SOIL WATER FLOW AND NITRATE TRANSPORT STUDY THROUGH HETEROGENEOUS VADOSE ZONE

Ph.D. THESIS

by

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ROORKEE- 247667, INDIA
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ROORKEE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis titled "**SOIL WATER FLOW AND NITRATE TRANSPORT STUDY THROUGH HETEROGENEOUS VADOSE ZONE**", in the partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy and submitted in the Department of Hydrology of the Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out during a period of January, 2013 to June, 2018, under the supervision of Dr. Brijesh Kumar Yadav, Associate Professor, Department of Hydrology, Indian Institute of Technology Roorkee, Roorkee.

The matter presented in the thesis has not been submitted by me for the award of any other degree of this or any other Institute.

Jahangeer

(JAHANGEER)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

(Brijesh Kumar Yadav)
Supervisor

Dated: June 04, 2018

Dedicated to my beloved parents

ABSTRACT

Nitrate, because of its intensive use as fertilizers/manure to increase the agricultural productivity of soils, is necessary to fulfil the demand of growing population. However, its high mobility in vadose zone is making it as a potential groundwater contaminant worldwide. In agricultural based economies, nitrate enrichment of groundwater has been appearing as a major threat to the local inhabitants especially in intensively cultivable areas. A high nitrate concentration in groundwater in these areas is due to heavy use of nitrogenous fertilizers in crop lands. In general, agricultural activities and dairy operations are identified as a major source of nitrate. The dairies and agricultural activities comprise a complex accumulation of multiple potential points and diffuse sources for nitrate contamination of vadose zone and underlying groundwater.

The vadose zone is the layer of soil present between the earth surface and water table, and is of utmost physical, chemical and biological importance. This zone is also associated with the recharge of groundwater, degradation and uptake of contaminants including nitrate, and thus, preventing them to percolate to the groundwater table. Conventionally vadose zone is considered as a homogeneous region for analyzing soil moisture flow and solute transport. But in reality, heterogeneity is invariably present in the vadose zones, and hence, non-uniform flow takes place leading to the non-equilibrium flow conditions. Most of the studies on nitrogen laid more focus on root zone nitrate dynamics and reach ability of nitrate to the adjoining water bodies from surrounding surface and shallow aquifers. Further, nitrate movement in vadose zone is mostly investigated considering uniform moisture flow and solute transport mechanisms and studies performed on nitrate dynamics through vadose zone considering the realistic approaches are at nascent stage. Therefore, the main focus of this study is to investigate the soil water flow and nitrate transport in heterogeneous subsurface at different scales using a series of laboratory and simulation experiments.

The aim of the conducting practical experiment was to characterize the flow and transport behavior of nitrate in subsurface under varying environmental conditions. Numerical runs were also conducted to predict the nitrate load to underlying groundwater resources of heterogeneous vadose zone using HYDRUS simulator. At plot scale, numerical simulation was performed considering the vadose zone heterogeneity for predicting accurate nitrate flux loading to groundwater under different rates of fertilizer applications. The experimental data of San Joaquin valley, California were used for these simulations. The nitrate leaching from the surface to the underlying water resources was simulated using dual porosity approach. Subsequently, a field scale study on the Nebraska

Management Systems Evaluation Area (MSEA) site, located within the Central Platte Natural Resources District (CPNRD) of the Platte River Valley, was performed for quantifying corn yield and nitrate leaching to the underlying groundwater resources. A lithologic framework was developed for the MSEA using Rock works considering the observed soil properties of the field site. Future climatic scenarios were also considered for predicting the nitrate leaching and the associated crop yield. The observed data at the laboratory, plot scale and field scale were compared with the breakthrough curves obtained by numerical simulation. The results of this study may help in protection of groundwater resources from vadose zone return flows and can be used directly in planning better fertigation scheduling of farmlands.

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Last, but certainly the most important GOD, who gave me the mental capability, strength to persevere and courage to succeed on my journey

June 04, 2018 **(Jahangeer)**

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NOMENCLATURE

C = contaminant concentration in soil solution [M/L^3];

C_m = Concentration in mobile zone [M/L^3];

C_{im} = Concentration in immobile zone [M/L^3];

D = diffusion-dispersion or hydrodynamic dispersion coefficient [L^2T^{-1}];

D_0 = free water diffusivity [L^2T^{-1}];

D_m = molecular diffusion coefficient [L^2T^{-1}];

D_R = Effective diffusion rate between soil solution and root surface [T^{-1}];

h = Soil water pressure head [L];

$h2$, $h3$ = Optimal pressure head points [L];

$h4$ = Wilting point pressure head [L];

hin = Initial pressure head [L];

h_L = Pressure head lower boundary [L];

$K_{(h)}$ = Unsaturated hydraulic conductivity [L/T];

$K_{(S)}$ = Saturated hydraulic conductivity [L/T];

K_m = Half saturation constant [ML-3];

$Lr(t)$ = Root length at time t [L];

Lm = Maximum root length [L];

n = Porosity of soil [%];

P = Empirical parameter [-];

P_c = Partition coefficient [-];

q = Darcy's velocity [LT^{-1}];

q_0 = Water flux at upper boundary [LT^{-1}];

q_L = Water flux at lower boundary [LT^{-1}];

S_C = Root water uptake [T^{-1}];

$Smax$ = Maximum root water uptake [T^{-1}];

t = Time [T];

μ_w, μ_s and μ_g = First-order rate constants for solutes in the liquid, solid, and gas phases [-];

γ_w, γ_s and γ_g = Zero-order rate constants for the liquid, solid and gas phases [-];

T_a = Actual transpiration [LT^{-1}];

T_P = Potential transpiration [LT^{-1}];

r_s = Solute transfer function [-];

v = The pore water velocity [LT^{-1}];

V_{rs} = Root surface volume [L^3];

V_T = Total soil volume [L^3];

V_{max} = maximum uptake rate of metal by root biomass [T^{-1}];

z = soil depth [L];

zr = normalized depth [-];

Zrj = root depth on jth day [L];

θ = volumetric moisture content [-];

θ_{in} = initial soil moisture content [-];

θr = residual moisture content [-];

θs = saturated moisture content [-];

θ_m = mobile moisture content [-];

θ_{im} = immobile moisture content [-];

$S_{e,m}$ = Effective saturation of the mobile region

$S_{e,im}$ = Effective saturation of the immobile region

a, n, m = empirical constants [-];

α, n and l = curve fitting parameters [-];

α_L = longitudinal dispersivity of the porous media [L];

$\alpha_{(h)}$ = Soil water availability factor [-];

β (z, t) = root density distribution function [L^{-1}];

λ = empirical parameter [-];

ρ_s = Bulk density of the soil [ML^{-3}];

Acronyms and Abbreviations

ADE	Advection Dispersion Equation
BTC	Breakthrough Curve
CCSM	Community Climate System Model
CPNRD	Central Platte Natural Resources District
CN	Courant Number
EONR	Economically Optimal Nitrogen Rate
FE	Finite Elements
GFE	Galerkin Finite Elements
IS	Indian Standard
MSEA	Management Systems Evaluation Area
PPM	Part Per Million
PN	Peclet Number
RCP	Representative Concentration Pathways
WRF	Weather Research and Forecasting

Chapter 1

INTRODUCTION

1.1. Introduction:

Groundwater is a major water resource for human activities and development. One third population of the world depends on groundwater for drinking and agricultural water consumptions (Hetzel et al., 2008). In arid and semi-arid regions, dependency on groundwater is even more critical where more than 60% of water requirement is catered from groundwater (Jha et al., 1999 ; Hetzel et al., 2008). Due to rapidly growing population, amplified human activities and climate change, groundwater resources are increasingly under pressure in terms of both quantity and quality. Considering the fact that groundwater remediation is very difficult and prohibitively expensive, groundwater monitoring and proper management is crucial to have sustainable access to safe water. Soil moisture flow and solute transport through upper lying soil strata, the vadose zone, of an aquifer is very crucial for quality and quantity control of the stored groundwater. Therefore, it is important to investigate the unsaturated soil hydrologic processes of the vadose zone thoroughly for effective management of the underlying groundwater resources.

Groundwater pollution is one of the major environmental problems in the world. Agriculture, industry and urbanization are main sources of groundwater pollution. Mining waste, road salt, and used motor oil may also leak into groundwater. Similarly, toxic chemicals from underground storage tanks, untreated waste from septic-tanks and leaky landfills can also pollute the groundwater resources. Out of these sources, agriculture and dairy farming related substances have impaired groundwater quality widely at several locations (Harter et al., 2002; Singh et al., 2013; Wable et al., 2017). Groundwater in these locations gets contaminated due to intense use of fertilizers, pesticides and by disposal of dairy wastes. Nitrate is one of the dominant pollutant derived from these intense agricultural and dairy farming practices as shown in figure 1. Nitrate in forms of fertilizers/manure is used to increase the agricultural productivity of land which leaches to the underlying groundwater resources along with the nitrate enriched dairy wastes. A high mobility of nitrate in the vadose zone is further making it as a potential groundwater contaminant worldwide.

Nitrate enrichment of groundwater has been appearing as a major threat especially in intensively cultivable areas of agricultural based economies like India (Singh et al., 1995; Kundu et al., 2008; Sankraramakrishnan et al., 2008). Excessive irrigation, and inappropriate soil management practices further amplifies this problem in these regions (Gärdenäs et al., 2005; Zhu et al., 2005; Mitsch & Day, 2006) where nitrate concentrations in underground water has been found to exceed the maximum contaminant level (MCL) of 50 mg/L for drinking water established by the U.S. Environmental Protection Agency (USEPA, 1990). The high nitrate level in drinking water is unsafe to pregnant women and aged people and may cause methemoglobinemia in infants (Spalding and Exner, 1993). Groundwater entriched with high nitrate may also pollute the adjoing surface water resources through base flow contribution leading to low dissolved oxygen level in the waterbodies which is inadequate to support natural aquatic life.

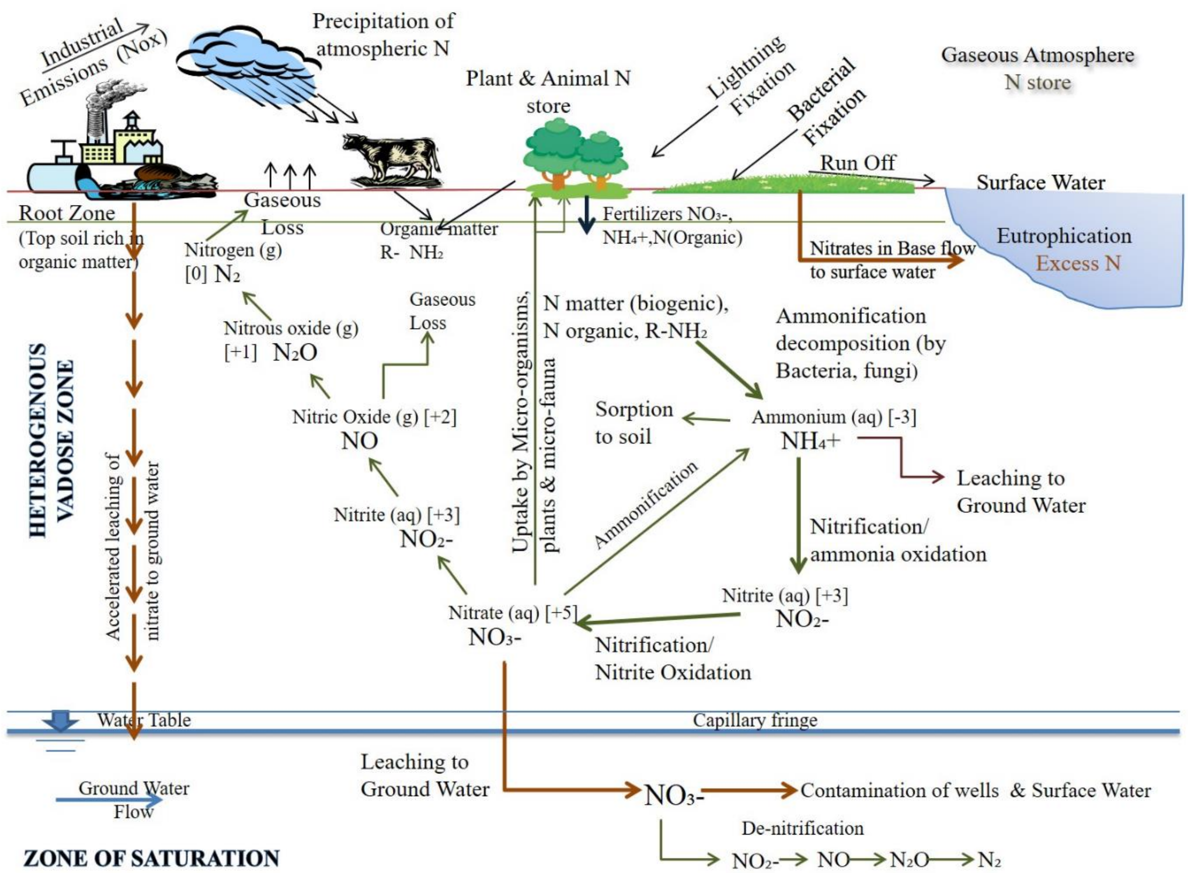


Figure 1-1 : Different source of Nitrate polluting to groundwater resources (adopted and modified from: USDA)

The soil moisture flux having dissolved solute, including nitrate, has to pass through the vadose zone before meeting to the underlying groundwater resources. The vadose zone is the layer of soil present between the earth surface and water table, and is of utmost physical, chemical and biological importance. Vadose zone, which is associated with the recharge of groundwater, degradation and uptake of contaminants, prevents surface pollutants to leach to the groundwater. Conventionaly, uniform flow through the vadose zone has been considered for computing solute load to the groundwatare resources by ignoring its heteroginity. However in the real field conditions, heterogeneity is ubiquitously present in the variably saturated zones due to varying characteristics of porous media, variability in soil moisture content, presence of plant roots, factures and (semi)impervious soil layers. Impact of this subsurface heterogeneity is further magnified under varying surface boundary condition.

The climatic/environmental variations and site specific land use pattern can also affect the subsurface flow and solute transport mechanisms significantly. Therefore, site prevailing environmental conditions and their variations are required to be considered for accurate prediction of soil moisture flow and solute transport through heterogeneous vadose zone considering various scenarios of crop yield. The flow and transport mechanisms through the partially saturated zone is also needed for predicting pollution load to the underlying groundwater resources and for implementation of its remedial measures (Yadav and Junaid 2014; Zhang et al. 2015).

Practical experiments and numerical tools are widely used in last few decades to improve our understanding of the water flow and contaminant transport processes in the vadose zone. Mathematical modeling plays important role in predicting transport of contaminants through vadose zone and its subsequent movement in underlying groundwater resources under varying (sub)-surface conditions for better management and remediation of polluted subsurface systems. However, lack of experimental/field data of heterogeneous vadose zone was always a limiting factor in scrutinizing the complexities of soil hydrologic processes. Limited flow and transport framework for vadose zone considering its heterogeniety are developed based on the practical and field measurement.. Therefore, to better analyze different flow and transport mechanisms in the unsaturated zone, an holistic integration between field characterization and mathematical modeling is critical (Nielsen et al.,1986).

1.2. Focus of the Study:

Nitrate fertilizers are indiscriminately applied to the agricultural farms in order to increase the fertility of soil leading to higher crop productivity. But leaching of excess nitrate to groundwater is degrading the water quality and also increasing the cost of the production to farmers. Due to presence of subsuface heterogeniety, preferential/non-equilibrium flow and transport processes in subsurface are gaining interest amongst the scientific community. Further, very limited literature is available dealing with soil water and solutes movement through hetrogeneous vadose zone having dynamic surface boundary conditions. Thus preferential flow of nitrate through hetorogeneous vadose zone is needed to be investigated thoroughly using practical and simulatipn experiments.

In this study a series of laboratory and simulation experiments were performed at different scales including laboratory, plot and field level for investigating nitrate movement through vadose zone. The practical experiments were conducted using one dimensional column, lysimeter and multidimensional tank setup followed by plot and field scale investigations. Present work deals with the experimental and modelling of nitrate leaching to the groundwater and hence will provide insights to the process of macropore flow and leaching of nitrate to the underlying groundwater resources.

1.3. The Objectives of the Study:

The main focus of this study is to investigate the soil water flow and nitrate movement through the heterogeneous vadose zone to underlying groundwater resources using a different levels of practical and numerical experiments. The specific objectives are

1. To investigate different mechanisms governing the process of soil moisture flow and nitrate movement in the heterogeneous vadose zone.
2. To investigate various modelling approaches used to model the preferential flow and non-equilibrium movement of nitrate in the subsurface.
3. To quantify actual nitrate flux moving from surface to groundwater resource using multidimensional and multiscale experiments under varying conditions.

1.4. Scope of the Work

Nitrate contaminated groundwater is a key environmental and water quality management issue. It is well recognized that in agriculturally intensive areas; pesticides and fertilizers may percolate through the subsurface and eventually pollute groundwater resources. The insights gained through this research work should be useful to researchers who are trying to manage nitrate polluted groundwater resources.

The present study will help in understanding the integrated water and nitrate transport process in the vadose zone that can be used in designing cost-effective and environment-friendly technologies of remediation of nitate contaminated soil water systems. Thus, the experimental and modeling outcomes of this study related to the processes of soil water and nitrate transport

transport could provide vital information towards sustainable land management and agricultural practices.

1.5. Organisation of the Dissertation

The thesis is divided into five chapters. In chapter (1), the background and focus of the study along with the objectives and scope of the proposed research work is discussed.

Chapter 2: Provides the review of literature pertaining to the modelling of preferential flow and nitrate transport in groundwater. Firstly contamination of groundwater by nitrate is discussed, followed by the discussion of various approaches for modelling the preferential movement of water and solutes in the vadose. In the next part, various studies involving experiments and modelling of nitrate through macropores is discussed.

Chapter 3: Present the detailed methodology followed in the present work. Detail of the practical experiments conducted using one dimensional column, Lysimeter and multidimensional tank setup followed by plot and field scale investigations is decsribed. This chapter incorporates various flow and transport equations which are used in modeling and also provides a solution strategy which is followed in the numerical simulations. It also describes the plot and field sites along with various parameters and atmospheric data which are input in the simulation runs.

Chapter 4: Presents the results and discussions of the soil water flow and the nitrate transport through vadose zone . Initially, the results of laboratory scale experiments are validated with the numerical model for the soil water flow and nitrate transport by consedering different modelling approaches. Simulated results of the plot scale and field scale for the nitrate leaching to the groundater are then validated using the available field data.

Chapter 5: Highlights the conclusions drawn from this study and recommends the areas for future research in the field of soil water flow and nitrate transport modeling.

The background information related to the text, such as derivation of basic governing equations used in the study, have been placed in the section on appendix.

Chapter 2

LITERATURE REVIEW

A comprehensive literature study has been done to understand soil moisture flow and nitrate transport through heterogeneous vadose zone. Various groundwater pollutants along with potential sources of nitrate are described first. Thereafter, various mechanisms used for water and solute movement through vadose zone are described. Simulation approaches for soil water and nitrate uptake by plant root biomass are also addressed. Realistic modelling approaches simulating preferential flow due to vadose zone heterogeneity are described in detail. Simultaneously, various numerical investigations and practical experiments conducted so far on non-equilibrium movement of nitrate in heterogeneous vadose zone are mentioned. Finally, use of popular models for predicting crop yield and optimum fertilizer requirement at watershed level is mentioned.

2.1. Soil water pollution by Nitrates

Numerous sources of pollutants such as hydrocarbons, heavy metals, and pesticides have been released to the soil surface polluting the underlying groundwater after moving through the vadose zone. The soil and water resources are the final receptors for such toxic chemicals posing potentials threats to human health (Chabukdhara et al., 2016). Due to these pollutants; physico-chemical, and biological properties of soil-water resources have been reformed severely, resulting in the continuous loss of soil water functions in sustaining the life. Groundwater is the main source of freshwater used by agricultural sector. However, excessive use of pesticides and fertilisers with intense irrigation practices posing a potential threat to quality and quantity of the groundwater resources. Amongst the various groundwater pollutants , nitrate is one of the most common pollutant throughout the world (Singh et al., 1995; Kundu et al., 2008).

Nitrate (NO_3) is the naturally occurring form of nitrogen and it is an integral part of the nitrogen cycle in our environment. The porous media comprising the vadose zone is capable of transporting the solute from surface to subsurface, and hence, an excessive amount of nitrogen applied with irrigation to crops can leach to the underlying groundwater resources (Yan et al., 2010). Nitrate is a highly mobile chemical species which is freely soluble in soil water while passing through the vadose zone. Many clinical trials on laboratory animals have shown that at higher doses of nitrate is potentially toxic. A high concentration of nitrate in drinking water above the maximum contaminate level (MCL) [50 mg/L] can also cause adverse impacts on human health and invariably causes methemoglobinemia in infants (USEPA 2012). Nitrate reduction into nitrite and its subsequent bonding with hemoglobin inside the human body form methaemoglobin which ultimately reduces the oxygen carrying capacity of the blood. Infants are most vulnerable to high nitrate concentration as foetal hemoglobin is more susceptible to nitrite affecting formation of HCl which may lead to infant death. Nitrate also effects the functioning of Thyroid gland in people with iodine deficiency in dietary (WHO, 2011). Higher intake of nitrate may also associate with cancer due to formation of N-nitroso compounds which are well known carcinogens. Although it is not clinically proven and needs more validation (WHO, 2011).

Since the groundwater is a major source of drinking water in many parts of the world, groundwater contamination by nitrate is of utmost importance. An understanding of various sources of nitrate and its fate and transport in soil water systems is of great important. Nitrate transported from polluted aquifers to their adjoining surface water bodies may induce an increased level of nutrients(eutrophication) affecting biodiversity, mammals, birds, and fish population adversely by producing toxins and reducing oxygen levels (Environmental Agency 2005). Besides this, denitrification processes contribute to the emission of greenhouse gases due to production of N_2O (Haag and Kaupenjohann, 2001).

The main sources of nitrate pollution are agriculture (Joosten et al., 1998; Harter et al., 2002; Shrestha and Ladha, 2002; Jordan and Smith, 2005; Liu et al., 2005) point sources such as septic systems (MacQuarrie et al., 2001) and dairy lagoons (Erickson, 1992) dissolved nitrogen in precipitation, and dry deposition (Zhu et al., 2005; Leskovar et al., 2016). Amongst these, agriculture has been identified as the major contributor (USEPA, 1990; Babiker et al., 2004; Gärdenäs et al., 2005; Mahvi et al., 2005; Thayalakumaran et al., 2008; Zhao et al., 2011) in polluting groundwater resources.

Nitrogen is applied to agricultural crops in several forms such as urea, ammonium compounds, calcium nitrate, and animal manure. All these substances are eventually converted to nitrate and transported away from the top vadose zone soil layer to the adjoining waterbody or groundwater (Gao et al., 1997; Jha et al., 2017). Denitrification converts nitrate to nitrogen or nitrous oxide gas and can diminish nitrate loading to water body and groundwater resources. This process generally occurs in areas where favorable geochemical conditions are met, viz. low O_2, organic carbon or reduced sulphur, and the presences of denitrifying bacteria. The hyporheic zone, riparian buffer zones, poorly drained soils and saturated zone with low dissolved O_2 are favorable environments for denitrifying bacteria. Figure 2.1 demonstrates the different mechanism of nitrate fate and transport in (sub)-surface.

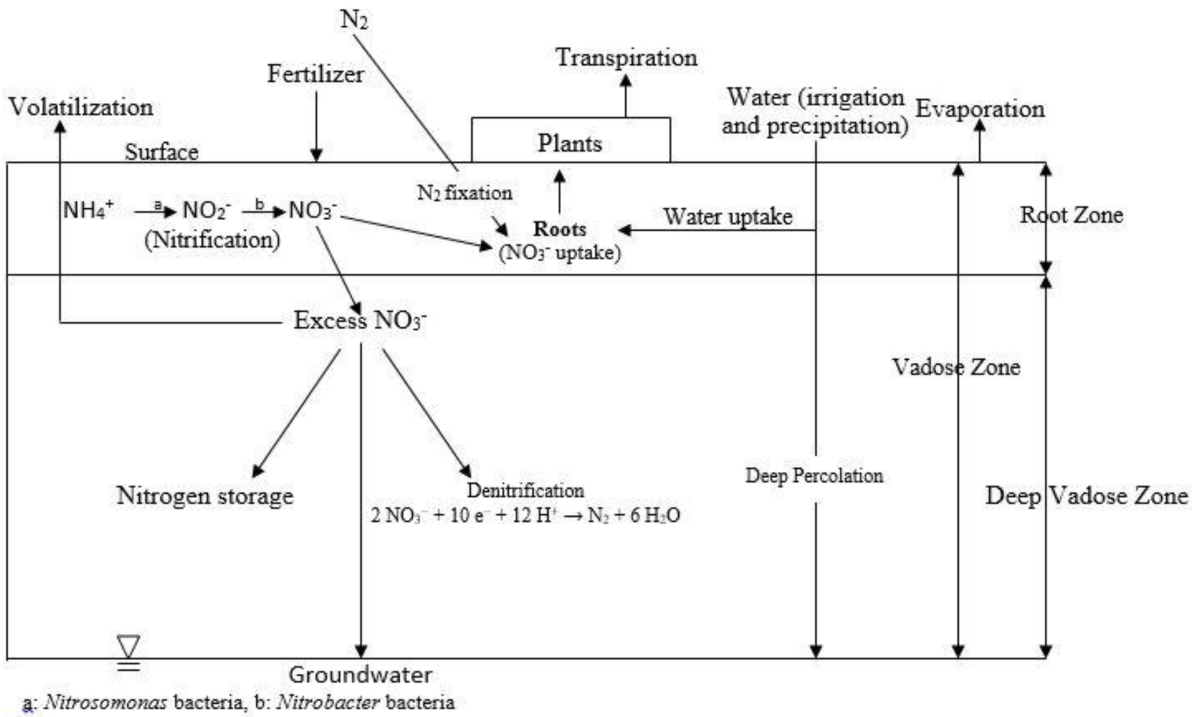


Figure 2-1: Fate and transport of nitrogen in vadose zone.

Urea, the most commonly used fertilizer, is hydrolyzed to ammonium in water by heterotrophic bacteria and then nitrified to nitrite and nitrate by autotrophic bacteria. The rate of conversion from nitrite to nitrate is more rapid than the nitrification of ammonium to nitrite in the soil media (Hanson et al., 2006). However, phosphorus isotope analysis of nitrate indicates that denitrification is not an important process under real field conditions (Martin et al., 1995). Figure 2.2 shows the impact of high nitrate application in agriculture on soil-water and surface water resources. Intense application of nitrate rich fertilizers also contribute in the emission of greenhouse gases which ultimately induce the climate change.

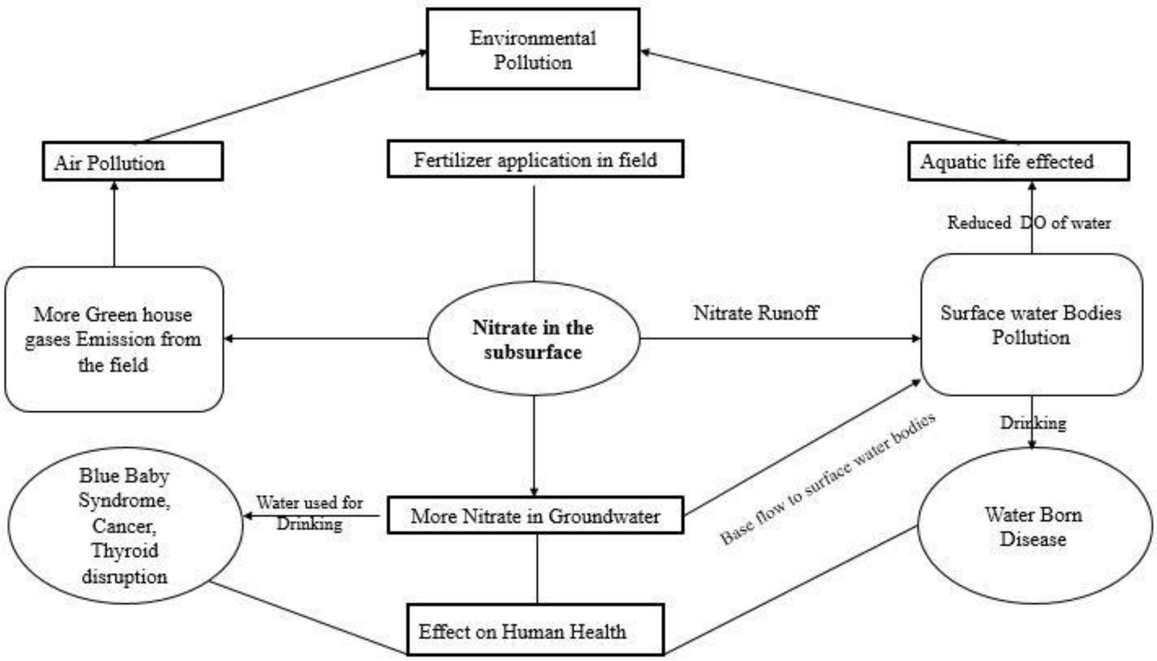


Figure 2-2: Impact of high nitrate application on (sub)-surface systems.

The modern agriculture practices with main focus in increasing the crop production is accompanied by intense use of fertigation. Intense fertigation infiltrates excess root zone nitrate into groundwater after passing though the deep vadose zone layers without sufficient denitrification (Singh et al., 1995; Bijay-Singh, and Singh, 2004; Leskovar and Othman, 2016). Groundwater quality degradation in rural areas is frequently attributed to agricultural practices involving the excessive use of fertilizers and pesticides (Suthar et al., 2009; Singh et al., 2013; Chopra and Krishan, 2014; Krishan et al., 2014; Wable et al., 2017). At present, groundwater contamination from agricultural nonpoint sources has become a ubiquitous environmental problem. Hallberg (1987) reported an almost linear increase in groundwater nitrate concentration over the last 20 years in United States.

Federal legislation in USA first recognized the potential impacts of nitrate leaching from agricultural area on water resources during the early 1970s, when the Safe Drinking Water Act, Clean Water Act, Federal Insecticide, Fungicide, and Rodenticide Act and other legislation related to water pollution were legislated. From that time, various efforts have been made by both the scientific and technical community and the agricultural industry for the better understanding of the role of agricultural practices in defining the fate of fertilizers and pesticides in surface and subsurface water resources and to improve agricultural activities accordingly (Harter et al., 2005).

2.2. Mechanisms of soil water and nitrate movement

Understanding the dynamics of soil moisture movement and solute transport is essential for evaluating the fate and transport of nitrate. Because of low available carbon sources in deep vadose zone (Dai et al., 2017), nitrate attenuation is quite poor which profoundly affect groundwater quality (Onsoy et al., 2005; Scanlon et al., 2010; Russo et al., 2013). The vadose zone act as the filter and a buffer zone as contaminants are retained, degraded and transformed during their transportation via this unsaturated zone, thereby controlling the movement of the nitrate load to the groundwater (Hansen et al., 2017; Min et al., 2017). Soils in deep vadose zone having reduced infiltration capacity generates an anaerobic condition (Mahvi et al., 2005) which may accelerate nitrate loss due to denitrification. Therefore, the soil moisture dynamics, soil hydraulic properties and biogeochemical parameters are the crucial factors for predicting nitrate transport and fate in soil water continuum (Yadav et al., 2009). Thus a thorough understanding of soil moisture movement and solute transport mechanisms in the vadose zone is critical in managing quality and quantity of groundwater resources (Denton et al., 2004; Harter et al., 2005; Min et al., 2018).

The vadose zone can be separated into two sections: the upper root zone and the lower deep vadose zone (Harter et al., 2004). A considerable amount of studies are conducted to investigate the nitrate mass balance in the root zone (Lafolie et al., 1997; Allaire-Leung et al., 2001; Stenger et al., 2002). Excess nitrate moving from top soil layers can contaminate the groundwater in absence of impeding layers present in the deeper layer (de Vries and Simmers, 2002). However the nitrate leaching to the groundwater depends on various other parameters such as land use practices (Bohlke and Denver, 1995; Sinha et al., 2009), depth of the water table, soil hydraulic properties, nitrogen loading at the surface, soil nitrogen dynamics such as denitrification and fertilization and irrigation practices (Ray and Kelly 1999; Almasri and Kaluarachchi, 2004a; Zhu et al., 2005).

Places with deeper water tables and high organic matter in vadose zone soils having low hydraulic conductivity are lesser prone to groundwater contamination as compared to places with shallow groundwater level having clean soils with high hydraulic conductivity (Bear, 1972). Studies have performed to understand the fate and transport of nitrate in the root zone but most of the studies on nitrogen laid more focus on root zone nitrate dynamics and its ability to reach the surrounding water body. Further, nitrate movement in vadose zone is investigated considering uniform moisture flow and solute transport mechanisms. Some studies performed on nitrate fate and transport through vadose zone has considered the realistic approaches like dual porosity but most of these studies are either limited to zero or one-dimension level batch/pot scale experiments (Delgado et al. 2014; Sharma et al. 2016).

2.3. Modeling crop yield and nitrate uptake

Roots are the key conduit for water and solute exchange between soil and plant system. Through root water uptake, soil water translocated from vadose zone to its surrounding atmosphere via root and shoot biomass (Feddes et al., 2001). Water and solute uptake by plants from vadose zone plays an important role in hydrology, agricultural and environmental science. Tempo-spatial soil moisture distribution in vadose zone is highly influenced by the root water uptake which is not necessarily uniform throughout the root depth (Quijano et al., 2012; Garg, et al., 2015). Thus a better understanding of soil moisture distribution in variably saturated zone along with plant water uptake is required for accurate quantification of nitrate movement below the root zone.

Land surface process such as infiltration, runoff and evapotranspiration are also dependent of soil moisture status and plant growth (Gao et al., 1997; Soylu et al., 2011; Garg et al., 2015). Therefore, water uptake by plants is a prerequisite in modeling solute transport, groundwater vulnerability to contamination (Yadav and Junaid, 2015), phytoremediation (Yadav and Mathur, 2008), nutrient uptake, groundwater recharge estimation, and in irrigation water management (Mathur and Rao 1999; Zhang et al., 2002; Leung et al., 2015).

Root water uptake rate and its pattern depends on root density and its distribution, soil moisture content, nutrients and prevailing weather condition (Ke et al., 2000; Ryel et al., 2004; Hodge et al., 2009; Albasha et al., 2015). Root water uptake models been developed based on the hydrological perspective are based on microscopic and macroscopic approaches (Mathur and Yadav, 2010). Microscopic models are single-root models with detailed description of water flow through and individual root. Whereas, macroscopic approach treat the entire root system as whole and a sink term representing plant water uptake is incorporated in soil water flow equation. The sink term representing the plant water uptake rate from a particular soil layer is considered as a function of soil water potential and root water extraction capacity.

Gardner (1960) made the first attempt to incorporate microscopic root water uptake into unsaturated soil moisture flow model. In this approach individual roots are considered as a narrow cylinder of uniform radius and a radial convergent flow towards the root is taken into account for quantifying the root water uptake rate. Application of this microscopic approach is limited to individual plant as it demand rich parameterization, complex geometrical and functional operation, and computational requirements (Molz, 1981).

Under the non-stressed condition, sink term is the transpiration demand that can be distributed across rooting depth as a function of root density distribution. However various experiments show that under stressed condition, water uptake profile deviates from its root distribution function (Bruckler et al., 2004; Faria et al., 2010). For reflecting water uptake function under soil moisture stress or oxygen stress, a stress reduction factor (Feddes, 1982) is linked to root water uptake function.

Numerous models have been proposed by the scientists over the decades to understand and quantify the uptake of solute by plant root biomass. These models classify into two general categories: empirical models and mechanistic models. The empirical models directly correlate the soil solute concentration with its presence in the different parts of the plant biomass using soil-plant uptake factor for a particular soil-plant system (Yerokun and Christenson, 1990). In these empirical models, the solute concentration in plant biomass and in the soil is assumed to be in equilibrium, and thus, the exposure time is not taken into account. Furthermore, these types of solute uptake relationship between the soil and plant is significant over a narrow range of solute concentration, relatively nontoxic range (Jiang and Singh, 1994; Kale and Sahoo, 2011; Jha et al., 2017).

Alternatively, mechanistic models simulate the solute uptake by plant roots mathematically using some uptake kinetics (Rao and Mathur, 1994; Mathur and Rao, 1999; Mathur, 2004; Verma et al., 2006). These models which consider the mechanistic approach of solute uptake can be subdivided in two categories; 1) passive and 2) active uptake types, based on the consideration of solute uptake parameters (Rengel, 1993).

Passive uptake mechanistic models are commonly used for quantifying solute uptake (Hoffland et al.,1990) as they do not contain any kinetic parameters of plant uptake as compared to the active uptake models. Passive uptake models consider the root biomass as an infinite sink and the solute uptake rate is assumed equal to the product of the water uptake rate and the contaminant concentration in soil water. This approach is oversimplified however, it seems reasonable for cases of very low solute concentrations where the potential rate of uptake exceeds solute transport to the root biomass. Nye (1966) and Leskovar et al. (2016) suggested improvement modification on this passive approach by considering a linear relationship between the nitrate uptake and nitrate concentration at the root surface to account for the root absorbing power. Such types of linear relationships between solute uptake and its concentration are however valid only for a very limited range of nutrient concentrations.

In active uptake mechanistic models (Rao and Mathur, 1994; Nedunuri et al., 1998; Mathur, 2004) the uptake of solute depends upon both the plant uptake capacity and the supply from the soil. In these models, the uptake of nitrate by root biomass is described by a Michaelis-Menten kinetics according to which the uptake increases with an increasing nitrate concentration in a curvilinear fashion such that it asymptotically approaches a maximum uptake. Nitrate transport from soil to the roots surface by mass flow describes contaminant movement with water through the soil when water is absorbed by plant roots to meet the plant transpiration requirements (Lehto et al., 2006; Yadav et al., 2009b; Yadav and Hassanizadeh, 2011). Gusman and Marino (1999) used the RISK-N model to predict the movement of nitrate in the saturated and unsaturated zone. They developed 1-Dimensional convection-dispersion equation (CDE), averaged spatially in the entire unsaturated zone, and a 2-D CDE in saturated zone to account for the movement of nitrate in the vadose zone and groundwater. Various nitrate assimilation processes such as ammonium adsorption, ammonia volatilization, nitrification, denitrification, leaching and plant uptake were considered in the model.

To see the impact of fertigation on nitrate leaching, crop simulation is required (Grabow et al., 2011). Crop simulation models characterize plant growth processes in form of a mathematical representations as a factor of interactions among genotype, environment, and crop management (Fischer et al., 2002; Hammer et al., 2002; Hansen 2002). Various generic crop modeling approaches have been used for simulating maize (Zea mays L.) development and growth. SUCROS, WOFOST and INTERCOM (Van Ittersum et al., 2003), STICS (Zimmer et al., 2003), and CropSyst (Stockle et al., 2003) are well known for simulating crop yield. Yang et al. (2004) developed the Hybrid Maize simulator for predicting the maize yield under non-limiting (fully-irrigated) and water-limited (rain fed) conditions based on daily weather data. Haishun Yang (2016) also developed Maize-N program that estimates fertilizer nitrogen rate for a corn crop. The program first simulates maize yield potential and then estimates the economically optimal N rate (EONR) of fertilizer for the computed maize yield.

