Regionalisation of nitrate leaching on pasture land in Southern Manitoba

By

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Abstract

Nitrogen is a key agricultural input which is considered to be crucial for crop growth, development, and yield. However, an excess application of anthropogenic nitrate in the form of fertilizers may result in the nitrate contamination of groundwater. A critical time in continental climates in Canada having long and cold winters is nitrate leaching during soil thawing since fast recharge fluxes may occur during that time. The objective of this research was to estimate leaching of nitrate upon the application of liquid hog manure on a pasture land in Southern Manitoba using physically based modeling and to further regionalise the point estimates of nitrate leaching fluxes at the field scale. Data for this research were taken from the Ph.D. study by Coppi (2012). During that study, the field site located in La Broquerie, Manitoba was divided into 6 types of plots namely - control-hayed, control-grazed, full-hayed, full-grazed, split-hayed, and split-grazed treatment plots. The control, full and split treatments plots represented no application of manure, one-time application in a year with full rate and two-times application in a year with half rates each time respectively. Haying and grazing were two types of forage harvesting treatments carried out on in the study site. Data on climate, soil texture, soil moisture, soil temperature, and nitrate concentrations in groundwater at 16 sensor stations (SS) during different manure application rates were observed for years 2008 and 2009 (Coppi, 2012). In this research, one-dimensional physically based modeling was applied using HYDRUS-1D to determine continuous recharge and nutrient leaching estimates from these data. The regionalisation of simulated leaching estimates was done using Cokriging which is a geostatistical interpolation approach. Results showed a good agreement of the simulated and observed soil moisture contents at 15, 45, 75 and 105 cm depths in the soil profile having RMSE between 0.7% and 5%, NSE between 0.39 and 0.99 and ME nearly equal to zero. On an average,

the recharge was estimated as 156.5 mm and 253.5 mm for the years 2008 and 2009 respectively. It was observed that about 42 mm of recharge out of 150 mm (about 28%), occurred during the snow-melt period of the year 2008 at SS-3. The difference in simulated and observed nitrate concentrations in groundwater was expressed in terms of RMSE between 0.023 and 5.12 mg NO_3-N L^{-1}, NSE between 0.66 and 0.96 and the ME between -1.03 mg NO_3-N L^{-1} and 1.05 mg NO_3-N L^{-1}. The areas which posed a risk to nitrate contamination of groundwater were the bare earth areas (BEA). The observed and simulated results showed that the groundwater nitrate concentrations in BEAs of both control-grazed and full-grazed plots were consistently higher than 10 mg NO_3-N L^{-1}. Overall, the cumulative nitrate leaching fluxes for control-hayed, full-hayed and control-grazed plots were below 2 kg NO_3-N ha^{-1} for both years. However, for full-grazed plots, the cumulative nitrate leaching flux was about 11 kg NO_3-N ha^{-1} and 6 kg NO_3-N ha^{-1} for 2008 and 2009 respectively. The cumulative leaching fluxes in BEAs were about 100 times larger than those in grassed areas. The non-accommodation of soil freezing and thawing processes in model simulations was one of the major limitations of this research since these processes are very important to evaluate solute redistribution, water balance, and snowmelt infiltration correctly in the frozen soils. Overall, HYDRUS-1D can be considered as a useful tool in quantifying the recharge and nitrate leaching estimates for pasture fields subjected to continental climates, and Cokriging can be considered as a reliable method for a study site where cross-correlations between variables are important to consider for carrying out interpolation.

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Nomenclature

α	Shape parameter, [L^{-1}]
a_i	undetermined weights assigned to u_i, [ ]
b_j	undetermined weights assigned to v_j, [ ]
c_k	Concentration of solute in liquid phase, [ML^{-3}]
c_k	Concentration of solute in solid phase, [MM^{-1}]
C_p	Specific heat of the air, [$L^2T^{-2}K^{-1}$]
c_r	Sink term concentraion, [ML^{-3}]
D	Hydrodynamic dispersion coefficient, [L^2T^{-1}]
$e_s - e_a$	Vapour pressure deficit of the air, [$ML^{-1}T^{-2}$]
G	Soil heat flux, [$ML^{-1}T^{-2}$]
h_3	Crop's wilting point, [L]
h_o	Pressure head at anaerobiosis point, [L]
h_{opt}	Optimal root water uptake, [L]
$K(\psi)$	Unsaturated hydraulic conductivity, [$L\,T^{-1}$]
K_s	Saturated hydraulic conductivity, [$L\,T^{-1}$]
m	Shape parameter, [ ]
$\bar{M}$	Mean value of observed data set
M_i	Observed data set, [ ]
n	Shape parameter, [ ]
n	Number of simulated and observed data set, [ ]
$N_{denitrification}$	Denitrification flux, [$M\,L^{-2}$]
$N_{leaching}$	Leaching flux of nitrogen below the root zone, [$M\,L^{-2}$]
N_{manure}	Amount of nitrogen added to soil through the application of manure or fertilizers, [$M\,L^{-2}$]
N_{runoff}	Amount (flux) of nitrogen in terms of runoff losses, [$M\,L^{-2}$]
N_{stored}	Amount of nitrogen initially stored or available in the soil, [$M\,L^{-2}$]
$N_{volatilization}$	Volatilization flux, [$M\,L^{-2}$]
q	Volumetric flux density, [LT^{-1}]
R	Coefficient of determination, [ ]
r	Correlation coefficient, [ ]
r_a	Aerodynamic resistance, [TL^{-1}]
R_n	Net radiation, [MT^{-3}]
r_s	Surface resistance, [TL^{-1}]
S	Sink term, [$L^3\,L^{-3}\,T^{-1}$]
$\bar{S}$	Mean value of simulated data set
S(h)	Rate of root water uptake per unit volume of soil, [T^{-1}],
S_e	Effective saturation, [ ]

S_i	Simulated data set, [ ]
S_p	Potential root water uptake rate, $[T^{-1}]$
t	Time, [T]
u_i	Primary data at *n* nearby locations
u_o	Estimate of interpolated paramter at the grid node or at location 0
v_j	Secondary data at m locations
z	Elevation, [L]
$\alpha(h)$	Root water coefficient, [-]
γ	Psychrometric constant, $[ML^{-1}T^{-2}K^{-1}]$
Δ	Slope of saturation vapour pressure and temperature relationship, $[ML^{-1}T^{-2}K^{-1}]$
θ	Volumetric water content, $[L^3L^{-3}]$
$\theta(\psi)$	Soil water retention function
θ_r	Residual water content, $[L^3L^{-3}]$
θ_s	Saturated water content, $[L^3L^{-3}]$
λ	Evapotranspiration, [L]
μ_s	First order decay constant of solute in solid phase, $[T^{-1}]$
μ_w	First order decay constant of solute in liquid phase, $[T^{-1}]$
ρ	Bulk density of soil, $[ML^{-3}]$
ρ_a	Average air density at any constant pressure, $[ML^{-3}]$
ψ	Pressure head, [L]

Acronyms

AWD	Alternate Wetting and Drying
BC	Boundary Condition
BEA	Bare Earth Area
CF	Continuously Flooded
CK	Cokriging
IDW	Inverse Distance Weighted
MASL	Metres Above Sea Level
ME	Mean Error
N	Nitrogen
N_2	Nitrogen Gas
N_2O	Nitrous Oxide
NN	Natural Neighbor
NH_4-N	Concentration of ammonium in water reported in terms of nitrogen
NO_3-N	Concentration of nitrate in water reported in terms of nitrogen
NSE	Nash-Sutcliffe Efficiency
OK	Ordinary Kriging
P	Phosphorous
PTF	Pedo Transfer Function
RMSE	Root Mean Square Error
SK	Simple Kriging
SS	Sensor Station
SWE	Snow Water Equivalent
TDR	Time Domain Reflectometry
VGM	van Genuchten-Mualem

Chapter 1: Background

Groundwater is one of the major freshwater source of consumed freshwater in Canada as about 9 million Canadians rely on it for drinking and household purposes (Environment Canada, 2013). However, the increasing agricultural and industrial activities resulted in groundwater contamination in various parts of the country (Environment Canada, 2010). Canadian agriculture has intensified during past few decades resulting in greater demands of groundwater for irrigational purposes, a regional increase in fertilizer use, and greater farm size and livestock numbers. This has led to an increase in the risk of groundwater contamination by nitrate and pathogens (Bruce, 2009).

Nitrogen is an essential nutrient and a key agricultural input which is considered to be crucial for crop growth, development and yield (Ribaudo et al., 2011). It is important for plants specifically in their metabolic processes such as the production of proteins, nucleic acids and other important molecules (ISAAP, 2015). Upon the application of nitrogen-rich manure or fertilizer to the soil, excess nitrate that is not consumed by the plants is accumulated in the soil and often leaches below the root zone, ultimately contaminating the groundwater. Generally, the risk of nitrate leaching increases during the periods of heavy rainfall and snow melt due to the high availability of surplus water that can carry the soluble nitrate along with it to the groundwater. Coarse textured soils with low water retention capacity, fast drainage, and high porosity are more prone to these losses compared to fine textured or clayey soils with higher water retention capacity and slow drainage. The extent of nitrate leaching also depends on denitrification during which, nitrate converts to nitrogen gas (N_2) by soil microorganisms under anaerobic conditions. Denitrification decreases the availability of nitrates in the soil so that the risk of nitrate leaching reduces.

The primary sources of nitrogen pollution in the environment are agricultural activities, stormwater, wastewater and few domestic sources (EPA, 2015). In Canada, many cases regarding nitrate contamination of groundwater have been observed. E.g., thousands of fishes were killed in Prince Edward Island due to leaching of nitrate into rivers and streams due to agricultural activities (Globe and Mail, 2008). In Manitoba, elevated nitrogen levels in Lake Winnipeg and at shallow depths in the Assiniboine Delta Aquifer located in South-Western Manitoba were observed (Burton et al., 2000). Frost (2006) reported the detection of more than 10 mg NO_3-N L^{-1} in groundwater for about 16% of all private wells in Manitoba. Environment Canada (2010) stated that more contaminated aquifers in Canada would be discovered in the coming decades due to emerging contaminants. The contaminated groundwater discharges into the lakes, streams, and wetlands.

Nitrate leaching is a serious concern for groundwater and surrounding surface water quality and also for human health if contaminated water is used for drinking purposes (Coppi, 2012). Nitrate concentration above 10 mg NO_3^--N L^{-1} in drinking water is linked to certain health problems such as stomach cancer in adults and *methaemoglobinaemia* in infants which decrease the ability of blood to carry oxygen in the body (Health Canada, 2013).

Manure is used to fertilize the soil for crop production (Wang et al., 2004). Liquid hog manure is another excellent source of nutrients for crop production in Manitoba since it is rich in mainly two important nutrients nitrogen (N) and phosphorous (P) on which Manitoba’s crop yield is dependent (Manitoba Agriculture, 2013). The nutrients present in manure are in stable organic forms and cannot be directly used by the crops. Hence, they need to be mineralized to an inorganic form before crops can use them (Ranjan et al., 2001). However, mineralization is a complex process which depends on soil type, weather conditions as well as the method of application of manure. Manure application must be based on the rate of mineralization and the quantity of nutrients which are readily available to the crops (Ranjan et al., 2001). Hence, knowledge about mineralization rate and the processes which govern this transformation is required for the sustainable management of manure which implies the effective use of nutrient present in manure. The basic concept behind the sustainable management of manure is to promote its value as an organic fertilizer and disregard considering it as a ‘waste product’.

Numerical simulation programs can simulate the physical and chemical processes occurring in the soil based on the integrated water flow, solute transport and heat transport equations, using soil properties and weather data. These are important and valuable tools for simulating such processes as well as determining how much nutrients are readily available in soil to be consumed by plants (Ranjan et al., 2001). After estimating available nutrients in the soil, the deficit can be added via manure application such that excess nutrients do not accumulate in the soil, therefore groundwater quality below the root zone is maintained (Ranjan et al., 2001). Physically based modeling reduces the amount of field work, cost and time required for studying the extent of nitrate leaching into the vadose zone under transient conditions (Saso, 2009). Moreover, a good understanding can be achieved regarding the relationship between timing and amount of nutrients to be applied and their uptake by the crops using numerical simulators (Dahan et al., 2014; Shekofteh et al., 2013).

One-dimensional physically based modeling can simulate groundwater recharge and nitrate leaching fluxes at a point scale. However, due to heterogeneities at the field scale, the behavior of these fluxes can be different at different points in the field depending on soil texture, the amount of manure applied and the groundwater table. Regionalisation refers to the prediction of values of the desired parameter at the un-sampled locations by taking into account data of parameter at sampled locations and the neighborhood distribution (Healy, 2010). There are several methods to carry out the regionalisation of point estimates such as simple empirical models which are suitable for estimating recharge and nitrate leaching fluxes in areas of low heterogeneity (Healy, 2010) and regression techniques which are applicable to the areas where sufficient data are available (Lorenz and Delin, 2007). In the recent decades, geostatistical techniques have widely been used in a number of different hydrological applications including nitrate leaching into groundwater and recharge estimation (Evers et al., 2004; Lee et al., 2006; Piccini et al., 2012). Kriging (Krige and Matheron, 1967; Matheron, 1967) is a geostatistical technique which allows the estimation of any parameter at unknown locations if the point estimates at neighbouring locations are known.

The objective of this research was to estimate nitrate leaching fluxes upon the application of liquid hog manure on a pasture land in Southern Manitoba using physically based modeling and to regionalise further the point estimates nitrate leaching fluxes at the field scale.

Chapter 2: Literature review

2.1 Nitrate in Canadian groundwater & environmental implications

Groundwater is a crucial and indispensable drinking water resource for 9 million Canadians. It is also regarded as a ‘hidden water resource’ for those who are not dependent on it or have not well understood and appreciated its value (Environment Canada, 2009).

In recent years, public concern and realization about worth and importance of groundwater have been triggered as a result of the occurrence of a number of events which affected the Canadian groundwater quality (Environment Canada, 2009). A few of these events were related to nitrate contamination of groundwater such as in Prince Edward Island where elevated nitrate concentration (>10 mg NO_3-N L^{-1}) were detected in 6% of drinking water domestic wells (Paradis et al., 2016) and in Assiniboine Delta Aquifer located in South-West Manitoba (Burton et al., 2000). Agricultural practices are one of the major sources of nitrate leaching resulting in the contamination of groundwater in Canada, mainly in Canadian Prairie province Manitoba. Lefebvre (2005) reported a 25% increase of nitrate concentration nationally in the Canadian groundwater from 5.9 mg NO_3-N L^{-1} in 1981 to 7.3 mg NO_3-N L^{-1} in 2001 resulting from agricultural lands with residual soil nitrogen. A study conducted by Rudolph et al. (2015) outlined the detection of elevated nitrate concentrations (>10 mg NO_3-N L^{-1}) in two agricultural fields located in the towns of Baden and Woodstock in Southern Ontario. Elevated concentrations of nitrate in groundwater associated with agricultural practices were also reported in the Grand Forks area located in the east of Kettle River basin as well as in areas surrounding Osoyoos located in the west of Kettle River basin of South Central British Columbia (Harker et al., 2015). There has been an increase in the risk of nitrate contamination of groundwater in the past decades due to several factors such as an increase in regional fertilizer use and in livestock (Bruce, 2009).

Agricultural producers are not yet able to adopt the Best Management Practices (BMPs) which are focussed to promote the value of manure as an organic fertilizer and disregard considering it as a 'waste product', for minimizing the nitrate contamination of groundwater in Canada. Hence, further research, monitoring, and enforcement of best management practices are required to achieve the desired objectives regarding the groundwater quality (Bruce, 2009).

The application of manure, especially to sandy soils, may pose a threat for losses of major nutrients and other compounds in groundwater (subsurface drainage and leaching) and surface water (snowmelt and run-off). Nitrate is soluble in water and is mobile in the soil pores. Unlike ammonium ions, nitrate ions do not get adsorbed to the negatively charged soil particles due to their negative charge. Hence they move below the root zone if there is an availability of excess soil water that can leach below the root zone. A region's overall hydrological and nitrogen balance greatly affect the leaching losses since these losses are dependent on the amount of surplus water available for groundwater recharge. In Manitoba, the extremely cold weather conditions from late September to early May allows the upper soil layer to freeze during these months. Soil thawing in early spring poses a potential threat for nitrate contamination of groundwater in Manitoba as most of the groundwater recharge occurs during this period (Wang et al. 2016, under review).

Another environmental concern that is linked with elevated N levels in groundwater is the eutrophication of surface waters bodies such as lakes and rivers. One of the potential causes of surface water eutrophication is the elevated nitrogen (N) concentrations in groundwater which is hydrologically connected with the nearby surface water bodies such as rivers and lakes. In aquatic environments, the elevated N and P concentrations trigger the growth of autotrophic algae as compared to other microorganisms which lead to an increase in dissolved oxygen consumption due to increased respiration. These algal blooms in the aquatic environments reduce the dissolved oxygen level in the water, as a result of which population of fish and other micro-organisms decreases in the surface water bodies (Carpenter et al., 1998). Lake Winnipeg, located in Manitoba, is the world's 10^{th} largest lake and is experiencing eutrophication since at least past thirty years (Coppi, 2012; Schindler et al., 2006). The increased nutrient load is from its main tributaries: Winnipeg River, Red River, and Saskatchewan River. The Red River supplies most of the annual P and N loadings to Lake Winnipeg as 54% and 30% respectively in spite of the fact that the volume of water contributed to the Lake Winnipeg by Red River is relatively small as compared to its other tributaries.

2.2 Human health concerns

Nitrate concentration above 10 mg NO_3^--N L^{-1} in drinking water is linked to certain health problems such as stomach cancer in adults and *methaemoglobinaemia* in infants which decrease the ability of blood to carry oxygen around the body (Health Canada, 2013). The drinking water threshold of 10 mg NO_3^--N L^{-1} was first suggested by Comly (1945), and later in 1951, Walton (1951) confirmed this standard based on incidents of *methaemoglobinaemia* in infants. Walton mentioned their study that no cases of *methaemoglobinaemia* were reported for the concentration of nitrate in drinking water being less than 10 mg NO_3^--N L^{-1}. The actual cause of *methaemoglobinaemia* in infants is nitric oxide, not nitrate (Addiscott and Benjamin, 2004). Nitrate is converted to nitric oxide in the gut which further oxidises hemoglobin present in blood to methaemoglobin reducing the amount of hemoglobin available for transport of oxygen. Nitrate is a relatively non-toxic compound of nitrogen as compared to its metabolites which can potentially cause several adverse health issues such as stomach cancer. Proper control and monitoring of nitrate-N levels in drinking water are always important to reduce such adverse health effects.

2.3 Nitrogen dynamics

Nitrogen is an important macronutrient which is required for a crop's proper growth and yield and is often inadequate in the agricultural soils (Manitoba Agriculture, 2013). Hence the application of nitrogen-rich fertilizers or manures is required to achieve the target crop yield. Application of nitrogen via fertilizers or manures allows it to enter the soil-N cycle. Soil-N cycle can be explained in terms of gains, internal transformations, removals, and losses of N in soil (Figure 1).

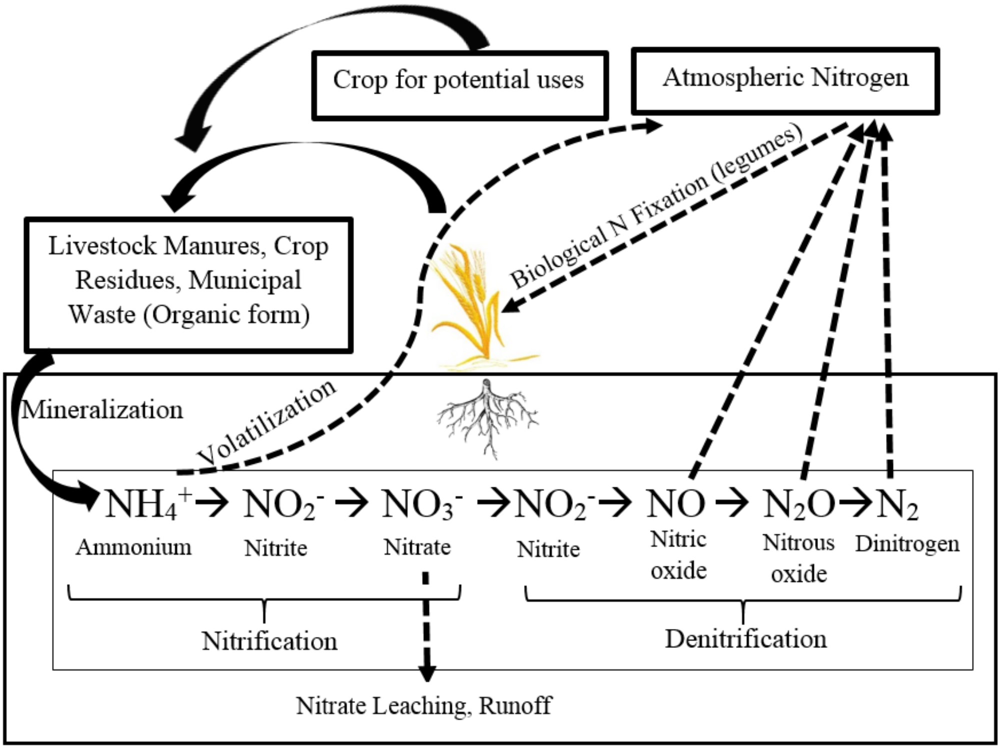

Figure 1: Soil-N cycle showing complex and dynamic behaviour of nitrogen in soil with many transformations (solid black lines) and potential losses (dashed lines)

Nitrogen in manure is mainly present in two different forms: organic nitrogen and ammonium nitrogen. It is also present in very small amounts in the form of nitrates. All these forms of nitrogen collectively add up to total nitrogen (Manitoba Agriculture, 2009). Soon after the application of manure, all of the nitrogen does not get available to plants for their use since they can only use the inorganic form of it. Ammonium-N (NH_4-N) is the primary inorganic form of nitrogen and is available immediately to the crops after manure application. Another form of inorganic nitrogen present in manure is nitrate-N (NO_3^-N), but it is present in negligible amounts. The organic form of nitrogen can be determined as the difference between total and ammonium nitrogen.

After application of manure to soil, nutrients go through various transformations which may affect their availability for use by plants. The organic nitrogen is converted to inorganic ammonium form by a process known as mineralization (Figure 1). In Manitoba, it has been determined that around 25% of manure's organic nitrogen is mineralized and becomes available to the next crop. The remaining amount becomes available for use during the following years at decreased rates (Manitoba Agriculture, 2009). Upon manure application, some of the ammonium-N undergoes a chemical process known as volatilization by which it gets lost to the atmosphere in the form of ammonia gas (Manitoba Agriculture, 2009). A number of losses through volatilization depends on various factors as follows:

- Soil cover: If the manure is properly covered by soil, it leads to the reduction in volatilization losses of ammonium-N. Injection of manure into the soil reduce these losses instead of the surface application.
- Soil pH: Alkaline soils with high pH and low concentration of H^+ ions favours the volatilization losses compared to low pH soils with high concentration of H^+ ions.
- Soil texture: Sandy soils with low cation exchange capacity can retain less ammonium-N leading to higher losses due to volatilization.
- Weather: Volatilization losses increase during warm weathers due to increase in the rate of NH_3 formation. Fast winds also increase NH_3 losses to the atmosphere due to increased rate of air exchange (Manitoba Agriculture, 2013).

The actually available ammonium-N that can be used by plants is calculated by the difference between manure's total ammonium content and percentage losses through the process of volatilization.

Although nitrate concentration in manure is very low, manured soils contain significant amounts of nitrate through the process of nitrification by which soil microorganisms transform nitrogen from ammonium to nitrate. There occurs an accumulation of nitrate-N (NO_3^--N) during the nitrification of ammonium-N. If the accumulated nitrates are not utilized by plants, they become prone to leaching below the root zone to contaminate the groundwater.

Immobilization is another process which occurs in the soil. It is known as the reverse process of mineralization. When microbes in the soil start feeding on plant available inorganic N due to limited amounts of organic N, they reduce the ammonium-N and nitrate-N from the soil solution and convert them to organic form.

Denitrification occurs in the soil only during anaerobic conditions. During this process, nitrates are reduced to nitrites and then further to N_2 (nitrogen gas) or N_2O (nitrous oxide) by the microorganisms. During anaerobic conditions, microorganisms use NO_3 for respiration instead of $O_{2.}$ This microbial process is favoured under certain conditions such as during large supply of NO_3 and limited amount of O_2 (saturated soils) or during warm temperatures when there is a high microbial activity in the soil (Manitoba Agriculture, 2013). Denitrification does not occur in dry soils when there is plenty of oxygen (O_2) present in the soil and can be utilised by microorganisms for respiration.

2.4 Liquid hog manure

Hog manure contains the nutrients which are required for crop production. It is a natural by-product of livestock production and can be regarded as an organic fertilizer. Applying hog manure to the soil recycles not only the soil nutrients but also improves soil tilth, aeration, structure, and water-holding capacity (Manitoba Agriculture, 2009).

Over the last century, there has been a gradual shift in livestock herding from extensive systems to the enclosed systems of barns and pastures (Haygarth and Jarvis, 2002). Hog population in Manitoba grew significantly from 600,000 in 1976 to 2.8 million in 2011 (Brisson, 2014). The average per-farm hog population also increased from 762 hogs/farm in 1976 to 4831 hogs/farm in 2011 (Brisson, 2014).

The significant increase in hog production in Manitoba over the last century has reduced the transportation costs of animals and feeds and motivated to store the animal waste (Coppi, 2012). The intensive production of hogs in Manitoba resulted in a need to import large amounts of nutrients to feed the livestock (Carpenter et al., 1998; Coppi, 2012). Since hogs cannot retain much of the nutrients ingested from feeds, they excrete a large part of them in the form of feces and urine which are further stored in earthen storages (Cooperband and Good, 2002).

On an average, each pig produces 161-178 kg of feces and urine per year (Müller, 1980) and every sow and their progeny excretes 20 t per year of manure. In Manitoba, hog manure is commonly stored in the anaerobic earthen storages where urine and feces are collected with wash water in open air pools. Urine and feces are mixed to form slurry that has suspended solids. Typically, the slurry has approximately 94 % moisture content (Haygarth and Jarvis, 2002). The composition of manure changes during its storage due to the prevailing anaerobic conditions. These conditions allow mineralization of organic N to its inorganic ammonium form. This also leads to the volatilization losses of ammonia (Cabrera and Gordillo, 1995). Two-thirds of N is in inorganic ammonium form which is dissolved in manure’s liquid phase, and the other one-third remains in an organic form associated with the solid phase (Cabrera and Gordillo, 1995).

2.5 Agricultural nitrogen balance

A healthy balance between nutrients added and removed from the soil is very important to ensure their optimal use and limit their accumulation in the soil (OECD and EUROSTAT, 2007). As explained in section 2.2, plants use nutrients available in the soil for their overall growth. However, if the nutrients removed from soil are more than nutrients added, soil begins to lose its fertility and limits the crop growth. It is then very important to maintain a balance of nutrients in soil in order to identify the areas of their surplus and deficits (OECD and EUROSTAT, 2007).

