrass (Agrostis tenuis var. Highlander), and white clover (Trifolium repens), Sericea lespedea (Lespedeza cuneata), Kentucky 31 fescue (Festuca arundinacea), soybeans (Glycine max cv. Bragg), and peanut (Arachis hypogaea) (Fail & Wochok, 1977; Kalra, et al., 1998; Mittra, et al., 2005; Jala & Goyal, 2006). However, most workers have noted the lack of nitrogen, phosphorous, and carbon in FA, to overcome this, they suggest limiting FA application to crops capable of fixating N at high amounts, like alfalfa, spinach and soybeans or applying nitrogen through the use of fertilizers.

2.2.2 Reservations About the Use of Flyash

The chemical composition of flyash can serve as a source of nutrients, as seen in Section 2.1.1.; however this same chemical composition is of concern because in addition to its nutrient content FA also has some trace elements which are known to be toxic. During the combustion process, FA gets concentrated with trace metals such as arsenic (As), selenium (Se), lead (Pb), copper (Cu), mercury (Hg), zinc (Zn), chromium (Cr), boron (B), nickel (Ni), and cadmium (Cd), among others, whose concentrations vary depending on the type of coal used (Adriano, et al., 2002). The reservation about using FA in agriculture stems from the possibility of these trace metals leaching out of the FA possibly affecting groundwater but most importantly, these trace metals may end up in the crop. Ferraiolo et al. (1990) noted that plant tissues had increased concentrations of S, Mo, B, and other non-essential trace elements such as Al, Se, and Sr; they suggested that Mo, As, Ba, Rb, W, and V showed an accumulating pattern on plant issue due to FA application. However, Ferraiolo et al. (1990) also noted the positive impacts of FA on an agricultural soil and agricultural production of potato, beet, and maize. Lokeshappa and Dikshit (2011) cite chromium as being the most important element limiting FA utilization in agriculture. The chromium can easily migrate from FA to water solution under common environmental conditions and has the potential to accumulate in the plants.

The potential for trace element leaching from FA is persistent and may limit the application in agriculture. The mechanism by which these trace elements are leached out is complex and depends on the pH of the invading solution and may be complicated by the dynamics of surface interactions (Van der Hoek & Comans, 1996; Iyer, et al., 2001; Iyer, 2002). It has also been shown that trace elements are not very soluble and generally remain in their insoluble form, causing the leaching to be a very slow process (Lokeshappa & Dikshit, 2011), however, under aggressive environments (pH < 4 and pH

> 9) trace element mobilization may occur due to dissolution at low pH or desorption at high pH (Jegadeesan, et al., 2008). These observations were reinforced by Kim (2002) who studied trace element leaching from FA over an extended period of time and found that most cations are only slightly soluble and the metals were only slightly more soluble when subjected to an acid leachant ($pH < 2$). The previous results show that the incorporation of FA into an agricultural system may indeed be possible without having a tremendous effect to human health. However, the results and conclusions regarding the leaching of trace elements from FA are varied and can contradict each other.

2.3 Flyash in Agriculture and Nitrate

The production of flyash in the U.S. has been steadily increasing since record keeping. The American Coal Ash Association (ACAA) reports that FA production in the U.S. increased from 17 Mt (million tons) in 1966 to 59 Mt in 2011, reaching a maximum of 76.5 Mt in 2002. Flyash use has followed a similar trend as the production with 1.4 % used in 1966 and 38.2 % used in 2011 (ACAA, 2011). The production and use of FA can be seen in Fig. 2.5, based on this figure it can be expected that both, the production of FA and FA use, will continue to increase at a seemingly steady pace. However, a large percentage of FA still remains unused. This FA will be stored (for future use) or sent to a landfill for disposal and burial. As seen on the previous sections, it is possible to increase FA utilization by incorporating it into an agricultural system. Many researchers have used FA to increase the production of several crops (See Section 2.2.1) however there exists contradictions regarding the potential of leaching trace elements from FA application to the soil (See Section 2.2.2).

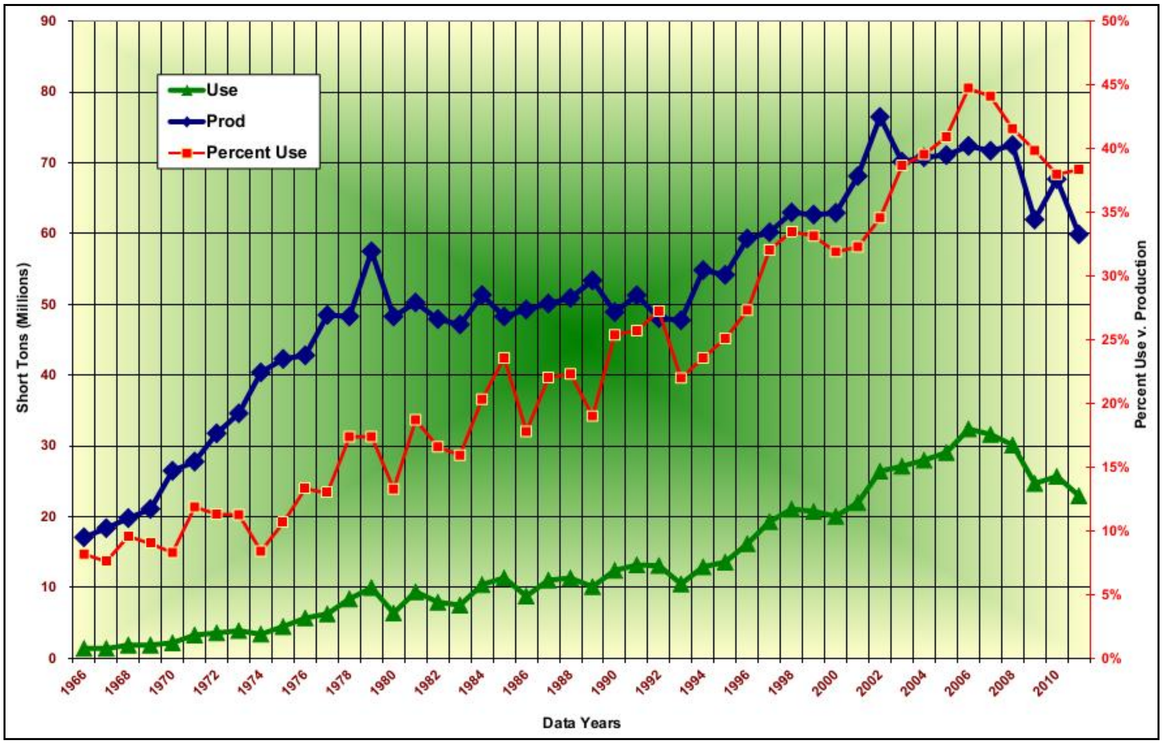

Figure 2.5. Flyash production and use, from 1966-2011 (ACAA, 2011)

The chemical composition of FA, which includes all the elements found in coal but at different concentrations, has been touted as a possible source for plant nutrients. However, the lack of nitrogen and phosphorous, essential nutrients for plant growth, has been noted by various researchers and would have to be provided via an external application, i.e., fertilizers. Using FA as part of a nutrient management system, researchers have proposed that FA may help reduce fertilizer use (Ferraiolo, et al., 1990). However, no previous studies were found to investigate the direct interaction between FA application and fertilizer savings. If FA is to be incorporated into a nutrient management system, it is important to evaluate any potential fertilizer savings so that all effects, both positive and negative, are known before making the decision to incorporate FA in agriculture at a large scale. The amount of flyash that remain unused warrant the need to explore different avenues for the beneficial utilization of an otherwise 'useless' coal combustion byproduct.

2.4 Objective

The objective of the present study is to investigate the relationship between rates of FA application and saturation levels of a sandy soil on the leaching of nitrate fertilizers. A Class-F flyash (CFFA) was used for this investigation. The FA was obtained from a co-generating power plant located in Trona, CA (obtained through Diversified Minerals Inc.). This co-generation facility obtains its coal source from various sources around Utah. Coals mined in Utah are mostly classified as bituminous and sub-bituminous. For this investigation a steady-state centrifuge-unsaturated flow apparatus (SSC-UFA) was used to investigate the hydraulic properties of the FA amended soil. The specific objective can be summarized as follows:

- Observe the leaching of nitrate as a function of time and soil moisture content.
- Observe the influence of flyash amendment on nitrate transport.
- Postulate an interpretation of the dynamics of nitrate transport under unsaturated conditions through different levels of flyash amendments.
- Analyze the effect of flyash amendment on the hydraulic properties of the soil.

CHAPTER 3

Materials and Methods

3.1 Materials

The following is a list of the materials used to conduct the unsaturated soil experiments:

- Bentonite (Montmorillonite K-10, Acros Organics)
- Sand (pure sand, 40-100 mesh, Acros Organics)
- Class F Flyash (Diversified Minerals Inc., Flyash source: Trona, CA co-generation power plant)
- Deionized water (DI Water. Source: Fisher Scientific, Nanopure)
- Ammonium Nitrate (NH_4NO_3 - Sigma-Aldrich A3795)
- Unsaturated Flow Apparatus, UFA:
    - Centrifuge - Beckman Coulter J6-MI
        - Rotor (JE-6B)
    - Volumetric Infusion Pumps (AVI Micro 210A)
    - Dispersion cap
    - Specimen holder
    - Specimen cup
    - Conical dispersion cap
    - Effluent collection chamber
    - Sample assembly cup
    - Plastic burettes and tubing
- Ion Chromatograph (Metrohm 882 Compact IC plus)

- Ion Chromatograph Auto-sampler (Metrohm 881 Autosampler)
- Conical Tubes - (BD Falcon)
- Polyethersulfone Membrane Filters - 0.2 microns (VWR Scientific)
- Gloves
- Lab coat
- Safety goggles
- Lab notebook

3.2 Methods

3.2.1 Soil Preparation

A sand-clay soil mix was prepared by mixing bentonite clay with pure sand. The soil mix was prepared with five percent bentonite by weight, this mix was treated as the base soil. Bentonite clay was added to the sand in order to improve its texture and workability, also, sand alone has faster infiltration rates and thus is prone to higher rates of leaching. Class F flyash (CFFA) was added as an amendment to the soil mixture at four different levels: 0%, 2%, 10%, and 20% flyash, by weight. The four amendment levels were designated as: no flyash (NFA), low flyash (LFA), medium flyash (MFA), and high flyash (HFA), respectively. The soil and FA amendment were mixed in batches of 1 kg in a medium container so as to leave room for the soil to be mixed thoroughly. Flyash particles are small, 60-90% of particles are less than 0.010 mm in diameter, and may get airborne easily. Therefore, mixing in a large container was considered the best alternative as mixing and transferring from another container may have resulted in a significant loss of FA particles.

3.2.2 Unsaturated Flow Apparatus

The steady-state centrifuge - unsaturated flow apparatus, SSC-UFA (simply referred to as UFA herein), shown in Fig. 3.1 was used to control hydraulic properties under unsaturated conditions for the study of the fate and transport of nitrate. Two identical specimen assemblies are attached to the UFA as shown in Fig. 3.2 during each test, for stability and validation purposes. The unsaturated soil in the UFA reaches steady-state when the weight of the specimen under observation does not change. The UFA must be stopped and the soil specimen is weighed, once the weight of the specimen does not vary over three consecutive weigh-ins, it is determined that the specimen has reached steady-state. The time it takes for a soil to reach steady-state depends on the physical and hydraulic properties of the soil, the rotation speed of the centrifuge, and the flowrate of the fluid being pumped through the soil.

The UFA allows the operator to control the variables of fluid flux and driving force in Darcy's Law. Darcy's Law states that the flux is equal to the hydraulic conductivity of the material times the driving force. Using the UFA the water is driven by both the matric potential gradient and the centrifugal force per unit volume, Darcy's Law then is given by Eq. 3.1(Conca et al., 1997):

$$q = -K(\psi)\left[\frac{d\psi}{dr} - \rho\omega^2 r\right] \tag{3.1}$$

Figure 3.1. Unsaturated flow apparatus and pump setup

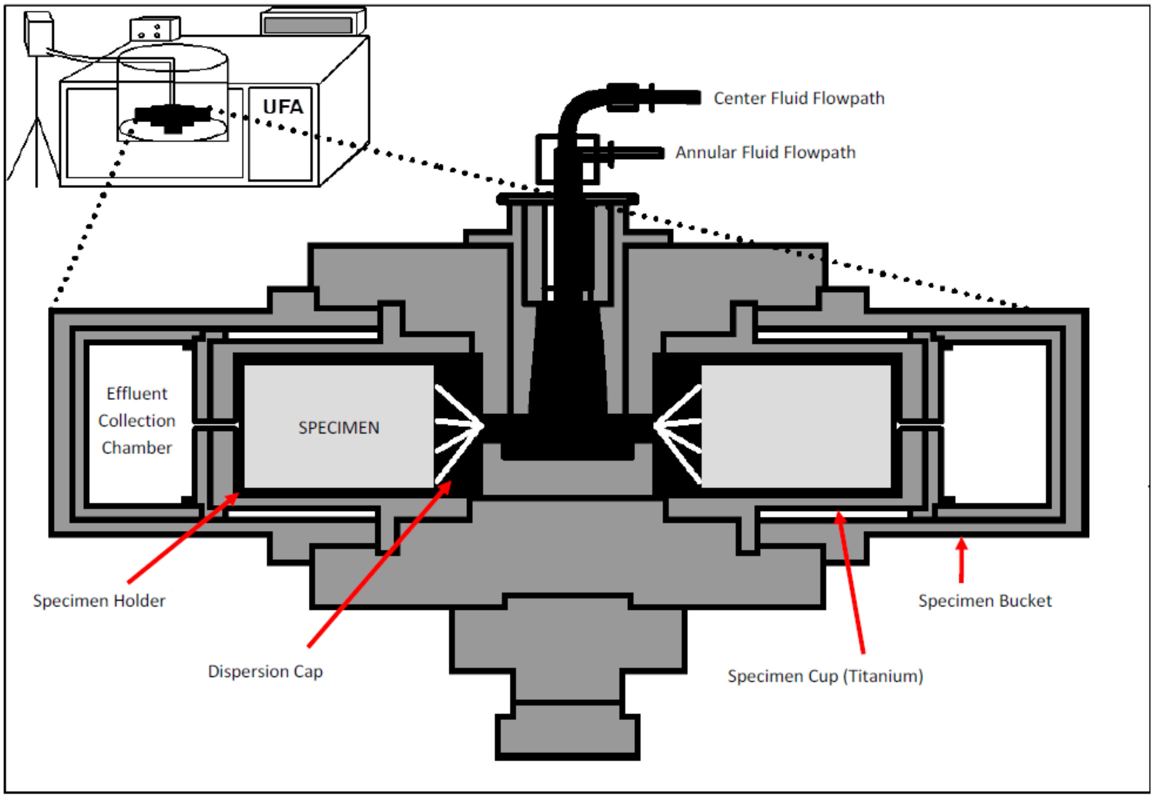

Figure 3.2. Schematic of SSC-UFA rotor. (Adapted from Conca and Wright, 1998)

where q is the fluid flux density into the sample, K is the hydraulic conductivity, ψ is the matric potential, $d\psi/dr$ matric potential gradient, $\rho\omega^2 r$ is the centrifugal force per unit volume, r is the radius from the axis of rotation, ρ is the fluid density, and ω is the rotation speed in radians per second. The hydraulic conductivity can be represented as a function of either matric potential or volumetric water content. If sufficient flux density exists, the matric potential is much less that the acceleration, $d\psi/dr \ll \rho\omega^2 r_.$ This is true above speeds of about 300 revolutions min^{-1}, provided that sufficient water flux density exists, Equation 3.1 then becomes:

$$q = -K(\psi)[-\rho\omega^2 r] \tag{3.2}$$

The dimensional analysis is:

$$(cm\ s^{-1}) = (cm\ s^{-1})(g\ cm^{-3}\ s^{-2}\ cm) \div 980.67(dynes\ cm^{-2} cm_{H_2O}^{-1}) \tag{3.3}$$

where dyne = g cm s^{-2}. The denominator converts the units from acceleration (g-force units) to a force per unit volume relative to water (ASTM-D6527A, 2008). The water flux density using the UFA is determined by the flowrate (set on the infusion pump) and the cross-sectional area of the specimen. Thus rearranging Eq. 3.2 and representing the hydraulic conductivity as a function of the volumetric water content gives Equation 3.4 (Menezes et al., 2011; Singh & Kuriyan, 2002).

