Development of a preliminary nitrogen index for different soil types in Quebec

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Abstract

Corn is a major crop in North America, with over 360,000 ha intensively cultivated in Quebec. Much of this Quebec cropland is also subsurface tile drained. Corn requires 120 to 180 kg/ha of nitrogen (N) to be applied to optimize yield, resulting in 43 to 65 thousand tonnes of N being applied to corn lands in Quebec. This addition of N has major environmental impacts, including the contribution to global warming via the emission of nitrous oxide and nitrate (NO_3-N) pollution of water bodies and groundwater, caused by fertilizer runoff and leaching. To explore more sustainable methods of corn production that reduce its contribution to global warming, this research aids in the development of a soil-type-dependent N index that include losses from nitrous oxide emissions, N uptake by the plant, N transformations in the soil, and NO_3 fluxes at tile drainage outlets. The developed N index is a ratio of N lost to the total available N.

Field work was conducted on four agricultural fields near St Hyacinthe, Quebec, to determine soil characteristics. An experimental field in St Emmanuel, Quebec was also considered using previously published data. DRAINMOD was used to simulate the hydrology of the sites in order to accurately simulate the NO_3 fluxes. DRAINMOD performed satisfactorily with indices of agreement (IOA) of 0.58 to 0.95 and Kling-Gupta Efficiencies (KGE) of 0.31 to 0.72. NO_3 fluxes were then generated using DRAINMOD-N II for the five sites and a total of three different soil textures (silty loam, sandy loam, and clay loam). Due to lack of data, it was only possible to calibrate DRAINMOD-N II at two of the sites. For these two sites, DRAINMOD-N II performed satisfactorily with IOA of 0.89 to 0.97 and KGE of 0.45 to 0.8. The soil N was calculated based on field work, and the remaining parameters were obtained from literature and agronomists.

Five fertilizer management practices were considered: 120, 122, 127, 180 and 222 kg N/ha. Sandy loams were found to leach the most NO_3 with simulated values of 52.39 to 82.12 kg N/ha. Clay loams leached more than the silty loams with simulated values of 11.6 to 33.77 kg N/ha and 32.6 to 55.13 kg N/ha, respectively. The N index showed that sandy loams were the most at risk for N losses with low index values of 0.2 to 0.36, followed by clay loams (0.32 to 0.59) and then silty loams (0.84 to 1.43). The N-index results indicate that N management is

most important on agricultural fields with sandy loam soil since the N index values were highest for the sandy loam sites regardless of fertilizer management practice. The abnormally high N index values for the silty loam sites were caused by an overestimation of soil N build up due to the timing of field measurements.

The accuracy of the N index is questionable due to limited data availability. Based on the findings of this research it is recommended that farmers and nutrient specialists focus primarily on tier one N indices, as a tier three N index is very data intensive. If the tier one N index flags the site as high risk, then one should proceed to a tier three index. If one does not have accurate data to perform a tier three N index, the results would be less reliable.

Résumé

Le maïs est une culture importante en Amérique du Nord, avec plus de 360 000 ha cultivés intensivement au Québec. Une grande partie de ces terres cultivables du Québec est également drainée par des drains souterrains. Le maïs nécessite l'application de 120 à 180 kg/ha d'azote (N) pour optimiser son rendement, ce qui se traduit par l'application de 43 à 65 mille tonnes d'azote sur les terres cultivées de maïs au Québec. Cet ajout d'azote a des impacts environnementaux majeurs, notamment la contribution au réchauffement climatique par l'émission d'oxyde nitreux et la pollution des plans d'eau et des eaux souterraines par les nitrates (NO_3-N), causée par le ruissellement et le lessivage des engrais. Pour explorer des méthodes plus durables de production de maïs qui réduisent sa contribution au réchauffement climatique, cette recherche aide à développer un indice N dépendant du type de sol qui comprend les pertes dues aux émissions d'oxyde nitreux, l'absorption d'azote par la plante, les transformations de l'azote dans le sol et les flux de NO_3 aux exutoires de drainage en tuyaux. L'indice N développé est un rapport entre le N perdu et le N total disponible.

Des travaux de terrain ont été menés sur quatre champs agricoles près de Saint-Hyacinthe, au Québec, afin de déterminer les caractéristiques du sol. Un champ expérimental à Saint-Emmanuel, au Québec, a également été considéré en utilisant des données publiées précédemment. DRAINMOD a été utilisé pour simuler l'hydrologie des sites afin de simuler avec précision les flux de NO_3. DRAINMOD a obtenu des résultats satisfaisants avec des indices de concordance (IOA) de 0,58 à 0,95 et des efficacités de Kling-Gupta (KGE) de 0,31 à 0,72. Les flux de NO3 ont ensuite été générés à l'aide de DRAINMOD-N II pour les cinq sites et un total de trois textures de sol différentes (limoneux sableux, franco-sableux et franco-argileux). En raison du manque de données, il n'a été possible de calibrer DRAINMOD-N II que sur deux des sites. Pour ces deux sites, DRAINMOD-N II a obtenu des résultats satisfaisants avec un IOA de 0,89 à 0,97 et un KGE de 0,45 à 0,8. L'azote du sol a été calculé en fonction du travail de terrain et les paramètres restants ont été obtenus de la littérature et d'agronomes.

Cinq pratiques de gestion des engrais ont été envisagées : 120, 122, 127, 180 et 222 kg N/ha. Les loams sableux ont été identifiés comme ceux qui lixivient le plus de NO3 avec des valeurs simulées de 52,39 à 82,12 kg N/ha. Les franco-argileux ont lixivié plus que les limons

sableux avec des valeurs simulées de 11,6 à 33,77 kg N/ha et 32,6 à 55,13 kg N/ha, respectivement. L'indice N'a montré que les limons sableux étaient les plus à risque de pertes d'azote avec des valeurs d'indice faibles de 0,2 à 0,36, suivis des franco-argileux (0,32 à 0,59) puis des limons sableux (0,84 à 1,43). Les résultats de l'indice N indiquent que la gestion de l'azote est la plus importante sur les champs agricoles avec un sol franco-sableux puisque les résultats de l'indice N étaient les plus élevées pour les sites de limon sableux, quelle que soit la pratique de gestion des engrais. Les valeurs anormalement élevées de l'indice N pour les sites de limon sableux ont été causées par une surestimation de l'accumulation d'azote dans le sol en raison du moment des mesures de terrain.

L'exactitude de l'indice N est discutable en raison de la disponibilité limitée des données. Sur la base des résultats de cette recherche, il est recommandé aux agriculteurs et aux spécialistes des éléments nutritifs de se concentrer principalement sur les indices N de niveau un, car un indice N de niveau trois nécessite beaucoup de données. Si l'indice N de niveau un signale que le site est à haut risque, il faut alors passer à un indice de niveau trois. Si l'on ne dispose pas de données précises pour réaliser un indice N de niveau trois, les résultats seraient moins fiables.

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Table of Contents

List of Tables

List of Figures

List of Abbreviations and Symbols

AGNPS	Agricultural non-point source pollution model
Anammox	Anaerobic ammonium oxidation
ANSWERS-2000	Areal non-point source watershed environment response simulation
APS	Ammonium persulfate
BMP	Best management practices
CAN	Calcium ammonium nitrate
CEC	Cation exchange capacity
CRAAQ	Centre de référence en agriculture et agroalimentaire de Quebec
DAP	Diammonium phosphate
ET	Evapotranspiration
IRDA	Institut de recherche et développement en agroenvironment
KGE	Kling-Gupta efficiency
Ks	Saturated hydraulic conductivity
N	Nitrogen
N_2	Molecular nitrogen
N_2O	Nitrous oxide
NERP	Nitrous oxide emissions reduction protocol
NH_3	Ammonia
NH_4	Ammonium
NIT-1	N Index Tool
NO_3	Nitrate
NOx	Nitrogen oxides
NSE	Nash-Sutcliffe efficiency
NUE	Nitrogen use efficiency
PBIAS	Percent bias
RSN	Residual soil nitrogen
RZWQM2	Root zone water quality model 2
SWAT	Soil and water assessment tool
UAN	Urea ammonium nitrate
WTD	Water table depth

Contribution of Authors

All the chapters in this thesis are authored by Calista Brown (first author) and Dr. Chandra A. Madramootoo. Calista conducted field and lab work, calibrated, and validated the model and performed statistical analysis and wrote the following chapters of the thesis. Dr. Madramootoo, the research supervisor and co-author, supervised and provided guidance throughout the research process and reviewed and edited the thesis chapters.

Chapter 1 - Introduction

1.1 Problem definition

Zea Mays (corn) is one of the most important crops in Canada. Quebec is the second largest producer of corn in the country, intensively cultivating over 360,000 ha of corn in 2022 (Statistics Canada, 2022a). Corn is a crop that requires significant amounts of nitrogen (N) to be applied in order to obtain an optimum yield, and recommended annual application rates range from 120-180 kg N/ha (Parent & Gagné, 2013).

However, organic and inorganic fertilizer use is directly linked to increased emissions of nitrous oxide (N_2O), a potent greenhouse gas, as well as the degradation of water quality and formation of algal blooms (Helgason et al., 2005; Carstensen et al., 2019). According to Helgason et al. (2005), N_2O emissions from N fertilizers and manure application account for 55% of the total N_2O emissions in Canada. On average, a cereal crop will only take up 20 to 50 percent of the applied N; some of the inefficiencies can be attributed to the volatile and mobile nature of N (Mosier et al., 2004). N can leave the application site through soil erosion, off-gassing, runoff, or leaching (Mosier et al., 2004). N losses from the field can also contribute to indirect N_2O emissions. For instance, Billen et al. (2020) found that a total of 21% of total agricultural N_2O emissions came from indirect emissions in an agricultural catchment of the Seine in France. The dominant indirect N loss occurs via underground migration routes, primarily the transport of dissolved nitrate (NO_3) (Singh et al., 2020).

Artificial drainage is very important for corn growth in humid climates such as eastern Canada which experiences significant precipitation resulting in fields with high water tables. High water tables can cause crops, such as corn, to have wet stress and will result in a decreased yield (Dayyani, 2010). As such, significant N fertilizer application and the implementation of tile drainage in these environments is necessary to optimize large-scale corn production in Quebec (Tomer et al., 2003). However, tile drainage allows for a virtually direct route for NO_3 contamination of surface water bodies; the NO_3 contaminated water is removed from the field and often directly discharged into a nearby surface water body. Indirect loss can be gauged by analyzing the NO_3 fluxes at tile drainage outlets (Singh et al., 2020). The ability to measure the amount of NO_3 being leached is important for managing water quality and minimizing the environmental impacts of agriculture in eastern Canada.

In an effort to improve the sustainability of corn production in Canada, this research developed N indices that are soil-type dependent. The indices included losses from N volatilization, N uptake by the plant, N transformations in the soil, and NO_3 fluxes at tile drainage outlets (Figure 1). NO_3 fluxes were generated using DRAINMOD-N II. Soil N changes were calculated based on field measurements and the remaining components were obtained from literature. This research was part of a larger project with a similar initiative to the Albertan Nitrous Oxide Emissions Reduction Protocol (NERP).

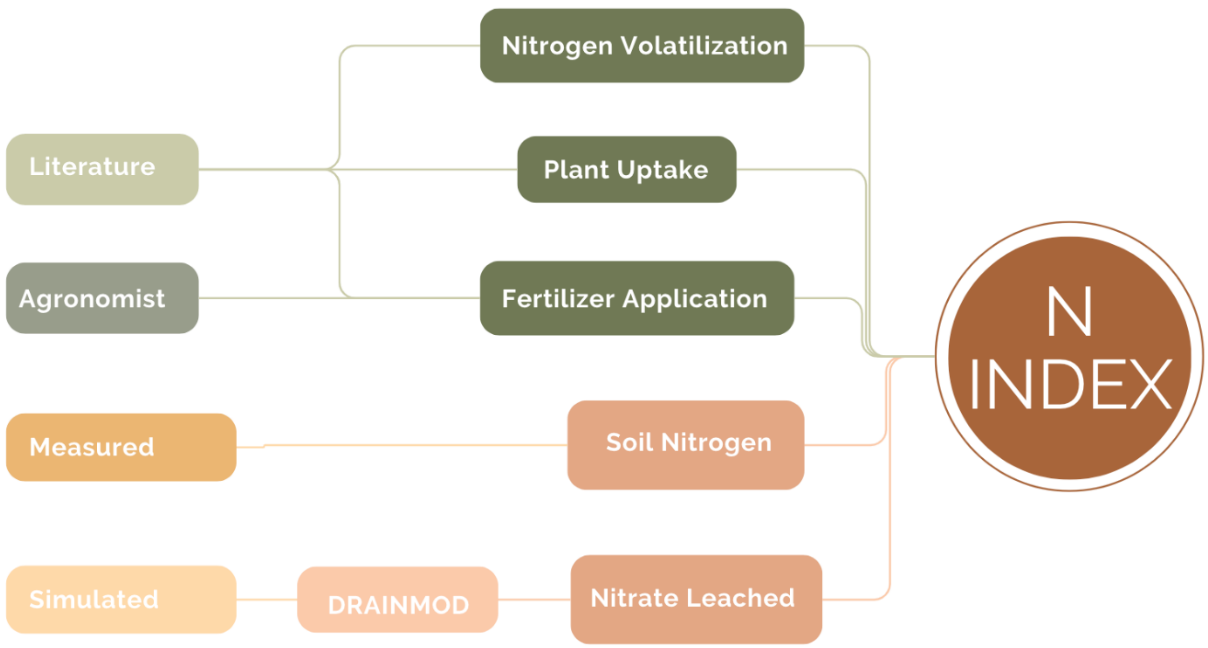

Figure 1. Graphical representation of global objective

This research was conducted on five corn fields in southern Quebec with three different soil types (silty loam, sandy loam, and clay loam). Historic data was collected by the Institut de recherche et développement en agroenvironment (IRDA) and Environment and Climate Change Canada and used in the modelling of NO_3 fluxes.

1.2 Objectives

The global objective of this research was to develop N indices for three different soil types. The study was conducted on five sites (sites A, B, C, D, E) which have a combined total of three soil types (silty loam, sandy loam, and clay loam). To complete this global objective the following specific sub-objectives were conducted:

i. Analyze the three soil types that were used in the study to determine the soil characteristics.

ii. Use base DRAINMOD to simulate the hydrology at the study sites.

iii. Use DRAINMOD-N II to simulate and analyze NO_3 leaching at the study sites.

iv. Use the DRAINMOD-N II simulations and literature data to develop an equation for the N losses to create an N index.

1.3 Scope

The research conducted is only applicable for sandy loam, silty loam, and clay loam soil types and the agroecological zone found in southeastern Quebec. The indices produced by this research are not applicable to all agroecological zones of Quebec nor all soil types. Due to insufficient data only two of the five DRAINMOD-N II models (the experimental field and one of the production fields) were calibrated and there were insufficient measured data to perform validation on any of the DRAINMOD-N II models.

Chapter 2 - Literature review

2.1 Nitrogen cycle

2.1.1 Overview

The N cycle is intimately linked with microbial activity and is considered one of the most intricate and dynamic biogeochemical cycles. It occupies a central role in terrestrial biogeochemistry, biological productivity, and climate change due to its significant influence on other nutrient cycles including carbon, sulphur, phosphorous, and iron (de Sousa, 2020). Changes in food production during the eighteenth-century Industrial Revolution and the 19th and 20th centuries Agricultural Revolutions have drastically altered the N cycle. The growing demand for food resulted in the synthesis of N fertilizers (Gonzalez-Lopez & Gonzalez-Martinez, 2021).

Although the N applied as fertilizer contributes to productive agriculture, excess N applied is lost to the environment. Prior to the use of synthesized N fertilizers biological N fixation and denitrification had similar yields, 140 Tg N/yr of reactive N added to the terrestrial system and 108 Tg N/yr of reactive N removed from the terrestrial system through denitrification (Gruber & Galloway, 2008). After the repeated excessive application of N fertilizers, the amount of reactive N added to terrestrial systems increased to 240 Tg N/yr while the amount of reactive N removed via denitrification only increased to 127 Tg N/yr (Gruber & Galloway, 2008). Therefore, denitrification cannot eliminate the excess reactive N that has been added to the system which results in significant losses of N to the environment. Field recoveries of N rarely exceed 50% as most of the N is lost through volatilization, leaching, soil erosion and denitrification processes (Gonzalez-Lopez & Gonzalez-Martinez, 2021). Figure 2 shows an outline of the N cycle in agriculture.

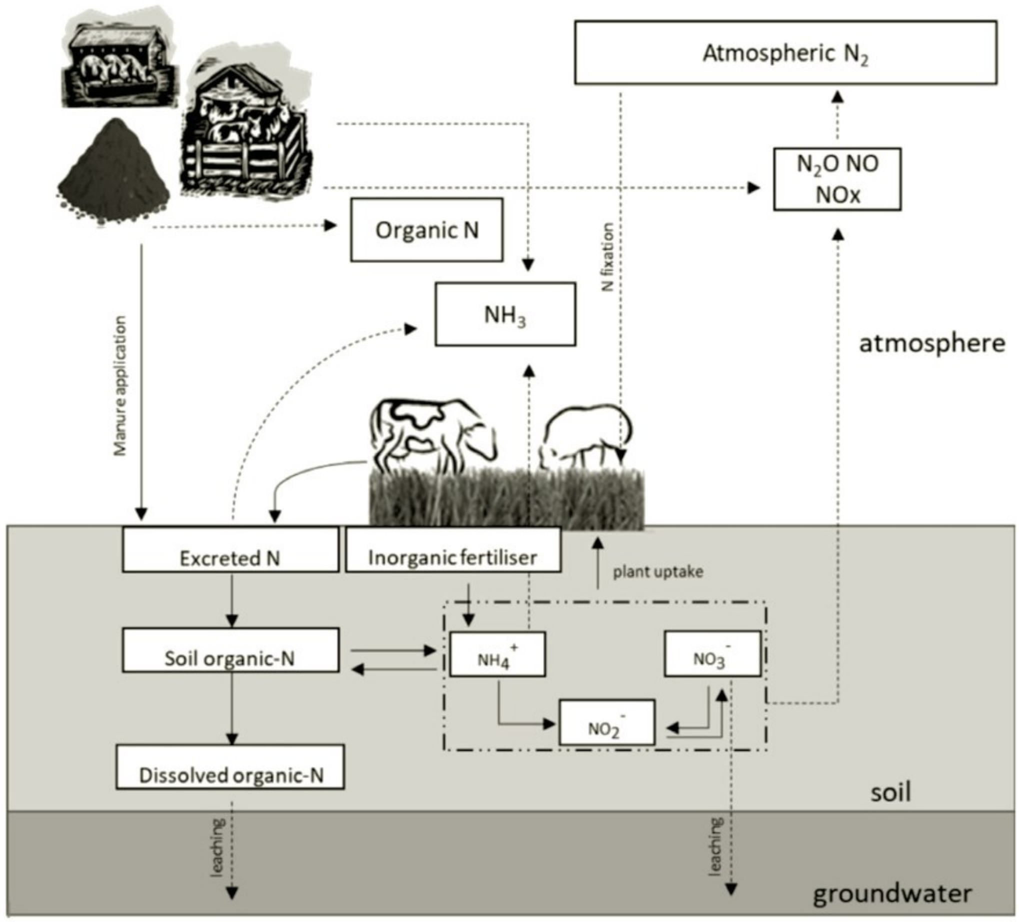

Figure 2. Nitrogen cycle in an agricultural crop context (Gonzalez-Lopez & Gonzalez-Martinez, 2021).

2.1.2 Nitrogen fixation

N is an essential nutrient for all living beings and is a component in amino acids, proteins, nucleic acids and chlorophyll (de Sousa, 2020). It is often the limiting factor for growth in terrestrial ecosystems and consequently it regulates biological activity (Roland et al., 2017). N in its elemental form, molecular nitrogen (N_2), makes up 78% of the Earth's atmosphere, however this form is not usable by most organisms (Gonzalez-Lopez & Gonzalez-Martinez, 2021). Gaseous N_2 must be fixed from the atmosphere before it is available for plant uptake. To convert N_2 into biologically available N (also called reactive N) such as ammonia (NH_3), and subsequently other reactive N species requires a large amount of energy to break the triple bond between the two N atoms (de Sousa, 2020).

$$N_2 + 8H^+ + 8e^- \rightarrow 2NH_3 + H_2$$

The interchange between N_2 and reactive N is predominantly controlled by a wide selection of microbial activities. This conversion has been developed by certain specialized microorganisms via biological N fixation and accounts for approximately 80% of the global process (Gonzalez-Lopez & Gonzalez-Martinez, 2021). Chemical fixation can also convert N_2 to reactive N, the energy required can be supplied by lightning (Stein & Klotz, 2016). However, these natural processes are theorized to account for less than 10% of the global process (Takai, 2019). N can also be fixed due to cosmic radiation when N_2O or NH_3 is produced by combining N and hydrogen and can be used as NH_3 fertilizer or it may be converted to other various fertilizers including urea (Stein & Klotz, 2016).