The nitrogen budget can be analysed by determining a mass balance between its input to the soil from agricultural and natural sources and removal by crops, pastures, and forages. A simple mass balance equation can be used to determine the surplus amount of nitrogen:

$$N_{surplus} = N_{manure} + N_{stored} - N_{denitrification} - N_{volatilization} - N_{leaching} - N_{runoff} - N_{crop\ uptake} \qquad (1)$$

where N_{manure} (kg/ha) is the amount of nitrogen added to the soil through the application of manure or fertilizers, N_{stored} is the initially stored nitrogen in the soil, $N_{denitrification}$ and $N_{volatilization}$ are the amounts of nitrogen removed by denitrification and volatilization processes, $N_{leaching}$ and N_{runoff} are the leaching and runoff losses, and $N_{crop\ uptake}$ is the Nitrogen uptake by plant roots. Positive $N_{surplus}$ represents the surplus of nitrogen in the soil which can be treated as a potential source of groundwater contamination whereas negative $N_{surplus}$ means the removal of nitrogen by the crops is more than the input through any of the sources. Negative $N_{surplus}$ indicates the declining fertility of the soil which can eventually lead to reduced crop productivity. Zero value of $N_{surplus}$ indicates the optimal use of nitrogen sources by the crop grown.

2.6 Tame pasture and bare-earth areas

Tame pastures are the agricultural fields cultivated with non-native grass or legume species and are used to achieve a list of purposes including grazing of livestock to recover and improve their health and nutrition, to minimize soil erosion and upgrade soil quality and to balance forage demand and supply during the periods of low forage production (Jacobs and Siddoway, 2007). The listed purposes of tame pastures are optimally achieved when the established crop is healthy and is functioning well to capture solar energy, facilitate nutrient and water cycling. In Manitoba, tame pasture is being used by the livestock producers since the beginning of homesteading in the province. The long and warm days in summers with an appropriate amount of soil moisture are the ideal conditions for pasture growth which prevails in the Canadian Prairies. In 1998, production of tame hay pasture was first recorded when 481.5 km^2 of land produced 195 million kgs of hay. The increase in livestock production over the years has steadily increased the production of pasture in Manitoba. Presently, around 7989 km^2 of land provides over 2721.5 million kgs of tame hay in Manitoba (Manitoba Agriculture, 2016)

Livestock grazing is a management practice which is used on tame pasture to achieve a well maintained and a healthy forage base, for providing nutrition to the livestock for their growth and development. Livestock grazing or mechanical harvesting of pastures is very important since it maintains the cycle of forage growth and utilization. The absence of crop harvesting, either by grazing or by mechanical means, can lead to the accumulation of dead plants on the land, which can further shade the photosynthetically active plant material, ultimately resulting in a reduction in capture of solar energy by plants that drive the system (Jacobs and Siddoway, 2007). In the grazed pastures, there exist a cycle of nutrient transfer from soil to pasture plants and vice versa, either through the excretes of grazing animals or through the dead plants (Williams and Haynes, 1990). As this cycle occurs, losses and gains of nutrients may occur via leaching, volatilization or through the addition of addition of fertilizers or manure. Grazing animals play an important role in carrying out the nutrient cycle through the soil. They ingest the herbage and ultimately encourage the growth of pasture plants and therefore intake more nutrients from the soil (Williams and Haynes, 1990). In grazed pastures, nutrient accumulation can occur when livestock tend to concentrate near areas such as mineral feeders, water troughs and shelters (Coppi, 2012; Williams and Haynes, 1990) resulting in higher deposition density of urine and feces than for other areas in pasture fields. Due to regular soil compaction, trampling and high concentration of nutrients, these areas often become bare. Apart from these areas getting larger with regular deployment of animals, the nutrient concentrations in the soil also rise due to further deposition of urine and feces over these areas (Dahlin et al., 2005), hence creating a serious threat of leaching of nutrients to the groundwater below.

2.7 Physically based modeling of nutrient leaching

Physically based models generally tend to represent the physical processes such as evapotranspiration, surface and subsurface flow and transport of solutes in soil that occurs in the real world. These processes can be simulated using empirical or partial differential equations, e.g. Richard's equation (Richards, 1931) which represents water flow in unsaturated soils (Section 3.4). Numerical simulation programs can simulate the physical and chemical processes occurring in the soil based on water flow, solute transport and heat transport equations, using soil properties and weather data. These are important and valuable tools for simulating such processes as well as determining how much nutrients are readily available in soil to be consumed by plants (Ranjan et al., 2001). Estimating the plant-available nutrients in the soil, the deficit amounts can be added via manure application such that they do not get accumulated in the soil and groundwater quality below the root zone is maintained (Ranjan et al., 2001). Physically based modeling reduces the amount of field work, cost and time required for studying the extent of nitrate leaching into the vadose zone under transient conditions (Saso, 2009)

Groundwater recharge and nutrient leaching are fundamentally time, and spatial variable processes and their estimation is difficult. A high degree of uncertainty is often associated with their estimation (Holländer et al., 2016). Physically based vadose zone modeling is a commonly used method for their estimation, e.g. Holländer et al. (2016) successfully used this method to estimate groundwater recharge on sandy soil in Southern Abbotsford, British Columbia, Canada subjected to mild and moist winters. They used data from a low-cost weather station and automated sensing techniques and concluded that this method is able to estimate transient recharge and nitrate leaching estimates which are controlled by heavy precipitation and water as well as nitrate infiltration events.

Liu et al. (2013b) used this method to estimate the impact of on-going and future long-term flood irrigation practices on the extent of nitrate leaching into the soil profile in an agricultural district of Jinghuiku, China with sandy clay loam soil and a semi-arid climate. They concluded that the introduction of flood irrigation increased the concentration and downward drainage fluxes of nitrate within the 2 m soil profile and also indicated the risk of elevation of N concentrations 1 m below the soil profile due to increasing future irrigation. Recently, Tan et al. (2015) used physically based modeling to simulate the movement of water and N transformations and transport in experimental lowland paddy fields subjected to Alternate Wetting and Drying (AWD) type as well as Continuously Flooded (CF) irrigations. Their results reflected the development of alternate aerobic and anaerobic conditions in the soil due to AWD type of irrigation leading to alternate nitrification and denitrification occurring in soil. During the dry (aerobic) conditions, nitrification of ammonium to nitrate took place which further denitrified to nitrogen gas (N_2) or nitrous oxide (N_2O) during the wet (anaerobic) conditions. They concluded the simulation of water and N movement using physically based modeling being an effective and reliable approach for the improved management of water and N for the sustainable production of rice.

There has been no such study found which used this method for estimation of groundwater recharge and extent of nitrate leaching in pasture fields of Southern Manitoba which are subjected to liquid hog manure applications with coarse soil texture and low hydraulic gradient groundwater flow.

2.8 Regionalisation of nitrate fluxes

Groundwater recharge and nitrate leaching fluxes are spatially variable quantities and are dependent on soil texture, manure/fertilizer application, groundwater table, and soil moisture content. One-dimensional (1D) physically based modeling generates groundwater recharge and nitrate leaching flux estimates at certain sampled locations in a field. However, due to heterogeneities at the field scale, these quantities can be potentially variable at un-sampled locations in the field. Regionalisation refers to the prediction of values of the desired parameter at the un-sampled locations by taking into account data of parameter at sampled locations and the neighbourhood distribution (Healy, 2010). It is a complex operation which takes into accounts various factors such as the distribution of sampled locations, omnidirectional consideration of observations and uncertainties of interpolation methods. Therefore the quality of results generated through spatial interpolation depends on the quality of inputs, spatial coverage, and model selection. There has been a development of different methods to carry out spatial interpolation such as local interpolation methods and geostatistical methods. Local interpolation methods are based on the assumption that each sampled point can influence the study area only up to a certain finite distance (Mitas and Mitasova, 1999). Different methods for this classification are Natural Neighbour (NN) interpolation (Sibson, 1981), Inverse Distance Weighted (IDW) interpolation (Bartier and

Keller, 1996), Thiessen polygons (Goovaerts, 2000) and Splines (Unser, 1999). Kriging (Krige and Matheron, 1967; Matheron, 1967) is the primary approach for geostatistical methods and was originally developed for the mining industry. Kriging methods of geostatistical interpolation consist of Simple (SK), Ordinary Kriging (OK), Universal Kriging and with further developments Cokriging (CK) was introduced which became applicable in environmental science, hydrogeology, remote sensing and natural resources (Bayraktar and Turalioglu, 2005; Chilès and Delfiner, 1999; Papritz and Dubois, 1999; Richmond, 2002; Tonkin and Larson, 2002). Several studies were carried out in recent decades to interpolate groundwater table using the geostatistical methods, and kriging was found to be optimal (Sun et al., 2009; Xiao et al., 2016; Yao et al., 2014). Recently, Wang (2017) carried out a study to spatially interpolate the groundwater recharge for a pasture land in Southern Manitoba and found Cokriging (CK) to be a potentially suitable method due to cross-variation of recharge with multiple soils and meteorological parameters. Similarly, leaching of nitrate below the root zone depends on various factors such as application and timing of manure, groundwater table, vegetation, soil texture and weather conditions. Therefore, Cokriging (CK) can be considered as a potentially suitable method for interpolating nitrate leaching fluxes taking into account the rate of manure application as a secondary variable. The non-accountability of the secondary variable in local interpolation methods (NN, IDW, Thiessen polygons, and Splines) as well as in Simple, Ordinary and Universal Kriging made these methods inapplicable for interpolating nitrate leaching fluxes.

Chapter 3: Methodology

3.1 Study area

The study site for this research was the Pasture and Swine Manure Management Site in La Broquerie, Manitoba (Figure 2). La Broquerie is one of the most concentrated areas of livestock production in Canada (Flaten et al., 2003). Its livestock density was 129 animals per km^2 in 2001. The study site had a total tame grassland area of 0.4 km^2. Before 2003, there was no application of manure or fertilizer to the study site (Coppi, 2012). The main vegetation of the pasture land was quackgrass (*Elytrigia repens L. Nevski*) and Kentucky bluegrass (*Poa pratensis L.*) (Wilson et al., 2010). About 89% of land in the rural municipality of La Broquerie falls under agriculture capability classes 3 to 6, which means the soil is suitable for grass forage production (Land Resource Unit, 1999). The soil texture in the study area was mostly sandy loam to gravel. At 2 m deep in the western half of study area, there was the presence of an impermeable clay layer (Coppi, 2012). Due to rapid drainage and low water retention of the coarse soil, it is not appropriate for annual crop production. Hence, most of the area was being utilized for grass forage production (Coppi, 2012). The dominant soil series were 70% Berlo loamy fine sand (imperfectly drained lacustrine) and 30% Kergwenan loamy sand to gravel (imperfectly drained outwash). The calcareous, coarse soil was under-layed partially by a 4 m thick clay layer which prevented free drainage and caused the groundwater table to rise up in spring during snow melt and heavy precipitation events (measured at SS-3, Figure 3) (Coppi, 2012).

The mean physical and chemical properties of soil in the study area are listed in table 1. The average stone weight percentage in the whole soil profile was determined to be 37%.

Table 1: Mean and standard error of soil physical and chemical properties at the study site determined in 2003 (modified after Coppi, 2012)

Soil Depth cm	**Parameter**	**pH**	**Total-N** g kg^{-1}	**NH_4^+-N** mg kg^{-1}	**NO_3^--N**	**Sand**	**Silt** %	**Clay**	**Texture Ɪ́** Class	**Stones** % weight	**Bulk Density** g cm^{-3}
0-30	Mean	7.9	0.77	1.95	1.73	82	10	8	Loamy Sand	31	1.68
	S.E.	0.0	0.08	0.22	0.18	1	1	0		2	0.11
30-60	Mean	8.3	0.32	0.94	1.24	87	10	3	Sand	41	2.04
	S.E.	0.0	0.06	0.15	0.10	2	2	0		2	0.12
60-90	Mean	8.4	0.17	0.45	0.71	93	6	2	Sand	39	1.94
	S.E.	0.0	0.05	0.09	0.04	0	0	0		2	0.09
90-120	Mean	8.6	0.13	0.31	0.54	93	5	2	Sand	36	1.96
	S.E.	0.0	0.03	0.05	0.04	0	0	0		2	0.09

ƗTextural classes based on the USDA classification.

Average bulk density of soil was determined in the field in August 2007 by excavating four soil pits to the depth of groundwater which was about 125 cm (Coppi, 2012) (Figure 3). The soil physical properties for each plot are listed in Appendix-A.

3.2 Experimental design

The study site was split into 12 plots (Figure 3). The experimental design conducted by the Department of Soil Science, University of Manitoba in 2003 was based on manure application and on forage utilization:

(a) Manure application treatment: There were three types of manure application treatments namely control, single (or full) and split. On control treatment plots, manure was never applied whereas, on single treatment plots, manure was applied with full rate according to the N requirement of pasture during spring (usually in May). On split treatment plots, manure was applied twice a year with half rates each time i.e. in spring and in fall.

(b) Forage utilization treatment: Forage utilization treatment was carried from June to August every year, and it consisted of baled dry forage removal (hay treatment) as well as grazing which was done by yearling beef steers (grazed treatment).

Based on above treatments, the study area was divided into six types of plots namely control-hayed, full-hayed, control-grazed, full-grazed, split-hayed and split-grazed in the year 2007 (Coppi, 2012). The grazed plots with control treatment covered an area of 8 ha whereas the grazed plots with single as well as split treatments had an area of 4 ha each. Each hay plot covered an area of 1.2 ha. The size of each plot was so adjusted that 8-10 animals and the standing forage of 1000-1150 kg dry matter per ha were always maintained. In the case of an excess number of animals and when standing forage became less than 400 kg ha^{-1}, some animals were removed from the plot. Haying was done once in a year to the respective plots, usually in June when grass was in its early head phonological stage (Coppi, 2012).

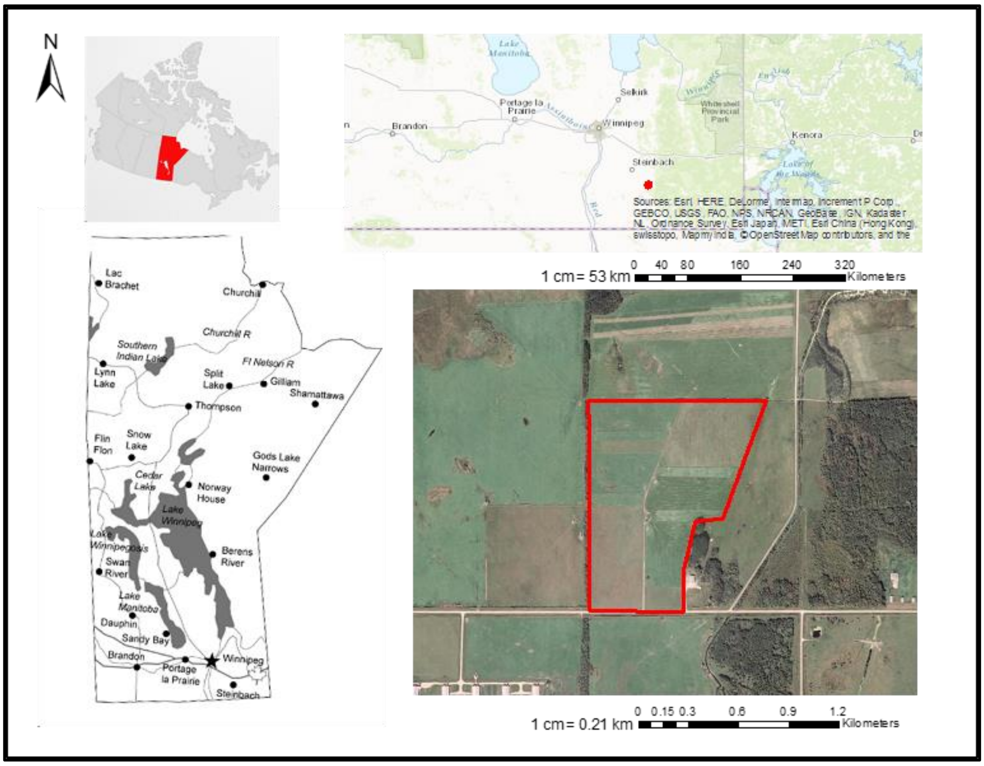

Figure 2: Location of the study site in Manitoba, Canada

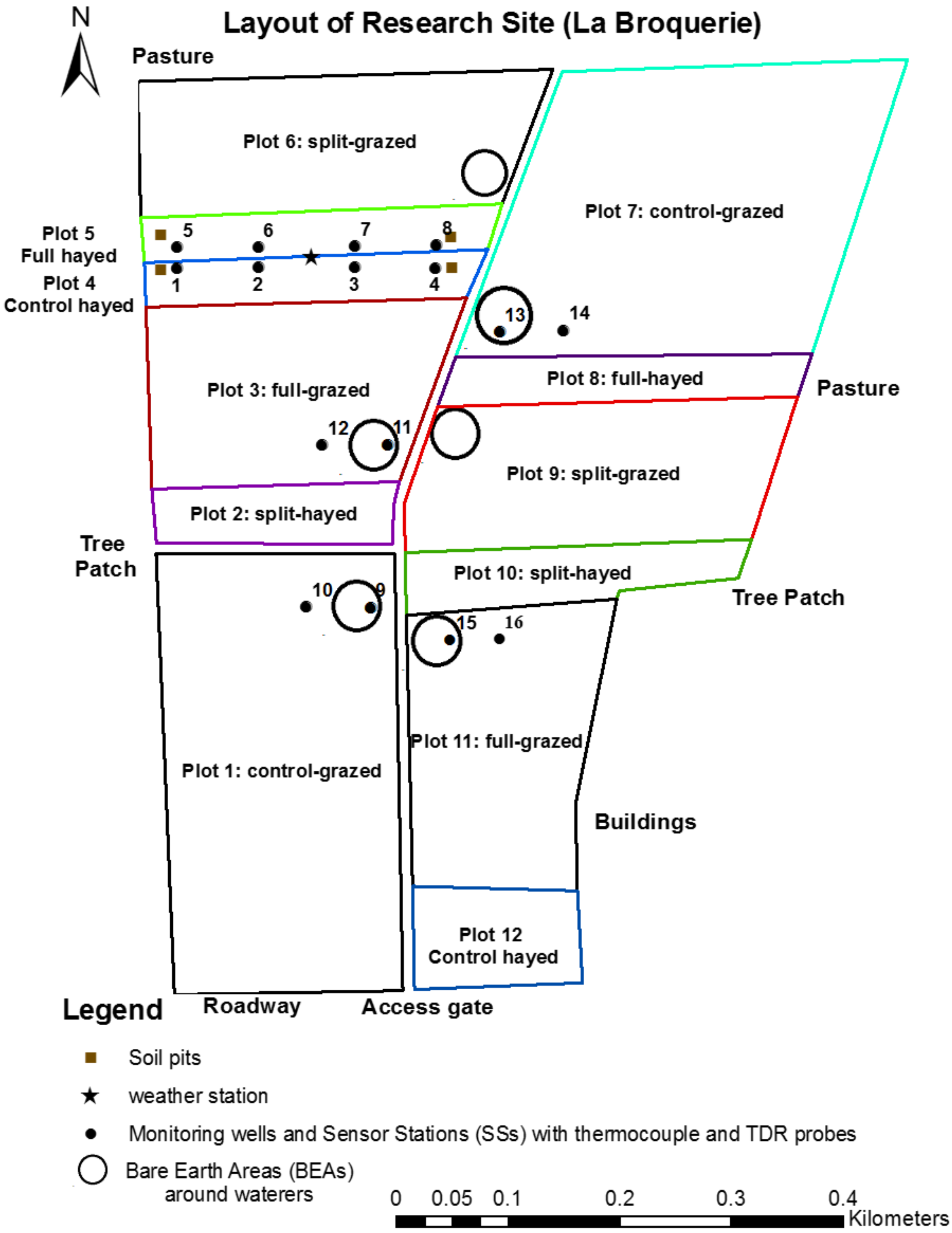

Figure 3: Layout of the research site in La Broquerie, the total size of which is 40 ha, showing the division of site into slurry and forage utilization treatments

3.3 Data analysis

The daily on-site weather conditions for years 2008 and 2009 were monitored using a Campbell Scientific weather station, equipped with a data-logger (CR1000, Campbell Scientific Canada Corp.) (Coppi, 2012). The weather station was installed at the boundary between plot 4 and 5 (Figure 3). It recorded the hourly (averaged to the daily values) meteorological data including precipitation, maximum and minimum air temperatures, solar radiation, relative humidity, wind speed and atmospheric pressure.

The annual rainfall precipitation was measured as 459 mm and 542 mm for years 2008 and 2009 respectively (Figure 4). Depth to groundwater was measured at SS-3 (Figure 5) on a daily basis for both years using a pressure transducer with a data logger (Aquistar PT2X with Aqua4Plus Control Software, INW, Kirkland, WA). Heavy precipitation events recorded in the year 2009 led the groundwater table to rise up to the ground surface (Figure 5).

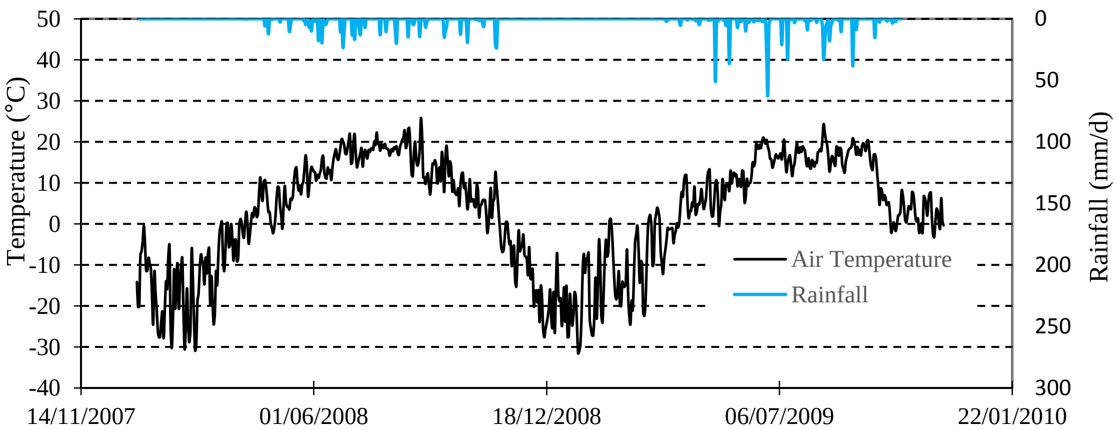

Figure 4: Daily mean observed air temperature and precipitation at Campbell Scientific weather station (Jan 2008 to Oct 2009). Data source (Coppi, 2012)

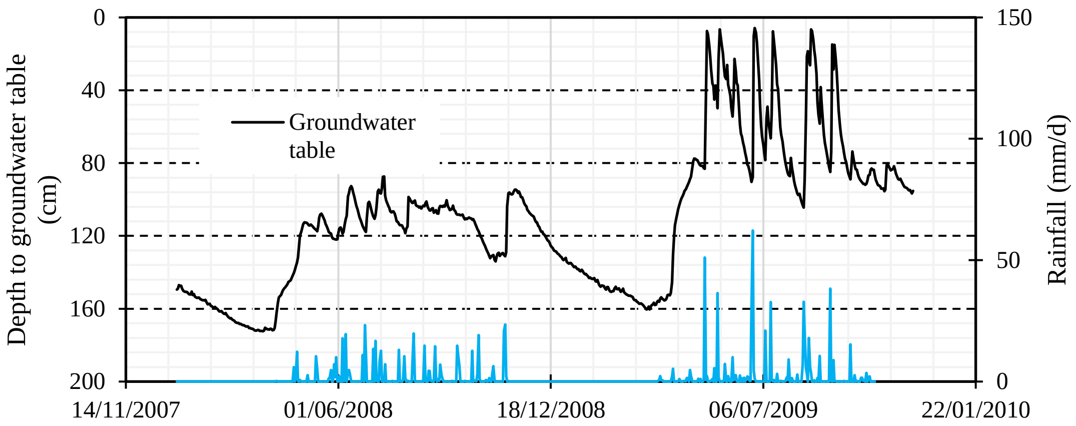

Figure 5: Depth to groundwater table from soil surface measured at SS-3 for the years 2007, 2008 and 2009. Elevation of monitoring wells was 303.52 m asl. (Data source: Coppi, 2012)

The daily soil moisture content at depths 15, 45, 75 and 105 cm for years 2008 and 2009 was measured using tensiometers and TDR probes at SS-1 to SS-8. Daily soil moisture content observations at SS-3 (depth 15 cm) increased after precipitation events (Figure 6). Soil moisture content was recorded to be less than 0.1 cm^3/cm^3 during the winter months due to the soil being in a frozen state (Figure 6). TDR probes measured such low values of soil moisture content in winter months due to the fact that dielectric constant of water in the form of ice is very low (about 4) as compared to its liquid form (about 80 at 20°C) (Jones et al., 2002).

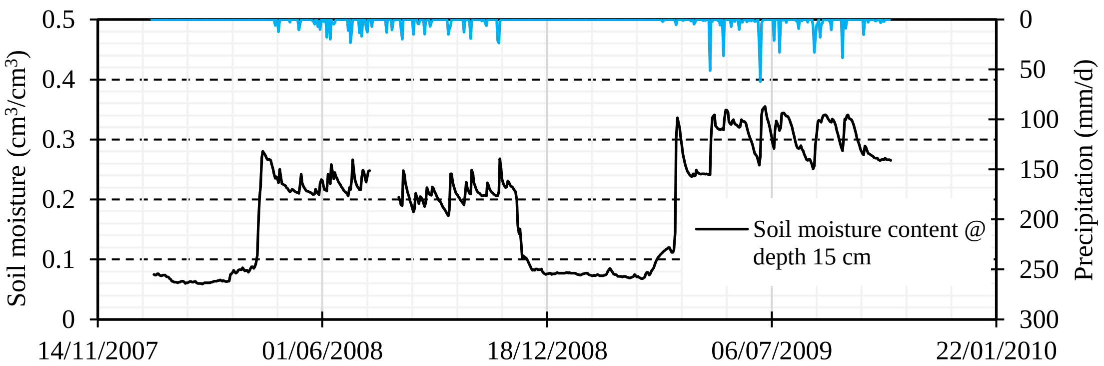

Figure 6: Observed soil moisture content at SS-3 (depth: 15 cm below soil surface). Data source (Coppi, 2012)

Surface application of liquid hog manure started in May 2004 at the study site (Coppi, 2012). The rates of application each year were based on the N requirement of pasture which was 123 kg plant available-N ha^{-1} $year^{-1}$ (Coppi, 2012). From 2004-2006, manure was applied at 142 kg plant available-N ha^{-1} $year^{-1}$ whereas, in 2007, 2008 and 2009, it was applied at 105, 119 and 224 kg plant available-N ha^{-1} $year^{-1}$. In single-treatment plots, manure was applied with full rate during the first week of May whereas, in split-treatment plots, it was applied with the half rate in May and then again with half rate at the beginning of October. Before each application, manure's organic-N and ammonium contents were measured with a hydrometer and Agros Nova Mk3 manure-N meter respectively. Based on these measurements, plant available-N concentration of manure was estimated as the difference between total and organic-N. At the time of application, it was assumed that 25% of the nitrogen available in the form of ammonium was volatilized as ammonia under cold and humid weather conditions. (Coppi, 2012). The chemical analysis of the manure samples carried out in a commercial laboratory in Winnipeg (Norwest Laboratory) was used to determine the actual plant available-N (Coppi, 2012). The manure characteristics are given Appendix-A.2.