$$K(\theta) = \frac{q}{(\rho\omega^2 r)} \tag{3.4}$$

where *K* is hydraulic conductivity, θ is the volumetric water content, q is flowrate, ρ is the density of the fluid, ω is the rotation speed, and r is the distance from the axis of rotation to the center of the soil sample. The hydraulic conductivity is a function of the volumetric water content, θ (Conca & Wright, 1998; Vogel, et al., 2000; Singh & Kuriyan, 2002). Using the UFA setup, the user controls the water flux, i.e., the flowrate being delivered from the infusion pumps, and the rotation speed. To run a de-saturation run the first step is to estimate the saturated hydraulic conductivity of the specimen. Once this has been determined, the maximum conditions to be used are calculated. The water retention curve (i.e. the K(θ) relationship described using Eq. 3.4.) is developed by operating the UFA under conditions similar to those shown in Table 3.1. the rotation speed (r) and flowrate (q) are increased and decreased, respectively, once it has been determined that the specimen has reached steady state. The soil water retention curve for a sand-clay mix is shown in Figure 3.3. The level of saturation for the specimen is given by Equation 3.5.:

$$\mathrm{S} = {}^{\theta}/_{\theta_{Sat}} \tag{3.5}$$

where S is the level of saturation and ranges from 0-1, θ is the volumetric water content at any given time and θ_{Sat} is the volumetric water content of a fully saturated sample. Using Equation 3.5 the saturation level is determined, the working range of saturation levels is then calculated along with the flowrate and rotation speed necessary to maintain a constant saturation level. The target saturation level ranges: 0.25-0.35 (low-saturation, LS), 0.45-0.55 (medium-saturation, MS), and 0.80-0.95 (high-saturation, HS) were chosen.

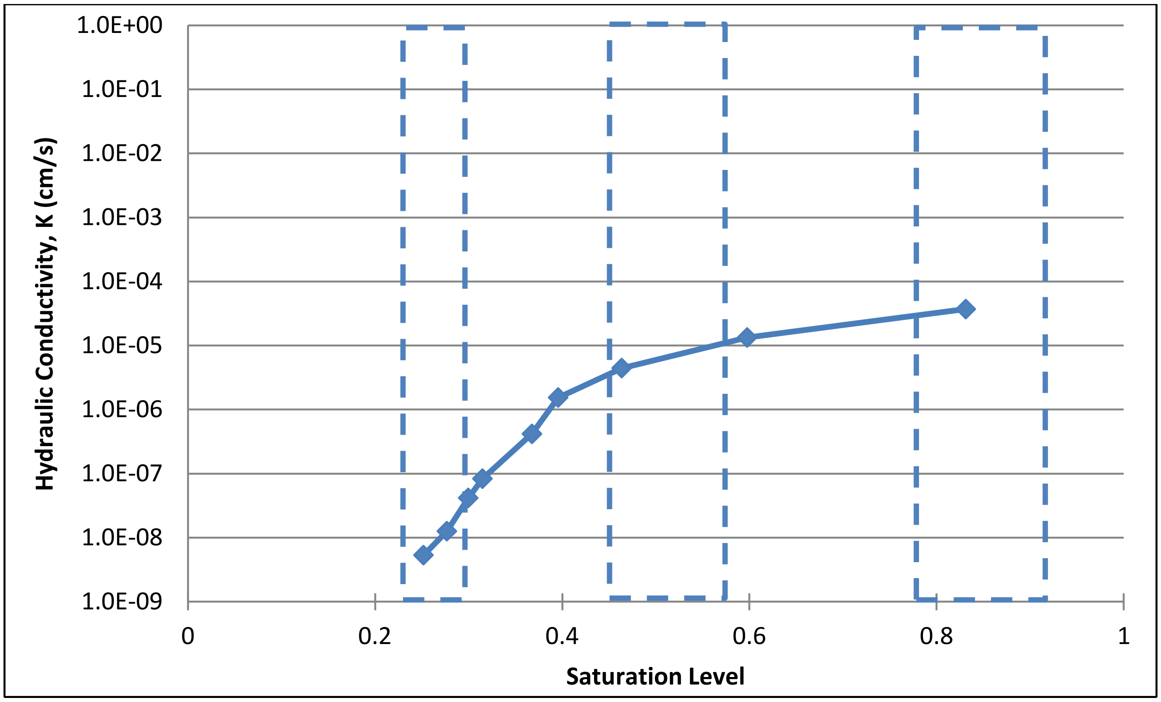

Figure 3.3. Water retention curve for clay-sand soil mixture. Dotted box represent the target range for low-, medium-, and high-saturation levels.

3.2.2.1 Preparation of a sample

The soil must be fully saturated before it is placed inside the UFA. The soil preparation was performed as described in ASTM-D6527. Start with a clean specimen holder and record its weight, a filter paper is placed at the bottom of the specimen holder and their combined weight recorded. The filter paper is sprayed with DI water so as to damp the paper without having too much water. After the filter paper has been wetted, the sample holder is filled with ~5 grams of soil at a time, the soil is compacted using a one-kilogram hand piston, once it is compacted the soil layer is sprayed with DI water and another layer of soil is added. Adding soil in small layers, compacting and damping the top of each soil layer enhances the cementing process therefore reducing the layering effect. Once the sample holder has been filled with soil, it is placed in a small beaker. Deionized water is carefully poured into the beaker until the water level reaches the maximum height of the sample holder. The sample holder is then covered and allow to rest for twelve hours, this is enough time for any air bubbles to be pushed to the top by the water seeping from the bottom of the sample holder. The sample holder and sample holder plus the filter paper are weighed and recorded.

3.2.2.2 Running the UFA for Hydraulic Conductivity De-saturation Curve

After the sample rests enough time to allow for any entrapped air to be pushed out by water then the sample is assumed to be fully saturated with no air bubbles entrapped. The weight of the sample holder and saturated sample is recorded. The specimen holder is placed on the table and the conical dispersion cap is placed inside the specimen holder, the sample holder is carefully lowered into the specimen holder, the sealing o-ring is placed on the sample holder whilst making sure that the soil remains untouched, finally the dispersion cap is screwed in place and lightly tightened. The effluent collection chamber is then placed on the table, specimen holder set on top and pressed down making sure it slides smoothly and evenly until it is tightly secured with the o-ring from the collection chamber. The specimen assembly is then attached to the UFA rotor making sure the air vent in the collection chamber is pointing upwards, finally the specimen bucket is positioned and tightened. The same process is repeated once more and two samples are inserted on the centered- and axial-line fed positions. After the two samples have been positioned and secured, the UFA is closed and programmed. The settings that need to be adjusted are the rotation speed and time for each step. Table 3.1 shows the typical settings for a complete de-saturation test.

Table 3.1.

Typical Settings for a Hydraulic Conductivity De-Saturation Test

Rotation Speed (RPM)	Flowrate (ml/hr)	Time
400	40	2 hrs
600	40	2 hrs
1000	30	2 hrs
1800	15	3 hrs
2000	5	4 hrs
2000	1	8 hrs
2000	0.5	8 hrs
2300	0.2	10 hrs
2500	0.1	14 hrs

The UFA's feed lines must be purged before the specimen assembly is connected to the rotor to ensure that there is no air bubbles entrapped. To prepare the feed lines, the plastic burette is filled with DI water and placed above the pumps. The line is opened and fluid is allowed to move though to the secondary stopper. The plastic burettes are then flushed to ensure that there is no air inside, and finally they are positioned in the piston casing inside the pump. The next step is to connect the feed line to the UFA, once connected set the pump rate at 99.9 ml/hr and start the pump until the fluid reaches the distribution mechanism inside the rotor and some fluid comes out and stop the pumps. This ensures that there will be no air to prevent the fluid from passing, furthermore, this guarantees that the sample will receive the fluid immediately after the pump has been started. After the pump lines have been prepped, the specimen assemblies are connected to the rotor as described above and the pump flowrate is set.

Once the time, speed, and flowrate are set in the UFA and pumps respectively, the UFA can begin operating. The pumps should begin operation only once the UFA has reached two thirds of the set speed, similarly the pumps are stopped only after the rotor reaches two thirds of the speed. The minimum speed and maximum flowrate varies for different soils and is based on their saturated hydraulic conductivity. The duration of each step is based on the time it takes for the fluid transport to reach steady-state under each of speed/flowrate combination settings and may vary for different soils. When the flowrate is too high, the volume being delivered by the pump must be monitored to ensure that the effluent collection chamber does not overflow, if this is the case the UFA must be stopped, effluent collection chamber must be emptied, and UFA restarted. At the end of each step the specimen holder is taken out, weighed, and placed back in position for the next step. At the end of the test, the specimen holder and soil is weighed one last time. The soil is then transferred to a drying cup, weighed, and is dried in a drying oven at 106^{o}C for 24 hours. Once the soil is dry, the weight of the dry soil is determined and recorded. The soil water retention curve can then be constructed using Equation 3.3

3.2.2.3 Running the UFA for Matric Potential

To determine the relationship between the level of FA amendment and matric potential and consequently water retention as a function of a force applied to the soil, a matric potential experiment was setup. The soil sample is prepared as described in Section 3.2.2.1, however, instead of using a dispersion cap on top of the specimen, a solid cap is used. Thus the soil starts from fully saturated and is de-saturated by changing the rotational speed of the centrifuge. Using centrifugation to determine matric potential, i.e., fluid retention, in a sample makes the assumption that a pressure and an acceleration are equivalent in their effect (Conca & Wright, 1998). This occurs only at equilibrium, when the sample is no longer draining. In this setup, UFA is setup and the sample drains until the matric potential gradient is equivalent and opposite to the centrifugal force at each point. The rotation speed is then raised to a new value similar to those shown in Table 3.2, and the sample drains until the matric potential gradient is equivalent and opposite to the centrifugal force. The pressure difference is calculated using Equation 3.6 (Conca & Wright, 1998)

$$P = \left({\rho\omega^2}/{2g} \right)(r_1^2 - r_2^2) \tag{3.6}$$

where P is the equivalent pressure difference (cm of H_2O), g is the acceleration due to gravity (981 cm/s^2), r_1 is the radial distance to the sample top (cm), r_2 is the radial distance to the sample bottom (cm), ω is the rotation speed (radians/s), and ρ is the fluid density (g/cm^3).

Table 3.2.

Typical Settings for a Matric Potential Experiment

Rotation Speed (RPM)	Time	Pressure Equivalent (kPa)
300	24 hrs	4.29
600	24 hrs	17.17
800	24 hrs	30.52
1100	24 hrs	57.70
1300	12 hrs	80.59
1500	12 hrs	107.30
1800	12 hrs	154.51
2100	12 hrs	210.31
2500	12 hrs	298.05
3000	12 hrs	429.20
3500	12 hrs	584.18
4000	12 hrs	763.02
4750	12 hrs	1075.97
5500	12 hrs	1442.58

3.2.2.4 Running the UFA for Nitrate Breakthrough Curve

To run the UFA for a breakthrough curve of nitrate, the soil samples were prepared as described in Section 3.2.2.1. The sample was placed inside the UFA in the rotor assembly connected to the feed lines. Initially, DI water was connected to the feed lines and was used until the soil sample reached steady state for the desired saturation range. After steady state was reached, the plastic burettes feeding the lines were replaced by ones filled with the nitrate solution. The UFA-setup was then reinitiated, maintaining the same flowrate, q, and rotational speed, ω. The UFA was stopped and leachate collected over small intervals for the first 2 to 3 pore volumes, after which the intervals were increased. The leachate was transferred to a clean and sterile conical tube for storage and transfer.

3.2.3 Ion Chromatograph

The samples collected from the UFA collection chamber as described in Section 3.2.2.3 were transferred to the Hydrogeology lab for Ion Chromatography (IC) analysis. The samples were analyzed based on Method 9056A of the EPA's Test Method SW-846 (U.S. EPA, 2007). The samples were stored refrigerated at 4 °C and analyzed within 48 hours after being collected to prevent any nitrate loss due to microbial interaction. The first step taken was to filter the samples using a 0.2 µm polyethersulfone membrane syringe filter, transferring the filtered sample into a clean conical tube. After the samples have been filtered, a two step dilution process was performed; in the first step, the original filtered sample is diluted one-hundred times, in the second step, the diluted samples are used and they are diluted ten-times, transferring to new tube at each step. The result of the two-step dilution is a sample dilution of one-thousand, which is within the range of detection for the IC instrument used. Once the samples have been analyzed in the IC, the nitrate concentrations for each sample can be calculated. A calibration sample, with known ion concentrations, was used for Quality Assurance (QA). The QA sample was run after every 5-10 samples. Further, to ensure Quality Control (QC) of the data analysis, a duplicate sample was analyzed at random approximately every 10-15 sample analysis.

CHAPTER 4

Results and Discussion

4.1 Hydraulic Properties

The hydraulic properties of the FA amended soil were evaluated using the methods described in Section 3.2.2. The average of the measured saturated volumetric water content (θ_{Sat}) and bulk density (ρ_b) for all the FA treatments are shown in Table 4.1. The standard deviations are shown in parenthesis. The results show that the bulk density of the soil samples increases linearly with the level of FA. Other workers (Basu, et al., 2009) have found that the bulk density decreases with the addition of FA, this is the case for this soil, however, the bulk density reflected in this study is the bulk density of the soil after it has been compacted into the soil column. The goal was to get a uniform compaction for all the soil samples, regardless of FA amendment level, and thus the bulk density increased. The results also show the level of FA added to the soil increases the water capacity, represented by the saturated water content. However, there is a significant decrease in the water capacity for the HFA (20% FA) as compared to the control (NFA).

Table 4.1.

Average Saturated Volumetric Water Content and Bulk Density (Standard Deviation Shown in Parenthesis).