2.4. Modeling soil water and nitrate movement in vadose zone

Understanding mechanisms of soil moisture flow through vadose zone is a prerequisite for simulating nitrate movement through variably saturated zone and for predicting nitrate load to the groundwater (Hendrickx and Flury, 2001; Harter et al., 2005; Dahan et al., 2009). Conventionally uniform flow is considered for quantifying water and solute fluxes joining groundwater table.

Uniform Flow

In uniform flow, water flows through entire soil matrix having uniform and stable wetting fronts parallel to the top soil domain (figure 2.3). The porous media is assumed to have interconnected pores all contributing in water flow and solute transport. The soil water flow and solute movement is described mathematically by Richard, and advective-dispersive equations, respectively. Richard's equation is derived from the Darcy's law and continuity equation for the movement of soil water in the porous media. The mass balance coupled with Fick's law is used in deriving advection dispersion equation which is used to predict the movement of nitrate in the vadose zone. The nitrate move with moving soil water is known as advective flux and it gets spreading due to dispersive and diffusive fluxes.

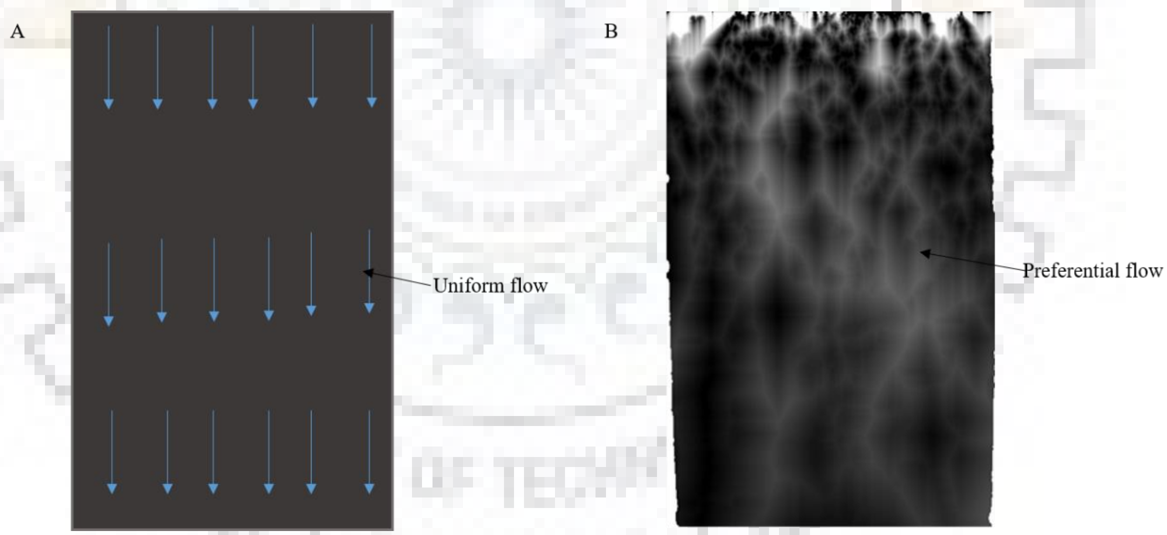


Figure 2-3: Uniform and preferential flow of soil water and solute through a vadose zone.

Nitrate moves from high to low concentration zone due to concentration gradient kwon as diffusive flux. Spreading and mixing of nitrate due to variation in velocities of the neighboring particles of fluid can occur at many scales due to the dispersive flux. The dispersion of solute at a microscopic scale occurs due to the velocity variation within the pores and due to the movement of the fluid around the soil particles (Srivastava et al., 1992; Toride et al., 2003; Yadav and Mathur, 2008). Macroscopic dispersion refers to the dispersion caused by inter fingering of materials of different permeability.

As some short of heterogeneity is present in vadose zone, consideration of uniform flow oversimplify the flow and transport mechanisms considerably. In such types of vadose zones, soil water flows along relatively high pervious pathways/cracks known as preferential flow as shown in figure 2.3.

Preferential Flow

In preferential flow, soil water and the dissolved solute bypasses a major fraction of the soil domain (Hendrickx and Flury, 2001) which increases the effective transport velocity of water and solutes. Preferential flow reduces the retention time of solute and increases the risk of groundwater contamination considerably (Larsbo et al., 2005; Radcliffe and Simunek, 2010).

Preferential flow can occur over a wide range of velocities in varying range of pore sizes (Beven and Germann, 2013). This means that preferential flow is not limited to transition and turbulent flow in large macropores, but can also occur under laminar flow cases having fluid films with a thickness of less than 100 μm along the sides of smaller pores (Nimmo, 2010). Regions of high preferential flow may or may not be connected directly to the soil surface or another source of water. Large scale preferential flow regions can be caused by weathering of parent material over long periods of time (karst formation, soil fissures). Smaller scale preferential flow regions can be the result of layered heterogeneity based on alluvial deposits, root growth and decay or animal burrowing activity, or surface cracks formed by clay shrink-swell potential (Beven and Germann, 2013). Preferential flow is complicated phenomena, difficult to measure and often, inferred from unexpectedly early water and chemical breakthrough in the vadose zone (D'Alessio et al., 2014).

Simunek et al. (2003) extensively reviewed various models used for simulating non-equilibrium flow and transport of water and solute in heterogeneous vadose zone. Various models such as single porosity model of Ross and Smettem (2000), dual–porosity models, dual-permeability model, multi-porosity and multi-permeability models are discussed by Simunek et al., (2003). While no domain geometry division is considered in single porosity models, in dual-porosity and dual-permeability models, flow domain is divided into two regions for providing a better representation of the actual scenario. In multi-porosity and multi-permeability models flow geometry can be divided into multiple domains. Dual-porosity and dual-permeability models, are used for modelling preferential flow phenomenon where flow region is divided into matrix and fractures. Fractures are considered to be the water conducting zone in both the approaches , whereas flow in matrix is considered to be absent in dual-porosity approach (Šimůnek and Genuchten, 2008). Thus, use of macroscale two-domain flow system seems to be the best available way of representing preferential flow (Beven and Germann, 1982; Šimůnek and Genuchten, 2008). The dual-porosity models allows water flow and solute transport to occur between the mobile and immobile phases and therefore also called as mobile-immobile models (Figure 2.3a). However, dual-permeability models are somewhat different from dual-porosity models. In dual-permeability models, mobile and immobile phases are replaced with "fast" and "slow" zones, respectively (Figure 2.3b) where both zones allow water and solute transport, but at different rates.

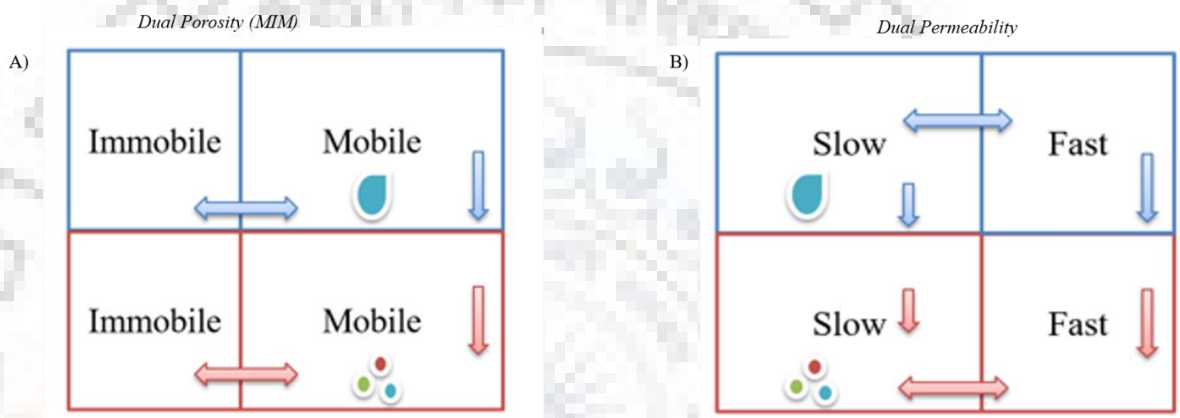


Figure 2-4: Different Conceptual models for soil water flow and solute transport in the subsurface: (a) dual porosity (mobile-immobile) and (b) dual-permeability. Adapted and modified from Šimůnek and van Genuchten (2008).

The mass transfer of water between matrix and macropores of the soil domain is driven by the gradient of pressure heads. The mass transfer for solute includes both convective mass transfer with moisture flow and diffusive mass transfer due to the concentration gradient (Šimůnek et al., 2008).

For modelling flow through dual porosity models, total moisture content in the soil domain is considered to be sum of moisture content in fractures and matrix. Matrix is considered to store, retain and exchange water from macro-pores (inter-aggregate pores) but no conduction of water takes place here (Wierenga, 1977; Köhne et al., 2006). Dual-porosity models formulated based on Richard's equation accounting for both gravity driven and capillary driven flows (Germann and Beven 1985). Solute Mass transfer is assumed to be proportional to the difference in effective saturation in two regions described by first order kinetics. Advantage of using water mass transfer coefficient is lesser number of parameters requires because only saturated and residual moisture content of the immobile (matrix) region is required additional to the rate coefficient. Inherent assumption is that there is no significant difference between the hydraulic properties of fracture and matrix regions (Gerke and Genuchten, 1993).

Researchers simulated the preferential flow using HYDRUS considering dual-porosity and dual-permeability approaches and optimized parameters using inverse solution technique (Haws et al., 2005; Akay et al., 2008; Lamy et al., 2009; Kodešová et al., 2010).In heterogeneous vadose zone, dual porosity can better represent the flow and solute transport to the underlying groundwater table. While in homogenous domain, where the porous media is mainly made of different sizes of soil particles, dual porosity approaches can also be used effectively for soil moisture flow and solute transport simulation. Uniform flux can be expected for the horizontal/lateral flows in saturated zone or the flow taking place against the gravity force. However, the soil moisture flux is expected to pass through the macro-pores of limited zone and bypass the remaining micro-pore of the soil matrix. Therefore in the present work, dual-porosity approach is used to predict preferential flow of water and nitrate through the vadose zone.

2.5. Review on preferential flow and nitrate movement in vadose zone.

Models for predicting the water flow in vadose zone relies on the assumption of continuity, i.e. hydraulic properties over the domain are uniform (Sposítu and Chu, 1982 cited in Germann and Beven 1985). Since vadose zone is composed of various soils, hydraulic properties vary with space (Botros et al., 2009). Further variation in soil moisture content changes the flow properties of soil media. Large variance in hydraulic properties results in non-uniform movement of water front through the soil with water moving from regions with higher conductivity by passing the low conducting matrix (Vogel et al., 2010). Dead roots, earthworm and ant bores also creates macro-pores or large void spaces (Li and Ghodrati, 1994; Pot et al., 2005; Jarvis, 2007) through which water moves very rapidly to the deeper parts of the vadose zone in considerably very less time. Solutes are advected with the flowing water through these macro-pores along with water. Researchers had studied the effects of preferential flow paths in soil on fluid and solute transport (Kelly & Pomes, 1998; Harter et al., 2005; Legout et al., 2009) and tried to model this phenomenon using Mobile-immobile/dual-porosity and dual-permeability approaches (Gerke and Genuchten, 1993; Ross and Smettem, 2000; Roulier and Jarvis, 2003; Haws et al., 2005; Pot et al., 2005; Gärdenäs et al., 2006; Šimůnek et al., 2008; Lamy et al., 2009; Vogel et al., 2010; Botros et al., 2012). Because of preferential flow of water and solutes through the macro-pores, there is very less time for water and solutes to equilibrate with the rest of the soil matrix creating non-equilibrium conditions in the soil matrix. Macro-pores which constitute a very small part of the soil matrix provide a channel through which most of the water and solutes flow to the deeper vadose zone very rapidly without equilibrating with the rest of the soil matrix.

Jarvis, (2007), reviewed studies conducted on the macro-pore flow in the soils. As water enters the macro-pores, because of larger hydraulic conductivity, water flows in a non-equilibrium manner bypassing the soil matrix, so as the soil approaches saturation macro-pore conductivity increases. Also, as per Jarvis, (2007) many authors have suggested that as the water potential increases towards saturation, non-equilibrium flow of water takes place. Germann and Beven, (1985) referred to macropore flow as "short circuiting" and gravity driven lasting for short times after cessation of water on soil surface contrary to the uniform flow of through the matrix.

To demonstrate the stable and unstable flow through partially saturated homogeneous sand, Babel et al. (1997) performed experimental and numerical study. Different boundary conditions like air dry and field capacity of the sand were applied to the study domain. It was found that the soil-water velocity remains constant regardless of the incident flux as long as the flux is smaller than the hydraulic conductivity. The antecedent wetness on the unstable flow reduce the soil water velocity significantly from air dry to field capacity conditions. To see the effect of soil texture and the impact of irrigation on the solute movement, Gupta et al. (2009) conducted laboratory and numerical experiments. For a specific soil texture, as the applied pressure head increases, nitrate movement along with moisture content also increases and the effect of the capillary forces on the emission rate of the pipe decreases. The effect of capillary forces in the flow domain on the emission rate of the pipe is negligible in the saturated conditions.

Richard's equation assuming local equilibrium of water content is incapable of predicting the actual wetting fronts of soil because of preferential flow (Gärdenäs et al., 2006; Ross and Smettem, 2000; Vogel et al., 2010). Ross and Smettem (2000) developed a one-dimensional model to simulate physical non-equilibrium water flow in soils using modifying form of Richard's equation by introducing one additional factor τ (equilibration time constant) which accounted for the non-equilibrium movement of water in the soil. The moving water fronts in soil were predicted and optimized the value of time constant τ using the predicted data. The proposed model is relatively simple and requires single parameter apart from soil hydraulic parameters. However time constant has to be optimized separately for each soil horizon for the vadose zone made of layered soil strata. Also, this model failed to predict the movement of solute front under non-equilibrium conditions as claimed by Simunek et al. (2003).

Vogel et al. (2010) who defined the non-equilibrium flow as the phenomenon where water content is lagging behind the water potential as given by the water retention curves. A two-dimensional model was developed in line with the model developed by Ross and Smettem (2000). It was tried to optimize the correlation length associated with modelling of non-equilibrium flow of water. It was concluded that the model developed by Ross and Smettem (2000) has to be refined further to predict the non-equilibrium water flow in heterogeneous vadose zone. However, the model developed by Vogel et al., (2010) is limited to the water flow predictions only. Germann and Beven (1985) also developed a model based on the concept of division of flow geometry into two regions. Flow in macro-pores is considered to be gravity driven only and is approximated by kinematic wave theory. They optimized various parameters for the developed model for 19 Dutch soils. This model does not require water retention characteristics of the macropores, and hence, number of parameters required is quite less as compared to the other models. However, only gravity driven flow was considered by neglecting the horizontal movement of water in the soil which occurs due to capillary action. Another drawback of this model is that uniform macropore system throughout the soil domain was considered, while in actual scenario, each macropore can have its own properties. Thus accuracy of this model for solute transport through macropores has to be verified.

Various simulation models such as VSAFT3 (Srivastava and Yeh, 1992), VSAFT2 (Yeh et al., 1993), Tough2 (Pruess, K., 1999), HYDRUS (Šimůnek et al., 2006; Šimůnek and Šejna, 2008) were developed for investigating the behaviour of soil moisture flow and contaminant transport in the subsurface. Jarvis (1994) developed MACRO (version 4.3 launched in 2001), one-dimensional model based on dual permeability approach, which is capable of simulating transport of solutes and pesticides. Mass-exchange between the domains is calculated with first-order expression. Convection-dispersion equation is used in this model development by neglecting dispersion in macropores, and therefore, the model application is limited for predicting solute transport in convection dominated cases. Using MACRO model of Jarvis (1994), Roulier and Jarvis (2003) modelled the leaching of pesticide due to preferential flow and optimized the parameters using inverse parameter estimation technique using SUFI. Concept of gravity driven flow in macropores proposed by Germann and Beven (1985) was used along with the first-order rate kinetics for exchange of water from macro-to-micropores. It was also assumed that reverse flow occurs once micropores becomes oversaturated with water, i.e. water starts moving from micro-to-macropores. A good fit was obtained with the modelled data and parameters were estimated by inverse modelling. Relatively more errors were found in fitting the modelled data to observations from the column experiments which were attributed to errors in simulating water outflow after rewetting of the soil. A lower value of degradation coefficient of the pesticide was taken resulting in overestimation of the pesticide concentration in the soil profile. They suggested better experimental design and use of other available models for better estimation and comparison of MACRO model with other available models.

Dušek et al.(2006) also modelled the transport of Cd during heavy rainstorm in heterogeneous vadose zone using S1D DUAL code, which is an extended version of HYDRUS 5 code., and the authors compared the simulation profiles of applied dual-permeability approach to the classical single permeability approach and suggested that dual-permeability model is better suited to simulate preferential flow as compared to single domain models. However, the model was not used for predicting movement of conservative solutes.

Modeling Nitrate movement using preferential flow

Most of the studies on nitrogen dynamics laid more focus on root zone nitrate dynamics and reach ability of nitrate to the sea from the shallow aquifers and very little is known about fate and transport of nitrate in vadose zone beyond root-zone (Onsoy et al. 2005). It was believed that deeper vadose zone is of not much importance because of lesser biological and chemical activity taking place there (Pionke and Lowrance, 1991 cited in Onsoy et al., 2005). But Stevenson (1986 cited in Onsoy et al., 2005) showed that “agricultural regions have considerably deeper vadose zones which contain appreciable amounts of organic matter. Large experimentation costs, spatial variability and long traveling times limits the study of nitrate movement in deeper vadose zone.

Kelly and Pomes (1998) studied the movement of nitrate from agricultural fields through vadose zone to the groundwater using N^{15} tracers and concluded that substantial amount of nitrate reaches to the groundwater which can be attributed to the preferential flow path taken by the water during the infiltration. They also studied the effect of spatial scale on hydraulic conductivity of the soil and concluded that hydraulic conductivity increases with scale because of the inclusion of more and larger preferential flow paths.

Akay et al. (2008) modelled flow dynamics during macropore-subsurface drain interaction and compared the results with the column experiments. Their objective was to study the effect of surface macropores to hastened movement of water to the subsurface drain. A three-dimensional grid was prepared with subsurface drain near the bottom of the domain and water table at the bottom of the domain with macropores of varying lengths. A three-dimensional Richard's equation was used having varying hydraulic conductivity for macropores with varying depths. It was observed that surface macropores behave differently as compared to the subsurface macropores. Surface macropores conveyed the water much rapidly as compared to the buried macropores and hydraulic non-equilibrium was found to be higher than buried macropores. They also found that, boundary conditions have to be changed for surface and buried macropores.

A column experiment was performed by Li and Ghodrati (1994) to study the effect of preferential flow on the movement of nitrate due to the presence of dead root in the soil. They compared their experimental results with various modelling approaches—and concluded that none of the model appropriately fitted the observed data, with mobile-immobile approach having the best fit of the used models.

To investigate the impact of microbial growth and mass balance on substrate interconversion and degradation Mburu et al., (2013) used the horizontal subsurface flow constructed wetlands systems. The model predicts organic matter, nitrogen and sulphur effluent concentrations and their reaction rates within the limit. Four pilot scale study considering subsurface horizontal-flow constructed wetlands for the removal of chromium and COD with some other nutrients from landfill site was conducted by Madera-Parra et al., (2015). It was observed that COD and chromium removal efficiency of the designed system was around 67 % and 50 to 58 % respectively. The nitrate found slightly higher in out flux as compared to the influx. To see the impact of carbon rich substrate on nitrate and bacteria transport in the subsurface Chung et al., (2017) performed column studies. In their study they performed two sets of column experiments one was with raw hydrochar and one with alkali mixed hydrochar. The removal of E. coli was not good when the sand columns were supplemented with raw hydrochar. In case of alkali mixed hydrochar more than 90% of E. coli removal efficiency was achieved in the column experiments.

The stochastic analysis of nonlinear reactive solute transport in a heterogeneous porous medium is a very computationally demanding task. Chaudhuri and Sekhar (2005) attempted to analyze the pollutant migration in the soil liner for one-dimensional solute transport problem. In the case of stochastic simulation mean concentration peak is higher than that of the deterministic case. The study indicates that the probability of exceeding the threshold concentration of pollutant is found to be sensitive to the variations in the key parameters like hydraulic conductivity, porosity dispersity of the random fields. Chaudhuri and Sekhar (2008) also attempt to assess the relative effects of various sources of uncertainties in probabilistic behavior of the concentration in a porous medium when the system parameters are modelled as random fields. The probabilistic behavior of the random response function was obtained by using a perturbation-based stochastic finite element method. This method work effectively well for mild heterogeneity. The proposed method is applicable for both one dimensional as well as multidimensional nitrate transport in the porous media.

To see the impact of precipitation and dissolution in porous media, Kumar et al., (2016) used homogenization techniques to provide a rigorous derivation of the small scale model. To find the impact of temperature on fluid flow an experimental and numerical study performed by Tiwari et al., (2014). A plate heat exchanger considering nano-fluid as homogeneous mixtures was used by the authors. The results of simulation were compared with laboratory data in order to verify the accuracy of the model. Validation of the computational fluid dynamics model indicated that simulation can be performed to predict the plate heat exchanger performance with reasonable accuracy considering nano-fluid mixture. Das et al., (2011) also present a numerical model of nonlinear reaction diffusion equation with fractional time derivative in the form of a quickly convergent series. The developed equation was used for modelling of nonlinear solution of contaminant transport in the subsurface.

Field scale modeling

Solute transport in partially saturated soils at the field scale is necessary for quantify the solute flux, assessing the level of contamination and for designing remedial measures. Ojha et al., (2014) provided an analytical solutions at local scale based on advective vertical transport of nitrate. The solution was then used to field-scale nitrate transport by considering lognormally distributed hydraulic conductivity of the field site to represent natural heterogeneity. The proposed method are limited to those filed conditions which have loamy sand and sandy loam soil profile. Further, Ojha et al.,(2015) investigated the role effective velocities and dispersion at the field-scale temporal moments of solute transport for preferential flow under rainfall through partially saturated zone. An analytical equation was developed for spatial temporal moments of solute travel times. The results were compared with Monte Carlo simulation and multidimensional numerical model for the calibration and they found that effective dispersion increases linearly with depth of the soil domain.

Obtaining surface soil moisture values at field-scale using ground-based measurements is expensive and time consuming. To fill this gap, Ojha and Govindaraju (2015) developed an analytical equation by using Richard equation and assumed log-normal distribution of the spatial surface saturated hydraulic conductivity field for surface soil moisture. For obtaining the response of surface soil moisture evolution, actual rainfall event of the area was utilized. The findings are helpful in upscaling of soil surface moisture content.

Onsoy et al. (2005) studied the movement of nitrate in a 15.8m deep heterogeneous vadose zone in California nectarine, where nitrate fertilizers were added in three categories: control, standard and high depending upon the amount of fertilizer application. Fertilizer experiment was carried for seven years and after that nitrate mass balance was calculated by including various parameters like fruit nitrogen level, nitrogen stored in the vadose zone, denitrification in root zone and in deep vadose zone, atmospheric losses and nitrate percolation to groundwater. It was found that there was a higher potential risk of nitrate leaching in high subplots as compared to standard plots. High level of non-detects were found in the deeper vadose zone, which authors attributed to the heterogeneity and flow non-uniformity. They mentioned that high number of non-detects in the vadose zone cannot be due to the denitrification losses in the deeper vadose zone because of very less organic matter present in that part and as the vadose zone at the site is highly heterogeneous and is having multiple layer of different textured soils, there is high variability in the hydraulic properties of the entire domain leading to high flow heterogeneity and preferential flow leading to hastened leaching of nitrate to the groundwater contrary to that predicted by mass balance approach.

Das et al. (2004) and Das and Hassanizadeh (2005) performed experimental and numerical study to investigate the impact of micro heterogeneity effect on flow properties of porous media in the upscaling of pore to core levels. For the sustainable groundwater utilization at Konan basin of Kochi, Japan, Jha et al., (1999) analysed the problem of increased groundwater withdrawals. The trend analysis of water utilization indicates that the groundwater demand would increase by 43 and 52%

by the years 2010 and 2025, respectively. The Groundwater table fluctuations over the entire basin vary appreciably in space and time, indicating a wide variation of natural recharge. It was concluded that besides the precipitation, stream-aquifer interaction also play a significant role in subsurface recharge. The aquifer hydraulic conductivity was varying from 65 to 804 m d^{-1} suggesting the presence of significant aquifer heterogeneity.

To find spatial variability of porous media which affect the soil water flow and nitrate transport, Machiwal et al., (2006) performed Infiltration and analysed the spatial characteristic in a field site of Kharagpur, India. They conducted 24 infiltration tests on squared grid pattern using double-ring infiltrometers. The experimentally collected data were fitted to several infiltration models and a best-fit model for each sites was identified. The parameters like sorptivity, transmissivity of soil media showed wide variation amongst all test sites. It was concluded that the study area has wide spatial variability of transport parameters. To see the impact of overusing and sea water intrusion on a coastal basin Rejani et al. (2008, 2009) were developed a groundwater simulation and optimization model. The sensitivity analysis shows that the aquifer system is more vulnerable to the river seepage, rainfall and interflow than the hydraulic conductivities and specific storage. It was found that optimal pumping schedules and cropping patterns differed significantly under the various scenarios, and the water table position improved significantly under the optimal hydraulic conditions.

To see the impact of irrigation and fertilizer application on groundwater quality of Nebraska MSEA site Spalding et al., (2001) performed a detailed study for the periods of six years. The watershed predominantly used for the corn farming. During their study variation in agricultural practices, irrigation management and seasonal behaviour of the climate can impact nitrate concentration of underlying groundwater resources. For the quantification of national terrestrial nitrogen budget for the developing countries Ascott et al., (2016) performed a study in three different aquifers at England and Wales. More than 35% water supply for public depend upon the groundwater of these aquifers. During experimental study they used vadose zone travel time and nitrate load at the surface of the filed area. They quantify and conclude that amount of nitrate stored in vadose zone of these underlying resources was 2.5 to 6 times more as saturated zone, it indicates that the vadose zone is an important store of reactive nitrogen.

In the Chtouka-Massa, Morocco basin 94% of fresh water resources used for agricultural activity. The aquifer extends over an area of 1250 km^2. The groundwater quality and quantity affected due to intensive use of nitrogen fertilizer in agriculture, over exploitation along with sea water intrusion in the particular watershed. Malki et al., (2017) were carried out several sampling in different sites of the study area to investigate the spatial variation of nitrate along with several other contaminant in groundwater of the study area. They found that water table was subjected to a gradual decline and nitrate concentrations exceed 50 mg/L, which is the threshold set by the World Health Organization. On the bases of their finding they suggest flood and sprinkler irrigation to drip irrigation for the improvement of agricultural practices.

Gärdenäs et al. (2006) used HYDRUS-2D to simulate the experiment of Roulier and Jarvis (2003) for simulating leaching of pesticide due to preferential flow from macropores. They compared the four approaches available in HYDRUS-2D: an equilibrium approach, mobile-immobile approach, dual-porosity approach, and dual-permeability approach. Parameters were used from Roulier and Jarvis (2003). They concluded that equilibrium approach and mobile-immobile approach largely fail to simulate the preferential flow of water, showing longer residence time and less drainage from the tile drains. Dual-porosity and dual-permeability approaches provided a better representation of the preferential flow phenomenon with dual-permeability approach having best fit to the observed data as compared to the rest of the approaches. Both the approaches overestimated the drainage rates, which authors suggested could possibly due to the percolation of water to shallow groundwater in actual scenario, whereas they have applied a no-flux boundary condition at the bottom of the domain. Drainage rate from dual-permeability approach showed that of the total drainage from the field most of it occurred from the macropore region of the domain. Authors also mentioned that cumulative drainage is sensitive to initial groundwater level. Leaching of MCPA was efficiently captured by the dual-porosity and dual-permeability approaches however; dual-porosity approach overestimated the leaching rates because no flow in the matrix is assumed. They suggested that vertical macropore flow surpassed the lateral flow of water in the unsaturated zone, but number of parameters required for dual-permeability model increases leading to their difficult experimental determination and longer CPU time required for the calculations.

Haws et al. (2005) used HYDRUS-2D to model the water and tracer dynamics in sub-surface drained fields. They compared the modelled results with the observed field data and also used the inverse modeling for parameter estimation. As per their observation, none of the approach was able to simulate the exact process of preferential flow, but dual-porosity approach approximated the observed water flow data. Although solute out fluxes from both approaches were not in accordance with the observed data, with dual porosity approach performing better and can be attributed to the assumption of material homogeneity in the soil column leading to late arrival time of solute at the drain. Parameters that were estimated from the solute flux data failed to simulate the actual out flux phenomenon as observed, probably because of less stringent optimization tools and homogeneity assumption. They also mentioned that "short-cutting" of pathways due to macropores are more evident in the two-dimensional modelling.

Kodesova et al. (2010) tried to optimize the various parameters for macropore flow in the dual-porosity approach using HYDRUS-2D/3D. They used tension disk infiltro meters and Geulph permeameter to determine the saturated and unsaturated hydraulic conductivity of the soil domain of their field site. Prasad and Mathur, (2007) have developed a genetic algorithm GA using artificial neural network (ANN) to find optimal solution to a soil water flow and contaminant problem. The developed methodology was applied to several case studies involving radial flow, uniform flow, heterogeneous steady soil water flow and solute transport and unsteady groundwater flow to predict the efficiency of the developed algorithm. The developed methodology considerable reduce the computational effort as compared to the methods widely used in the past.

An artificial macropore was created in a sandy soil by Lamy et al. (2009) to study the preferential flow followed by simulating the process with dual-permeability approach in HYDRUS 2D. Analysis showed that the model simulations over-predicted the tracer transport with faster elution times as compared to the observed experimental data. The model correctly predicted the two peaks—larger one corresponding to macropore flow and smaller one corresponding to matrix flow, but the elution time of both peaks was under-predicted showing faster leaching of the solutes than the observed one which is in line with the past research mentioned by Gardenas et al. (2006) and Haws et al. (2005).

Understanding the impact of climate change on soil hydrological processes and groundwater resources is fundamental for sustainable water management and protection of water quality in the future. Climate change can influence groundwater resources directly through interactions with rivers and lakes and indirectly through groundwater recharge (Cherkauer and Sinha 2010). Varied precipitation patterns (spatiotemporal and intensity changes) can cause chloride and nitrate in the vadose zone to infiltrate into aquifers and deteriorate groundwater quality (Gurdak and Qi, 2006; Gurdak and Roe, 2009). An indirect effects of climate change on groundwater quality can be caused by groundwater table decline due to enhanced pumping as a result of future population growth and increasing water demand where the effected hydraulic head can lead to upward leakage of groundwater with poor water quality. Thus impact of climate change is considered in this study for predicting cop yield and associated nitrate leaching flux to subsurface for a site of Nebraska state.

A review of literature reveals that few models have been developed to analyse water flow and nitrate transport through heterogeneous vadose zone. However, most of these developed models are applied at either laboratory scale or used in predicting nitrate transport at field without investigating its transport parameters practically. Because of the complexity of the soil-plant-atmospheric continuum, very limited field studies are conducted for observing the behaviour of nitrate in heterogeneous vadose zone. Thus both numerical and practical experiments are required to investigate the nitrate fate and transport under varying environmental conditions. In this study transport of nitrate through heterogeneous porous media at different scales is investigated using column, lysimeter, tank, field and watershed scale. The spatial and temporal variation of nitrate concentration in soil is simulated using different modelling approaches. Zero to multidimensional laboratory experiment are performed for the validation of simulation runs. The laboratory small scale practical and numerical experiment considering heterogeneity are useful to characterize the soil water and solute transport parameter for the preferential flow dynamics.

CHAPTER 3

METHODOLOGY

To achieve the specified research objectives, a series of practical experiments and simulation runs were performed at different scales of study domain varying from laboratory to plot and field/watershed levels. Preliminary experiments were conducted first to characterize the porous media used in laboratory experiments and related modelling runs. Practical experiments were then conducted using one dimensional column, small lysimeter followed by two and three dimensional tank setups. Thereafter, numerical runs were performed for these practical experiments along with numerical investigations of a plot and a watershed level field studies. The objective of conducting the laboratory scale experiments was to predict the flow and transport parameters involved in nitrate movement considering uniform and heterogeneous vadose zones. Impact of soil moisture variability was also investigated using these experiments. Both point and distributed sources of nitrate pollutant were considered along with the varying environmental conditions to estimate the nitrate flux to the underlying groundwater resources of the targeted study domains. Richards and advection dispersion equations were used for simulating nitrate flux considering the uniform and mobile -immobile approaches of flow through vadose zone. The developed methodology was then applied to a plot scale study conducted by Onsoy et al. (2005) at San Joaquin Valley, California. The numerically obtained nitrate flux considering the uniform and preferential flows was compared with the observed nitrate mass of the experimental vadose zone. Thereafter, a field scale numerical study was performed for the Nebraska MSEA watershed located within the Central Platte Natural Resources District (CPNRD) of the Platte River Valley. The Hybrid Maize and Maize N models were used for prediction of corn yield and for fertilizer estimation respectively. The corn yield for the watershed was simulated for six years (1991-1996), considered as the baseline period, and for a future climatic scenario of six years (2055-2060). The predicted corn yield for these future years was then used to estimate optimal rate of nitrogen fertilizer application at the field site. Finally, nitrate transport through the vadose zone of MSEA site was simulated for predicting the nitrate load to the underlying groundwater resources under past and future climatic conditions. The figure 3.1 shows the schematic diagram of the entire methodology followed in this study for investigating nitrate movement through the vadose zone.

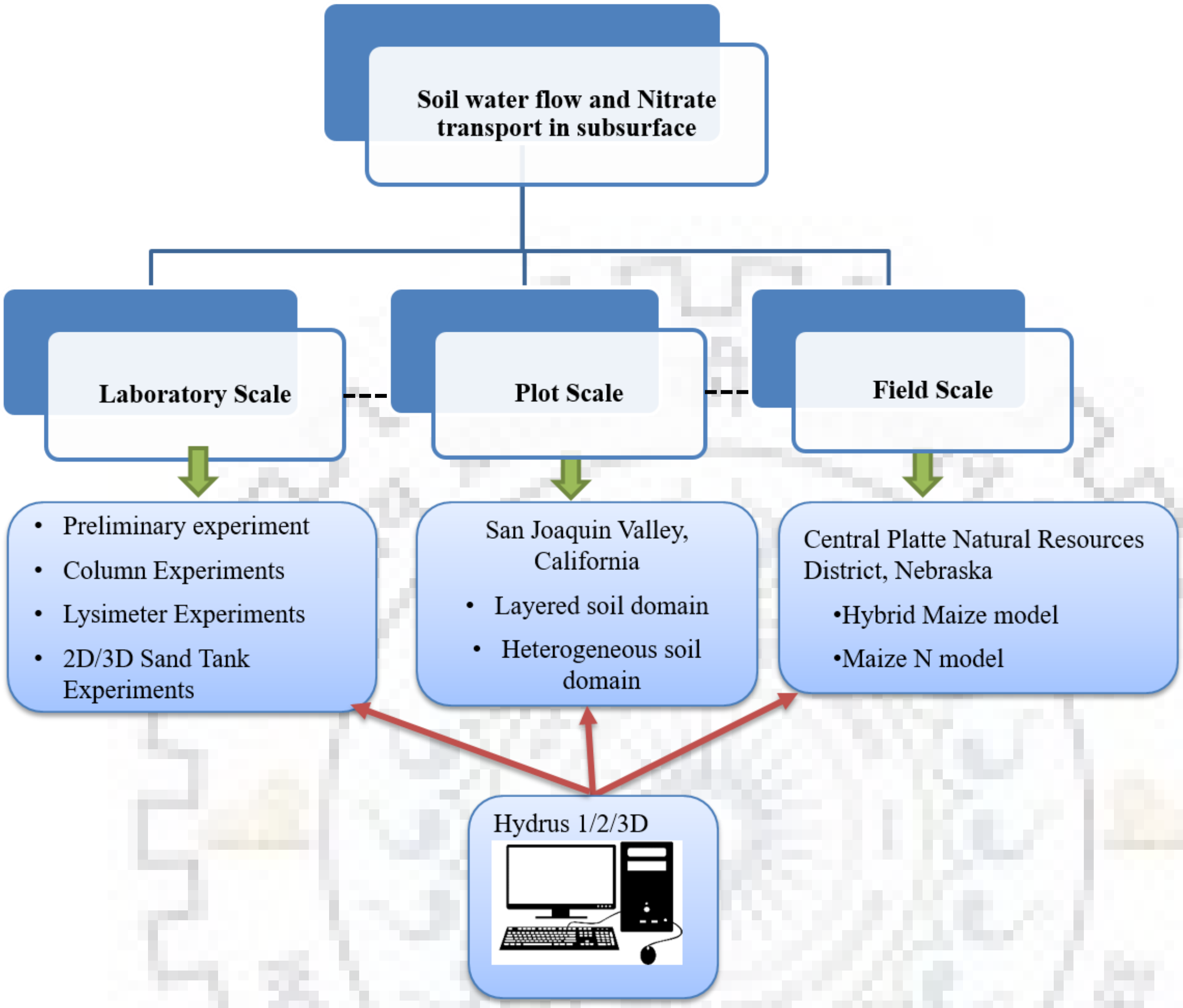


Figure 3-1: Overview of the research methodology used in this study to predict nitrate movement through variably saturated zone under varying environmental conditions

3.1. Laboratory Experiments:

The soil parameters like soil particle size, bulk density, particle density, organic content, and the soil moisture retention curve were determined in laboratory to characterize the porous media. The porous media used in the laboratory experiments was IS grade II supplied by Ennore Tamil Naidu, India. The bulk and particle densities, and porosity were determined using the standard procedures as mentioned in Appendix-I. Sieve analysis was performed using a sieve shaker to get the particle distribution of the porous media. The grain size distribution of used soil material are listed in table 3.1. The soil water flow parameter obtained from preliminary laboratory experiment are presented in the table 3.2. Preliminary experiments column, lysimetric and tank setups were conducted to get the idea of equilibrium time.