The source of nutrients in BEAs (Bare Earth Areas) was through the deposition of urine and feces by steers. Williams and Haynes (1990) explained that most of the N ingested by steers from pasture are not utilised (about 60-99 %) and get excreted with urine and feces. An event of urination can provide highly localised rates of N-application to the soil at anywhere between 500-1000 kg N ha^{-1} even though 20-60 % urea can be lost as ammonia through volatilization (Williams and Haynes, 1990).

The concentration of nitrate in groundwater at SS-1 to SS-16 was dependent on the type of manure-treatment plot and BEAs. Starting from SS-1 to SS-4 located in the control-hayed plot (plot 4) and SS-5 to SS-8 located in the full-hayed plot (plot 5), the observed nitrate concentrations in groundwater were always below 1 mg NO_3-N L^{-1} in 2008 and 2009 (Figure

7 and Figure 8). Therefore, the average concentration of these SS's was taken and used as observed data for numerical modeling.

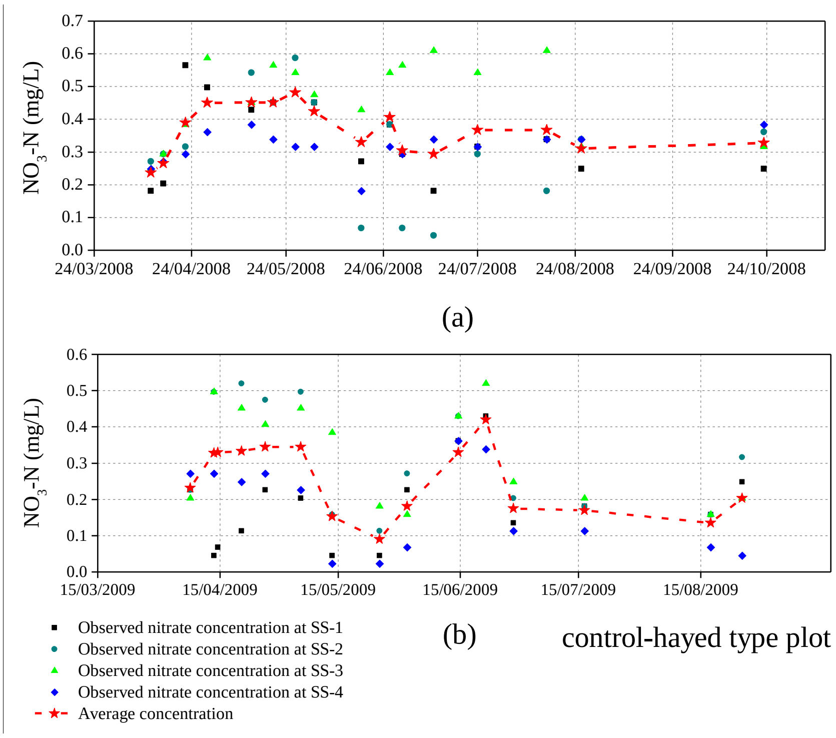

Figure 7: Observed nitrate groundwater concentrations at SS-1 to SS-4 and their average for the years (a) 2008 and (b) 2009

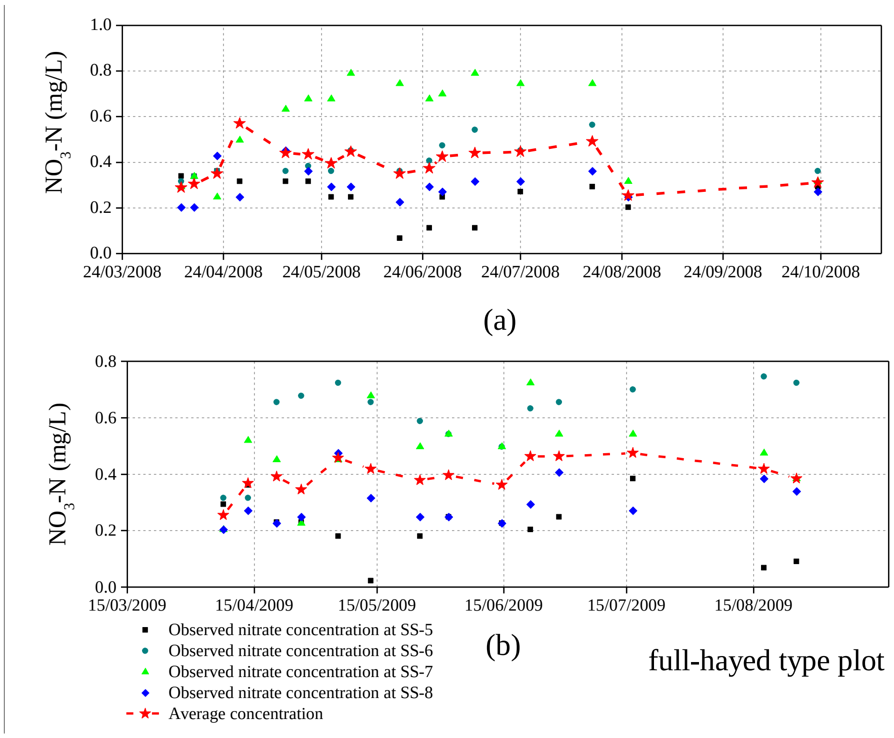

Figure 8: Observed nitrate groundwater concentrations at SS-5 to SS-8 and their average for the years (a) 2008 and (b) 2009

For SS-12 & SS-16, located in full-grazed plots, the concentration of nitrate in groundwater was between 2-8 mg NO_3-N L^{-1} for most of the time in both years of study (Figure 9). The increased concentrations at these SSs as compared to control-hayed, full-hayed and control-grazed plots were mainly due to the application of manure at full rates in early spring and less removal of nitrate due to the utilization of forage by animal grazing (Coppi, 2012). Forage utilization treatment by haying removed a larger amount of nitrate from the soil as compared to that by animal grazing. This resulted in a lesser concentration of nitrate in groundwater at plots where haying was adopted (Coppi, 2012) (Figure 7, Figure 8 and Figure 9).

SS-9 & SS-13 were located in BEAs of control-grazed plots whereas the SS-11 & SS-15 were located in the BEAs of full-grazed plots. The nitrate concentration in groundwater at all of these SSs was significantly greater than in other parts of the study area and the drinking water threshold of 10 mg NO_3-N L^{-1} (Figure 10). As mentioned before, the BEAs of control-grazed plots received lesser amounts of nitrogen via animal excretes, hence the concentration of nitrate in groundwater at these spots was lower than the BEAs of full-grazed plots (Figure 10).

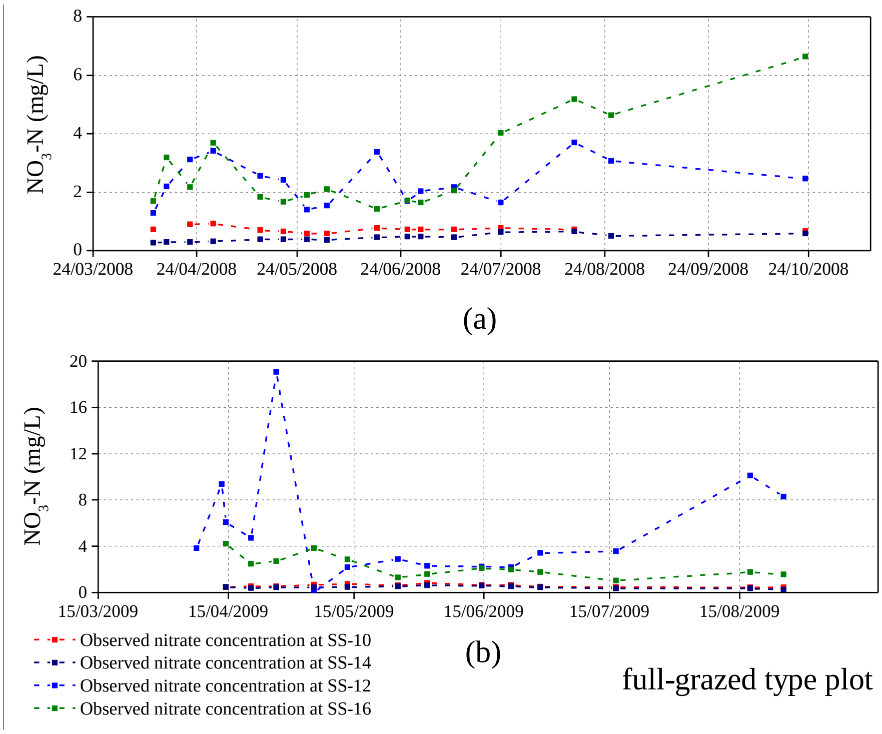

Figure 9: Observed nitrate groundwater concentrations at SS-10, SS-12, SS-14 & SS-16 for the years (a) 2008 and (b) 2009

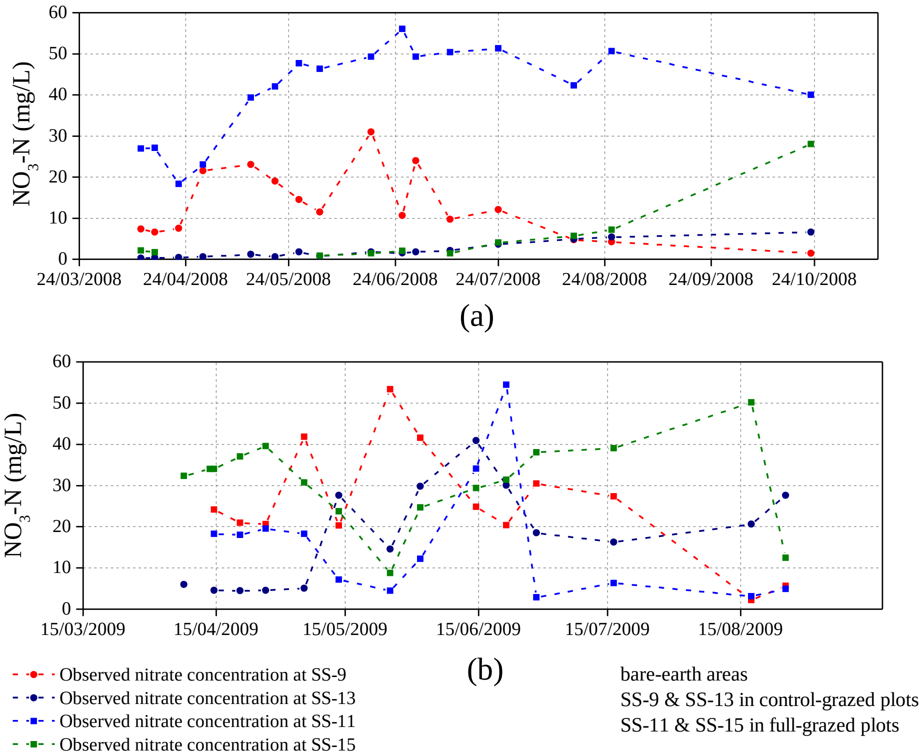

Figure 10: Observed nitrate groundwater concentrations for SS-9, SS-11, SS-13 & SS-15 for the years (a) 2008 and (b) 2009

3.4. Vadose zone modeling

HYDRUS-1D version 4.16 (Simunek et al., 2008) is a physically based numerical modeling program which allows simulating one-dimensional (1D) flow of water, heat, and solute in the variably saturated zone. This tool was used in the present study to estimate recharge and leaching of nitrate from the surface application of liquid hog manure.

Water flow: The variably saturated water flow was simulated in HYDRUS-1D using Richards equation (Richards, 1931) :

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(\psi)\left(\frac{\partial \psi}{\partial z}\right) - S\right] \tag{2}$$

where ψ [L] represents pressure head, θ [L^3L^{-3}] is the volumetric water content, t [T] represents time, z [L] is the elevation, S [$L^3L^{-3}T^{-1}$] is the sink term and unsaturated hydraulic conductivity is represented by $K(\psi)$ [LT^{-1}] which is a function of ψ and saturated hydraulic conductivity K_s [LT^{-1}]. The hydraulic conductivity, $K(\psi)$, and soil water retention, $\theta(\psi)$ functions were estimated based on van Genuchten-Mualem (VGM) model (Mualem, 1976; van Genuchten, 1980):

$$\theta(\psi) = \begin{cases} \theta_r + \frac{\theta_s - \theta_r}{[1+|\alpha h^n|]^m} & \psi < 0 \\ \theta_s & \psi \geq 0 \end{cases} \tag{3}$$

$$K(\psi) = K_s S_e \left[1 - \left(1 - S_e^{\frac{1}{m}}\right)^m\right]^2 \tag{4}$$

where θ_s [L^3L^{-3}] is the saturated water content, θ_r [L^3L^{-3}] is residual water content and α [L^{-1}], n [-] and m [-] are the shape empirical parameters, K_s [LT^{-1}] represents saturated hydraulic conductivity, and S_e [-] is the effective saturation.

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} \tag{5}$$

The estimation or the actual measurement of the VGM parameters (α, n, m, θ_s, θ_r and K_s) is complex, time-consuming and expensive. Hence, these parameters were estimated using a built-in function ROSETTA (Schaap et al., 2001b) which makes use of soil textures classified on the basis of USDA system.

Root water uptake: The Feddes-type function (Feddes et al., 1978) representing evapotranspiration effect to the water distribution was used to estimate the root water uptake flux. The default parameterization of 'Pasture' integrated into HYDRUS-1D representing the pasture crop type was used (parameters h_o, h_{opt}, h_2, and h_3 explained in next paragraph). The sink/source term mentioned in equation 2 was determined as per equation 6 below:

$$S(h) = \alpha(h)S_p \tag{6}$$

where S(h) [T^{-1}] represents the rate of root water uptake per unit volume of soil, α(h) [-] and S_p [T^{-1}] are root water coefficient and maximum or potential root water uptake rate respectively (Feddes et al., 1978). In equation 6, it was assumed that water uptake for soil being close to saturation is equal to zero. The 'close to saturation' condition is considered to be wetter than an arbitrary "anaerobiosis point", h_o. For pressure head less than the crop's wilting point (h_3), root water uptake is considered equal to zero. The optimal root water uptake is considered between the pressure head h_2 and h_{opt}. For pressure head between h_2 and h_3 and between h_o and h_{opt}, water uptake increases and decreases linearly with pressure head respectively. For pasture crop, h_o, h_{opt}, h_2, and h_3 values are listed in table 3.

Evapotranspiration: The estimation of potential evapotranspiration was done using the Penman-Monteith equation (equation 7) (Allen et al., 1998) for which the input data such as wind speed, daily average temperature, solar radiation, relative humidity were used.

$$\lambda\,\mathrm{ET} = \frac{\Delta(R_n - G) + \rho_a C_p \frac{e_s - e_a}{r_a}}{\Delta + \gamma\left(1 + \frac{r_s}{r_a}\right)} \tag{7}$$

where R_n [MT^{-3}] represents the net radiation, soil heat flux is represented by G, ($e_s - e_a$) [$ML^{-1}T^{-2}$] is the vapour pressure deficit of the air, ρ_a [ML^{-3}] is the average air density at any constant pressure, C_p [$L^2T^{-2}K^{-1}$] represents the specific heat of the air, the slope of saturation vapour pressure and temperature relationship is represented by Δ [$ML^{-1}T^{-2}K^{-1}$], γ [$ML^{-1}T^{-2}K^{-1}$] is the psychrometric constant, and r_s and r_a [TL^{-1}] are the (bulk) surface and aerodynamic resistances.

Soil freezing and thawing: The standard code of HYDRUS-1D version 4.16 (Simunek et al., 2008) was used in this study. The freezing and thawing of water inside the soil pores was not simulated with the standard code. However, a 'snow hydrology' function was used which assumed that precipitation was in the form of snow when the air temperature was below 2°C and in the form of rain when the air temperature was above 2°C and a linear transition occurred between these two limiting temperatures (Jarvis, 1989).

Snow water equivalent (SWE): HYDRUS-1D allows inputting an initial layer of snow on the ground that melts proportionally to the air temperature. Snow water equivalent can be defined as the amount of liquid water (in cm) in the snowpack if it is allowed to melt completely. The SWE for La Broquerie was not available for both years of study. However, Government of Manitoba (2008) reported the SWE range of 25 – 50 mm in 2008 and 2009 for most areas of southern Manitoba and . SWE of 50 mm was considered in this study for both years.

Solute transport: In a variably saturated rigid porous medium, the transport of solute in one-dimensional advective-dispersive manner is governed by the partial differential equation:

$$\frac{\partial\theta c_k}{\partial t} + \rho \frac{\partial\overline{c_k}}{\partial t} = \frac{\partial\left(\theta D\frac{\partial c_k}{\partial z}\right)}{\partial z} - \frac{\partial q c_k}{\partial z} + \emptyset_k - Sc_r \tag{8}$$

where θ [L^3L^{-3}] signifies the volumetric water content, c_k [ML^{-3}] and $\overline{c_k}$ [MM^{-1}] are concentration of solute in liquid and solid phase respectively, ρ [ML^{-3}] signifies the bulk density of soil, q [LT^{-1}] is the volumetric flux density, D [L^2T^{-1}] represents the hydrodynamic dispersion coefficient, $\emptyset$ [$ML^{-3}T^{-1}$] represents the chemical reaction of solutes involved in a sequential decay chain of first order, for example, nitrification of species of nitrogen, S [T^{-1}] is the sink term which represents the root water uptake in water flow equation, c_r [ML^{-3}] represent the sink term concentration, the chemical species (e.g NO_3^-, NH_4^+ and other major ions) are represented by the subscript k. Sc_r represents the passive root nutrient uptake (Liu et al., 2013b; Simunek et al., 2008). The nitrogen uptake by roots was simply estimated by multiplying root water uptake and soil mineral nitrogen concentration.

Nitrification of species of NH_4+ to the species of NO_3- is represented by the parameter $\emptyset$ in equation 9a and 9b and is obtained as follows for NH_4+ and NO_3- (Liu et al., 2013b)

$$\emptyset_{\mathrm{NH_4^+}} = -\mu_{w,\mathrm{NH_4^+}}\theta c_{\mathrm{NH_4^+}} - \mu_{s,\mathrm{NH_4^+}}\theta \bar{c}_{\mathrm{NH_4^+}} \tag{9a}$$

$$\emptyset_{\mathrm{NO_3^-}} = \mu_{w,\mathrm{NH_4^+}}\theta c_{\mathrm{NH_4^+}} + \mu_{s,\mathrm{NH_4^+}}\theta \bar{c}_{\mathrm{NH_4^+}} \tag{9b}$$

where μ_w [T^{-1}] and μ_s [T^{-1}] represent the rate (first order) constant for the solutes in liquid as well as solid phase respectively.

Assumptions: Nitrification of ammonium to nitrate was considered in the modeling process with an assumption that ammonium was directly transformed to nitrate instead of its intermediate conversion to nitrite. Nitrification from nitrite to nitrate is a very fast process and hence neglected (Hanson et al., 2006). Ammonium was assumed to adsorb on negatively charged soil particles based on linear adsorption isotherm also known as Henry's adsorption isotherm. Denitrification of NO_3 (nitrate) to N_2 (nitrogen gas) or N_2O (nitrous oxide) was not considered since it seldom occurs in unsaturated soil conditions. 25% of ammonium present in the slurry was assumed to be volatilized as ammonia during its surface application under the cold, humid conditions (Coppi, 2012). Surface runoff was neglected since it was unlikely to happen in coarse-textured soils with low soil water retention and flat terrains.

Initial and boundary conditions: The initial conditions for flow and solute transport model were assigned according to the observed soil moisture content, nitrate, and ammonium concentrations in the soil water at different depths.

“Atmospheric BC with surface runoff” was used as upper BC (Boundary Condition) since the meteorological (external) conditions controlled the potential water flux across the upper boundary. Few examples of external conditions controlling potential water flux could be the ponding of the surface due to rapid warming and frequent precipitation, large variation in temperature with the change of season and the dynamic moisture conditions of the soil. There was a significant seasonal groundwater fluctuation at the study site; hence “variable pressure head” was employed as the lower boundary condition which estimated the flux depending on the position of the groundwater table.

For the upper boundary, Cauchy (third-type) boundary condition was used to describe the concentration flux at the soil surface (equation 10) whereas a free drainage boundary condition was used as a bottom boundary condition to allow free drainage of solute flux in the soil profile.

$$-\theta D \frac{\partial c_k}{\partial z} + q c_k = q_0 c_{k0} \tag{10}$$

where q_o and c_o represent the water flux and concentration of the infiltrating fluid [ML^{-3}].

3.5 Model calibration

Model calibration can be defined as the process of manipulating the model input parameters such as water flow parameters, solute transport parameters, initial conditions or boundary conditions within a reasonable range such that the model becomes tuned for a particular problem and yields results with a close match to the observations e.g. soil moisture content, pressure heads, etc. (Šimůnek et al., 2012). The prediction of VGM parameters in HYDRUS-1D was made using ROSETTA. Since ROSETTA was developed using soil samples from the USA and European countries, the program could generate an inaccurate prediction of VGM parameters if the soil samples were taken from other places such as Canada (Simunek et al., 2008). Hence, to provide an authentic description of the soil properties, 'inverse modeling' was implemented which used a Marquardt-Levenberg (Marquardt, 1963) type of technique based on a weighted least-squares approach. It used the observed and/or solute transport data for the inverse estimation of soil hydraulic, solute and/or heat transport parameters (Šimůnek et al., 2012). The VGM parameters θ_s (saturated water content), θ_r (residual water content), α, n and m (shape empirical parameters) and K_s (saturated hydraulic conductivity) were initially estimated using ROSETTA (table 2). These parameters were then calibrated based on observed soil moisture data at different depths.

3.6 Model performance

Model calibration and performance were evaluated by comparing the observed and simulated soil moisture and groundwater nitrate concentration data for different time periods using various quantitative measures of uncertainty, namely, root mean square error (RMSE), Nash–Sutcliffe efficiency (NSE) (Nash and Sutcliffe, 1970) and mean error (ME). A general assumption behind these model evaluation criteria is that the simulated and observed dataset are continuous such that the data values are not restricted to some particular values. Although the observed data are not contentious since they are based on hand sampling with an interval of two weeks (Coppi, 2012). Thus, they have equal intervals and are handled as contentious data here. Thus, the three quantitative measures are used in this research.

$$\mathrm{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(M_i - S_i)^2} \tag{11}$$

where n is the number of simulated and observed data set to be compared, M_i and S_i are the observed and simulated data set points. For a perfect match between the observed and simulated dataset, RMSE should be 0.

$$\mathrm{NSE} = 1 - \frac{\sum_{i=1}^{n}(M_i - S_i)^2}{\sum_{i=1}^{n}(M_i - \bar{M})^2} \tag{12}$$

where $\bar{M}$ represents the mean of observed dataset points.

$$\mathrm{ME} = \frac{1}{n}\sum_{i=1}^{n}(M_i - S_i) \tag{13}$$

In addition to the above measures of uncertainty, the model performance for this study was also evaluated by the coefficient of determination, R, which is defined as the square of the correlation coefficient, r:

$$R = r^2 = \left(\frac{\sum_{i=1}^{n}(M_i - \bar{M})(S_i - \bar{S})}{\sqrt{\sum_{i=1}^{n}(M_i - \bar{M})}\,\sqrt{\sum_{i=1}^{n}(S_i - \bar{S})}}\right)^2 \tag{14}$$

where $\bar{M}$ and $\bar{S}$ are the mean values of observed and simulated date set respectively. The coefficient of correlation lies between 0 and 1. A value of 0 indicates no correlation between observations and simulations where as a value of 1 implies a strong correlation and a perfect fit between the two datasets.

3.7 Sensitivity analysis

A sensitivity analysis represents how different sources of uncertainty in the input parameter could be apportioned such that their effect can be quantified on the model output, and to screen the sensitive parameters for calibration.

Robustness is used in this research not by its original means but by the definition that the model was considered to be robust if the method chosen provided the results which were reliable and were low-sensitive (<10%) to the changes in input parameters. This definition was also used by Holländer et al. (2016) where robustness was defined as the ability of their recharge estimation method to provide a reliable recharge estimate although most input data were derived from different degrees of uncertainty.

The fundamental targets, chosen for sensitivity analysis were soil moisture and nitrate leaching fluxes since a recent study by Holländer et al. (2016) showed that the estimated groundwater recharge was more sensitive to alterations in soil moisture values than to the soil temperature. Since the nitrate leaching fluxes are highly dependent on recharge, their sensitivity to model parameters was also analysed. The parameters *n*, α, and K_s were varied to determine their impact on the simulated soil moisture, recharge and nitrate leaching. The vegetation parameters, as shown by Liu et al. (2013a) had a minimal impact on groundwater recharge estimates than changes accounting to the VGM parameters. Therefore, vegetation parameters were not considered in the sensitivity analysis of recharge.

One of the most common and simplest approaches to carrying out sensitivity analysis is changing one factor at a time to see the effect the output (Czitrom, 1999). While changing one parameter at a time, all other parameters are kept constant. The feasibility and applicability of this method have been testified in a recent study conducted by Oostrom et al. (2013) who evaluated the sensitivity of the variant cross-correlation parameters. Therefore, the calibrated recharge was considered as the baseline for the sensitivity analysis while changing α and n by ±5%, ±10% and ±20% at each time. Ks was changed at a larger scale (Ks*2, Ks/2, Ks*4, Ks/4) to account for soil heterogeneity and thus its impact on recharge and nitrate leaching.