	NFA	LFA	MFA	HFA
θ_{Sat}	31.22% (0.86%)	34.97% (0.59%)	34.04% (0.55%)	29.54% (1.20%)
ρ_b	1.51 (0.02)	1.59 (0.01)	1.67 (0.02)	1.83 (0.03)

The unsaturated hydraulic conductivity was evaluated for a specific set of conditions, flowrate (q) and rotation speed (ω), set at the infusion pump and the UFA, respectively. The initial conditions were chosen such that, the hydraulic conductivity was as close as possible to the saturated hydraulic conductivity. The soil sample was weighed periodically in order to empty out the leachate from the effluent collection chamber, preventing it from overflowing. Once the weight remained constant (±0.1 g) over two consecutive measurement, it was assumed that the soil had reached steady-state. Upon reaching steady-state conditions the flowrate and rotation speed were adjusted so as to reduce the hydraulic conductivity. This procedure was repeated until the hydraulic conductivity had been reduced by five orders of magnitude, taking an average of ten distinct steady-state hydraulic conductivity samples. The results were plotted in Fig. 4.1. and show that FA addition improves the water retention and decreases hydraulic conductivity.

The level of FA seems to shift the K(θ) function to the right, almost linearly, however, the HFA amendment behaved differently. The K(θ) function of HFA initially remains closer to saturation and decreases quasi-linearly. The plot of the K(θ) shows that HFA has two inflection points, when the soil is close to fully saturated and as it approaches the residual water content, in contrast the other three samples have one inflection point, located near the halfway-point between the saturated and residual water content. Furthermore, these results show that in terms of unsaturated hydraulic conductivity, there seems to be little change between MFA and HFA, therefore, there seems to be little advantage to the hydraulic conductivity by doubling the amount of FA from 10 percent to 20 percent. These results are also important in quantifying the effect of flyash on the hydraulic properties of the soil. Research on flyash amended soil has focused largely on the crop yield resulting from flyash applied at different rates, however, there seems to be a discrepancy in the recommended amount of FA. Researchers have proposed using from 10-200 ton ha-1 (Kalra, et al., 1998; Basu, et al., 2009) up to 1120 ton ha-1 (Adriano, et al., 2002), and 5-40% wt/wt (Ghodari, et al., 1995; Kalra, et al., 1997; Pathan, et al., 2003; Basu, et al., 2009), however there seems to be a lack of consensus as to the optimal amount of flyash added as an amendment. Several workers have proposed 20% (wt/wt FA) as an optimal amount for several factors, however, based on the results presented in Fig. 4.1. there is not a significant improvement of 20% FA over 10% FA.

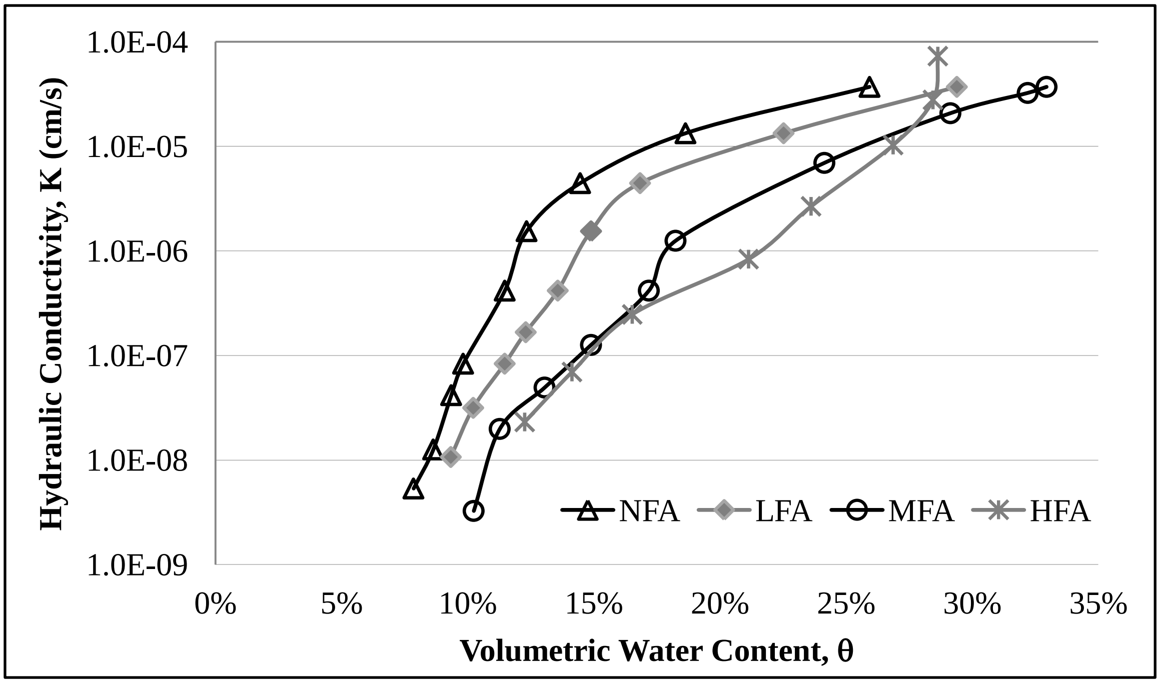

Figure 4.1. Hydraulic conductivity of soil as a function of volumetric water content

In addition to the unsaturated hydraulic conductivity, a separate experiment was setup to investigate the water retention of the FA amended soils. The procedure for this experiment was described in Section 3.2. Each experiment was conducted over ten consecutive days. The experiments for NFA and MFA were stopped 36 hours prior to completion due to mechanical failure of the apparatus; however, the data obtained was enough to provide the trends observed in Figure 4.2. The results show that the water retention increases with an increase of FA. It is observed that there is little difference between the control (NFA) and the low-flyash application (LFA). The data shows that a soil amended with 2% FA will hold about the same amount of water as a sample without FA amendment. However, as the level of flyash is increased, the water retention is also increased. Assuming the trend continued for LFA and MFA, it can be seen that the residual water content (the water content that will be retained by the soil regardless of the pressure applied) clearly correlates with the level of FA added to the soil. The increased water retention properties of FA amended soil has been attributed to the small particle size of the flyash (Ghodrati, et al., 1995; Kalra, et al., 1997) which changes the soil texture and classification, depending on the amount of FA. In contrast with the unsaturated hydraulic conductivity, it can be seen that 20% FA is significantly different from 10%.

Incorporating FA into an agricultural soil management program can now be evaluated based on two objective criterion: a) improve hydraulic conductivity (i.e., lower the hydraulic conductivity) of the soil, therefore, slowing down the leaching of water and fertilizer and b) improve moisture retention. A decision can be made based on these two criteria. Based on the hydraulic conductivity data, it would be recommended to use 10%

FA; however, addition of 20% FA offers a major improvement to moisture retention, as compared to 10% FA, 2% FA, and 0% FA additions. It is expected that the improved hydraulic properties of the soil with the FA amendment, would also contribute to the soil structure, porosity, and workability of the soil. Furthermore, the reduced hydraulic conductivity and increased moisture retention offer the potential to retain nitrogenous fertilizers for a longer period of time, thus allowing a longer contact time between the plant root and nitrate leading to nitrate savings through improved nitrogen use efficiency and reduced rates of leaching.

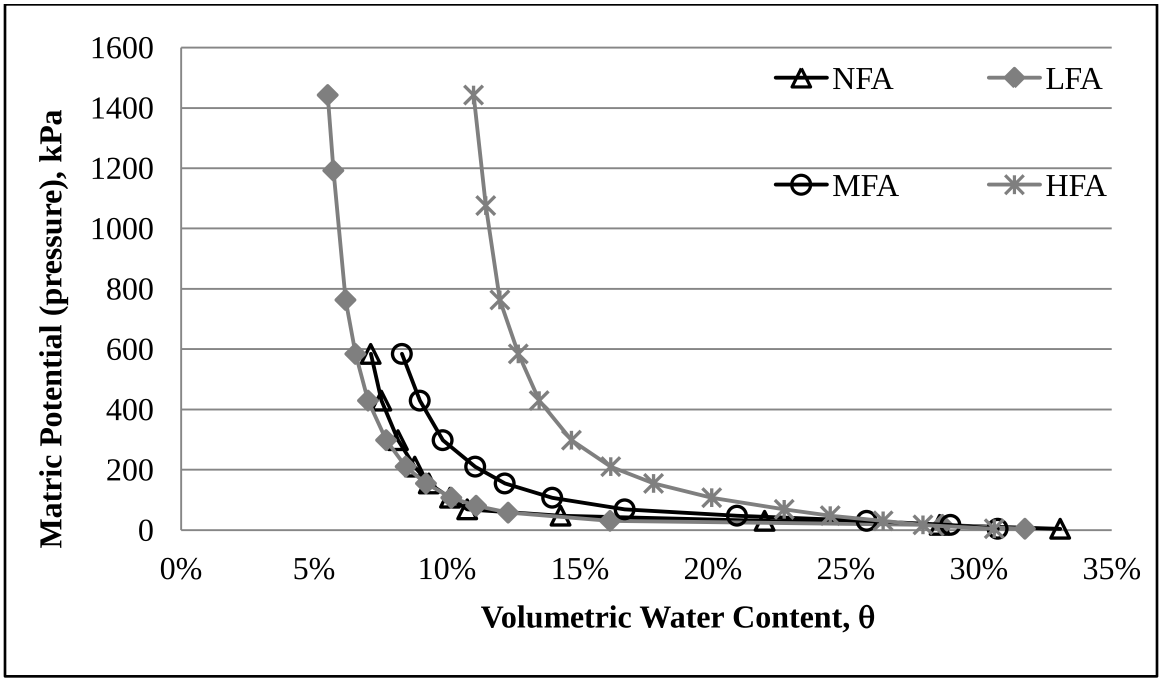

Figure 4.2. Soil-water characteristic curve of FA amended soils

Using the data obtained from Table 4.2 the plant available water storage capacity (AWSC) was calculated using Equation 4.1

$$\theta_{AWSC} = \theta_{FC} - \theta_{PWP} \tag{4.1}$$

where θ_{FC} is the volumetric water content at field capacity and θ_{PWP} is the permanent wilting point. The field capacity of soil is the volumetric water content of a soil after infiltration stops, the soil is drained, and the matric potential starts to take a role in the drainage process. This is typically considered to occur at a matric potential equivalent to -10 to -33 kPa. The permanent wilting point is the minimal soil moisture the plant requires not to wilt and typically occurs at a matric potential equivalent to -1.5 MPa. The estimated θ_{AWSC} were 18.84 %, 16.67 %, 19.76 %, and 16.15 %, for NFA, LFA, MFA, and HFA, respectively. The water holding capacity, therefore is only improved with the addition of 10% FA as the other two samples are shown to decrease the plant available water of the soil.

4.2. Nitrate Transport in Flyash Amended Soils

To assess the different levels of FA amendment's effect on nitrate leaching, a small cylindrical soil sample was prepared and subjected to a centrifugal force using the unsaturated flow apparatus (UFA). Controlling the centrifugal acceleration, i.e., the rotation speed of the UFA centrifuge, and the fluid flux, i.e. flow rate delivered through the external infusion pumps, allows the user to 'impose' the hydraulic conductivity of the soil. The volumetric water content values obtained during the experimental determination of the hydraulic conductivity, shown graphically in Fig. 4.1., were converted to saturation levels using Eq. 3.5. After calculating the saturation levels for each amendment level and plotting K Vs. S, three saturation ranges and their corresponding operating conditions (q and ω) were determined. Three target saturation levels were chosen, namely, 0.30 (low saturation), 0.55 (medium-saturation), and 0.85 (high-saturation). Though initially, the target saturation levels were 0.25, 0.50, and 0.90, respectively, it was difficult to constantly maintain a soil sample under such high saturation level. Additionally, the amount of FA used as amendment reduced the hydraulic conductivity; conversely, the level of FA increased the moisture retained for a given hydraulic conductivity, making it difficult to reach the low saturation levels within good operational conditions. Thus the target saturation levels were adjusted accordingly.

The physical and hydraulic properties of the soils are shown in Appendix A. The experimental saturation level (and their respective standard deviation) of soils subjected to high-saturation conditions (target saturation = 0.85) were: 0.86 (0.05), 0.75 (0.02), 0.82 (0.01), and 0.92 (0.01), for the NFA, LFA, MFA, and HFA samples respectively. The difference between the operational conditions (q and ω) accounts for the nature of the changing hydraulic properties based on the level of FA contained. The results from Table A.1. demonstrate that the percent of flyash has an inverse effect on the saturated volumetric water content. The results are consistent for samples subjected to medium- and low-saturation conditions. The pattern of decreasing θ_{Sat} as the level of FA is increased and the data plotted on Fig. 4.1, sheds some light onto why there is a sharp decrease in hydraulic conductivity. These results show that when the soil is close to saturation, a small change in hydraulic conductivity will cause a large decrease in volumetric water content, leading to increased drainage when the soil is close to being fully saturated for all the samples, except for the HFA soil. It is therefore, important to understand the difference in soil-solution behavior with a change in saturation level.

Samples subjected to medium saturation (target saturation = 0.55) are presented in Fig. 4.4., and the corresponding data shown in Table A.2. The average saturation level achieved for these samples (and respective standard deviation) were: 0.44 (0.01), 0.48 (0.01), 0.54 (0.02), and 0.62 (0.00), for the NFA, LFA, MFA, and HFA samples, respectively. Table A.2. shows that θ_{Sat} decreases with an increase of FA while the soil bulk density increases with increasing percent of FA. Samples subjected to low saturation (target saturation = 0.30) are presented in Fig. 4.5., and the corresponding data shown in Table A.3. The average saturation level achieved for these samples (and respective standard deviation) were: 0.28 (0.01), 0.34 (0.01), 0.39 (0.02), and 0.41 (0.00), for the NFA, LFA, MFA, and HFA samples, respectively. These samples follow the same trend as those subjected to medium and high saturation: θ_{Sat} decreases and the soil bulk density increases with increasing percent of FA. During the experiments, the operating conditions were adjusted to be as close to the target saturation as possible, however, the variability in micro-pore structure, soil column packing, and soil composition changed the hydraulic properties of the soil. Data obtained from Fig. 4.1. was used as a guide to estimate the operating conditions, however, these estimates varied and thus the experimental saturation level was different from the target.

The leachate from the soil samples subjected to the specific saturation level was collected and analyzed for nitrate concentrations. The experimental results obtained are presented on Figures 4.3, 4.4, and 4.5. The dimensionless nitrate concentration C/C_0 was plotted on the *y-axis* and the effective pore volume, after nitrate injection began, was plotted on the *x-axis*. C is the concentration of the leachate collected at the outlet in the effluent collection chamber and C_0 is the concentration of the solution at the inlet. Here, the effective pore volume is defined as the average pore volume occupied by the fluid for the specified level of saturation. When the soil is fully saturated effective pore volume is equal to the total pore volume; an unsaturated soil sample will have a lower effective pore volume than the total pore volume. Two parameters that can be extracted from a breakthrough curve are: (a) the breakthrough point, defined at the point when $C/C_0 = 0.1$ and (b) the exhaustion point, also known as the equilibrium point, defined at the point when $C/C_0 = 0.9$. The breakthrough point defines the point at which the invading solute starts displacing the inner solute and begins to be detected at the outlet. The exhaustion point is the point at which the sorbent is no longer adsorbing any solute and the inlet and outlet concentrations begin to equilibrate and will tend to reach a concentration of $C/C_0 = 1$. An ideal breakthrough curve, with no adsorption or retardation would be represented by a step function (or a piston flow) in which C/C_0 would remain at zero until and would jump to $C/C_0 = 1$ instantly after one pore volume. However, a non-ideal solute and sorbent will create a sinusoidal due to adsorption of the invading fluid onto the solid particles (soil) and mixing between the invading soil and pore fluids.