Due to the high energy requirement of N fixation, only a few specialized prokaryotes (oxygenic and anoxygenic phototrophic bacteria, chemoautotrophic and chemoheterotrophic bacteria, and aerobic and anaerobic bacteria) called diazotrophs can use N_2 as a source of N for their nutrition (de Sousa, 2020). Although many different types of bacteria can carry out N fixation, they all have a similar enzyme complex that catalyzes the reduction of N_2 to NH_3 (or ammonium (NH_4) at neutral pH), nitrogenase. Once the N_2 is converted to NH_3 it can be assimilated in proteins and other organic molecules. The diazotrophs can be free-living, semi symbiotic, and symbiotic fixators (Gonzalez-Lopez & Gonzalez-Martinez, 2021). Free-living fixators do not need to associate with other organisms to fix N and fix relatively low amounts of N (up to 50 kg/ha per year). Semi-symbiotic fixators are associated with low specificity to the roots of various plants and do not produce nodules, they have a slightly higher capacity of fixation than the free-living fixators (up to 200 kg/ha per year). Symbiotic fixators are strictly associated with another organism and when associated with plants, the plant produces nodules. The host provides nutrients for the diazotrophs allowing for a high fixation capacity (up to 400 kg/ha per year) (Gonzalez-Lopez & Gonzalez-Martinez, 2021). The symbiotic associations between bacteria belonging to the genus *Rhizobium* and legumes has the largest implications for humans. These symbiotic fixators are associated with many legumes that are important crops worldwide (alfalfa, soybeans, chickpeas, etc.) and are used as bio-fertilizers to naturally increase N fixation and improve yield of various crops (de Sousa, 2020).

2.1.3 Assimilation and ammonification

N assimilation is the incorporation of inorganic N into organic compounds such as amino acids. In assimilation, the inorganic compound NH_3 can be directly used by microorganisms and/or their symbiotic partners. Most plants absorb inorganic N as NH_3 and NO_3 from the soil through their roots. N is then assimilated, transformed, and mobilized inside the plant. In aerobic soil most inorganic N is supplied as NO_3, in anaerobic soils NH_3 tends to be the dominant form of inorganic N (Yousuf et al., 2022). The principal route of assimilation is the incorporation of NH_3 in glutamate that is transformed in glutamine by the enzyme glutamine synthetase (Gonzalez-Lopez & Gonzalez-Martinez, 2021).

NH_3 available for assimilation is not solely supplied through N_2 fixation, but also through ammonification. Ammonification is the conversion of organic N into NH_3/NH_4 through the breakdown of compounds containing N including proteins and amino acids. The process is performed by various microorganisms including bacteria such as *Bacillus*, *Proteus*, and *Pseudomonas* (de Sousa, 2020). The microorganisms secrete various enzymes for the hydrolysis of the nitrogenous compounds and NH_3 and an assortment of N containing products are released during decomposition. Depending on the organism the catabolism of organic N can produce a variety of N waste products including NH_3, urea, and uric acid. Urea and uric acid can be used as N sources by organisms that have ureases and/or uricases. In anaerobic soils, NO_3 is reduced by bacteria to generate NH_3 in a process called dissimilative NO_3 reduction to NH_3 (Gonzalez-Lopez & Gonzalez-Martinez, 2021).

2.1.4 Nitrification and Anammox

Soil microbes can convert reduced N (NH_3/ NH_4) in the soil to NO_3 in a process called nitrification; this occurs best in slightly alkaline to neutral pH levels and aerobic conditions including well-drained agricultural environments (Bergamasco et al., 2019; Szajdak, 2021). Recently it has been discovered that nitrification can also occur as a one step process in which the bacteria *Nitrospira* can oxidize NH_4 to NO_3 (Gonzalez-Lopez & Gonzalez-Martinez, 2021). More commonly, nitrification is a two-step process carried out by chemolithoautotrophic microorganisms; the first step, nitritation, is the oxidation of NH_3 to nitrite by the bacteria *Nitrosomonas* and the second step, nitratation, is the oxidation of nitrite to NO_3 by the bacteria *Nitrobacter* (Yousuf et al., 2022). Nitrification rates can increase due to increased NH_3 concentrations in soil due to fertilizer application. The increased nitrification can result in acidification of the soil as H^+ ions are released during the process:

$$2\mathrm{NH_4^+} + 3\mathrm{O_2} \longrightarrow 2\mathrm{NO_2^-} + 4\mathrm{H^+} + 2\mathrm{H_2O}$$
$$2\mathrm{NO_2^-} + \mathrm{O_2} \longrightarrow 2\mathrm{NO_3^-}$$

The acidification of soil results in higher mineral solubility, however, the increased rates of nitrification negatively impact soil fertility (Gonzalez-Lopez & Gonzalez-Martinez, 2021). This is because NO_3 is highly soluble and is easily leached if they are not rapidly adsorbed by plant roots. Due to its positive charge, NH_4 is more resistant to leaching as it can be well retained by clay particles and humic soil. In addition, the nitrifying microorganisms have reduced efficiency in soils that are more acidic.

The microorganisms described above are generally aerobes that are autotrophic, however, NH_3 can be oxidized in anoxic conditions. Bacteria such as *Anammoxoglobus*, *Brocadia*, and *Jettenia*, have an Anammox (Anaerobic Ammonium Oxidation) process in which NH_3 is oxidized anaerobically by nitrite (or less frequently NO_3) and produces gaseous N (Gonzalez-Lopez & Gonzalez-Martinez, 2021).

$$NH_4^+ + NO_2 \longrightarrow N_2 + 2H_2O$$

This process occurs in every anaerobic environment where both NH_4 and nitrite are present (Gonzalez-Lopez & Gonzalez-Martinez, 2021). It is most common in marine anoxic sediments and sewage plants; however, it can occur in waterlogged agricultural soils. Large N inputs can stimulate annamox and result in the loss of approximately 5-10% of applied fertilizers in agricultural soils (Nie et al., 2019).

2.1.5 Denitrification

NO_3 can also be removed from the soil profile through denitrification, the conversion of NO_3 to nitrite, NO_x, and N_2 gas by microbes in anoxic conditions (Szajdak, 2021). In agriculture, denitrification is viewed as a negative process as it removes NO_3, which are often added to fields as fertilizer. Most denitrifying microbes belong to the phylum Proteobacteria and are facultative heterotrophs (ie. *Bascillus, Escherichia*, *Nocardia*, and *Staphylococcus*) that only partially oxidize NO_3 to nitrite (de Sousa, 2020). Other genera can complete NO_3 reduction to N_2. Only bacteria that can completely reduce NO_3 can be considered as true denitrifying and this process, previously believed to occur only in anoxic conditions, can occur under both aerobic and anaerobic conditions (Gonzalez-Lopez & Gonzalez-Martinez, 2021). In denitrification, NO_3 acts as the terminal electron acceptor in anaerobic respiration and is sequentially reduced to NO_2^-, NO, N_2O, and N_2.

$$\mathrm{NO_3^-} \longrightarrow \mathrm{NO_2^-} \longrightarrow \mathrm{NO} \longrightarrow \mathrm{N_2O} \longrightarrow \mathrm{N_2}$$
$$2\mathrm{NO_3^-} + 10\mathrm{e^-} + 12\mathrm{H^+} \longrightarrow \mathrm{N_2} + 6\mathrm{H_2O}$$

NO, N_2O and N_2 are gaseous and once produced can diffuse to the atmosphere from soil and water. Denitrification reductases are inhibited in soils with a pH lower than 7, particularly nitrous oxide reductase which reduced N_2O to N_2 (Knowles, 1982). However, denitrification can still occur in acidic soils but at a decreased rate. It is more likely that incomplete reduction of NH_3 will occur in acid soils and result in increased N_2O emissions. Denitrification rates also decrease at lower temperatures (Dorland & Beauchamp, 1991).

2.2 Nitrogen in agriculture

2.2.1 Nitrogen fertilizers

N is one of the most important macronutrients for plants and is considered necessary to reach optimum crop yields (Mosier et al., 2004). N fertilizer has contributed significantly to the tripling of global food production over the past 50 years, and the annual production of N fertilizer has increased over six-fold since 1962 (Mosier et al., 2004). Over the last century, it is estimated that more than a quarter of the world's population has been fed by synthetic N fertilizers (Ramankutty et al., 2018). N fertilizer exists under two main categories: organic and inorganic.

Organic N fertilizer comes from sources such as livestock manure and crop residues. In contrast, inorganic fertilizers are man-made and include NH_3, urea, urea ammonium nitrate, ammonium phosphate, and ammonium sulphate (Rochette et al., 2018; Szajdak, 2021). Most of the global N demand is for the production of cereal crops. On average, a cereal crop will only take up 20 to 50% of the applied N; some inefficiencies can be attributed to the volatile and mobile nature of N (Mosier et al., 2004). N can leave the application site through soil erosion, off-gassing, runoff, or leaching (Mosier et al., 2004). N that leaches into groundwater can then be removed from the field through subsurface drainage and discharged into surface water. The transport of this N reduces the retention capacity of the field (denitrification of NO_3-N) and poses the risk of eutrophication of surface waters (Carstensen et al., 2019).

Inorganic and organic fertilizer application is a primary factor in determining N losses (Cooke & Verma, 2012). Higher amounts of fertilizer are associated with higher N losses. When fertilizer is overapplied, it can result in a build-up of NO_3 in the soil profile. The residual NO_3 is susceptible to leaching due to the mobile nature of N (Skaggs et al., 2012). Inorganic fertilizers are also often 'quick-release,' meaning the N in the fertilizer will rapidly become plant-available when introduced to water. 'Quick-release' fertilizers should be applied at low rates when the crop is taking up N, or their use will notably increase the amount of dissolved N available for leaching. Some inorganic fertilizers are considered 'slow-release' and are designed to delay the release of plant-available N and allow for a higher application rate. N fertilizer applied as urea will quickly be hydrolyzed to NH_4 and carbon dioxide by urease, and the organic N from organic fertilizers can be converted to bioavailable N by soil microbes in a process called mineralization (Gonzalez-Lopez & Gonzalez-Martinez, 2021).

Organic fertilizers contain mainly organic forms of N that are unavailable and must be mineralized (converted to NH_4 by soil microbes) before plants can utilize the N (Gutser et al., 2005) (Figure 2). The application of organic fertilizer increases soil carbon which affects N cycling, particularly denitrification. Increased soil carbon stimulates microbial growth and activity and provides the organic carbon required by soil denitrifiers (Cameron et al., 2013). Increased carbon supplies are generally associated with lower N_2O:N_2 ratios due to the increased denitrification (Saggar et al., 2013). It should be noted that soil carbon can also be increased by applying urea, a man-made inorganic fertilizer, as well as applying organic fertilizers.

Fertilizer timing also impacts the amount of N losses. Many farmers will apply a pre-plant fertilizer treatment in spring and early summer. This timing of application coincides with warming temperatures and increased rainfall. If there is excess rainfall and drainage occurs beyond the crop root zone, then N leaching is likely to occur (Jabloun et al., 2015). In a split application approach fertilizer is often applied in two applications the timing of which best suit the N uptake of the plant, this reduces the amount of excess N in the soil profile and reduces N losses (Wang & Li, 2019). Manure is sometimes applied in the fall after harvest with the assumption that the N will remain in the soil for the next growing season. Ejack et al. (2021) found that the fall application of manure in cold humid environments such as eastern Canada did not provide plant available N to spring cereals.

2.2.2 Losses of nitrogen to water

Large amounts of N can be lost to water via leaching, leached N is predominantly in the form of NO_3, but nitrite and NH_4 can also be lost. Due to its negative charge, NO_3 is the main form of N lost through leaching because it does not adsorb as readily to soil and clay particles as the positively charged NH_4 (de Sousa, 2020). NO_3 is also highly soluble, which results in NO_3 being easily dissolved in subsurface water and makes it susceptible to leaching. Environmental concerns of NO_3 leaching are mainly related to eutrophication and water acidification of surface water bodies. The volatilization of leached N is also a point of concern ((Wang & Li, 2019)).

Soil biota plays a prominent role in nutrient cycling and availability. Protozoa in soils accelerate the mineralization of NH_4 and the denitrification of NO_3 (Gonzalez-Lopez & Gonzalez-Martinez, 2021). Water content in soil dramatically impacts the rate of the interactions between microorganisms and protozoa. When soil is drier, it inhibits the ability of protozoa to mineralize N and reduces denitrification rates (de Sousa, 2020). Because of this dependence on water, decreasing the water held in the field via subsurface drainage allows for an aerobic environment to form and reduces protozoan activity (de Sousa, 2020). The decreased protozoan activity can result in less mineralization of N and lower denitrification rates, resulting in more NO_3 leaching due to increased NO_3 in the soil profile. Fields that are under subsurface drainage also have increased risks of NO_3 leaching, this is due to the direct transport of NO_3 rich water that was drained from the field to surface water bodies (S. Singh et al., 2020).

N leaching depends on several factors, including fertilization level, type and timing of application, method of fertilizer application, soil properties, crop type and fertilizer requirements, and plant nutrient uptake (Katz, 2020). Weather conditions also majorly impact the amount of N leaching (Jabloun et al., 2015). N will leach when the soil water content exceeds the maximum soil water holding capacity. This is because the soil water will drain from the root zone and will carry N, mainly as soluble NO_3, with it (Meisinger & Delgado, 2002). This means high precipitation environments in places like eastern Canada have an increased risk of NO_3 leaching.

2.2.3 Losses of nitrogen to the atmosphere

N can off-gas in many different forms including N_2O, nitrogen oxides (NO_x), NH_3, and N_2. The rates of N off-gassing depend on several factors including fertilizer application, climate, tillage practices, irrigation practices, and soil type. Studies have found that with increased fertilizer application the amounts of N_2O-N and NO_x-N increase but still only amount to 1-2% of the total N applied (Halvorson & Del Grosso, 2013; X. J. Liu et al., 2005). NH_4 forming fertilizers are particularly susceptible to NH_3-N volatilization, and it has been reported that it can account for up to 50% of total N losses from a field (International Plant Nutrition Institute [IPNI], 2016). Excess NH_4 in the soil surface will lead to the volatilization of NH_4 into NH_3 gas, and chances of volatilization increase in soils with more basic pH levels (Rochette et al., 2013).

NH_3-N volatilization is affected by soil type, pH, temperature, and moisture content. More alkaline soils tend to result in higher rates of NH_3-N volatilization, this is because the relationship between NH_3-N and NH_4-N concentrations is highly pH dependent (Rochette et al., 2013). At a higher pH, there is more NH_3-N than NH_4-N resulting in increased NH_3-N off-gassing. Soil texture is highly related to the cation exchange capacity (CEC) of a soil, the finer textured soils such as clay have higher CEC (Gaines & Gaines, 1994). Soils that have a higher buffering capacity due to characteristics like high CEC, high clay content, and high soil organic matter, will be more resistant to changes in pH and therefore NH_3-N volatilization is less likely in these kinds of soils (Rochette et al., 2013). Increased soil temperature increases urea solubility which increases the volatilization of NH_3-N, warmer soil temperatures also tend to correspond with when N is applied to fields (early summer months of May-June). If soil moisture is high NH_3-N volatilization is increased due to the hygroscopic nature of urea. After urea hydrolyzes it can be lost via volatilization. Jantalia et al. (2012) found that NH_3 volatilization resulted in losses of 0.1 to 4% of the N fertilizer applied in irrigated fields that applied urea fertilizers.

Agricultural land use is also highly associated with N_2O emissions. Since the pre-industrial era atmospheric N_2O concentrations have risen from ~270 ppb to 332 ppb in 2019 (Fowler et al., 2015). Approximately 60% of the anthropogenic contribution to this increase is due to agricultural activities (Syakila & Kroeze, 2011). N_2O is a powerful greenhouse gas that accounts for approximately 6% of global warming as of 2019 (World Meteorological Organization (WMO), 2019). Approximately 66% of N_2O emissions from soil are caused by microbial processes (Gonzalez-Lopez & Gonzalez-Martinez, 2021). N_2O emissions from agriculture, like most N losses, are mainly a function of N applied as fertilizer. Up to 70% of annual emissions of N_2O worldwide are a result of nitrification and denitrification (Butterbach-Bahl et al., 2013). To reduce emissions, soils should be well aerated and drained to prevent anoxic environments from forming and reduce denitrification. The sum of the N lost due to N_2O, NO_x and NH_3 off gassing can range from 3.3 to 5.8% (Halvorson & Del Grosso, 2013; Jantalia et al., 2012)

It is also important to note that although losses due to N_2 off-gassing are poorly documented, N_2 emissions have been reported as being up to ten times the N_2O losses in a field (Chen et al., 2019; Pan et al., 2022). Laboratory studies have reported losses of up to 70% of the applied N in conditions that are optimal for denitrification (Cardenas et al., 2017). N_2 emissions represent an inefficient use of N and potential economic losses for farmers.

2.2.4 Plant nitrogen uptake

Plant available N in the soil takes two primary forms, NO_3 and NH_4. Plants absorb the N through their root systems when fertilizer is applied to soil. The availability of N to the plant depends on the physiological capacity of the roots to uptake and assimilate N. Soil moisture and texture are the main factors that control the capacity of the roots. Generally, the preferred form of N for plant uptake is NH_4, however, the preferred N form depends on plant adaptation to soil conditions (Gonzalez-Lopez & Gonzalez-Martinez, 2021). Soils with low pH and anaerobic conditions tend to produce more NH_4 and plants adapted to these kinds of soils preferentially uptake NH_4. Plants adapted to soils with high pH and aerobic conditions tend to prefer NO_3 due to its higher abundance. NH_4 is the primary form of N taken up by corn plants, however, crops require both NO_3 and NH_4 for proper growth (Warncke & Barber, 1973). In corn crops maximum N uptake occurs during vegetative growth, between the point when the plant grows 9 leaves (V9) and 18 leaves (V18) (Abendroth et al., 2011).

2.2.5 Soil nitrogen

N in soil can be divided into two main categories, organic N and mineral N. A substantial proportion of total N in soil is organically bound (0-90%) (Szajdak, 2021). Organic N stability is largely dependent on temperature and moisture trends. At lower average temperatures and higher moisture levels soil organic matter increases (Haas et al., 1957). Organic matter in soils has declined due to cultivation of virgin soils, however, cultivated soils in the Midwest have reached an equilibrium of organic matter levels (Haas et al., 1957). Reduced tillage techniques, legume rotations, and prudent fertilizer application can help stabilize or possibly increase soil organic matter over time. Inorganic N is either applied as fertilizer or mineralized by microorganisms. The amount of inorganic N that remains in the soil after harvest is referred to as residual soil N (RSN). RSN contains soluble and particulate forms of N that are easily transported from agricultural land to waterways, particularly NO_3 (Rasouli et al., 2014). RSN can also be used to fertilize crops in the following growing season. It is also possible for the RSN to become unavailable to plants due to soil microorganisms decomposing plant residues in a process called immobilization (Szajdak, 2021). As the decomposition proceeds and microorganism populations decline, the inorganic N becomes available to plants again.

2.2.5 Nitrogen indices and balance

N losses from agricultural land use are negatively affecting surface water, groundwater, and air quality. In order to minimize agriculture's negative impact to the environment it is necessary to minimize the off-site transport of N by developing and implementing best management practices (BMP) (Delgado et al., 2010). To accomplish this, it is important for nutrient managers and conservationists to have a fast and effective tool that can assess the effects of current and alternative management practices of N losses (Delgado et al., 2008). Over the past 30 years, various N index tools have been developed, including the Nitrate Leaching Index, the Nitrate Available to Leach Index, the Ontario N Index, Nitrogen Loss and Environmental Assessment Package, LEACHMN, and the GIS N Index Tool (NIT-1) (Reynolds et al., 2016). N indices are tools of varying complexity that simulate the N losses from agricultural fields.

The estimation of agricultural N losses is incredibly difficult due to the complexities of the N cycle. Often detailed models that consider numerous N pathways need to be used to estimate N losses from a field accurately. However, these complex models are time-consuming and not user-friendly. Shaffer and Delgado (2006) proposed a tiered approach to NO_3 leaching indices in which each tier would be more accurate but also require more input data. The tier one N index would require non-numeric inputs and would be used to separate fields that have medium, high, and very high NO_3 leaching potential from sites that have low and very low NO_3 leaching potential. A tier two N index would involve the use of application models and the introduction of off-site effects, interpretation, and normalization. Lastly, a tier three N index would require detailed research models, field measurements, off-site effects, interpretation, and normalization. A tiered approach would allow for N indices to be applied at a global scale while also allowing for refinement of accuracy (Delgado et al., 2006).

Delgado et al. (2010) recommend a field scale approach that incorporates the N balance into the index to better account for all possible agricultural losses of N. An N balance is a type of nutrient balance which is used to calculate the difference between the N input and output in a system. Nutrient balances represent nutrient flow in a system and are often used to produce sustainability indicators such as N Use Efficiency (NUE) (Bassanino et al., 2007). Often these balances are used as policy tools to reduce NO_3 leaching risks and are used to assess the efficacy of environmental measures. It is a well-known approach used for nutrient management in agriculture and can be used to determine if there is a deficit or surplus of nutrient application (Oliveira et al., 2022). Therefore, its inclusion in N indices is a logical progression and necessary to better assess BMP.