3.8 Regionalisation of point estimates

The leaching flux of nitrate at 16 SSs was regionalised for the entire study site (40 ha) using ArcGIS 10.2 built-in function 'Cokriging' (ESRI, 2014). Kriging makes use of only one data type at the target location to map the surfaces. Therefore, the existing spatial correlations between secondary data points and primary attribute are not taken into account using kriging (Journel, 1989). Cokriging, being an extension of Ordinary Kriging can potentially manage the estimation process from several data types (e.g. manure application and leaching flux) to improve the performance of regionalisation. Hence, it was considered as a potential method in the La Broquerie case. The Cokriging equation can be expressed as following:

$$u_0 = \sum_{i=1}^{n} a_i u_i + \sum_{j=1}^{m} b_j v_j \tag{15}$$

where u_o is the estimate at the grid node or at location 0; u_i is the primary data at n locations nearby, v_j is secondary data at m locations, a_i and b_j are the undetermined weights assigned to u_i and v_j and varies between 0 and 1. Unbiasedness in the estimates is assured if the weights of primary data sum to 1 and that of secondary data sum to 0 (Yalçin, 2005):

$$\sum_{i=1}^{n} a_i = 1 \text{ and } \sum_{\mathrm{j}=1}^{\mathrm{m}} b_j = 0 \tag{16}$$

The additional cross-correlation between various parameters makes Cokriging to perform better than Kriging (Ahmadi and Sedghamiz, 2008). The primary variable of interest was nitrate flux that leached below the root zone. Cross-correlations between nitrate flux and manure application were considered to improve the prediction of resulting map. Since the soil type at study area was mainly loamy to gravelly sand which was considered to be highly uniform and moreover, the distribution difference of precipitation at study area was ignored due to the small size of the study area (40 ha).

Inverse Distance Weighing (IDW) is a deterministic interpolation method by which weights are assigned to the points where interpolation of any variable has to be done based on the known value of that variable at neighboring point locations in the study area. The value of weights was calculated as the inverse of the distance between the point where interpolation has to be done and the neighbouring points of known value of a variable of interest.

$$u\ (x) = \frac{\sum_{i=1}^{N} w_i(x) u_i}{\sum_{i=1}^{N} w_i(x)} \tag{17}$$

$$w_i = \frac{1}{d\ (x, x_i)^p} \tag{18}$$

where *u* is the variable to be interpolated using a known point *x*, *i* represents the set of points where interpolation has to be done and their corresponding weights represented by *w*, *d* represents the distance between a known point and the point where value of variable is unknown, *p* represents a power parameter (Bartier and Keller, 1996).

Natural Neighbor (NN) interpolation method is also based on weights assigned to an unknown point, similar to IDW. However, these weights are assigned using closest neighboring points.

The interpolated map using estimated nitrate leaching fluxes at 16 SSs did not extend through the entire study area but only a limited boundary of those 16 SSs. To overcome this problem, 15 virtual SSs were assumed (17-31) through the boundary of the study area (in different plots) such that a resulting interpolated map that covers the entire study area could be obtained. It was assumed that nitrate leaching fluxes for similar plots were equal and hence the virtual SSs were assigned equal flux values corresponding to one of the 16 SSs depending on the plot type.

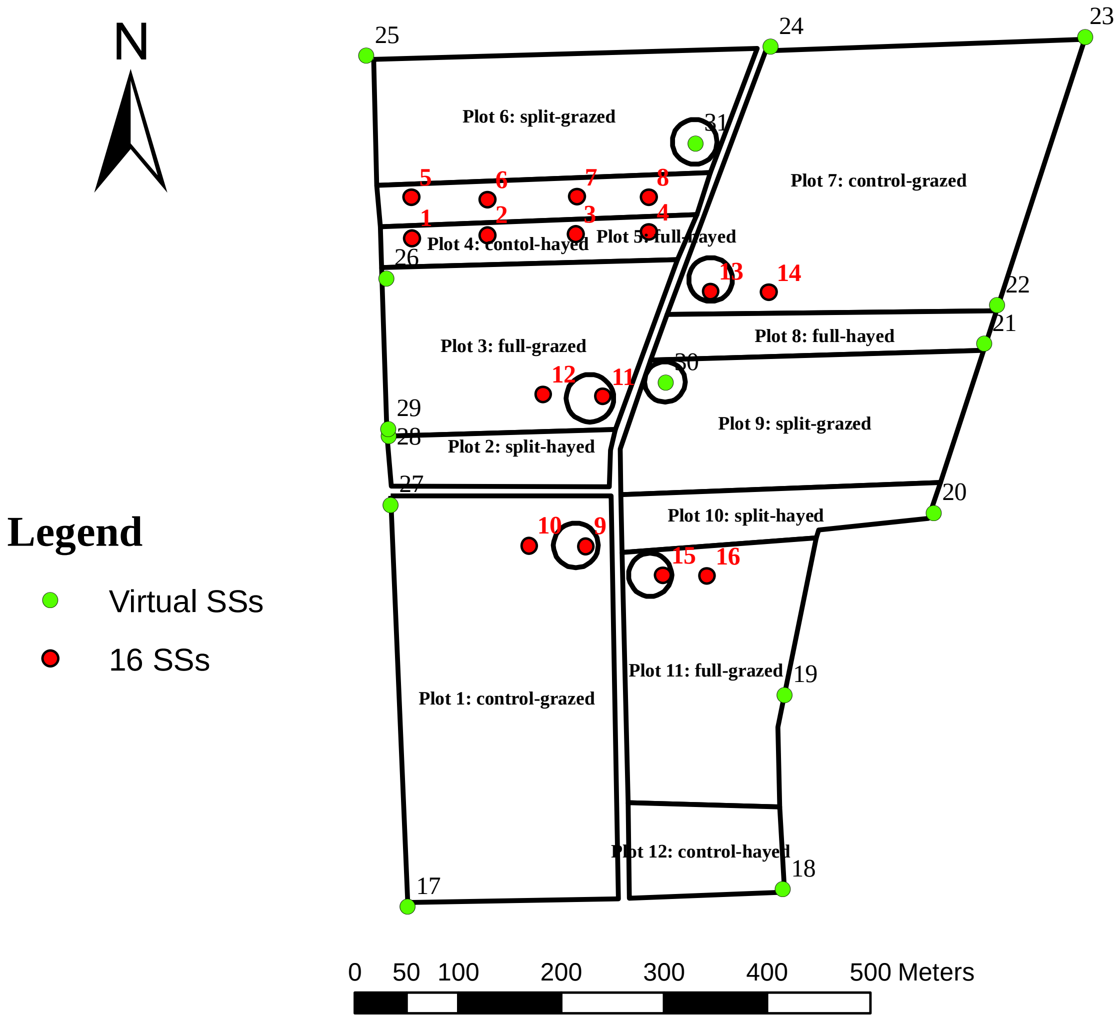

Figure 11: Data points used (16 SSs and additional virtual SSs) to generate an interpolated map that represents the nitrate leaching flux for the entire study area

Chapter 4: Parameterization

Various types of soil hydraulic, solute as well as heat transport parameters are required as input for variably-saturated models. The unsaturated soil hydraulic properties impact the soil moisture characteristic curve as well as the hydraulic conductivity function. A soil moisture characteristics curve, also known as soil water retention curve can be defined as a relationship between soil water content, θ and matric suction, ψ (Fredlund and Xing, 1994). The unsaturated hydraulic conductivity $K(\theta)$ is dependent on the water content of the soil system which reduces with increasing matric suction (ψ) in soil and is required for modeling water and solute transport in the soil. However, its measurement in the field as well as in laboratory is difficult, expensive and time-consuming. Therefore various analytical models are implemented in HYDRUS-1D which can estimate the unsaturated hydraulic properties (Simunek et al., 2008) such as Brooks and Corey (1964), van Genuchten (1980), Vogel and Cislerova (1988), Kosugi (1996) and Durner (1994). The van-Genuchten-Mualem model was explained in section 3.4 which makes the use of parameters θ_s (saturated water content), θ_r (residual water content), α, n and m (shape empirical parameters) and K_s (saturated hydraulic conductivity).

Soil hydraulic parameters: The VGM parameters estimated using ROSETTA (Schaap et al., 2001a) are listed in table 2 for all the SSs.

Table 2: VGM parameters estimated by PTF

Soil Sampling location	Depth [cm]	θ_r [cm³/cm³]	θ_s [cm³/cm³]	α [1/cm]	n [-]	K_s [cm/d]
	0 to 30	0.04	0.33	0.03	1.82	81.0
SS-1	30 to 60	0.03	0.25	0.04	1.91	30.9
	60 to 90	0.04	0.26	0.03	2.85	179.5
	90 to 200	0.04	0.26	0.03	2.85	167.4
	0 to 30	0.04	0.33	0.03	1.82	81.0
SS-2	30 to 60	0.03	0.25	0.04	1.91	30.9

	60 to 90	0.04	0.26	0.03	2.85	179.5
	90 to 200	0.04	0.26	0.03	2.85	167.4
	0 to 30	0.04	0.33	0.03	1.82	81.0
SS-3	30 to 60	0.03	0.25	0.04	1.91	30.9
	60 to 90	0.04	0.26	0.03	2.85	179.5
	90 to 200	0.04	0.26	0.03	2.85	167.4
	0 to 30	0.04	0.33	0.03	1.82	81.0
SS-4	30 to 60	0.03	0.25	0.04	1.91	30.9
	60 to 90	0.04	0.26	0.03	2.85	179.5
	90 to 200	0.04	0.26	0.03	2.85	167.4
	0 to 30	0.04	0.33	0.04	1.68	60.5
SS-5	30 to 60	0.04	0.25	0.03	2.37	64.3
	60 to 90	0.04	0.26	0.03	2.84	179.3
	90 to 200	0.04	0.26	0.03	2.86	171.1
	0 to 30	0.04	0.33	0.04	1.68	60.5
SS-6	30 to 60	0.04	0.25	0.03	2.37	64.3
	60 to 90	0.04	0.26	0.03	2.84	179.3
	90 to 200	0.04	0.26	0.03	2.86	171.1
	0 to 30	0.04	0.33	0.04	1.68	60.5
SS-7	30 to 60	0.04	0.25	0.03	2.37	64.3
	60 to 90	0.04	0.26	0.03	2.84	179.3
	90 to 200	0.04	0.26	0.03	2.86	171.1
	0 to 30	0.04	0.33	0.04	1.68	60.5
SS-8	30 to 60	0.04	0.25	0.03	2.37	64.3
	60 to 90	0.04	0.26	0.03	2.84	179.3
	90 to 200	0.04	0.26	0.03	2.86	171.1

Table 3: Root water uptake coefficients (Simunek et al., 2008)

Plant	**h_o (cm)**	**h_{opt} (cm)**	**h_{2H} (cm)**	**h_{2L} (cm)**	**h_3 (cm)**
Pasture	-10	-25	-200	-800	-8000

Solute transport parameters: For modeling solute transport process in HYDRUS-1D, nitrate was assumed to not adsorb on the soil particle due to its negative charge. Whereas, ammonium adsorbed to the soil particles with an adsorption coefficient (K_D) of 3.5 cm^3 g^{-1} (Hanson et al., 2006). The nitrification rate, μ_w (day^{-1}), also known as first-order decay constant in the nitrification chain reaction was initially chosen as 0.2 day^{-1} (Hanson et al., 2006) but was then calibrated for each layer based on the observed nitrate concentrations in groundwater. The longitudinal dispersivity was considered as one-tenth (20 cm) of transport length (200 cm) (Gelhar et al., 1992; Hanson et al., 2006).

Model initial conditions:

Table 4: Initial N conditions at the study site (modified after Coppi, 2012)

Plot	Depth (cm)	NO_3^--N (kg ha^{-1})			NH_4^+-N (kg ha^{-1})			Total N (kg ha^{-1})		
		2007	2008	2009	2007	2008	2009	2007	2008	2009
Control grazed	0-30	7.46	9.10	21.80	9.31	10.73	9.09	16.77	19.83	30.89
	30-60	2.50	1.62	11.74	1.97	3.36	4.72	4.47	4.98	16.46
	60-90	0.84	0.00	6.72	1.13	1.68	2.18	1.97	1.68	8.91
	90-200	0.88	0.00	3.50	0.81	1.41	1.94	1.69	1.41	5.44
Full grazed	0-30	10.23	22.71	112.04	7.71	10.30	12.41	17.94	33.01	124.45
	30-60	2.65	1.62	19.62	2.63	4.38	6.02	5.29	6.00	25.64
	60-90	1.81	0.00	8.69	1.09	1.52	2.53	2.90	1.52	11.22
	90-200	1.98	0.00	6.23	0.79	1.76	1.98	2.78	1.76	8.21
Control hayed	0-30	4.66	5.50	43.70	8.39	9.82	15.21	13.05	15.31	58.91
	30-60	3.25	1.46	12.99	1.37	2.52	5.96	4.62	3.98	18.95
	60-90	0.81	0.00	7.37	0.96	1.47	2.54	1.78	1.47	9.91
	90-200	0.85	0.00	1.70	0.60	1.36	2.15	1.44	1.36	3.85
Full hayed	0-30	6.51	9.07	121.14	13.28	11.82	14.69	19.79	20.89	135.82
	30-60	1.55	0.00	19.73	1.51	3.35	4.79	3.06	3.35	24.51
	60-90	0.83	0.00	6.98	0.88	1.58	1.73	1.71	1.58	8.71
	90-200	0.93	0.00	3.60	0.73	1.61	1.63	1.66	1.61	5.23

Chapter 5: Results

5.1 Water-flow model calibration

The observed soil moisture content at 15, 45, 75 and 105 cm depths for SS-1 to SS-8 was used for calibration. Simulated and calibrated soil moisture content at SS-3 ranged from dry condition at ~0.05 cm^3/cm^3 to fully saturated conditions at 0.30 to 0.35 cm^3/cm^3 (Figure 12). The simulated soil moisture content at the other SSs are very similar and are given in Appendix-B.

Comparison of VGM parameters estimated by PTF and those by inverse calibration showed small differences in the residual and saturated soil moisture contents (θ_r and θ_s) as well as in α values, whereas n values were changed significantly (both increased and decreased) after calibration. For example, θ_r, θ_s and α values, before and after calibration, did not change significantly for SS-3, whereas n decreased (1.82 to 1.58) for layer 1 and increased (2.85 to 5) for layer 3 (tables 2 and 5).

The difference in observed and simulated soil moisture and soil temperature were analysed by means of RMSE between 0.7% and 5%, and between 1.26 and 5.36 respectively, NSE between 0.39 and 0.99, and between 0.55 and 0.97 respectively (table 6). The ME between the observed and simulated moisture content was always below 0.01 cm^3/cm^3 which showed no tendency for under-prediction and over-prediction. However, the ME between the observed and simulated soil temperatures was between -2.96°C and 2.14°C.

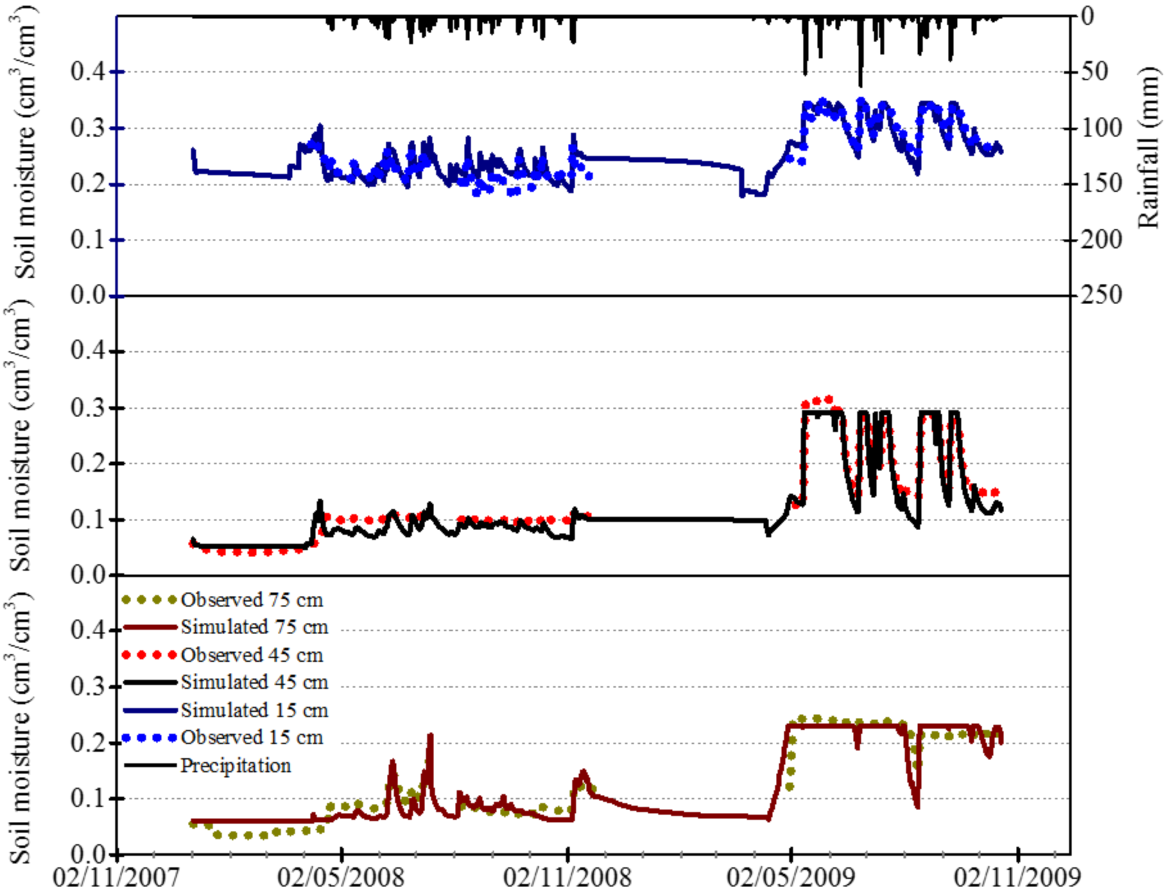

Figure 12: Observed v/s simulated soil moisture contents at depths 15, 45 and 75 cm

Table 5: VGM parameters after calibration

Soil Sampling location	Depth [cm]	θ_r [cm^3/cm^3]	θ_s [cm^3/cm^3]	α [1/cm]	n [-]	K_s [cm/d]
SS-1	0 to 30	0.04	0.42	0.002	1.96	158.0
	30 to 60	0.02	0.26	0.02	2.80	30.0
	60 to 90	0.04	0.21	0.03	2.85	179.5
	90 to 200	0.04	0.26	0.03	2.85	200.0
SS-2	0 to 30	0.04	0.33	0.03	1.81	81.0
	30 to 60	0.03	0.25	0.03	3.57	30.9
	60 to 90	0.04	0.25	0.03	4.55	179.5
	90 to 200	0.04	0.21	0.06	1.99	167.4
SS-3	0 to 30	0.09	0.34	0.03	1.58	81.0
	30 to 60	0.03	0.28	0.05	2.10	30.9
	60 to 90	0.04	0.23	0.05	5.00	179.5
	90 to 200	0.04	0.26	0.03	1.50	167.4
SS-4	0 to 30	0.04	0.24	0.01	2.05	81.0
	30 to 60	0.03	0.23	0.03	4.69	45.0
	60 to 90	0.01	0.26	0.04	3.51	179.5
	90 to 200	0.04	0.22	0.09	2.52	167.4
SS-5	0 to 30	0.04	0.31	0.01	1.80	100.0
	30 to 60	0.03	0.31	0.02	2.44	30.9
	60 to 90	0.04	0.28	0.03	1.47	179.5
	90 to 200	0.04	0.25	0.03	2.85	167.4
SS-6	0 to 30	0.02	0.42	0.01	2.70	100.0
	30 to 60	0.03	0.34	0.02	2.34	57.6
	60 to 90	0.04	0.25	0.05	3.68	185.3
	90 to 200	0.04	0.25	0.03	2.85	167.4
SS-7	0 to 30	0.04	0.32	0.02	1.90	81.0
	30 to 60	0.03	0.29	0.02	4.50	30.9
	60 to 90	0.04	0.25	0.03	4.00	179.5
	90 to 200	0.04	0.26	0.03	2.50	167.4
SS-8	0 to 30	0.04	0.32	0.02	1.90	81.0
	30 to 60	0.03	0.33	0.02	2.67	30.9
	60 to 90	0.04	0.25	0.03	4.00	179.5
	90 to 200	0.04	0.26	0.03	2.50	167.4

Table 6: Model performance

		Soil Moisture			Soil Temperature		
	Depth [cm]	RMSE [cm^3/cm^3]	ME [cm^3/cm^3]	NSE [-]	RMSE [°C]	ME [°C]	NSE [-]
SS-1	15	0.042	-0.003	0.96	4.80	-1.76	0.55
	45	0.032	-0.001	0.84	3.18	-1.15	0.88
	75	0.027	-0.005	0.78	2.33	-0.52	0.92
	105	-	-	-	1.87	-0.06	0.94
SS-2	15	0.021	0.0007	0.92	5.36	-2.96	0.66
	45	0.016	-0.0015	0.95	2.77	-1.22	0.88
	75	0.038	-0.003	0.81	2.61	1.38	0.83
	105	-	-	-	1.85	0.33	0.88
SS-3	15	0.018	-0.003	0.99	3.88	-2.55	0.71
	45	0.025	0	0.88	2.52	-1.69	0.93
	75	0.029	0.002	0.83	1.72	-0.87	0.96
	105	0.014	0	0.39	1.26	-0.44	0.97
SS-4	15	0.022	0.001	0.79	N/A	N/A	N/A
	45	0.024	0	0.87	N/A	N/A	N/A
	75	0.028	-0.005	0.93	N/A	N/A	N/A
	105	-	-	-	N/A	N/A	N/A
SS-5	15	0.028	0	0.87	4.05	-0.45	0.75
	45	0.034	0.001	0.86	2.64	0.50	0.86
	75	0.031	-0.001	0.40	2.61	1.38	0.83
	105	0.029	0	0.87	3.01	2.14	0.73
SS-6	15	0.033	-0.002	0.94	2.84	-0.17	0.92
	45	0.029	-0.007	0.92	2.17	-0.03	0.94
	75	0.018	-0.003	0.96	1.97	0.45	0.94
	105	-	-	-	2.07	0.90	0.93
SS-7	15	0.026	-0.005	0.89	2.72	-0.20	0.93
	45	0.032	-0.002	0.86	1.96	0.08	0.95
	75	0.033	0.009	0.90	1.84	0.57	0.95
	105	0.034	0.008	0.81	2.04	1.03	0.93
SS-8	15	0.028	0.004	0.85	N/A	N/A	N/A
	45	0.026	0.006	0.89	N/A	N/A	N/A
	75	0.050	0.024	0.68	N/A	N/A	N/A
	105	0.007	-0.003	0.72	N/A	N/A	N/A

N/A: Observed data were not available.

5.2 Recharge

The recharge estimated at SS-3 using the VGM parameters and after carrying out inverse calibration was simulated to be 150 mm and 256 mm for years 2008 and 2009 respectively and the corresponding recharge-precipitation for both the years was calculated as 32.7% and 49% respectively. In general, for all SSs (1-8) where recharge was estimated, its value varied between 119 and 186 mm for 2008 and between 227 and 279 mm for the year 2009 (table 7).

Table 7: Recharge (mm) and recharge-precipitation ratio (%) for SS-1 to SS-8 in years 2008 and 2009

		Recharge (mm)		**Recharge-Precipitation ratio (%)**	
	Sensor Station	**2008**	**2009**	**2008**	**2009**
After Calibration	1	169	264	36.8	50.6
	2	166	279	36.1	53.4
	3	150	256	32.7	49.0
	4	186	256	40.5	49.0
	5	145	227	31.6	43.5
	6	119	238	25.9	45.6
	7	164	254	35.7	48.7
	8	153	254	33.3	48.7
	Min	119	227	25.9	43.5
	Max	186	279	40.5	53.4

The recharge-precipitation ratio for all the SSs was simulated between 25.9% to 40.5% for the year 2008 and between 43.5% to 53.4% for 2009. Recharge estimated for SS-3, using VGM parameters directly derived from PTF was 165 mm (10% larger than the calibrated value of 150 mm) and 279 mm (8.9% larger than the calibrated value of 256 mm) for years 2008 and 2009 respectively.

Most of the recharge, for SS-3, occurred during the period of snow-melt in April 2008. About 42 mm of it occurred during this month which was about 28% of total recharge in 2008, whereas for the next year, 2009, about 110 mm of recharge occurred during the month of

June when due to high precipitation, water table rose close to the surface leading a shorter path for the incoming flux to meet the water table.

5.3 Sensitivity analysis

During sensitivity analysis, the VGM parameters *n*, *α*, and K_s were evaluated as explained in section 3.4 for the depth 45 cm, within the root zone (50 cm depth). The parameter which showed the largest sensitivity to soil moisture content was *n* (Figure 13). The parameter *α* showed a lower sensitivity than *n* and the least sensitive parameter to soil moisture content was determined to be K_s (Figure 13). For SS-3 (depth: 45 cm), changing *n* from -20% to +20% impacted the soil moisture content from -28% to +149% for 2008 and from -12% to +121% for the year 2009. However, the change in recharge by changing *n* from -20% to +20% was less as compared to the changes in soil moisture content.

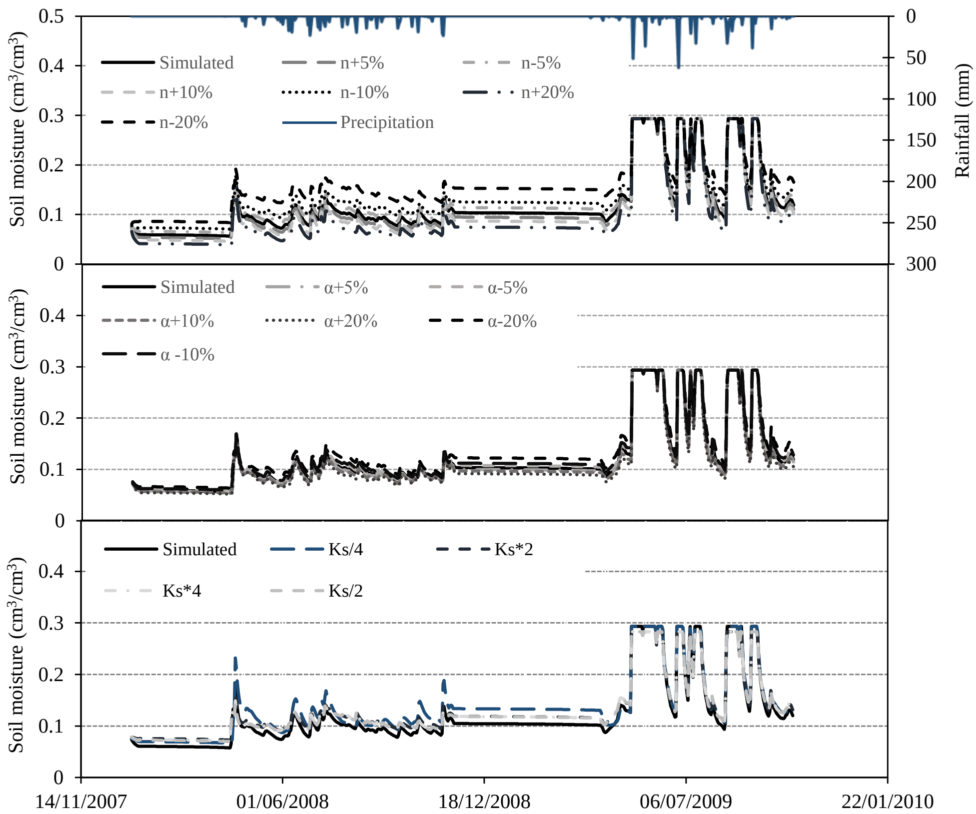

Figure 13: Sensitivity analysis of α, n and K_s on soil moisture content at 45 cm depth

In 2008, recharge was reduced by 0.8% when n was reduced by 20% whereas it increased by 0.8% when n was increased by 20%. A similar behaviour of deviation in recharge was achieved for the year 2009. It increased by 4.2% on increasing n by 20% whereas it reduced by 6.1% when n was reduced to $0.8 \times n$ (reduced by 20%). Therefore, the results indicated at least one magnitude smaller changes in recharge estimates as compared to soil moisture.