The experimental results for the samples subjected to high saturation are presented in Figure 4.3. These results show that all four samples reach the breakthrough point after 0.7 effective pore volumes (EPV). After the samples have reached the breakthrough point, their respective concentrations rise rapidly until they reach the exhaustion point. The rate at which the concentrations rise is almost identical, with LFA having the steepest ascent followed by NFA, MFA, and HFA, respectively. The LFA and NFA samples reach the exhaustion point after 1.4 EPVs followed thereafter by MFA and HFA which reach this point at around 1.6 EPVs. The ascending curves, in the region between breakthrough and exhaustion, for the MFA and HFA are similar to those of NFA and LFA, but are shifted to the right. This shift is indicative of nitrate retardation, however, the difference is minimal. After the samples have reached the exhaustion point, the concentrations remain semi-constant around $C/C_0 = 1$ with very little variation between samples.

Results obtained from samples subjected to medium saturation are presented in Figure 4.4. These samples all have a distinct breakthrough point and converge near the exhaustion point. The samples reach the breakthrough points after only 0.2, 0.4, 0.6, and 0.8 effective pore volumes for LFA, NFA, MFA, and HFA, respectively. All samples then reach the exhaustion point at around 1.9 EPVs. After this, the concentrations rise at a slower rate and reach $C/C_0 = 1$ after 3 effective pore volumes and remain close to this concentration for the rest of the study. The results show that at medium saturation, the level of FA starts to have a more noticeable role in the transport of nitrate. It is observed that at medium saturation, the retardation of nitrate increases with an increase of flyash, expressed by the breakthrough curves being shifted to the right as the level of FA is increased. Furthermore, after the nitrate exhaustion point has been reached the NFA, LFA, and HFA concentrations stay at, or a little above, $C/C_0 = 1$; however, the MFA samples stay below 1. The behavior of the MFA breakthrough could be due to the reduced anion exclusion induced by the FA addition.

The results for those samples subjected to a low saturation are presented in Figure 4.5. These results are more complicated than the previous two cases. It can be seen that the level of FA has a direct impact on the retardation of the nitrate breakthrough curve, evidenced by the curves shifted to the right (while C/C_0 is increasing) with an increase in

FA. The NFA samples reach the breakthrough point at 0.3 EPV while the LFA, MFA, and HFA samples all reach breakthrough point at 0.6 EPV. The exhaustion point is reached at approximately 1.4, 1.4, 1.7 and 2.2 EPVs, for NFA, LFA, MFA, and HFA, respectively. Unlike the previous saturation levels, the nitrate concentrations of samples subjected to low saturation fluctuate and are generally above $C/C_0=1$. With the exception of LFA, all samples have nitrate concentrations $C/C_0 > 1$ after they reach the exhaustion point. After reaching the exhaustion point, the concentrations of LFA all remained below $C/C_0 =1$. This further reinforces the hypothesis that FA addition can potentially reduce anion exclusion effects between nitrate and the soil.

Initially it was presumed that these high concentrations could be part of the operational error, however, the quality check (QC) and quality assurance (QA) samples revealed that the nitrate samples are within 3% maximum error. Some of the samples subjected to low saturation have a concentration of up to $C/C_0 = 1.13$. Additionally, the possibility of operational or detection error was ruled out because three of the samples subjected to low saturations had concentrations >1.0 after the exhaustion point. Further research onto the phenomena observed in Figure 4.5, and to a lesser extent on Figures 4.3 and 4.4, points to anion exclusion as being the cause of these concentrations that surpass the input concentrations.

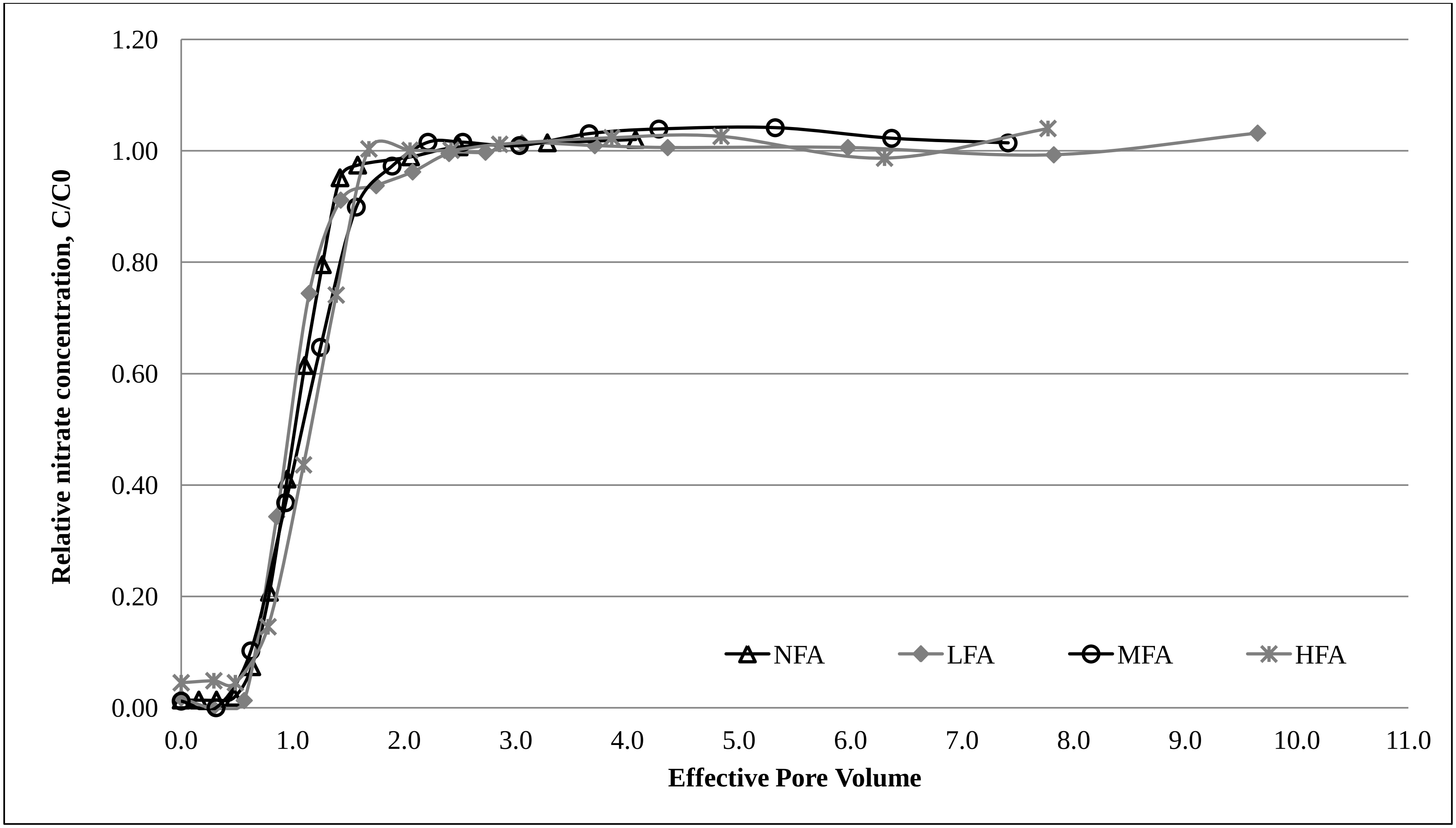

Figure 4.3. Nitrate breakthrough curve for soils subjected to high-saturation

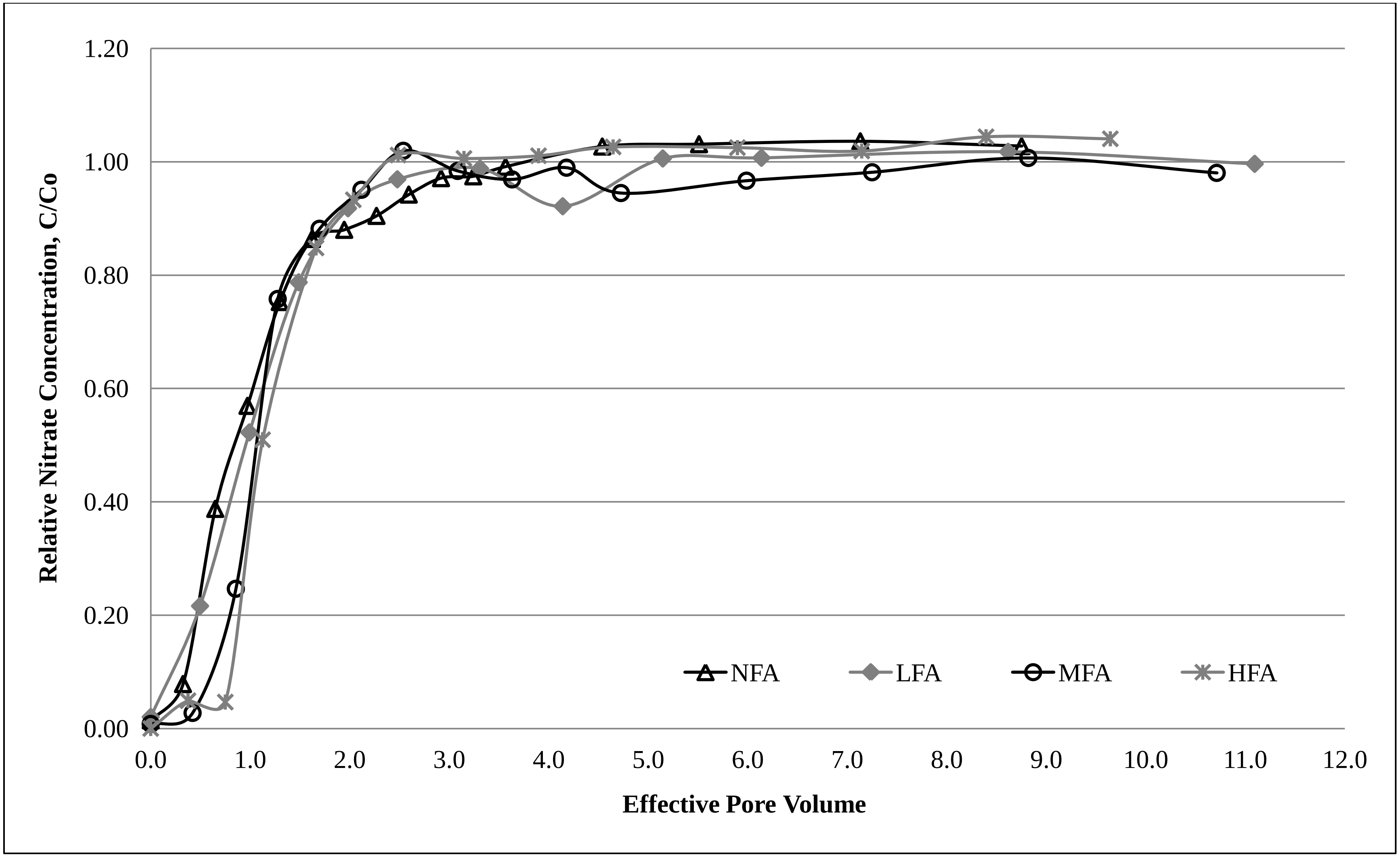

Figure 4.4. Nitrate breakthrough curve for soils subjected to medium-saturation

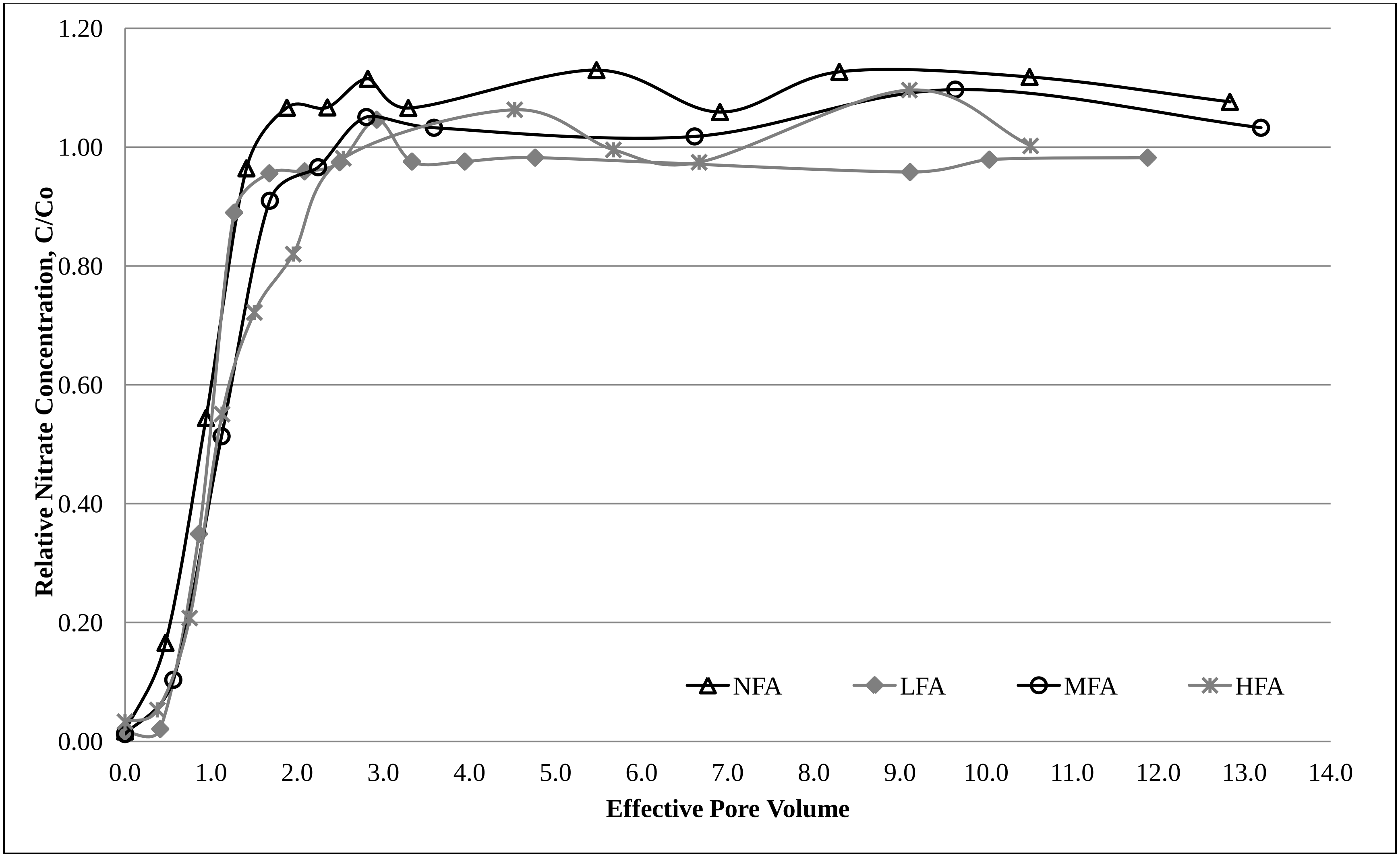

Figure 4.5. Nitrate breakthrough curve for soils subjected to low-saturation

Nitrate mobility in soil is influenced by electrostatic interactions between negatively charged NO_3^- ions and either soil minerals or soil organic matter (Allred, 2007). When the dissolved anions are larger than the water molecules, they are repelled by electrostatic forces, causing these anion molecules to be pushed to the center of the pore (i.e. away from the pore walls) where the average transport velocity is higher (Gvirtzman & Gorelick, 1991). The anion exclusion phenomena can be explained by diffusive double-layer theory and the van der Waals interaction between the invading fluid and the particle walls.