Table 3-1: Mass fraction of various gain sizes in the sieve analysis of soil

Grain diameter (mm)	Mass(g)	Mass (%)
1.0	41.7695	9.51
0.5	248.9623	56.71
0.25	109.5451	24.95
>0.25	38.7098	8.82
sum	438.9867	100

Table 3-2: Physical and chemical properties of the experimental porous media

Porous media	Sand ($g\ hg^{-1}$)	Silt ($g\ hg^{-1}$)	pH	EC (s/m)	OMa	Bulk Density (g/cm3)
Sand	92.8	4.2	5.5	4.9	0%	1.65

3.2. Column Experiment

To investigate the vertical flow of nitrate through variably saturated zone a vertical column setup made of plexi-glass was fabricated. The column was mounted on a frame to make it stable during the experiments. The column was 120 cm in length with an inner diameter of 15 cm. The column was packed homogeneously with the porous material (IS grade II medium sand) having a particle size of 0.5 -1.0 mm. Before using column, sand was washed and oven dried at 105^0C for 24 hours to make it free from organic contents. The column was filled with the porous media up to a height of 90 cm from the bottom. Water table was maintained at a height of 30 cm from the lower boundary leaving the remaining 60 cm soil mass as an unsaturated zone. A head space of 30 cm was allowed at the top of the soil surface. There were four sampling ports at a distance of 40, 55, 70 and 90 cm from the source taken at the top of the column. Soil hydraulic parameters like soil-water velocity, hydraulic conductivity, dispersivity etc. were estimated using tracer experiments in the designed column setup. A stock solution containing 100 ppm of nitrate was then prepared by dissolving potassium nitrate in millipore water. A constant water table was maintained throughout the experimental period and a constant influx of 150 ml/h of the solution was applied at the top surface using a peristaltic pump and was allowed to drain from the bottom boundary. The schematic diagram of this experimental setup is shown in Figure 3.2

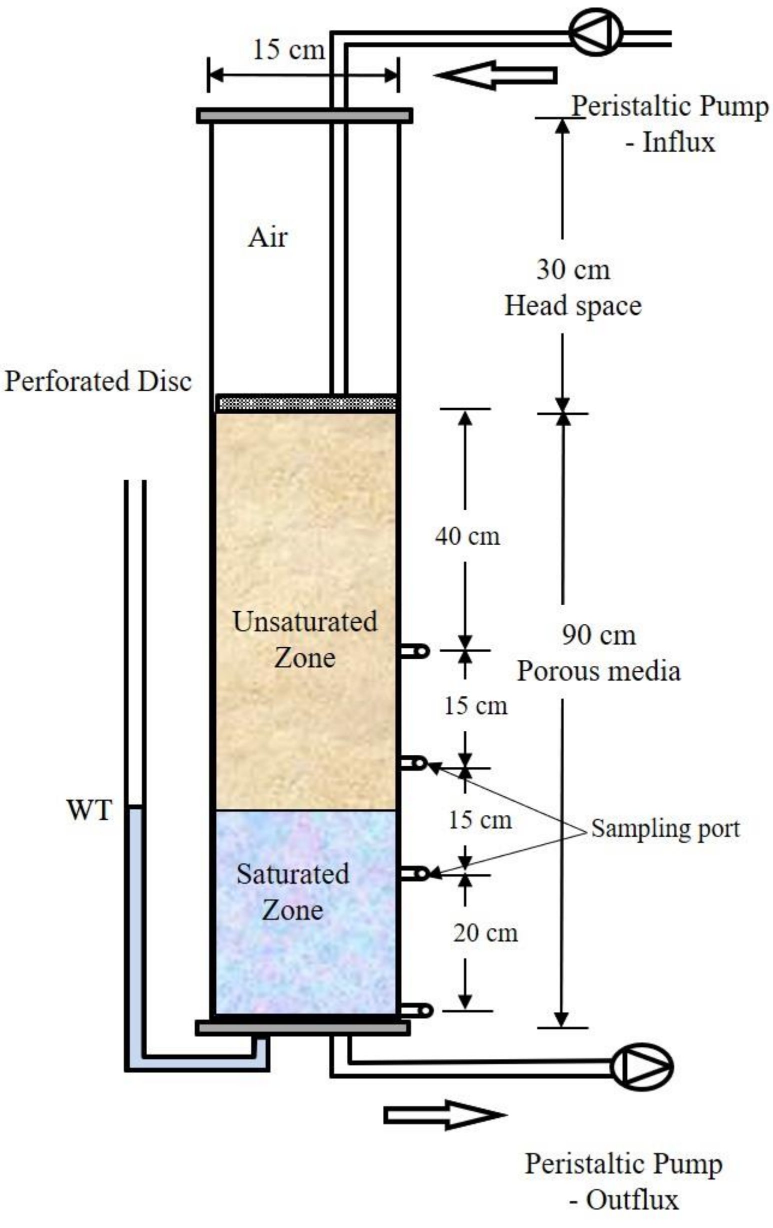


Figure 3-2: Schematic diagram of the column set-up used for characterizing soil moisture flow and nitrate transport through variably saturated zone.

The soil water was collected at various time intervals to measure the concentration of nitrate at different sampling ports of the column setup. Extraction syringes were attached to the sampling ports via needles passing through the Teflon septas to the soil-water mass of the column setup. Sampling was done for the time duration of 27 hours at regular interval of 2 hrs. The collected samples were then analysed for nitrate concentration using Single Beam Spectrophotometer (Spectroquant pharo 100).

3.3. Lysimeter Experiments:

To study the impact of soil moisture heterogeneity on nitrate transport, lysimeter experiments were performed under varying soil moisture content. The lysimeter (Figure 3.3) was consisted of a glass tank of dimension 28 cm long x28 cm breadth x30 cm high. The lysimeter was filled homogeneously with the organic content free sand in over-saturation condition and was then allowed to drain to obtain the field capacity, which was about 80% of the porosity, of the considered porous media before starting the experiments. Thereafter, laboratory experiments were performed for saturated soil moisture content level by allowing the water table to stand at the top surface of the lysismeter. The lysimeter was connected to a peristaltic pump to provide a flux of 150ml/hour with 100 PPM nitrate concentration. The water samples were collected from two drainage ports situated at the bottom and were analysed using spectrophotometer for the Nitrate concentration. The Lysimeter was mounted on a weighing balance to perform the mass balance. Samples were also collected from two side ports located at 18 cm vertical depth from the top surface of the porous media. BTCs were obtained by taking average concentration of nitrate from these points.

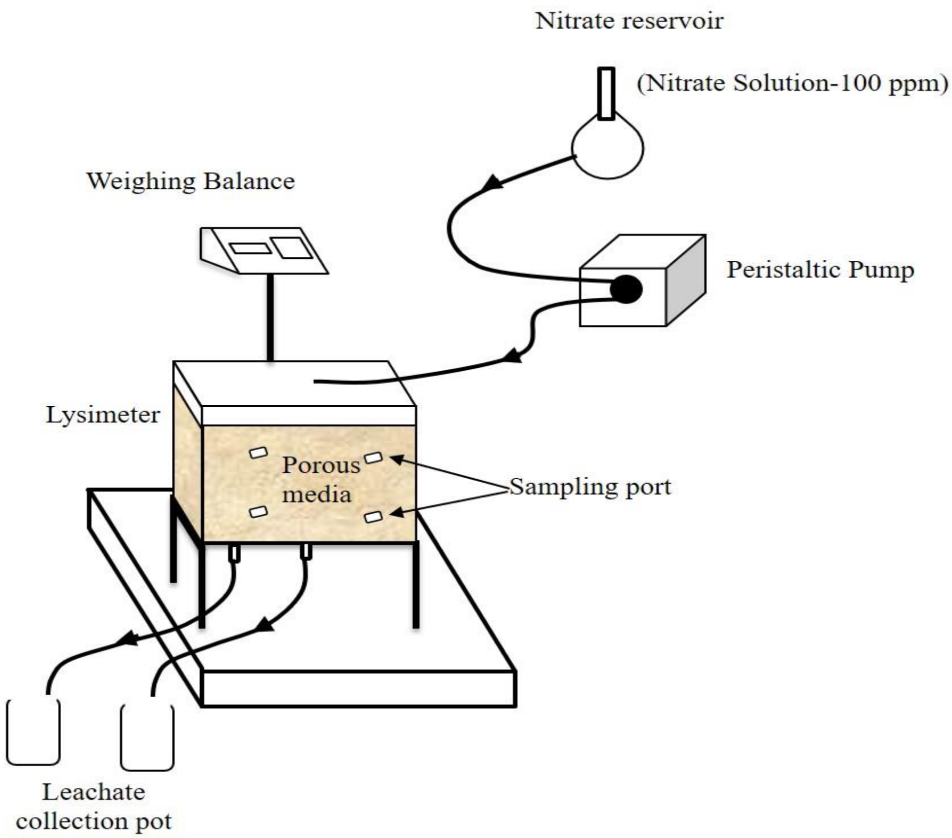


Figure 3-3: Schematic representation of Lysimeter setup used in laboratory to investigate the impact of soil moisture content on nitrate movement through variably saturated soil.

3.4. Tank experiment

3.4.1. Two dimensional tank experiments:

A series of two dimensional experiments were carried out to investigate the soil moisture flow and nitrate transport considering the transient flow conditions. A two dimensional sand tank was fabricated of 0.7 mm thick glass sheet and stainless steel embedded with three horizontal layers of sampling ports having vertical distance of 30 cm (Figure 3.4). The porous medium was packed homogeneously for conducting steady state experiments. The physical and chemical properties (Table 3.2) obtained from the earlier laboratory experiments were checked and used for these experiments. To see the role of drainage and recharge fluxes, a three sets of the simulation experiment was conducted considering- a) drainage flux from bottom of sand tank, b) applied recharge flux at top surface under transient condition. Subsequently, the role of subsurface flow on nitrate transport was evaluated in same setup under transient flow conditions. Different boundary conditions used for this simulation are shown in figure 3.5

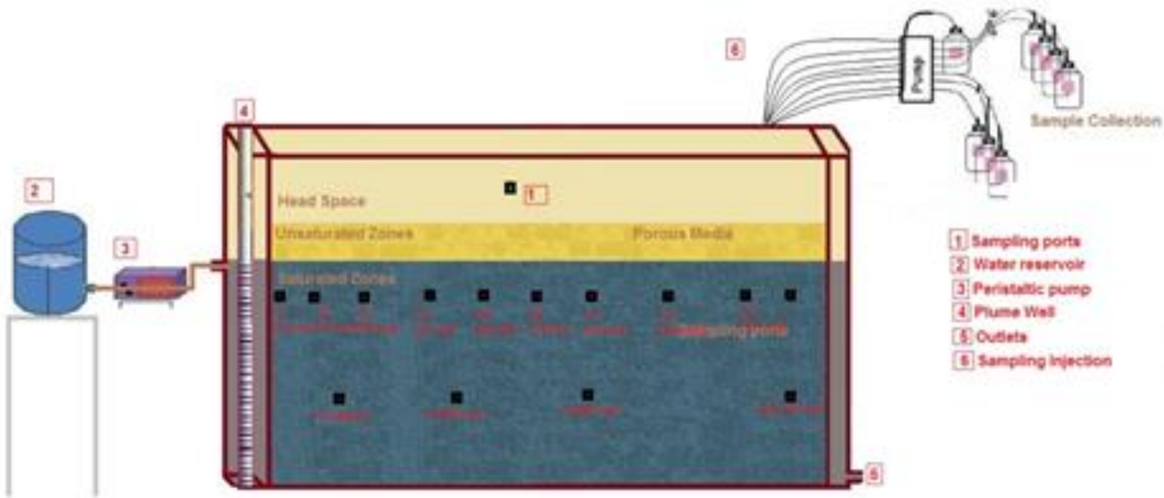


Figure 3-4: Schematic diagram of the two dimensional sand tank setup having saturated and unsaturated zones and sampling ports.

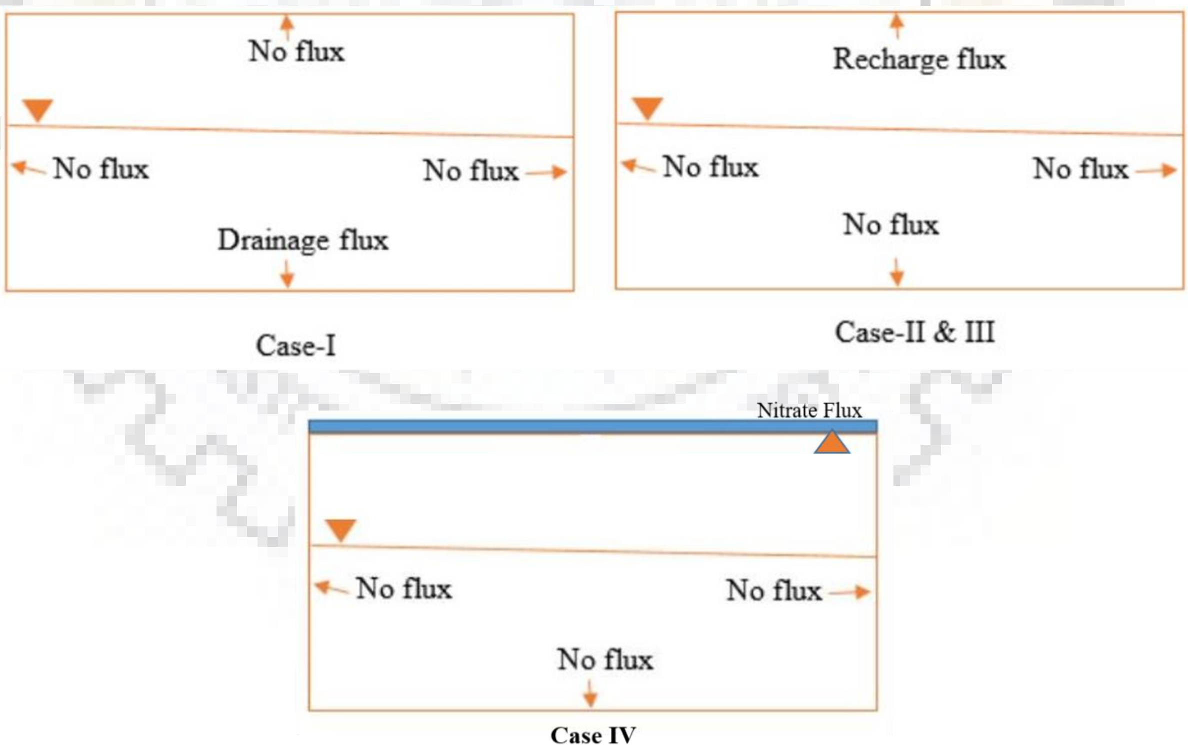


Figure 3-5: Applied boundary conditions in simulation domains in different cases

Four different cases of flow regimes were considered in conducting laboratory experiments using the 2D tank setup. In the case I, the flux was allowed to drain freely from the saturated zone having dimension of 6.0 m x 2.0 m. No-flow boundaries were considered at the top and at the sides in flow model. A height of 1.45 m was maintained for the water table before starting the drainage. The soil-water parameters θs=0.3, θr=0, K's =9.6 m/day which were measured in laboratory were then used for simulating the study domain. In the second case, recharge flux of 3.55 m/day was applied at the soil surface over a width of 0.5 m on the top of the flow domain. The water table level was maintained at 0.65 m, and a no-flow boundary was considered above the water table on the right side of the flow domain as shown in figure 3.5. The measured soil parameters and hydraulic conductivity of 8.40 m/day were used in simulating the experimental domain. Likewise in third case, a constant water flux of 3.29 m/day was imposed at the top surface having lower node at constant pressure head of ψ = -0.615 m. Subsequently in the fourth case, a set of solute transport experiments were performed applying nitrate at top surface. A constant flux of 150 mL/hrs having 300 ppm nitrate concentration was allowed to flow in horizontal direction. The pore water samples were collected hourly in triplicates from the sampling ports and were analysed using spectrophotometer. The errors associated with the estimated values are evaluated using the observed data.

3.4.2. Three Dimensional Tank Experiment:

To investigate the transport of nitrate in subsurface, a series of laboratory and numerical experiments were performed considering the mobile-immobile zones in an experimental subsurface domain. A large three dimensional sand tank setup was used for this purpose to mimic the real field conditions and to neglect/ minimize the chances of bypass of solute and solvent through tank and soil boundary interphases. The laboratory experiments were conducted in the sand tank and subsequently the characterized domain was simulated for water flow and nitrate transport using HYDRUS 3D (Jirí Šimůnek, van Genuchten, & Šejna, 2008). The experimental setup was fabricated of 7 mm thick glass sheet with dimensions of 60 cm long by 30 cm wide by 60 cm high (figure 3.6). The tank is embedded with three layers of horizontal and vertical sampling ports. The sampling ports are made of stainless steel tubes having diameter of 0.3 mm and depth of 05cm, 10cm, 15cm, 20cm and 25cm. The inlet and outlet ports are installed on each side of the tank at heights of 35 cm and 02 cm respectively. The tank was filled with the organic free sand having physiochemical properties listed in table 3.2. A filtration screen is fixed on the inlet and outlet ports to prevent passing of the experimental media to the connecting tubes used for water flow. The sand tank was filled in over saturated condition, and was then left open to drain the excess water to achieve the field capacity condition of the soil. Thereafter, nitrate solution of 300 ppm concentration was applied as a distributed source at steady state rate using a sprinkler for 70 hours. The pore water samples were collected from the different sampling ports situated at different locations to monitor the nitrate concentration. The schematic diagram and various details of the tank setup is shown in the figure 3.6.

The single beam spectrophotometer was used to analyze the collected soil water samples for nitrate concentration. The absorbance readings were taken at a wavelength of 410 nm and the nitrate concentration in pore water was computed using the calibration curve having R^2 value of 0.998. The soil water properties used in simulation experiment are listed in table 3.3.

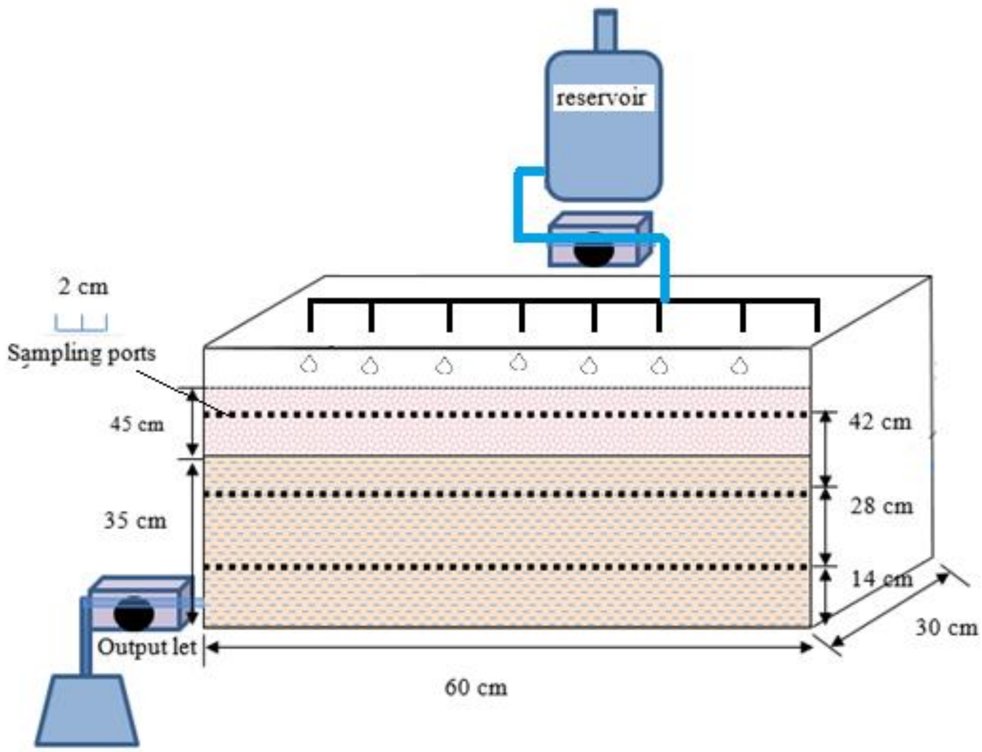


Figure 3-6: The sand tank setup used to investigate the nitrate transport in subsurface. The square dots show the location of the sampling ports (2 cm apart in horizontal direction) embedded in three horizontal layers situated 14 cm apart vertically from each other. Two layers are on front of setup and the third layer is embedded between these two layers on the rear wall of the setup.

Table 3-3: Parameter of hydraulic function used in laboratory conditions

Parameter	Sand tank	Single porosity model	15% mobile region
Porosity (n) [%]	33±2	33±2	33±2
Hydraulic Conductivity K [cm/day]	350.2	350.2	350.2
Saturated water content θ_s ([-]	0.410	0.410	0.0615
Residual water content θ_r [-]	0.057	0.057	0.0085

3.4.3. Numerical Modelling:

For predicting soil moisture flow and breakthrough curves at different depth of the soil profile, the classical advection-dispersion equation for solute transport was used along with the soil water flow equation. Transport of nitrate in subsurface depends upon advection, dispersion and diffusion fluxes. For modeling soil water flow Richards's equation is used by integrating continuity equation with the Darcy's law as (Celia et al., 1990).

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left[K(h)\frac{\partial h}{\partial x}\right] + \frac{\partial}{\partial y}\left[K(h)\frac{\partial h}{\partial y}\right] + \frac{\partial}{\partial z}\left[K(h)\frac{\partial h}{\partial z}\right] - S_c \qquad (3.1)$$

where, θ is the water content of the soil profile [L^3L^{-3}], h is the pressure head of the soil profile [L], t is time [T], x, y, and z are the spatial coordinates of the soil domain [L], S_c is a sink term representing the water uptake by plant root biomass[T^{-1}], $K(h)$ is the unsaturated hydraulic conductivity of the unsaturated soil [LT^{-1}]. Richards equation is highly nonlinear as the unsaturated hydraulic conductivity and soil moisture content (θ) are the dependent parameter of hydraulic head (h). So, for solving this equation, the soil constitutive relationship between the dependent variable h and nonlinear terms K and θ are required. Out of various soil water constitutive relationships, the most popular ones is by Van Genuchten, (1980). The close form $\theta - h$ relationship used by fitting mathematical equations to field experiments data using Van Genuchten method yields

$$\theta(h) = \begin{cases} \theta_s & h > 0 \\ \theta_r + \left[\theta_s - \theta_r\right] \Big/ \left[1 + |\alpha h|^n\right]^m & h < 0 \end{cases} \qquad (3.2)$$

Where θ_s is the saturated water content, θ_r is the residual water content (irreducible) and θ is the moisture content at the soil matrix potential, h, n, m, α are curve fitting parameters. Total moisture content (θ) in the soil domain was considered to be sum of moisture content in mobile θ_m and immobile θ_{im} regions. The moisture flow equation in its mixed form coupled by a non-uniform sink term (Yadav and Mathur, 2008) and water transfer function can be written in 3D form as:

$$\frac{\partial \theta_m}{\partial t} = \frac{\partial}{\partial x}\left[K_x(h)\frac{\partial h}{\partial x}\right] + \frac{\partial}{\partial y}\left[K_y(h)\frac{\partial h}{\partial y}\right] + \frac{\partial}{\partial z}\left[K_z(h)\frac{\partial h}{\partial z} + K(h)\right] - S_m - \Gamma_w \tag{3.3}$$

$$\frac{\partial \theta_{im}}{\partial t} = -S_m - \Gamma_w \tag{3.4}$$

Where Γ_w is the water transfer rate between the mobile and immobile region [T^{-1}], The K and h relationship given by

$$K(h) = K_s S_e^l \left[1 - \left(1 - S_e^{1/m}\right)\right]^2 \tag{3.5}$$

Where K_s is the saturated hydraulic conductivity of the soil, $m = 1 - 1/n$ and l is the pore connectivity parameter taken as 0.5 in the above hydraulic conductivity function (Mualem Yechezkel, 1976) and S_e is the effective saturation. The water transfer K_s rate between the mobile and immobile region is assumed to be proportional to the difference in effective saturation between mobile and immobile regions (Van Genuchten and Wierenga, 1976).

$$\Gamma_w = \omega\left(S_{e,m} - S_{e,im}\right) \tag{3.6}$$

Where ω is a first order water transfer coefficient, $S_{e,m}$ and $S_{e,im}$ are the effective saturation of the mobile and immobile regions defined as

$$S_{e,m} = \frac{\theta_m - \theta_{m,r}}{\theta_{m,s} - \theta_{m,r}}$$

$$S_{e,im} = \frac{\theta_{im} - \theta_{im,r}}{\theta_{im,s} - \theta_{im,r}} \tag{3.7}$$

For nitrate transport in a variably-saturated soil profile, Fick's law coupled with the mass balance equation yields the following modified form of the advective-dispersive equation (Yadav and Mathur, 2008) for simulating nitrate movement in vadose zone

$$\frac{\partial(\rho_s S_D)}{\partial t} + \frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial x_i}\left[D_{ij}\theta\frac{\partial C}{\partial x_i} - q_i C\right] + S_c - \Gamma_s$$

$$\frac{\partial(\rho_s S_D)}{\partial t} + \frac{\partial(\theta C)}{\partial t} = S_c + \Gamma_s \tag{3.8}$$

Where C is the nitrate concentration in the soil solution (mg per unit volume of soil solution), S_D is the amount of solute adsorbed by the soil solids (mg of contaminant per Kg of soil), q_i is the i^{th} component of soil water flow velocity [LT^{-1}] (i, j = 1, 2, 3), ρ_s is the bulk density of soil, q is the soil water flux. The tensor of hydrodynamic dispersion coefficient (or diffusion-dispersion coefficient) D_{ij} is the pore water velocity dependent function and is evaluated by adding the mechanical dispersion and molecular diffusion coefficients (Scheidegger, 1960) as:

$$D_{ij} = \left(\alpha_L - \alpha_T\right)\frac{v_i v_j}{v} + \alpha_T v \delta_{ij} + D_o \qquad (3.9)$$

Where α_L and α_T are longitudinal and transverse dispersivities $[L]$, v is the pore water velocity q/θ δ_{ij} is the Kronecker delta ($\delta_{ij} = 1$ if $i = j$, and $\delta_{ij} = 0$ otherwise), and D_o is the molecular diffusion $[L^2T^{-1}]$.The solute transfer function Γ_s between mobile and immobile region is considered to be proportional to the difference in solute concentration between mobile and immobile regions.

$$\Gamma_s = \omega_s\left(C_m - C_{im}\right) + \begin{cases} \Gamma_w C_m & \Gamma_w > 0 \\ \Gamma_w C_{im} & \Gamma_w < 0 \end{cases} \qquad (3.10)$$

Where C_m and C_{im} are the concentration in mobile zone and immobile zone respectively.

3.4.4. Simulation Procedure

For the numerical simulation of moisture flow and contaminant transport in vadose zone, the finite element based HYDRUS-2D/3D was used as it provides various approaches for solute transport including (non)-equilibrium model for the (single)-dual porosity types of flow situations. A simulation domain was created in 3D having elemental size of X: 60 cm, Y: 30 cm and Z: 60 cm. The targeted element size was 10 cm with stretching factor of unity. The five observation nodes were considered at vertical positions of 4 cm, 28 cm, and 42 cm.

Uniform flow can be expected for the horizontal/lateral flows in saturated zone or the flow taking place against the gravity force. In simulation of three dimensional tank experiments, both uniform and preferential flow approach were applied. A dual-porosity model with water mass transfer term was considered for simulating the preferential flow. In dual porosity approach, three more parameters were introduced apart from the standard van Genuchten-Maulem model, these were residual and saturated water content in the immobile zone and the water mass transfer term from immobile zone (matrix) to mobile zone (macro-pores). The parameters used for vadose zone having different mobility are listed in table 2. Residual water content of the mobile domain was considered to be zero (Jarvis, 2007; Kodešová, et al.,2010). In dual-porosity approach, movement of solutes is also restricted mainly to the mobile zone, and a solute transfer term was taken for the movement of solutes from matrix to macro-pores and vice versa.

Initial and Boundary Conditions

The initial condition was taken in form of soil pressure head decreasing linearly from water table to the top soil surface. The soil moisture content was measured in laboratory which was found at -98 cm. The atmospheric boundary condition was applied on top of the soil domain, and a constant water head was applied at the lower boundary condition to represent water table. For nitrate transport, a constant flux boundary condition was applied on top and a free drainage flux was taken at the bottom of the soil domain. A no-flux boundary condition was applied on the sides of the soil column considering no water and solute was leaving and entering the domain. The simulation time for the 3 dimensional tank setup under different modelling approach was 70 hours. Initial time step was taken as 0.001hr, minimum time step was 0.0001 hr while maximum time step was 3.5 hours.

3.5. Plot scale study:

A 12 year fertilizer trial beginning in 1982 was performed at Kearney research site formerly known as Fantasia Nectarine by Harter et.al (2005). It was a flood-irrigate 0.8 ha orchard at University of California on the Kings River alluvial fans having semiarid, mediterranean climate. Groundwater table varied from 12- 20 m during fluctuating seasons.

Nitrogen fertilizer was applied to a set of random blocks with varying application rates (110 and 365 kg N ha-1 for low and high plots respectively). Soil core sampling was done by drilling 62 soil cores of 15.8 m length to estimate the moisture content and nitrate levels in the soil after fertilization trial was over (Onsoy et al., 2005). Bulk density of the soil core samples varied from 1.3 to 1.9 g cm^{-3} with an average of 1.6 g cm-3. A constant bulk density of 1.45 g cm-3 was used to account for the compression of soil during core drilling.

Out of total 62 core samples, 19 were used for the determination of hydraulic parameters of the soils. A multistep outflow technique was used to determine the relationships between the soil hydraulic properties. In multistep outflow technique, air pressure in the suction chamber was increased in several discreet steps during the course of time varying from several days for sand to several weeks for clay. Each increase in air pressure forces water to flow out of the soil core until the soil water suction in pores matches the applied air pressure. The soil Hydraulic properties for 97 soil core samples were determined (Botros et al., 2009).

The entire subsurface domain is divided into 8 lithofacies depending on the type and characteristics of the soil at varying depths (Fig.3.7). These lithofacies in order from top to bottom are as Sandy loam (SL1), clay (C), sand (predominantly, S1), paleosol hardpan (HP1), sandy loam with intercalations (SL2), Sand (S2), Clayey-silty and loamy material (CTL), sandy loam (SL3) and paleosol hardpan (HP2). Sandy soil has higher hydraulic conductivity and hence water drains out of these soil domains quickly as compared to clay which have high water retention capacity due to smaller pore sizes, thus preventing rapid water flow through the soils. This heterogeneity along with macropores leads to the non-uniform flow of water and irregular water fronts in the soil. Onsoy et al. (2005) and Botros et al. (2009) found that hydraulic conductivity data for the soil core samples was lognormally distributed indicating high variability in hydraulic properties of the soil domain.

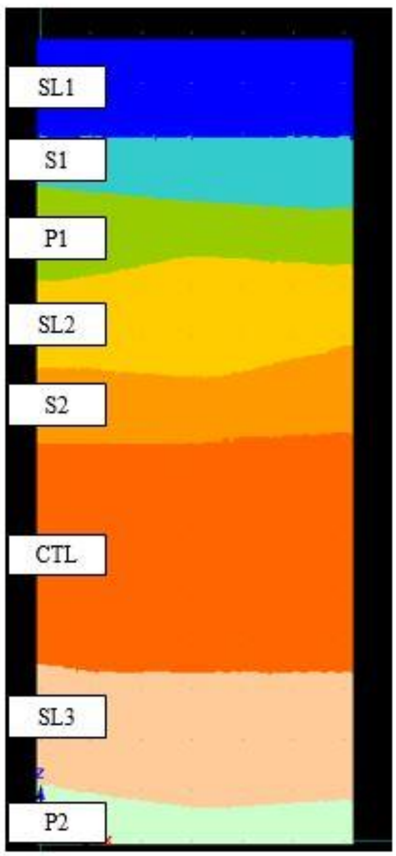


Figure 3-7: Vadose zone profile of experimental plots conducted at San Joaquin Valley. There are total eight soil materials found at the experimental site having soil domain of 15.8m depth and 6.1m wide

3.5.1. Simulation Experiments

Uniform and preferential (dual-porosity) flow approaches are used for quantifying nitrate load to the underlying groundwater resources of San Joaquin valley. The governing equations used for flow and nitrate transport simulations are already mentioned in numerical modelling section of three dimensional sand tank experiments. Root zone is assumed to be consisted of all nodes for which potential root uptake distribution coefficient is greater than zero. Root water uptake term is considered to vary linearly over each element. Transport equation often shows oscillatory behavior, especially when the transport process is advection dominant with small dispersivity. In such cases, two dimensionless numbers called as Peclet number (PN) and Courant number (CN) are used to characterize space and time discretization. The Peclet number characterizes the spatial discretization and defines the predominant type of solute transport process in relation to coarseness of finite element mesh. In order to maintain a low PN (advection < dispersion), a dense mesh is desirable and numerical oscillations can be eliminated with PN < 5. Courant number is associated with temporal discretization, and is used in calculating the maximum permitted time step (when CN < 1). Stability criterion is product of PN and CN which is used to stabilize the numerical solution and limit oscillation in Galerkin finite element method.

The two dimensional rectangular domain of 6.10m*15.8m width and length was constructed using HYDRUS simulator. The entire soil domain was divided into 8 polygons and surfaces were generated to account for the layered structure of the soil (Figure 3.7). A finite element grid consisting of 29611 nodes and 58466 finite elements of 5 cm was then constructed. Soil domain was then divided into 8 soil materials of varying dimensions as found in the soil cores. The simulation period of 7 years (2557 days) through 1990-1996 was considered.

Initial and boundary conditions:

Since groundwater was considered to be at a depth of 15.8 m, so the initial conditions was taken to be in linearly decreasing from the lowest nodal point with pressure head value at the lowest point given as zero and at the surface of the domain it is taken as -100 cm. The atmospheric boundary condition was applied on top of the soil domain, while constant water head (h=0) was applied at the lower boundary representing the water table. Precipitation and evaporation data were taken from Denton et al., (2004). A no-flux boundary condition was applied on the sides of the soil column considering no water and solute is leaving and entering the soil domain. In the equilibrium approach, water and solute fronts are assumed to be moving uniformly in the entre soil domain. While in a non-equilibrium approach, it is assumed that only small proportion of the soil domain is mobile zone, rest of the soil domain is immobile zone, although exchange of water and solute between mobile and immobile zone is considered. Table 3.4 shows the various hydraulic parameters which were used for the soil materials.

Table 3-4: Various parameters and their values for each soil type input in the equilibrium approach

Material type	θr	θs	α	n	K_s
SL1	0.057091	0.265545	0.021545	1.924273	8.713
S1	0.071875	0.283625	0.054	4.748625	247.06
P1	0.12625	0.28275	0.007625	2.0415	14.88
SL2	0.103583	0.292583	0.009083	2.414417	12.67
S2	0.094625	0.348	0.033	4.4445	301.37
C-T-L	0.175533	0.356533	0.009167	2.2148	17.54
SL3	0.045	0.262455	0.007091	2.454182	9.552
P2	0.120889	0.270778	0.008444	2.163333	8.9

To simulate solute transport additional parameters like bulk density (1.45), longitudinal dispersivity (10) and transverse dispersivity was $1/10^{th}$ of the longitudinal dispersivity were considered for the simulation domain

Water and nitrate uptake by plants

Plant water and solute uptake was also considered in the simulation model. Total root depth was taken as 1.8 m of the top vadose zone. The sink term represents the volume of water removed per unit time from a unit volume of soil by the plant. Feddes parameters were used for the uptake of water depending on the varying water head conditions of the soil. Two main mechanisms involved in the solute uptake by plants are active and passive uptake (Hopmans and Bristow, 2002). The passive nitrate uptake represents the mass flow of nitrate into roots with water while active uptake represents the movement of nitrate into the roots induced by other factors than mass flow. A passive uptake term was used to account for the uptake of solute by plant roots from the soil**.**

At favourable moisture conditions, the actual water uptake by the roots is maximum at a given root depth for the atmospheric conditions. It diminishes with unfavorable moisture conditions. Feddes (1982) introduced a macroscopic sink term to simulate the actual water uptake rate as a function off the maximum extraction rate (Smax) and the soil water pressure head:

$$S(z,t) = \alpha(h)*Smax \tag{3.11}$$

Where, α (h) is the dimensionless parameter representing soil water availability factor and a function of pressure head. It is being assumed here that root density is constant throughout the entire root depth zone. In this study root density is considered to vary linearly from top to lowest part of the root zone. . Assuming that the water uptkae root rate is proportional to the local root density (Perrochet, 1987; Skaggs et al.,2006; Yadav and Mathur, 2008) the actual water uptake term at a particular depth can be expressed as

$$S(z,t) = \alpha(h)*\beta(z,t)*T_p \tag{3.12}$$

Where β (z,t) is the root density distribution function such that β (z,t) dz gvies the fraction of the root located between depth z and z+dz. It distributes the potential transpiration over the entire root domain as a factor of local root density and must be equal to the unity when integrated over the entire root zone. α (h) accounts for transpiration reduction caused by either soil moisture limitation condition or deficient aeration condition at the root zone and is mathematically expressed by the following equation:

$$\phi(h) = \begin{cases} 0 & h \geq h_4 \ or \quad h \leq h_1 \\ \dfrac{h-h_1}{h_2-h_1} & h_1 \leq h \leq h_2 \\ 1 & h_2 \leq h \leq h_3 \\ \dfrac{h_4-h}{h_4-h_3} & h_3 \leq h \leq h_4 \end{cases} \tag{3.13}$$

Water uptake in a completely saturated soil is considered to be 0 i.e. at h1. Also it is zero near wilting point pressure head i.e. at h4. Water uptake is considered to be optimal between h2 and h3, whereas water uptake increases between h1 and h2, and decreases between h3 and h4 (Šimůnek and Hopmans, 2009). In our simulation study we used active and passive root uptake by plant to see the impact on nitrate load to the underlying water resource under different root uptake scenarios.

In dual-porosity model with water mass transfer term was considered for simulating the macropore flow. In dual porosity approach, three more parameters are introduced apart from the standard van Genuchten-Maulem model, these are residual and saturated water content in the immobile zone and the water mass transfer term from immobile zone (matrix) to mobile zone (fractures). The movement of solutes is mainly restricted to the mobile zone, and a solute transfer term is used for quantifying the movement of solutes from matrix to fractures and vice versa

Table 3.5 shows the various parameters used in the dual-porosity approach. Residual water content of the macropore domain is considered to be zero (Jarvis, 2007; Kodešová et al., 2010).

Table 3-5: Parameters for each soil type used in the dual-porosity approach

Material type	θr	θs	α	n	Ks	L	θri	θsi	ω
SL1	0.057	0.16	0.014	1.714	8.713	0.5	0	0.1	0.02
S1	0.074	0.19	0.0521	4.624	247.06	0.5	0	0.1	0.02
P1	0.126	0.183	0.0071	1.923	14.88	0.5	0	0.1	0.02
SL2	0.104	0.193	0.00796	2.178	12.67	0.5	0	0.1	0.02
S2	0.095	0.248	0.0297	4.405	301.37	0.5	0	0.1	0.02
C-T-L	0.176	0.257	0.00756	2.018	17.54	0.5	0	0.1	0.02
SL3	0.045	0.162	0.00573	2.421	9.552	0.5	0	0.1	0.02
P2	0.121	0.171	0.0075	2.094	8.9	0.5	0	0.1	0.02

The obtained cumulative nitrate flux drained from the lower boundary of the vadose zone was computed under different modeling approach and compared each other. On the bases of mass balance for both uniform and preferential flow, the residual amount of the nitrate in the vadose zone estimated and compared with the observed filed results.

3.6. Watershed scale studies:

To investigate the impact of fertilizers applied in field on groundwater resources, a watershed scale experimental study is used here for numerical investigations. The objective of this study was to find the impact of climate change on nitrate leaching to the groundwater resources of the MSEA Site. Effects of soil heterogeneity and different physical-chemical properties on water flow and nitrate transport in the vadose zone were also evaluated. Lithologs of the site were developed using

Rockwork tool which provides spatially varied soil properties of the site. Nitrate leaching from soil surface to groundwater in the site was simulated using HYDRUS simulator.

The study area is part of the Nebraska MSEA site located within the Central Platte Natural Resources District (CPNRD) of the Platte River Valley. The study area covers the Upper Platte basin delineated by the Nebraska Department of Natural Resources (DNR), which extended from western Nebraska to east within longitude range of -104 to -97 (Spalding and Exner, 1993). High plains aquifer is the primary aquifer in this area and the Platte River is in the middle of the basin. The sediment types throughout the basin is mainly silt and sand with clay at some small portions. The figure 3.6.1 demonstrate the site location and sampling well at the site.