Delgado et al. (2006) highlighted the importance of other nutrients in the development of an N index. When using an N index that only pertains to N, a nutrient manager could decide on BMP that optimize the efficiency of N and simultaneously compromise the efficiency of another nutrient. The current N index made by Delgado et al. (2006) simultaneously evaluates both N and phosphorous and is applicable in different agroecosystems in the United States and internationally. However, the index is not sensitive to abrupt changes in NO_3 leaching driven by sudden events such as high precipitation or irrigation (Delgado et al., 2006).

2.3 Drainage and water table management

2.3.1 Subsurface drainage in Quebec

In places with wet climates, the water table is relatively high. This high water table can result in waterlogging and stress crops, which can reduce yield (Dayyani, 2010). Using drainage systems, the water table can be lowered, excess soil water removed, and natural drainage improved. Consequently, soil health and productivity, as well as the productivity of the crops, will be improved (Satchithanantham et al., 2014). Subsurface drainage is a standard method of drainage used in agriculture as it allows for rapid drainage of excess soil water, higher land trafficability, and increased soil aeration. The most common method of subsurface drainage used is tile drainage, the implementation of perforated pipes approximately one meter below the soil surface (Figure 3). Groundwater can enter the perforated pipes and is removed from the field through gravity or a pumped outlet, this artificially lowers the water table. Subsurface discharge can then be released into a mitigation pond to reduce NO_3 concentrations or is directly channeled into a surface water body.

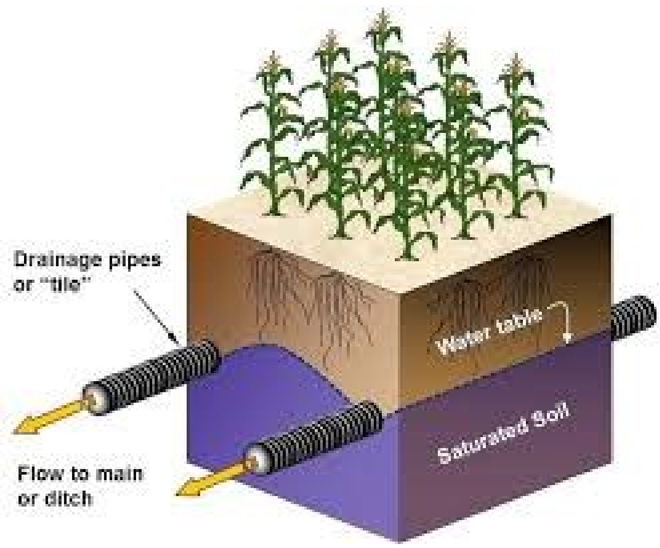

Figure 3. Diagram of tile drainage (Image from Scherer et al. (2014)).

It was estimated that in 2002 there were 735 000 ha of tile-drained crop land in Quebec (Gollamudi, 2006). Subsurface drainage is necessary in environments like eastern Canada for several reasons. Intensive cropping of cereals and vegetables is conducted on heavy soils such as clay, clay loams, and fine sands and silts (Dayyani, 2010). The cultivated lands tend to be flat, and these soils tend to have low hydraulic conductivity and can easily be waterlogged which can lead to flooding.

On average, Quebec receives a large amount of rain, 79-138 cm of precipitation annually, and the precipitation routinely exceeds evapotranspiration by 300-700 mm (Statistics Canada, 2022b). These factors together result in fields that absorb and hold large amounts of water which can damage crops and limit growth if unregulated. In addition, the growing season is quite short and drainage in humid regions removes excess water from the root zone and improves field trafficability which allows for timely planting and harvesting (Evans & Fausey, 1999). Artificial drainage reduces surface runoff which results in less soil erosion and particulate pollutant transport, however, fields with artificial drainage systems contribute more water to stream flow than naturally drained fields. A major downfall of subsurface drainage is that it acts as a more or less direct route for excess water contaminated with nutrients, particularly NO_3-N, to surface bodies of water (Carstensen et al., 2019). The water drained from the fields is often rich in NO_3 and contributes to non-point source pollution from agriculture. NO_3 loads in tile-drained water can be as high as 95% of the total N losses from a field (Gollamudi et al., 2007). Therefore, it is important to quantify the nutrient loading coming from tile drainage to protect and preserve water quality in Quebec.

2.3.2 Corn production in Quebec

Corn is the primary cash crop in Quebec and is the most important crop in eastern Canada. Corn in Canada is grown mainly for grain and is used in ethanol production, food production, and silage and animal feed. Corn is Canada's third largest grain crop and in 2006, 96% of corn grown in Canada was grown in the East and 33% of Canada's total corn production was in Quebec (330, 000 ha) (Pesticide Risk Reduction Program et al., 2006). Over the last couple of decades, there has been a slight increase in the area cropped for corn in Quebec. In 2021, Statistics Canada (Statistics Canada, 2022a) reported a total of 361,000 ha of corn cropland in Quebec, an increase of about 30,000 ha over 15 years.

Corn has a high potential productivity and yield has been increasing over the past couple of years in Quebec (Statistics Canada, 2022a). To reach optimum yield corn requires high N. To achieve this, farmers will apply high rates of N fertilizer to their fields, ranging from values of 120-180 kg N/ha (Parent & Gagné, 2013). Split application of N is common for corn, usually N is applied at time of seeding and again at the V6 (6 leaves) stage of growth (Clark, 2020). The addition of this N can lead to high rates of NO_3 losses due to leaching and contamination of groundwater. In addition, corn can be planted in rotation with soybeans which provides many benefits including reduced N use due to N fixation.

Corn is planted late April to early May when soil temperatures are warming. Corn should be planted in soil that is at least 10°C to encourage rapid germination, uniform emergence, and to protect against seedling blights (Pesticide Risk Reduction Program et al., 2006). Corn can be planted on a variety of soils as long as they are well-drained. Corn in Quebec benefits greatly from tile drainage due to the high water table and the prevalence of impermeable clay soils from glacial retreat. The shallow water tables combined with the relatively impermeable soil can lead to flooding and water stress for corn crops in spring and fall when there are heavy rain events. This makes tile drainage a necessity to obtain the optimal yield of corn in Quebec. The loss of NO_3 associated with increased N fertilizer application is exacerbated by the implementation of tile drainage as it removes the NO_3 contaminated water rapidly and directly discharges into surface water bodies. This highlights the importance of monitoring NO_3 fluxes of corn fields in Quebec.

2.4 Drainage simulation modelling

2.4.1 Hydrologic and nitrogen models

Hydrologic processes in agricultural watersheds are incredibly complex and difficult to evaluate. Hydrologic models are simplified representations of actual hydrological systems that are used to simulate these complex processes and pinpoint problems and find solutions through best management practices (Dayyani, 2010). Hydrologic models are often paired with water quality models which allow for a wider application. Hydrologic and water quality models play an important role in many areas of agricultural hydrology such as pollutant source detection, impacts of fertilizer application strategies on water quality, climate change impacts, agricultural drainage plans, etc. Generally hydrologic water quality models have two purposes, to formalize scientific understanding of a hydrological system and to provide testable predictions (Solomatine & Wagener, 2011).

Hydrologic and water quality models are generally categorized into two main groups, conceptual and physically based models (Solomatine & Wagener, 2011). Conceptual models use simplified descriptions of hydrological process using simplified mathematical relationships. Most models used in practical applications are conceptual models. Physically based models are based on the laws of conservation of mass, momentum, and energy and generally use more detailed representations of physical processes (Solomatine & Wagener, 2011). However, physically based models have high data demand and often have scale-related issues. The parameters required by these models may be measured at a scale that is not representative of the scale that is being modeled and at least some of the parameters cannot be derived through measurements. This means that these models still require calibration of a few key parameters. As such, these models are usually applied in a similar way as the conceptual models.

Hydrologic and water quality models can also be categorized as continuous simulation models and event-based models (V. P. Singh, 1995). Continuous simulation models are used for long-term purposes such as estimation of effects of climate change and agricultural management practices. Event based models are used for short-term purposes such as flood forecasting and evaluating structural management practices. These models can range in scope from large watershed scales to small field size scales.

In order to properly use a model, it is important to have a clear understanding of the model's original purpose, under what conditions it performs well, accuracy of results, assumptions made and limitations (Dayyani, 2010). It is important to select a model that meets the needs of the water resource problem that is being addressed. To meet the objectives of the current study, the main requirements of the model were: (1) simulates hydrologic and nutrient transport processes in tile drained agricultural land at the field scale, (2) functions well in cold wet climates analogous to eastern Canada, (3) ability to incorporate fertilizer management scenarios, and (4) ability to carry out continuous simulations. Common hydrological and water quality models that were considered for this research include: Annualized Agricultural Non-Point Source Pollution Model, AnnAGNPS (Young et al., 1989), Areal Non-point Source Watershed Environment Response Simulation, ANSWERS-2000 (Bouraoui & Dillaha, 1996), Root Zone Water Quality Model 2, RZWQM2 (Hanson et al., 1998), Soil and Water Assessment Tool, SWAT (Arnold et al., 1998), and DRAINMOD (Skaggs, 1980). These models are briefly outlined below.

2.4.2 AnnAGNPS model

The AnnAGNPS model (Young et al., 1989) was developed to predict non-point source pollutant loadings in agricultural watersheds to aid in determining BMPs. It is a distributed parameter, physically based model that can be used to simulate the surface runoff, sediment, nutrients, and pesticide movement within agricultural watersheds. The model uses the SCS-Curve number method to calculate runoff volume and the TR-55 method to calculate runoff rate (Dayyani, 2010). Daily input data is required, and output data is on an event, monthly, or annual basis. AnnAGNPS has been validated in eastern Canadian sites. The model was used to estimate runoff volumes for both a site in south-western Ontario and the St Esprit watershed in Quebec and the model results during the growing season were acceptable for both sites (Das et al., 2004; Perrone, 1997). However, the model does not use mass balance calculations for inflow and outflow and there is not tracking of nutrients and pesticides from one day to the next (Dayyani, 2010).

2.4.3 Answers-2000 model

ANSWERS-2000 (Bouraoui & Dillaha, 1996) was developed to simulate average annual runoff and sediment yield from agricultural watersheds. It is a non-point source management model that allows for simulations to be run at field or watershed scales and simulations can be long or short term. It is a physically based, distributed parameter, continuous simulation model that works with an ArcInfo GIS interface for data input and processing. Bai et al. (2004) found that the model adequately simulated runoff during the growing season in Ontario. Both N and phosphorous are simulated in ANSWERS and are based on interactions between four pools of N and phosphorous each. N leaching is simulated through the estimation of N percolation, total Kjeldahl N and denitrification. However, the model does not have chemical routing processes and does not allow for proper fertilizer inputs, and it has non-significant baseflow simulations (Deb & Shukla, 2011).

2.4.4 RZWQM2 model

RZWQM2 (Hanson et al., 1998) was developed to simulate major physical, chemical, and biological processes in agricultural watersheds. It is a one-dimensional, process-based, field scale model that accounts for water, chemical, and heat transport, plant growth, evapotranspiration, organic matter/N cycling, pesticides, and management practices. The model can be used to predict the impacts of management practices on the movement of NO_3 and pesticides to runoff, drainage water, and deep percolation. Craft et al. (2018) found that RZWQM2 is capable of simulating shallow drainage systems in the Midwest and NO_3 losses due to drainage were accurately predicted. Some limitations of the RZWQM2 model are that it requires extensive input data, and it can only simulate vertical movement of water and chemicals (Ma et al., 2012).

2.4.5 SWAT model

SWAT (Arnold et al., 1998) is a conceptual, continuous, physically based watershed scale model that simulates impact of land management practices on water, chemical, and sediment yields. The model is based on eight components including hydrology, weather, sedimentation, soil temperature, crop growth, nutrients, pesticides, and management practices (Dayyani, 2010). The model accounts for varying weather, soil types and land uses, and has been used successfully in eastern Canada. Gollamudi et al. (2007) reported that SWAT satisfactorily simulated sediment and nutrient transport for two agricultural fields in Quebec. However, they found that the simulations on a daily or monthly basis were less reliable with a short calibration period (Gollamudi et al., 2007). Although subsurface drainage is incroporated in the model, the method is very simple and does not consider detailed information of the tile-drainage system (Dayyani, 2010). SWAT divides watersheds into hydrologic response units which results in the requirement of hundreds of input files. Without a reliable interface, management of the input files is difficult.

2.4.6 DRAINMOD model

DRAINMOD (Skaggs, 1980) is a deterministic, field-scale model that simulates the hydrology of poorly drained, high water table soils with an emphasis on agricultural drainage. It was designed with the intent of designing and evaluating agricultural drainage and water management systems. The model simulates the performance of different water management systems including subsurface drainage, controlled drainage, and subirrigation, over long periods of time. The model uses approximate methods to calculate a water balance for the soil profile as a closed system (Skaggs, 1980). The water balance is calculated using vertical soil columns extending from the surface to the impermeable layer with a unit surface area at drain mid-spacing (Figure 4). The water balance is conducted on a day-by-day, hour-by-hour basis and consists of rain, infiltration, ET, drainage, surface runoff, subirrigation, vertical seepage, and distribution of soil water in the profile. The water balance for the soil profile for a time increment of Δt can be expressed as (Skaggs, 1980):

$$\Delta V_a = D + ET + DS - F \qquad Eq\ 1$$

Where ΔV_a is the change in air volume, D is the lateral drainage, ET is evapotranspiration, DS is deep seepage, and F is infiltration. All parameters are measured in centimeters. Lateral drainage, ET, deep seepage and infiltration are all functions of the water table elevation, soil water content, soil properties, drainage parameters, crop type and growth stage, and atmospheric conditions. The amount of runoff and storage for a time increment of Δt can be expressed as (Skaggs, 1980):

$$P = F + \Delta S + RO \qquad Eq\ 2$$

Where P is precipitation, F is infiltration, ΔS is the change in volume of water stored on the surface, and RO is runoff. All parameters are measured in centimeters.

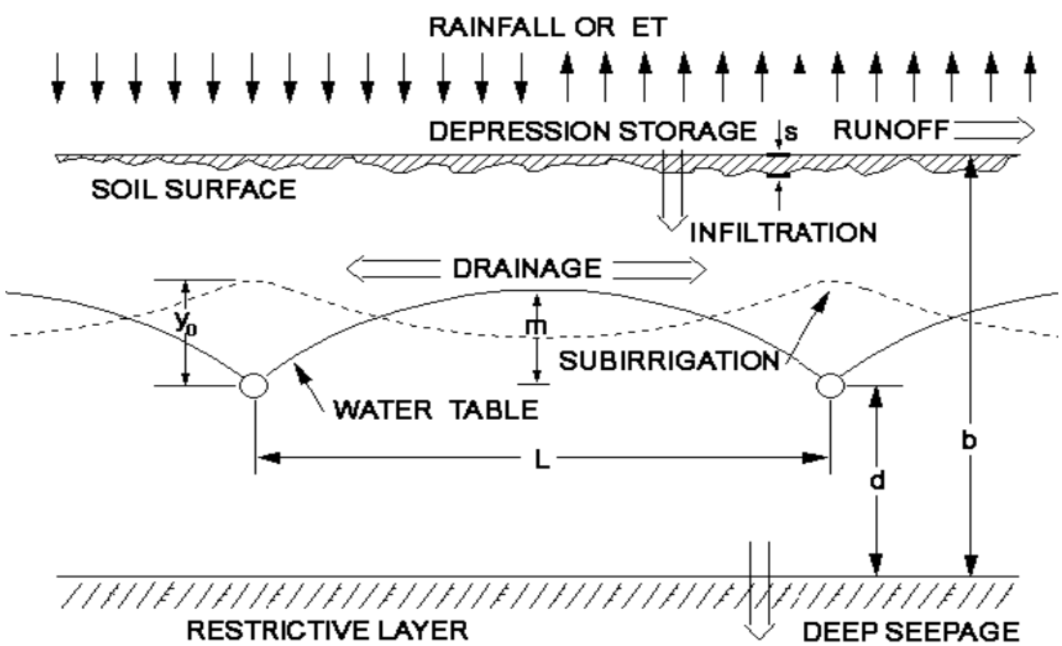

Figure 4. Schematic of the hydrologic processes simulated by DRAINMOD (Skaggs, 1980).

The model inputs required include soil characteristic, crop parameters, drainage system parameters, and weather and irrigation data. Model outputs include surface runoff, subsurface drainage, infiltration, ET, WTD, and crop water stresses. The rates of infiltration, ET, and surface and the distribution of soil water in the profile are calculated using various approximate methods that have been tested for a wide range of soils and boundary conditions (Skaggs, 1980). The physically based Green-Ampt equation is used to calculate the infiltration component in DRAINMOD. ET is calculated using the Thornthwaite method, however, it is possible to input an ET file if the user has measured ET data or would like to use a different method to estimate ET (e.g., Penman-Monteith or Hargreaves). Surface runoff depends on the average depth of surface depression storage and begins once the depressions are filled (Skaggs, 1980). Drain outflow is calculated using a corrected Hooghoudt's steady state equation and flow is assumed to only occur in the saturated zone. The model also uses Kirkham's steady state flow equation is to calculate subsurface drainage flux from ponded surfaces. Darcy's law is used to calculate deep seepage rates.

DRAINMOD also includes a N submodel, DRAINMOD-N II, which is a field-scale, process-based model that simulates carbon and N dynamics in drained agricultural lands for a wide range of soil types, climatic conditions, and management practices (Youssef & Skaggs, 2006). The submodel is a detailed N model that considers three pools of N: NO_3-N, ammoniacal-N, and organic N. Ammoniacal-N is an optional N pool that may be turned off if its formation is unlikely due to environmental conditions. The model considers atmospheric deposition, application of mineral and organic N fertilizers, plant uptake, mineralization, denitrification, NH_3 volatilization, and NO_3 and ammoniacal N losses via runoff and subsurface drainage (Figure 5). The model also includes a carbon submodel due to the complex relationship between N mineralization and immobilization processes and carbon dynamics during organic matter decomposition (Youssef et al., 2005).

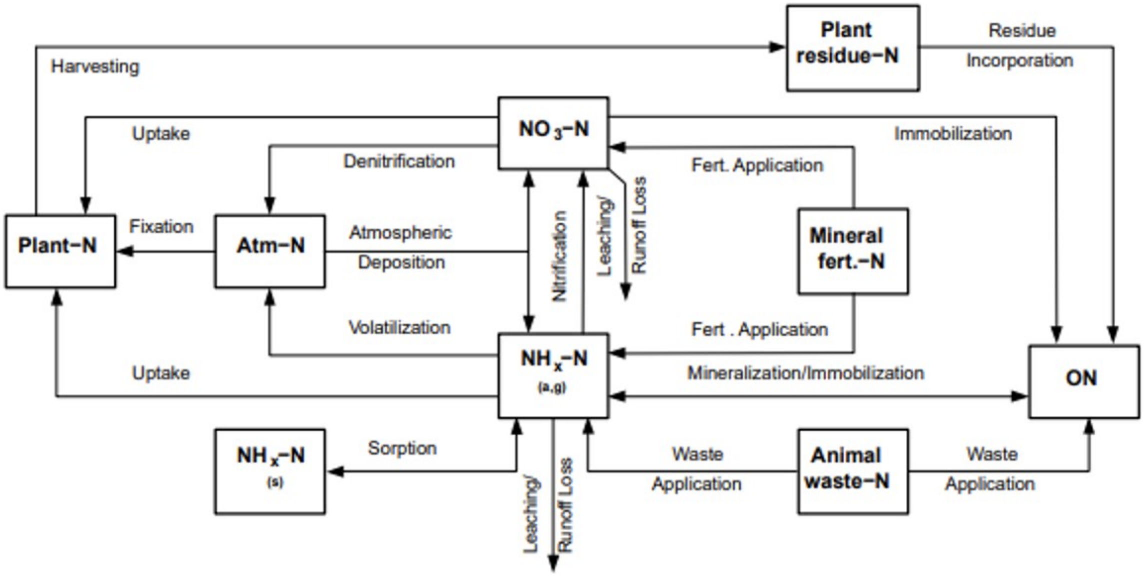

Figure 5. Nitrogen cycle considered in DRAINMOD-N II (Youssef et al., 2005).

The DRAINMOD-N II outputs include daily NO_3 and ammoniacal N concentrations in soil water and drainage discharge, daily organic content of the top 20cm of soil, and cumulative rates of N processes. Average daily soil water fluxes and soil water contents are provided by base DRAINMOD. Youssef and Skaggs (2005) found that DRAINMOD-N II reliably predicted to model annual and cumulative NO_3 losses in tile drained fields in North Carolina and Indiana. There is a lack of studies using DRAINMOD-N II in Canada, however, its precursor DRAINMOD-N, was successfully used to simulate NO_3 concentrations in drainage outflows in southern Ontario (Yang et al., 2007).