As stated earlier, parameter α showed a less sensitive behaviour on soil moisture as well as on recharge estimates. On increasing α by 20%, the recharge was reduced by 1.2% in 2008 and increased by 1.7% in 2009 whereas a reverse behaviour was observed on reducing α by 20%, recharge increased by 1.6% in 2008 and reduced by 3.6% in 2009.

Changing K_s at a larger scale accounted for greater changes in groundwater recharge. Ks*2 resulted in 4% increase in recharge, Ks/2 lead to 3.6% decrease, Ks*4 increased it by 10% and lastly Ks/4 reduced the groundwater recharged by 9.6%.

5.4 Water balance

A water balance for the La Broquerie Pasture and Swine Manure Management Site was evaluated for the years 2008 and 2009 using the calibrated model. The daily simulated soil moisture contents, evapotranspiration and water fluxes at 50 cm depth were used for the water balance analysis since the depth of 50 cm represented the end of the root zone. The total precipitation at the study site for years 2008 and 2009 was 488 mm and 542 mm respectively (Figure 14) whereas the actual evapotranspiration simulated by HYDRUS-1D was 259.2 mm (53.2% of precipitation) for 2008 and 221.4 mm for 2009 (40.9% of precipitation).

The water storage changes were determined on a monthly basis for both the years. The summer months were dry for both years which resulted in a deficit in the water balance. The surplus water in the soil was observed during the periods of snowmelt in April-May or during the events of heavy rainfall for both the years (table 8).

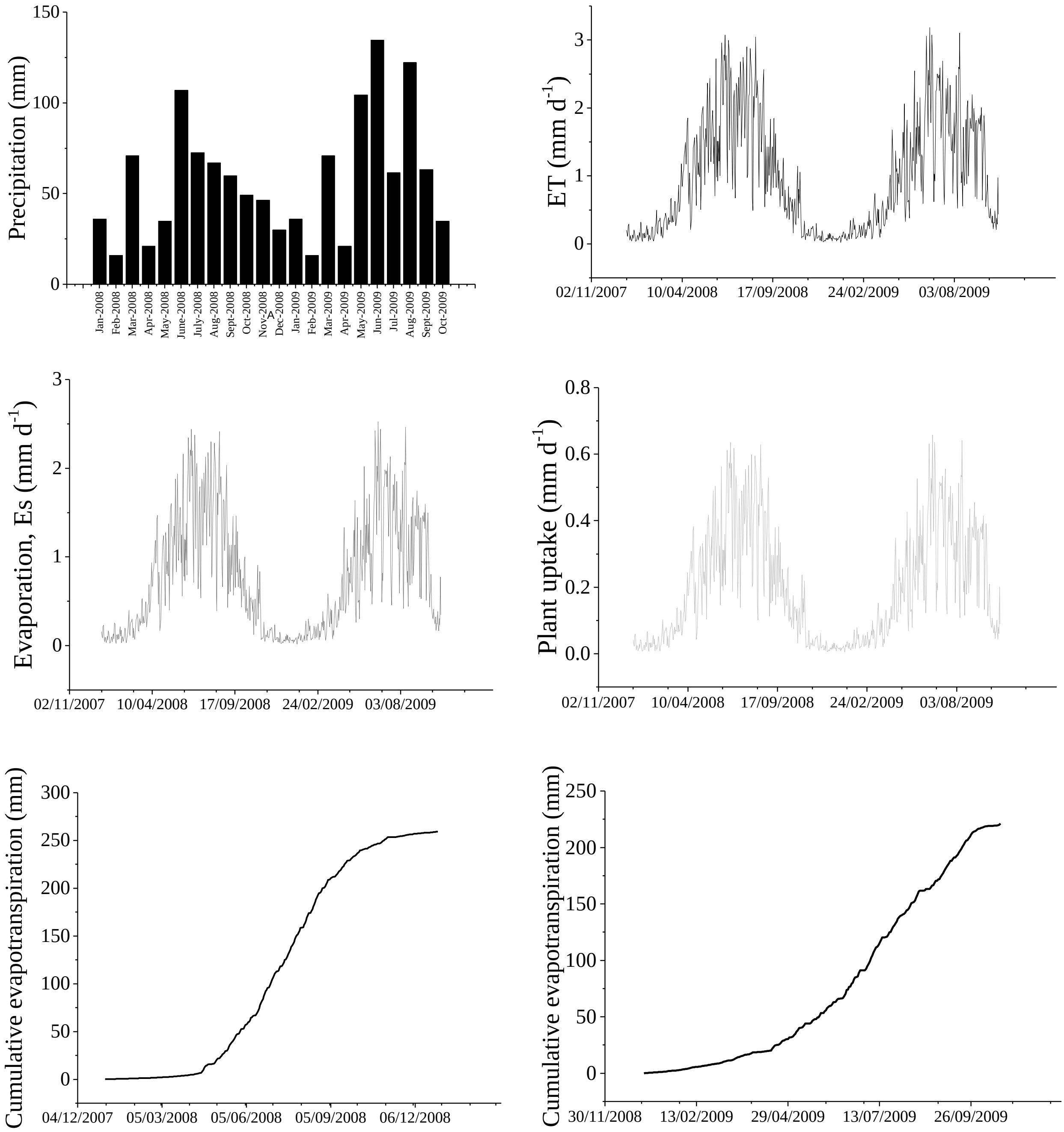

Figure 14: Monthly precipitation, actual evapotranspiration (AET), simulated root water uptake and evaporation

Table 8: Monthly water balance for 2008 and 2009 (SS-3)

Month-Year	Infiltration (mm)	ET (mm)	Downward flux at 50 cm depth (mm)	Upward flux at 50 cm depth (mm)	Recharge (mm)	Storage changes (mm)
Jan-08	0.0	0.8	0.3	0.2	0.1	-0.9
Feb-08	0.0	1.0	0.0	0.1	-0.1	-0.9
Mar-08	11.0	2.2	0.0	0.0	0	8.8
Apr-08	120.0	12.2	62.0	0.0	42	45.9
May-08	27.0	36.3	8.0	0.0	12	-17.3
Jun-08	63.8	43.7	11.0	0.0	15	9.1
Jul-08	65.0	55.2	18.0	3.0	19	-5.2
Aug-08	58.0	52.3	7.0	1.0	10	-0.3
Sep-08	42.0	29.5	12.0	0.0	12	0.5
Oct-08	27.0	15.3	18.2	0.0	22.2	-6.5
Nov-08	25.0	7.7	18.0	0.0	18	-0.7
Dec-08	0.0	3.0	0.0	0.0	0	-2.9
Jan-09	0.0	2.9	0.0	0.0	0	-2.8
Feb-09	0.0	5.4	0.0	0.0	0	-5.3
Mar-09	0.0	10.2	0.0	0.0	0	-10.2
Apr-09	9.9	13.2	0.7	10.7	-10	6.7
May-09	101.0	25.8	84.5	43.0	41.5	33.7
Jun-09	114.0	33.8	75.0	10.4	64.6	15.5
Jul-09	54.0	48.5	79.0	46.0	33	-27.5
Aug-09	110.0	32.1	66.0	11.7	54.3	23.6
Sep-09	60.0	43.0	68.0	10.4	57.6	-40.5
Oct-09	12.0	6.5	15.6	0.0	15.6	-10.1
Total						
2008	438.8	259.2	154.5	4.5	150.0	29.6
2009	460.9	221.4	388.9	132.4	256.5	-17.0

5.5 Solute transport model calibration

The solute transport parameters related to N transformations were calibrated based on the observed nitrate concentration in groundwater at all SSs for 2008 and 2009. The calibrated parameters were ammonium adsorption coefficient, K_D (cm^3g^{-1}) and nitrification rate, μ_w (day^{-1}), also known as first-order decay constant in the nitrification chain reaction. The detailed parameters for each layer for all SSs can be seen in table 9. It can be seen in table 9 that K_D values obtained after calibration varied between 1.5 and 4.5 cm^3g^{-1} whereas μ_w varied between 0.1 and 0.7 day^{-1} for different SSs.

Table 9: Solute transport (N transformations) parameters obtained after model calibration

Soil Sampling location	Depth [cm]	Ammonium adsorption coefficient, K_D (cm^3g^{-1})	First-order decay constant, μ_w (day^{-1})
	0 to 30	2.3	0.2
SSs-1, 2, 3 & 4	30 to 60	3.5	0.2
	60 to 90	3.5	0.2
	90 to 200	3.5	0.1
	0 to 30	1.5	0.1
SSs-5, 6, 7 & 8	30 to 60	3.5	0.2
	60 to 90	2.5	0.4
	90 to 200	3.5	0.2
	0 to 30	3.5	0.4
SS-9	30 to 60	4.5	0.4
	60 to 90	3.5	0.7
	90 to 200	3.5	0.2
	0 to 30	3.5	0.2
SS-10	30 to 60	3.5	0.1
	60 to 90	3.5	0.2
	90 to 200	3.5	0.4
	0 to 30	3.5	0.4
SS-11	30 to 60	4.5	0.4
	60 to 90	4.5	0.4
	90 to 200	3.5	0.1
	0 to 30	4.5	0.2
SS-13	30 to 60	4.5	0.3
	60 to 90	3.5	0.2
	90 to 200	4.5	0.3

	0 to 30	3.5	0.2
SS-14	30 to 60	3.5	0.2
	60 to 90	3.5	0.1
	90 to 200	3.5	0.1
	0 to 30	3.5	0.2
SS-15	30 to 60	3.5	0.2
	60 to 90	3.5	0.2
	90 to 200	3.5	0.2
	0 to 30	3.5	0.2
SS-16	30 to 60	3.5	0.2
	60 to 90	3.5	0.5
	90 to 200	3.5	0.2

The differences in observed and simulated nitrate concentration in groundwater were analysed by means of RMSE between 0.023 and 5.12 mg NO_3-N L^{-1}, NSE between 0.66 and 0.96 and the ME between -1.03 mg NO_3-N L^{-1} and 1.05 mg NO_3-N L^{-1} (table 10). Figures 15-20 show the observed versus simulated nitrate concentration in groundwater for all SSs.

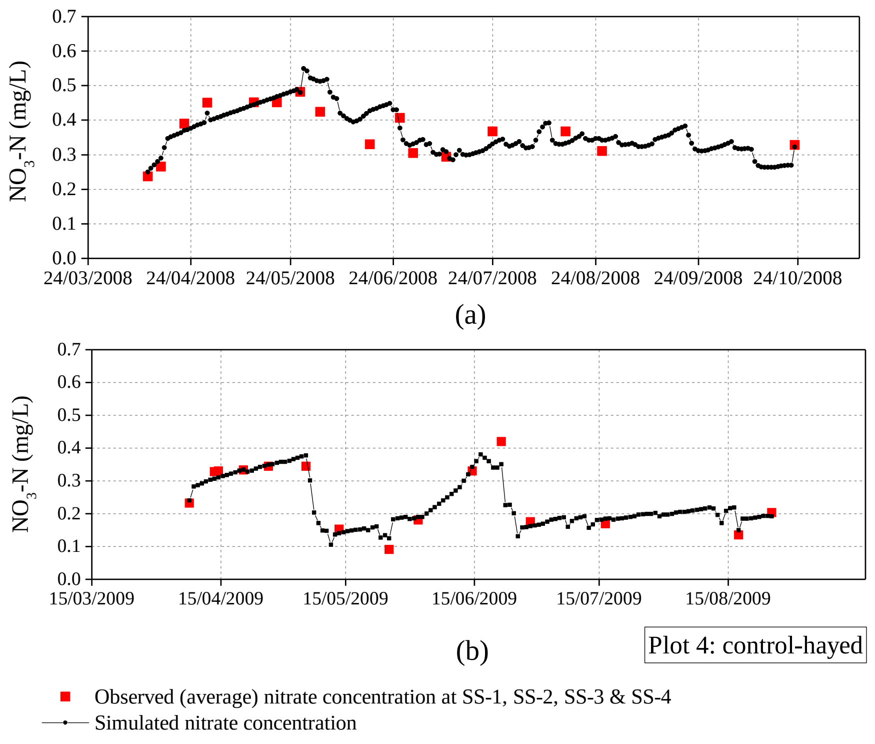

Figure 15: Simulated v/s observed nitrate concentration in groundwater for (a) 2008 and (b) 2009 for SSs 1, 2, 3 & 4

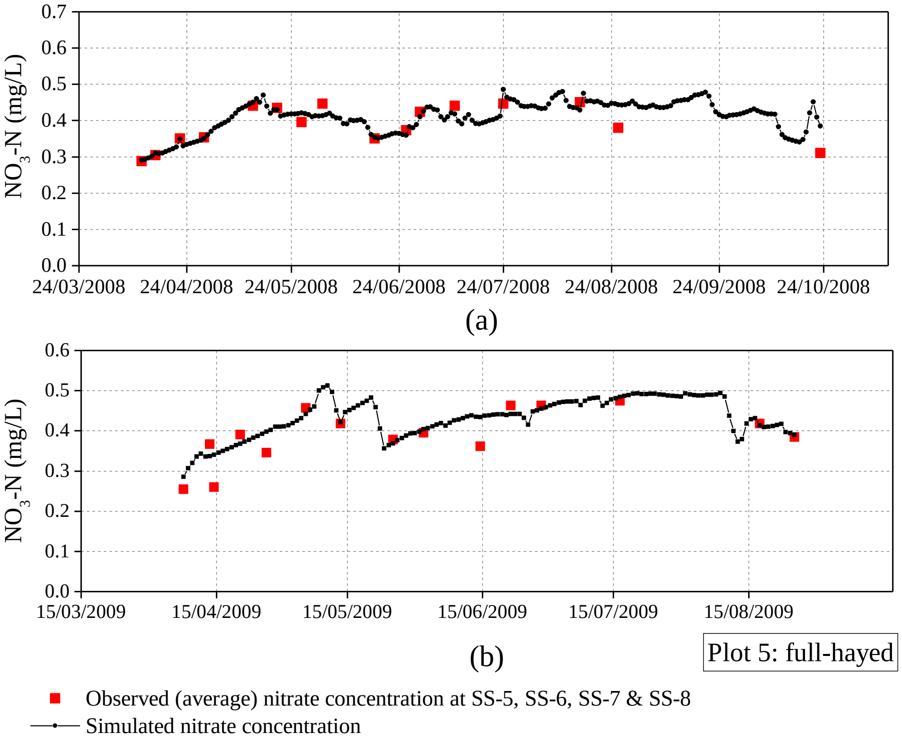

Figure 16: Simulated v/s observed nitrate concentration in groundwater over the years (a) 2008 and (b) 2009 for SS-5, SS-6, SS-7 & SS-8

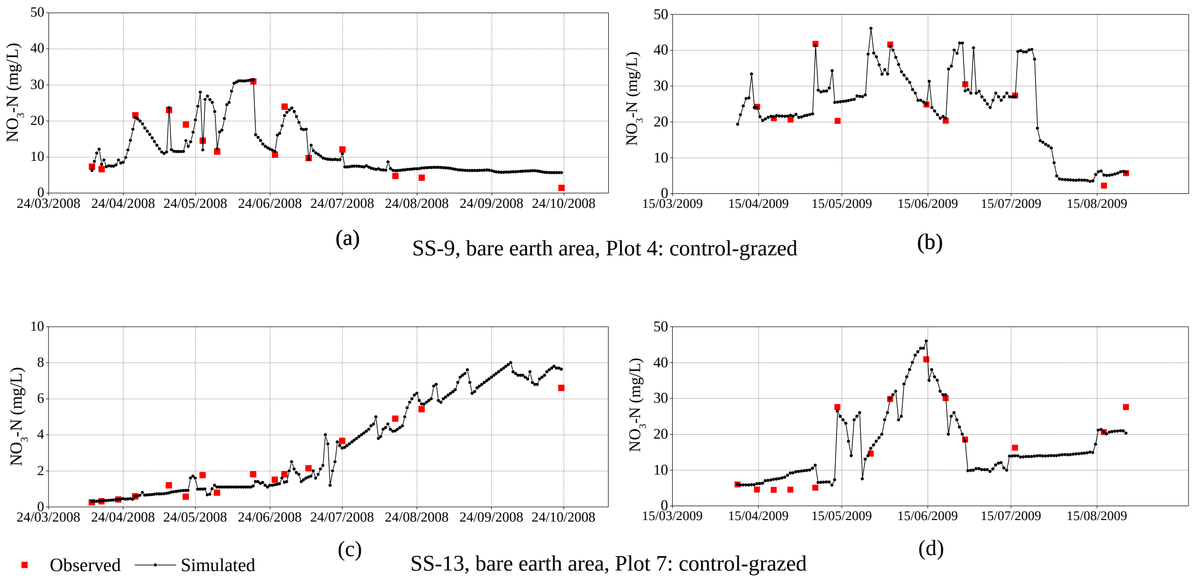

Figure 17: Simulated v/s observed nitrate concentration in groundwater during the years for the BEAs (SS-9 and SS-13 in plots 4 and 7 respectively) over the years (a), (c) 2008 and (b), (d) 2009

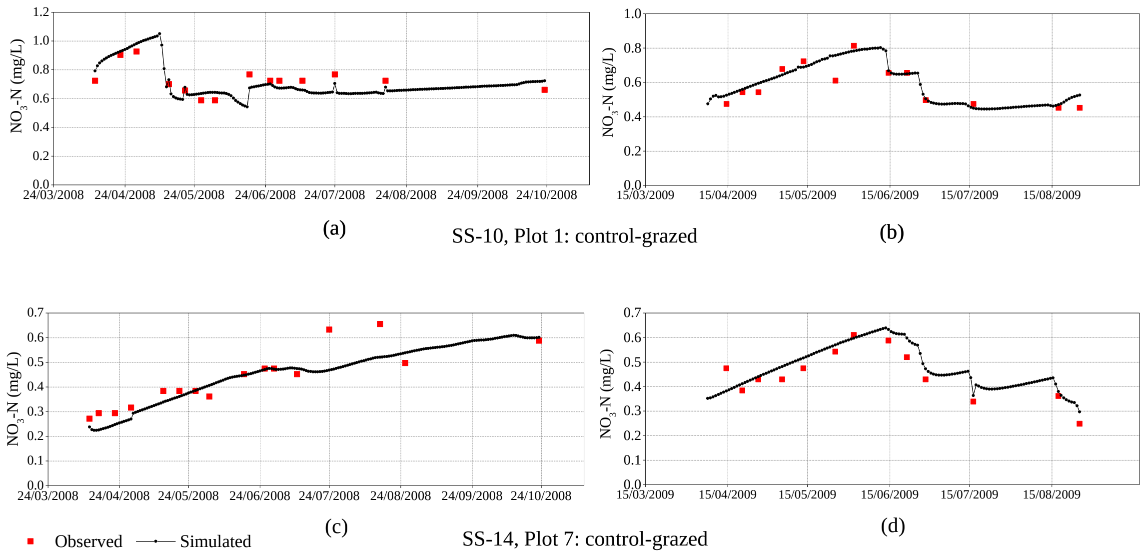

Figure 18: Simulated v/s observed nitrate concentration in groundwater for SSs 10 & 14 in plots 1 and 7 respectively over the years (a), (c) 2008 and (b), (d) 2009

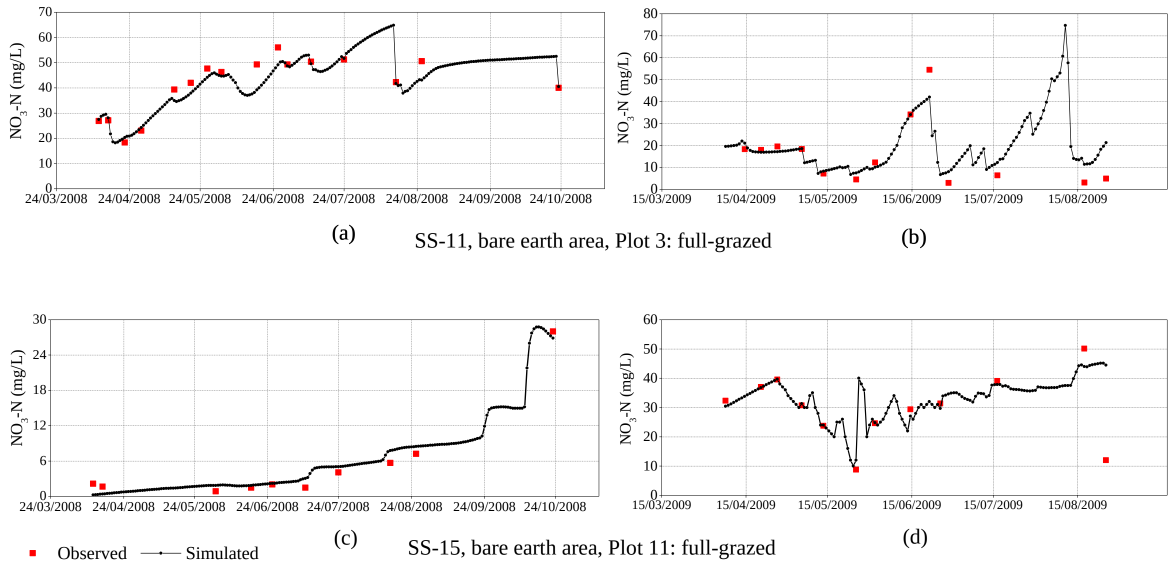

Figure 19: Simulated v/s observed nitrate concentration in groundwater during the years for the BEAs (SSs 11 and 15 in plots 3 and 11 respectively) over the years (a), (c) 2008 and (b), (d) 2009

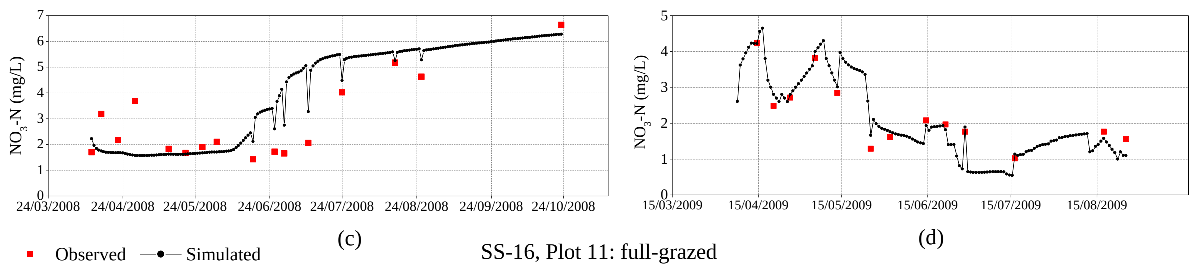

Figure 20: Simulated v/s observed nitrate concentration in groundwater for SS-16 in plot 11 over the years 2008 and 2009

Table 10: Performance of the solute transport model

		Nitrate concentrations in groundwater (mg L^{-1})			
	Year	RMSE [mg L^{-1}]	ME [mg L^{-1}]	NSE [-]	r^2
SSs-1, 2, 3 & 4 (control hayed plot)	2008	0.023	0.36	0.80	0.81
	2009	0.024	0.25	0.93	0.93
SSs-5, 6, 7 & 8 (full hayed plot)	2008	0.029	0.38	0.71	0.75
	2009	0.034	0.38	0.71	0.74
SS-9 (BEA in control grazed plot)	2008	2.08	-0.08	0.93	0.94
	2009	3.69	-0.72	0.92	0.93
SS-10 (control grazed plot)	2008	0.05	0	0.70	0.74
	2009	0.05	-0.02	0.76	0.83
SS-11 (BEA in full grazed plot)	2008	2.86	1.05	0.93	0.93
	2009	5.12	0.04	0.86	0.95
SS-13 (BEA in control grazed plot)	2008	0.48	0.12	0.93	0.95
	2009	3.22	-0.58	0.92	0.95
SS-14 (control grazed plot)	2008	0.06	0.02	0.71	0.77
	2009	0.05	-0.03	0.70	0.80
SS-15 (BEA in full grazed plot)	2008	1.43	-0.34	0.96	0.97
	2009	2.95	-1.03	0.91	0.93
SS-16 (full grazed plot)	2008	0.86	-0.02	0.66	0.70
	2009	0.46	0.04	0.74	0.75

5.6 Crop nitrogen uptake

The root NH_4^+ and NO_3^- uptake were simulated in HYDRUS-1D as 'passive root uptake' since the concentrations of both NH_4^+ and NO_3^- in soil were always above the pasture N requirement. The root N uptake in hayed plots was significantly greater than the grazed plots (Figure 21). The uptake process became faster after the application of manure in full-hayed (fig 20 (c), (d)) and full-grazed treatment plots (fig 20 (g), (h)) as pasture started to grow quickly and utilize the crop-available N after the application of manure during both years. The simulated cumulative total N uptake by grass pasture for control-hayed, full-hayed, control-grazed and full-grazed treatment plots were 9, 72.4, 2.6 and 11.4 kg/ha/year respectively whereas the observed cumulative total N uptake for the same plots were 10 ± 1, 67 ± 7, 3 ± 0.1 and 11 ± 0.5 kg/ha/year respectively (Coppi, 2012).

For both years, N was mostly utilized by roots in NO_3^- form which accounted for about 76.2% of the total N uptake on an average. Since there were no observed root N uptake data available at monthly or weekly intervals, only the yearly observed cumulative N uptake was compared with the simulated values as mentioned in the previous paragraph.