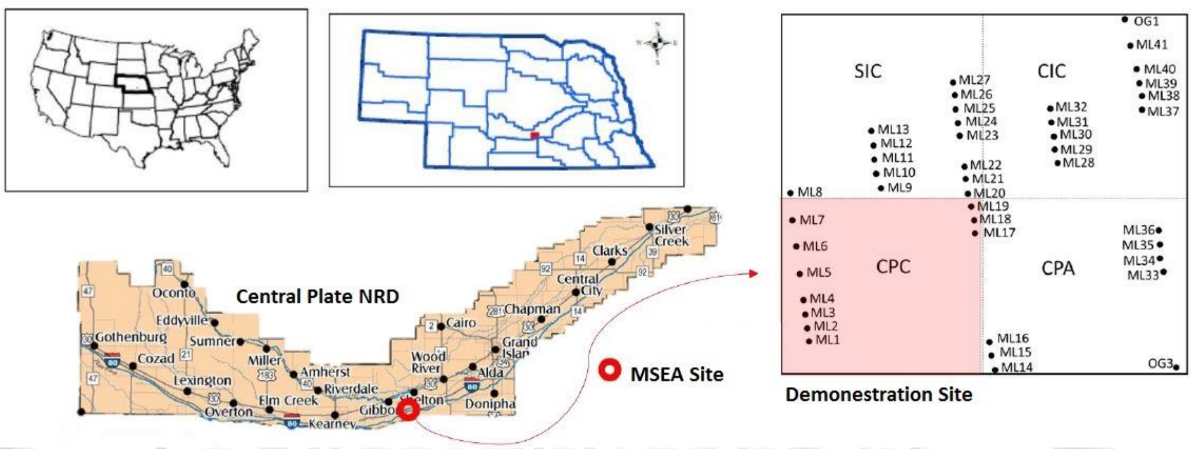


Figure 3-8: Shows description of MSEA site at Central Platte Nebraska's Natural Resources Districts and the location of the site on NRD map with multilevel samplers

3.6.1. Simulation procedure

The entire simulation was performed in three steps using different simulation tools. Hybrid Maize, Maize N, and HYDRUS are for prediction of corn yield, fertilizer estimation and for the nitrate leaching to groundwater respectively. Corn yield under different time periods, baseline (1991-1996 and future case (2055-2060), was simulated using the Hybrid Maize model. Predicted corn yields under different climate periods was then used to estimate optimal nitrogen fertilizer application rates at the field site using the Maize-N model. Finally, nitrate transport in the vadose zone under MSEA site was simulated using soil moisture flow and solute transport equations. Figure 3.9 demonstrate the whole methodology applied at this watershed scale study.

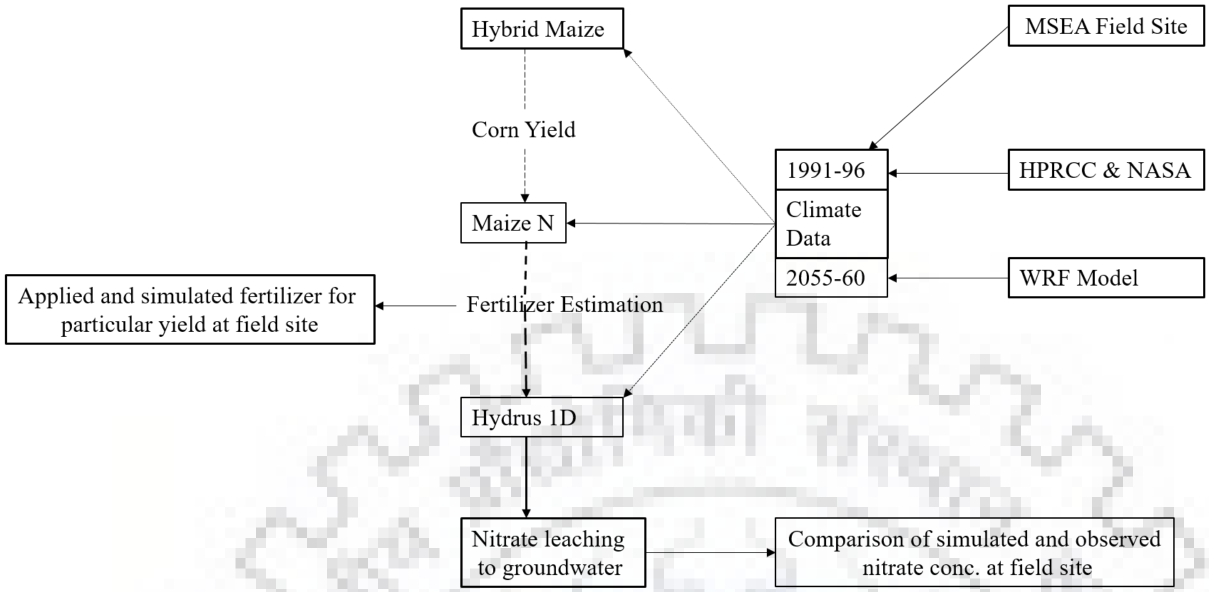


Figure 3-9: Flow chart for the methodology followed at watershed scale.

HPRCC and NASA services were used for obtaining the past climatic data of the site.. For the generation of future climate data sets, the downscaled climate data at a resolution of 24×24 km^2 were created using Weather Research and Forecasting (WRF) model. WRF is a regional climate change model that downscales the climate change predictions from the Community Climate System Model (CCSM4). The CCSM4 is a global climate change model that simulated the Representative Concentration Pathways (RCP) 8.5 scenario which corresponds the worst climate scenario with a high greenhouse gas emission pathway. A set of data from 2006 to 2010 was used to control and validate the WRF model and the future predicted climate data set is from 2055 to 2060. The 5-year mean annual precipitation and temperature of the whole basin were predicted to be 59.3 cm/year and 14.1 °C during 2055-2060. These datasets were used for predicting the corn yield using Hybrid – Maze simulator of the region under the considered climatic conditions.

<u>*Estimation of Nitrate Fertilizer*</u>

The required nitrate fertilizer was simulated based on the crop yield under the considered climatic conditions. Initially Hybrid Maize model was used for the prediction of corn yield under past and future climatic variables. Hybrid-Maize crop simulation model describes growth and development processes of maize (Zea mays L.) as the factors of weather, soil properties, and management factors. The main purpose of this simulation was to allow the maize producers, crop consultants, and the researchers to hypothetically explore the impact of weather and management factors on crop performance, with the goal of better understanding site yield potential, year-to-year variation in yield

potential, and potential management options that affect the corn yield. Hybrid-Maize simulates the growth of a maize crop under non-limiting or water-limited (rain fed or irrigated) conditions based on daily weather data. It 1) assess the overall site yield potential and its variability, 2) evaluate changes in attainable yield using different choices of planting date, maize variety, and plant density, 3) analyze maize growth in specific years, 4) explore options for irrigation water management, and 5) conduct in-season simulations to evaluate actual growth and forecast final yield starting at different growth stages. Hybrid maize was used for the corn yield analysis under different climatic scenarios. To estimate the required fertilizers for a particular crop yield Maize N was used.
Maize-N model used for estimating fertilizer rate for the crop. The estimation is based on user input information on the current maize crop, last season crop, basic soil properties, fertilizer management and manuring, crop residue management and tillage, and long-term weather data of the field. The program first simulates maize yield potential and its year to year variation. Thereafter it simulates mineral N released from mineralization of soil organic matter, crop residues and manures. Maize-N model can also estimate recovery efficiency of applied N fertilizers. Finally, the model estimates the economically optimal N rate of fertilizer for the current maize crop.

3.6.2. Quantifying Nitrate leaching from vadose zone

Hydrus1D is used for variably saturated media for prediction of nitrate load to the groundwater. The simulation tool provides various approaches for solute dynamics, including zero and first order solute decay reactions. It also incorporates the physical and chemical non-equilibrium processes to account for the exchange of solutes between mobile and immobile regions and for kinetic sorption models respectively. At the field scale study, fertilizer application in form of urea was used. Urea breakdown into ammonium compound which ultimately converted into nitrate. The equation used for the moisture flow and solute transport are described above in 3D sand tank experiment. In addition for the field scale simulation, modified form of the advection dispersion considering the first order decay of nitrate is given as:

$$\frac{\partial \theta_{c1}}{\partial t}+\frac{\partial \theta_{\rho s1}}{\partial t}+\frac{\partial a_{ygi}}{\partial t}=\frac{\partial}{\partial x_i}\left(\theta D_{ij1}^{w}\frac{\partial c_1}{\partial x_j}\right)+\frac{\partial}{\partial x_i}\left(\alpha_v D_{ij1}^{g}\frac{\partial g_1}{\partial x_j}\right)-\frac{\partial q_i c_i}{\partial x_i}-Sc_{r,1}\left(\mu_{w,1}+\mu'_{w,1}\right)\theta c_1 \quad (3.14)$$
$$-\left(\mu_{s,1}+\mu'_{s,1}\right)\rho s_1-\left(\mu_{g,1}+\mu'_{g,1}\right)\alpha_v g_1+\gamma_{w,1}\theta+\gamma_{s,1}\rho+\gamma_{g,1}a_v$$

Where, ρ is bulk density of the soil, c, s, and g is the solute concentration in the liquid phase, solid phase and gaseous phase, μ_w, μ_s , and μ_g are first-order rate constants for solutes in the liquid, solid, and gas phases, respectively; $\mu_{w'}$, $\mu_{s'}$, and $\mu_{g'}$ are similar first-order rate constants providing connections between individual chain species, γw, γs and γg are zero-order rate constants for the liquid, solid and gas phases, respectively. Q_i is the i-th component of the volumetric flux density, a_v is the air constant, S_c is the sink term for uptake by plants, c_r is the concentration of the sink term, D_{ijw} and D_{ijg} are the dispersion coefficient tensor of water and gas phase respectively. The root water and nitrate uptake by plants are used as described above under the plot scale study part.

Initial and boundary conditions:

The soil profile was considered to be in hydrostatic equilibrium with the local groundwater level. The initial fertilizer concentration in the subsurface were considered as zero. The groundwater nitrate concentration measured during 1991 were used as the initial nitrate concentration. An atmospheric boundary condition was implemented at the top surface, which required daily precipitation, irrigation and potential evaporation and transpiration values. A variable pressure head boundary condition was implemented at the bottom boundary of the soil domain.. The simulation period of 6 years (2190 days) was considered for both past and future climate variables. Initial time step was taken as 0.001 days, minimum time step was 0.0001 days while maximum time step was 25 days.

Moisture flow and nitrate transport in heterogeneous vadose zone is very complicated process. Efforts has been made in past to investigate the movement of nitrate either using experimental or numerical study at a particular scale. However both the numerical and practical experiment are needed to be investigated at various levels. Therefore, small scale practical experiment were performed to characterize the flow and transport parameter which were used for executing the subsequent large scale investigations. The conceptualized frame work developed for practical experiments at different dimensions were finally used in investigating real plot and field scale studies.

Chapter 4

RESULT AND DISCUSSION

This chapter presents the results and discussions of laboratory, plot and field scale studies performed for the soil water flow and nitrate transport through heterogeneous vadose zone. Results of different laboratory experiments like column, lysimeter and multidimensional tank setups are presented first along with the numerical runs. Outcome of plot and field scales numerical investigations are described next. Results of equilibrium and non-equilibrium approaches applied to layered and heterogeneous soil domains of plot scale study having low and high nitrate application rates are discussed using 2/3D simulation runs. A comparative analysis is presented between the observed and computed nitrate mass retained in the vadose zone. The predicted nitrate leaching associated with particular crop yield under past and future climatic conditions at Nebraska MSEA site are presented in last. The climatic periods of 1991-1996 and 2055-2060 are considered at this field site to represent past and future scenarios for prediction of nitrate leaching to the underlying groundwater resources.

4.1. Preliminary and column experiment:

Preliminary results were obtained using laboratory methods. To characterize the particle distribution of the porous media, sieve analysis was performed using a sieve shaker. The results are presented in tables 4.1 and 4.2

Table 4-1: Mass fraction of various gain sizes in the sieve analysis of soil

Grain diameter (mm)	Mass(g)	Mass (%)
1.0	41.7695	9.51
0.5	248.9623	56.71
0.25	109.5451	24.95
>0.25	38.7098	8.82
sum	438.9867	100

Table 4-2: Physical and chemical properties of the experimental porous media

Porous media	Sand (g hg^{-1})	Silt (g hg^{-1})	pH	EC (s/m)	OMa	Bulk Density (g/cm3)
Sand	92.8	4.2	5.5	4.9	0%	1.65

The table shows that the selected porous media a typical medium sand having a particle size of 0.5 -1.0 mm. various physical and chemical properties of this porous media are listed in table 4.2.

The applied nitrate at surface in form of fertilizers/fertigation passes through the variably saturated zone before reaching to the underlying groundwater resources in field. To mimic these conditions, a large column set-up having diameter of 15 cm and length of 120 cm with 23 sampling ports was fabricated. The porous media was filled in the column till 90 cm depth with no background concentration of nitrate. A constant water flow 150 ml/hr having 100 ppm concentration of nitrate was applied at the top surface of the soil column and a constant water table was maintained at 30 cm from the bottom of the column using a peristaltic pump. The filled sand in the column setup water was fully saturated up to a height of 30 cm and the remaining 60 cm was kept unsaturated. The applied nitrate flux at the top surface of the column setup was allowed to move down from the lower boundary of the experimental setup. Concentration of nitrate was measured routinely at various depths of the soil profile by collecting soil water from various sampling ports along the depth. The relative concentration of nitrate was plotted as a function of time at different depths, known as breakthrough curves (BTCs), for the column systems.

Figure 4.1 shows the BTC observed at location 40, 55, 70 and 90 cm depth from top surface of the column setup. In all these BTCs, initially the concentration of nitrate was zero which started increasing after some time when the solute front arrived to the respective sampling ports before reaching to an equilibrium condition. The relative concentration at 40 cm depth reach a maximum value of 0.91(Figure 4.1) after about 13 hours while it takes 24 hours for 90 cm port to attain the plateau value. This shows the lag time of advective flux required in physical movement of the solute. No significant difference was observed between the equilibrium/plateau concentrations of nitrate observed at different ports. This shows that the nitrate adsorption by the selected porous media can be neglected. A diffusive front of nitrate at 40cm port is having sharper front as compared to the lowermost port indicating a role of dispersive and diffusive transport of nitrate in the setup. As groundwater velocity was kept quite high during the experiments, dispersive flux played dominant role as compared to the diffusive flux. The nitrate concentration profile with variation of simulation time (Figure 4.2) indicates the flow and transport behavior of nitrate in the column setup.

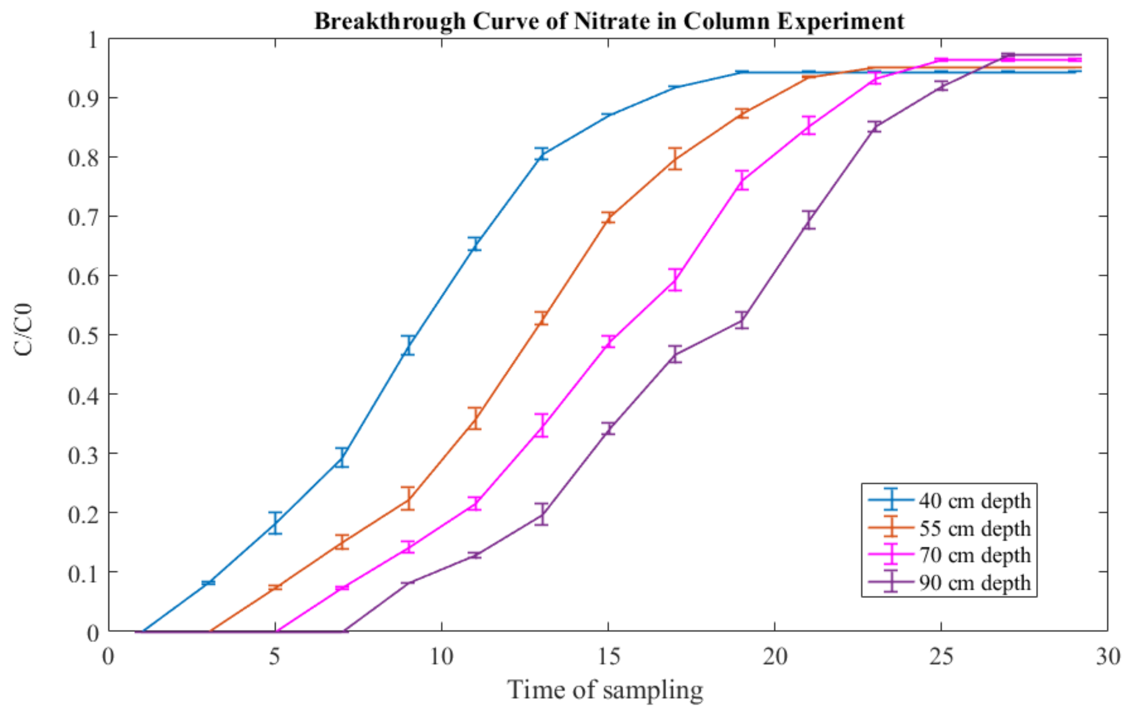


Figure 4-1: Breakthrough curve of nitrate at different depth of the column experiment. Error bar shows average of triplicate samples analysed using spectrophotometer.

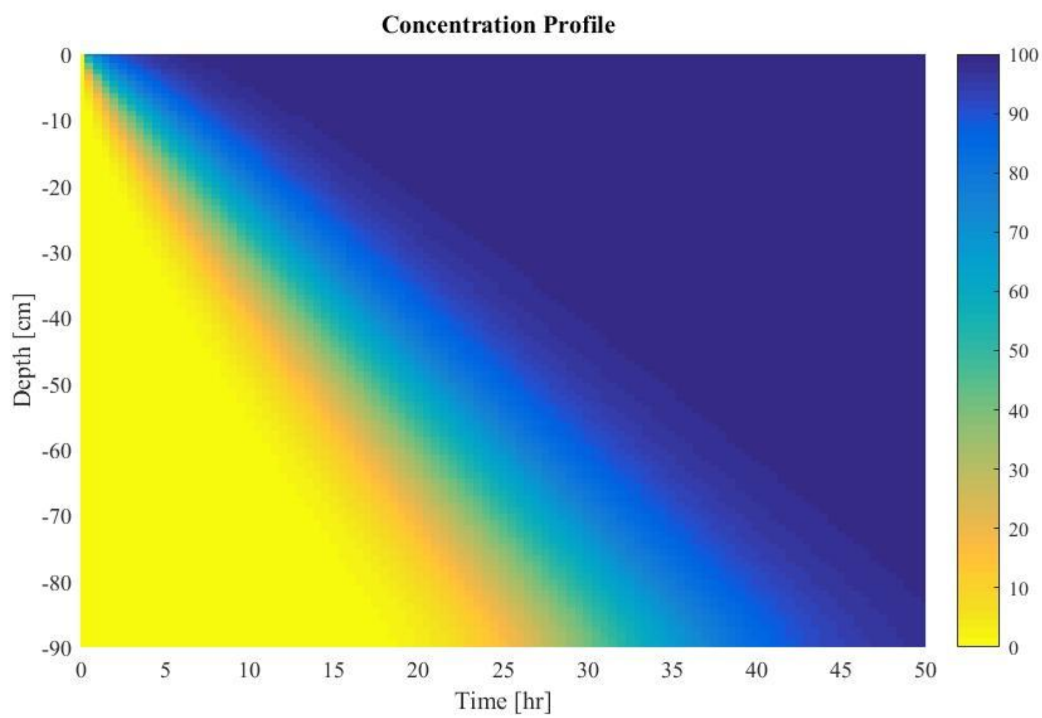


Figure 4-2: Nitrate concentration profile variation with time during simulation domain.

.Value of the dispersivity derived from column was ranging from 4.56 to 5.95 cm for partially saturated zone and ranging from 7.31.to 8.56 cm for fully saturated zone. Moreover, the dispersivity value in column increases with the travel distance due to the scale-dependent effect. This dependency of soil dispersity on soil moisture content and domain scale are in line with the observed results mentioned by Raymundo et.al. (2012). These obtained soil water and nitrate transport parameter are used for the subsequent series of laboratory and simulation experiments.

4.2. Lysimeter experiment:

To see the impact of moisture content on nitrate load to the underlying groundwater table, results of the lysimeter experiments are shown here. Two sets of experiments were performed at100% saturation and 80% saturation i.e. filed capacity of porous media. A peristaltic pump was connected with the lysimeter to provide a constant flow of 100ppm standard nitrate solution with flow rate of 150mL/hour. The potassium nitrate solution was used as standard for applying a constant flux of 100ppm nitrate solution. The concentration of nitrate was measured routinely at various depths of the soil profile by collecting soil water from four sampling ports. Two of these sampling ports were situated at 18 cm (O_1) at the remaining two were situated at the bottom of the lysimeter i.e. at 24 cm (O_2). The soil water collected from these ports were analysed using Single Beam Spectrophotometer 'Spectroquant pharo 100'. An arithmetic average of nitrate concentration was taken from these two depths. The sampling analysis was performed in triplicates. The breakthrough curve of obtained concentration during the both experiment was plotted (Figure 4.3). Before conducting the lysimeter experiment at varying moisture content, diurnal water loss in form of evapotranspiration was quantified using a mass balance. The obtained evapotranspiration loss was used in the maintaining the steady state condition of lysimeter experiments.

The soil water samples were collected from the ports in a time interval of two hours till the nitrate concentration in the collected samples became stable. The experimentally observed concentrations of nitrate under varying moisture content are listed in table 4.3. Figure 4.3 shows that time taken by nitrate to move through the lysimeter filled with 80% saturated sand was more than the time taken by same concentration of nitrate solution to move at 100% saturation. It was observed that the equilibrium concentration at the different observation depths for both saturation levels is similar. The trend of nitrate movement flux is also quite similar for the varying moisture content. The nitrate BTC for fully saturation case has sharper front as compared to the 80 % saturation case. This indicates that the role of advective dispersive flux was dominant over the diffusive flux. The observed and simulated (Figure 4.4) BTCs clearly indicate that a high water content present in the soil domain lead to the accelerated movement of nitrate to the underlying groundwater resources.

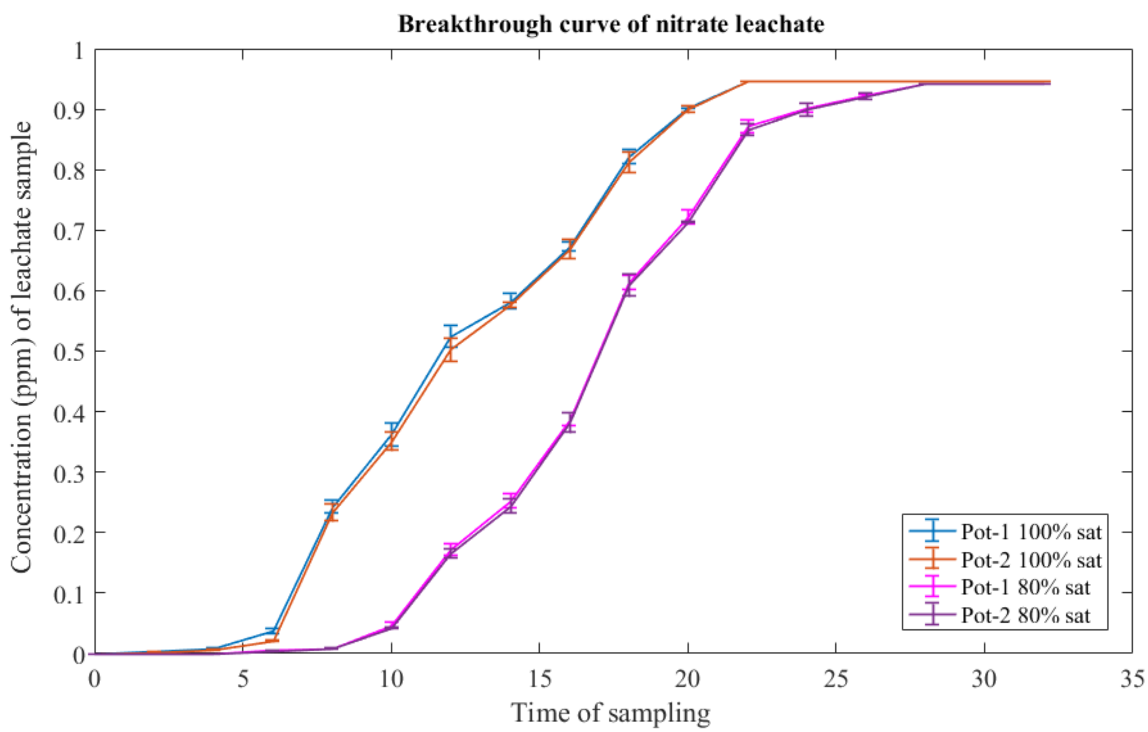


Figure 4-3: The breakthrough curve of observed nitrate concentration in the Lysimeter setup at 100 % saturation and at field capacity. The error bar shows average of triplicate sample analyzed by spectrophotometer

Figure 4.4 shows the simulated breakthrough curves at sampling port which is quite similar to the experimental results. In simulation domain three nodes (N_1, N2 and N_3) were considered at the depth of 14, 18 and 24 cm from the top surface. The simulation runs are showing the similar trend like the laboratory results. A flat shape of curves at deeper location as compared to the top nodes showing the impact of dispersion and diffusion fluxes on nitrate transport through the selected porous media. Figure 4.5 shows the nitrate concentration profile at different simulation times. The time difference between the equilibrium concentrations not in proportion to their physical distance emphasizes the impact of initial moisture content of the porous media. Similar trend of BTC is observed for the 80% saturated case (figures 4.6 - 4.7), however, the absolute concentration of nitrate was observed same as 100% saturation case in all the sampling ports. In case of 80 % saturation level, travel time was more as compared to the fully saturated case.

Table 4-3: Laboratory observation of nitrate concentration during lysimeter experiment.

Time (hrs).	Conc. of nitrate(ppm) 100% saturation.		Conc. of nitrate(ppm) 80% saturation.	
	Port 1(O_1)	Port2(O_2)	Port1(O_1)	Port2(O_2)
0	0	0	0	0
2	0.33	0.24	0	0
4	0.77	0.65	0	0
6	3.736	2.56	0.56	0.45
8	24.24	22.35	0.89	0.77
10	36.236	32.12	4.65	4.23
12	52.368	48.26	17.23	15.61
14	58.26	57.66	21.33	18.41
16	64.27	62.91	33.73	30.17
18	82.12	79.25	62.35	58.89
20	94.25	89.00	72.23	71.34
22	94.61	94.22	88.21	85.61
24	94.61	94.22	90.23	88.92
26	94.61	94.22	92.45	90.21
28	94.61	94.22	94.26	92.24
30	94.61	94.22	96.26	94.61
32	94.61	94.22	96.26	94.61

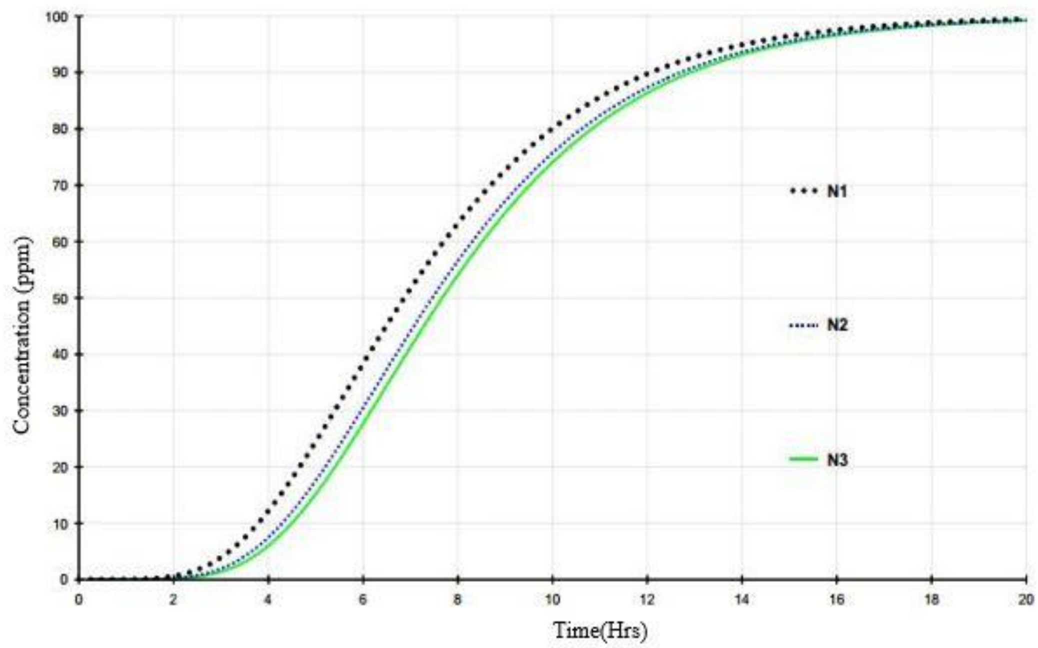


Figure 4-4: Simulated concentration profile for 100 % saturated porous media at different sampling port of the Lysimeter setup. The N_1, N_2 and N_3 node represent the observation port at the depth of 14, 18 and 24 cm from the top layer of the porous media.

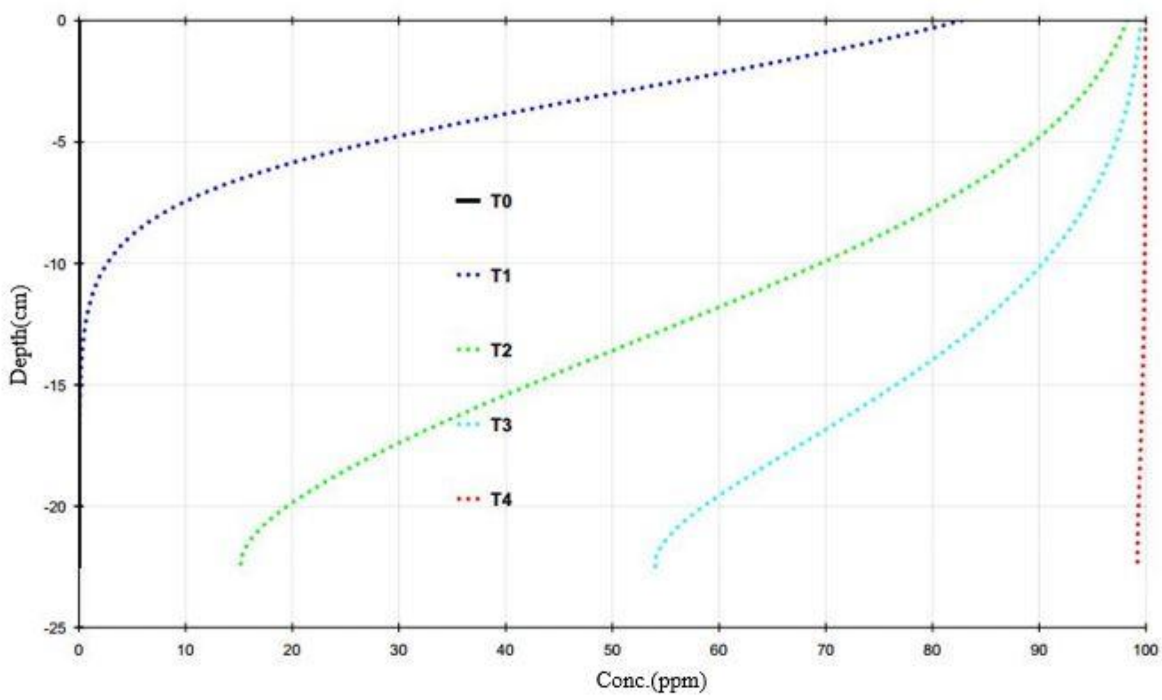


Figure 4-5: Nitrate concentration profile vs porous media depth during simulation at different time intervals for 100 % saturation level.

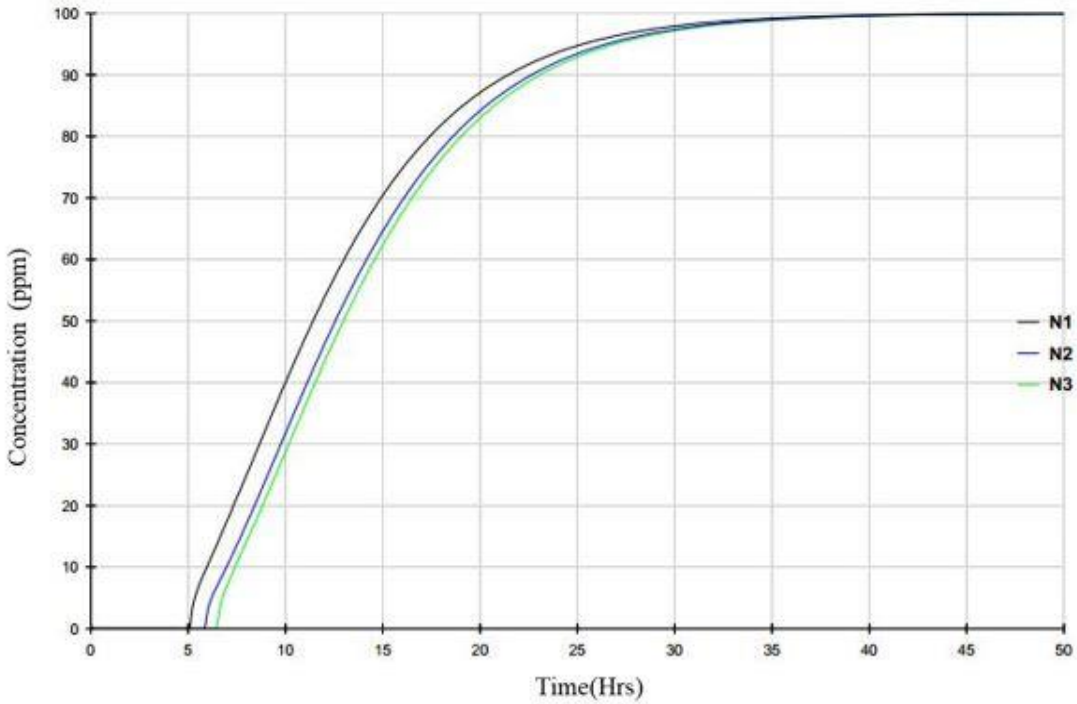


Figure 4-6: Simulated concentration profile for 80 % saturated porous media at different sampling port of the lysimeter setup The N_1, N_2 and N_3 node represent the sampling port position at the depth of 14, 18 and 24 cm from the top layer of the porous media.

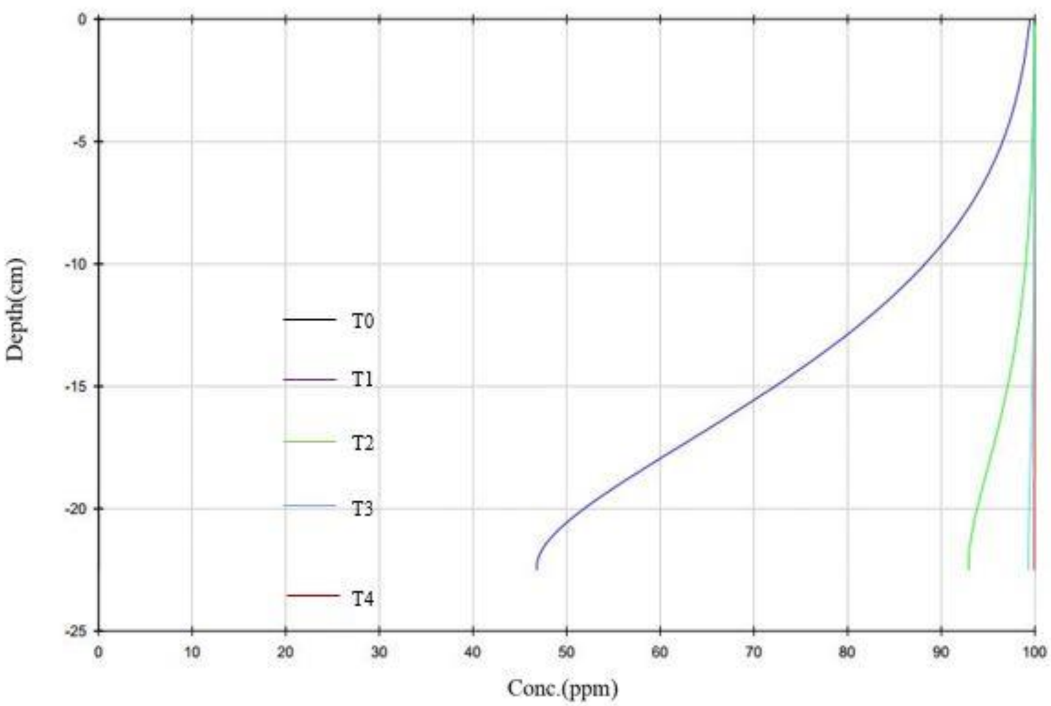


Figure 4-7: Nitrate concentration profile vs porous media depth during simulation at different time intervals for 80 % saturation level.

The above mentioned column and lysimeter experiments were performed under steady state conditions. To investigate the impact of transient flow in variably top boundary condition, two dimensional tank experiments were performed.

4.3. Two Dimensional Tank Experiments

The main focus of this study is to investigate the role of drainage flux, recharge flux and infiltration on the subsurface flow and subsequently, the nitrate movement in partially saturated zones. The water flow and solute transport properties were investigated experimentally using the preliminary experiments. A series of two dimensional experiments were carried out considering different boundary conditions in different four case studies. In first case, effects of drainage flux were evaluated by applying the constant drain flux as bottom boundary condition to the sand tank setup. Similarly, in second case, role of recharge flux was evaluated by applying the constant research flux taken as the top boundary condition. Likewise, for nitrate transport, the nitrate flux was allowed at top boundary in last case of experiments. The outcomes of these practical and numerical experiments are presented in four sub-sections.

4.3.1. Impact of drainage flux on subsurface conditions:

A constant drain flux was considered at the bottom boundary of this study domain and the subsurface changes were evaluated on a basis of the comparative position of the water table. The measured and simulated positions of water table at different time scales were plotted and shown in figure 4.8. A change in the location of water table shows depletion in water table with progression of time. This shows that the increasing drainage flux causes lowering of water table i.e. extension of partially saturated zones. Which indicates that the drain flux is responsible for the change in subsurface water storage condition along with the distribution of different zones in subsurface, especially in shallow aquifer system. The comparative analysis of the observed and simulated hydraulic parameters gives the associated percentage difference as listed in table 4.4.