2.4.7 Model Selection

Based on the requirements of the current study DRAINMOD and DRAINMOD-NII were selected. Few models are applicable for drainage simulations in soils with high water tables and DRAINMOD is one of the most widely used models developed for this specific purpose (Ewemoje et al., 2010). DRAINMOD and DRAINMOD-N II have been shown to accurately simulate hydrologic and nutrient transport in artificially drained soils with high water tables. The model uses a field scale which is appropriate for the input data available, and the goals of this research and it has been successfully used in eastern Canada (Dayyani, 2010; Yang et al., 2007).

DRAINMOD-N II also has the ability to incorporate fertilizer management scenarios and can carry out continuous simulations.

Chapter 3 - Materials and Methods

3.1 Experimental approach

A simplified N balance was used to produce an N index for three different soil types. The N index accounts for the N fertilizer applied, leached N, volatilized N, plant N uptake, and N fixed in the soil (Figure *1*). The index was applied to five different fields in southern Quebec. The volatilized N and plant uptake were obtained from the literature. The N fertilizer applied was obtained from a local agronomist and CRAAQ recommended values (Parent & Gagné, 2013). The N fixed in soil was measured and the N leached was simulated using DRAINMOD-N II. The soil N and the input data collected for the DRAINMOD-N II simulations were obtained through a mix of field and lab work conducted on the five agricultural fields.

3.2 Site description

The research was conducted at five intensively cultivated corn fields in southern Quebec, located within the St Lawrence Lowlands (Figure 6). Sites A, B, C and D are all located near St Hyacinthe, site A is 12km north-northeast, site B is 14 km northeast, site C is 18 km south, and site D is 33.5 km south-southeast of the city. Site E is at St. Emmanuel and is located 51 km southwest of Montreal near Coteau-du-Lac. All sites are located within agroecological zone 10, the temperate sub-humid zone (Plevin et al., 2014). Agriculture is a dominant form of land-use in the St Lawrence Lowlands ecoregion because it is a relatively flat area with highly fertile soil and the primary soil type is clay. The dominant crop grown in the area is corn; in 2006 corn cropland in the St Lawrence Lowlands accounted for 39% of Canada's total corn cropland (Larocque et al., 2010). According to the Government of Canada (2021), the risk of contamination of surface water by N in the St Lawrence Lowlands is high to very high. This increased risk is due to the higher precipitation rates in Central and Atlantic Canada in conjunction with the increasing rates of fertilizer application. Monthly rainfall in St Hyacinthe can range between 20 to 105 mm, with approximately two-thirds of the annual rainfall occurring over the growing season (May-Oct) (Figure 7).

Figure 6. Map of site locations. Satellite image obtained from Google Earth Pro.

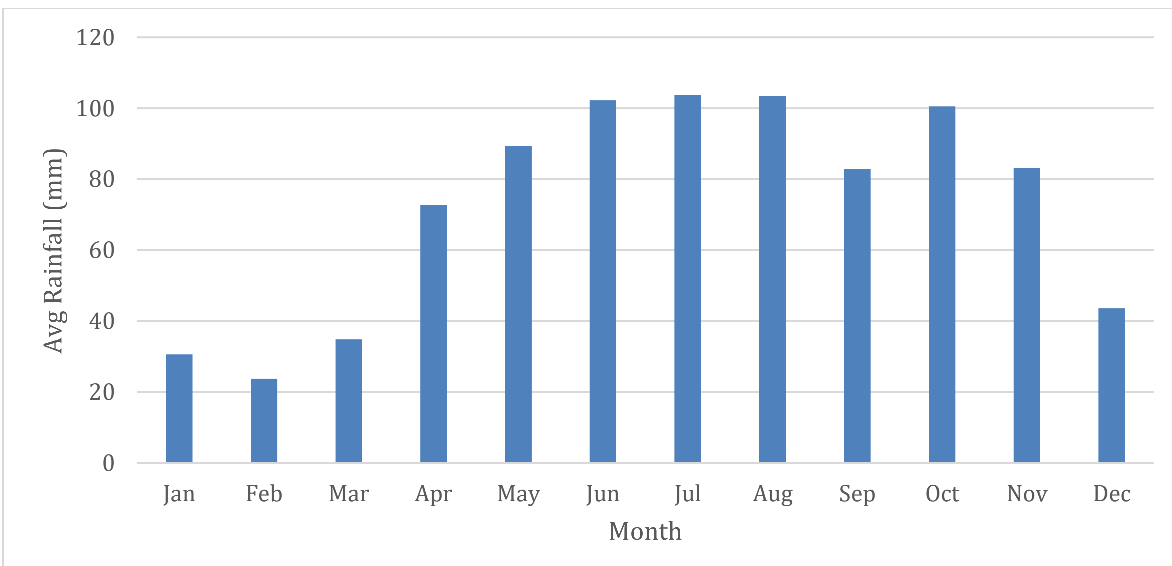

Figure 7. Average monthly rainfall from 1981 to 2010 at St Hyacinthe, QC (Environment Canada, 2024)

Sites A, B, C and D are commercial farms that predominantly grow corn and all field sites have conventional free drainage. Sites A, B, C, and D were under mono-cropped corn from 2020 to 2023. Site A is a 23.4 ha field located on St Hyacinthe silty clay loam. Site B is a 37.9 ha field on St Hélène sandy gravelly loam, site C is a 52 ha field on St Rosalie clay, site D is a 28.5 ha field on lightly to moderately stony Mawcook loam (Table 1). The sites range from very poorly drained to well drained and soil pH ranged from acidic to neutral (Table 1). All sites are relatively flat with average slopes under 0.5%.

Table 1. Soil descriptions of the study sites.

Site	Soil Type	Drainage	pH	Bulk Density (g/cm3)
A	St Hyacinthe silty clay loam	Poorly drained	7.4	1.2
B	St Hélène sandy gravelly loam	Well drained	7.5	1.13
C	St Rosalie clay	Imperfect drainage	5.8	1.1
D	Mawcook loam lightly to moderately stony	Poorly drained	7.4	1.1
E	Soulanges sandy loam	Very poorly drained	5.5	1.6

Site E is an experimental research site that was constructed in 1992 and has a mix of free drainage, sub-irrigated and controlled drainage plots (Elmi et al., 2000). Site E is a 4.2 ha comprised of a Soulanges sandy loam (Table 1). Site E was arranged in a split plot design in which two N fertilizer rates were used and factorially combined with two water table management practices (subirrigation at a WTD of 0.6 m and free drainage at a depth of 1 m). For the purposes of this research, only the plots that were under free drainage and a fertilizer application rate of 120 kg N/ha were considered. The field was seeded for grain corn on May 8, 1998 and May 4, 1999 (Helwig et al., 2002). For detailed design and instrumentation refer to Tait et al. (1995).

All sites applied inorganic fertilizers including urea, ammonium persulfate (APS), diammonium phosphate (DAP), calcium ammonium nitrate (CAN), and urea ammonium nitrate (UAN). Site C also applied organic fertilizer in the form of diluted pig slurry. Sites A, B, and C applied fertilizer pre-sowing and site E used a split fertilizer application method (presowing and at V7 stage of corn growth). Field management practices at all sites are detailed in Table 2. Site D field management was not obtained, and standard practices of split fertilizer application and amounts were assumed based on CRAAQ recommendations (Parent & Gagné, 2013). The fertilizer types (34-0-0 CAN and 18-46-0 DAP) were based on Elmi et al. (2000), which resulted in a very high application of CAN fertilizer to achieve the CRAAQ recommended 180 kg N/ha.

Table 2. Field management practices at study sites.

Site	A	B	C	D	E	
Year	2022	2022	2022	2022	1998	1999
Date of first tillage	08-May	04-May	05-May	-	-	-
Depth of tillage (cm)	8.3	6.35	5	5	5	5
Sowing date	09-May	07-May	07-May	08-May	08-May	04-May
1st fertilizer application date	04-May	07-May	07-May	07-May	08-May	04-May
Fertilizer formula	45-0-0 (Urea)	45-0-0 (Urea)	6-24-6 (APS)	18-46-0 (DAP)	18-46-0 (DAP)	18-46-0 (DAP)
Application rate	170kg/ha	165 kg/ha	56 kg/ha	128 kg/ha	128 kg/ha	129 kg/ha
2nd fertilizer application date	08-May	07-May	07-May	08-Jun	08-Jun	10-Jun
Fertilizer formula	23-0-5 (CAN)	17-7-10 (CAN)	32-0-0 (UAN)	34-0-0 (CAN)	34-0-0 (CAN)	34-0-0 (CAN)
Application rate	220 kg/ha	280 kg/ha	187 kg/ha	461.8 kg/ha	285 kg/ha	286 kg/ha
3rd fertilizer application date	-	-	07-May	-	-	-

Fertilizer formula	-	-	diluted pig slurry	-	-	-
Application rate	-	-	45 000 kg/ha	-	-	-

3.3 Data collection

3.3.1 Weather data

Daily temperature and precipitation data were collected from Environment Canada for the calibration years (2022 for sites A, B, C, and D and 1998 and 1999 for site E) and the validation years of 2008 and 2009 for site E. Sites A, B, C, and D weather data were collected from the St. Hyacinthe 2 weather station and dates with missing values were retrieved from the Granby weather station. Site E weather data were obtained from the Coteau-du-Lac weather station and dates with missing values were obtained from the Valleyfield weather station. The weather data were used to create four separate weather files necessary for the DRAINMOD simulations, one precipitation file and one temperature file for the sites near St Hyacinthe (A, B, C, and D) and site E.

3.3.2 Soil data

Soil data were obtained primarily by IRDA. Soil pH was measured using the soil pH in water method, NH_4-N and NO_3-N were measured using the 2.0M KCl extraction method, total carbon and N were measured using the CN combustion method, bulk density was measured using the cylinder method, and the sand, silt, and clay percentages were measured using the hydrometer test (Carter & Gregorich, 2007). Additional lab work was performed for three of the five sites (A, B, and C) at the MacDonald campus. Site D was not resampled due to time limitations and the sufficiency of data collected by IRDA. Sampling was performed randomly using the zigzag method (Carter & Gregorich, 2007). Three samples were taken per field, at each sampling location 800g of soil were collected at depths of 0-20 cm and 20-40 cm. Soil at a depth of 0-20 cm was collected using a spade and soil at a depth of 20-40 cm was collected using a soil auger. Composite samples were made in the lab by thoroughly combining equal proportions of soil collected at the 0-20 cm depth and the 20-40 cm depth.

Lab work was conducted to determine the particle size distribution and the soil water retention curves at the three sites (A, B, and C). All lab work was conducted on the prepared composite samples and three replicates were performed per site for each test. The hydrometer test using the methodology outlined in Carter and Gregorich (2007) was used to ascertain the particle size distribution. Two different devices were used to determine the soil water retention curves, the Sandbox for pF Determination (Eijkelkamp Soil and Water; Model 0801) was used for lower pressures (0-0.1 bar) and the Pressure Membrane Apparatus (Eijkelkamp Soil and Water; Model 0803) was used for higher pressures (1-15 bar). The Sandbox was used to determine pF at six pressures (0.001, 0.0025, 0.01, 0.0316, 0.0631, and 0.1 bars) and the Pressure Membrane Apparatus was used to determine pF at seven pressures (1, 2, 3, 4, 5, 7, 10, and 15 bars) for a total of thirteen pF measurements. The pressures between 0.1 and 1 bar were not measured due to lack of the necessary equipment. The measured soil data and soil water characteristic curves were used in the creation of the soil files necessary to run DRAINMOD.

3.3.3 Water table depth

Water table depth (WTD) was recorded by IRDA for sites A, B, C and D. Three HOBO Loggers (Onset; Model U20L) were installed at each site and recorded the combined atmospheric and water pressure at half-hour increments. To extrapolate the WTD relative to the ground surface the following equation was used:

$$WTD = H - LC + CS + \frac{PP - PA}{G} \qquad Eq\ 3$$

Where H is the elevation of the piezometer cap, LC is the length of the rope added to the piezometer, CS is the height of soil above the piezometer cap, PP is the pressure read by the piezometer, PA is the atmospheric pressure, and G is the gravitational acceleration (9.806 m/s2). All variables must be in the same unit. This equation was developed by IRDA.

For site E the WTD was measured three times a week in 1998-1999 and once every week in 2008-2009 using Leveloggers (Solinist Canada Ltd.; Model 3001) in observation wells that were installed during the growing season (Dayyani, 2010; Singh, 2013). The discharge for the tile drains was also measured for site E using tipping buckets (Dayyani, 2010). For the detailed methodology refer to Dayyani (2010) and Singh (2013). The WTD and discharge volume were used for calibration and validation of the DRAINMOD simulations.

3.3.4 Nitrate in tile drainage water

NO_3 concentrations at tile drainage outlets were measured by IRDA at site C and NO_3 fluxes were taken from Dayyani et al. (2010) for site E. At site E, discharge water was stored in 20L buckets to form composite samples, 20 mL sub-samples were taken, and NO_3-N was measured using a modified colorimetric method. Total NO_3-N losses from tile drains were calculated by multiplying the NO_3-N concentrations by the drainage volume over the growing season. For site C, samples of drainage water were taken directly from the drainage outlet and NH_3-N and NO_3-N were measured using the colorimeter method (Carter & Gregorich, 2007). A total of 11 samples were taken from March to December and since drainage flow volume was not measured at site C, total N losses were not calculable. Drainage flux was not measured due to the lack of instrumentation. The 11 concentrations were assumed to be a daily flux for calibration purposes. The NO_3 fluxes were used to calibrate the DRAINMOD-N II simulations.

3.4 DRAINMOD and DRAINMOD-NII simulations

3.4.1 DRAINMOD hydrology simulations

DRAINMOD hydrology simulations were conducted for all five sites. The simulations conducted take the different soil physical and chemical properties found at each site into account. The different weather at site E compared to sites A, B, C and D was also considered in the simulations. The hydrology of the sites needed to be accurately simulated before the NO_3 fluxes required for the N index could be simulated.

3.4.2 Model input parameters

DRAINMOD was selected for this study due to its friendly user interface and relatively straightforward input requirements. The model is specifically tailored towards agricultural watersheds in humid environments and has been proven to work in environments analogous to the ones of interest in this study (Dayyani, 2010; Helwig et al., 2002; Madramootoo, 1990). Many of the input parameters are automatically calculated by DRAINMOD meaning fewer direct measurements are required. For DRAINMOD to accurately simulate the WTD for a given site it requires input parameters specific to the site of interest. Some of the parameters are known, and some are measured, or estimated. The known and measured parameters must be used and estimated parameters may be subject to change during calibration. Therefore, it is important to obtain accurate input parameters to minimize calibration time and to ensure realistic simulated output values.

Base DRAINMOD requires two weather files (temperature and precipitation), one soil file and one crop file. The weather and soil files can be created using the Utilities function in DRAINMOD to convert the files to a DRAINMOD readable format. Weather files include the dates, the maximum and minimum temperatures, and the daily precipitation. All days with a rainfall amount of zero were deleted as DRAINMOD does not recognize the zero input in the precipitation files. Weather data for the year prior to the calibration and validation years were also included to ensure sufficient warming of the model.

Soil files include the soil water characteristic curve data per layer, depths of each soil layer, saturated hydraulic conductivity (Ks), root depth and max root depth. For simplicity, four of the five sites (A, B, C, and D) were assumed to be homogenous and only one layer of soil was assumed. Four soil layers were considered for site E due to a more comprehensive understanding of the field site.

The soil water characteristic curves were measured in a lab for sites A, B and C. Due to the incomplete sampling of the soil at site D, the soil water characteristic curve was generated instead of measured. The soil water characteristic curve was generated using the Van Genuchten model and the Rosetta3 model was used to generate the Van Genuchten parameters. To generate these parameters Rosetta3 required the input of the percent sand, silt, and clay of a soil as well as the optional input of bulk density, volumetric water content at field capacity, and the volumetric water content at the permanent wilting point. For this study, the sand, silt, and clay percentages were measured using the hydrometer method and only these data were input into Rosetta3. The soil water characteristic curves used for site E were obtained from Bourke (2011) in which

SPAW (Soil Plant Atmosphere Water Model) was used to generate the curves (Figure A1). Several points from each curve were taken to create the soil files for DRAINMOD.

The crop file (.cin file) is created by editing the crop parameters within the model interface. The default corn130.cin file in DRAINMOD was used as a base file. The crop file includes the cropping window, growing season, planting date reduction parameters, excess and deficit water stress parameters, root depths, sum of excess water (SEW), first and second work periods, and weir settings. The crop growing season was modified based on the field management at each site (Table *2*). The remaining parameters were retrieved from the DRAINMOD User's Guide (Workman et al., 1994).

By default, DRAINMOD generated evapotranspiration (ET) data using the input files and the Thornthwaite method (Thornthwaite, 1948), monthly ET factors, latitude, and the heat index. In this study, the monthly ET factors used were taken from Caldwell et al. (2007) for sites A, B, C and D and from Dayyani (2010) for site E. Drainage data required for DRAINMOD was obtained from Info-sols for sites A, B, C, and D and from Dayyani (2010) for site E (Table *3*).

The calibrated parameters were the Ks and the volume drained versus the WTD. These parameters were changed within reasonable ranges for the soil type, the starting point for Ks was the value generated by Rosetta3 and the values were changed at rates of 0.1cm/hr within the range of 0.1-7.4 cm/hr (Dayyani, 2010). The volume drained versus WTD relationships were initially generated by DRAINMOD and edited based on the curves for North Carolina soils found in the DRAINMOD manual (Skaggs, 1980). For simplicity, the impacts of seepage were omitted in this study. Additional input parameters can be found in Table *3*.

Table 3. DRAINMOD input parameters for hydrologic simulations.

Soil Physical and Chemical Properties	Site							
	A	B	C	D	E			
					L1	L2	L3	L4
Bottom depth of layer (cm)	300	300	300	300	25	50	75	300

Saturated Hydraulic Conductivity (cm/hr)*	0.45	0.4	0.89	0.41	7.4	6.8	5.2	3
Wilting Point (cm3/cm3)	0.223	0.139	0.195	0.168	0.068	0.068	0.068	0.068
Clay Fraction	0.107	0.082	0.151	0.319	0.1	0.2	0.39	0.39
Silt Fraction	0.622	0.266	0.53	0.411	0.34	0.22	0.29	0.29
Soil Classification	Silty Loam	Sandy Loam	Silty Loam	Clay Loam	Sandy Loam			
Bulk Density (g/cm3)	1.2~	1.13	1.1	1.1	1.63	1.6	1.49	1.49
Soil Ph	7.4	7.5	5.8	7.4	5.5	5.5	5.5	5.5
Drainage Plans								
Distance from surface to impermeable layer (cm)	300	300	300	300	300			
Drainage Coefficient (cm/d)	1.2	1.2	1.2	1.2	1.5			
Initial Depth to Water Table (cm)	30	30	30	30	30			
Maximum Surface Storage (cm)	2.5	1.5	1.5	2.5	2.5			
Depth of Drains (cm)	100	100	100	100	100			
Drain Spacing (m)	21	18.5	35.36	16.06	15			
Drain Pipe Diameter (cm)	10	10	10	10	7.6			
Effective Radius (cm)	0.35	0.35	0.35	0.35	0.35			

* Calibrated parameters

~ Bulk density at site A was not measured, value obtained from Scheuler (2000) for silty loam soil type

All drainage plan data for sites A, B, C and D were obtained from Infosols

All data for site E were obtained from Dayyani (2010)

3.4.3 Model calibration and validation

The models were calibrated for the year 2022 for sites A, B, C, and D and the years 2008 and 2009 for site E. The model for site E was validated for the years 1998 and 1999 and there were insufficient data to validate the models for sites A, B, C, and D. The observed WTDs used for model calibration for sites A, B, C, and D were measured by IRDA in 2022. The WTDs used for calibration of the site E model were obtained from Singh (2013) and the WTDs used for validation were obtained from Dayyani (2010). All models were calibrated using observed WTDs, only the model for site E was calibrated using drain discharge volumes in addition to WTD.

Identifying the specific causes of the models' over or underestimation requires a comprehensive evaluation of the model setup, input data, and assumptions, as well as a critical examination of how they collectively impact the simulation results. After a sensitivity analysis and due to the recommendations of Skaggs et al. (2012), the models were calibrated by adjusting Ks and the volume drained versus the WTD.

3.4.4 DRAINMOD-NII Nitrogen Simulations

NO_3 fluxes at drainage outlets were simulated using the DRAINMOD-N II submodel. Similar to the hydrology model the DRAINMOD-N II simulations considered the different soil physical and chemical properties and weather patterns found at each site. The models were run with five different fertilizer application practices: 180 kg N/ha and 120 kg N/ha inorganic split application, 121.85 kg N/ha and 127.1 kg N/ha single inorganic presowing application, and 222.05 kg N/ha single organic and inorganic presowing application.