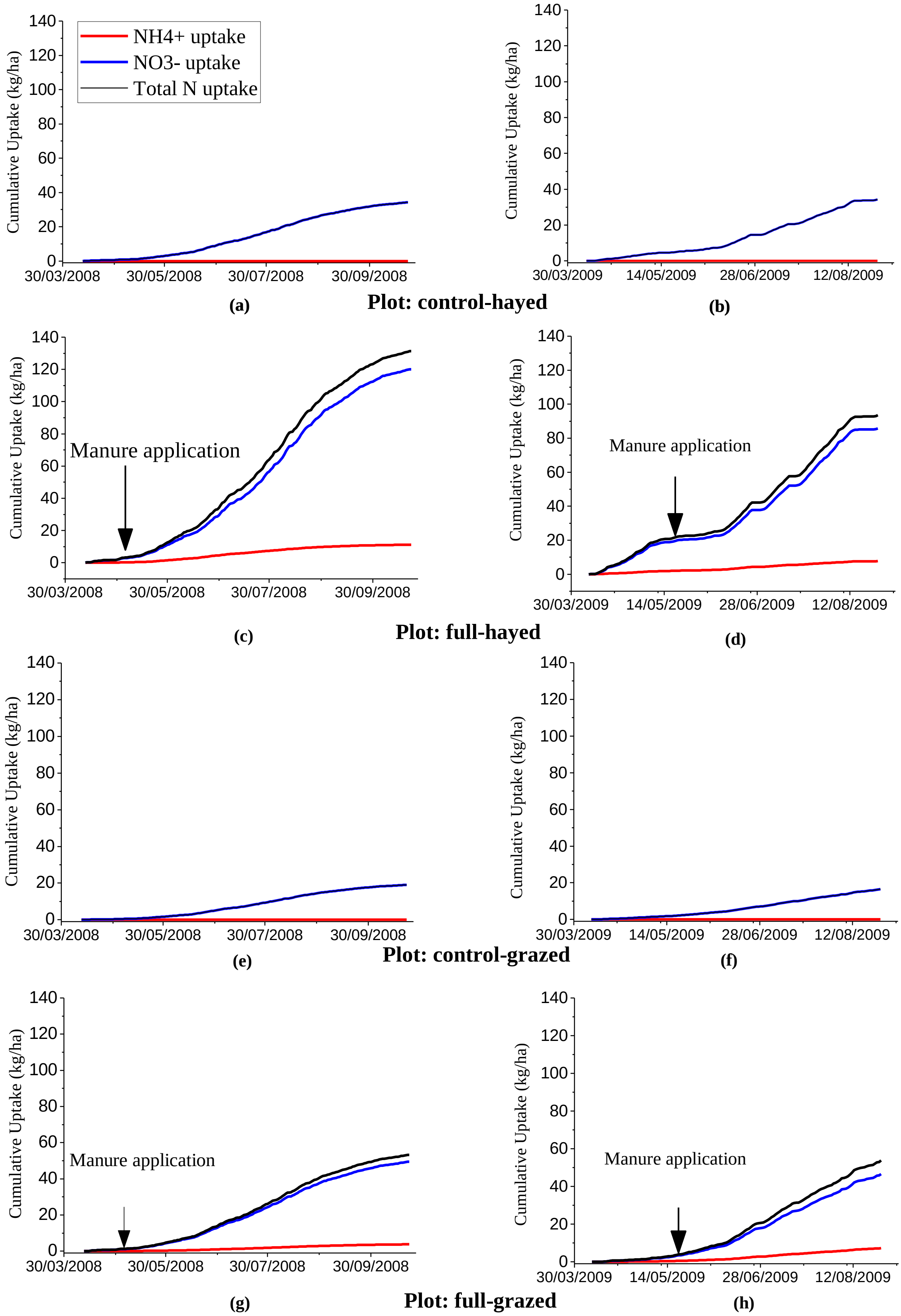

Figure 21: Simulated cumulative N (NH_4^+, NO_3^- and total) uptake (kg/ha) for different plots during 2008 (a), (c), (d), (g) and 2009 (b), (d), (f), (h)

5.7 Nitrate and ammonium leaching

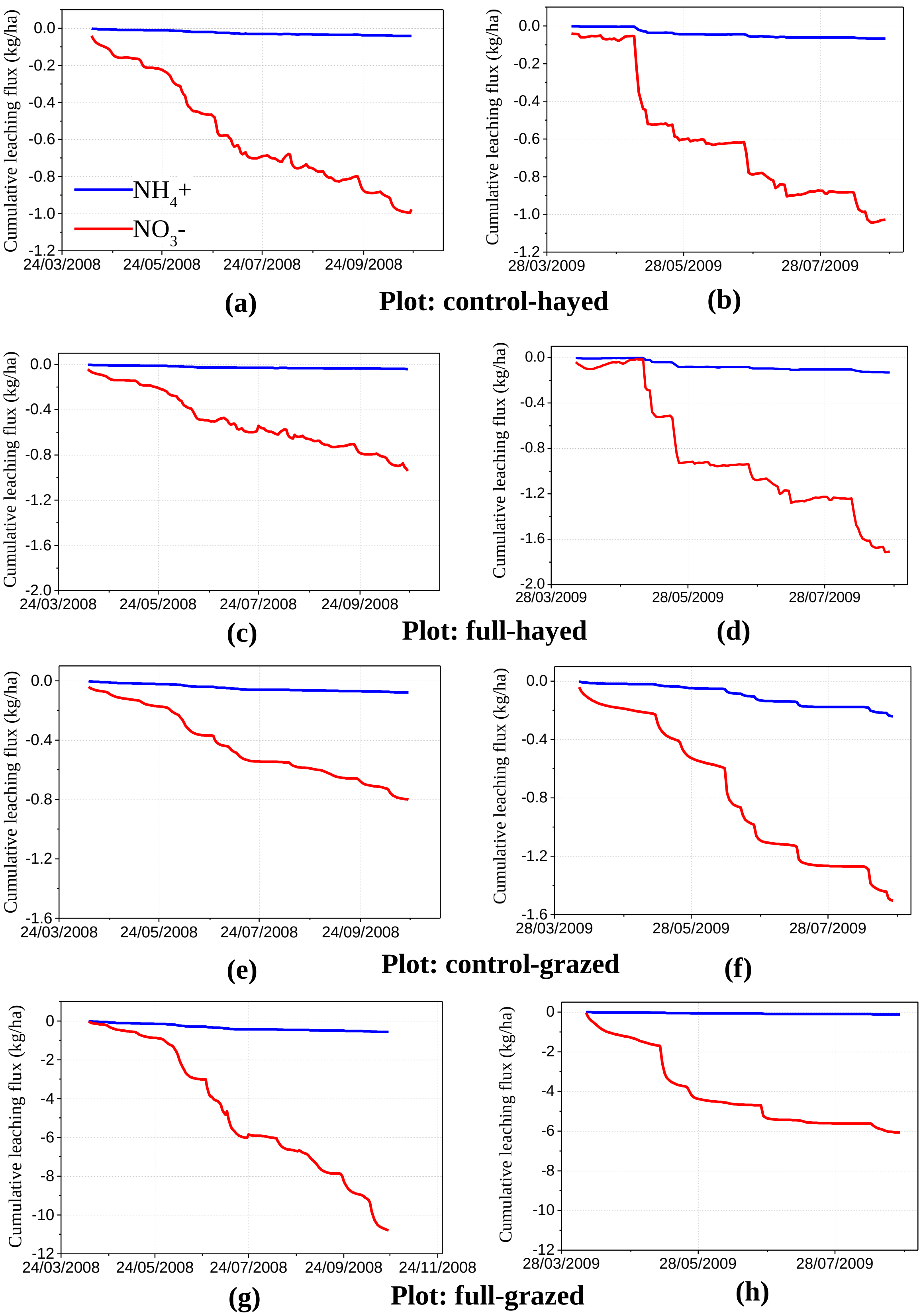

Figure 22: Cumulative NH_4^+ and NO_3^- leaching (kg/ha) for different plots during 2008 (a), (c), (d), (g) and 2009 (b), (d), (f), (h)

Figure 22 shows the cumulative N leaching fluxes at 50 cm depth (root zone depth) during 2008 and 2009. The cumulative vertical leaching flux of NH_4^+ for all types of treatment plots was always less than 0.3 kg/ha/year since the concentration of NH_4^+ in soil was always below 0.02 mg L^{-1} as mentioned by Coppi (2012). In plots where manure was applied once (full treatment) or twice a year (split treatment), NH_4^+ leaching fluxes were less than 1 kg/ha/year (Figure 22) even though manure contained N mostly in the ammonium form.

NO_3^- was observed to be transported downward quickly into the soil along with the leaching water. The cumulative NO_3^- leaching flux varied differently according to the plot type. For example, the cumulative NO_3^- leaching fluxes for control-grazed and control-hayed treatment plots were 0.97 kg/ha and 0.80 kg/ha respectively for 2008 and 1.50 kg/ha and 1.02 kg/ha respectively for 2009. Since manure was applied in full-hayed and full-grazed treatment plots, the NO_3^- leaching fluxes for these plots were larger than those observed in control treatment plots.

Results indicated that even after the application of manure in full-hayed plot, the leaching fluxes (0.94 kg/ha in 2008 and 1.7 kg/ha in 2009) were somehow comparable to that in control-treatment plots whereas the fluxes increased to 10.8 kg/ha in 2008 and 6.0 kg/ha in 2008 for the full-grazed type plot.

There were significant NO_3^- leaching fluxes simulated in the BEAs (Figure 23). As mentioned before, the BEAs in both full-grazed and control-grazed plots were generated due to the animal congregation. The NO_3^- leaching fluxes for BEAs in control grazed plots were 262 kg/ha in 2008 and 429 kg/ha in 2009 whereas, for BEAs in full-grazed plots, the leaching fluxes were 1080 kg/ha in 2008 and 714 kg/ha in 2009.

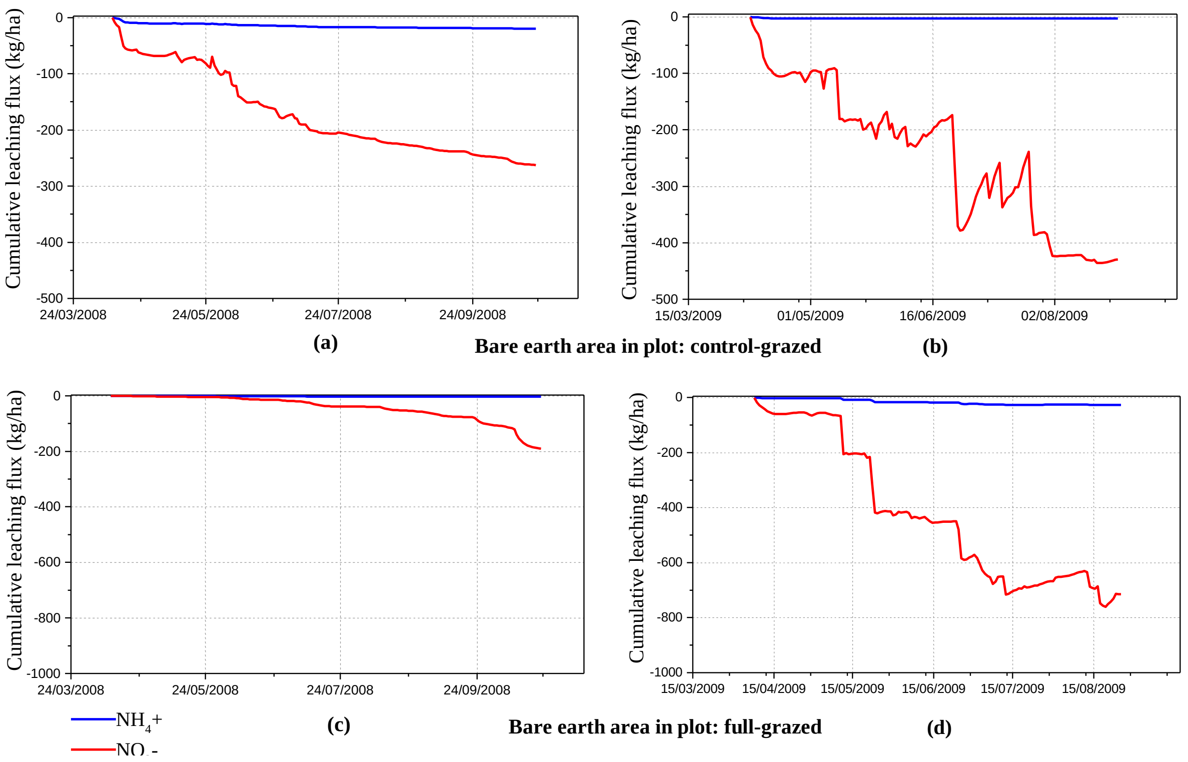

Figure 23: Simulated cumulative N (NH_4^+ and NO_3^-) leaching fluxes (kg/ha) for BEAs in different plots during 2008 (a), (c) and 2009 (b), (d)

5.8 Sensitivity analysis (nitrate leaching)

The sensitivity of VGM parameters *n*, *α*, and K_s on nitrate leaching was evaluated as explained in section 3.7. The parameter which showed the largest sensitivity to nitrate leaching was *α* (Figure 24). The parameter K_s showed a lower sensitivity than *α* and the least sensitive parameter to nitrate leaching was determined to be *n* (Figure 24). Nitrate leaching was reduced by 4.79% when *n* was reduced by 20% whereas it increased by 4.45% when *n* was increased by 20%. On increasing K_s to K_s*5, the nitrate leaching was increased by 6.4 %. However, it reduced by 2.42 % when K_s was decreased to K_s/25.

Parameter *α* showed the highest sensitivity on nitrate leaching. Leaching increased by 12.5 % on decreasing *α* by 20% whereas it decreased by 6.95 % when *α* was increased by 20 % (Figure 24).

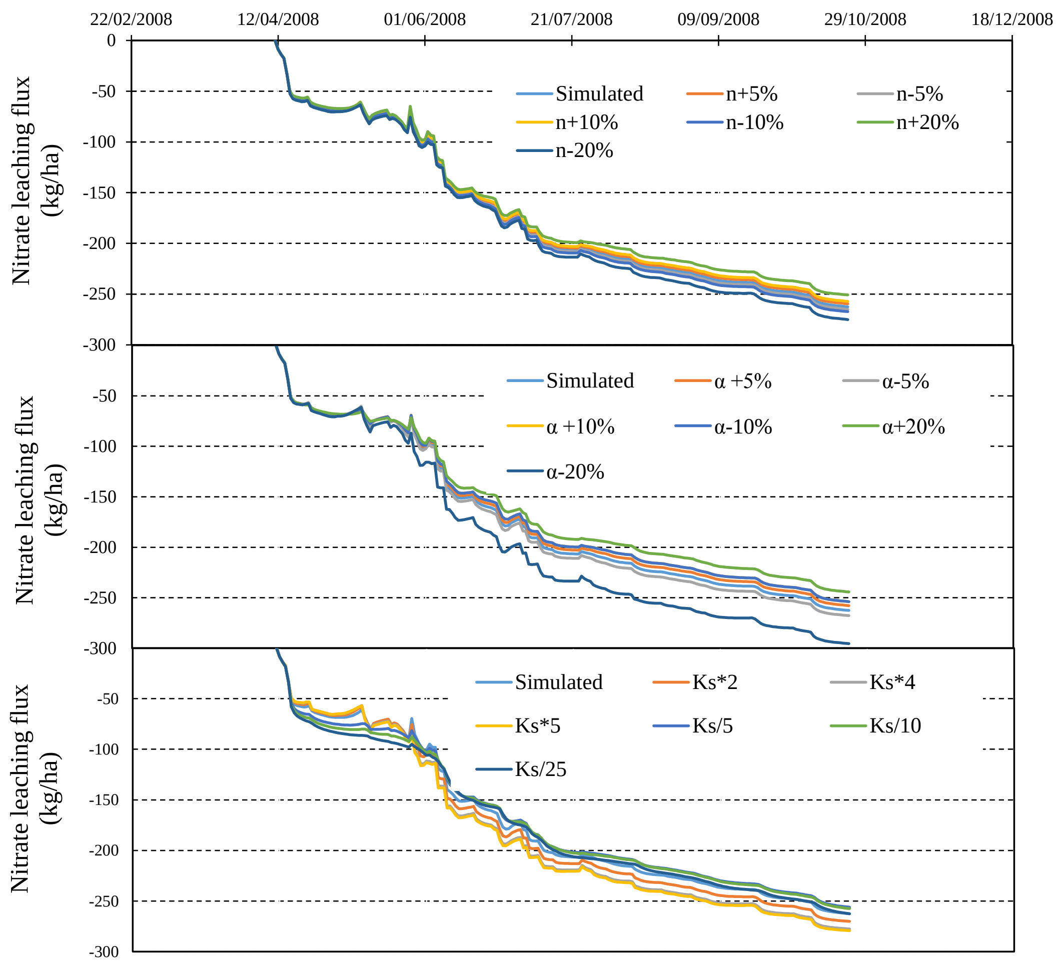

Figure 24: Sensitivity analysis of α, n, and K_s on nitrate leaching (kg/ha) at SS-9

5.9 Nitrogen balance

It is critical to analyze the N balance for understanding how efficiently the grown pasture utilized the N added to soil via liquid hog manure and how much N was lost due to various processes. The dominant inputs of N to the soil were through the application of liquid hog manure in single-treatment plots and through animal excretion in the BEAs. Control treatment plots did not receive any slurry throughout the period of study, so the pasture grown in these plots utilized N available in the soil from previous years. N uptake by the roots of grown pasture and leaching were regarded as output N components which prevented the nitrate leaching. The leaching losses were greater in the BEAs as compared to the other parts of the field due to no vegetation and thus no root N uptake (table 11). The N uptake efficiency for the full-grazed plots was approximately 37.5 % (average for years 2008 and 2009) of the applied N and leaching losses were greater in this plot due to lower N use efficiency by the pasture roots.

Table 11: Components of N balance in a 200 cm depth soil of the pasture field during the years 2008 and 2009

		Initial N Ґ	**Residual forage** Ŧ	**Manure applied**	**Cattle deposition** ƅ	**N Leaching**	**Crop N Uptake**	**N available for next year** ɗ
		(kg ha^{-1})	(kg ha^{-1})	(kg ha^{-1})	(kg ha^{-1})	(kg ha^{-1})	(kg ha^{-1})	(kg ha^{-1})
Control Hayed	2008	20.89	16.03	-	-	0.97	34.20	1.75
	2009	22.12	12.61	-	-	1.03	34.40	-
Full Hayed	2008	26.22	56.07	119.00	-	0.94	131.30	69.05
	2009	27.43	65.25	224.00	-	1.70	93.40	221.58
Control grazed	2008	24.89	32.12	-	-	0.80	19.01	37.20
	2009	27.90	53.02	-	-	1.50	16.40	63.02
Full grazed	2008	28.90	132.37	119.00	-	10.70	53.20	216.37
	2009	42.29	82.90	224.00	-	6.07	53.70	289.42
BEA (control-grazed)	2008	67.80	-	-	1327	262.00	-	1132.80
	2009	64.50	-	-	2040	429.00	-	835.50
BEA (Full-grazed)	2008	83.60	-	-	291	191.00	-	1092.60
	2009	99.10	-	-	4225	714.00	-	585.10

Ґ Sum of Initial NH_4^+-N and NO_3^--N accumulated in the soil profile at the end of previous year (Table 4 and Coppi, 2012)

Ŧ N from the residual forage (uncut pasture) from previous year (Coppi, 2012)

ƅ N added via cattle deposition on the bare earth areas(Coppi, 2012)

ɗ N available for next year including accumulated and residual N associated with the current year

5.10 Regionalisation of nitrate leaching

The gross nitrate leaching fluxes at 31 SSs as an average of years 2008 and 2009 were regionalised using Cokriging, and a mean value for the entire study area was obtained as 12.9 kg/ha (Figure 25). The nitrate leaching flux inside BEAs of control-grazed plots averaged to 360 kg/ha whereas in full-grazed plots its value averaged to 925 kg/ha for both years. BEAs had an (mathematical) effect on outside their specific site due to a high gradient of nitrate leaching flux on the boundaries of these areas (approx. 1:925) (Figure 25). However, it is very important to note that leaching flux was largest inside the bare earth areas and just outside the boundary of bare earth area, the flux reduced significantly e.g. it was about 925 kg/ha inside BEA of plot 11 and reduced to 110-300 kg/ha 25 m away from boundary and further reduced to 8-15 kg/ha when measured about 50 m away (Figure 27).

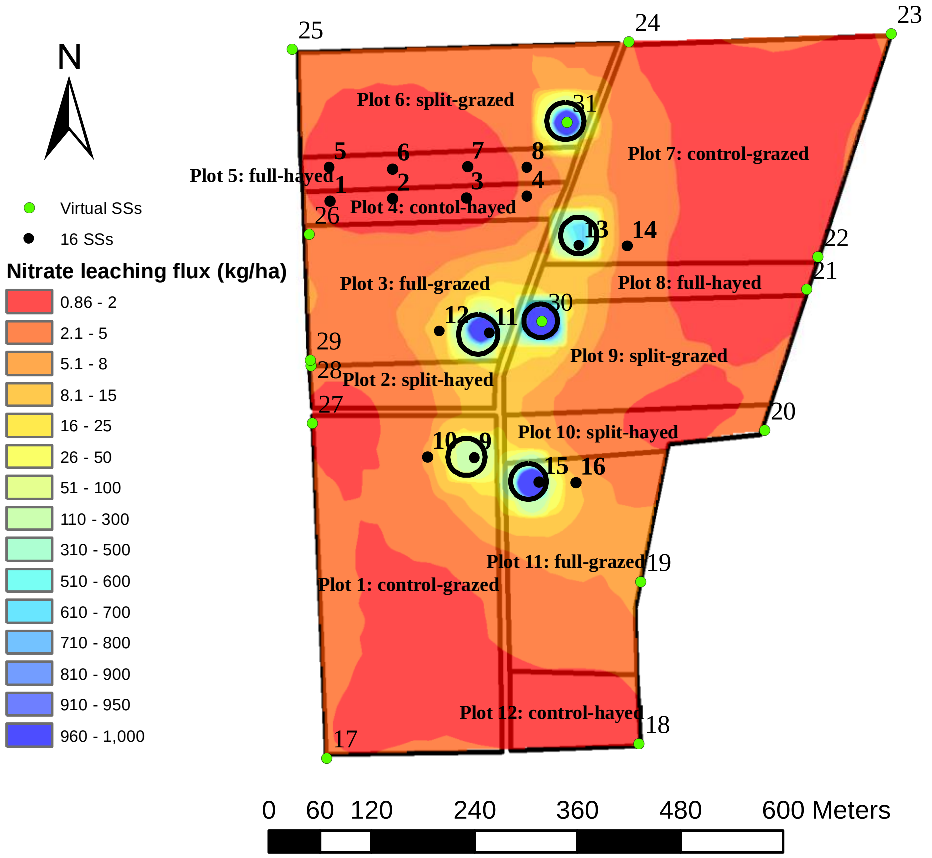

Figure 25: Nitrate leaching fluxes across the study area regionalised using Cokriging (average leaching rate: 12.9 kg/ha/year)

The study area separated into two categories: the red area that remained unaffected from nitrate excretion by beef cattle and leaching flux in this area was below 10 kg/ha/year, the blue area which received most of the nitrate excreted by beef cattle (Figure 26, next page). The flux in the blue area was between about 11-1000 kg/ha/year. Furthermore, a comparison of average nitrate leaching fluxes resulting from different methods of interpolation was made. Using Cokriging, its value was averaged as 12.9 kg/ha (Figure 25) whereas it was 274, 264 and 259 kg/ha using Kriging (Figure 38, Appendix-C), Inverse Distance Weighing (IDW) (Figure 39, Appendix-C) and Natural Neighbors (NN) (Figure 40, Appendix-C) respectively. There was a significant difference in the value of leaching flux regionalised using different methods of interpolation. The chapter on discussion (Chapter 6) discusses the comparison of these methods and the best-fitted method that can be used to interpolate nitrate leaching fluxes for the La Broquerie case.

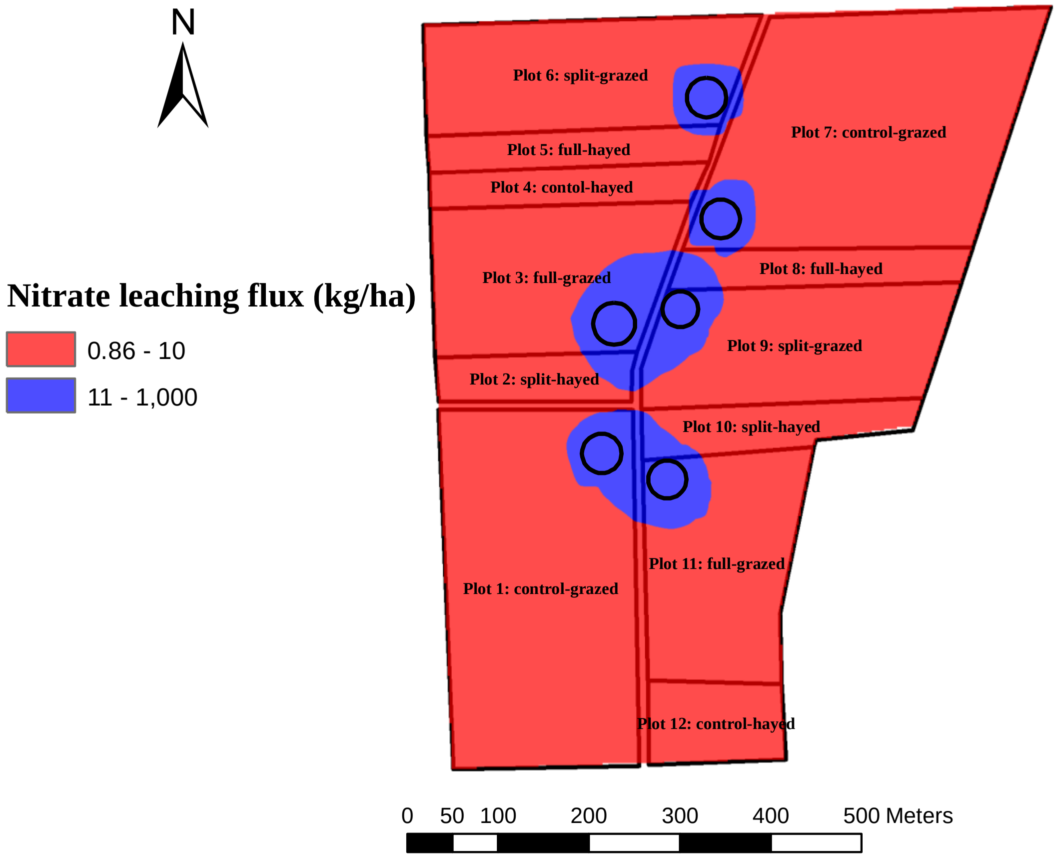

Figure 26: Nitrate leaching fluxes classified into two ranges, Blue area: affected by nitrate excreted by beef cattle (11-1000 kg/ha), red area: unaffected by nitrate excreted by cattle (0.86-10 kg/ha)

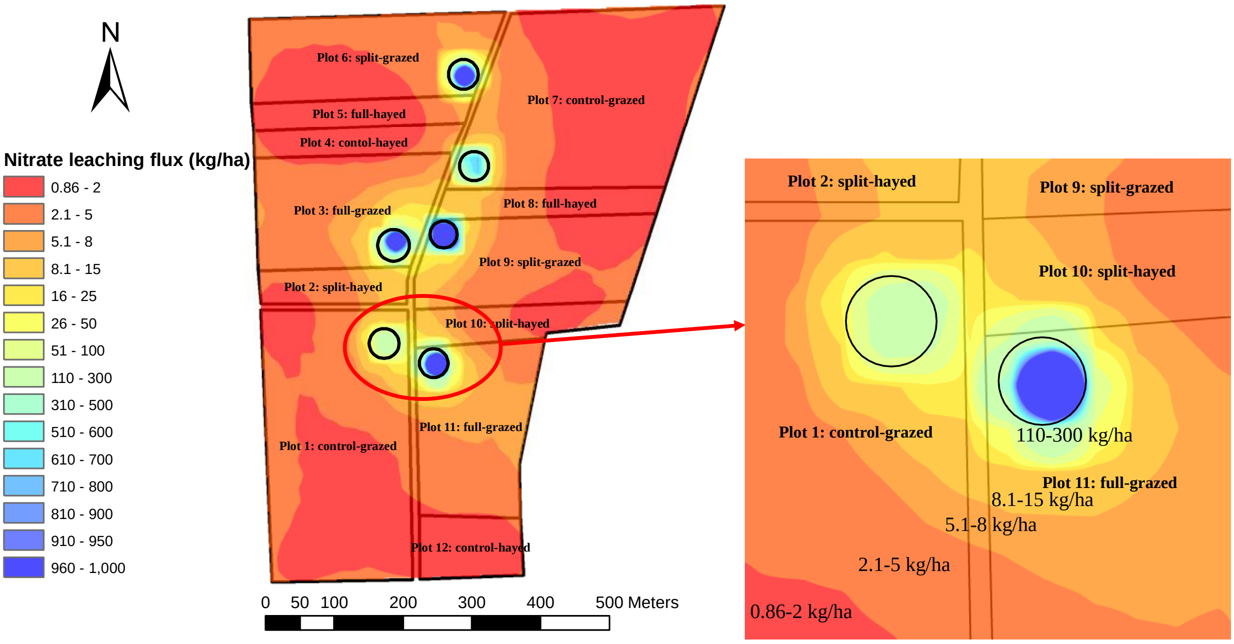

Figure 27: Nitrate leaching flux just outside the boundary of BEAs in plot 1 and plot 11

Chapter 6: Discussion

The overall error in simulated soil moisture content based on the observed values was between 0.6 to 5% as expressed by RMSE and between 0.39 and 0.99, expressed by NSE. The mean error (ME) was nearly equal to 0 in almost all simulations. Overall, the NSE and ME verified a good agreement between the simulated and observed soil moisture values. The temporal variations in soil moisture content were based on spring snowmelt and precipitation events throughout the year. It was observed that soil moisture content increased in the year 2009 due heavy precipitation events.