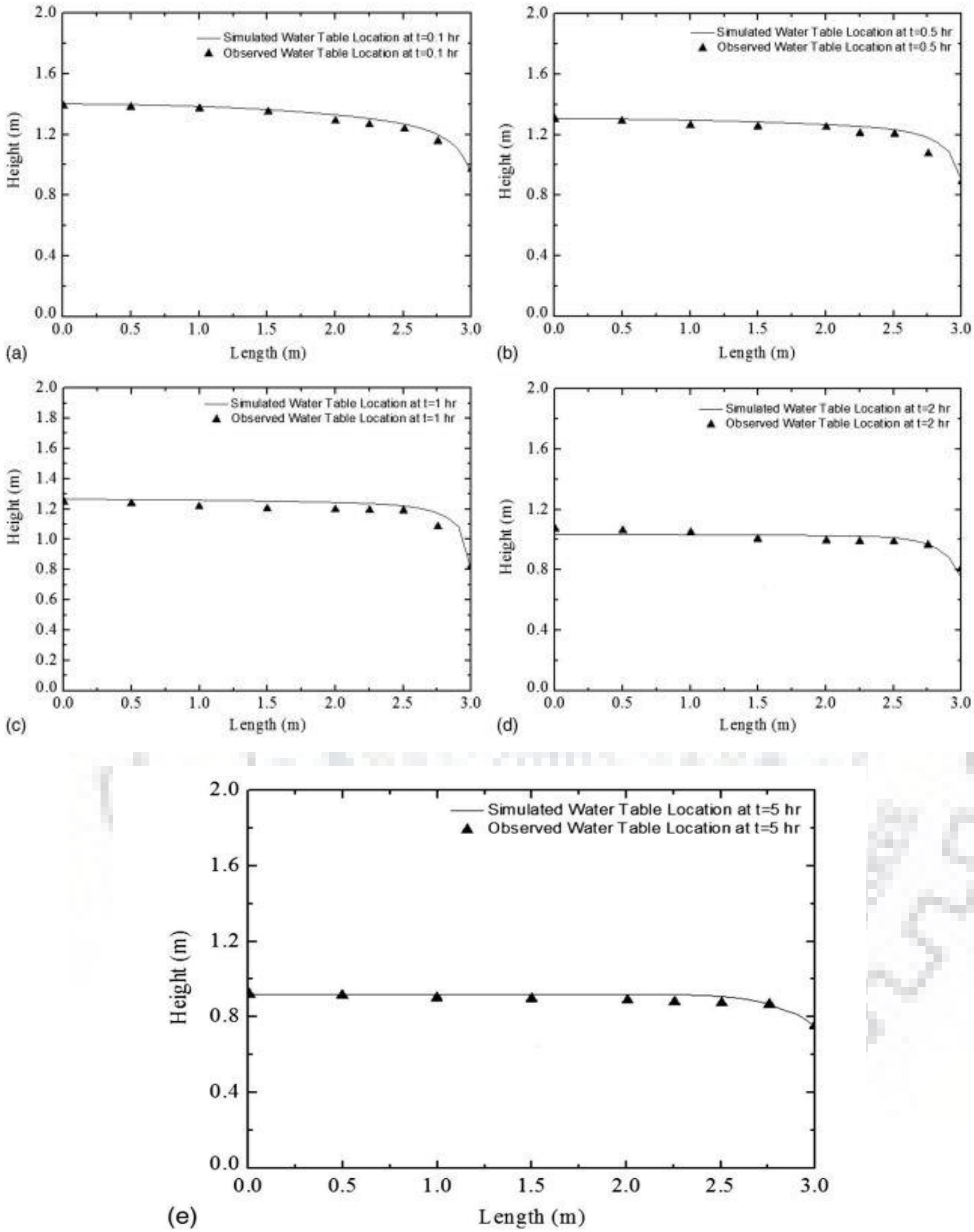


Figure 4-8: Role of drainage flux on water table location in the experimental and simulation domain under transient conditions at (a) 0.1 h; (b) 0.5 h; (c) 1 h; (d) 2 h; (e) 5 h

Table 4-4: Observed and simulated hydraulic parameters in the case of drainage flux applied at bottom boundary conditions of study domain

Parameter	Observed value	Simulated value	% difference
θs	0.25	0.30	14.67
θr	0.013	0.01	27.01
Ks	0.31	0.40	20.75

4.3.2. Impact of recharge flux on subsurface conditions:

A constant recharge flux was applied at the top boundary of the study domain. The increasing water storage volume caused the upward movement of the water table location at a slower rate as compared with the drainage case. The location of the water table is shown in figure.4.9 at 2, 3, 4, and 8 hrs. The associated percentage error between the simulated and observed data is listed in table 4.5.

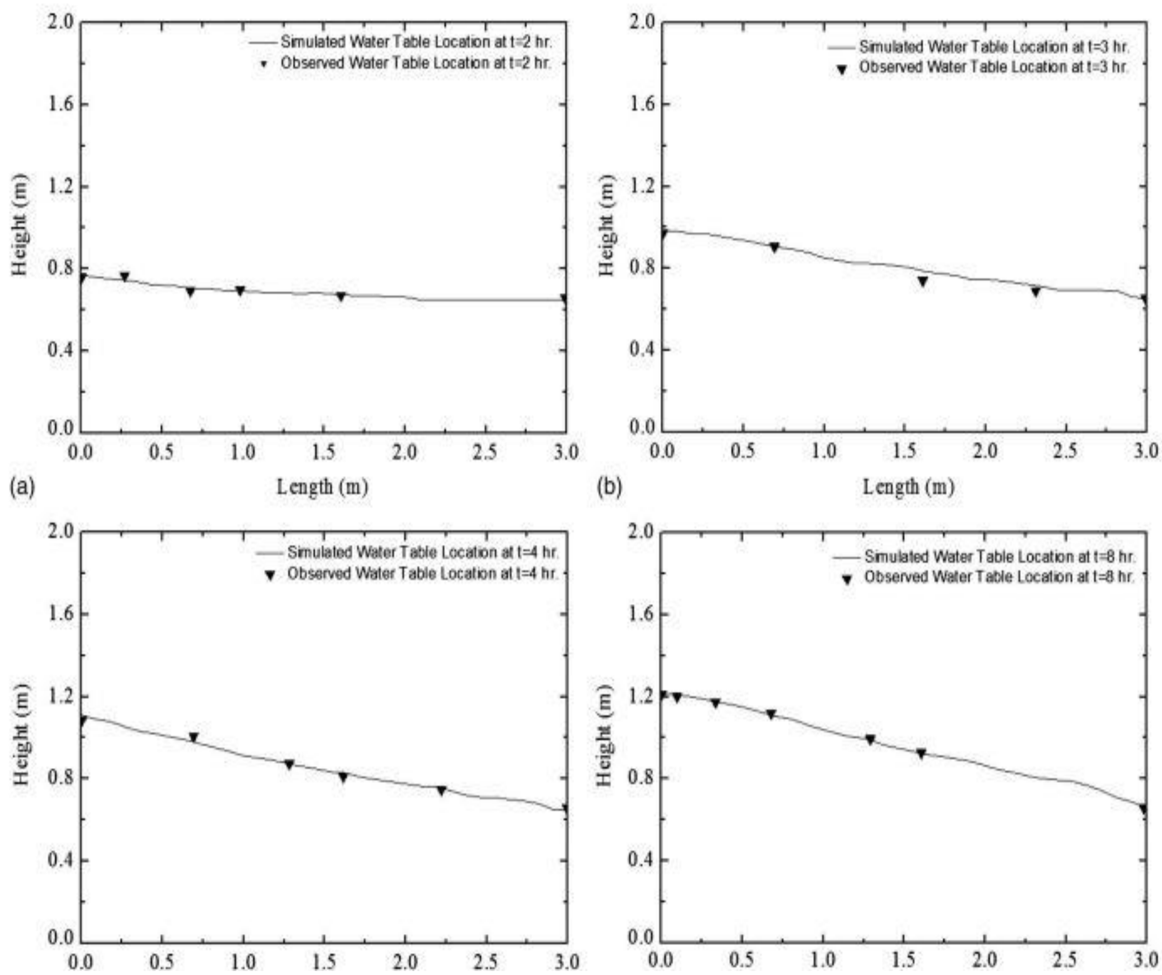


Figure 4-9: Role of recharge flux on the water table profile under transient conditions at study time: (a) 2 h; (b) 3 h; (c) 4 h; (d) 8 h

Table 4-5: Observed and simulated hydraulic parameters in the case of recharge flux applied at top of study domain

Parameter	Observed value	Simulated value	% difference
θs	0.24	0.30	17.33
θr	0.012	0.01	21.88
Ks	0.29	0.35	15.71

4.3.3. Transient infiltration in column setup

A constant water flux was allowed to the flow domain in vertical direction at the top boundary. The measured and simulated result showed the decreasing water table elevation with increasing water volume (Figure 4.10). Initially, water front moved at faster rates, but started decreasing at later stage. A comparative analysis between the observed and simulated water content is shown in table 4.6.

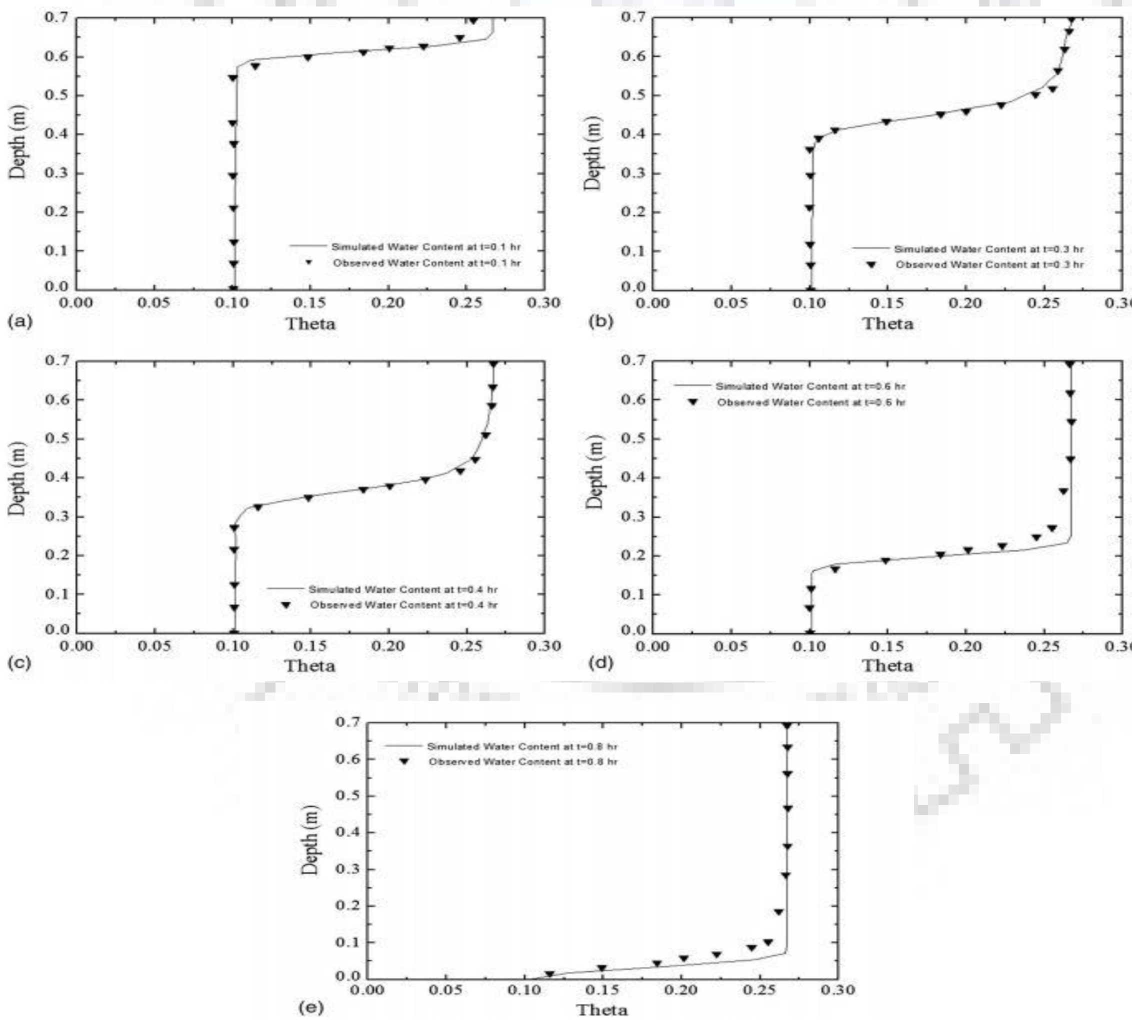


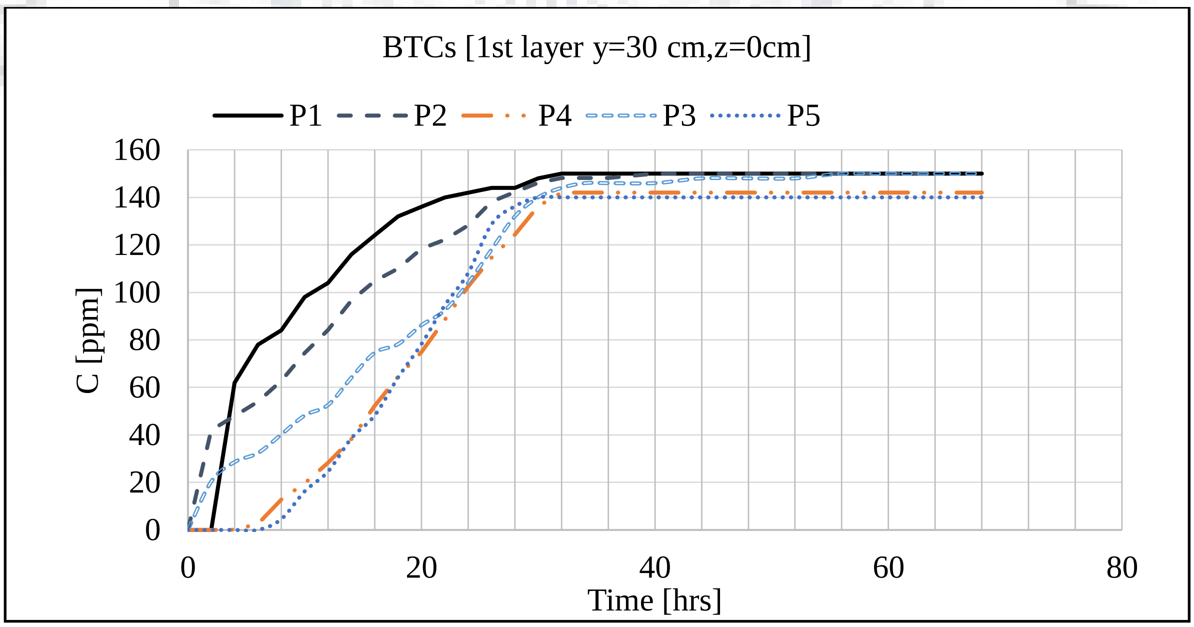
Figure 4-10: Water content profile in the case of the transient infiltration in the study domain at (a) 0.1 h; (b) 0.2 h; (c) 0.4 h; (d) 0.6 h; (e) 0.8 h

Table 4-6: Observed and simulated hydraulic parameters in the case of transient infiltration

Parameter	Observed value	Simulated value	% difference
θs	0.25	0.28	09.75
θr	0.10	0.07	26.04
Ks	0.30	0.34	11.47

4.3.4. Role of transient water flow on nitrate transport

A constant flux of nitrate was allowed to flow in horizontal direction in this two-dimensional domain. The BTCs show that the nitrate concentration increases with time and reaches to the peak concentration, thereafter it decreases with evolution of time as sown in figure 4.11. To represent the concentration profile, the concentration isolines are plotted in figure 4.12. Initially, the top observation points (P1-P5) having high peak concentration, which decreases with increasing concentration of middle area of the soil domain (P10-P14). This shows that nitrate transported downward primarily because of advective flux and toward the down gradient sides by dispersive flux. The advective flux dominated the transport mechanisms in this study and was highly affected by the recharge flux in the vertical direction. Therefore, the recharge flux in the study domain with nitrate pollution carried more nitrate load to the groundwater table.



(a)

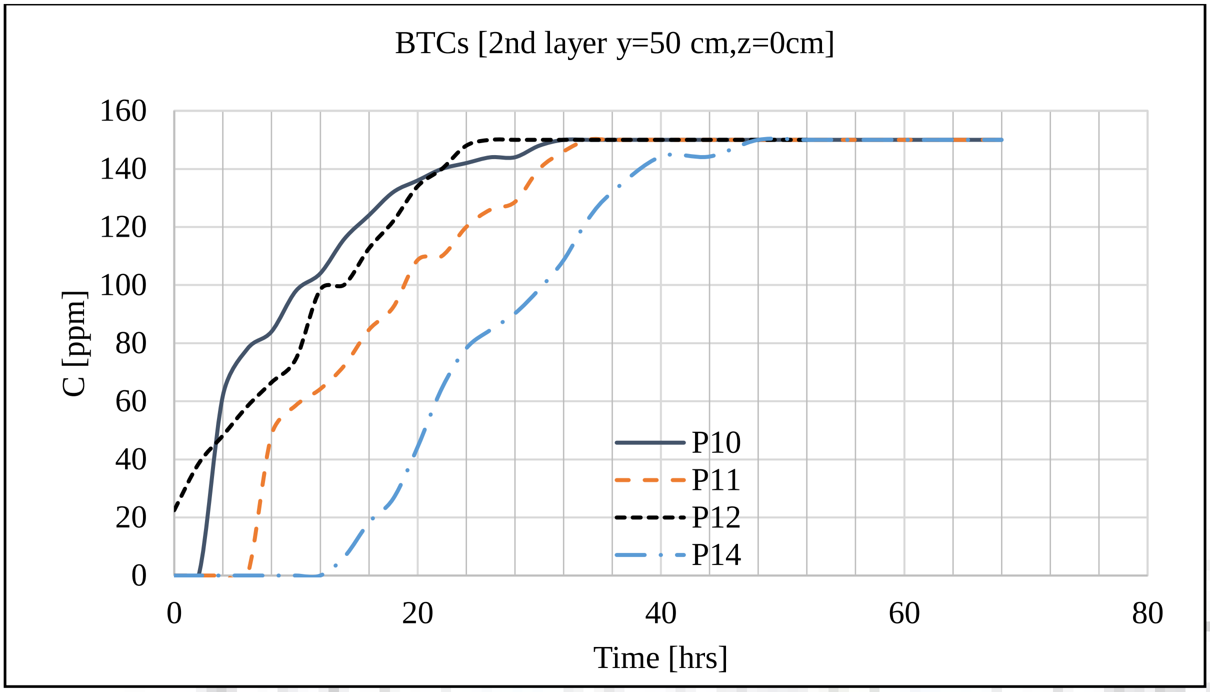


Figure 4-11: Experimental breakthrough curve of nitrate at different ports, (a) ports P1-P5 installed in 1st layer (b) port P10-P14 installed in 2nd layer

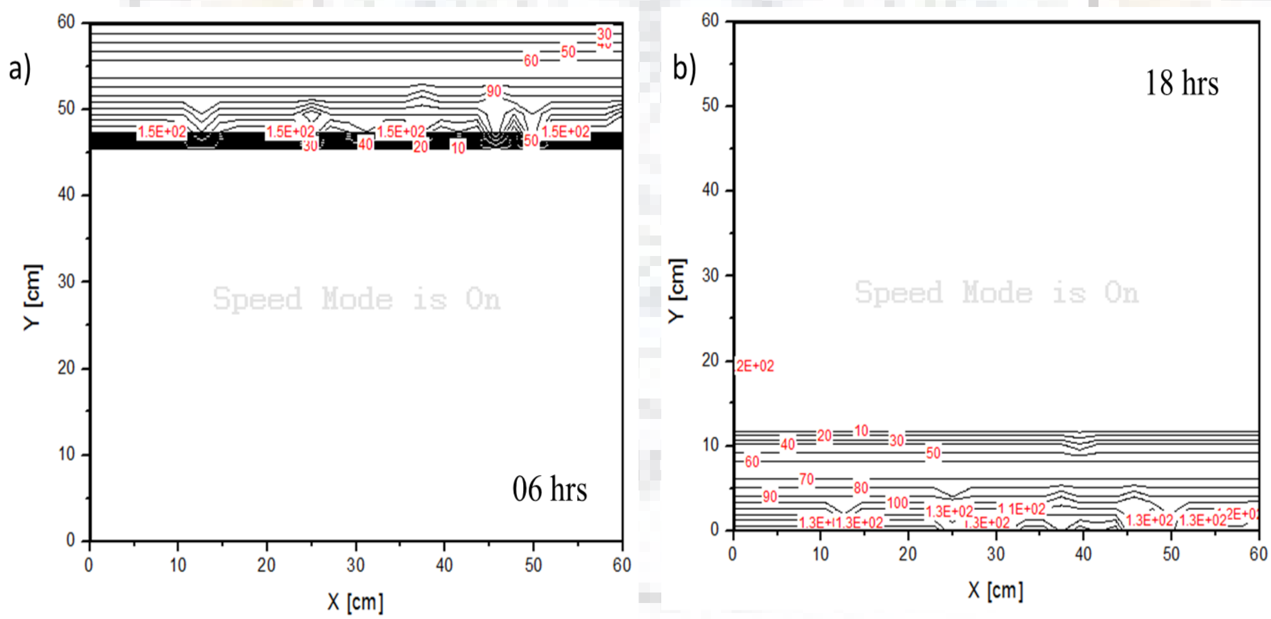


Figure 4-12: Concentration isolines of the nitrate in the study domain at time: (a) t= 06h; (b) t =18h

4.4. Three dimensional tank experiment:

In this experiment, transport of nitrate is investigated in vadose zone using laboratory sand tank considering single and dual-porosity approaches. Nitrate containing water having concentration of 300 ppm was applied as a distributed source from top surface using a sprinkler. The nitrate concentration was observed at different observation ports and compared with the simulated data. Different varying degrees of mobile-immobile zones were considered and it was found that 15 % of mobile zone compared well with the observed results.

Breakthrough curves for nitrate movement through the created unsaturated zone considering single and dual porosity (mobile and immobile regions) approaches are obtained for the tank setup. The observed cumulative flux of nitrate along with the simulated flux for single as well 15% mobile region is sown in figure 4.13. The observed breakthrough curve shows the higher cumulative nitrate flux at bottom as compared to the single porosity model. However, the simulated BTC considering the 15 % mobile zone was matching well with the observed quantity.

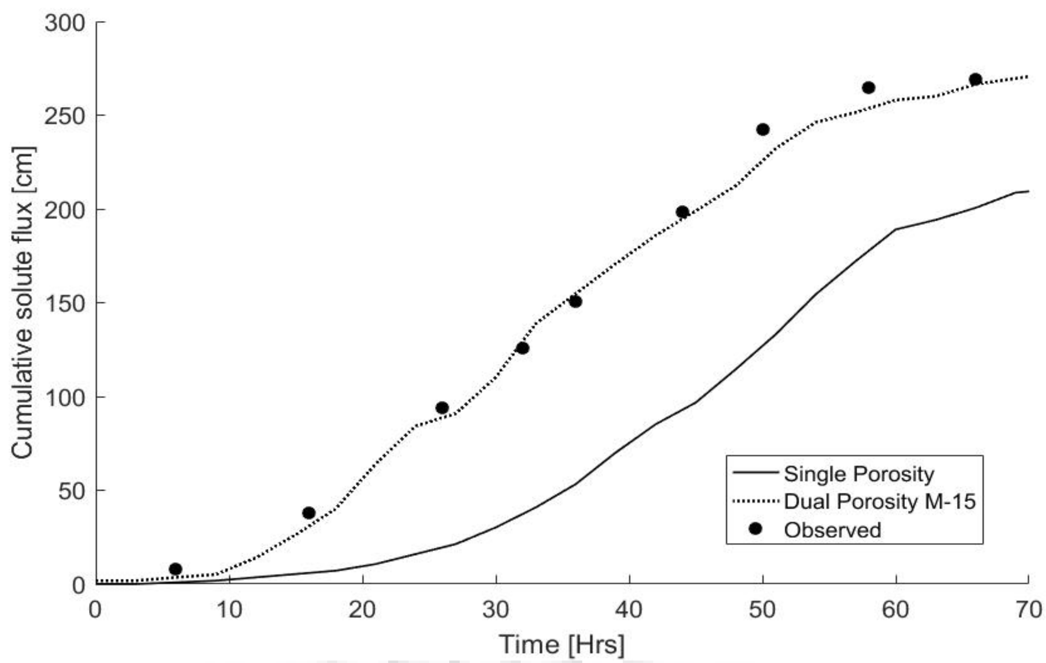


Figure 4-13:Represent the cumulative nitrate flux at bottom of the sand tank (black dots) and simulation domain having single porosity (solid line) and dual (dotted line) porosity model.

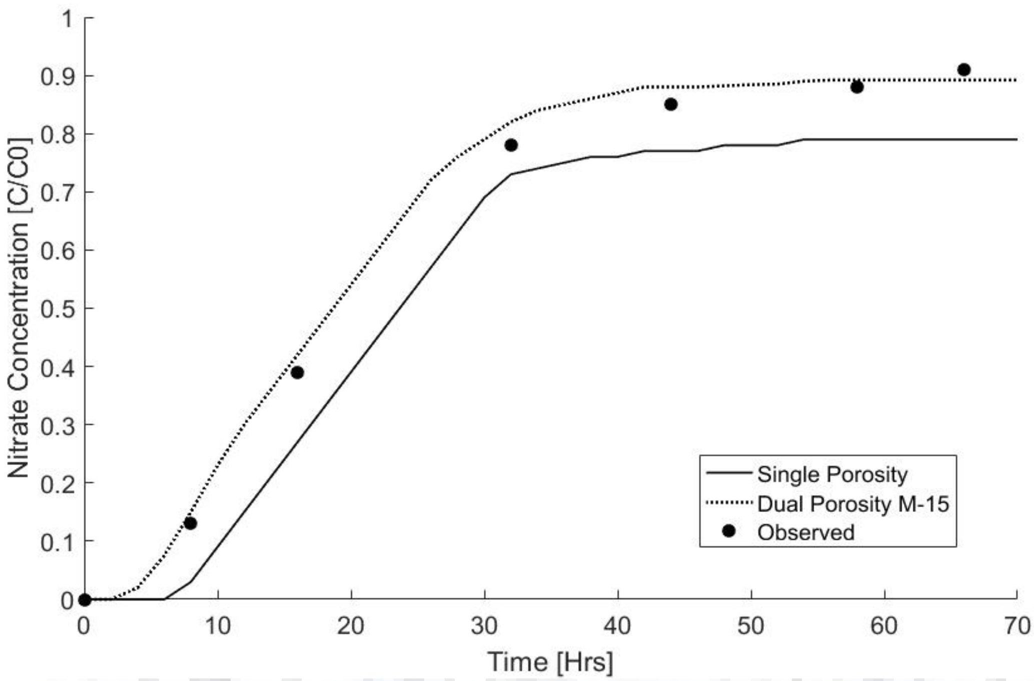


Figure 4-14: Represent the nitrate concentration at bottom of the sand tank (black dots) and simulation domain having single porosity (solid line) and dual (dotted line) porosity model.

Similarly, figure 4.14 shows that the time of arrival of nitrate to groundwater table was earlier for observed and dual porosity models as compared to the single porosity model. The peak of equilibrium nitrate concentration is also high in observed and dual porosity BTCs then the single porosity model. As soil water in dual-porosity approach moves faster than the single porosity approach, higher advective flux of nitrate is entering the groundwater in the dual porosity approach as compared to the uniform flow case. This indicates that vulnerability of groundwater to nitrate contamination increases as mobility in soil domain decreases.

4.4.1. Stored nitrate mass in vadose zone:

In subsurface system, the transport behaviour of nitrate changes due to relative storage of soil water and nitrate in micro and macro pores. Therefore, the storage mass of nitrate in unsaturated zone was computed for the both single and dual porosity approaches with varying mobile regions. The nitrate storage at different observation nodes was computed for dual porosity and single porosity approaches during the entire period.

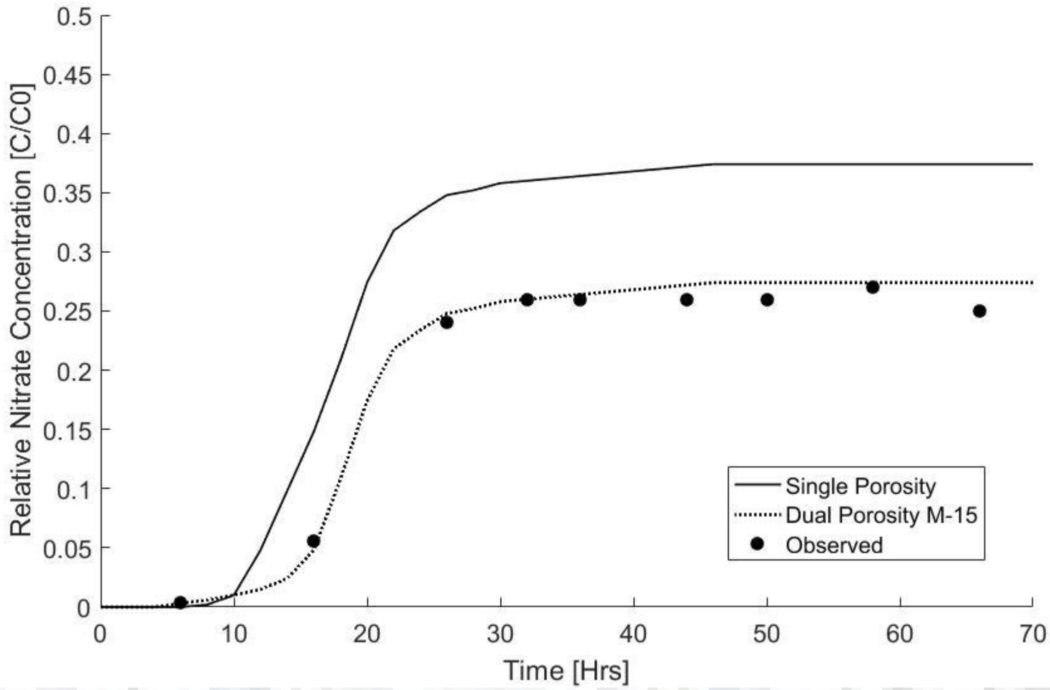
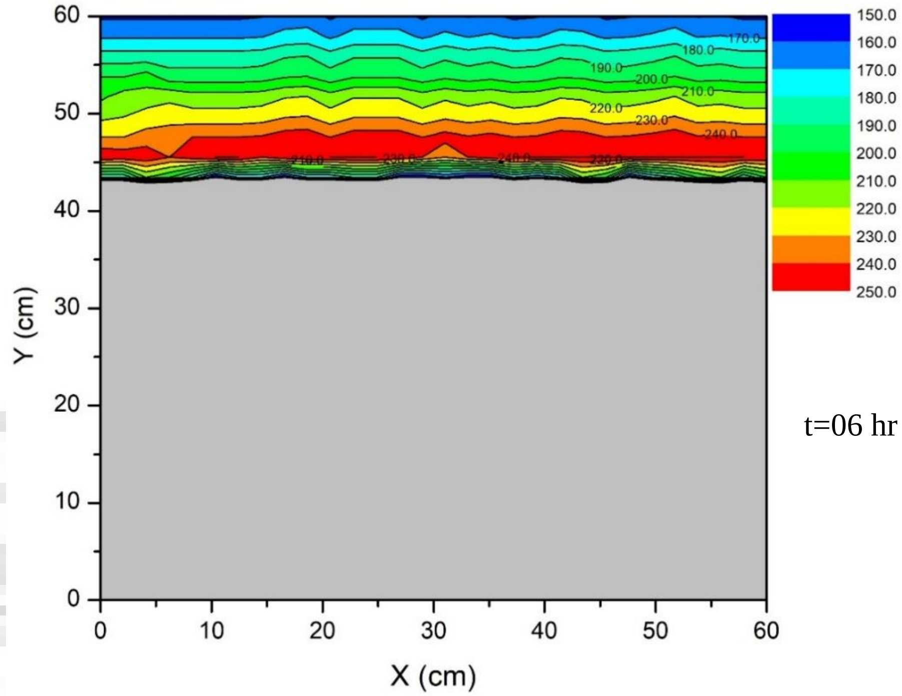


Figure 4-15: The relative nitrate concentration at inflow (C_0) and outflow (C) domain of the unsaturated zone during experimental period. The black dots represent the laboratory observed results, solid and dotted line shows single and dual porosity (15% mobile region) models.

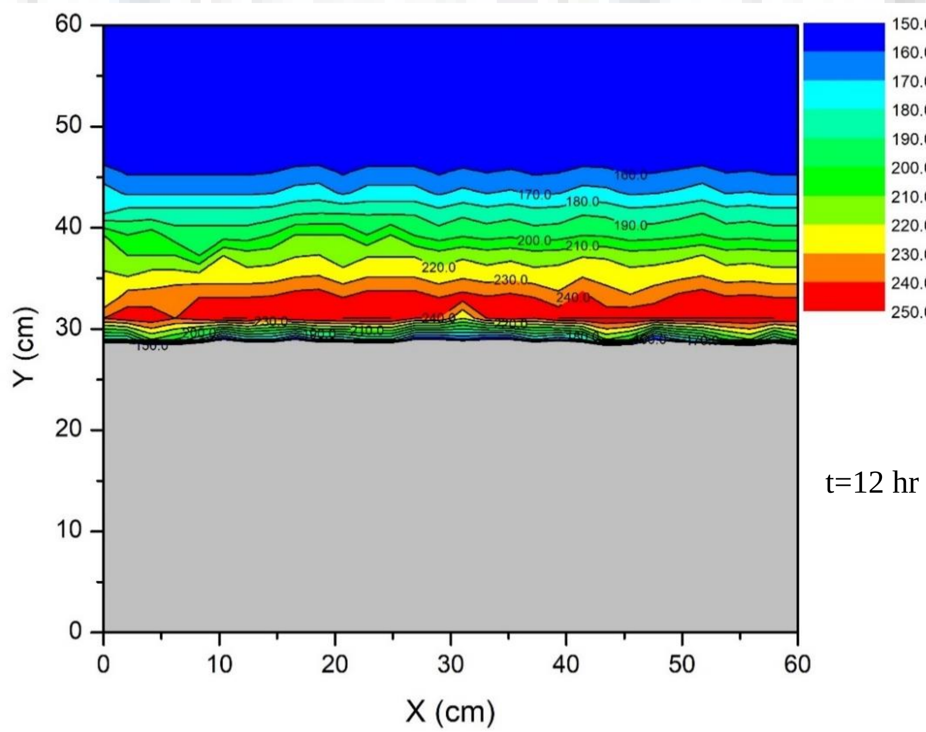
The progression of relative nitrate concentration of all three cases i.e. laboratory, dual and single porosity model are shown in figure 4.15. The obtained relative concentration curve for stored concentration shows the higher retention of nitrate in single porosity model than dual porosity followed by sand tank experiments. The overall results of stored concentration for all three domain having mobility region clearly shows the nitrate contamination increases as mobility in domain decreases.

4.4.2. Nitrate transport in vadose zone:

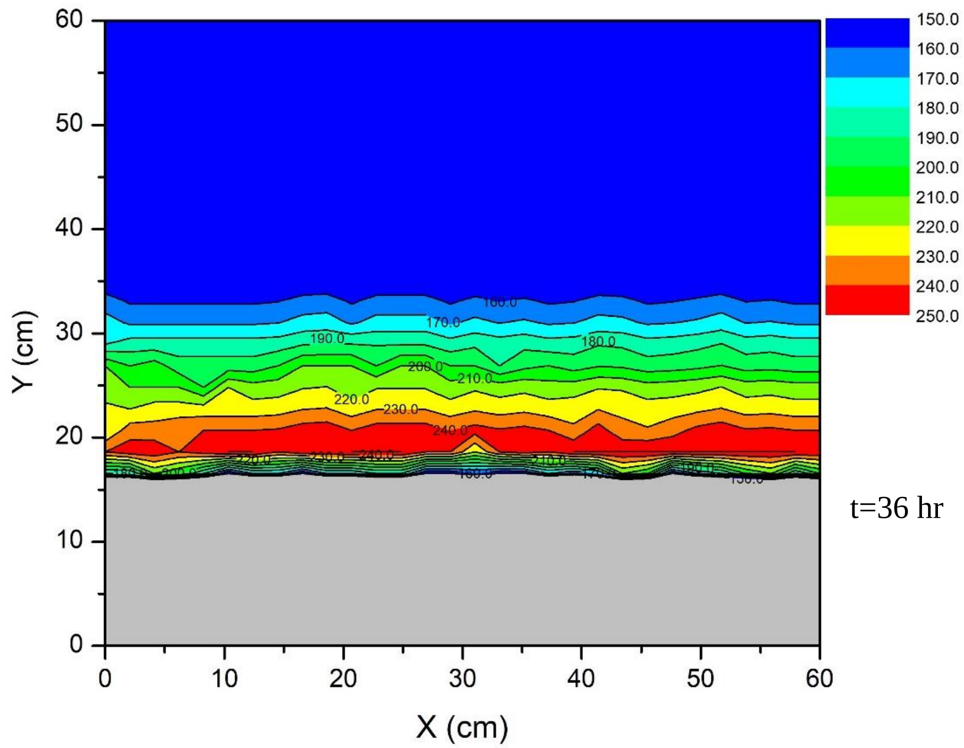
The concentration isolines of nitrate in sand tank and dual porosity model having 15 % mobile regions are presented in figures 4.16 -4.17. The laboratory sand tank observed nitrate plume movement in vertical direction is plotted as a function of space in figure 4.16. The spatial nitrate concentration isolines of domain clearly indicates the movement of nitrate in vertical direction. In which the maximum concentration of 254 ppm of nitrate was found nearby the bottom sampling port. At the equilibrium time, the bottom nitrate concentration was higher than middle and there was no concentration found at top sampling port due to the vertical movement of nitrate flux. Similarly, the simulated nitrate movement in domain having 15% mobile region are presented in figure 4.17, which shows similar flow pattern and time of arrival of plume as observed in experimental setup. To compare the concentration line, the concentration isolines of simulated nitrate concentrations are also plotted (figure 4.17). This shows the advective flux was dominating transport mechanisms. The comparative analysis of experimentally observed and simulated data shows high level of correlation and matching quite well. The mass balance analysis of laboratory and simulation experiment results presented in the table 4.7.



Y (cm)
X (cm)
150.0
160.0
170.0
180.0
190.0
200.0
210.0
220.0
230.0
240.0
250.0
t=06 hr



Y (cm)
X (cm)
150.0
160.0
170.0
180.0
190.0
200.0
210.0
220.0
230.0
240.0
250.0
t=12 hr



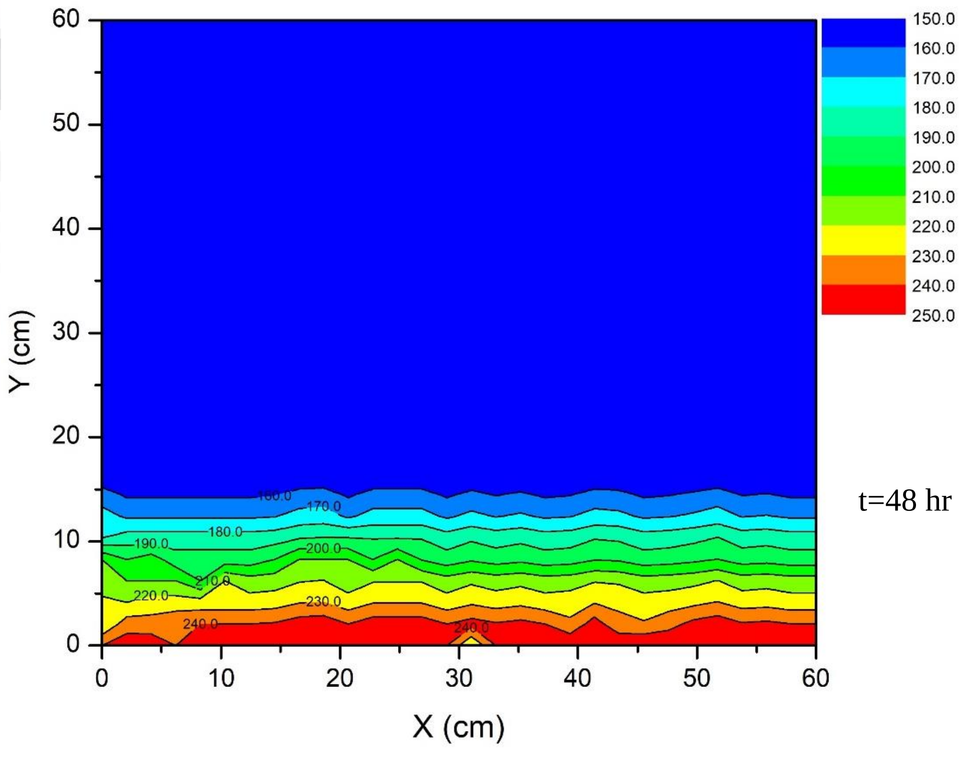


Figure 4-16: Concentration isolines representing the nitrate flow path in laboratory setup at different time, t=06 hrs., t=12 hrs., t=24 hrs., t=48 hrs.