3.4.5 Model input parameters

Model input parameters used for the hydrological models were maintained for the N submodel. In addition to those parameters, the soil physical and chemical properties, soil temperature data, fertilizer management practices, and the yield and uptake data were added (Negm et al., 2017). The new soil physical and chemical properties included wilting point, silt, sand, and clay percentages, bulk density, soil pH, and the distribution coefficient. The distribution coefficient was assumed to be 2.5 for all sites and the specific properties and soil temperature data can be found in Table 4. The temperature at the bottom of the soil was taken to be the average long term air temperature. This was found by averaging the yearly air temperature recorded by Environment and Climate Change Canada at the same weather stations that were used to create the weather files. Simulations were run for each of the five sites at five different fertilizer management practices for a total of 25 simulations. The fertilizer management practices at sites A, B, C, D, and E were used for the simulations (Table *2*). DRAINMOD-N II requires fertilizer input to be categorized by type of N (urea, NH_4, NO_3, and organic fertilizer) and requires fertilizer application in the unit of kg N/ha. The amount of fertilizer applied in kg/ha (Table 2) was converted to the amount of N applied in kg N/ha using the chemical breakdown of the fertilizer types and the application rates. The N application breakdown for each fertilizer treatment can be found in

Table 5. For yield and uptake data refer to Thorp et al. (2009), the study was performed in the Midwest USA and was taken to be analogous to Eastern Canada.

Table 4. DRAINMOD-NII input parameters for nitrogen simulation.

Soil Temperature Parameters		
Soil Thermal Conductivity Coefficient	TKA = 0.39, TKB = 1.33	Negm et al., 2017
Avg. air temperature below which precipitation is snow (ºC)	0	Negm et al., 2017
Snowmelt base temperature (ºC)	2.5	*
Critical ice content to stop infiltration ($cm^3\ cm^{-3}$)	0.3	Negm et al., 2017
Snow melt coefficient ($mmd^{-1}\ ^{o}C^{-1}$)	5	Negm et al., 2017
Temperature at the bottom of the soil profile (ºC)	6.44	
Nitrogen Transport Parameters		
Longitudinal Dispersivity (cm)	5	*
Tortuosity	0.5	Negm et al., 2017
Tolerance	0.0001	
Minimum time step (day)	0.001	
Rain NO3-N concentration ($mg\ L^{-1}$)	0.32	~
Rain NH4-N concentration ($mg\ L^{-1}$)	0.34	~
Air NH3-N concentration ($mg\ L^{-1}$)	0	~
Nitrification Transformation Parameters		

Michaelis-Menten max rate (µg Ng^{-1}soil)	10	~
Parameters half-saturation constant (µg Ng^{-1}soil)	30	~
Optimum temperature (°C)	22	~
Empirical shape coefficient	0.35	~
Denitrification Transformation Parameters		
Michaelis -Menten max rate (µg Ng^{-1}soil)	1.5	*
Parameters half-saturation constant (µg Ng^{-1}soil)	30	*
Optimum temperature (°C)	30	*
Empirical shape coefficient	0.13	~

* Calibrated values
~ Default values in DRAINMOD

Table 5. Nitrogen applied at sites A, B, C, D and E.

Fertilizer Management Practice	Urea (kg N/ha)	Ammonium (kg N/ha)	Nitrate (kg N/ha)	Organic N (kg N/ha)	Total N (kg N/ha)
Site A	76.5	25.3	25.3	NA	127.1
Site B	74.25	23.8	23.8	NA	121.85
Site C	30.312	17.928	14.96	158.85	222.05
Site D	0	101.5	78.5	NA	180
Site E	0	71.5	48.5	NA	120

3.4.6 Model calibration and validation

Due to insufficient data only two of the five N simulations, site C and E, were calibrated. Site C was calibrated for the year 2022 and site E was calibrated for the year 1999. There were insufficient data to validate the simulations for any of the sites. The 11 daily NO_3 fluxes at site C were used for model calibration for the simulation at site C and were measured by IRDA in 2022. The NO_3 fluxes at site E were obtained from Dayyani (2010) and used for calibration and validation of the simulation for site E.

The model was calibrated by adjusting the following parameters: snowmelt base temperature, longitudinal dispersivity, the Michaelis-Menton maximum rate of denitrification, denitrification parameters half-saturation constant, and the denitrification optimum temperature (Dar & Singh, 2022).

3.5 Statistical performance indicators

To properly assess a hydrological model at least one measure of relative error and one measure of absolute error must be considered (Legates & McCabe, 1999). In this study, four measures of relative error and one measure of absolute error were used to assess model performance. The measures of relative error include Percent Bias (PBIAS), Nash-Sutcliffe Efficiency (NSE) (Nash & Sutcliffe, 1970), Kling-Gupta Efficiency (KGE) (Gupta et al., 2009), and Index of Agreement (IOA) (Willmott, 1981).The one measure of absolute error used was the Coefficient of Residual Mass (CRM). These parameters are defined as:

$$PBIAS = \frac{\sum_{i=1}^{N}(O_i - P_i)}{\sum_{i=1}^{N} O_i} * 100 \qquad Eq\ 2.$$

$$NSE = 1 - \frac{\sum_{i=1}^{N}(O_i - P_i)^2}{\sum_{i=1}^{N}(O_i - \bar{O})^2} * 100 \qquad Eq\ 3.$$

$$KGE = 1 - \sqrt{(r-1)^2 + (\frac{\sigma_{sim}}{\sigma_{obs}} - 1)^2 + (\frac{\mu_{sim}}{\mu_{obs}} - 1)^2} \qquad Eq\ 4.$$

$$IOA = 1 - \frac{\sum_{i=1}^{N}(P_i - O_i)^2}{\sum_{i=1}^{N}(|O_i - \bar{O}| + |P_i - \bar{O}|)} \qquad Eq\ 5.$$

$$CRM = \frac{\sum_{i=1}^{N}(P_i - O_i)}{\sum_{i=1}^{N} O_i} \qquad Eq\ 6.$$

Where O_i is the ith observed observation, P_i is the ith predicted observation, $\bar{O}$ is the average of observed values, r is the linear correlation between observations and simulations, σ_{sim} is the standard deviation of the simulated values, σ_{obs} is the standard deviation of the observed values, μ_{sim} is the mean of the simulated values, and μ_{obs} is the mean of the observed values.

PBIAS indicates the tendency for predicted values to over or underestimate the observed values and will be positive or negative, respectively. The optimal value for PBIAS is 0% meaning no difference between observed and predicted value. In hydrology, an acceptable value of PBIAS is within the range of ±25% (Moriasi et al., 2007) (Table 6). NSE is a normalization of the variance of the observation series (Krause et al., 2005). An optimal NSE value is 1, if NSE is positive then the model is a better predictor than the mean, if NSE is negative then the mean is a better predictor than the model. Generally, for a model to be deemed acceptable the NSE value must be 0.36 or greater (Eryani et al., 2022) (Table 6). KGE is a modification of NSE that accounts for the underestimation of flow variability that is common with NSE (D. Liu, 2020). KGE must be larger than 0.4 for a model's performance to be deemed satisfactory (Knoben et al., 2019) (Table 6).

IOA accounts for the difference between means and the proportional changes. IOA can range from 0 to 1, a value of zero indicates there is no agreement between the observed and predicted value and a one indicates perfect agreement. IOA values above 0.6 were considered to mean the model was acceptable (Table 6). CRM is a measure of whether the model is over or under predicting values, a positive value conveys an overestimation and a negative value conveys an underestimation (Bourke, 2011).

Table 6. Values of statistical indices that indicate sufficient hydrological model performance for calibration and validation of DRAINMOD and DRAINMOD-NII models.

Statistical Index	Satisfactory Value
PBIAS	± 25%
NSE	> 0.36
KGE	> 0.4
IOA	> 0.6

3.6 Nitrogen balance and index

3.6.1 Nitrogen balance input and output data

The outputs and inputs used were from the simplified N balance depicted in (Figure 8). The index is as follows:

$$N_{losses}(kg\ N\ ha^{-1}) = N_{app} - N_{uptake} - N_{gas} - N_{leach} - N_{soil} \qquad Eq\ 7.$$

Where all components are measured in kg N/ha. N_{app} is the nitrogen applied as fertilizer, N_{uptake} is the nitrogen taken up by the corn grain, N_{gas} is the nitrogen that has off gassed as NO_2, NH_3 and NO_x. N_{soil} is the nitrogen left in the soil after harvest, both organic nitrogen and inorganic nitrogen were considered.

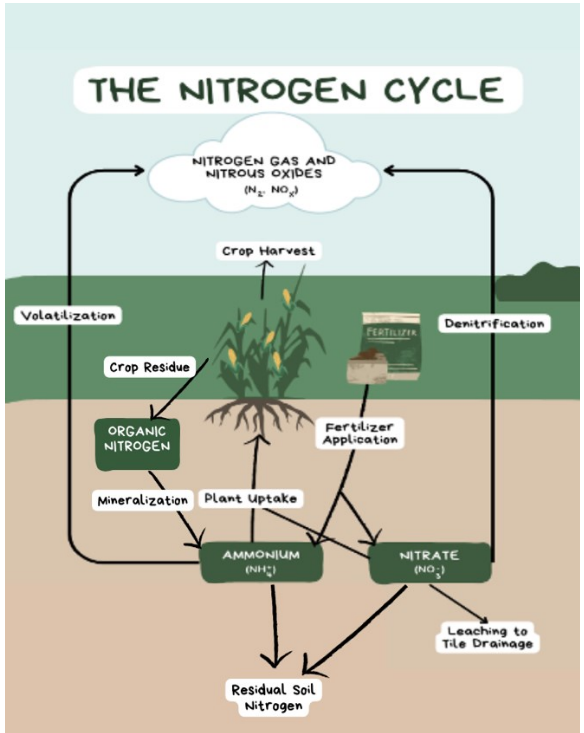

Figure 8. Simplified nitrogen balance for nitrogen balance.

N leaching was simulated using DRAINMOD-NII. The fertilizer applied was provided by a local agronomist for sites A, B, and C, 120 kg N/ha was applied at site E and an application of 180 kg N/ha was assumed at site D based on the CRAAQ recommendations for corn crops (Parent & Gagné, 2013). N taken up by the plant was assumed to be 104 kg N/ha, only the grain N was considered based on the assumption that the cob, stalks, and leaves were used in plant residue recycling (Abbasi et al., 2020; Delgado et al., 2023). It was assumed that 2% of the applied fertilizer was lost as N_2O-N and NO_x-N and 3.8% of the applied N was lost as NH_3-N (Halvorson & Del Grosso, 2013; Jantalia et al., 2012). The N_2 losses were assumed to be double the N_2O-N losses (Pan et al., 2022). Therefore, total N volatilization was taken to be 7.8% of the applied N (Delgado et al., 2023). The change in soil N was calculated based on the lab work conducted by IRDA. Total N as well as inorganic soil N were measured using the CN combustion method in November of 2021 and May of 2022. The change in soil N was calculated by subtracting the amount of total N measured in 2022 by the amount measured in 2021. If N_{losses}

was calculated to be positive it suggests an accumulation of N in the system, if negative it suggests that more N is leaving the system than is being added.

3.6.2 Nitrogen index

The N index was developed using a simplified N balance. The following empirical equation was used to create a simple user-friendly N index:

$$N\ index = \frac{N_{app}}{N_{uptake} + N_{gas} + N_{leach} + N_{soil}} \qquad Eq. 8$$

Where all components are measured in kg N/ha. N_{app} is the nitrogen applied as fertilizer (both organic and inorganic), N_{uptake} is the nitrogen taken up by the corn grain, N_{gas} is the nitrogen that has off gassed as NO_2, NH_3 and NO_x. N_{soil} is the total nitrogen left in the soil after harvest, both organic nitrogen and inorganic nitrogen were considered. Stanford and Smith (1972) found that most soils had similar N mineralization rates and the most reliable N rate constant was 0.054± 0.009 week^{-1}. Since the rate constant was found to be low for most soil types and the developed index was for a year time scale, the time dependent N mineralization was not considered.

If the N index calculated is greater than one then there is more N being applied to the system than lost, if it is equal to one then the amount applied is equal to the amount that leaves the system, and if it is less than one then the amount of N applied is less than the amount that is leaving the system. The N-index was calculated for each site using the fertilizer management practice that resulted in the highest simulated NO_3 leaching. The N index was calculated for each soil type on a yearly basis.

Chapter 4 – Results

4.1 Field measurements

4.1.1 Particle size distribution

Soil at site A was measured to be 23.0% sand, 66.2% silt, and 10.7% clay. Soil at site B was 65.2% sand, 26.6% silt, and 8.2% clay. Soil at site C was 31.6% sand, 53.3% silt, and the 15.2% clay. Soil at site D was 27.0% sand, 41.1% silt, and 31.9% clay. Using the soil classification triangle, sites A and C were classified as silty loams, site B was classified as a sandy loam, and site D was classified as a clay loam (Figure 9).

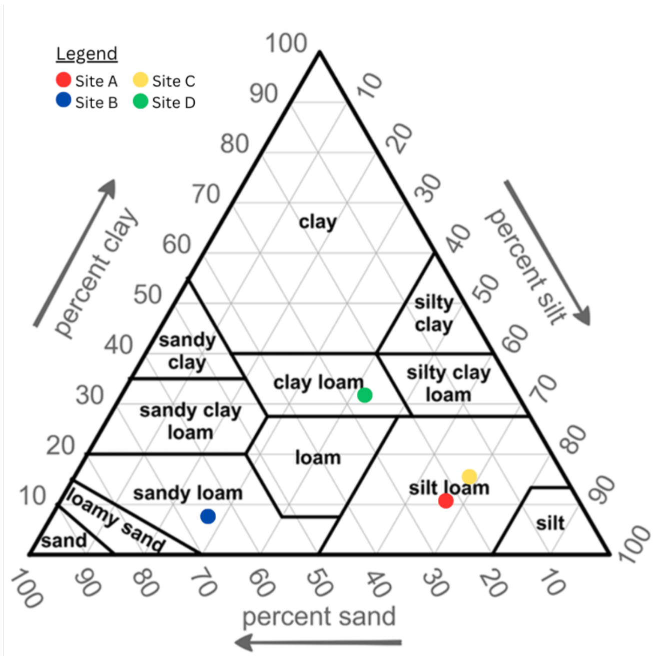

Figure 9. Soil classification triangle showing sites A, B, C and D.

4.1.2 Soil water characteristic curves

Site A had a field capacity of 0.65 cm^3cm^{-3} and a wilting point of 0.22 cm^3cm^{-3}, site B had a field capacity of 0.50 cm^3cm^{-3} and a wilting point of 0.14 cm^3cm^{-3}, site C had a field capacity of 0.52 cm^3cm^{-3} and wilting point of 0.19 cm^3cm^{-3}, and site D had a field capacity of 0.43 cm^3cm^{-3} and wilting point of 0.17 cm^3cm^{-3} (Figure 10).

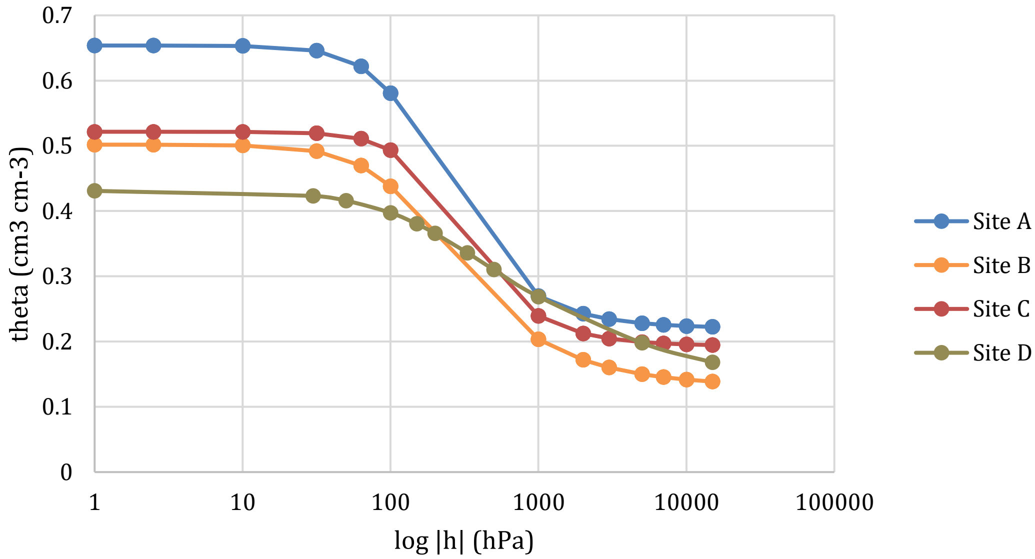

Figure 10. Soil water characteristic curves for sites A, B, C, and D using composite samples of soil from 0-20 cm and 20-40 cm depths.

4.1.3 Soil nitrogen

The total soil N measured at sites B, C, and D all increased over the course of a year. Total N increased the most at site B by 459 kg N/ha, it increased by 220 kg N/ha at site D and increased the least at site C by 11 kg N/ha (Table 7). The inorganic N measured at all sites ranged from 1.3% to 2% of the total N.

Table 7. Total, organic, and inorganic nitrogen at sites B, C, and D in 2021 and 2022.

Site	Year	Total N kg N/ha	Inorganic N kg N/ha	Organic N kg N/ha
B	2021	3106	43.0	3063
	2022	3565	49.3	3516
C	2021	2162	30.3	2131
	2022	2173	31.3	2141
D	2021	2035	26.0	2009
	2022	2255	45.7	2209

4.1.4 Water table depths

The WTDs measured at site A ranged from 0 (soil surface) to 68 cm (below the soil surface), site B ranged from 0 to 108 cm, site C ranged from 0 to 101.5 cm, and site D ranged from 2.9 to 108.9 cm. All of the sites followed similar trends in WTD versus time, with increased depth during the hottest summer months (July-August) and shallower WTDs at the beginning (May-June) and ending (September-October) of the growing season (Figure 11).

4.1.5 Nitrate measurements

The NO_3 concentrations ranged from 0 to 0.76 kg N/ha with an average value of 0.14 kg N/ha and an interquartile range of ±0.16 kg N/ha (Table 8). The value measured on April 8th, 2022, was considered an outlier due to it being outside of the interquartile range by a value of 0.6 kg N/ha.

Table 8. Measured nitrate fluxes at site C.

Date	Nitrate Flux (kg N/ha)
3/21/2022	0.29
3/29/2022	0.12
4/8/2022	0.76
5/17/2022	0.11
5/26/2022	0.03
6/8/2022	0.13
7/13/2022	0.04
7/22/2022	0.06
8/9/2022	0.02
10/28/2022	0.00
11/25/2022	0.01
12/8/2022	0.14

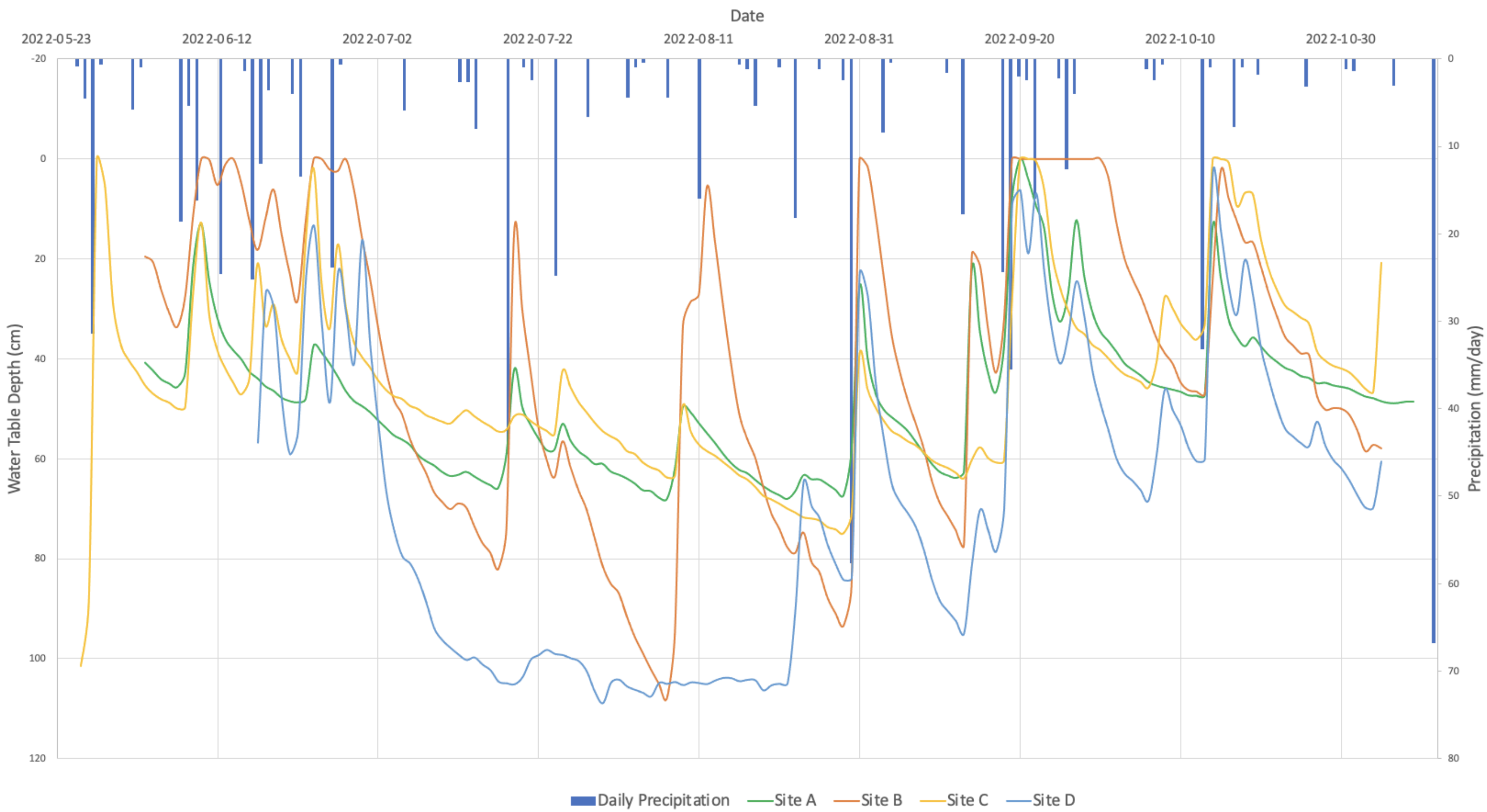

Figure 11. Water table depths measured at sites during the 2022 growing season.