The diffuse double-layer theory quantitatively describes soil solution anion and cation concentration distributions with respect to the distance from a soil particle. Clay particles have an inherently electronegative charge and can exert an electrostatic on a negatively charged ion if it is close enough. The clay's overall negative charge is compensated by exchangeable cations held on the surface by coulomb forces; this combination of the negative charge on the clay surface and the counteracting charge from the cations create the electrical double layer around individual clay particles (Tindall & Kunkel, 1999). A graphical representation of the diffuse double layer is presented in Figure 4.6; the concentrations of cations and anions in these layers are controlled by the balance of electrostatic forces. When the diffuse double-layer is fully developed, anions, such as NO_3^-, will have a zero concentration value at the side of the pore, immediately adjacent to the soil surface, and with increasing distance from the soil surface the concentration of NO_3^- will increase rapidly to a point beyond which it levels off to a constant value (Allred, 2007). This interaction is called anion exclusion. This repelling of negatively charged ions can create a '*parabolic*' concentration profile in which the concentration is highest at the middle of the pore and decreases parabolically to a concentration of zero at the particle surface.

The resulting concentration profile can create a region with concentration which is higher than the averaged solution concentration. For this reason, it is believed that the observed concentrations $C/C_0 > 1.0$ are a result of anion exclusion which are most evident with when the samples were subjected to low saturations and observed in Figure 4.5. These results are in accordance with those discussed by B. Allred (2007) in which he found that anion exclusion was affected primarily by the level of saturation, additionally, he found the anion exclusion was also enhanced by the ionic strength of the invading solution rather that the nitrate concentration alone. The previous results were obtained from a transient unsaturated soil column; the present work differs in that these experiments were carried out under steady state unsaturated conditions. It appears that anion exclusion is also enhanced by the lower saturation level under steady state saturation, though to a lower level as that experienced by the transient experiments conducted by Allred (2007). Figure 4.5, shows that the addition of 2% FA effectively counteracts any repelling forces, which may be attributed to the ferro-aluminous nature of the FA matrix and its positively charged adsorption sites. Increasing the level of FA to 10% and 20% seems to have a slight effect in reducing anion exclusion; however, its effects are difficult to distinguish from those effects exerted by the soil without flyash (NFA).

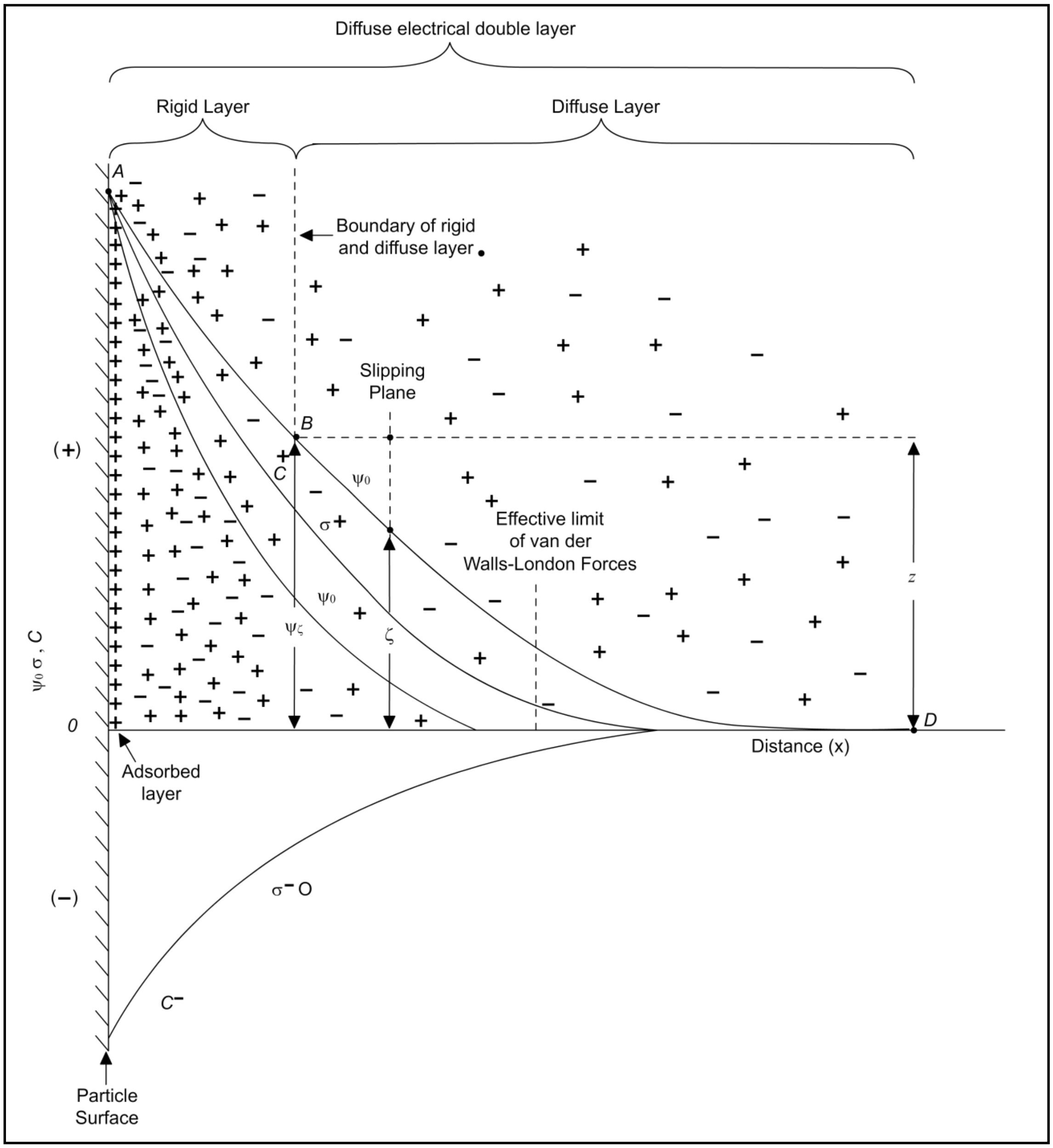

Figure 4.6. Representation of the diffuse double-layer (Tindall & Kunkel, 1999)

Though the results from Figure 4.5 seem to indicate that FA addition to the soil mitigates anion exclusion of nitrate, it is difficult to distinguish between possible adsorption of nitrate onto the FA particles and reduced anion exclusion effects. In an effort to assess the respective effect of nitrate adsorption and reduced anion exclusion the adsorption of nitrate was calculated. The adsorption coefficient (K_d) describes how well a constituent will be adsorbed onto the soil. The K_d of nitrate was calculated using two methods: (*i*) derived from the steady-state saturation and breakthrough curve experiments and (*ii*) through the use of batch experiments and isotherms. For the first method the retardation factor (R_f) is calculated from the breakthrough curves using Equation 4.1 (Dudukovic, 2005):

$$R_f = \int_0^{p_{max}} \left(1 - \frac{c}{c_0}\right) dp \tag{4.2}$$

where R_f is the retardation factor (dimensionless), p is the pore volume and p_{max} is the maximum pore volume of the breakthrough curve. Equation 4.2 integrates the area under the breakthrough curve and subtracts this area from the area under the equilibrium concentration $C/C0 = 1$. After the integral of Equation 4.2 has been calculated, the value is then substituted into Equation 4.3 (Tindall & Kunkel, 1999; Site, 2001) to obtain the adsorption coefficient.

$$R_f = 1 + \left(\frac{\rho_b}{\theta}\right) K_d \tag{4.3}$$

where, as before, R_f is the retardation factor, ρ_b is the soil bulk density (g cm^{-3}), θ is the average volumetric water content, and K_d is the adsorption coefficient (L Kg^{-1}). Rearranging the variables yields Equation 4.4:

$$K_d = \left(R_f - 1\right)\left(\frac{\theta}{\rho_b}\right) \tag{4.4}$$

The results obtained from Equation 4.4 are presented in Figure 4.7 below. Though physically, a negative K_d value does not make much sense, this negative value has been attributed to anion exclusion effect discussed above. As previously predicted, it appears that the flyash amendment has a positive effect in reducing anion exclusion effect when compared to the control; this is especially evident for the medium (MS) and low saturation (LS), respectively.

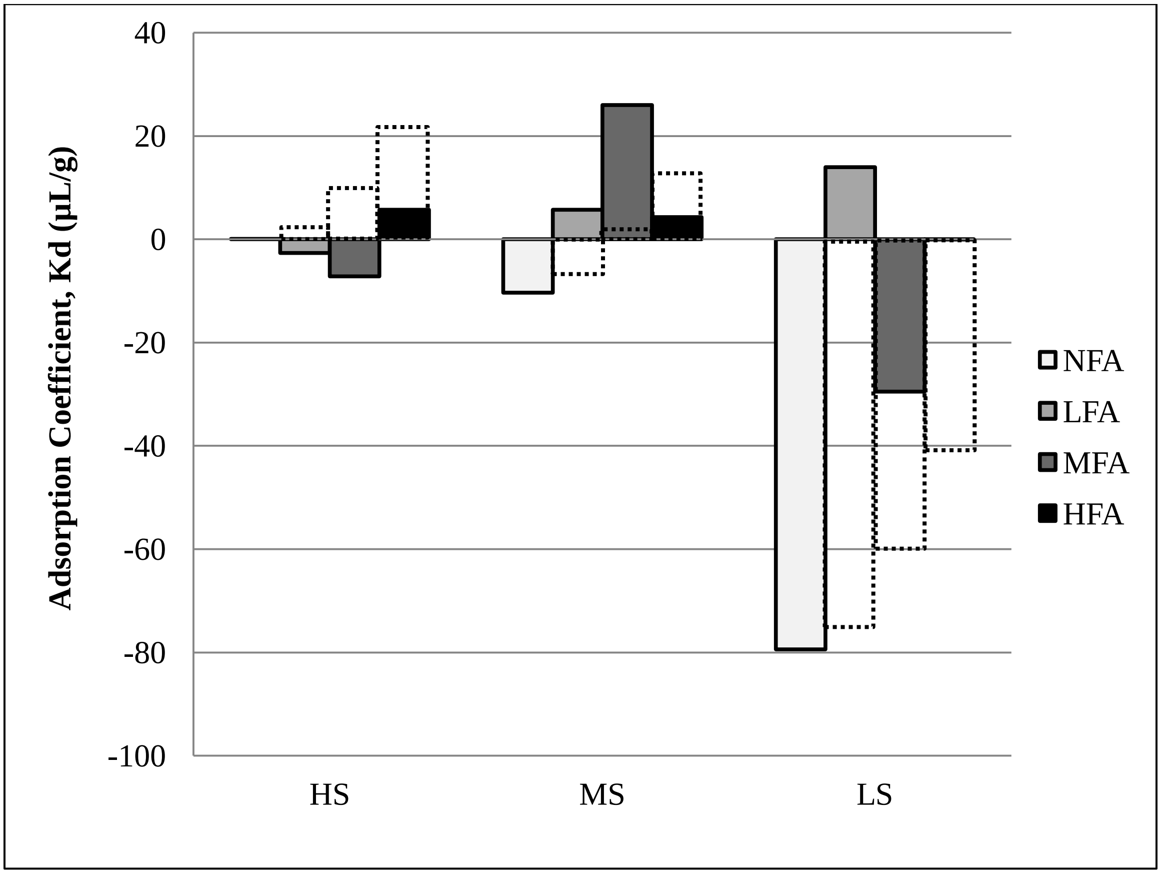

Figure 4.7. Adsorption coefficient for the three levels of saturation (dashed bars are the expected values)

Additionally, the adsorption coefficient was also calculated using a batch experiment and isotherms, method (*ii*), using a linear isotherm. For this method, a known weight of soil (sorbent) is placed in a vial with a measured volume of solution of known concentration. This vial was shaken for a time appropriate to reach equilibrium; the vial was centrifuged to separate solid and liquid phases and the concentration of liquid determined. The mass of sorbate per unit mass of sorbent was obtained by the difference between initial and equilibrium concentrations. These steps were repeated for five additional samples with solutions at different initial concentrations. Plotting the mass of solute sorbed per unit weight of solid, C*, versus the concentration of the solution after equilibrium was reached, (C_e), in a log-log plot will yield a straight line, as seen in Figure 4.8. The line from Figure 4.8 is related to the Equation 4.5:

$$C^* = K_d C_e \tag{4.5}$$

The adsorption coefficient of nitrate on FA was then calculated from Figure 4.8 as K_d = 0.1092 (L Kg^{-1}). It is recognized that a linear isotherm does not provide the most accurate estimate for the distribution coefficient, as evidenced by the low coefficient of determination, R^2=0.56; a non-linear Freudlich isotherm gives a better estimate with an R^2 value of 0.91. However, the linear isotherm was used for comparative purposes because method (*i*) described above assumes linear adsorption. Comparison of the distribution coefficient using both method (*i*) and (*ii*) indicates that anion exclusion is reduced by FA addition. The K_d from the batch experiment has a value of 109.2 µL/g. Using the K_d from the batch experiment and the K_d for the control samples for each saturation level a weighted K_d was calculated. The weighted value is the value that is expected as a result of the anion exclusion and FA addition. Therefore, the samples subjected to low saturation are expected to have a K_d of -75.6, -60.5, and -41.7 µL/g for the LFA, MFA, and HFA, respectively. However, the measured values of K_d (based on equations 4.3 and 4.4) were: -79.4, 14.0, -29.5, and -0.1 µL/g for the NFA (control), LFA, MFA, and HFA, respectively. The other values (measured and expected are shown in Table 4.2.