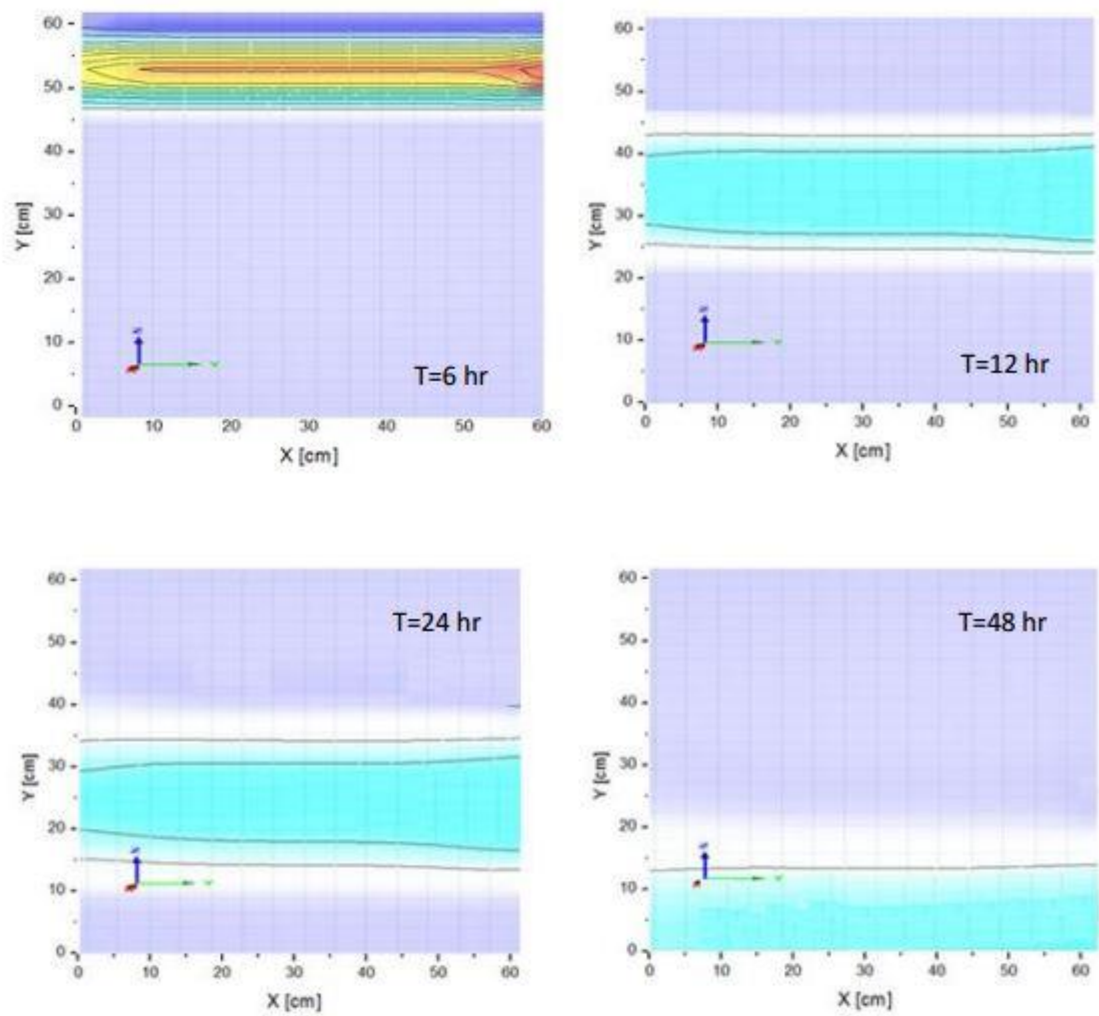


Figure 4-17: The simulated nitrate flux movement in study domain having 15% mobile region, at different time, t=06 hrs., t=12 hrs., t=24 hrs., t=48 hrs.

Table 4-7: Mass balance analysis of the simulated domain subjected to experimentally observed sand tank results.

Domain Properties	Influx mass [g]	Out flux mass [g]	Sorption mass [g]	Differences [-]	% (Error)
Sand tank experiment	2.7	2.4	0.25	-	-
Single porosity model	2.7	2.30	0.40	-0.1	4.16
15% mobile region	2.7	2.42	0.28	+0.02	-0.833

Results show that there are significant differences in the nitrate leaching pattern to groundwater using the two different modeling approaches. It is found that leaching of nitrate is very less in case of equilibrium approach which is in accordance with the results found by Gärdenäs et al.(2006), who suggested that equilibrium approach fails to predict the preferential flow and suggested that dual-porosity approaches is more realistic for modeling movement of water and solute in vadose zone. Since equilibrium approach assumes that water and solute fronts move uniformly along the whole soil domain, it takes time for the moisture and solute fronts to reach the bottom of the soil profile. Moreover, since solutes are moving slowly in the soil domain, it can be said that solute get longer time of residence in unsaturated zone which can ultimately affect the functionality of indigenous micro-organisms responsible for degrading most of the organic pollutants (Yadav and Hassanizadeh 2011: Basu et al., 2015). Whereas in dual-porosity approach, water and solutes move preferentially through the mobile zone of the solute which has high conductivity for water resulting in hastened flow and transport of solutes to deeper parts of the domain in considerably lesser time. Leaching patterns of nitrate from different nitrate concentration plots observed by Onsoy et al.(2005) is in accordance with these findings. However, they attributed this preferential flow to the heterogeneity of the deep vadose zone. It is observed here that even in a homogeneous unsaturated zone, role of macro/micro pores in mobility of soil water and solute movement cannot be ignored.

4.5. Plot Scale Simulations:

Uniform and preferential (dual-porosity) approaches were considered for simulating the movement of soil water and solute (nitrate) in deep and heterogeneous vadose zone of San Joaquin valley, California. Plant water and nitrate uptake mechanisms were also taken into account for precise estimation of the nitrate mass dynamics. The equilibrium and non-equilibrium (mobile-immobile) approaches were considered for low and high nitrate application cases at plot scale for the prediction of soil moisture and nitrate flux considering the heterogeneity of the vadose zone. Inter and intra layer heterogeneity of the soil domain was considered for the vadose zone comprised of eight layers of soils.

A two dimensional rectangular domain of 6.10m×15.8m width and depth is considered having a simulation mesh size of 1 cm. A simulation period of 730 days throughout the 1990-1996 period was considered. The initial condition is taken in linearly decreasing way from the lowest nodal point with pressure head value as zero, and -100 cm at the surface of the domain. The atmospheric boundary condition prescribing daily values of water fluxes including precipitation, irrigation, and evapotranspiration is applied on top of the soil domain, while constant water head of zero value is applied at the lower boundary. Precipitation and evaporation data were taken from Denton et al.(2004). For nitrate transport, the applied nitrate flux was considered at the top surface and zero concentration gradient was taken at the lower boundary of the vadose zone. A no-flux boundary condition was applied on both sides of the soil domain considering no water and solute is leaving and entering the soil domain. For the simulation runs all input like irrigation, evapotranspiration and soil lithology data was taken from Harter et al.(2005), Onsoy et al. (2005) and Botros et al. (2009). It was found that non-equilibrium approach uses higher CPU time as compared to equilibrium approach.

4.5.1. Nitrate transport in layered soil domain:

In this case, fate and transport of nitrate is investigated in deep vadose zone using equilibrium and dual-porosity model for mobile-immobile, (water concentration, mass transfer) domain regions. Here, simulation considered for the uniform and the two varying degree i.e. 60% and 80% of immobile regions.

Cumulative flux of nitrate transported at bottom of the soil domain after passing through the layered soil domain along with the nitrate mass retained in the vadose is predicted considering the three simulation approaches. The simulated cumulative flux of nitrate for 60% and 80% immobile regions and equilibrium approach is shown in figure 4.18. The breakthrough curve shows a higher cumulative nitrate flux at bottom in 80% immobile domain than 60% immobile case followed by the equilibrium approach.

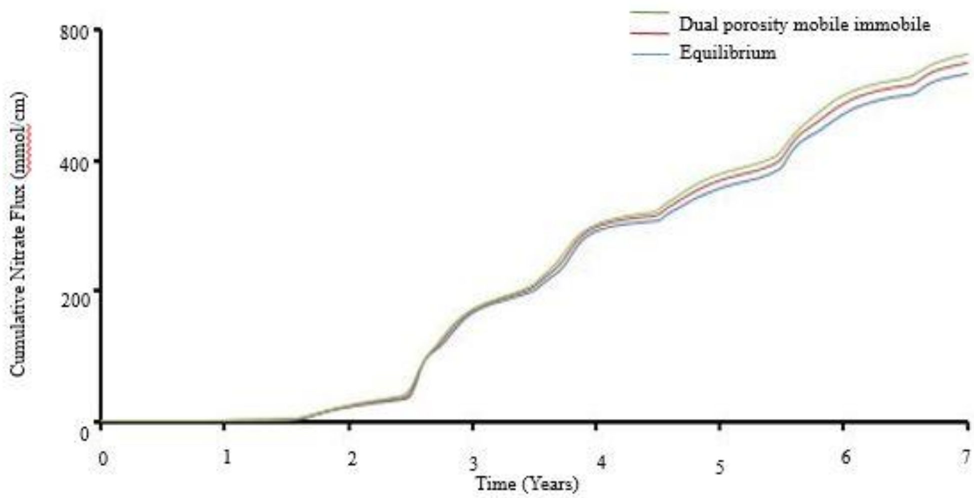


Figure 4-18: Cumulative nitrate flux at bottom transported through layered vadose zone having 60% (red line), 80% (green line) immobile regions and equilibrium approach (blue line) for seven years.

The simulated nitrate flux leaving the vadose zone for both the equilibrium and dual porosity approaches suggests that equilibrium approach under-predicted the leaching of nitrate to the underlying groundwater resources of the study area. This seems to be justified because in dual-porosity approach, nitrate is flowing through the zone of higher conductivity and bypasses the rest of the soil matrix. In equilibrium approach, nitrate moves uniformly giving more opportunity to soil micro pores to retain it which leads to longer travelling time of the nitrate to the groundwater.

The nitrate retention in vadose zone soil water in different layers is computed for 60% and 80% immobile cases along with the equilibrium approach. The average stored concentration of nitrate obtained using these three cases is shown in figures 4.19 - 4.20 for each layers of the vadose zone. A higher retention of nitrate mass in equilibrium model is observed as compared to the dual porosity model. The 60% dual porosity case shows more nitrate mass retention as compared to the 80 % immobile domain. Similarly, the layer wise stored nitrate varies with depth showing a decreasing retention trend for all the cases. Figure 4.19 shows variations in nitrate concentration in different soil layers with progression in time. The maximum concertation of nitrate in 1st layer is 31.37 mg/l and 36.45 mg/l for dual porosity model having 80 % and 60% immobile domain respectively. The equilibrium model shows a higher peak of nitrate in all the layers. The overall results of layer wise nitrate concentration for both the approaches show that the nitrate contamination in groundwater increases with decrement in mobile zone value.

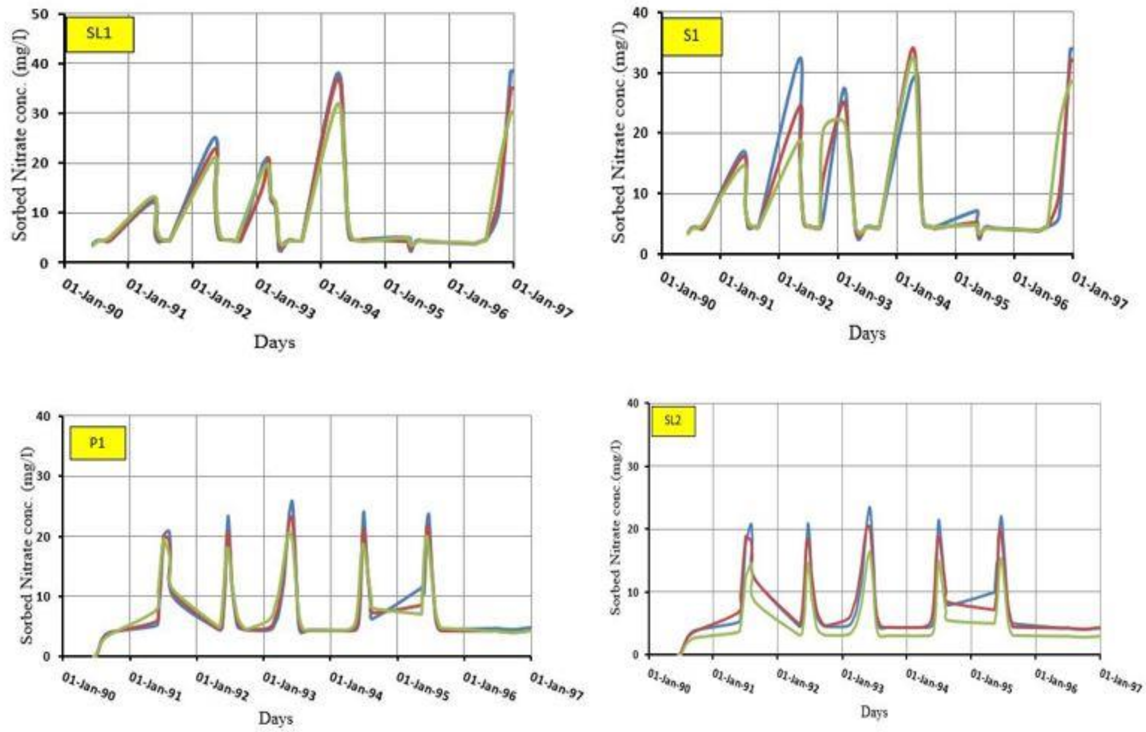


Figure 4-19: Variation in nitrate concentration in layers SL1, S1, P1 and SL2 during the transport in domain for dual porosity and equilibrium approaches.

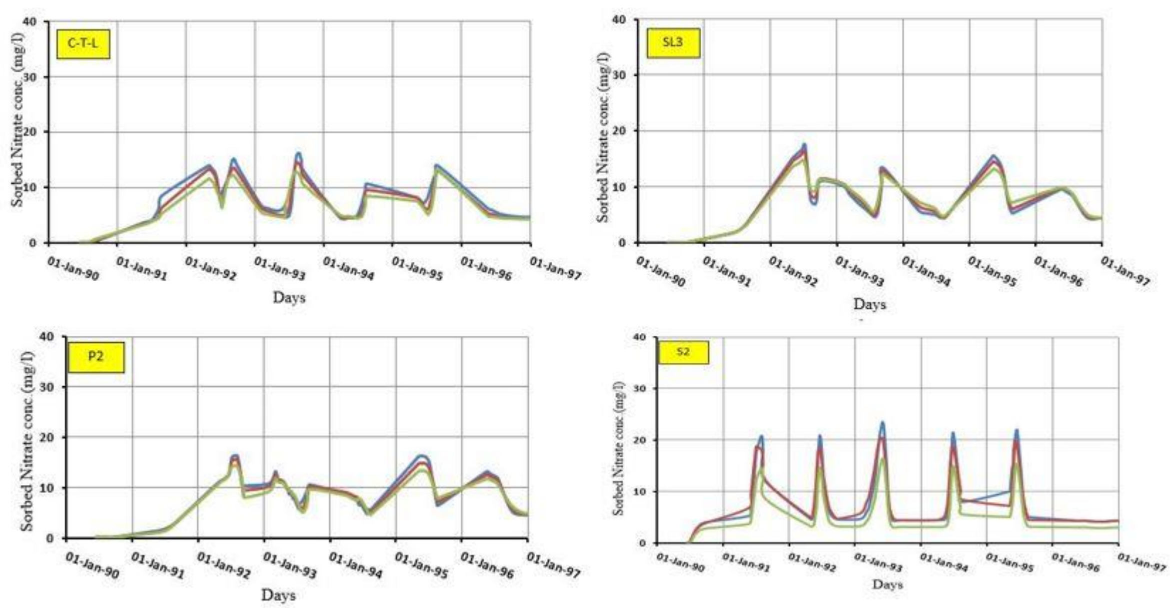


Figure 4-20: Variation in nitrate concentration in layers CTL, SL3, P2 and S2 in domain for dual porosity and equilibrium approach.

4.5.2. Nitrate transport in heterogeneous soil domain:

Here, heterogeneous of individual lithofacies is used for predicting transport of nitrate considering equilibrium and dual-porosity approaches. Botros et al. (2009) suggested that 15 to 20 % region of soil domain really participate in soil water flow and contaminant movement in the study area. Simulation experiment were performed considering equilibrium and non-equilibrium modeling approaches to see the impact immobile zone varying from 20 to 80% on underlying groundwater resources.

Figure 4.21- shows the leaching patterns of cumulative nitrate flux for equilibrium and non-equilibrium approaches. The figure shows that leaching of nitrate is higher in dual porosity (mobile immobile) as compared to equilibrium approach.

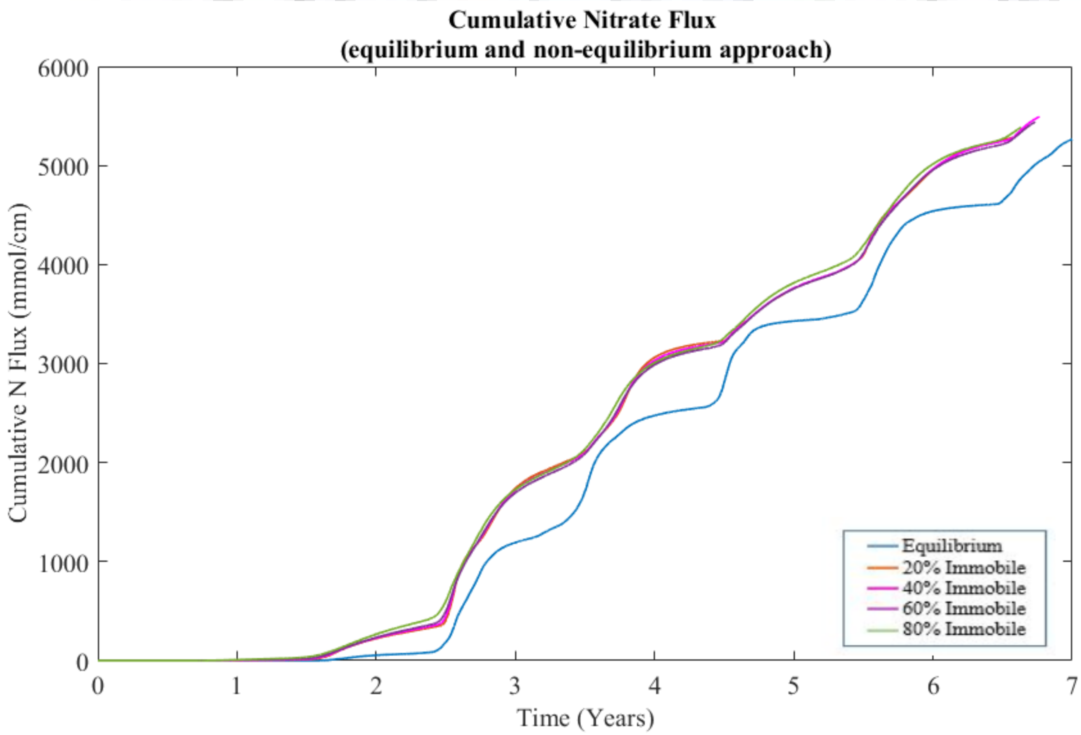


Figure 4-21: Variation of cumulative nitrate flux using equilibrium and dual porosity (20, 40, 60, and 80%) approaches

Variation in nitrate concentration with time of progression is shown figures 4.22-4.23 for the low and high nitrate application plots using equilibrium and dual porosity approaches. Different proportion of mobile and immobile zones presumed in dual porosity approach shows that nitrate peaks are more prominent for higher values of immobile zone.

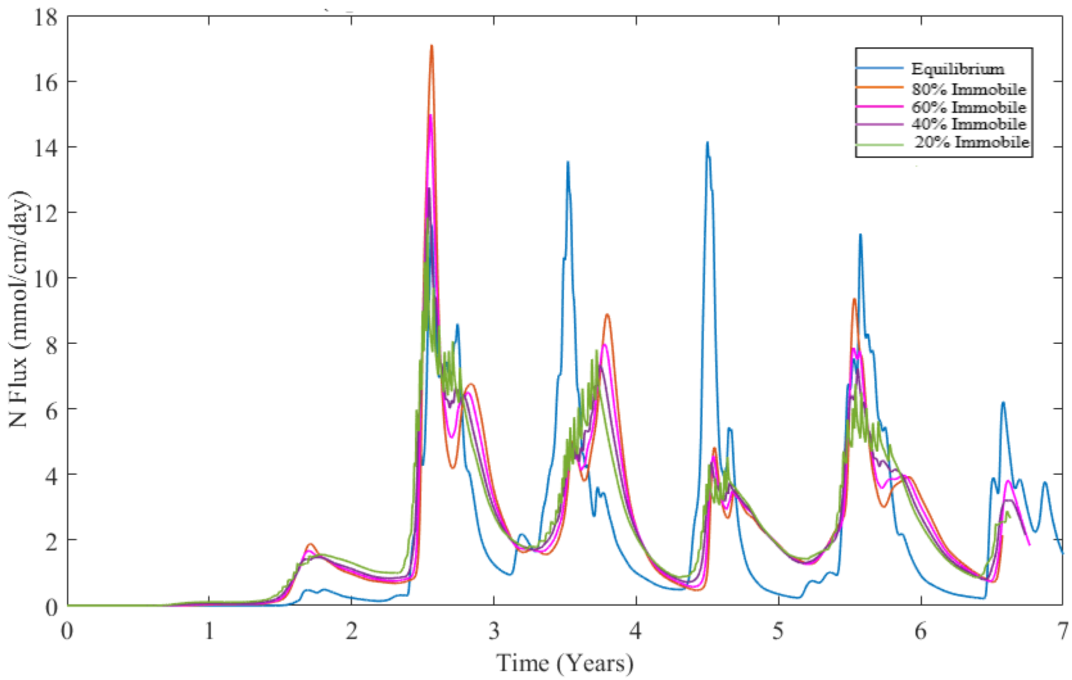


Figure 4-22: Variation of nitrate flux at low nitrate application plot using equilibrium and non-equilibrium (20, 40, 60 and 80%) approaches

Nitrate mass stored in the vadose zone was computed (figure 4.24) for the dual porosity approach having different mobile immobile portion of the soil domain. It was found that as the degree of immobility increases a less nitrate mass is retained in the soil profile.

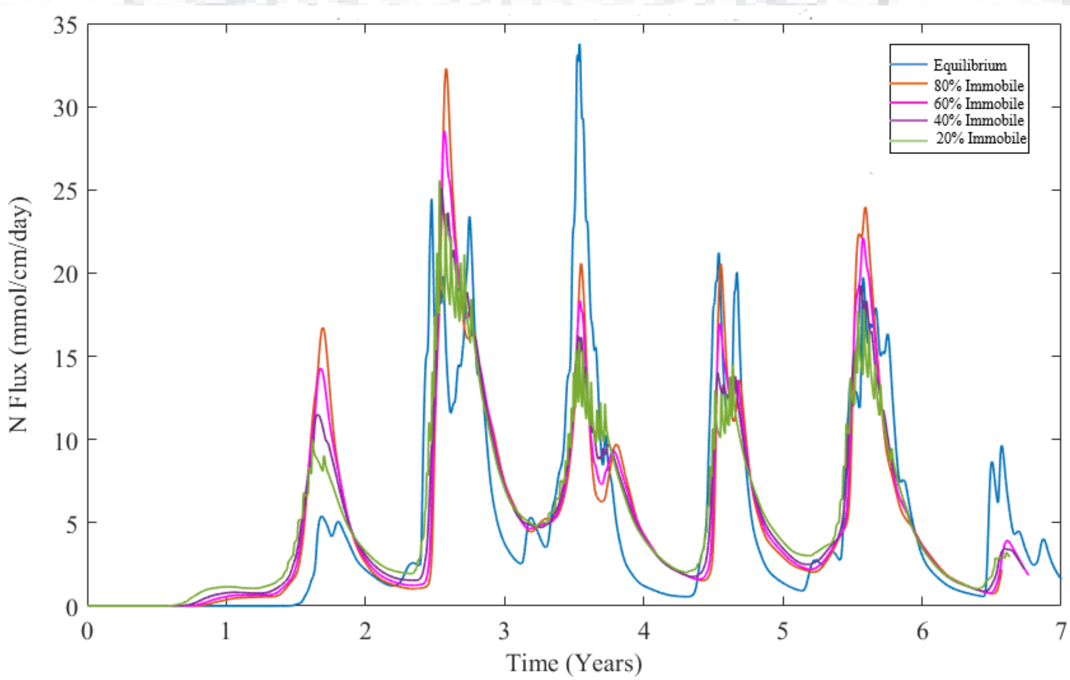


Figure 4-23: Variation of nitrate flux at high nitrate application plot using equilibrium and non-equilibrium (20, 40, 60 and 80%) approaches

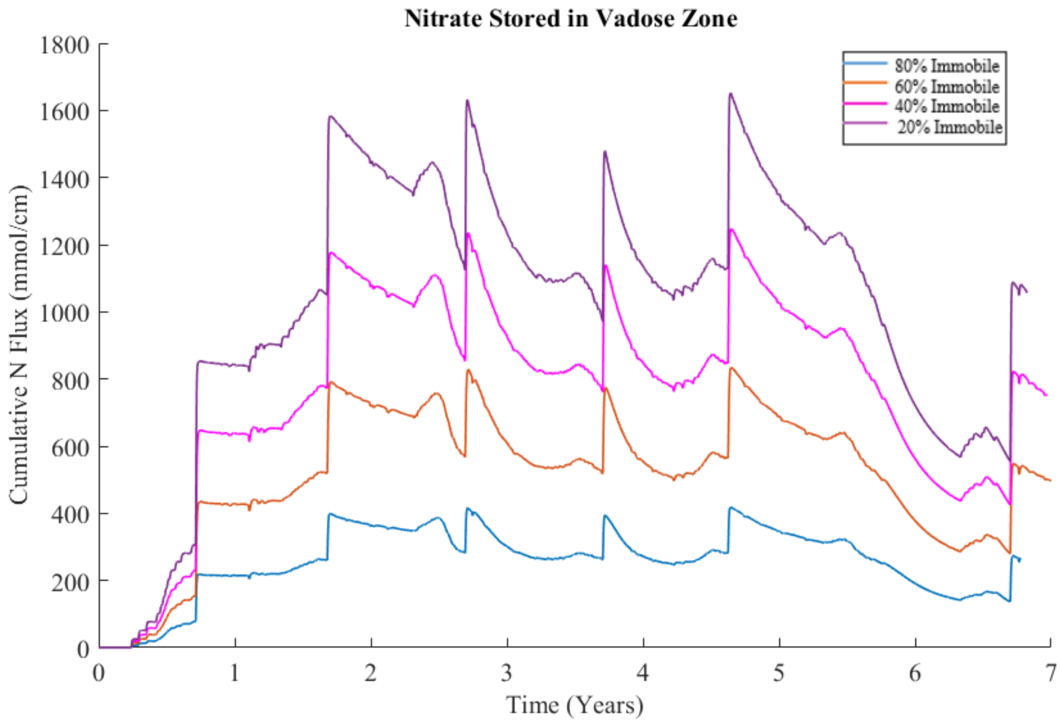


Figure 4-24: Computation of nitrate stored mass in vadose zone under different degree of immobile zone considered in non-equilibrium modelling approach

To see the impact of plant on nitrate flux, root uptake terms were incorporated in the simulation of soil water flow and nitrate movement through the vadose zone. The cumulative root nitrate uptake at low and high nitrate application plots in non-equilibrium modelling approach is presented in figure 4.25. The results clearly indicates that more amount of nitrate is taken up by plants in high nitrate application plot considering the active and passive uptake mechanisms. The solute uptake by plant at high subplot was almost two times of the low subplot in both active and passive root uptake model.

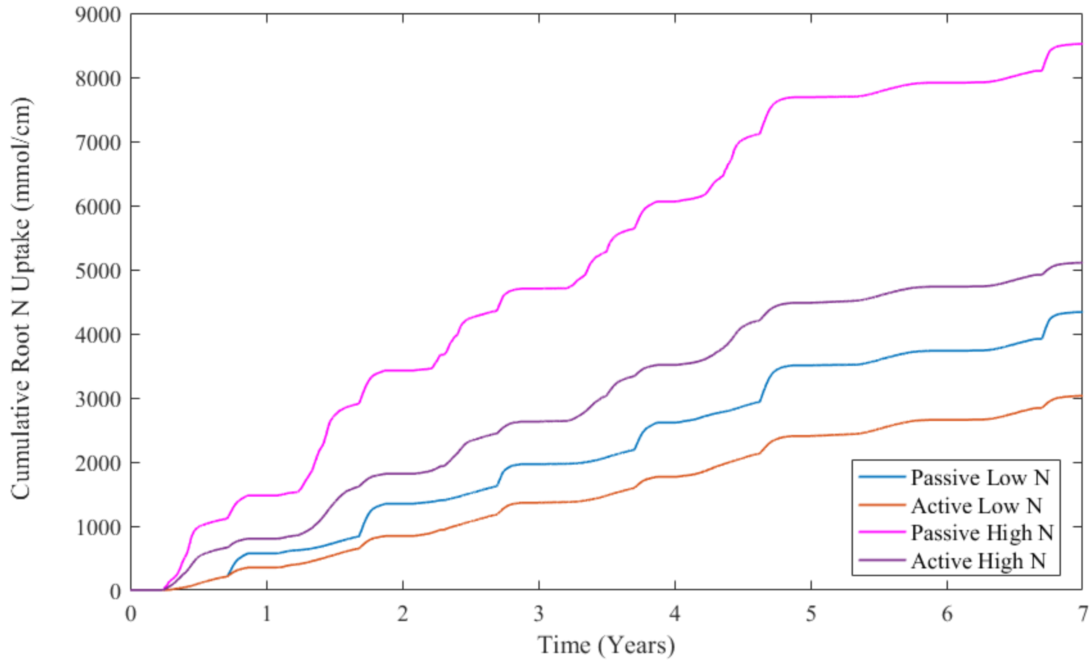


Figure 4-25: Cumulative nitrate uptake by plant in non-equilibrium approach at low and high subplots.

Nitrate flux at bottom boundary of the soil domain was estimated to predict the effect of root uptake by plants on nitrate leaching under planted and non-planted conditions at both low and high subplot nitrate application plots. Figure 4.26 shows the nitrate leaching flux under different cases in dual porosity modelling approach. More nitrate flux leach to the groundwater table under non-planted case. Indeed leaching of nitrate to the water table also affected by the fertilizer application at the plot. The travel time of nitrate flux to reach the groundwater was quite low in case of unplanted case in comparison with the planted case for both high and low nitrate application plots. A travel time of 1.5 and 2.7 years was observed for without and with planted cases for both low and high subplots.

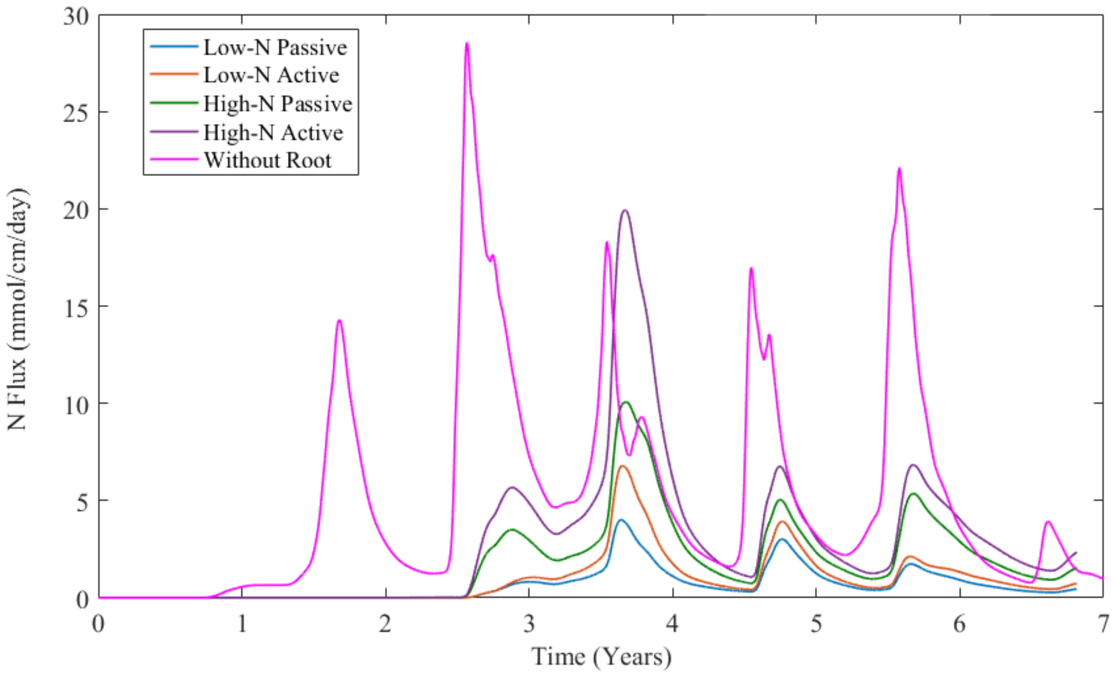


Figure 4-26: Nitrate leaching flux at low and high subplot for both planted and unplanted conditions in non-equilibrium modelling approach.

A sensitivity analysis is conducted to identify the relative importance of the model parameters used in soil water flow and nitrate transport simulation through vadose zone. The important parameters like the intra transfer coefficient of soil water and nitrate through mobile and immobile zone are very crucial (Therrien and Sudicky, 1996: Prasad and Mathur, 2007: Ma et al., 2015) for such types of modelling. Therefore, the base value of water and nitrate transfer coefficients, denoted by Γ_w and Γ_s respectively, are taken to perform the sensitivity analysis. These parameters are changed (reduced/increased) five times of their base values for this purpose. Figure 4.27 shows the cumulative nitrate flux at constant boundary in low nitrate application plot using different values of water transfer coefficient Γ_w taken as high (0.1), medium (0.02) and low (0.004). The results show that more nitrate reaches to the water table under high water transfer coefficient (figure 4.28). Table 4.8 shows the sensitivity analysis of nitrate flux under different water transfer coefficient values. A similar type of trend on model output was observed by varying the value of this parameter.

Table 4-8: Sensitivity analysis of nitrate flux under different water transfer coefficient values.

Parameter Γ_w value	Cumulative nitrate flux (mmol/cm)	Nitrate flux (mmol/cm/day)
High	5900	13.5
Medium	5400	10.8
Low	5050	10.4

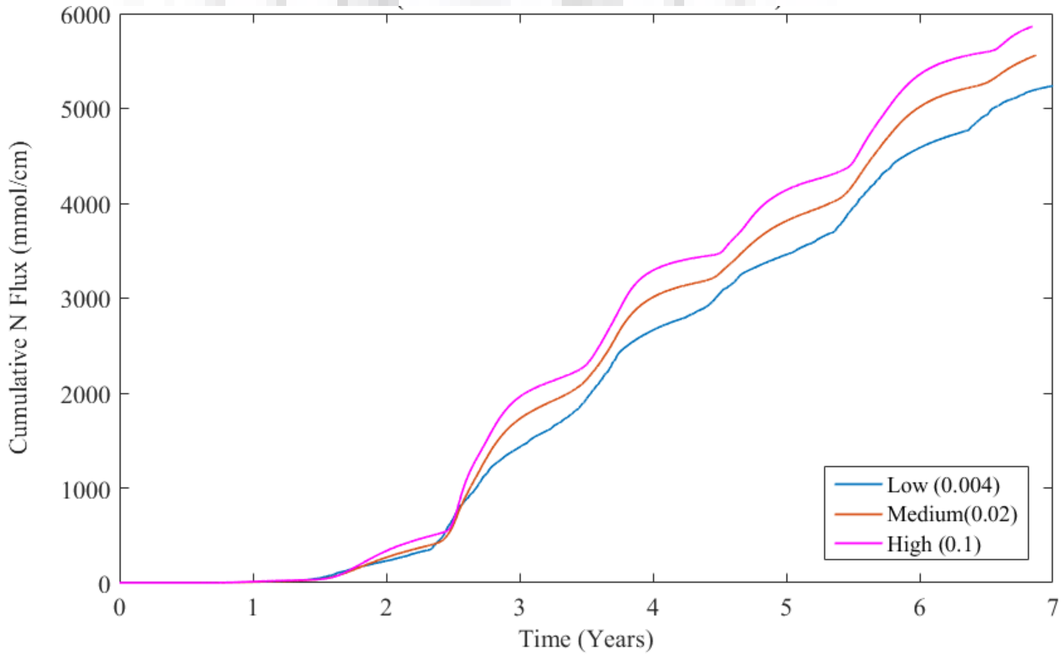


Figure 4-27: Cumulative nitrate flux under different values of water transfer coefficient at low nitrate application plot

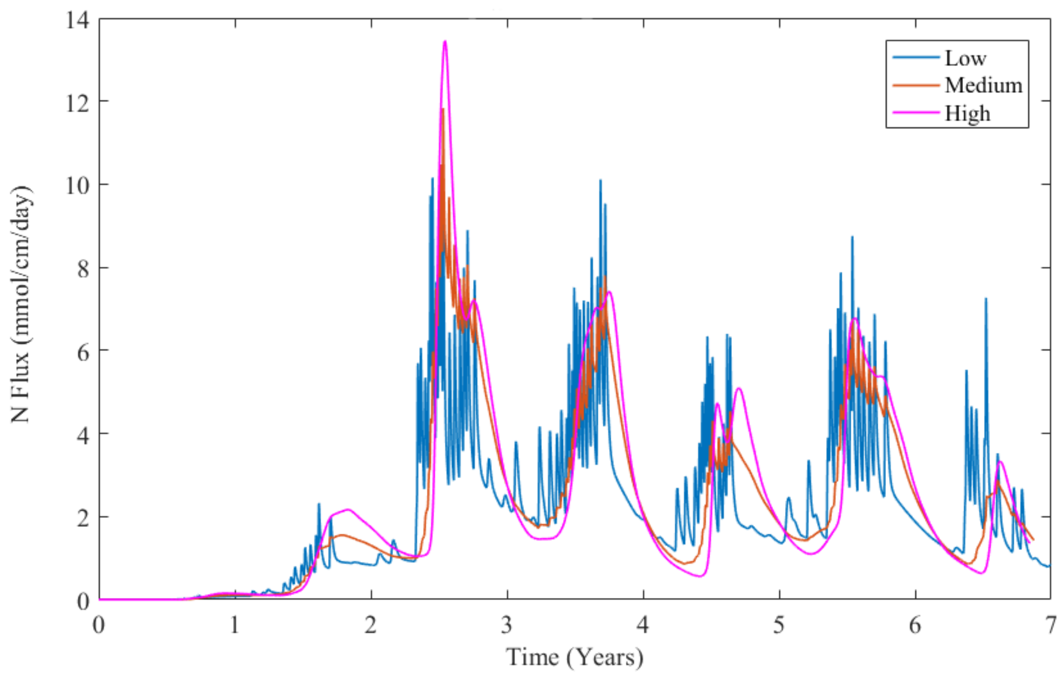


Figure 4-28: Nitrate flux under different water transfer coefficient at low nitrate application plot in non-equilibrium modelling approach

Likewise, different values of solute transfer coefficient were considered representing high (0.165), medium (0.033) and low (0.0066) values of the model parameter. Figure 4.29 shows that more nitrate leaches down to water table when a lower solute transfer coefficient value is considered. About 1.75 times more nitrate load is reaching to groundwater for the lower value of Γ_s as compared with the base and high value cases. However no significant change was observed by increasing the value of Γ_s from the considered base value. Thus care must be taken while choosing the lower values of this parameter at real filed site. Fig 4.30 shows the nitrate flux under different solute transfer function values fortifying a high sensitivity of model output on lower values of Γ_s. Table 4.9 shows the value of nitrate flux under different solute transfer values.