4.2 Model simulations

4.2.1 Hydrologic modelling

The DRAINMOD model was calibrated for WTD and compared to field data collected in the growing season of 2022 for sites A, B, C, and D. WTD in conjunction with drainage outflows are more commonly used for calibrating DRAINMOD (Skaggs et al., 2012). However, the drainage outlets were inaccessible for sites A, B, and D and the drainage volumes were not measured at site C. As such, WTD was the only parameter used for calibration. Figures 12 to 15 present the observed and simulated daily average WTDs over the growing season for the calibration period. The model responded well to the rainfall fluctuations in all sites, after precipitation events both the simulated and the observed WTD decreased and increased over time during periods of no rain. Generally, the simulated WTDs followed closely with the observed WTDs, and both followed similar trends.

The DRAINMOD simulations for site E were calibrated using WTD for 2008 and 2009 and validated using WTD and volume drainage for 1998 and 1999. The observed WTD were point measurements instead of the continuous measurements collected for sites A, B, C and D. The simulated WTDs for 1998, 2008, and 2009 followed similar trends and comparable depths as the observed WTDs (Figures 16 to 18). The simulated WTD for 1999 followed the same trends as the observed WTD. However, the simulated depths were lower than the observed WTDs for the entire growing season (Figure 19). The simulated drainage volumes were similar to the observed drainage volumes, with the highest volumes in June and July of 1998 and October of 1999 (Figure 20).

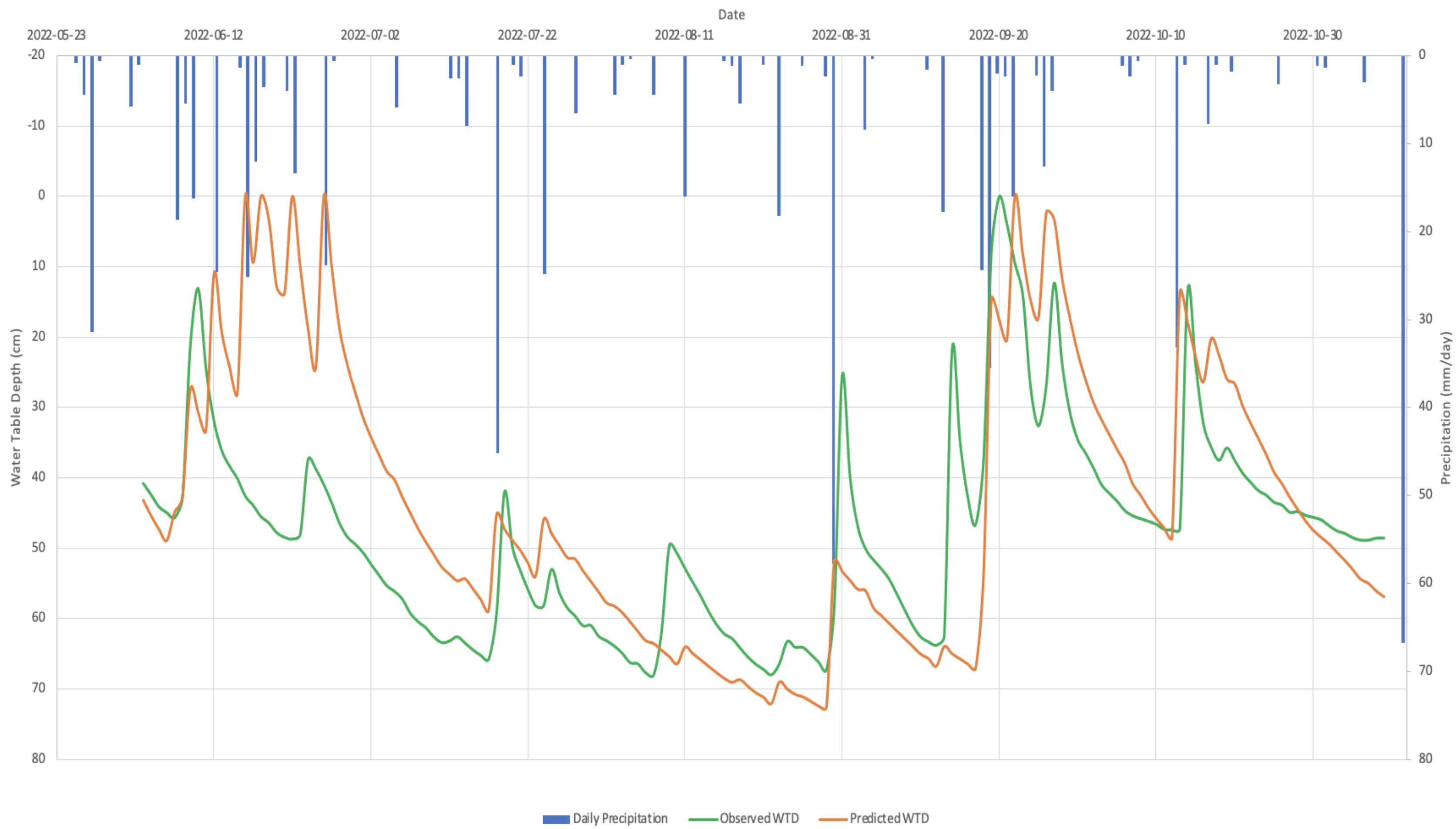

Figure 12. Simulated and observed water table depths at site A in 2022.

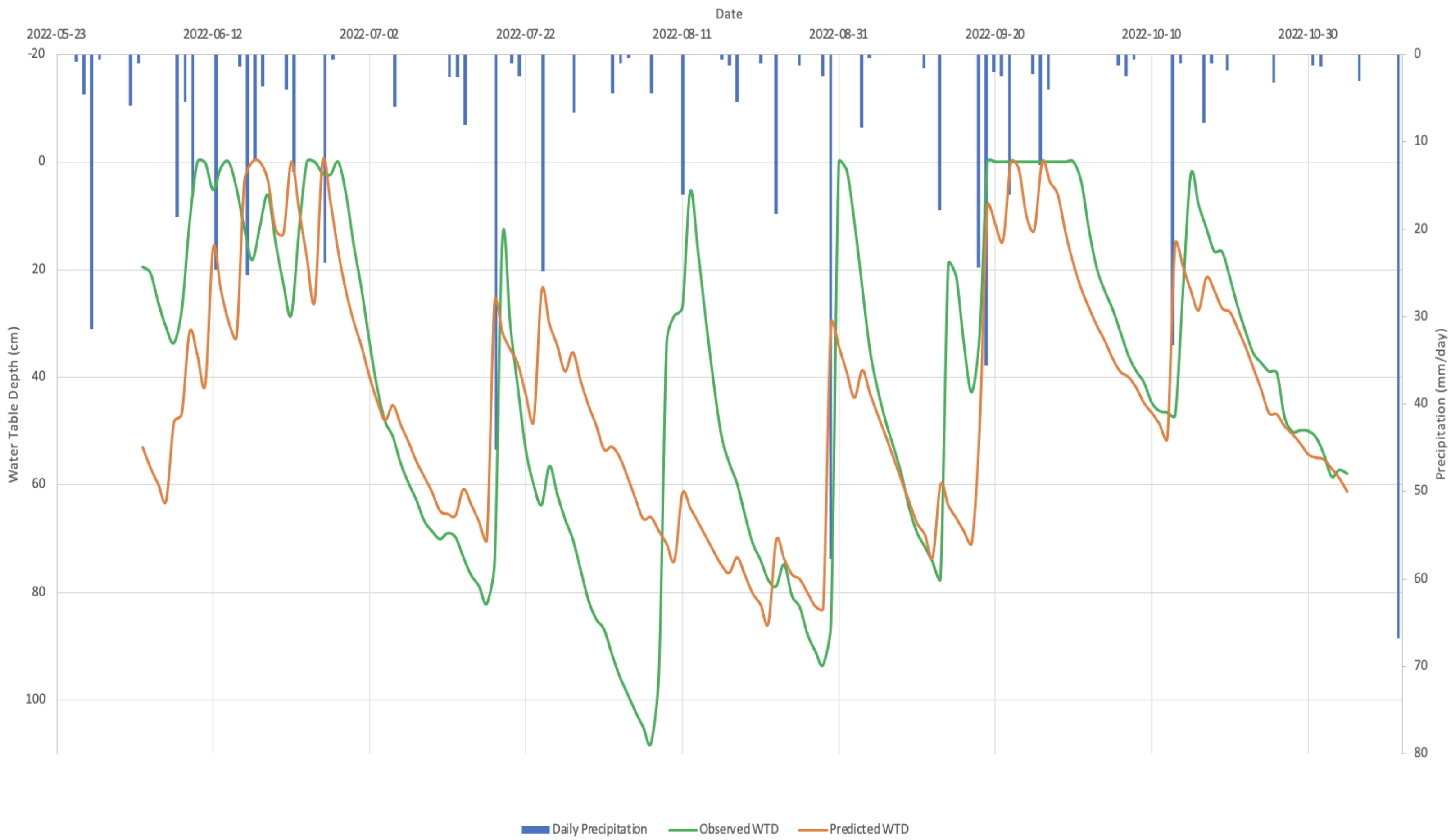

Figure 13. Simulated and observed water table depths at site B in 2022.

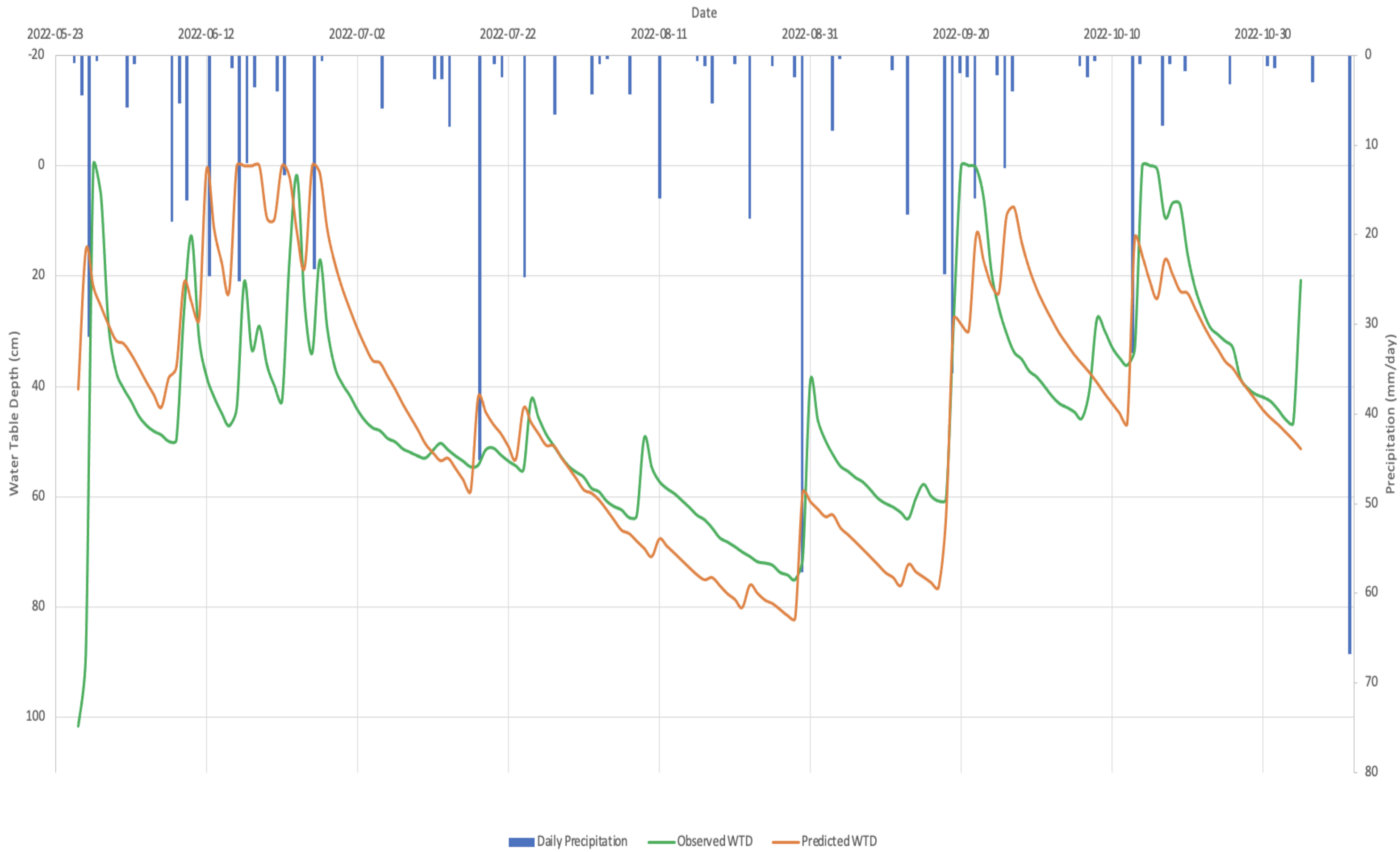

Figure 14. Simulated and observed water table depths at site C in 2022.

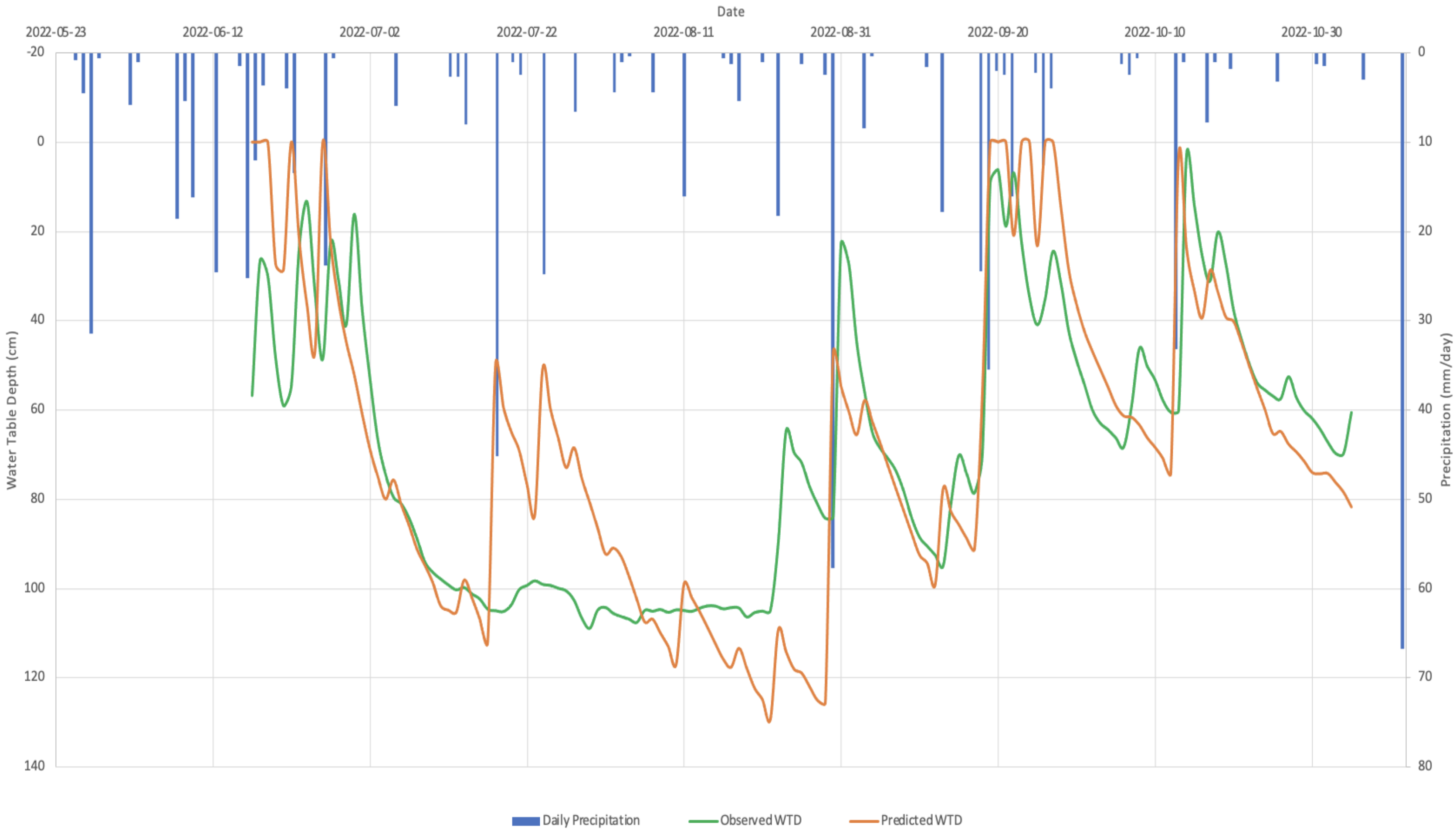

Figure 15. Simulated and observed water table depths at site D in 2022.

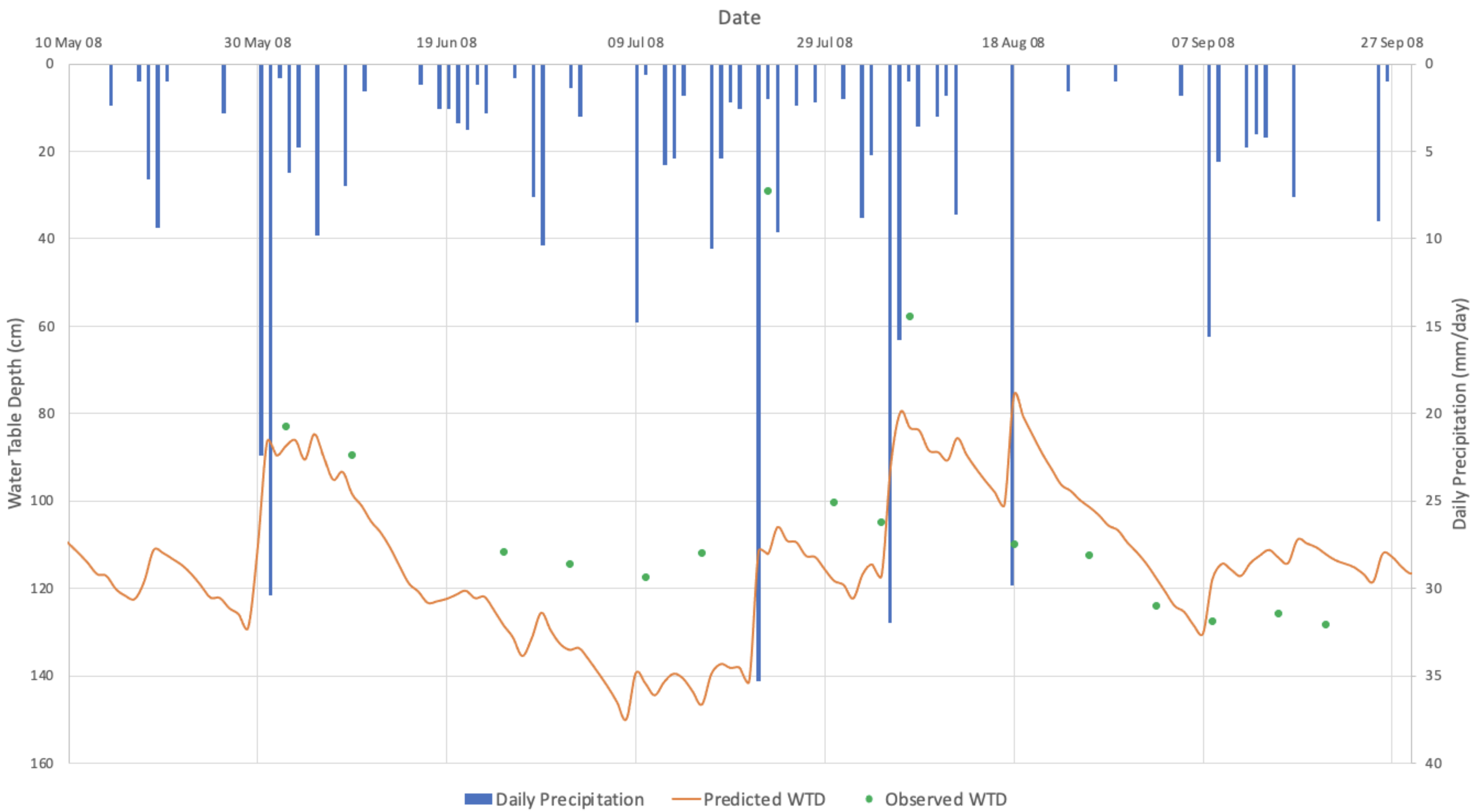

Figure 16. Simulated and observed water table depths at site E in 2008 for DRAINMOD calibration.