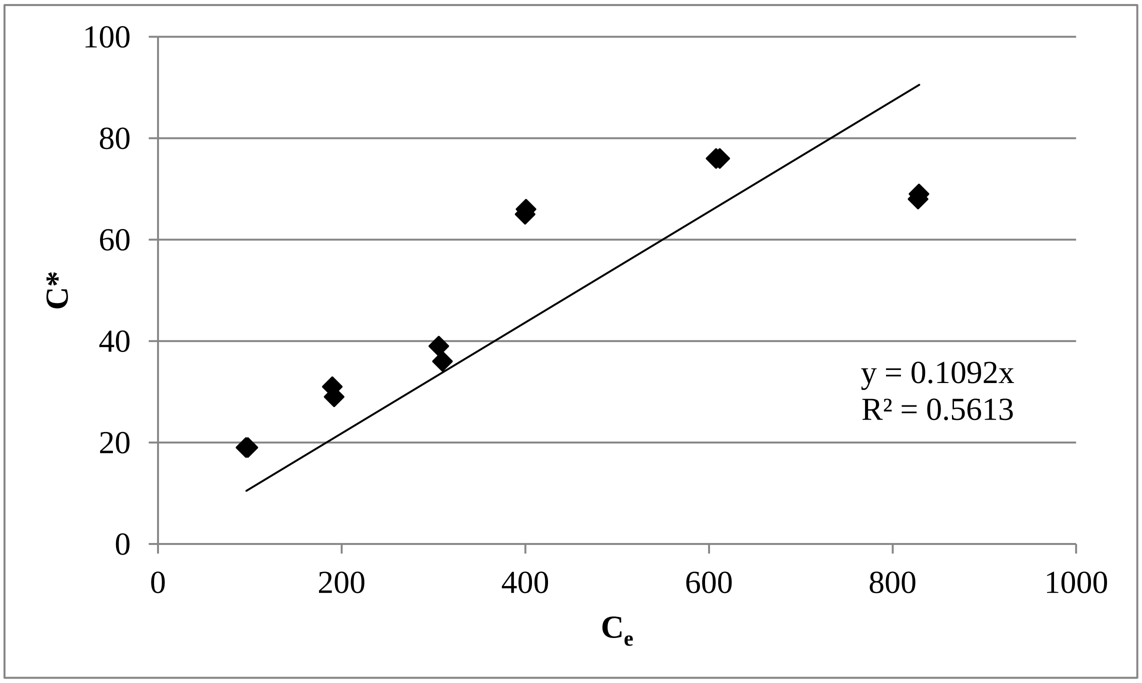

Figure 4.8. Linear isotherm for flyash adsorption coefficient determination

It can be observed that the expected K_d (based on the weighted average of the control and the % of flyash added to the sample) and the experimental values (based on Eq. 4.3 and 4.4) are not in agreement. At high saturation, based on the behavior of the control and the capacity of flyash to adsorb nitrate, we expected to see a positive K_d value for all FA amended samples, however, only the HFA sample had a positive value but was lower than the predicted value. The other two samples, LFA and MFA, both had negative values. The difference in predicted values and observed values is indicative that anion exclusion still has a major role in the transport of nitrate. The K_d values for the samples subjected to low saturation, shown in Table 4.2, indicate that the anion exclusion effect on nitrate has been reduced. This is evident by comparing the expected and

Table 4.2

Observed and Expected Values for K_d (All Values Shown in μL/g. Nitrate Adsorption Coefficient on Flyash is $K_d = 109.2$ μL/g)

	NFA	**LFA**	**MFA**	**HFA**
Low Saturation				
K_d	0.05	-2.63	-7.19	5.69
K_d expected	-	2.23	10.96	21.88
Medium Saturation				
K_d	-10.36	5.71	26.00	4.29
K_d expected	-	-7.97	1.60	13.56
High Saturation				
K_d	-79.38	13.97	-29.50	-0.06
K_d expected	-	-75.61	-60.52	-41.66

observed values. The output nitrate concentrations of the control (NFA) sample subjected to low saturation were greater than the input concentration as shown in Fig. 4.5, i.e. $C/C_0 > 1.0$. This is the result of anion exclusion, where the negatively charged nitrate ions are repelled from the negatively charged soil particles, this repelling action causes the nitrate ions to travel through the pores faster than the bulk soil solution as was described by Allred (2007). Flyash has the ability to adsorb some nitrate, as discovered through the batch experiments, it is able to adsorb 109.2 µL of nitrate for every gram of flyash. Using this value and the K_d observed for the control sample the expected values were determined, meaning the nitrate should still experience some anion exclusion, however, the amount of FA added should also be able to adsorb some of the nitrate passing through. These expected and observed K_d values are shown in Fig. 4.7 and Table 4.2. The expected values are all highly negative, however, the observed values are much smaller than the predicted values, indicating that the anion exclusion effect on nitrate has been neutralized due to the FA addition. It must also be noted that the percent FA addition does not correlate to an equivalent increase in the adsorption of nitrate, that is to say that 20% FA is ten times more efficient at adsorbing nitrate than the 2% FA addition. The reasons for this could be the heterogeneity of samples. Though the appropriate measures were taken to assure samples were as homogeneous as possible, there is some room for samples to be a little different from each other. Additionally, it is assumed that not all FA added will come in contact with the bulk soil solution; thus, as the percent of FA added to the soil increases, the possibility for micro-aggregates of FA (or FA not coming into contact with the pore fluid) also increases. This could be the reason why the LFA and MFA have a higher K_d (observed) than the HFA samples subjected to medium saturation. Similarly, the LFA sample has a higher K_d (observed) than the MFA and HFA samples when subjected to low saturation.

4.3 Sulfate Leaching From Flyash Amended Soils

The leachate collected from the samples was analyzed for fluoride, chloride, nitrite, bromide, phosphate, and sulfate. As expected, the leachate samples did not contain any F^-, Cl^-, Br^-, NO_2^-, or PO_4^-, however, the samples did contain significant amounts of sulfate (SO_4^-). Most flyash will contain some amount of sulfur (in the form of sulfate) for two possible reasons: (i) any sulfur that was not used up during the combustion process will end up in the flyash and (ii) in an effort to comply with emissions regulations, coal burning power plants will employ a technique known as flue-gas desulfurization (FGD). The FGD process uses a liming agent to remove sulfur dioxide (SO_2) from the exhaust gases before they are released to the atmosphere; this process thus, adds sulfur onto the flyash, as flyash can be used as the liming agent and is typically collected from the FGD compartment.

The results for the samples subjected to high, medium, and low-saturations are presented in Figures 4.9, 4.10, and 4.11, respectively.   Sulfate concentrations are plotted on the *y-axis* and effective pore volume in the *x-axis*. The negative pore volumes represent the sample as it is reaching the desired saturation level (while the sample is fed with DI water). Once the sample reaches steady state, the input line is switched from DI water to nitrate; this is represented at a pore volume of zero.   The results show that the amount of sulfate is proportional to the amount of FA in the soil, as expected. The results also show that sulfate is leached out rapidly, i.e., the sulfate concentrations drop very fast, and after four pore volumes (or less) it seems that these concentrations have reached a plateau. Additionally, the results for LFA and MFA seem to have a drastic decrease in concentration after the inlet feed line is changed from DI water to nitrate.

Released sulfate can be beneficial for plant nutrition. Sulfur is one of the secondary macronutrients discussed in Chapter 2, it plays an important role in the overall nutrition of plants. Sulfur is essential for the synthesis of amino acids required to produce proteins, additionally, it is also required for the production of chlorophyll and for the utilization of other essential nutrients. Tucker (1999) states that sulfur is just as important as nitrogen for optimizing crop yield by enhancing the efficiency of nitrogen to produce proteins, therefore, increasing size and weight of grain crops. It is important, then that a nutrient management system include sufficient nitrogen, however, the nitrogen use efficiency may be enhanced by providing sufficient sulfur. It can then be concluded that FA will enhance nitrogen use efficiency by providing a sufficient and steady source of sulfur. Though the present study cannot determine the extent to which the sulfur released will be used by the plant, the fact that the sulfur is released and made available can serve as a starting point for future discussion or research.