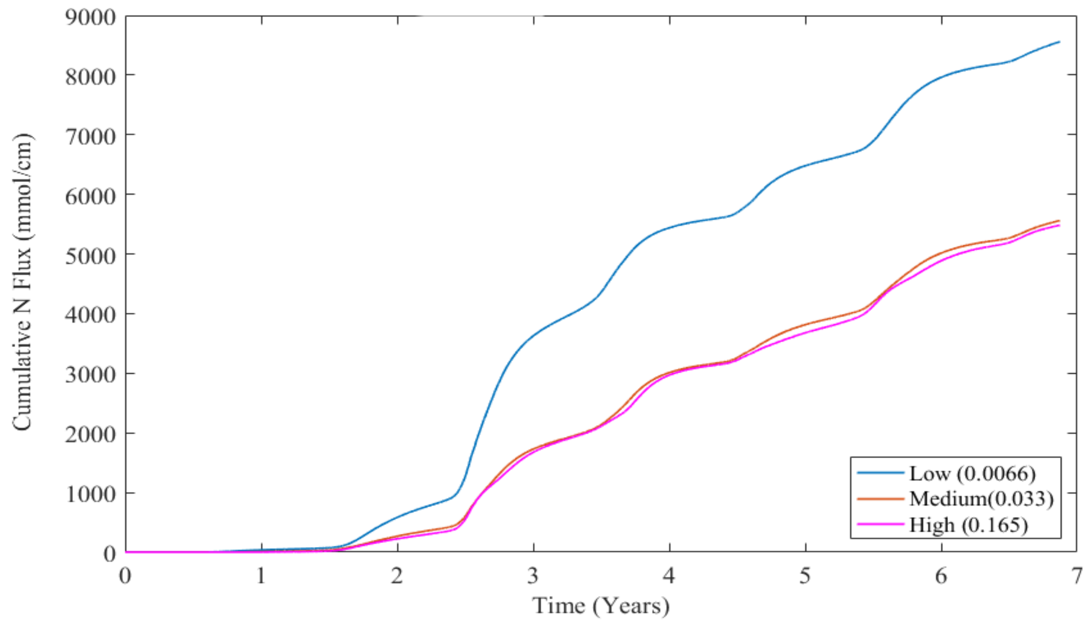


Figure 4-29: Cumulative nitrate flux under different solute transfer coefficient at low nitrate application plot

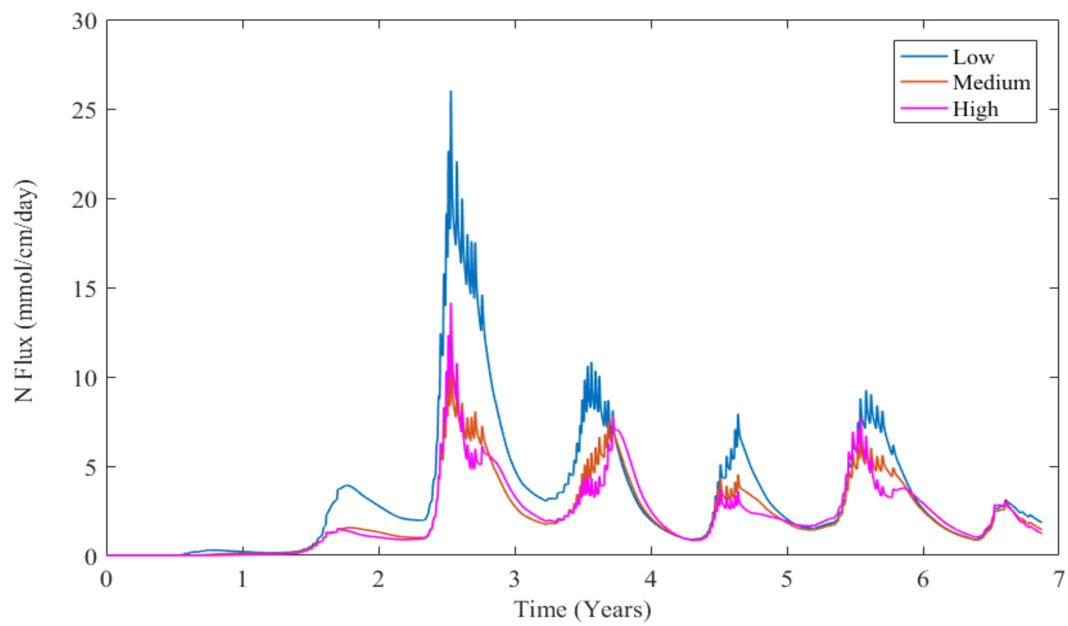


Figure 4-30: Nitrate flux under different water transfer coefficient at low nitrate application plot

Table 4-9: Sensitivity analysis of nitrate flux under different solute transfer coefficient values.

Parameter Γ_s value	Cumulative nitrate flux (mmol/cm)	Nitrate flux (mmol/cm/day)
High	4700	14.7
Medium	4800	12
Low	8700	27

Sensitivity analysis was also performed using the observed residual water content by varying its value by 80 to 85 % value of the observed quantity. The figure 4.31 shows that cumulative nitrate flux decreases with decreasing the value of residual water content. Figure 4.32 shows the effect of this parameter on nitrate flux simulated at lower boundary of the study domain.

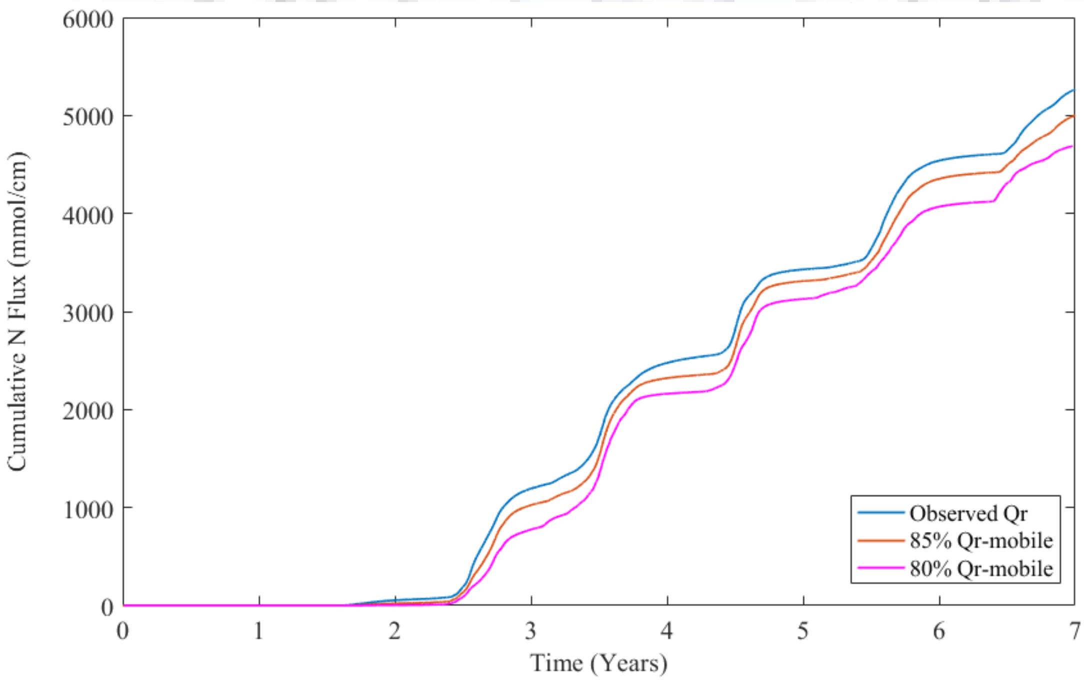


Figure 4-31: Cumulative nitrate flux under different residual water content value at low nitrate application plot in non-equilibrium modelling approach

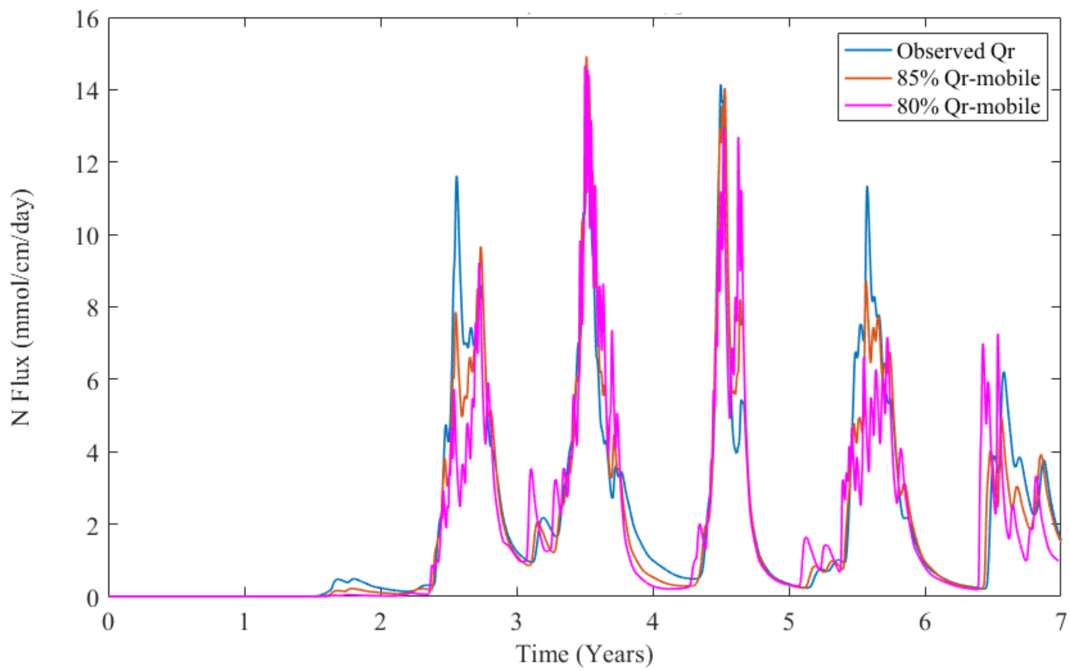


Figure 4-32: Nitrate flux under different residual water content value at low nitrate application plot in non-equilibrium modelling approach

Similarly, figures 4.33- 4.34 represent the cumulative nitrate flux and nitrate flux under different value of residual water content at the high nitrate application plot in non- equilibrium modeling approach of the simulation domain.

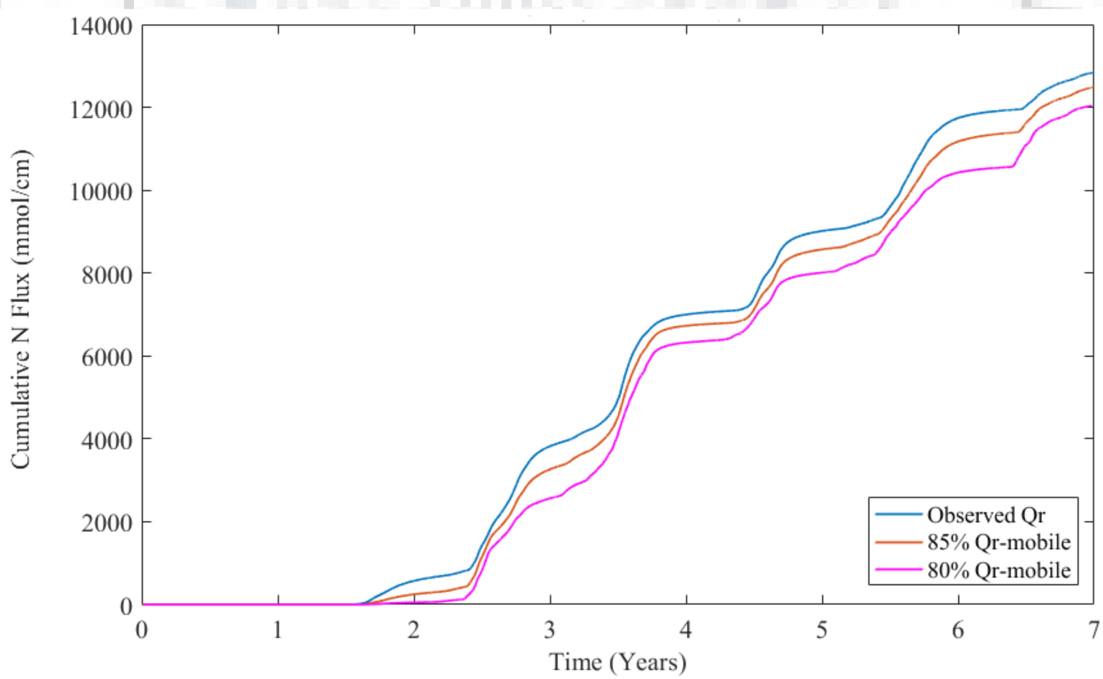


Figure 4-33: Cumulative nitrate flux under different residual water content value at high nitrate application plot in non-equilibrium modelling approach

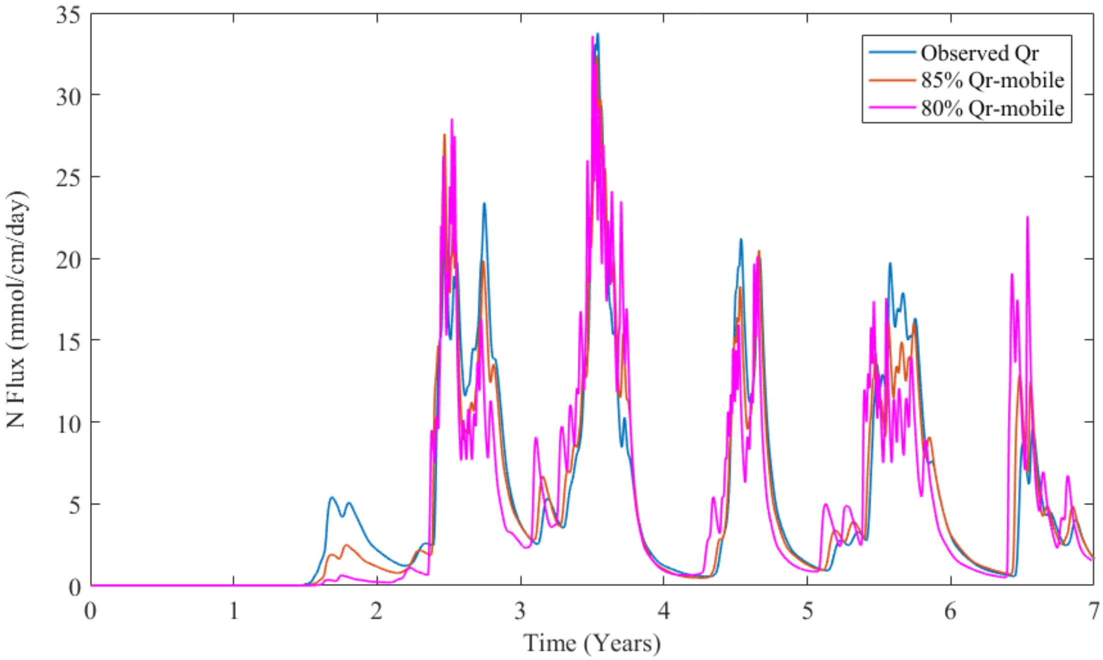


Figure 4-34: Nitrate flux under different residual water content value at low nitrate application plot in non-equilibrium modelling approach

To explore more about the effect of residual water content on soil water flow and nitrate transport in vadose zone simulation runs were also performed using equilibrium approach. The cumulative nitrate flux at the bottom boundary of the study domain is presented for both low and high plots in figures 4.35- 4.36, respectively. The cumulative nitrate flux was observed low in case of all mobile domains having 80 and 85 % water content value. This indicates that in equilibrium modelling approach, more nitrate mass retain in the domain and less solute flux leach out to the lower water table boundary.

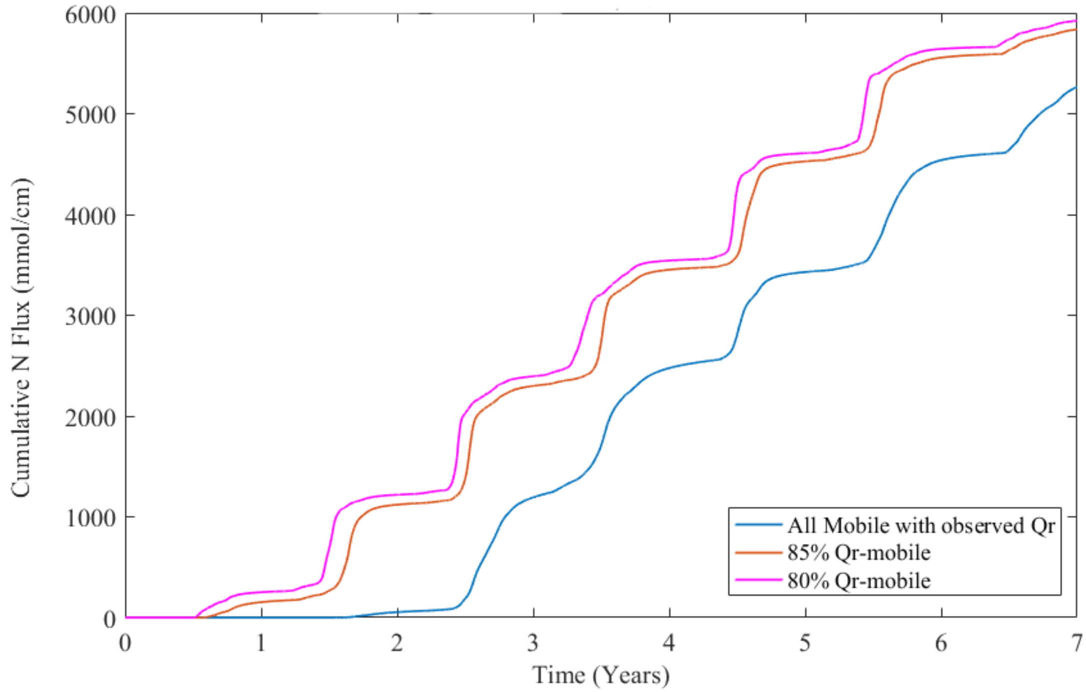


Figure 4-35: Cumulative nitrate flux under different residual water content value at high nitrate application plot in equilibrium modelling approach.

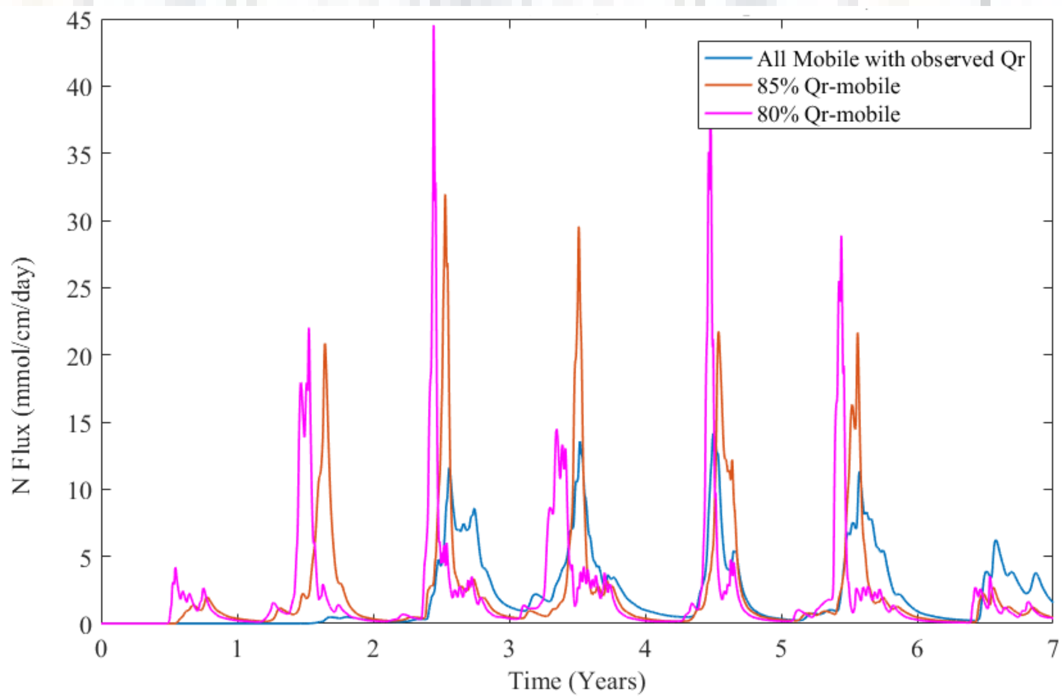


Figure 4-36: Cumulative nitrate flux under different residual water content value at high nitrate application plot in equilibrium modelling approach.

Results show that there are significant differences in the leaching pattern of nitrate to groundwater using the two different modeling approaches. It is found that leaching of nitrate is very less in case of equilibrium approach which is in accordance with the results found by Gardenas et al. (2006), who suggested that equilibrium approach fails to predict the preferential flow. Thus dual-porosity approaches more suitable for modeling non-equilibrium movement of water and nitrate transport through heterogeneous vadose zone. Since equilibrium approach assumes that water and solute fronts move uniformly along the whole soil domain, it takes more time for the moisture and solute fronts to reach the bottom of the soil profile. Moreover, since solutes are moving slowly in the soil domain, it can be said that solutes get longer time to be acted upon by micro-organisms and/or taken up by plants leading to their faster attenuation which further reduces out flux of solute from the soil domain. Whereas in dual-porosity approach, water and solutes move preferentially through the mobile zone which has high conductivity for water and solutes resulting in hastened flow and transport of solutes to deeper parts of the domain in considerably lesser time. Leaching patterns of nitrate from standard and high plots in both the approaches are in accordance with Onsoy et al. (2005) who suggested that nitrate leaching increases with increased application of nitrate at surface. Furthermore, they suggested that nitrate leaching can be attributed to preferential flow path taken by the water and nitrate fronts thus leading to hastened removal of nitrate from the soil which is well supported by dual-porosity approach used in this study.

4.6. Field scale studies;

The main objective of the field scale study was to predict the impact of climate change on corn yield and nitrate leaching to the underlying water resources. Past climate data (1991-1996) and forecasted future climatic variables of the period from 2055 to 2060 were used for the prediction of corn yield and nitrate leaching to the groundwater. For the prediction of corn yield under variable climatic condition, Hybrid Maize simulator was used during the study period. To estimate the fertilizer application for the particular yield, Maize N simulator was used. Finally for the estimation of nitrate leaching to the groundwater, Hydrus1D simulator was used considering the prevailing field conditions. The field study area was part of the Nebraska MSEA site, which is located within the Central Platte Natural Resources District (CPNRD) of the Platte river valley. Shallow and rapidly recharged High Plains alluvial aquifer water having average nitrate concentration between 30 to 32 mg/L is mainly used for irrigation in this region. The soil parameters of subsurface lithology of the study area are listed in table 4.10. The depth of water table varied between 8.99 and 9.48 m in the study area. Well logs of the area shows that silt and silt loam type of soils are present from land surface to a depth of 3 m. Sand and gravel formed the majority of the contiguous layers in the deeper portion of the site. The solute parameter and field data used for this simulation are listed in tables 4.11- 4.12 respectively. The climate of the study area was continental and temperate, with annual mean temperature and precipitation of 10°C and 623 mm, respectively. For this study the past climate data taken by HPRCC and NASA are used and the future climate data created by Weather Research and Forecasting (WRF) model at a resolution of 24×24 km are utilised. The WRF represent regional climate change model which downscales the climate change predictions from the Community Climate System Model (CCSM4). The CCSM4 is a global climate change model that simulates the Representative Concentration Pathways (RCP) 8.5 scenario which corresponds the worst climate case with a high greenhouse gas emission pathway. In this work the downscaled forecasted climatic data are used.

Table 4-10: Soil parameter used in modeling

Soil type	Organic matter (%)	Bulk Density (kg m^{-3})	van Genuchten-Mualem Parameter					
			θr	θs	α [m^{-1}]	n	Ks[md^{-1}]	l
Loam1	1300	1.8	0.049	0.402	0.7	1.58	0.25	0.5
Loam2	1300	1.4	0.051	0.396	0.96	1.51	0.16	0.5
Sandy loam	1650	0.3	0.034	0.390	3.57	1.43	0.56	0.5
Loam3	1300	1.2	0.058	0.398	1.29	1.46	0.12	0.5
Longitudinal dispersivity, D_L [m]			1.16	Transverse dispersivity, D_T [m]				0.2

Table 4-11: Solute transport parameter used in simulation;

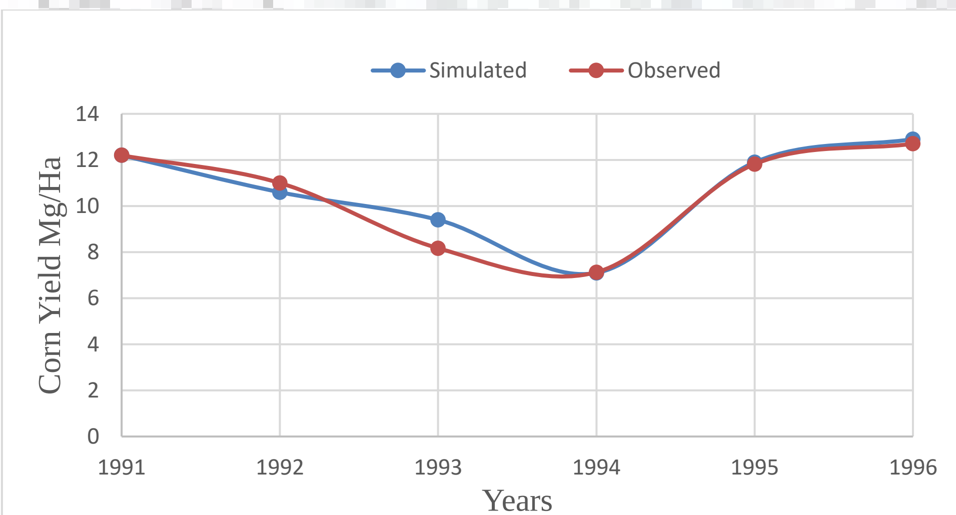
Root Dist. Parameters [m]		Solute Transport (Nitrate-N)	
Max. root d	1.8	Urea to ammonium 1st order rate, μ [d^{-1}]	0.38
Max. intensity d	1.4	Ammonium to nitrate 1st order rate, μ [d^{-1}]	0.20
		Ammonium adsorption coeff., Kd [m^3 kg^{-1}]	3.5×10^{-3}

Table 4-12: Field scale study data used in the simulation (Spalding et al 2001)

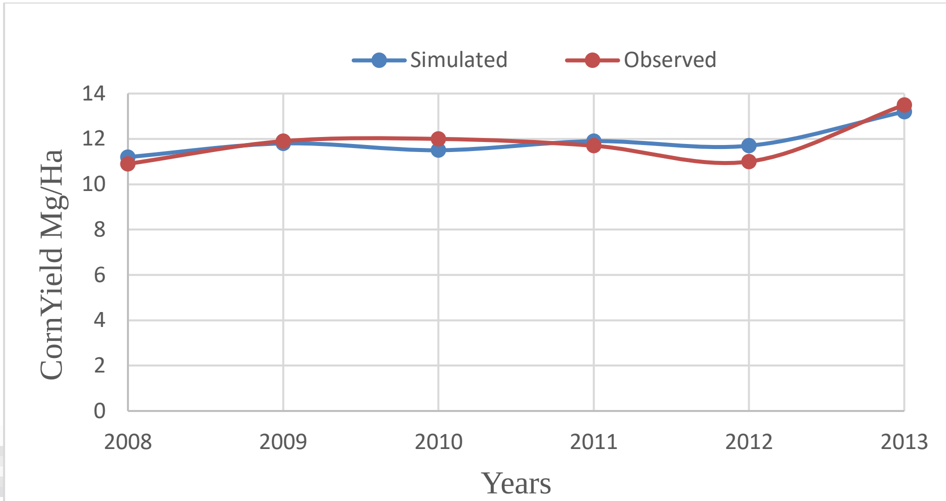
Nitrogen Application[kg ha^{-1}] and irrigation field data					
Year	Residual	Irrigation	Starter+Sidedress /Fertigation	Preplant	Irrigation water
1991	85	92	24	-	335
1992	70	54	46	-	208
1993	21	24	90	68	79
1994	68	31	62	98	107
1995	83	95	188	-	307
1996	74	45	80	112	152

4.6.1. Estimation of corn yield:

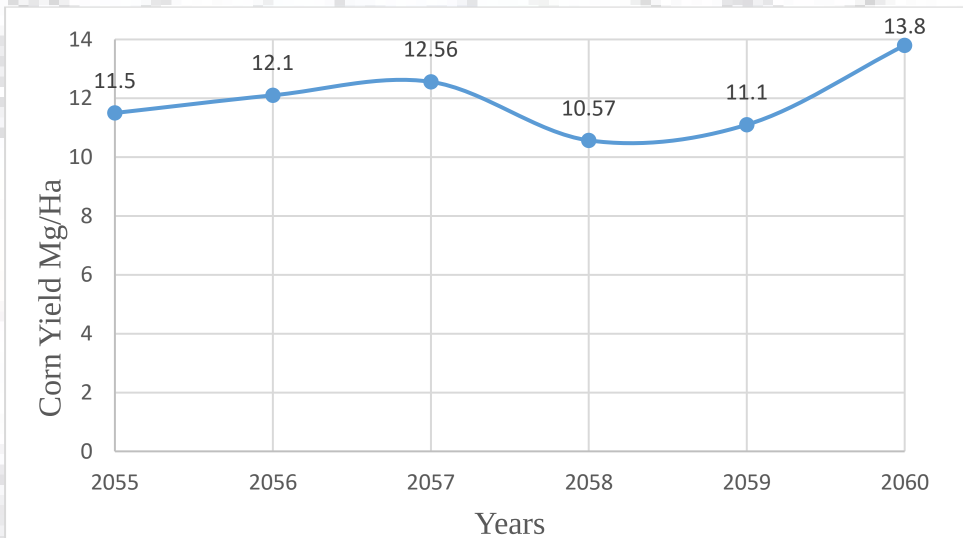
The simulated corn yield is compared with the observed data as shown in figure 4.37. For this, climatic variables, field data and applied fertilizer along with irrigation data are used for the past and future climate conditions. The figure 4.37(a, b, c) shows the simulated and observed corn yield for the past, intermediate and future climate conditions. The figure shows that the simulated value of corn yield are matching closely with the observed (Spalding et al., 2001) values for the period of 1991-96. The trend line of observed and simulated corn yield under intermediate time (2008-13) is also quite similar (figure4.37 b). The figure 4.37c shows the trend line of corn yield under future climate condition and have the maximum value of 13.8 Mg/ha for the year of 2060.



(a)



(b)



(c)

Figure 4-37: Comparison of observed and simulated corn yield under different climate scenarios.

4.6.2. Water flux in the study domain;

Figure 4.38 demonstrates the soil moisture dynamics of the vadose zone for both future (2055-60) and past climate (1991-96) conditions. Water flow into or out of the study domain depends on water flux at the surface and at the bottom boundary. However changes in volume of water in the entire vadose zone is mainly controlled by surface water flux. During the course of simulation, the total volume of water in the domain decreases under both future and past climate conditions (Figure 4.39). However the total volume of water reduces faster in the future condition, which can be attributed to the higher transpiration rates in future. The predicted future actual transpiration rate is almost 2.5 times than the past conditions.

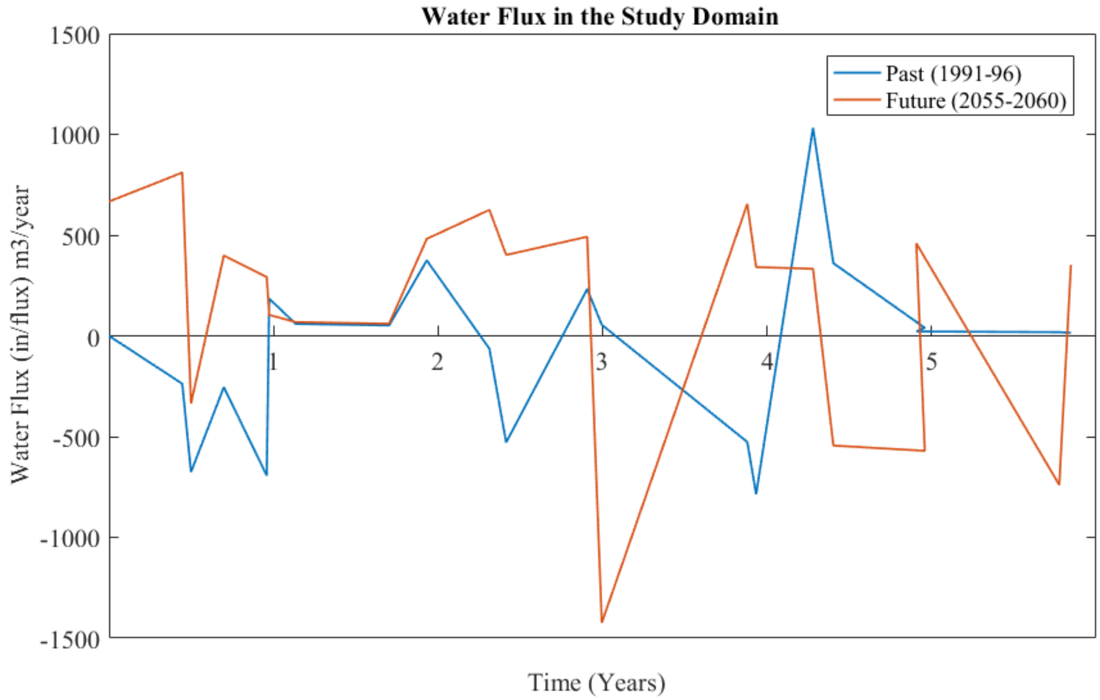


Figure 4-38: Water flow into or out of the entire flow domain where negative values are for increase in moisture content.

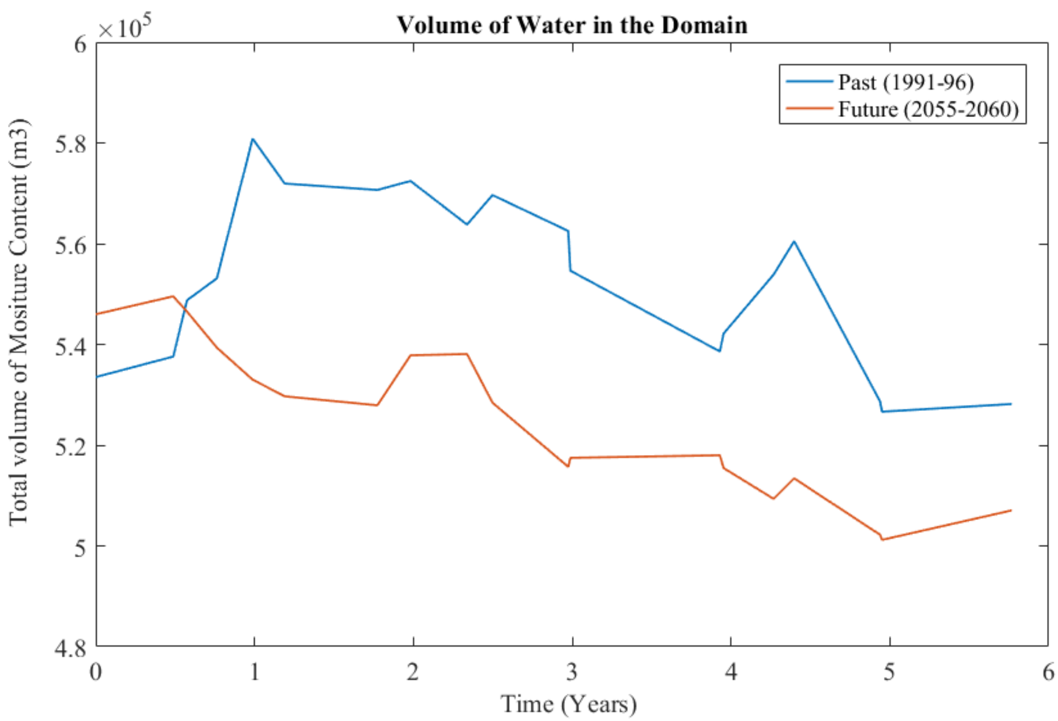


Figure 4-39: Volume of water in the entire flow domain

4.6.3. Nitrate Flux:

Nitrate leaching is influenced by multiple factors, including surface fertilizer loading, precipitation, soil type, water holding capacity, cropping, and fertilizer application. As shown in the figure 4.40, the total mass of nitrate in the entire flow domain starts with a sharp increase in the first year of the simulation for both past and future climatic conditions. Then the amount of nitrate continuously increases in the past climate condition. In contrast, the mass of nitrate gradually reduces under the future climate condition. The reduced nitrate mass in future can be explained based on the climate induced impacts on the application of nitrate fertilizer, nitrification of Urea, and bottom groundwater flux.

During 1991 to 1996, irrigation water was applied at the surface with respect to precipitation rate, except for the year 1995 in which field was irrigated with almost three times greater amount of water as compared to the other years in order to increase the grain yield. Similarly, the yearly amount of irrigation water added at the surface under future climate scenario is specified relative to the precipitation amount during the growing season of each year (table 4.13) considering the same rate and timing taken as in the past. The amount of nitrate applied via irrigation is higher in the past than in the future climate condition. This effect could partially explain the smaller mass of nitrate in the domain under future climate condition.

Nitrogen mineralization and nitrification depend on temperature and precipitation. Under future climate condition, slightly increased temperature will enhance evapotranspiration rate and decrease soil water content in the root zone, which may reduce the mineralization reaction and lead to smaller amount of urea converted to nitrate. This effect could also partially explain the smaller mass of nitrate in the domain under future climate condition.