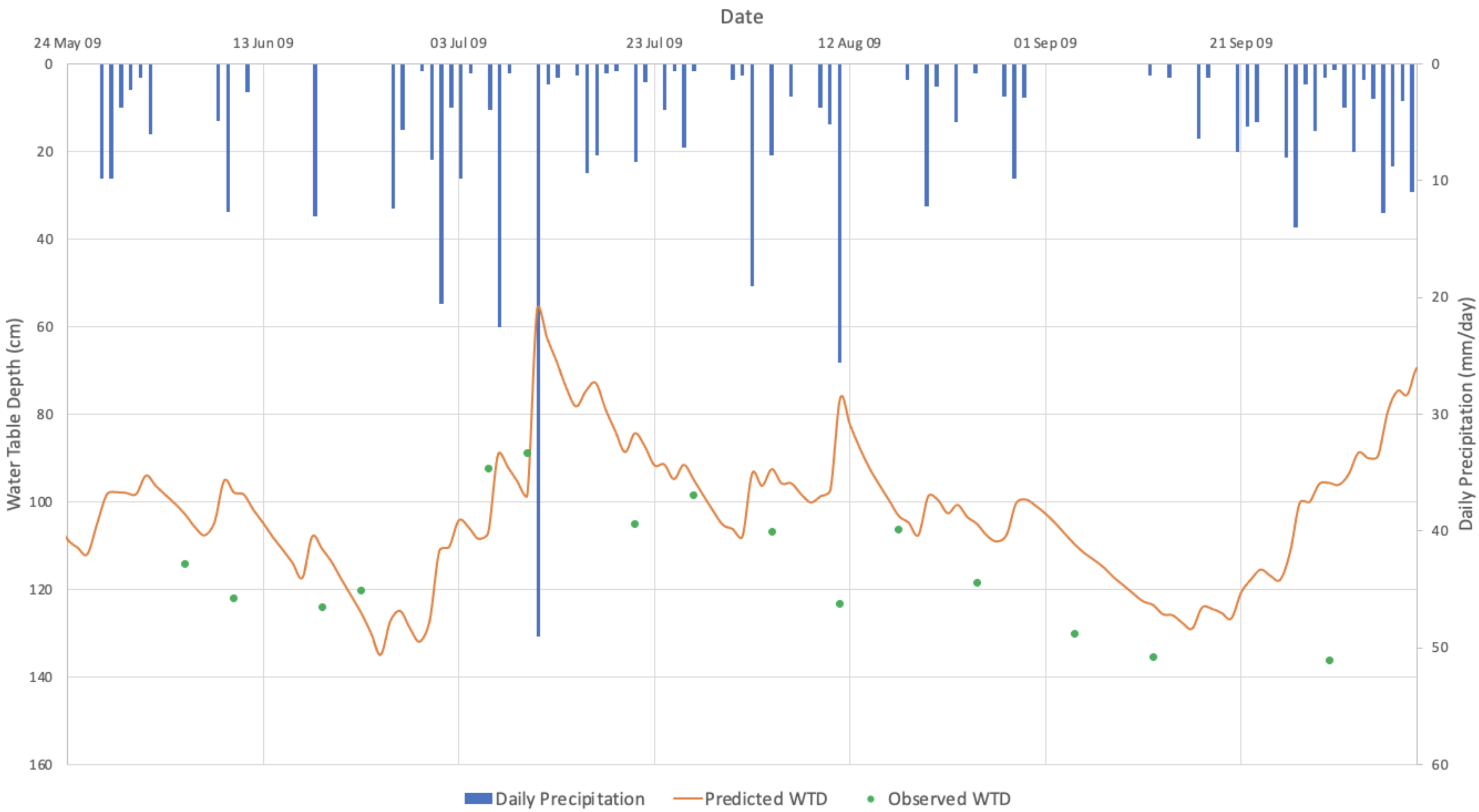

Figure 17. Simulated and observed water table depths at site E in 2009 for DRAINMOD calibration.

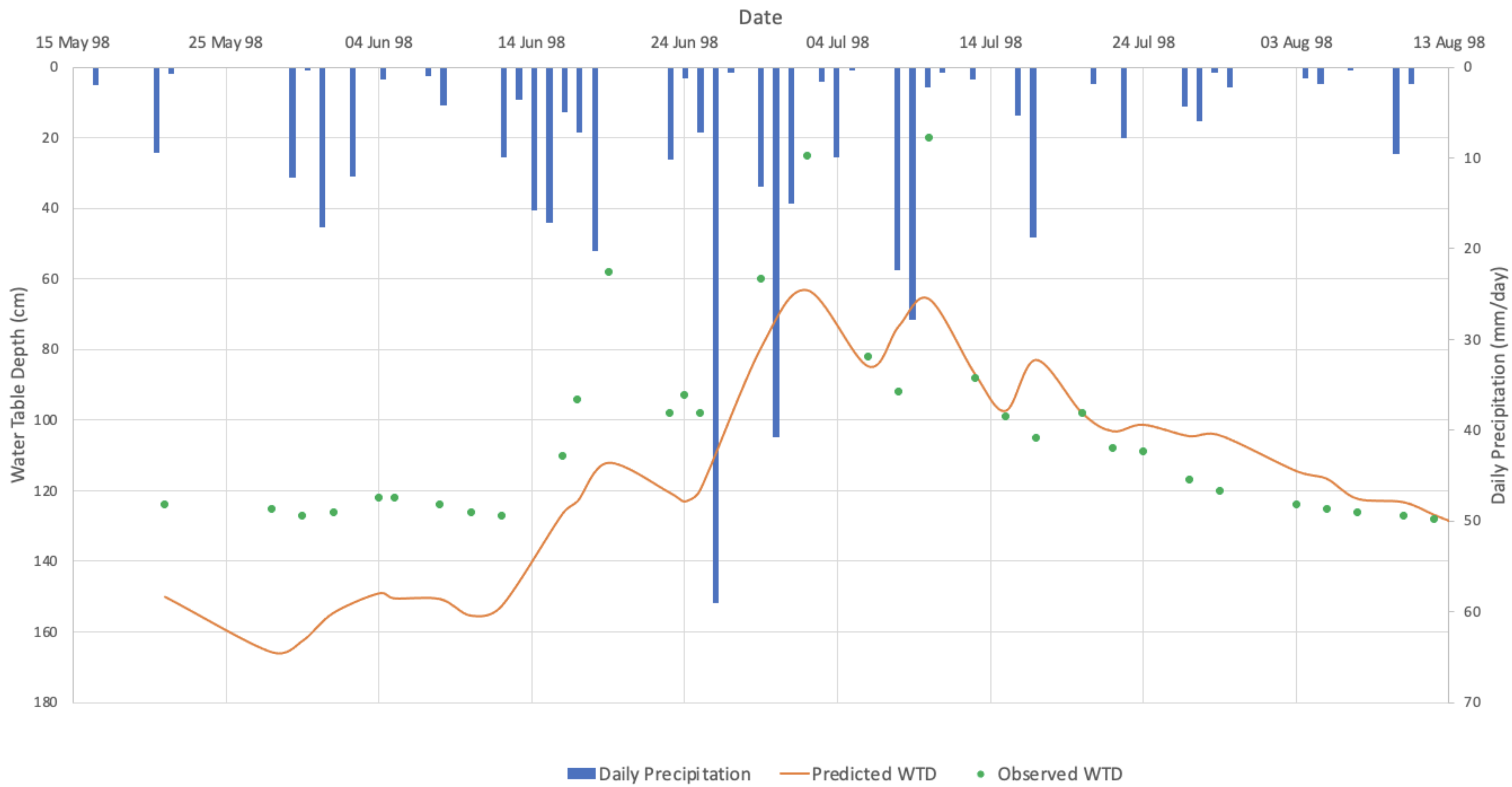

Figure 18. Simulated and observed water table depths at site E in 1998 for DRAINMOD validation.

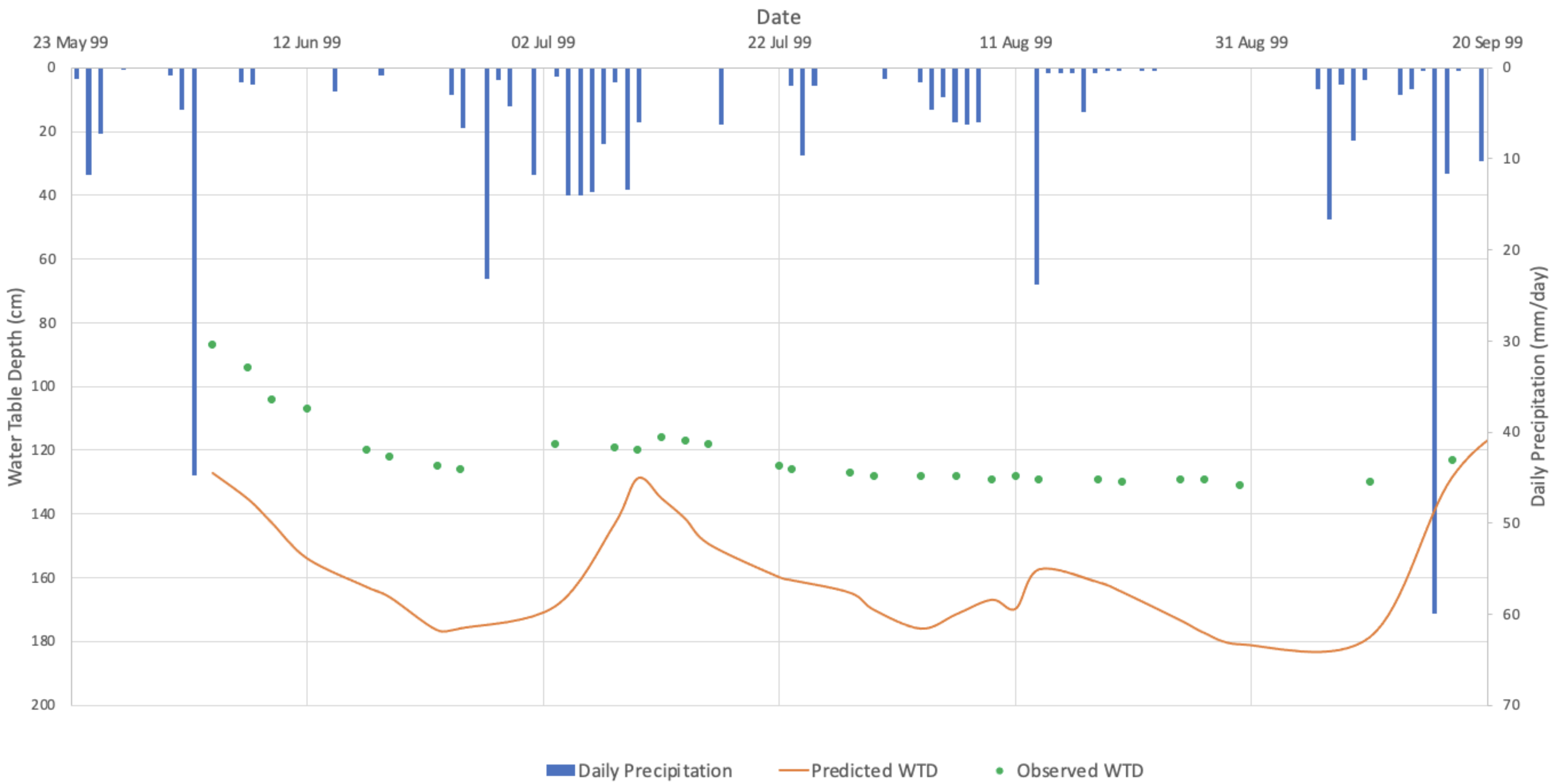

Figure 19. Simulated and observed water table depths at site E in 1999 for DRAINMOD validation.

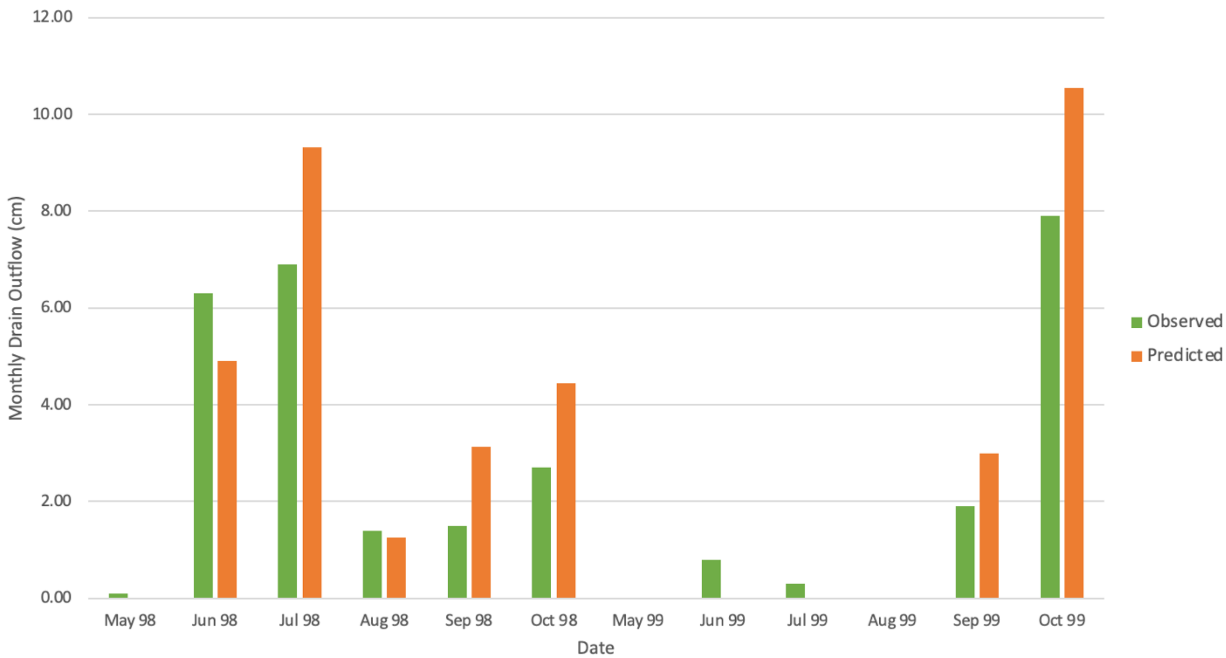

Figure 20. Simulated and observed drainage volumes at site E in 1998 and 1999.

4.2.2 Nitrate simulations

The DRAINMOD-N II simulations were only calibrated for sites C and E using the NO_3 fluxes in drainage water. For site C, a total of 11 daily NO_3 fluxes measured during the growing season of 2022 were used to calibrate the simulation. For site E, monthly NO_3 fluxes measured during the growing season of 1999 were used for calibration. The simulated daily NO_3 fluxes at site C in 2022 were similar to the observed NO_3 fluxes with the exception of an overestimation of NO_3 on May 17 (Figure 21). The simulated monthly NO_3 fluxes at site E in 1999 were similar to the observed values with the highest NO_3 fluxes occurring in October (Figure 22).

The NO_3 leached was modelled for five different fertilizer management practices and the NO_3 leached over all sites ranged from 2.09 kg N/ha to 82.12 kg N/ha (Table 9). The NO_3 leached at site A ranged from 22.93 to 33.77 kg N/ha, 52.39 to 82.12 kg N/ha for site B, 11.6 to 21.41 kg N/ha for site C, 32.6 to 55.13 kg N/ha for site D, and 2.09 to 2.27 kg N/ha for site E. The simulated NO_3 leached at site E was an order of magnitude lower than all other sites.

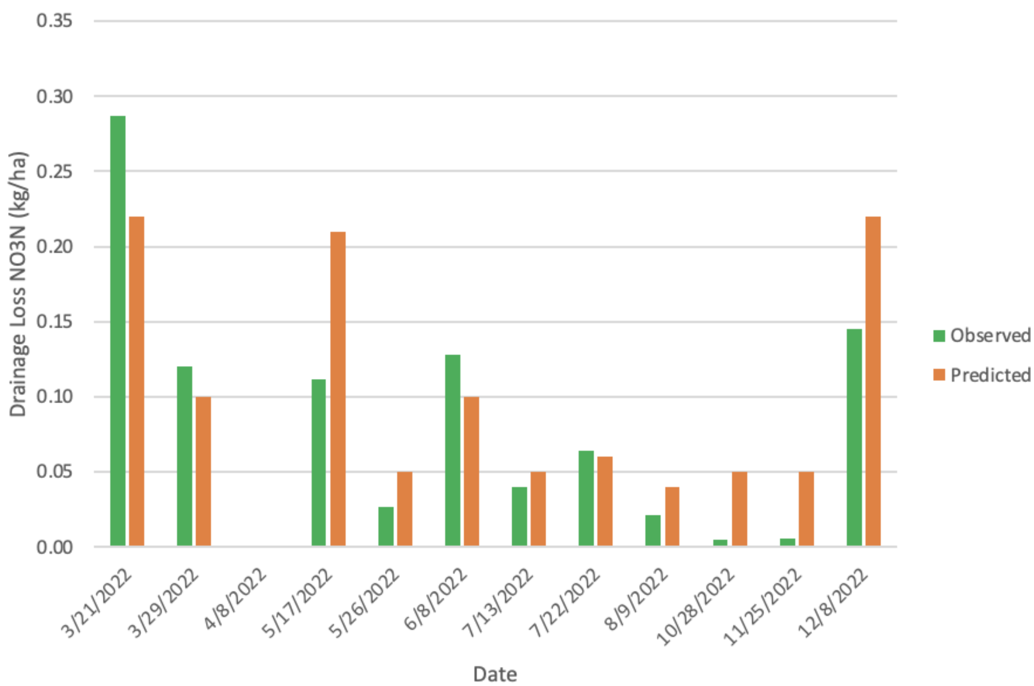

Figure 21. Simulated and observed daily drainage nitrate fluxes at site C in 2022.

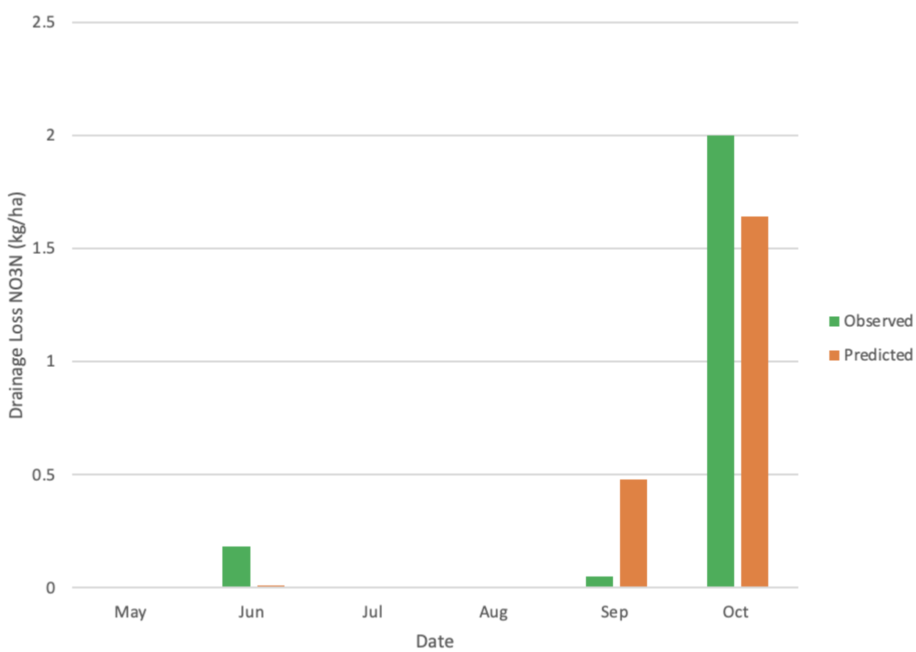

Figure 22. Simulated and observed monthly drainage nitrate fluxes at site E in 1999.

The fertilizer management practice of a single presowing application of 121.85 kg N/ha using urea and CAN fertilizer resulted in the lowest simulated NO_3 leaching for all sites. The fertilizer management practice of a split application of 180 kg N/ha using DAP and CAN fertilizer resulted in the highest simulated NO_3 leaching for all sites except for site C. Site C had the highest simulated NO_3 leaching under a single presowing application of 222 kg N/ha using APS, UAN, and organic fertilizer (diluted pig slurry).