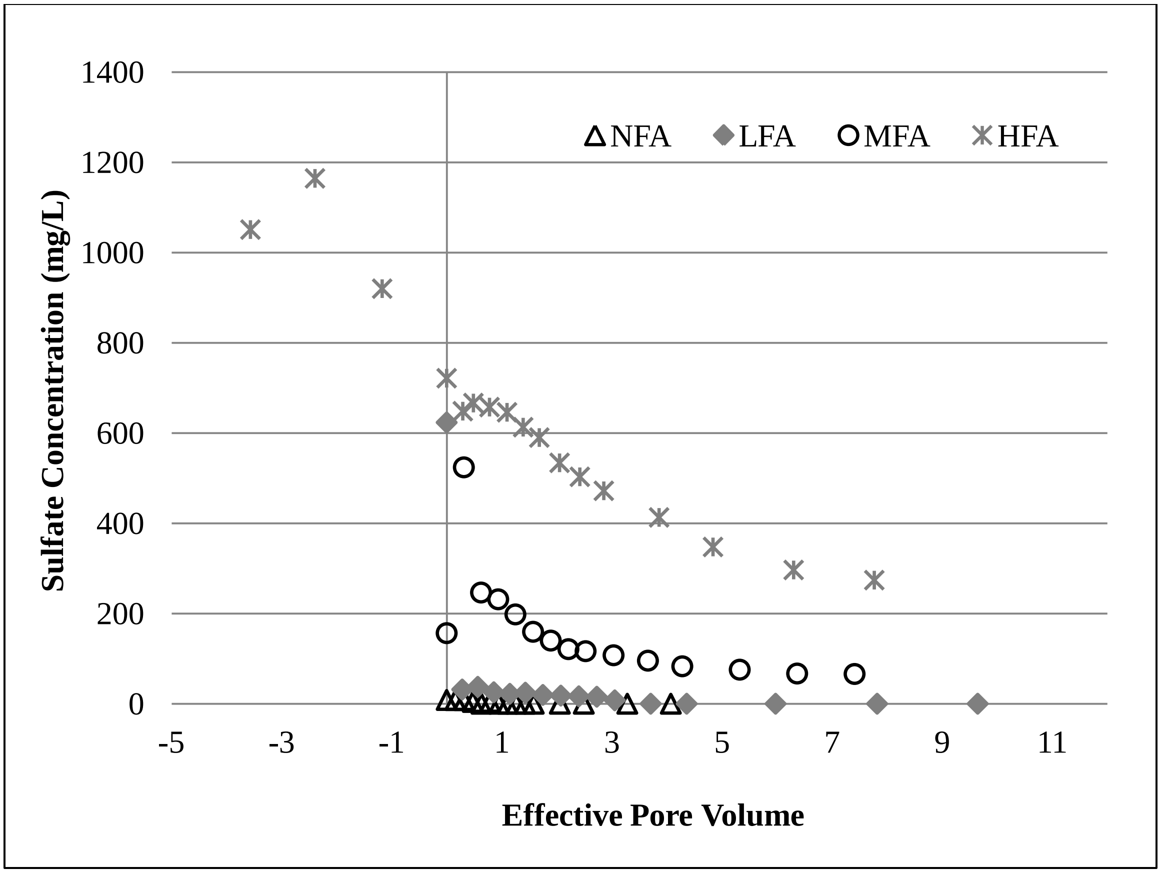

Figure 4.9. Sulfate leaching from soils subjected to high-saturation

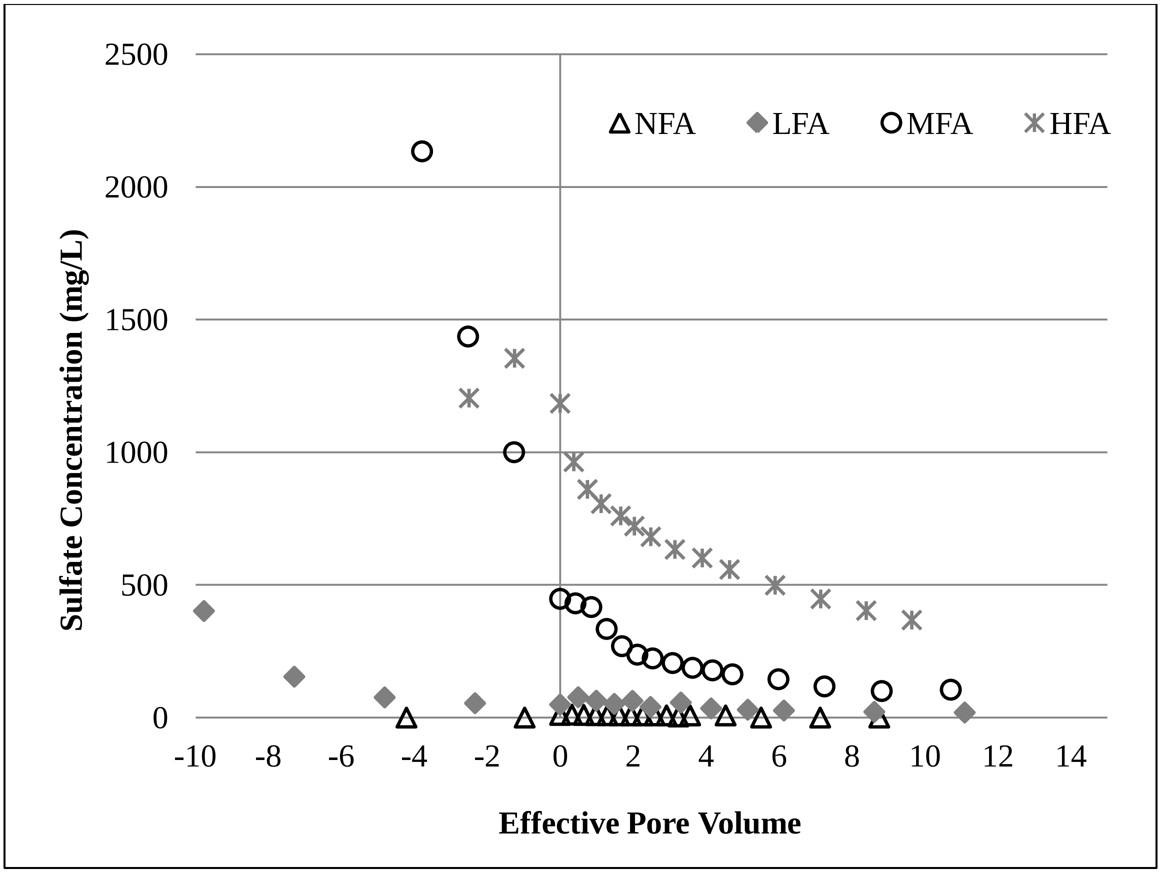

Figure 4.10. Sulfate leaching from soils subjected to medium-saturation

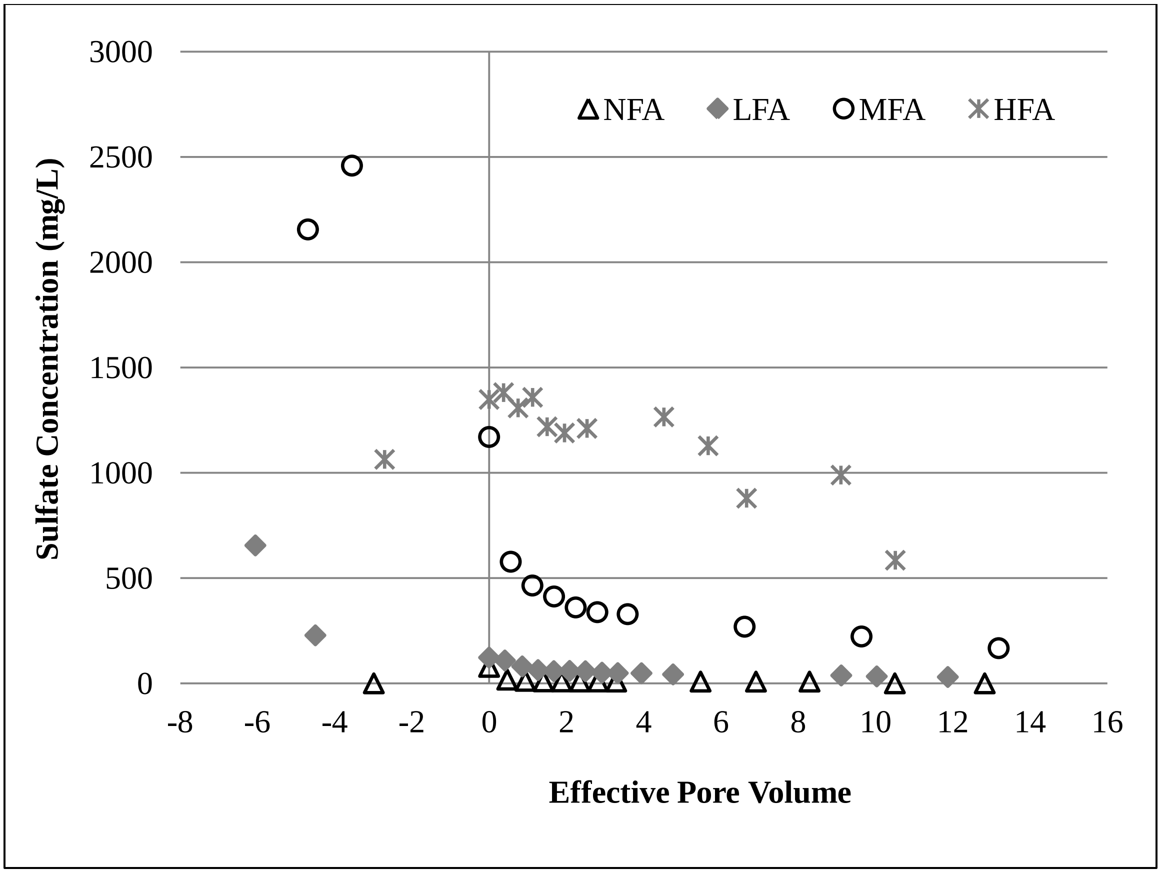

Figure 4.11. Sulfate leaching from soils subjected to low-saturation

4.4 Estimating Hydraulic Properties of Flyash Amended Soil

It has been shown that there is a relationship between the soil-water characteristic curve for a particular soil and the properties of the unsaturated soil (Frendlund & Xing, 1994). In 1980, M. Th. van Genuchten proposed an equation (4.6) relating volumetric water content and matric potential:

$$\Theta = \left[\frac{1}{1+(p\psi)^n}\right]^m \tag{4.6}$$

where Θ is the normalized volumetric water content (i.e., $\Theta = (\theta - \theta_r)/(\theta_s - \theta_r)$); *p, n,* and *m=1-1/n* are three different soil parameters. Equation 4.1 is the equation frequently used to estimate parameters to describe unsaturated soil behavior. A modified version of the above equation, Equation 4.7 was used in this study:

$$\theta = \theta_s \left[\frac{1}{ln[e + (\psi/a)^n]}\right]^m \tag{4.7}$$

where θ is the volumetric water content, θ_s is the saturated volumetric water content, ψ is the matric potential (matric suction), and *a=1/p, n,* and *m* are all hydraulic estimating parameters. The *a, n, m* parameters determine the shape of the soil-water characteristic curve, as the one shown in Figure 4.2. In order to obtain an estimate for these parameters (*a, n,* and *m*), a non-linear multivariable regression analysis was performed. A numerical computing software, Matlab, was used to determine the parameters. The regression analysis takes the experimental θ and ψ as inputs (same data is plotted in Fig. 4.2). The mathematical development and the numerical implementation of the approximating function, Equation 4.7, is presented in Appendix B. Though in theory, the initial estimates for the *a, n,* and *m* parameters should be arbitrary, it was found that the initial estimates have a high sensitivity to initial conditions; this is because the calculation requires matrix inversion, which may result in really large or small values, causing the numerical model to crash or output a erroneous answer. The results obtained from this numerical approximation are shown in Table 4.3 and the graphical estimates shown in Figure 4.12 below.

Table 4.3.

Estimate of a, n, and m Parameters

	NFA	**LFA**	**MFA**	**HFA**
a	17.6962	15.6729	24.7742	36.4479
n	3.4959	6.4282	1.6898	1.4663
m	0.6488	0.5249	0.8431	0.5986
Error	1.097E-04	1.399E-04	8.070E-05	1.462E-05

The error presented in Table 4.2 is the standard error for the multivariable regression analysis. It can be observed from Figure 4.12 that the estimated values are very close to the experimental values. Additionally, it was observed that the *a* parameter will have the biggest impact on the curve, causing the estimated values to move left or right, depending on the value for the *a* parameter. The *n* and *m* parameters control the slope of the curves and where the inflection point falls. Though, not fully optimized, the multivariable regression analysis proved to be an effective and accurate method to estimate the *a*, *n*, and *m* parameters to describe the estimating $\theta(\psi)$ function.

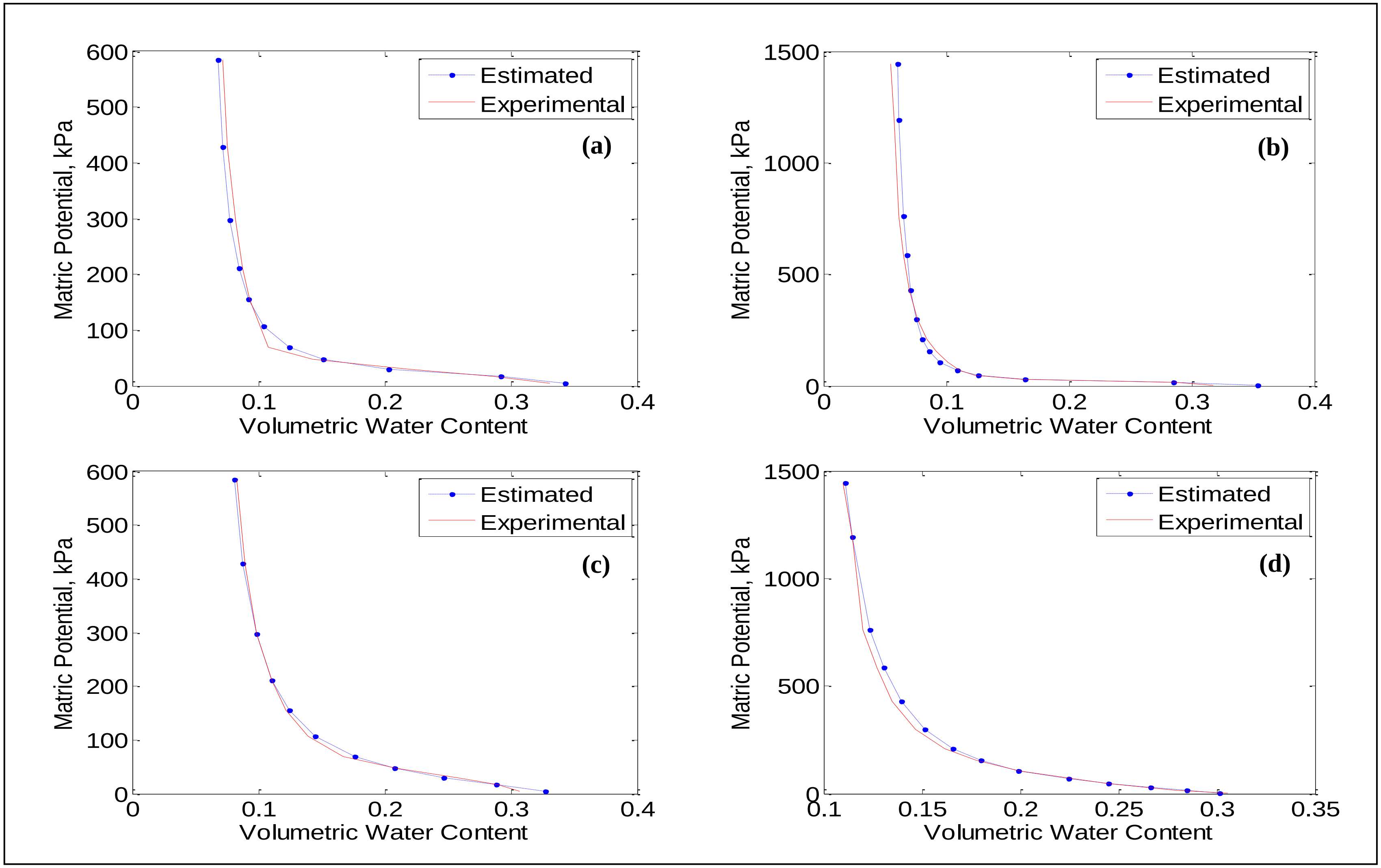

Figure 4.12. Experimental and estimated matric potential for: (a) NFA, (b) LFA, (c) MFA, and (d) HFA

CHAPTER 5

Conclusion

It has been shown that the addition of flyash onto a sandy soil has the potential to mitigate nitrate leaching. Using the steady-state centrifuge - unsaturated flow apparatus (UFA) soil samples were subjected to unsaturated conditions and maintained at a constant volumetric moisture content; the results presented here demonstrate that under steady state conditions, the anion exclusion effect of nitrate increases with a decrease in level of saturation. These results are similar to those found by Allred (2007), however, those experiments were performed under transient conditions. It was found that several soil properties were affected by the FA amendment level: (a) soil bulk density increased with an increase in FA content, (b) saturated volumetric water content decreased with increased FA, (c) hydraulic conductivity decreased with increased FA, and (d) moisture retention was increased as FA content was increased.

Though previous researchers have shown that the soil bulk density decreased with increased FA application, the present study found the opposite effect. It was shown that the bulk density of FA amended soils were increased by a small amount compared to the control samples. The increased bulk density owes to the fact that the FA are very small particles with about 65-90% of particles that have a diameter <10 µm; these small particles fill in the voids between the sand and clay soils and thus increase the overall bulk density of the soil. Additionally, it is believed that this also contributed to the observed reduction in saturated volumetric water content. Voids that were previously filled with water are now filled with these FA particles, thus reducing the amount of water that the soil can uptake. Decreased saturated volumetric water content does not appear to have any effect on the hydraulic behavior of the soil.

The most significant effects of FA addition was observed on the hydraulic properties of the soil.   Considering unsaturated hydraulic conductivity as a sole factor, it is evident that the best FA amendment level is provided by 10% FA addition. Though 20% would also decrease the unsaturated hydraulic conductivity, there seems to be little change between MFA and HFA and therefore only provides minimum advantage to the hydraulic conductivity while doubling the amount of flyash. At the time of writing, the author could not find any agreement as to the amount of FA addition as soil amendment; therefore, the results presented here are a significant advance towards a quantifiable and generalizable standard for the amount of FA addition, considering that the purpose of the amendment is to change the unsaturated hydraulic conductivity of the soil.

In addition to lowering the hydraulic conductivity, it was shown that the level of FA amendment has a significant impact on the moisture retention ability of the soil. Matric potential is the force which causes capillary forces between soil particles; these capillary forces create a negative pressure, preventing fluid to be flushed out, i.e., increases the moisture retention of the soil. These results demonstrate that FA addition has a positive effect on water retention of the soil. The results obtained in this study show that a 2% FA addition actually increases drainage, while both the 10% FA and 20% FA additions cause a significant increase in water retention of the soil. Unlike unsaturated hydraulic conductivity, the results obtained from the matric potential experiments indicate that 20% FA would be favorable over a 10 % FA amendment because water retention is significantly increased.

The leachate collected from the samples subjected to the three levels of saturation was analyzed for all major anions. Results indicate that FA will release a significant amount of sulfate, however, it appears that this release is fast. After only several pore volumes, sulfate concentrations had leveled out. Research indicates that this sulfate release may be beneficial for the plants because sulfate tends to increase nitrate use efficiency of the plants. An increase in nitrate use efficiency can potentially lead to a healthier crop with increased yield. Though the present study cannot fully determine if this sulfate release will in fact increase nitrate use efficiency, and thus reduce nitrate losses, it can be postulated as a possibility based on previous studies, such as the one byTucker, 1999.

The purpose of the leaching experiments presented in this study was to investigate the possibility of using FA to mitigate nitrate losses due to leaching. It was observed that the saturation level had a significant effect on nitrate concentrations of the leachate from soils not amended with FA. The leachate concentrations from these samples were higher than the average concentration of the invading fluid for this samples. Initial tests showed that the non amended soil (NFA) was creating anion exclusion of nitrate and therefore increasing nitrate losses due to leaching. This was confirmed by the calculated adsorption coefficient an its negative value. It was therefore hypothesized that the addition of FA as an amendment to this soil had the potential to reduce anion exclusion and therefore reduce nitrate losses due to leaching. The breakthrough curves obtained from the experimental data of the leaching sample experiments revealed that FA can reduce anion exclusion. The latter statement was validated by calculating the adsorption coefficient of each sample subjected to the different levels of saturation. Under high saturation conditions, the LFA and MFA samples actually seem to increase anion exclusion, while HFA completely mitigates it. Under medium saturation, all FA amended soils mitigated anion exclusion, but the MFA soil amendment yielded the best results. Under low saturation, it was shown that all FA amendments were efficient in reducing anion exclusion: LFA amendment yield the best results, followed by HFA, and MFA, in that order.

The present study has demonstrated that the addition of FA can, indeed, mitigate nitrate losses due to leaching by reducing anion exclusion of nitrate. Additionally, it was shown that the ideal FA amendment level is between 10-20% wt/wt. When deciding the amount of FA to be used as a soil amendment several factors should be considered: (a) possibility of trace elements leaching (not considered in this experiment); (b) decreased saturated volumetric water content; (c) increased soil bulk density; (d) decreased unsaturated hydraulic conductivity; (e) increased moisture retention; (f) decreased nitrate losses; and (g) increased sulfate release. These are all characteristics that may be beneficial to an agricultural system if applied correctly. Additionally, the possibility of increased nitrate use efficiency by the plants could be proved in this experiment and leaves room for future investigation. Considering the above characteristics would be influenced by adding FA as a soil amendment, the agriculturists can decide which soil characteristics need the most improvement and can now decide on the amount of FA to be used based on the performance offered by the 10% or 20% FA addition. It can be concluded that the level of flyash added as an amendment does in fact reduce anion exclusion of nitrate solution; therefore, FA offers the possibility of reduced nitrate losses. Reduced nitrate losses means farmers may benefit by applying less fertilizers while still producing comparable crop yields. Additionally, the FA incorporation to a properly managed agricultural system can reduce nitrate leaching into aquifers.