The trend of surface nitrate flux is similar between the past and future climate conditions shown in figure 4.42. The similar trend of surface flux is due to similar irrigation scheduling of irrigation water that also determines the trend of nitrate uptake by plants. Root nitrate uptake is higher during 2055 than in 1991(figure 4.41) because a higher solute flux (figure 4.42) is added to the system during the first year along with the increased water infiltrated from the soil surface due to high rainfall events during the year 2057. The trend of bottom nitrate flux, however, is very different between the past and future climate conditions (figure 4.43). Under the past climate condition (1991-1996), groundwater level fluctuated more often than during the future predicted conditions, and therefore, an excessive mass of nitrate was able to enter the vadose zone of the MSEA site.

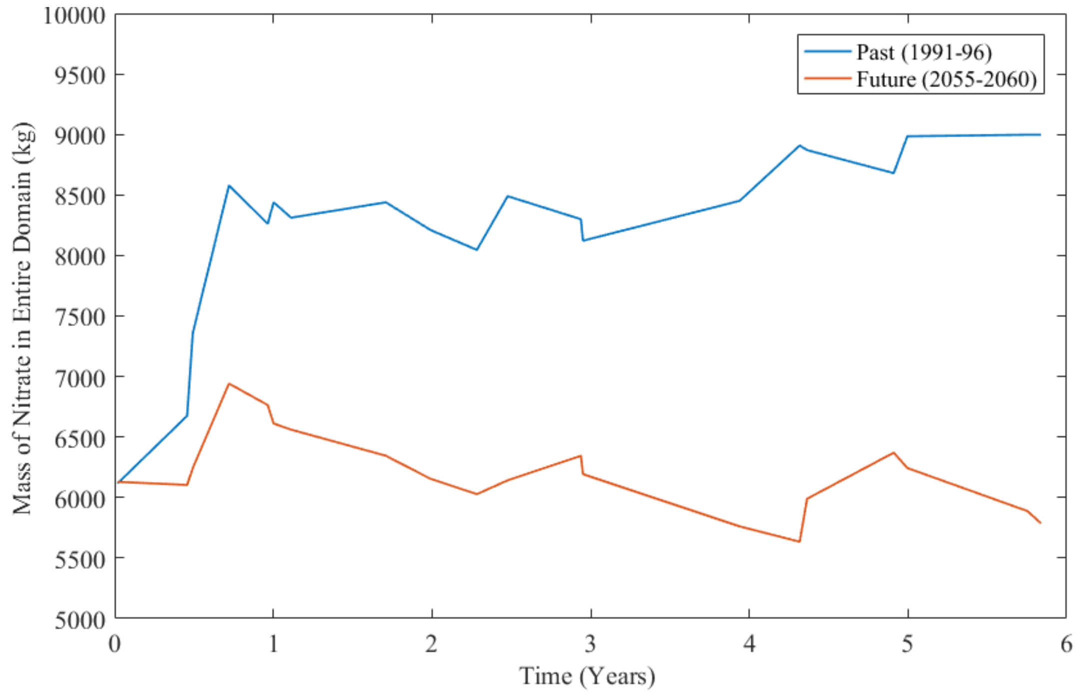


Figure 4-40: Total mass of nitrate in study domain during past and future climate condition

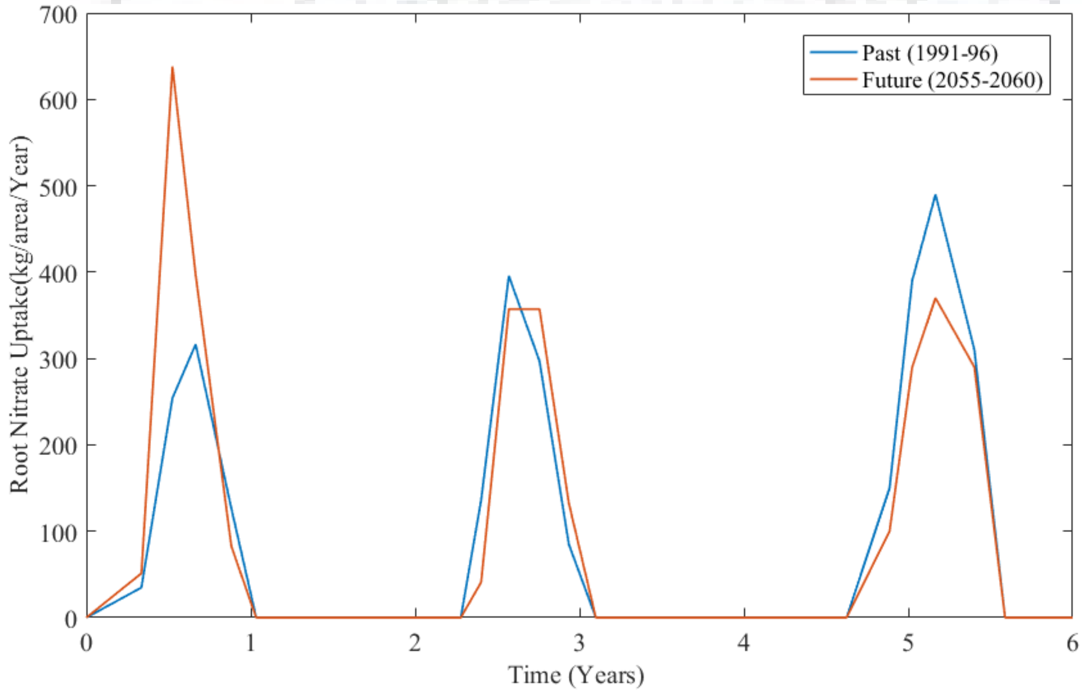


Figure 4-41: Root uptake during past and future climate conditions.

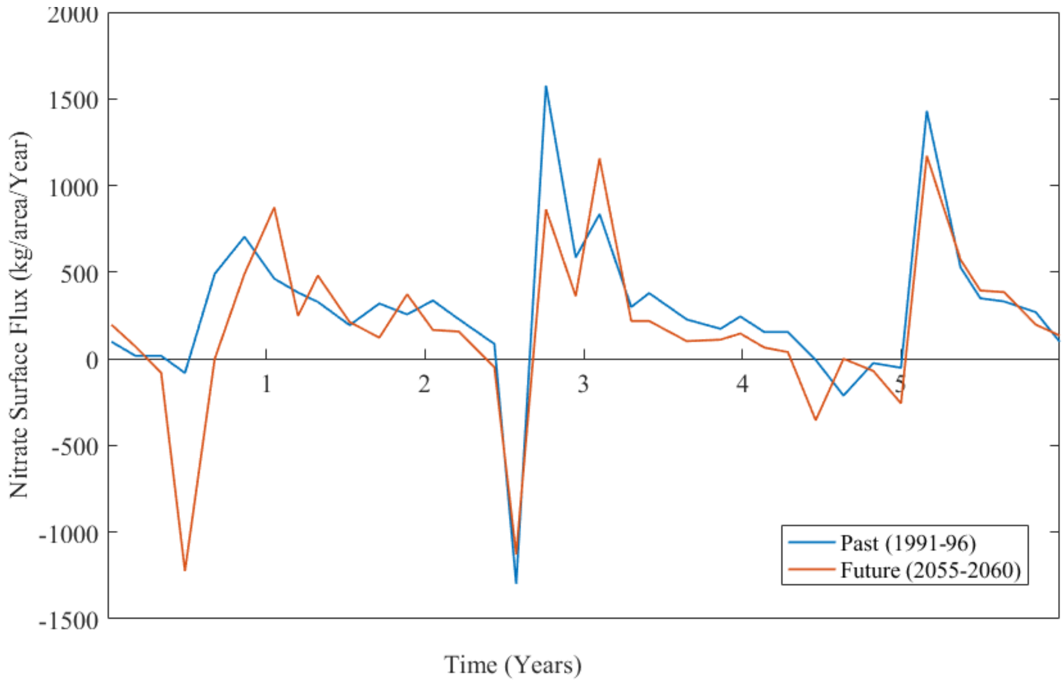


Figure 4-42: Nitrate surface flux comparison during past and future climate.

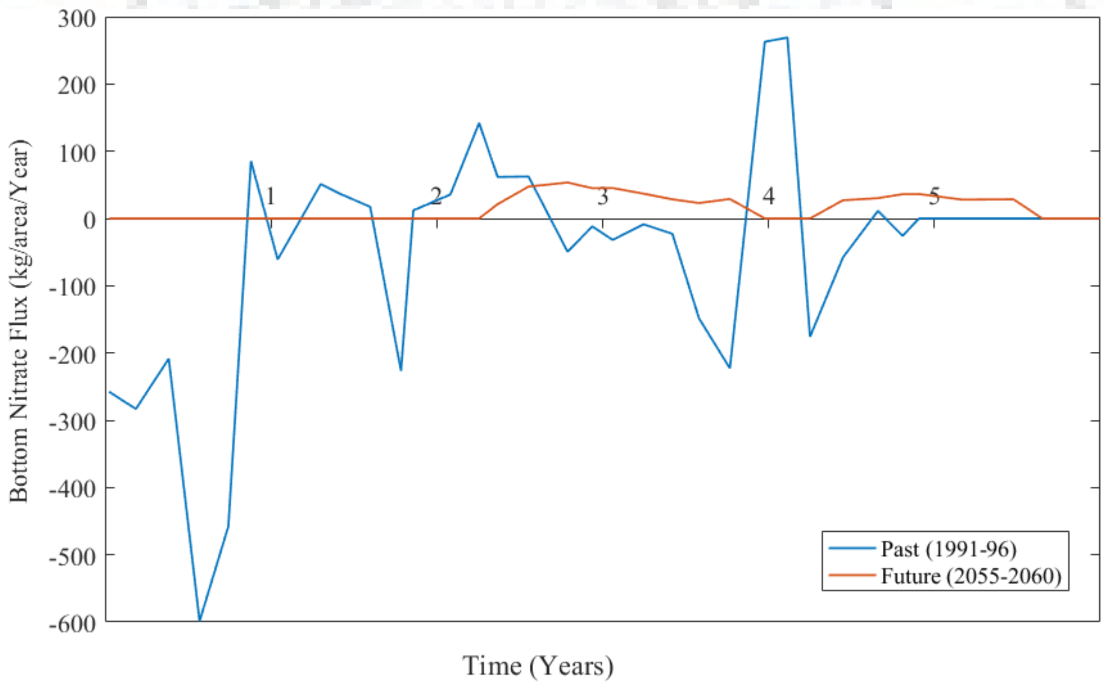


Figure 4-43: Bottom nitrate flux comparison during past and future climate.

Figure 4.44 shows the nitrate concentration at the bottom layers (9.5m depth) of the filed site during past and future climate conditions. Spatial nitrate concentration depends on soil heterogeneity, surface applied fertilizer as well as on the residual nitrate concentration in the field. At the bottom of the domain, nitrate concentration mainly controlled by groundwater elevation fluctuations. Since, groundwater elevation is decreasing over time under future climate data (Figure 4.39), bottom nitrate flux (Figure 4.43) changes are showing negative values (negative flux means nitrate is removed from the system) with minor oscillations as compared with the past. However nitrate concentration is varying significantly in shallow groundwater. At the bottom layer, although nitrate concentration is decreasing under future climate data, some small parts of the domain is showing slightly increasing values as compared with the past which seems due to impact of soil heterogeneity.

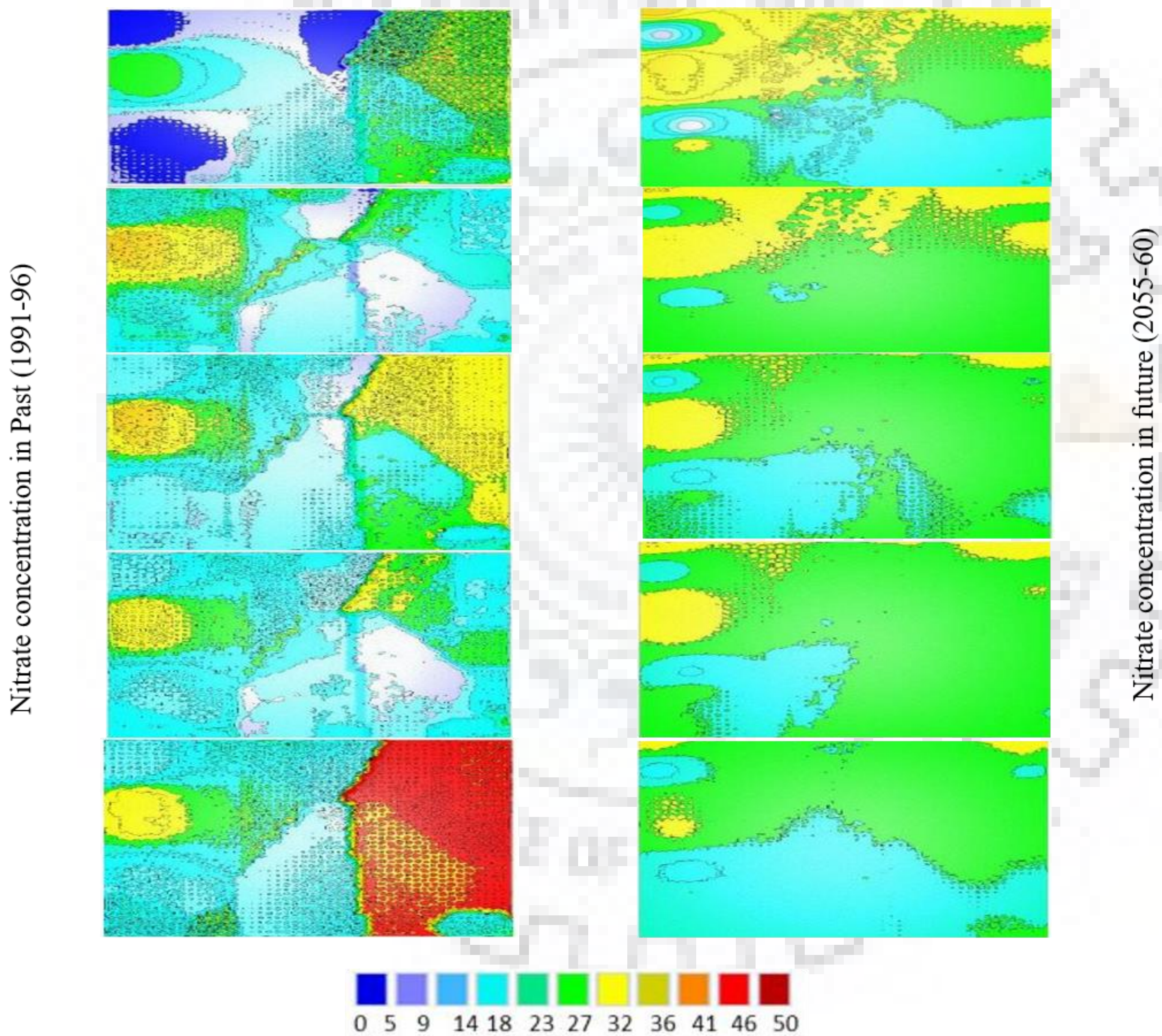


Figure 4-44: Nitrate concentration profile at the bottom of soil domain during past and future climatic scenarios.

At all these different cases of soil heterogeneity or presence of micro and macro pores along with the variability in moisture content indicates that output obtained from non-equilibrium model shows a better agreement with the observed value at laboratory and field scales. The above results and discussion shows the finding of this study are in line for different scale taken as column, lysimeter, tank, plot and field scale levels.

Chapter 5

SUMMARY AND CONCLUSIONS

The main focus of this study is to investigate the soil moisture flow and nitrate movement through the heterogeneous vadose zone to underlying groundwater resources using a series of laboratory, plot and field scale experiments. A comprehensive literature review was conducted first to get insight of the processes involved in soil moisture flow and nitrate movement along with different modelling approaches under varying environmental conditions, which can help in managing groundwater resources effectively. The main mechanisms of controlling simultaneous movement of soil water and solute transport through the vadose zone along with water and nitrate uptake by plant roots biomass are identified first. The governing equations representing preferential flow are formulated by including the water and nitrate transfer between mobile and immobile zones of the vadose zone for different types of heterogeneity.

Preliminary experiments are conducted first for deducing basic parameters of soil moisture flow and nitrate transport through variably saturated porous media under controlled conditions. To investigate the vertical flow of nitrate through variably saturated zone a large scale column setup made of plexi-glass was fabricated. The column was packed homogeneously with the porous material having a particle size of 0.5 -1.0 mm. The column was filled with the porous media up to a height of 90 cm from the bottom. Water table was maintained at a height of 30 cm from the lower boundary leaving the remaining 60 cm soil mass as an unsaturated zone. A head space of 30 cm was allowed at the top of the soil surface. There were 4 sampling ports at a distance of 40, 55, 70 and 90 cm from the source taken at the top of the column. Soil hydraulic parameters like soil-water velocity, hydraulic conductivity, dispersivity etc. were estimated using tracer experiments in the designed column setup. The results shows a lag time of advective flux required in physical movement of the solute. No significant difference was observed between the equilibrium/plateau concentrations of nitrate obtained from different observation ports. This shows that the nitrate adsorption by the selected porous media can be neglected. A diffusive front of nitrate at the top sampling port is having sharper front as compared to the lowermost port indicating a role of dispersive and diffusive transport of nitrate observed in the experiments setup. As the groundwater velocity was kept quite high during the experiments, dispersive flux played dominant role as compared to the diffusive flux. . Values of the dispersivity derived from column was ranging 4.56 to 5.95 cm for partially saturated zone and ranging from 7.31.to 8.56 cm for fully saturated zone.

Thereafter, impact of soil moisture heterogeneity on nitrate transport was investigated using a lysimeter setup consisted of glass sheet having dimension of 28 cm long x28 cm breadth x30 cm high. The lysimeter was filled homogeneously with the organic content free sand in over-saturation condition and was then allowed to drain for overnight to obtain the field capacity, which was about 80% of the porosity of the considered porous media before starting the experiments. Two sets of experiments were performed at100% saturation and 80% saturation. The Lysimeter setup results show that the nitrate movement in the soil profile is accelerated with increase in the water content of the profile. The nitrate equilibrium concentration was obtained at 24hrs for saturated soil profile while it took 32 hrs for the 80% saturation level of the same profile. Thus level of soil moisture content plays and important role in a homogeneous vadose zone for ground water contamination by conservative pollutants like nitrate.

In the third part of the study a series of two dimensional experiments were carried out to investigate the soil moisture flow and nitrate transport considering the transient flow conditions. A two dimensional sand tank was fabricated of 0.7 mm thick glass sheet and stainless steel embedded with three horizontal layers of sampling ports having vertical distance of 30 cm. To see the role of drainage flux, recharge flux, the three sets of the simulation experiment were conducted considering- a) drainage flux from bottom of sand tank, b) applied recharge flux at top surface under transient condition. Subsequently, the role of subsurface flow on nitrate transport was evaluated in same setup under transient flow conditions. The results showed that water table position decreased significantly when applying drainage flux and increased when applying the recharge flux at the top boundary. Similarly, a constant water flux was applied on the top surface to investigate the impact of infiltration on the soil moisture flow regime in the unsaturated zone. Further, a constant flux of nitrate, the elected conservative solute, was allowed to flow in the horizontal direction in the study domain to evaluate the role of the subsurface flow on nitrate movement. The BTCs and concentration isolines showed that advective flux dominated the nitrate transport and was affected highly by the recharge flux in the vertical direction. Therefore, the recharge flux in an area with nitrate pollution caused more nitrate load at the groundwater table as compared with the drainage flux.

Subsequently, a series of 3 D laboratory and numerical experiments were performed considering the mobile-immobile zones in a subsurface domain. A three dimensional sand tank setup was used for this purpose to mimic the real field conditions and to neglect/minimize the chances of bypass of solute and solvent through tank and soil boundary interphase. The experimental setup was fabricated of 7 mm thick glass sheet with dimensions of 60 cm long by 30 cm wide by 60 cm height. The tank is embedded with three layers of horizontal and vertical sampling ports. The sampling ports are made of stainless steel tubes having diameter of 0.3 mm and depth of 05cm, 10cm, 15cm, 20cm and 25cm. The nitrate concentration was observed at different observation ports and compared with the simulated data. Different varying degrees of mobile-immobile zones were considered and it was found that 15 % of mobile zone compared well with the observed results. The observed breakthrough curve shows the higher cumulative nitrate flux at bottom as compared to the single porosity model. However, the simulated BTC considering the 15 % mobile zone was matching closely with the observed quantity. The nitrate concentration isolines of the experimental domain clearly indicate the movement of nitrate in vertical direction. In which the maximum concentration of 254 ppm of nitrate was found nearby the bottom sampling port. At the equilibrium time, the bottom nitrate concentration was higher than middle and there was no concentration found at top sampling port due to the vertical movement of nitrate flux. The comparative analysis of experimentally observed and simulated data shows high level of correlation and matched well to each other. The mass balance analysis shows that the computed mass in the study domain in single porosity model was quite less than the observed amount. However, the sand tank experimental results were quite close to the dual porosity model. The results of this study clearly indicate that the conventional single porosity based modelling cannot be used for accurate prediction of the nitrate movement and its subsequent loading to the underlying groundwater resources.

At plot scale simulations, equilibrium and non-equilibrium approaches were used for quantifying nitrate load to 15.8 m deep groundwater resources of San Joaquin valley. The entire soil domain is divided into 8 lithofacies depending on the type and characteristics of the soil at varying depths. Uniform and preferential flow cases were taken for simulating the movement of water and solute through deep and heterogeneous vadose zone along with plant water and nitrate uptake sink terms. The equilibrium and mobile-immobile approaches were considered for low and high nitrate application cases for prediction of nitrate flux at the lower boundary of the vadose zone. Two cases of heterogeneity in the soil domain were considered in form of layered and inter layer heterogeneity. It was found that non-equilibrium approach uses higher CPU time as compared to equilibrium approach. In the equilibrium approach, it is assumed that whole soil domain is having uniform hydraulic properties and no preferential flow is taking place. For numerical runs, a mesh size of 1 cm was taken for discretizing the entire soil domain. A simulation period of 730 days through 1990-1991 was considered.

Results show that there are significant differences in the leaching pattern of nitrate to the groundwater using the two different modeling approaches. It is found that leaching of nitrate is quite less in case of equilibrium approach which is in accordance with the results found by Gardenas et al. (2006), who suggested that equilibrium approach fails to predict the preferential flow. The authors concluded that dual-porosity approach is more suitable for modeling non-equilibrium movement of water and solute in vadose zones. Since equilibrium approach assumes that water and solute fronts move uniformly along the whole soil domain, it takes more time for the moisture and solute fronts to reach the bottom of the soil profile. Moreover, since solutes are moving slowly in the soil domain, it can be said that solutes get longer time to be acted upon by micro-organisms leading to their degradation which further reduces out flux of solute from the soil domain. Whereas in dual-porosity approach, water and solutes move preferentially through the mobile zone of the solute which has high conductivity for water and solutes resulting in hastened flow and transport of solutes to deeper parts of the domain in considerably lesser time. Leaching patterns of nitrate from low and high plots in both the approaches are in accordance with Onsoy et al. (2005) who suggested that nitrate leaching can be attributed to preferential flow leading to hastened removal of nitrate from the soil. Heterogeneity of porous media influence the horizontal and vertical movement of soil moisture flow and nitrate transport in the vadose zone. Soil having high saturated hydraulic conductivity and low residual water content have lower water holding capacity, which enhance moisture infiltration and nitrate leaching to the vadose zone. Though there are discrepancies in the prediction of nitrate leaching and storage in the vadose zone and model over-predicted the storage of nitrate in the deeper vadose zone which is contradicting to the observed data and can be attributed to the no-flow assumption in the matrix which under natural conditions conducts water flow and solute transport. Moreover a much finer spatial discretization is preferable to decrease the mass balance errors and better spatial resolution of the data. Further, denitrification losses in the deeper vadose zone, which is although very less, should be considered for better assessment of nitrate mass balance in the vadose zone.

Finally, the field scale numerical runs are conducted for the Nebraska MSEA site located within the Central Platte Natural Resources District (CPNRD) of the Platte River Valley, for quantifying corn yield and nitrate leaching to the underlying groundwater resources. A lithologic framework was developed first for the MSEA using Rock works considering the observed spatially varied soil properties of the field site. Future climatic scenarios were considered for predicting the nitrate leaching and the associated crop yield. It was observed that heterogeneous vadose zone influenced the horizontal and vertical distribution of soil water content and water flux as well as nitrate leaching. A coupled hydrological model and future climate data from WRF climate model was used to assess the impacts of climate change on nitrate leaching at corn field in MSEA site, Nebraska. The primary focus was to evaluate the impact of climate change on nitrate concentration distribution in variably saturated media. Yearly average precipitation was higher under future climate condition compared with past climate (1993-1996) while the percentage of precipitation occurred during the growing season decreased from 84% to 77% of total in future. The predicted potential evapotranspiration for the future climate data is little lower than the existing scenario, but, actual evapotranspiration is quite more than the past climatic conditions. Higher evapotranspiration rate will increase root water and nitrate uptake resulting in drier soil condition which may slow down the nitrification process of urea to nitrate. Thus a reduced mass of nitrate in the vadose zone is expected in the root zone system of the MSEA site under future climatic condition. In the saturated part of the subsurface, nitrate concentration majorly depends on groundwater elevation fluctuations. Groundwater elevation is projected to decline under future climate data, and therefore, nitrate load to groundwater resources is expected to decrease considering that land use and fertigation rates remain unchanged. However, a rising global demand for food, agricultural activities are expected to be intensified and which may change the management practices impacting nitrate leaching rate.

Thus, heterogeneous properties of vadose zone are found to have major impact on nitrate distribution in root zone and its subsequent loading to saturated zone. Impacts of climate change and population growth on agricultural activities affecting nitrate leaching at sites can be performed through application of this developed framework. Though the adopted modeling approach is not able to completely match with the field observed data, a gap between the observed and the simulated data by convention modelling approaches has been reduced significantly. Therefore, the methodological framework can be used for better planning of fertigation scheduling to minimize groundwater contamination.

Scope for Future Work

Presence of other pollutants can be considered in soil water system to investigate their impact on fate and transport of nitrate in the vadose zone. Further, sensitivity of environmental factors with each another can provide more accurate guidelines for customizing root zone conditions optimally Further, denitrification losses in the deeper vadose zone, which is although very less, can be considered for better assessment of nitrate mass balance in the vadose zone.

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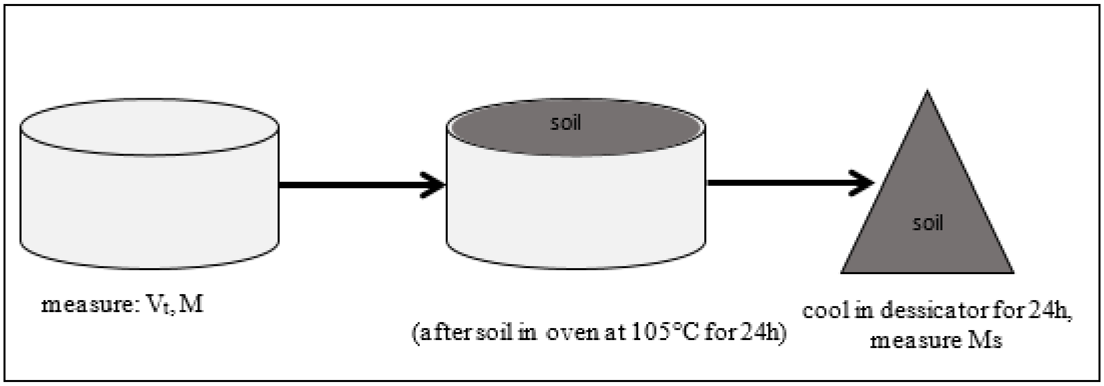
Appendix

Appendix 1: Estimation of porous media parameters

Mass of soil was oven dried at 105 °C for 24 hours and then cooled in the desiccator. It was then weighed till a constant weight was obtained



Weight of dry soil M= weight of soil with Petri dish M_p – weight of empty Petri dish P

Petri dish volume =V_t

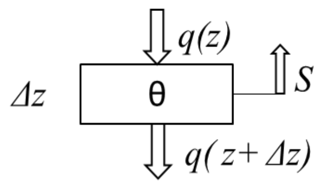
Bulk density $\boldsymbol{\rho}_s$=M/V_t

Porosity, n= 1-$\boldsymbol{\rho}_b/\boldsymbol{\rho}_s$

Appendix 2: Richards' equation derivation

Consider the moisture balance of a porous media mass shown in the Figure. Inflow into the porous mass is denoted by q(z) [LT^{-1}] and outflow from the layer is q(z+Δ z). S is the sink term representing the amount of water taken up by plants (volume of water per unit volume of soil per unit time). The change in moisture content θ over time, t can then be written as

$$J_{dis} = -\alpha_L v \frac{\partial C}{\partial z} = -\alpha \frac{q}{\theta} \frac{\partial C}{\partial z}$$



By taking into account the definition of partial derivative it is possible to write this Equation as:

$$\frac{\partial \theta}{\partial t} = -\frac{\partial q}{\partial z} - S \qquad \text{(X1)}$$

Describing moisture flow in porous media system by using Darcy's law. For one dimensional vertical flow, the volumetric flux q can be written as:

$$q = -K(h)\frac{\partial H}{\partial z} \quad \text{-- >>>} \quad q = -K(h)\frac{\partial (h+z)}{\partial z} \qquad \text{(X2)}$$

where K(h)is the hydraulic conductivity of the porous media (function of soil water pressure head) [LT^1], H is the hydraulic head (h+ z) sum of pressure head and gravitational head [L]

By combining the equation (X1) and equation (X2) obtained the Richard’s equation

$$c(h)\frac{\partial h}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\frac{\partial h}{\partial z} + K(h)\right] - S \qquad \text{(X3)}$$

Equation (X3) is a second order, partial differential nonlinear equation. This equation demonstrate the variably saturated flow of a single fluid neglecting that air phase role in the moisture flow through unsaturated zone. Equation (X3) could be modified into the h and θ based form as follows.

$$c(h)\frac{\partial h}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\frac{\partial h}{\partial z} + K(h)\right] - S \qquad \text{(X4)}$$

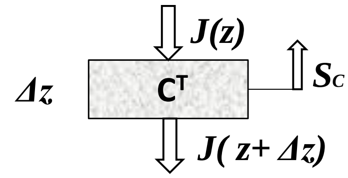
$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(\theta)\frac{\partial \theta}{\partial z} + K(\theta)\right] - S \qquad \text{(X5)}$$

Where $c(h)\ \partial\theta / \partial h$ is the specific moisture capacity of the soil [1/L] and $D(\theta) = K(\theta)/C(\theta)$ is the of the soil moisture diffusivity [L^2T^{-1}].

Appendix 3: Advection-dispersion equation derivation

Consider the pollutant balance of a soil layer of Δz thickness shown in the Figure. The pollutant influx into the layer is denoted by J(z) [$ML^{-2}S^{-1}$] and out flux from the layer is J(z+Δ z). Sc is the amount of nitrate uptake by plant roots [$ML^{-3}S^{-1}$]. Then, the change in total soil nitrate concentration C^T over time t can

$$\frac{\partial C^T}{\partial t} = \frac{J(z) - J(z + \Delta z)}{\Delta z} - S_C$$



The partial derivative of above equation as:

$$\frac{\partial C^T}{\partial t} = \frac{\partial J}{\Delta z} - S_C \quad \text{(Y1)}$$

Here, (C^T) total nitrate concentration in soil volume, It is the sum of nitrate in the soil solution and retained on the soil matrix can be written as

$$C^T = \theta C + \rho_S S_D \quad \text{(Y2)}$$

Here C is the nitrate contaminant concentration in the soil solution [ML^{-3}], θ is the volumetric soil moisture content [L^3L^{-3}], ρ_s is the bulk density of the soil [ML^{-3}] and S_D is the nitrate retain in the soil [MM^{-1}].

The total flux J in equation (Y1) includes the change in the nitrate concentration due to advection, dispersion and diffusion and is represented as:

$$J = J_{adv} + J_{dis} + J_{diff} \quad \text{(Y3)}$$

where J_{adv}, J_{dis}, J_{diff} are the advective, dispersive and diffusive fluxes respectively.

Advective flux: Advection causes the pollutant to move with the flow velocity and given by:

$$J_{adv} = v\theta C = qC \quad \text{(Y4)}$$

where v is the soil water velocity [LT^{-1}], q is the soil water flux and θ is the volumetric moisture content.

Diffusive flux: When contaminant move due to the concentration gradient it is called diffusion. Diffusion is mathematically described by Fick's law which states that the net rate of pollutant transport is proportional to the negative gradient of its concentration and can be modified for unsaturated porous medium as

$$J_{diff} = -\tau D_0 \theta \frac{\partial C}{\partial z} = -D_m \theta \frac{\partial C}{\partial z} \qquad \text{(Y5)}$$

where τ is the tortuosity factor (dimensionless) which accounts for the increased distance of transport due to tortuous path of the pollutant particle in porous media. D_0 and D_m are the free water diffusivity and molecular diffusion coefficients respectively [L^2T^{-1}].

Dispersive flux: This is because of spreading and mixing of the solute due to variation in velocities of the neighboring particles of fluid and can occur at many scales. The dispersion at a microscopic scale occurs due to the variation of velocity within the pores and due to the tortuous movement of the fluid around the soil particles. Macroscopic dispersion refers to the dispersion resulting from the inter fingering of materials of different permeability. Mechanical dispersion is mathematically described in the same way as molecular diffusion by using the Fick's law as:

$$\frac{\partial(\rho_S S_D)}{\partial t} + \frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z}\left[D\theta \frac{\partial C}{\partial z} - qC \right] - S_C \qquad \text{(Y6)}$$

where α_L is the longitudinal dispersivity of the porous media in the direction of flow [L] and v is the soil water velocity.

Now by adding all the above mentioned fluxes, the resultant flux

$$J_{adv} + J_{dis} + J_{diff} = qC - D\theta \frac{\partial C}{\partial z} \qquad \text{(Y7)}$$

Where $D = \tau D_0 + \alpha_L\, q/\theta = \tau D_0 \alpha_L v$

Here D is the hydrodynamic dispersion coefficient and it is soil water velocity dependent function [L^2T^{-1}]. The modified form of advection-dispersion equation is obtained by substituting the equation (Y2) and (Y3) into equation (Y1).

$$\frac{\partial(\rho_S S_D)}{\partial t} + \frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z}\left[D\theta \frac{\partial C}{\partial z} - qC \right] - S_C \qquad \text{(Y8)}$$

Brief Bio-data of the Author

Summary:

The author graduated from SVBP University Meerut, in India with Bachelor of Technology in Biotechnology in 2010. He completed an M.Tech. in Environmental Engineering from National Institute of Foundry and Forge Technology Ranchi, India in 2012. Subsequently, He joined his doctoral studies at Indian Institute of Technology, Roorkee pursuing research on “Soil Water flow and Nitrate Transport through Heterogeneous Vadose Zone”. He was selected for the Indo- US Water Advanced Research and Innovation (WARI) Fellowship by the Indo- US Science and Technology Forum, government of India to undertake a 6 months visiting research Intern at the University of Nebraska Lincoln, USA in 2017.

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- M.Tech., Environmental Engineering from National Institute of Foundry and Forge Technology Ranchi (CGPA 8.57); 2010-2012
- B.Tech., Biotechnology from Sardar Vallabh Bhai Patel University of Agriculture and Technology Meerut, Uttar Pradesh (CGPA 7.91); 2006-2010

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- Student Travel Grant by Japan geoscience Union to attend JpGU Meeting 2018 held in, Chiba, Japan.
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- CSIR Travel support 2017 American Geophysical Union to attend AGU Fall Meeting 2017 held in, New Orleans, Louisiana, USA.
- Received Young research fellowship 2017 to participate in 5th IYRW conference held in

Malaysia

- University of Nebraska, USA Travel fellowship 2017 to participate in Sixth International Conference on Climate Change Adaptation, held in University of Toronto, Canada.
- Awarded Indo-US WARI Fellowship (2016) from IUSSTF, India to work as Visiting Research scholar at University of Nebraska Lincoln USA.
- Science and Engineering Research Board (SERB) ITS Award 2016 to attend AGU Fall Meeting 2016 held in, San Francisco, USA.
- Senior Research Fellowship from 2015-2017 and Junior Research Fellowship from 2013-2015 for completion of PhD at IIT Roorkee.

Publications during this Doctoral Research:

International/National Journals

1. **Jahangeer**, Pankaj Kumar Gupta, Brijesh Kumar Yadav (2017) "Transient water flow and Nitrate Movement Simulation in Partially Saturated Zone." *Journal of Irrigation and Drainage Engineering*. https://doi.org/10.1061/(ASCE)IR.1943-4774.0001238
2. **Jahangeer**, Brijesh Kumar Yadav (2017) "Spatial and Temporal Nitrate transport in deep heterogeneous Vadose Zone of India's Alluvial Plain" *Water Science and Technology Library*. https://doi.org/10.1007/978-981-10-5789-2_13
3. **Jahangeer** and Brijesh K. Yadav. "Nitrate transport modelling through vadose zone considering mobile-immobile approach using sand tank experiments" *Journal of Irrigation and Drainage Engineering*.– In revision
4. **Jahangeer** and Brijesh K. Yadav " Impact of moisture content on nitrate leaching to soil and groundwater using experimental and numerical modelling." Under preparation
5. **Jahangeer** , Brijesh Kumar Yadav and Thomas Harter "Soil water flow and nitrate movement simulation through deep and heterogeneous variably saturated zone of San Joaquin valley, California" Under preparation
6. **Jahangeer** , Brijesh Kumar Yadav , Haishun Yang, Chittaranjan Ray and Yusong Li "Prediction of corn yield and Nitrate-N leaching to the groundwater under future climatic scenarios" Under preparation

International Conferences

1. **Jahangeer** and Yadav B.K., (2018), "Modeling of Soil Moisture Flow and Nitrate Movement using mobile-immobile approach in Soil column experiment". JpGU Meeting, Makuhari Messe, Chiba, Japan. 20-24 May 2018
2. **Jahangeer** and Brijesh Kumar Yadav (2018), "Numerical modeling of Moisture flow and Nitrate-N transport through unsaturated porous media in laboratory condition" International Conference on "Sustainable Technologies for Intelligent Water Management" Department of Water Resources Development & Management, IIT Roorkee, India.16-19 Feb. 2018)
3. **Jahangeer,** Pankaj Kumar Gupta and Yadav B.K., (2017), "Numerical simulation of water flow and Nitrate transport through variably saturated porous media in laboratory condition using HYDRUS 2D". AGU Fall Meeting, New Orleans, Louisiana, USA, 11-15 December 2017
4. **Jahangeer**, Pankaj Kumar Gupta and Brijesh K. Yadav (2017), "Modeling of water flow and Nitrate dynamics through partially saturated porous media in laboratory condition using HYDRUS-2D." The 5th International Young Researchers and Workshop on River Basin Environment and Management 28-29 October 2017 held at University of Malaysia Pahang, Malaysia
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8. Brijesh K. Yadav, **Jahangeer** and Thomas Harter (2014) "Soil Moisture Flow and Nitrate Movement Simulation through Deep and Heterogeneous Vadose Zone using Dual – porosity Approach" AGU Fall Meeting, San Francisco, California, USA, 15-19 December 2014