The sensitivity analysis was carried out to check the robustness of simulated recharge and nitrate leaching. The most sensitive parameter to the variations in soil moisture content was *n*. The changes in recharge as a result of changes in VGM parameters were always less than 5% on a point scale (Figure 28), which proves the robustness of model in terms of recharge estimation. The estimated recharge using the VGM parameters directly derived from PTF was 4% and 3.6% larger than that after calibration for 2008 and 2009 respectively and verified the low sensitivity of the model output to the VGM parameters. Changing Ks to a larger scale (Ks*2, Ks/2, Ks*4, Ks/4) accounted for soil heterogeneity and thus its impact on recharge. Changing Ks to Ks*2, Ks/2, Ks*4, Ks/4 resulted in differences of recharge up to 10% which proved its low sensitivity to the groundwater recharge (Figure 28).

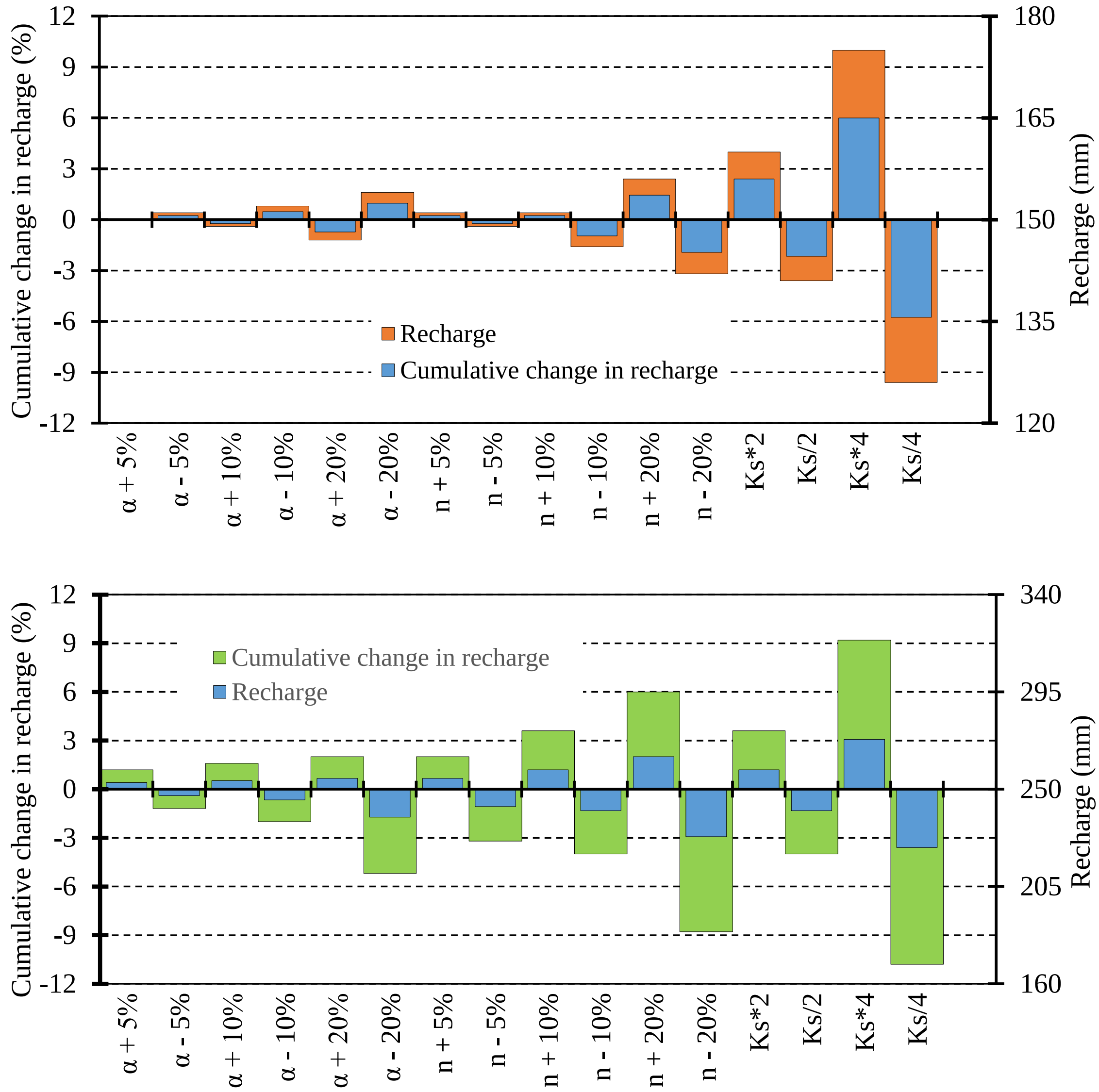

Figure 28: Changes in cumulative recharge for the year (a) 2008 and (b) 2009 as a result of changes in VGM parameter for SS-3

On an average, the recharge was estimated as 156.5 mm and 253.5 mm for the years 2008 and 2009 respectively. It was observed that most of the recharge, 42 mm out of 150 mm (about 28%), occurred during the snow-melt period of the year 2008 from April 11th to April 30th (Figure 29) for SS-3. Similar recharge values were observed for other SSs. These findings agree with the rise in soil moisture content that was also observed after the snowmelt, and the precipitation events occurred throughout the year (Figure 6 and Figure 12 for temporal variations in soil moisture at 15 cm depth of SS-3). The increase in soil moisture content after precipitation or snowmelt events was mainly observed in the top layer of soil. At

75 cm and depths below, soil moisture was observed to be constant with time mainly due to the fact that root density decreases with increasing depth which leads to a lesser effect of evapotranspiration (Figure 12 for daily soil moisture at 75 cm depth of SS-3). Even after the precipitation events, the soil moisture at lower depths (e.g. at 75 cm, Figure 12) did not change significantly with time which can be explained as (a) the upper soil layers (up to 60 cm depth) were of low hydraulic conductivity and had more water retention capacity due to the presence of loamy material (b) delayed change in soil moisture due to increased time of travel of the infiltrating water to the lower depths. It can also be observed that for SS-3 (layer 3, 60-90 cm), the value of parameter *n* changed significantly from 2.85 to 5 and for SS-2 (layer 3, 60-90 cm), it changed from 2.85 to 4.55 after calibration. These changes can be considered to be associated with high stone content in the soil layers due to which the soil moisture was subjected to faster drainage and the resulting shape of relation between soil moisture content and time showed high fluctuations during the heavy precipitation events. The parameter *n* in the VGM parameterization defines the steepness of the soil water retention curve between saturation and permanent wilting point. An increasing *n* results into a stronger reduction of soil water with increasing suction. Thus, soil water percolate easier downwards.

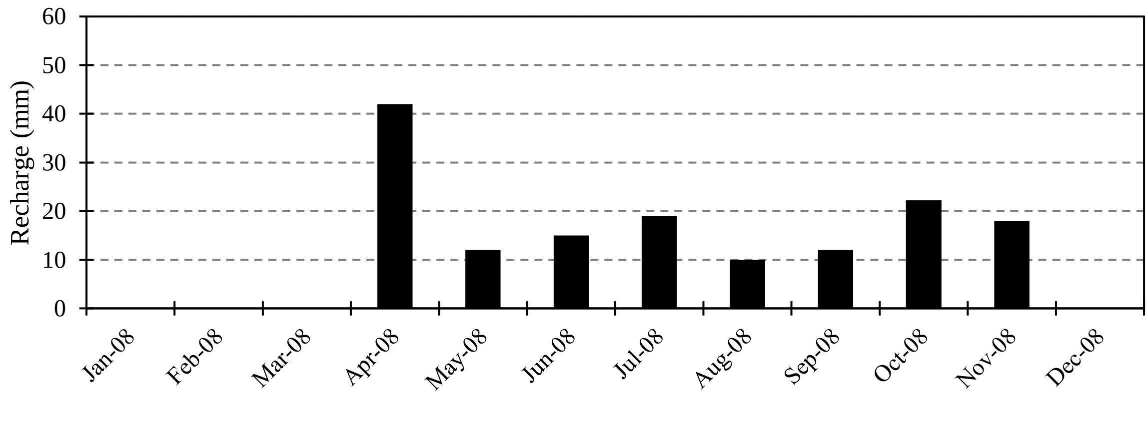

Figure 29: Monthly simulated recharge (mm) in 2008

The water flow within the vadose zone is driven by the soil moisture (Holländer et al., 2016). So a good agreement between the observed and simulated soil moisture as expressed by overall RMSE of 0.7 - 5%, NSE of 0.39 - 0.99 and approximately '0' ME were the basis of robust recharge estimation by the chosen method.

Soil freezing and thawing processes were not simulated with the standard HYDRUS-1D code. Therefore, the soil moisture content at different depths was only calibrated for periods from early spring (after the snowmelt) to the early winter (before the soil freezing). The non-accommodation of soil freezing and thawing processes in model simulations was one of the major limitation of this research since these processes are very important to evaluate solute redistribution, water balance, and snowmelt infiltration correctly in the frozen soils (Saito et al., 2008). This disadvantage was clearly observed while calculating the monthly water balance for both years of study (2008 and 2009). The monthly water balance, shown in table 8 showed that there was negligible evapotranspiration in the winter months (November-March). As the standard code of HYDRUS 1-D was not able to simulate soil freezing and thawing, water fluxes in the form of evapotranspiration were observed in the modeling results (e.g. evapotranspiration of 2.2 mm in March 2008 and 10.2 mm in March 2009). Overall, there was a surplus of 29.6 mm and a deficit of 17 mm water observed in the soil profile for years 2008 and 2009 respectively.

The performance of the model in simulating the transport of nitrate in the soil profile as expressed by RMSE between 0.023 mg L^{-1} and 5.12 mg L^{-1}, ME between -1.03 mg L^{-1} and 1.05 mg L^{-1}, NSE between 0.66 and 0.96 and r^2 between 0.7 and 0.97 is shown in table 10. The solute transport parameters obtained after calibration, K_D (1.5 - 4.5 cm^3g^{-1}) and μ_w (0.1 - 0.7 day^{-1}) (table 9), were lying within the range of values reported in the literature. Ranjbar and Jalali (2013) mentioned in their study that ammonium adsorption increased linearly with the increased amounts of NH_4+ added to the soil and hence the adsorption coefficient, K_D

which varied between 1.438 to 4.474 cm^3g^{-1}. Another study conducted by Boatman and Murray (1982) reported the K_D range from 2.7 to 5.8 cm^3g^{-1} on marine sediments. The first order decay coefficient, μ_w was lying within the range reported in the literature as 0.02-0.5 day^{-1} by Lotse et al. (1992) and 0.24 – 0.72 day^{-1} were reported by Misra et al. (1974).

The sensitivity analysis of VGM parameters on nitrate leaching showed a maximum increase in nitrate leaching flux by 12.5% on decreasing α by 20% whereas the flux decreased by 6.95% when α was increased by 20%. Parameter n was the least sensitive parameter to nitrate leaching. The model was considered to be robust considering such range of variations in the nitrate leaching fluxes on changing VGM parameters.

The concentration of ammonium in groundwater was always observed to be less than 0.2 mg L^{-1}. So the model was considered to be calibrated if the simulated concentration of ammonium in groundwater was less than 0.2 mg L^{-1} at all time periods. Nitrate concentrations in groundwater in control and full-hayed plots averaged to be less than 1 mg L^{-1} throughout the sampling campaign. Thus, the accumulation of nitrate in groundwater was generally not a concern with grass harvest by haying. The application of manure with greater than N requirement in 2009 did not increase nitrate concentration in groundwater (Figure 16). Therefore, it can be stated that nitrate concentration in groundwater was generally unaffected by the application of manure in hay treatment plots. Di and Cameron (2002) also reported a low concern for nitrate leaching in cut (hay) grasslands subjected up to 400 kg N ha^{-1} especially when applications are made during spring when air temperatures are low.

Nitrogen stored in the soil for control-hay plot was about 14-15 kg ha^{-1} for both years of study whereas the stored N in full-hayed plots was about 36.7 kg ha^{-1} in 2008 and 178.9 kg ha^{-1} in 2009 due to spring manure applications in both years. The results suggested that the roots of pasture grass intercepted most of the nitrate and thereby prevented its leaching to groundwater.

Trends in groundwater nitrate concentrations in grazed plots varied with time among different manure treatment combinations. Since control-grazed plots did not receive any slurry throughout the study period, the simulated and observed groundwater nitrate concentrations were always below 1 mg NO_3-N L^{-1} in these plots whereas in full-grazed plots, the concentrations varied between 1-7 mg NO_3-N L^{-1} NO_3-N for both years of study. Overall, the results indicated that for all the treatment plots including control-hayed, full-hayed, control-grazed and full-grazed, the groundwater nitrate concentrations were always below the drinking water threshold of 10 mg NO_3-N L^{-1}.

The areas which posed a risk to nitrate contamination of groundwater were the BEAs. The observed and simulated results showed that the groundwater nitrate concentrations in BEAs of both control-grazed and full-grazed plots were consistently higher than 10 mg NO_3-N L^{-1} (Figure 17 and Figure 19). The N accumulated in soil through deposition of urine and feces was leached to the groundwater during these events. Furthermore, in BEAs, there was no plant uptake of N, promoting the leaching losses.

Overall, the cumulative nitrate leaching fluxes for control-hayed, full-hayed and control-grazed plots were below 2 kg NO_3-N ha^{-1} for both years (Figure 22). However, for full-grazed plots, the cumulative nitrate leaching flux was about 11 kg NO_3-N ha^{-1} and 6 kg NO_3-N ha^{-1} for 2008 and 2009 respectively (Figure 22). The N leaching fluxes for all the plots showed a stepped increasing trend. This trend can be explained on the basis of snowmelt and precipitation events, especially in 2009 when due to heavy precipitation, this kind of trend in cumulative leaching fluxes was observed (Figure 22 and Figure 23).

The cumulative leaching fluxes in BEAs were about 100 times larger than those in grassed areas. Also, these fluxes were larger in BEAs of full-grazed plots as compared to the BEAs in control-grazed plots. This was mainly due to the fact that cattle spent more time in full-grazed plots before they were removed from the plot due to the minimum requirement of biomass. Overall, these results suggested a concern for nitrate leaching to the groundwater in BEAs. The ammonium leaching fluxes were always below 1 kg NH_4^+-N ha^{-1} since model simulations showed that all of the available ammonium was quickly converted to nitrate by the process of nitrification.

Overall, HYDRUS-1D simulated reasonable results for both water flow and nitrate transport processes occurring in the study area for the years 2008 and 2009. It can be considered as a suitable and a reliable tool for estimating recharge and nitrate leaching on pasture fields of South-Western Manitoba subjected to the application of liquid hog manure under the continental climatic conditions.

Cokriging allowed considering the cross-correlation of nitrate leaching with the application of manure. The other methods of interpolation such as Kriging, Natural Neighbor, and Inverse Distance Weighing did not allow the cross-correlation between two parameters. The average leaching flux determined using Cokriging was 12.9 kg/ha (Figure 25) whereas it was 274, 264 and 259 kg/ha using Kriging (Figure 38, Appendix-C), Inverse Distance Weighing (IDW) (Figure 39, Appendix-C) and Natural Neighbors (NN) (Figure 40, Appendix-C) respectively. Since the observed data on nitrate leaching fluxes were not available, it was expected that similar plot types would have same values of nitrate leaching fluxes. For example, the leaching fluxes in control treatment plots were always below 1 kg/ha and for full treatment plots, they were about 10 kg/ha, as obtained by physically obtained modeling. It was assumed that these fluxes were strictly dependent on the plot type, manure application, and forage removal treatments. The BEAs had high fluxes only within their boundaries and just outside their boundaries, the fluxes reduced significantly. Very high average leaching fluxes of nitrate were obtained using Kriging, IDW, and NN since the interpolation using these methods was done considering only one variable of interest (leaching fluxes).

The regionalisation results (Figure 25 and Figure 27) showed the effect of BEAs outside their boundaries due to a high gradient of nitrate leaching flux on the boundaries of these areas (approx. 1:925). This can be justified on the basis that beef cattle were mostly loafing inside the perimeter of BEAs where they excreted most of the nitrogen ingested via grazing and also in some areas outside the perimeter to travel from one BEA to other. Therefore, the flux was greater than 10 kg/ha in some areas outside the BEAs as well. Regionalisation results showed the risk of nitrate leaching only in BEAs and areas around them (Figure 26, blue region). However, the rest of the study area (Figure 26, red region) was found not to be prone to nitrate leaching. Furthermore, there was another attempt made to figure out what would be the situation if there were no BEAs in the study site (Figure 30). The average nitrate leaching flux for the entire study area under this scenario was estimated as 3.6 kg/ha.

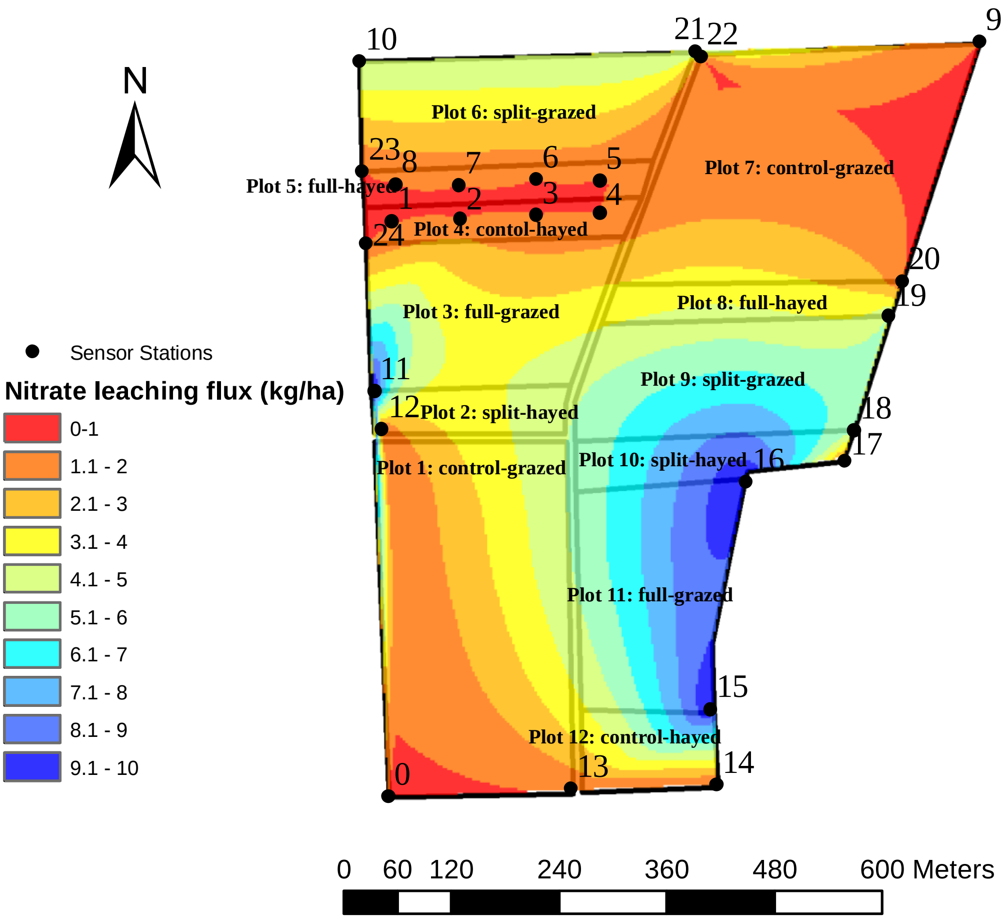

Figure 30: Nitrate leaching in a scenario when the study site consisted of no BEAs. Average flux: 3.6 kg/ha

As explained earlier, the focus of Best Management Practices (BMPs) is to achieve an efficient use of available resources (e.g. hog manure) such that the environmental risks concerned with them being unused are controlled. In this study, it was found that only Bare Earth Areas were at risk of nitrate leaching and groundwater contamination. The Best Management Practice for the study area would be to adopt haying as a forage harvesting technique since the nitrate leaching fluxes were minimum in plots where haying was adopted as a harvesting treatment. The removal of N by haying would not allow its accumulation in soil and will ultimately prevent its leaching to the groundwater.

Another concern which can be subjected as the area of further research relating this study site is increase in the production of beef cattle at the study site. If the cattle production at study site increases, more number of cattle would be required to be sent to the study area for grazing purposes, ultimately increasing the number and size of Bare Earth Areas which would lead to a greater risk of nitrate leaching and contamination of groundwater by nitrate.

Conclusions

This research showed how the daily meteorological data and soil physical properties were used to simulate daily soil moisture and yearly recharge values at different SSs of the study area. The model was calibrated on the basis of daily soil moisture content at different depths and was found to simulate robust recharge values. The low sensitivity of groundwater recharge on the VGM parameters proved the robustness of the adapted method.

Simulation results suggested that two years of liquid hog manure application to the hay pasture on a coarse sand soil did not cause the significant accumulation of nitrate in the shallow groundwater. Even during the snowmelt and heavy precipitation events, the shallow groundwater nitrate concentrations never exceeded 10 mg NO_3-N L^{-1}. This was likely due to the uptake of nitrate by plant roots. Following the same manure application treatments in the grazed pasture plots, the concentration of nitrate in groundwater was not an environmental concern even though it occasionally rose closer to the drinking water threshold. In contrast, nitrate concentrations above the drinking water threshold were simulated in BEAs throughout the vegetation period. Leaching of large amounts of nitrate to the groundwater occurred in these areas.

HYDRUS-1D simulated the soil moisture content and groundwater nitrate concentrations with a good agreement with the observed values. On the other hand, the standard HYDRUS-1D code was not able to simulate freezing and thawing of soil which was the major drawback of this research. Cokriging allowed the cross-correlation of nitrate leaching with the application of manure and improved the prediction of resulting map. Regionalisation results suggested that BEAs and some areas around their periphery were under the concern of nitrate leaching.

Overall, HYDRUS-1D can be considered as a useful tool in quantifying the recharge and nitrate leaching estimates for pasture fields subjected to continental climates, and Cokriging can be considered as a reliable method for a study site where cross-correlations between variables are important to consider carrying out interpolation.

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Appendix-A (Data)

Appendix A.1:

Table 12: Manure characteristics (modified after Coppi, 2012)

Timing	Fall 06	Spring 07	Fall 07	Spring 08	Fall 08	Spring 09
Date of Application	October 3, 2006	May 9, 2007	October 3, 2007	May 5, 2008	November 6, 2008	May 20 2008
NH_3 (kg/m^3)	3.35	3.83	3.11	3.23	3.23	3.95
Moisture %	96.4	92.6	95.8	90.2	95.7	87.0
Electrical Conductivity (dS/m)	28.9	26.6	22.0	18.0	18.6	9.0
pH	7.6	7.3	7.1	6.9	11.0	5.8
Ammonia (mg NH_3-N / L)	3410	4118	3705	3746	3630	3575
Nitrate mg NO_3-N / L	9.0	1.3	1.0	2.6	3.0	0.7
Total N % of Fresh Weight	0.49	0.53	0.51	0.58	0.52	0.64
Organic N % of Fresh Weight	0.15	0.12	0.14	0.20	0.16	0.28

Appendix A.2

Table 13: Rates of manure application and amounts of nutrients applied per m^2. Values for the split treatments in fall are standardized to rates for a full application treatment. In spring 2009 a double amount of manure (2x N crop removal rates) was applied (modified after Coppi, 2012)

Timing	fall 06	spring 07	fall 07	spring 08	fall 08	spring 09
Date of Application	03-Oct-06	09-May-07	03-Oct-07	05-May-08	06-Nov-08	20-May-08
Application Rate l/m^2	4.435	3.12	4.31409	3.615645	4.257055	6.661875
Estimated Available N applied kg N / m^2	0.012765	0.010434	0.01332	0.011766	0.013098	0.0222
Total Nitrogen kg N / m^2	0.021201	0.016317	0.021645	0.020535	0.021867	0.041847

Table 14: Mean monthly air temperature and monthly rainfall for the growing seasons (April to October) from 2006 to 2009 and long term climate (mean temperature and rainfall) for the years 1971 to 2000 (Coppi, 2012).