5.1 Future Work

The present study investigated the effect of a flyash amendment at different levels and its effects on nitrate transport under steady state unsaturated conditions. It was shown that the addition of FA can reduce the anion exclusion effect experienced by nitrate ions passing through a sandy soil. Though this is a thorough experiment, there is still much room for investigation. A similar study can be setup to investigate nitrate transport, however, instead of a continuous flow a plug flow can be used. A plug flow experiment may be able to help determine the maximum nitrate that FA amended soils may adsorb. A plug flow experiment can be used to perform a mass balance analysis and therefore help understand the effect of FA on the nitrate transport. Batch experiments for the different FA amended soils can help determine the total adsorption expected and can be compared to the adsorption observed from the breakthrough curves. Performing batch experiments for each of the three FA amended soils might eliminate the possibility of some FA not being in contact with the bulk solution and can thus be a better approximate of the Kd values expected; comparing these batch experiment K_d (using isotherms) can help determine if the effect observed was due to the reduction of anion exclusion of nitrate.

Future work shall also perform further analysis in order to fully understand and better evaluate the reduced anion effect seen in this study. Future work may also analyze the ionic strength of the solution passing through the soil to investigate if FA can reduce nitrate transport under different ionic strength solutions that include nitrate, in addition to the ionic strength, the effect of the solution concentration can also be investigated. Varying the nitrate concentration in solution may be able to broaden the possible applicability of FA in an agricultural system. Tucker (1999) suggests that sulfur ranks equal to nitrogen in importance as a plant nutrient because sulfur is an essential component in the synthesis of amino acids required to manufacture proteins. Therefore, the sulfur, just like nitrogen, plays an essential role in optimization of crop yield and quality, it is also known that plants that have a large nitrogen requirement must also have an adequate amount of sulfur in order to optimize nitrogen utilization. It was shown in this study that FA releases some sulfur, in the form of sulfate; further analysis must be performed to investigate whether this sulfate release can optimize nitrogen utilization and consequently reduce nitrogen leaching. Small scale crop experiments may help in the further understanding of FA on the crops and nutrient management.

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APPENDIX A

Results for Nitrate Transport Through Flyash Amended Soil

Table A.1.

Results Data for Nitrate Transport Subjected to High-Saturation

	NFA	**LFA**	**MFA**	**HFA**
ω (rpm)	400	450	600	600
q (ml/hr)	30	44	35	35
θ_{Sat}	34.97% (2.37%)	36.14% (0.49%)	32.34% (0.28%)	30.97% (0.40%)
ρ_b	1.60 (0.02)	1.59 (0.00)	0.02 (0.00)	1.79 (0.01)
NO_3 Conc. (C_0, mg/L)	438.5 (0.00)	424.0 (1.41)	421.0 (0.00)	423.0 (4.24)
Solution pH	4.68 (0.00)	5.13 (0.00)	5.13 (0.00)	5.74 (0.00)
θ_{Avg}	30.17% (1.77%)	26.95% (0.80%)	26.67% (0.43%)	28.34% (0.19%)
S_{avg}	0.86 (0.05)	0.75 (0.02)	0.82 (0.01)	0.92 (0.01)
Pore Volume (ml)	14.735 (1.00)	15.23 (0.21)	13.63 (0.12)	13.05 (0.17)

Table A.2.

Results Data for Nitrate Transport Subjected to Medium-Saturation

	NFA	**LFA**	**MFA**	**HFA**
ω (rpm)	1600	1500	1850	1650
q (ml/hr)	20	34	18	20
θ_{Sat}	33.63% (0.03%)	33.65% (0.85%)	31.99% (0.49%)	30.84% (0.27%)
ρ_b	1.63 (0.00)	1.67 (0.03)	1.75 (0.01)	1.79 (0.00)
NO_3 Conc. (C_0, mg/L)	422.7 (0.00)	421.0 (0.00)	436.0 (8.49)	418.0 (0.00)
Solution pH	4.87 (0.26)	4.92 (0.00)	5.15 (0.00)	5.33 (0.00)
θ_{Avg}	14.63% (0.24%)	16.29% (0.22%)	17.15% (0.63%)	19.01% (0.09%)
S_{avg}	0.44 (0.01)	0.48 (0.01)	0.54 (0.02)	0.62 (0.00)
Pore Volume (ml)	14.17 (0.01)	14.18 (0.36)	13.48 (0.21)	13.00 (0.12)

Table A.3.

Results Data for Nitrate Transport Subjected to Low-Saturation

	NFA	**LFA**	**MFA**	**HFA**
ω (rpm)	3500	2000	3000	3800
q (ml/hr)	1	2	1.5	1
θ_{Sat}	35.68% (0.45%)	33.80% (0.18%)	32.33% (0.03%)	30.21% (0.43%)
ρ_b	1.59 (0.00)	1.68 (0.00)	1.75 (0.00)	1.83 (0.00)
NO_3 Conc. (C_0, mg/L)	424.0 (0.00)	454.0 (2.83)	444.0 (0.00)	453.0 (0.00)
Solution pH	4.925 (0.18)	4.94 (0.00)	5.00 (0.00)	5.15 (0.00)
θ_{Avg}	10.11% (0.07%)	11.62% (3.96%)	12.70% (0.14%)	12.53% (0.41%)
S_{avg}	0.28 (0.00)	0.34 (0.12)	0.39 (0.00)	0.41 (0.01)
Pore Volume (ml)	15.04 (0.19)	14.24 (0.08)	13.62 (0.01)	12.73 (0.18)

APPENDIX B

Numerical Approximation of Matric Potential

B.1 Mathematical Development of the Nonlinear Gauss-Newton Method for Matric Potential

When an equation has a non-linear dependence on its parameters such as the equation:

$$f(x) = a_0(1 - e^{-a_1 x}) + e \tag{B.1}$$

a linear regression cannot be performed because the function has a nonlinear dependence on its parameters. The Gauss-Newton method is one algorithm for minimizing the sum of the squares of the residuals between data and nonlinear equations. The key concept underlying the technique is that a Taylor series expansion is used to express the original equation in an approximate, linear form. Then, least-squares theory can be used to obtain new estimates of the parameters that move in the direction of minimizing the residual. To illustrate how this is done, first the relationship between the nonlinear equation and the data can be expressed generally as

$$y_i = f(x_i; a_0, a_1, \ldots, a_m) + e_i \tag{B.2}$$

where y_i = a measured value of the dependent variable, $f(x_i; a_0, a_1, \ldots, a_m)$ = the equation that is a function of the independent variable xi and a nonlinear function of the parameters $a_0, a_1, \ldots, a_m$, and e_i = a random error. The nonlinear model can be expanded in a Taylor series around the parameter values and curtailed after the first derivative. For example, for a three-parameter case,

$$f(x_i)_{j+1} = f(x_i)_j + \frac{\partial f(x_i)_j}{\partial a_0}\Delta a_0 + \frac{\partial f(x_i)_j}{\partial a_1}\Delta a_1 + \frac{\partial f(x_i)_j}{\partial a_2}\Delta a_2 \tag{B.3}$$

where *j* = the initial guess, *j+1* = the prediction, $\Delta a_0 = a_{0,j+1} - a_{0,j}$; $\Delta a_1 = a_{1,j+1} - a_{1,j}$; and $\Delta a_2 = a_{2,j+1} - a_{2,j}$. Thus, we have linearized the original model with respect to the parameters. Eq. (B.3) can be substituted into Eq. (B.2) to yield

$$y_i - f(x_i)_j = \frac{\partial f(x_i)_j}{\partial a_0}\Delta a_0 + \frac{\partial f(x_i)_j}{\partial a_1}\Delta a_1 + \frac{\partial f(x_i)_j}{\partial a_2}\Delta a_2 + e_i \qquad \text{(B.4)}$$

or in matrix form,

$$\{D\} = [Z_j]\{\Delta A\}\{E\} \qquad \text{(B.5)}$$

where [Zj] is the matrix of the partial derivatives of the function evaluated at the initial guess j; {D} contains the differences between the measurements and the function values, and {ΔA} contains the changes in the parameter values. For the present case, the equation describing the relationship between water content and the parameters can be estimated as:

$$\theta_i = \theta(\psi; a, n, m) + e_i \qquad \text{(B.6)}$$

where θ_i = the measured volumetric water content, $\theta(\psi; a, n, m)$ = the equation that is a function of the independent variable ψ and the *a*, *n*, and *m* parameters, and e_i = a random error. For convenience, this model can be expresses in abbreviated form by omitting the parameters,

$$\theta_i = \theta(\psi) + e_i \qquad \text{(B.7)}$$

The estimating function is defined by (Frendlund & Xing, 1994):

$$\theta(\psi) = \theta_s \left[\frac{1}{\ln\left(e + \left(\psi/a\right)^n\right)}\right]^m \qquad \text{(B.8)}$$

The partial derivatives of the estimating function are then defined by:

$$\frac{\partial\theta}{\partial a} = \theta_s m \left[\ln\left(e + \left(\psi/a\right)^n\right)\right]^{-m-1} \left[\frac{n\left(\psi/a\right)^{n-1}\left(\psi/a^2\right)}{e + \left(\psi/a\right)^n}\right]^m \qquad \text{(B.9)}$$

$$\frac{\partial\theta}{\partial n} = -\theta_s m\left[\ln\left(e + \left({}^{\psi}/_{a}\right)^{n}\right)\right]^{-m-1}\left[\frac{\left({}^{\psi}/_{a}\right)^{n} ln\left({}^{\psi}/_{a}\right)}{e+\left({}^{\psi}/_{a}\right)^{n}}\right]^{m} \tag{B.10}$$

$$\frac{\partial\theta}{\partial m} = -\theta_s\left[\ln\left(e + \left({}^{\psi}/_{a}\right)^{n}\right)\right]^{-m} ln\left[\ln\left(e + \left({}^{\psi}/_{a}\right)^{n}\right)\right] \tag{B.11}$$

where, a, n, and m = nonlinear parameters, ψ is the matric potential, θs = saturated volumetric water content and $\theta(\psi)$ = the equation which estimates the volumetric water content for a given ψ. It follows then that [Z$_j$], the matrix of the partial derivatives of the function evaluated at the initial guess j, is constructed:

$$[Z_j] = \begin{bmatrix} {}^{\partial\theta_1}/_{\partial a} & {}^{\partial\theta_1}/_{\partial n} & {}^{\partial\theta_1}/_{\partial m} \\ {}^{\partial\theta_2}/_{\partial a} & {}^{\partial\theta_2}/_{\partial n} & {}^{\partial\theta_2}/_{\partial m} \\ \vdots & \vdots & \vdots \\ {}^{\partial\theta_M}/_{\partial a} & {}^{\partial\theta_M}/_{\partial n} & {}^{\partial\theta_M}/_{\partial m} \end{bmatrix} \tag{B.12}$$

where M = the number of data points and ${}^{\partial\theta_i}/_{\partial k}$ = the partial derivative of the function with respect to the kth parameter evaluated at the ith data point. The vector {D} contains the differences between the measurements and the function values,

$$\{D\} = \begin{Bmatrix} \theta_1 - \theta(\psi_1) \\ \theta_2 - \theta(\psi_2) \\ \theta_M - \theta(\psi_M) \end{Bmatrix} \tag{B.13}$$

And the vector {ΔA} contains the changes in the parameter values,

$$\{A\} = \begin{Bmatrix} \Delta a \\ \Delta n \\ \Delta m \end{Bmatrix} \tag{B.14}$$

Applying linear least-squares theory to Eq. (B.4) results in the following normal equations:

$$\left[\left[Z_j\right]^T\left[Z_j\right]\right]\{\Delta A\} = \left\{\left[Z_j\right]^T\{D\}\right\} \tag{B.15}$$

Thus, the approach consists of solving Eq. (B.10) for {DA}, which can be employed to compute improved values for the parameters, as in

$$a_{j+1} = a_j + \Delta a \tag{B.16}$$

$$n_{j+1} = n_j + \Delta n \tag{B.17}$$

$$m_{j+1} = m_j + \Delta m \tag{B.18}$$

The procedure is repeated until the solution converges - that is, until

$$|\varepsilon_a|_k = \left|\frac{a_{k,j+1} - a_{k,j}}{a_{k,j+1}}\right| 100\% \tag{B.19}$$

falls below an acceptable stopping criterion.

B.2 Implementation of Gauss-Newton Method in the Numerical Model (Matlab Code)

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%          Modified van Genuchten Multivariable Regression for a, n, m estimation          %
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
clear all
clf
clc
%Read the data from excel file "experiment.xls", where: 1st column = theta
experimental, 2nd column = psi, and 3rd column = theta saturated
[NUMERIC, TXT]=xlsread('experiment.xls');
 Texp=NUMERIC(:,1);
psi=NUMERIC(:,2);
Tsat=NUMERIC(1,3)
```

```
 %Theta_Experimental.  Transpose so it is converted to a row vector
Texp = Texp'
 %Total number of samples
M = length(Texp);
 %Psi_Experimental. Transpose so it is converted to a row vector
psi=psi'
 %Theta_Saturated
T=Tsat;
%Initial Estimated Values
a=25.5;
n=1.11;
m=.52;

%f is the Theta Estimating function
f=inline('T*(log(exp(1)+(psi/a)^n))^-m','T','psi', 'a', 'n', 'm');
 %These are the partial derivatives of the f() function w.r.t. a, n, m, respectively
dfa=inline('m*T*(log(exp(1)+(psi/a)^n))^(-m-1)*((n*(psi/a)^(n-1)*(psi./a.^2))/(exp(1)+(psi/a)^n))','T','psi', 'a', 'n', 'm');
dfn=inline('-m*T*(log(exp(1)+(psi/a)^n))^(-m-1)*(((psi/a)^n)*log(psi/a))/(exp(1)+(psi/a)^n)','T','psi', 'a', 'n', 'm');
dfm=inline('-T*((log(exp(1)+(psi/a)^n))^(-m))*(log(log(exp(1)+(psi/a)^n)))','T','psi', 'a', 'n', 'm');
```

```
error=1;

iter=0;

 while error > 0.0001

            for k=1:M

                        Z(k,1)=dfa(T,psi(k),a,n,m);

                         Z(k,2)=dfn(T,psi(k),a,n,m);

                         Z(k,3)=dfm(T,psi(k),a,n,m);

             end

             A=transpose(Z)*Z;

             B=inv(A);

            for k=1:M

                        D(k,1)=Texp(k)-f(T,psi(k),a,n,m);

            end

             C=transpose(Z)*D;

            DA = B*C;

            a= a+DA(1);

            n= n+DA(2);

            m= m+DA(3);

            %Calculating Sum of differences squared

            sum=0;

             for i=1:M

                        sum = sum + (Texp(i)-f(T,psi(i),a,n,m))^2;

            end
```

```
        error=sum/(M-3);

        iter=iter+1

end

% Display the final values of a, n, m, and error

a

n

m

error

% Calculate values of theta and assign to the array "Est"

for i=1:M

        Est(i) = f(T,psi(i),a,n,m);

end

 % Plot experimental and Estimated values

plot(Est,psi,'-.b.')

hold on

plot(Texp,psi,'-r')

set(gca,'fontsize',16)

xlabel('Volumetric Water Content')

ylabel('Matric Potential, kPa')

hleg1=legend('Estimated','Experimental');
```