Year	**-----2006-----**		**-----2007-----**		**-----2008-----**		**-----2009-----**		**Long-term average**	
Month	Mean Temp (°C)	Rainfall (mm)	Mean Temp (°C)	Rainfall (mm)	Mean Temp (°C)	Rainfall (mm)	Mean Temp °C	Rainfall mm	Mean Temp (°C)	Rainfall (mm)
April	8.9	12	4.0	7	3.2	21	3.5	23	4.1	21
May	11.9	23	12.3	122	8.7	45	8.2	103	11.9	59
June	17.4	50	17.9	109	15.2	98	14.9	134	16.6	95
July	21.3	42	20.6	60	18.0	73	16.3	71	19.1	80
August	18.5	26	16.9	51	18.4	67	16.7	113	18.1	69
September	12.8	94	12.3	25	12.5	60	16.6	63	12.1	60
October	3.9	36	6.2	97	6.0	49	3.3	29	5.4	39
Season	13.5	283	12.9	470	11.7	413	11.4	535	12.5	422

Table 15: Soil physical properties for each plot type in the study area

Plot	Sample depth	Sand %	Silt %	Clay %	USDA Texture Class	Stones %
Plot 1: control-grazed	0-1	89	5	6	Sand	37.7
	1-2	93	5	2	Sand	44.0
	2-3	93	5	2	Sand	41.0
	3-4	94	4	2	Sand	38.8
Plot 2: split-hayed	0-1	83	11	6	Loamy Sand	27.4
	1-2	91	7	2	Sand	41.6
	2-3	93	5	2	Sand	43.1
	3-4	93	5	2	Sand	36.6
Plot 3: full-grazed	0-1	83	9	8	Loamy Sand	29.0
	1-2	61	36	3	Loamy Sand	50.9
	2-3	92	6	2	Sand	44.2
	3-4	93	5	2	Sand	41.7
Plot 4: control-hayed	0-1	79	11	10	Loamy Sand	40.2
	1-2	89	7	4	Sand	52.5
	2-3	92	6	2	Sand	46.4
	3-4	93	5	2	Sand	42.4
Plot 5: full-hayed	0-1	81	11	8	Loamy Sand	39.6
	1-2	89	7	4	Sand	50.4
	2-3	94	4	2	Sand	43.5
	3-4	93	5	2	Sand	42.6
Plot 6: split-grazed	0-1	81	9	10	Loamy Sand	35.9
	1-2	89	7	4	Sand	43.2
	2-3	93	5	2	Sand	45.7
	3-4	94	4	2	Sand	34.3
Plot 7: control-grazed	0-1	81	11	8	Loamy Sand	32.3
	1-2	89	7	4	Sand	39.1
	2-3	93	6	1	Sand	42.5
	3-4	91	7	2	Sand	43.5
Plot 8: full-hayed	0-1	83	9	8	Loamy Sand	31.8
	1-2	91	5	4	Sand	36.3
	2-3	93	5	2	Sand	35.0

	3-4	93	5	2	Sand	39.4
Plot 9: split-grazed	0-1	85	10	5	Loamy Sand	33.3
	1-2	89	8	3	Sand	39.2
	2-3	92	7	1	Sand	36.5
	3-4	93	6	1	Sand	33.8
Plot 10: split-hayed	0-1	81	12	7	Loamy Sand	26.8
	1-2	89	9	2	Sand	34.0
	2-3	93	6	1	Sand	35.6
	3-4	94	5	1	Sand	34.2
Plot 11: full-grazed	0-1	81	12	7	Loamy Sand	19.4
	1-2	89	8	3	Sand	30.0
	2-3	93	6	1	Sand	30.0
	3-4	93	6	1	Sand	26.5
Plot 12: control-hayed	0-1	81	10	9	Loamy Sand	22.5
	1-2	87	8	5	Loamy Sand	30.8
	2-3	93	6	1	Sand	24.8
	3-4	93	6	1	Sand	19.4

Appendix-B (Soil water)

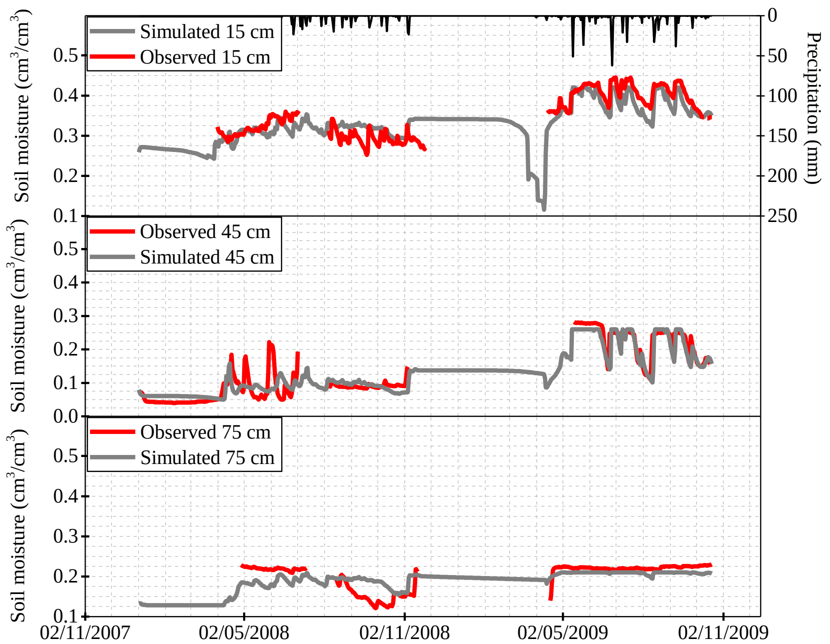

Figure 31: Observed v/s simulated soil moisture contents at depths 15, 45 and 75 cm using the VGM parameters derived from inverse optimization for SS-1

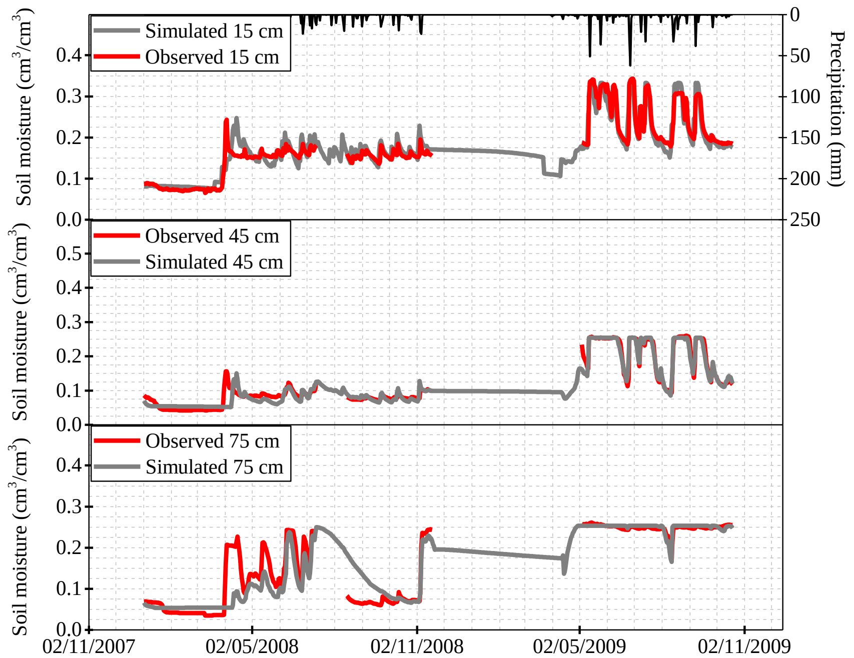

Figure 32: Observed v/s simulated soil moisture contents at depths 15, 45 and 75 cm using the VGM parameters derived from inverse optimization for SS-2

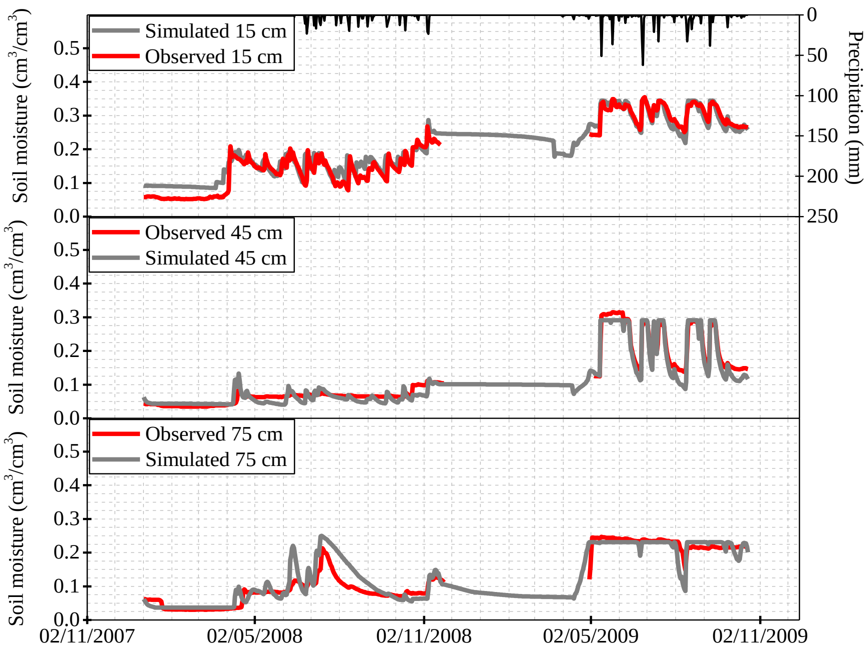

Figure 33: Observed v/s simulated soil moisture contents at depths 15, 45 and 75 cm using the VGM parameters derived from inverse optimization for SS-4

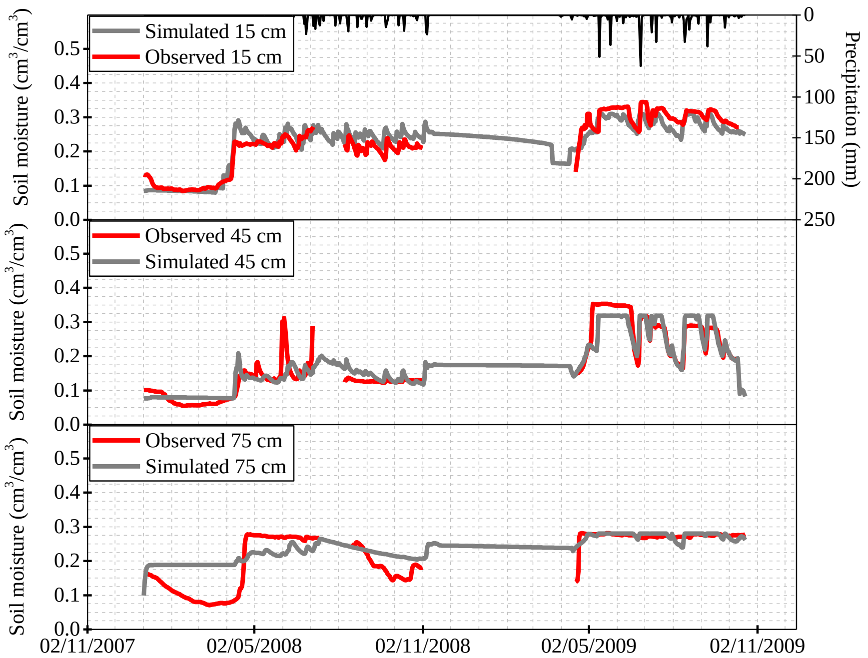

Figure 34: Observed v/s simulated soil moisture contents at depths 15, 45 and 75 cm using the VGM parameters derived from inverse optimization for SS-5

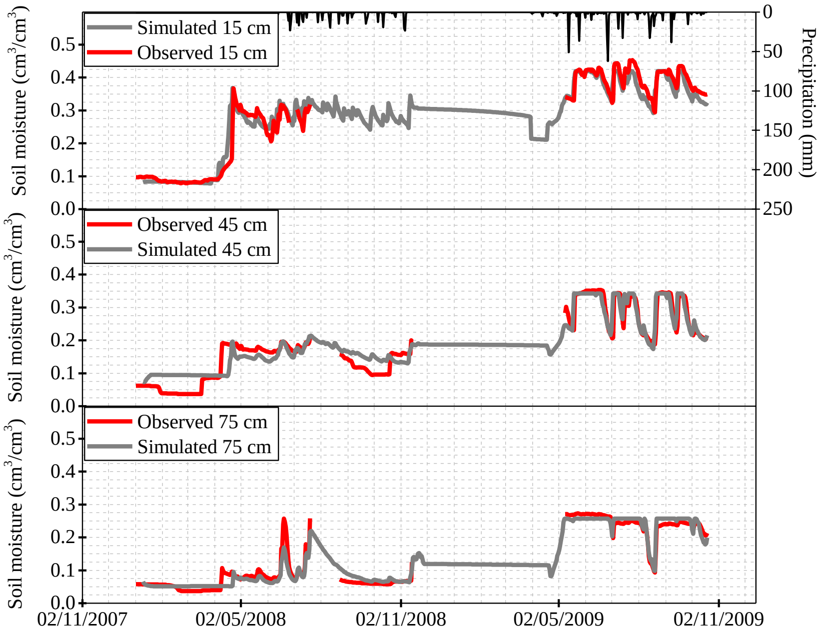

Figure 35: Observed v/s simulated soil moisture contents at depths 15, 45 and 75 cm using the VGM parameters derived from inverse optimization for SS-6

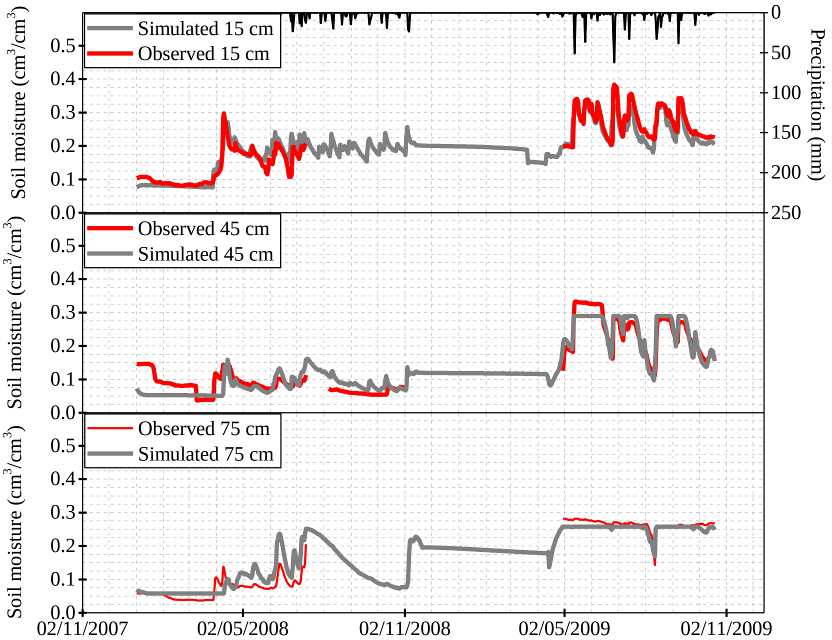

Figure 36: Observed v/s simulated soil moisture contents 15, 45 and 75 cm using the VGM parameters derived from inverse optimization for SS-7

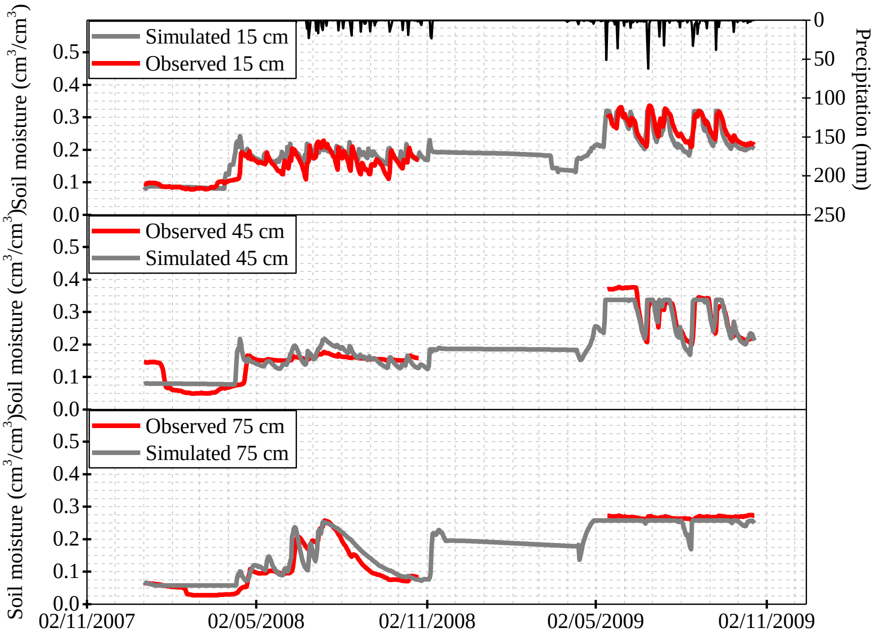

Figure 37: Observed v/s simulated soil moisture contents at depths 15, 45 and 75 cm using the VGM parameters derived from inverse optimization for SS-8

Appendix-C (Nitrate leaching)

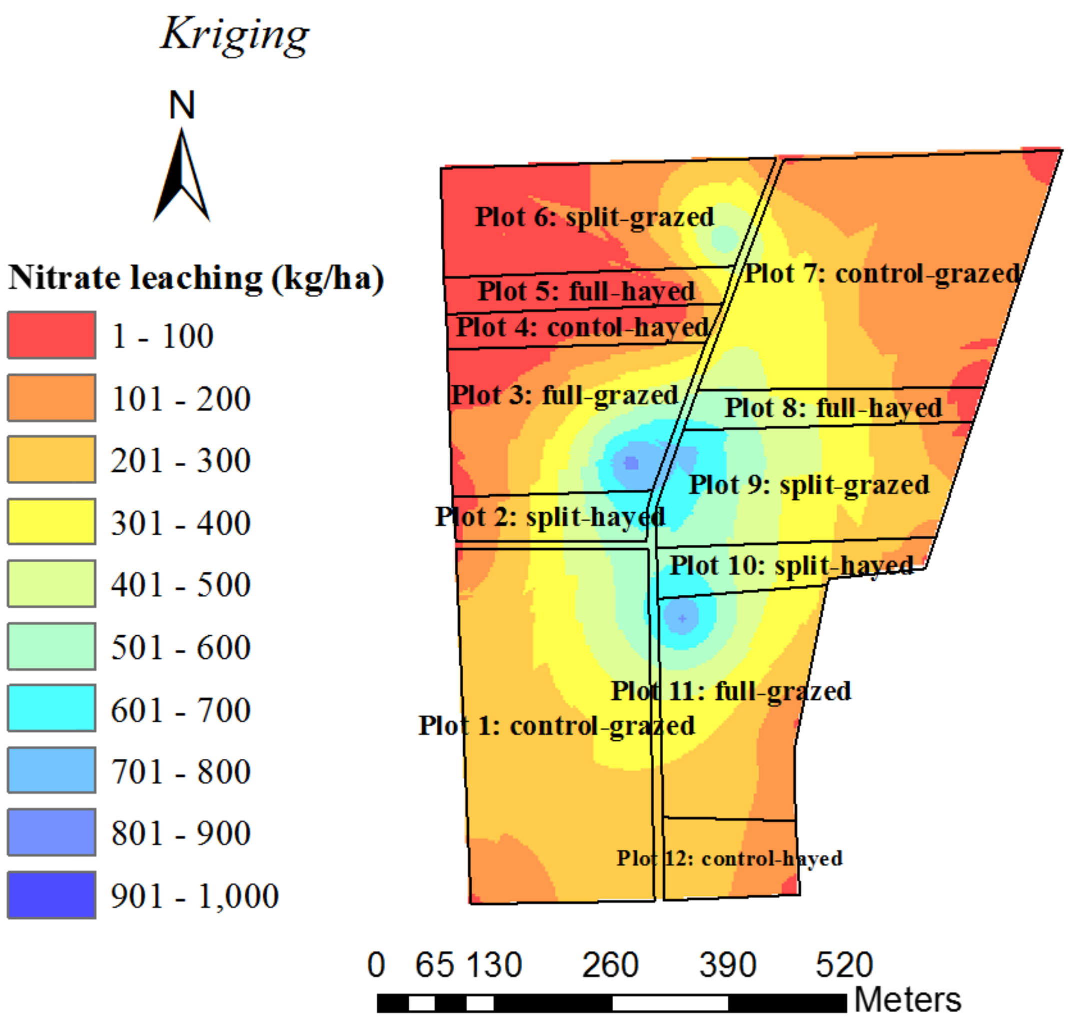

Figure 38: Nitrate leaching fluxes across the study area regionalised using Kriging (average leaching rate: 274 kg/ha/year)

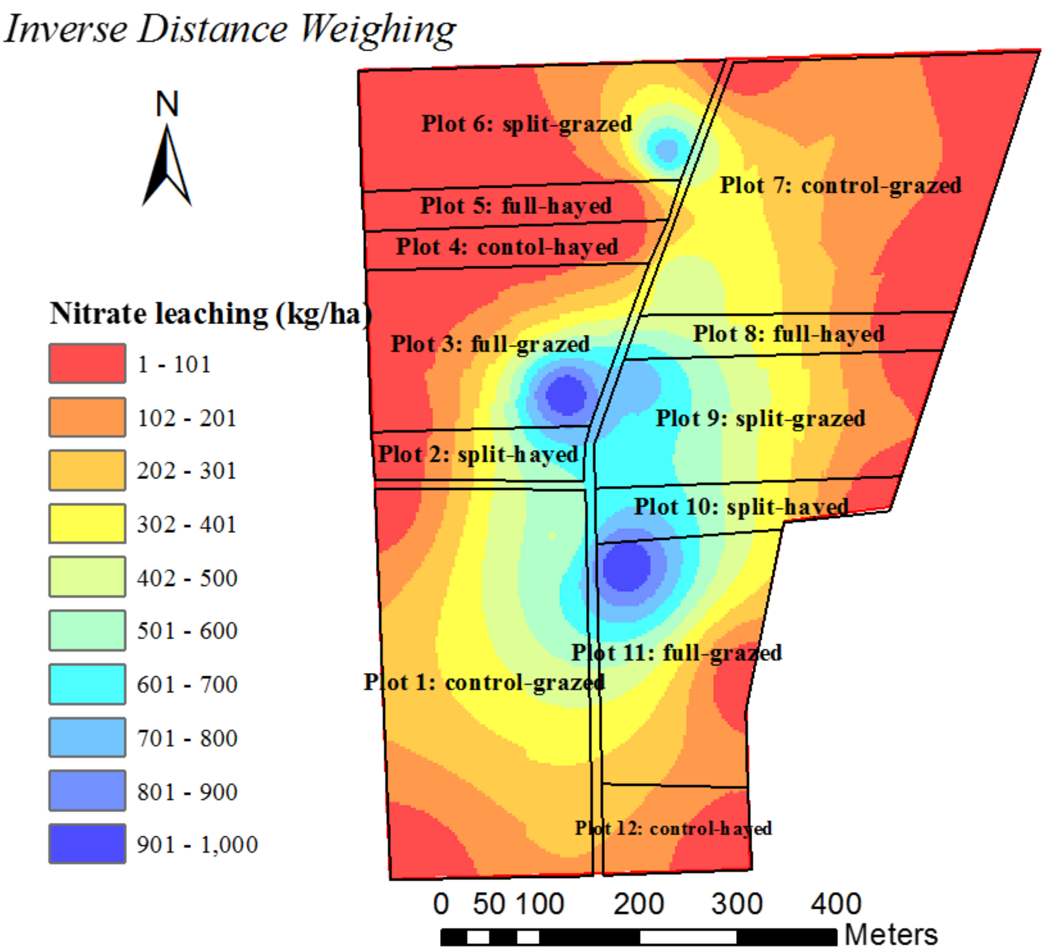

Figure 39: Nitrate leaching fluxes across the study area regionalised using Inverse Distance Weighing (IDW) (average leaching rate: 264 kg/ha/year)

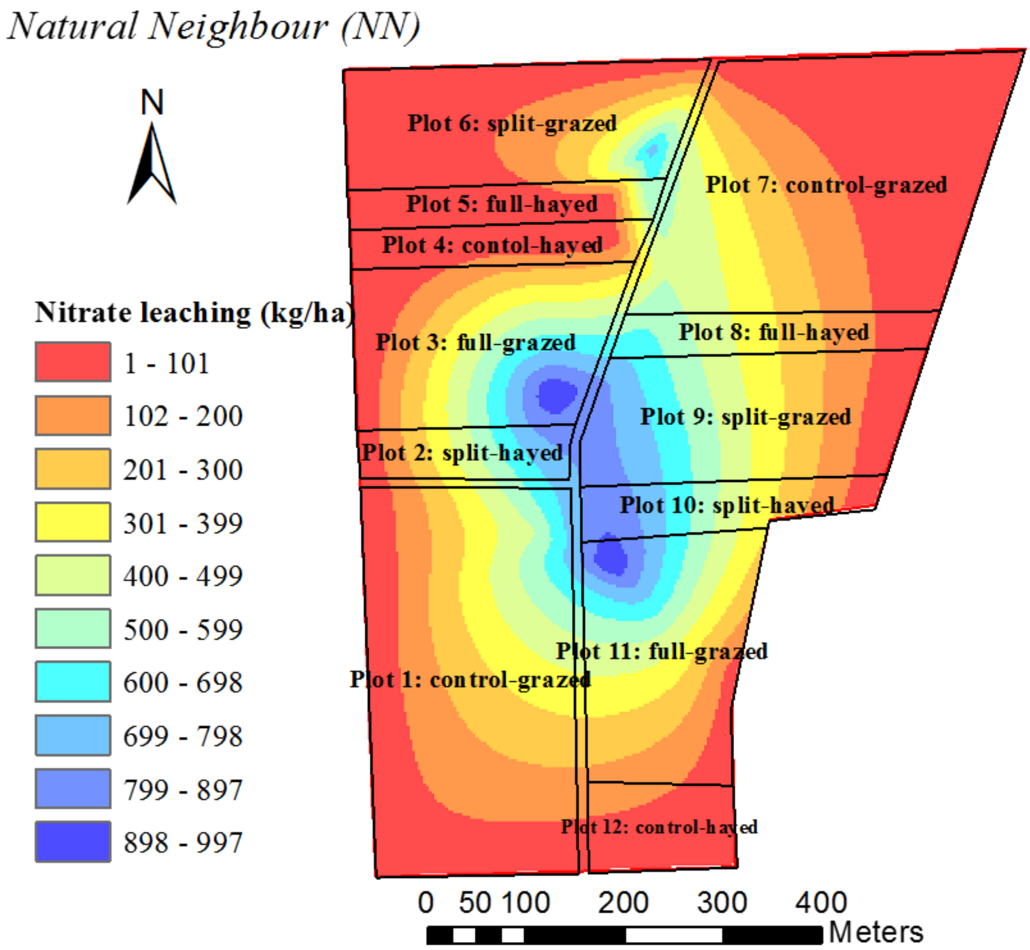

Figure 40: Nitrate leaching fluxes across the study area regionalised using Natural Neighbor interpolation (average leaching rate: 259 kg/ha/year)