Table 9. Simulated nitrogen leached at each site at differing fertilizer application regimes.

Total Nitrogen Applied (kg N/ha)		127.1	121.85	222	180	120
Application Timing		presowing	presowing	presowing	split	split
Fertilizer Type		Urea/CAN	Urea/CAN	APS/UAN/Organic	DAP/CAN	DAP/CAN
Nitrogen Leached at Each Site (kg N/ha)	A	23.46*	22.93	24.58	33.77	24.33
	B	55.08	52.39*	58.67	82.12	57.96
	C	11.68	11.6	21.41*	17.66	13.77
	D	34.38	32.6	36.33	55.13*	36.53
	E	2.1	2.09	2.11	2.27	2.13*

* simulated nitrate leached at site with the observed fertilizer management practice

4.2.3 Assessment of model performance

Due to insufficient data, the hydrology simulations were calibrated but were not validated except for the site E simulation. Only two of the five NO_3 simulation (site C and E) were calibrated and there were insufficient measured data to perform validation on any of the NO_3 simulations. The statistical indices used for calibration and validation were PBIAS, NSE, KGE, IOA, and CRM.

The statistical parameters were used to calibrate DRAINMOD hydrology simulations by comparing the simulated and observed WTDs. The site E DRAINMOD simulation was assessed by comparing the observed and simulated drainage discharge volumes as well as WTD. It is deemed necessary to compare simulated and observed drainage volumes to properly calibrate a DRAINMOD simulation (Skaggs et al., 2012). Calibrating for drain outflow generally functions better than calibrating for only WTD because a wide range of values are obtainable from high to low flows, including periods of no drain outflow (Dayyani, 2010). However, there was insufficient observed data to calibrate any of the models using drainage discharge except for site

E. The statistical indices for the calibration and validation of the hydrology simulations can be found in Table 10. All sites performed acceptably according to PBIAS, and all sites except site E performed acceptably according to the IOA. The NSE for sites A, C, and E was not within the acceptable range, however, the KGE for these sites was either within range or very close. KGE for all sites showed that the model was a better predictor than the mean WTD as all calculated KGE values were over -0.41(Knoben et al., 2019). The model generally underestimated the WTDs for all sites except site B during calibration. During validation the model overestimated the WTD and the drainage discharge volumes. The model performed acceptably for the validation of the site E simulation for the 1998 and 1999 WTD and discharge volumes.

Table 10. Colour coded statistical indicators for DRAINMOD performance based on water table depths and drainage volumes (where DV is indicated).

	Site	PBIAS (%)	NSE	KGE	IOA	CRM
Calibration	A	9.1	-0.08	0.41	0.79	-0.076
	B	-8.2	0.48	0.6	0.82	0.082
	C	2.7	0.28	0.65	0.83	-0.027
	D	1.4	0.47	0.37	0.88	-0.014
	E 2008	*-4.15*	*0.19*	*0.44*	*0.66*	*0.042*
	E 2009	*12.8*	*-1.3*	*-0.35*	*0.51*	*-0.13*
	E total	4.5	-0.05	0.31	0.58	-0.045
Validation	*E 1998*	*-1.03*	*0.69*	*0.65*	*0.94*	*0.01*
	E 1999	*-9.22*	*-3*	*-0.06*	*0.51*	*0.092*
	E total	-4.92	0.682	0.72	0.84	0.049
	E (DV 1998)	*-22.1*	*0.66*	*-0.14*	*0.92*	*0.22*
	E (DV 1999)	*-24.2*	*0.81*	*0.34*	*0.97*	*0.24*
	E (DV total)	-22.9	0.76	0.64	0.95	0.23

DV = drainage volume

The DRAINMOD-N II simulations were also assessed using these indices to compare simulated and measured drainage water NO_3 concentrations. It should be noted that due to inadequate measured data only the DRAINMOD-N II simulations for site C and site E were calibrated and none of the models were validated. The DRAINMOD-N II simulations all performed acceptably according to the calculated statistical indices (Table 11).

Table 11. Statistical indicators for DRAINMOD-N II performance

	Site	PBIAS (%)	NSE	KGE	IOA	CRM
	C	-20.7	0.67	0.8	0.89	0.21
Calibration	E	4.5	0.89	0.45	0.97	-0.045

4.3 Nitrogen index

The calculated N index ranged from 0.84 to 1.43 for silty loams, 0.32 to 0.59 for clay loams, and 0.20 to 0.36 for sandy loams (Table 12). For a breakdown of the N balance and the calculation of N index values refer to Appendix Tables B1 to B5. The N index for silty loams had the widest range and was the most reactive to changes in fertilizer rates, clay loams had the second widest range and was relatively reactive to changes in fertilizer rates, and sandy loams had the smallest range and was the least reactive to changes in fertilizer rates. The N index increased for all soil types as the amount of kg N/ha increased. Silty loam had the highest N index values, followed by clay loam, and then sandy loam.

Table 12. Nitrogen Index for different soil textures under five fertilizer management practices.

		Nitrogen Index				
	Fertilizer (kg N/ha)	120	122	127	180	222
Soil Texture	Silty loam	0.84	0.86	0.89	1.16	1.43
	Clay loam	0.32	0.33	0.34	0.46	0.59
	Sandy loam	0.20	0.20	0.21	0.29	0.36

Chapter 5 - Discussion

5.1 Field measurements

5.1.1 Particle size distribution

Particle size distribution was determined using three sample locations per site. Although depth was accounted for through the use of a composite sample, the spatial variability of soil may not have been adequately covered. Soil type varies widely based on spatial variability and as such the soil types determined through lab work are broad simplifications of the soil type found in the fields (Wendroth et al., 2011). However, the soil types determined match the official soil series reported in Info-sols and were considered accurate enough for the purposes of this research (Gombault et al., 2022).

5.1.2 Soil water characteristic curves

Sites A and C are silty loams and have similar wilting points, the field capacity of site A, however, is 0.13 cm^3cm^{-3} higher than the field capacity at site C. The clay loam (site D) had a higher wilting point than the sandy loam (site B) but had a lower wilting point than the two silty loam sites. It is expected that the clay loam site would have a wilting point that is higher than both the silty and clay loam because the fine particles in the clay loam should hold onto more water than the larger silty and sandy particles of the other sites (Tuller & Or, 2004). When all curves were generated using the Van Genuchten method, the expected relationship was observed (Figure A2). However, upon further investigation, both the measured and generated curves gave similar results when input into DRAINMOD. This is likely because the Van Genuchten generated soil water characteristic curve values were relatively close to the measured. The largest difference in wilting point for sites A, B, and C was 0.11 cm^3cm^{-3} and the for field capacity it was 0.22 cm^3cm^{-3} , this difference is within experimental error. As such, it was decided to use the measured curves for sites A, B and C and the Van Genuchten curve for site D in the DRAINMOD simulations.

5.1.3 Soil nitrogen

The total soil N measured at each site increased from 2021 to 2022 for sites B, C, and D which suggests an accumulation of N in the soil of both inorganic and organic N. The developed

N balance used the change in soil N over the course of a year which accounts for the N that remains in the soil over long periods of time. As a result, the soil N was considered a loss of the N applied as per Delgado et al. (2023), this was because the change in soil N was positive meaning that some of the N applied remained in the soil. The increase in both organic and inorganic N in soil was an unexpected trend as most agricultural fields experience either a plateau or decrease in soil N over time (Haas et al., 1957). The soil N at sites B and D increased by 220 and 459 kg N/ha, respectively. Not only was the increase unexpected but an increase of this magnitude was very abnormal. The observed increase was likely due to the timing of the measurements. The soil samples in 2021 were taken post-harvest and the samples in 2022 were taken after sowing. This means that the 2022 measurements were taken shortly after fertilizer was applied to the fields which would result in higher soil N measurements while the 2021 measurements were taken after soil N was depleted. The soil N was calculated from three spot samples per site. Soil N is spatially variable and is greatly affected by the application of fertilizer. In addition, the soil N is only a snapshot of one year and does not provide the general trends of soil N over a long period. It is possible the changes observed in 2021 to 2022 were outliers and not representative of the overall trends. These discrepancies should be considered when analyzing the results of the N index.

5.1.4 Water table depths

The silty loam sites (A and C) had shallow WTD that remained relatively stable throughout the growing season, hovering around a depth of 60 m. The sandy loam site (B) had the most reactive WTD, and depth decreased quickly after rainfall events and rapidly increased shortly after. The clay loam site (D) had the deepest WTD of the four sites in 2022. The soil type, precipitation and the drainage are factors that impact WTD drastically. All sites had tile drainage installed at a depth of one meter meaning the drainage does not account for the WTD differences at the sites. The precipitation was measured at a nearby weather station and not at each site independently, this means that a rainfall event could have been observed at the weather station that did not impact one or more of the fields. Alternatively, there could have been a rainfall event at one of the fields that was not observed at the weather station. This could explain why the WTD at site D remained stable for most of July and August despite a large precipitation event observed at the weather station on July 18. It can also explain the drastic increase in the WTD at site B on August 11 despite the relatively small rainfall event observed at the weather station. The soil type explained the reactivity of the WTD to precipitation. Sandy soils are well draining soils that have high infiltration, whereas clayey soils are poor draining and have low infiltration (Rose, 2004). This would explain why the sandy loam site had the most reactive WTD and the clay loam had the least reactive WTD with the silty loam sites laying somewhere in-between.

5.1.5 Nitrate measurements

There were only 12 total NO_3 flux measurements, eleven of which were considered in this research. It was not possible to have a well-rounded understanding of the NO_3 fluxes based on the limited data. The NO_3 fluxes were measured using one sample per measurement and are not representative of the total NO_3 fluxes that were observed at the site. Additionally, drainage volumes greatly impacted the NO_3 flux, however, they were not measured for site C. The point measurement of NO_3 data was assumed to be the daily NO_3 flux and was used to calibrate the DRAINMOD-N II simulation for site C. The assumption that the single point measurement was the daily flux could be a source of error that would result in underestimation of NO_3 leaching.

5.2 Model simulations

5.2.1 Hydrologic modelling

To accurately model NO_3 leaching it is integral that the driving hydrologic parameters are simulated accurately (Youssef et al., 2005). Drainage volumes, average daily soil water fluxes, and soil water contents simulated by DRAINMOD have significant impact on the simulated NO_3 leaching. As such, it is important that the DRAINMOD simulations are properly calibrated to ensure the most accurate NO_3 leaching simulations possible. This is particularly important due to the inability to calibrate the majority of the NO_3 simulations. There are slight variations in the trends, at sites A, B, and D, in which the peaks of the simulated WTD did not match the timing or intensity of the observed WTD. This may be due to a difference in precipitation observed at the weather station versus the precipitation observed at the sites. For example, at site B there was an observed spike in the WTD on August 11, 2022 that was not reflected in the simulated WTD.

This could be due to a large precipitation event that occurred at site B but was not observed at the nearby weather station.

The WTDs at site E were lower than were observed at sites A, B, C and D, particularly in the years 1999 and 2009. This could be due to the lower precipitation observed near Coteau-du-Lac compared to St Hyacinthe. Over 25 years (1998-2022) St Hyacinthe received a yearly average of 1041mm, and Coteau-du-Lac received a yearly average of 977mm. On average, over the last 25 years Coteau-du-Lac receives 30mm less precipitation during the growing season than St Emmanuel. In 1999 and 2009 at Coteau-du-Lac, the precipitation was 589mm and 579mm, respectively, during the growing season. In contrast, the precipitation in 2022 at St Hyacinthe was 638mm during the growing season, a difference of about 50mm.

5.2.2 Nitrate simulations

While there was good agreement between the observed and simulated NO_3 fluxes there were very limited data available for calibration of the DRAINMOD-N II simulations. A total of eleven daily measurements for site C and six monthly measurements for site E. With such limited data the calibration of the two DRAINMOD-N II simulations is questionable. Additionally, there were insufficient data for the calibration of the sites A, B, and D simulations and insufficient data for the validation of all the simulations.

NO_3 leached from site E was very low compared to the other sites (Table 13). This could be due to 1999 being a particularly dry year during the growing season (Figure 23). The WTD was low throughout the entire growing season and only came above the drainage depth in early June. If the WTD remained below the depth of drains, there would be minimal to no drainage and consequently minimal to no NO_3 flux in the drainage water. DRAINMOD predicted an even lower WTD than was observed and this was likely why the DRAINMOD-N II simulations predicted NO_3 leaching values that were an order of magnitude lower than all other sites and why the values did not change notably under different fertilizer application strategies. As such these NO_3 leaching values were not comparable to the other sites.

The simulated NO_3 leached was highest for site B, one of the sandy loam sites. NO_3 leached at sites A and C, the two silty loams sites, were the lowest simulated values. Simulated NO_3 values at site D, the clay loam site, were between the values for the sandy loam and silty loam sites. The high NO_3 leached in sandy loams compared to the silty loam and clay loams agrees with literature (Gaines & Gaines, 1994; Sogbedji et al., 2001). The NO_3 leached depends heavily on soil type because NO_3 leaching depends on the movement of water in soil. Sandy soils have higher water permeability and lower CEC than silty and clay soils which results in sandy soils retaining less water and less NO_3 than silty and clayey soils (Gaines & Gaines, 1994).

Table 13. Heat map of simulated nitrogen leached at each site at differing fertilizer application regimes.

Total Nitrogen Applied (kg N/ha)		127	122	222	180	120
Application Timing		presowing	presowing	presowing	split	split
Fertilizer Type		Urea/CAN	Urea/CAN	APS/UAN/Organic	DAP/CAN	DAP/CAN
Nitrogen Leached at Each Site (kg N/ha)	A	23.46	22.93	24.58	33.77	24.33
	B	55.08	52.39	58.67	82.12	57.96
	C	11.68	11.6	21.41	17.66	13.77
	D	34.38	32.6	36.33	55.13	36.53
	E	2.1	2.09	2.11	2.27	2.13

Note: Site E is not coded in the heat map due to low measured values

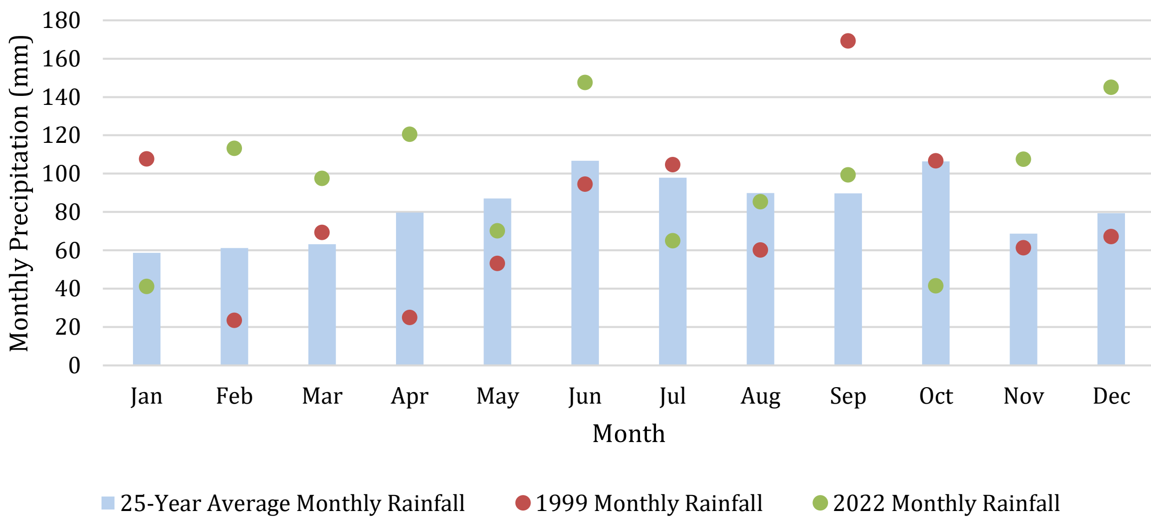

Figure 23. Monthly Precipitation at Coteau-du-Lac over the last 25 years.

However, the silty loam sites were expected to leach more NO_3 than the clay loam site. Clayey soils have lower water permeability and higher CEC than silty soils and should therefore retain more NO_3 than silty soils (Lambe & Whitman, 1969). A potential reason for this discrepancy was the use of the Van Genuchten method instead of measured soil water characteristics. The clay loam site was the only site that used the Van Genuchten method and the generated wilting point laid in-between the measured wilting points of the sandy and silty loam sites. Clay soils would be expected to have a wilting point lower than both sandy and silty soils (Tuller & Or, 2004). Since the model used the characteristic curve that had a higher wilting point than the silty loams it would assume that the clay loam site retains water less efficiently than the silty loams and would therefore leach more NO_3.

Leached NO_3 was highest during split application compared to the single applications (Table 13). This was an unexpected observation as the split application process was implemented specifically to reduce N losses and has been considered successful in many cases (Wang & Li, 2019). The split application regime also used DAP fertilizer, the most widely used phosphorous fertilizer in the world (Maqsood et al., 2022). It provides both phosphorous and NH_4 and is touted for its alkalinization of soil which increase phosphorous plant uptake (Maqsood et al., 2022). It is likely that this was observed due to the consistent high precipitation after the second application of fertilizer in early June.

Another possibility was that there was no use of urea in the two split application regimes. Urea introduces organic carbon to the soil as well as N. Organic carbon stimulates microbial growth and activity and is required for the process of denitrification (Youssef et al., 2005). Increased denitrification would result in more volatilization of N and lower NO_3 leaching due to lower available leachable N. DRAINMOD-N II takes the carbon cycle into account in the calculation of NO_3 leached and therefore the exclusion of added carbon may have resulted in higher NO_3 leached values. Despite much more total N being applied in the 222 kg N/ha fertilizer management practice, the simulated NO_3 leached was generally not as high as the simulated NO_3 leached for the 180 kg N/ha regime. This was likely due to the use of organic fertilizer in the 222 kg N/ha application regime which also introduces organic carbon to the system.

5.3 Nitrogen index

The N index developed for this research was a simplified type three N index (Shaffer & Delgado, 2002). The NO_3 index proposed by Shaffer and Delgado (2002) requires a tier three approach in fields with fluctuating shallow water tables such as those found in eastern Canada. Tier three N indices require the most intensive data input of the three tiers and requires site specific field data and computer simulation modelling of NO_3 leached (Paz et al., 2009).

The N index for both clay loam and sandy loam were between zero and one for all fertilizer application rates (Figure 24). This suggests that for all the fertilizer management practices observed, more N was lost than was applied for the silty loam and clay loam sites. The silty loam site N index was between zero and one for the application rates of 127 kg N/ha and below. At an application rate of 180 kg N/ha and 222 kg N/ha the N index for the silty loam sites were above one, meaning that more N was applied than was lost and N was accumulating in the soil (Figure 24).

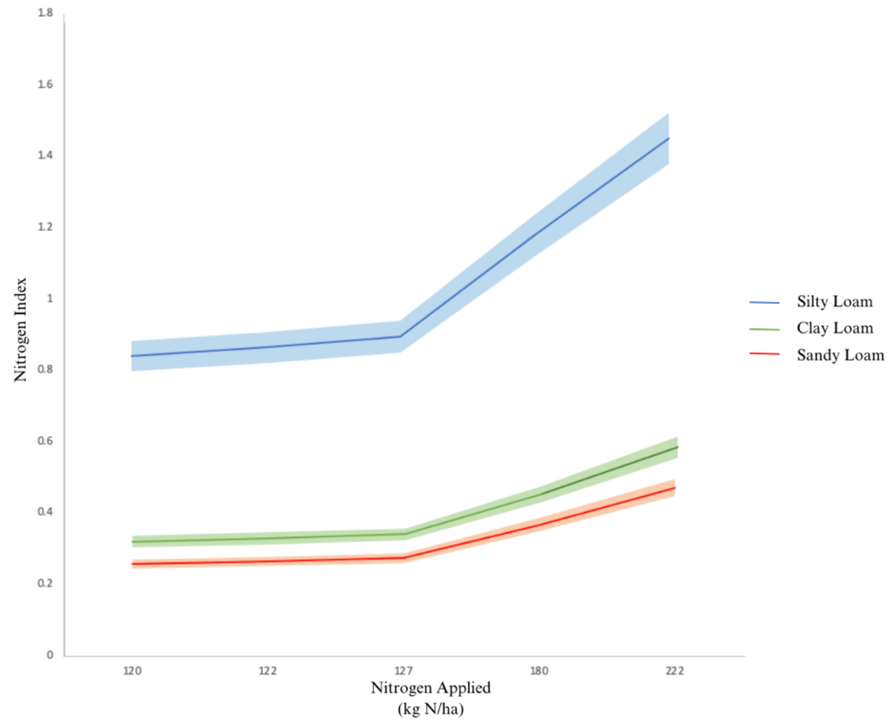

Figure 24. Nitrogen index for three soil types with error bands of +/-5%.

The observed build-up of N was unexpected but can be explained by the index not accounting for all N outputs which could result in an underestimation of N leaving the system. The primary losses of N that were not considered included losses due to runoff and deep seepage. In addition, the N losses that were considered were greatly simplified with the exception of NO_3 leaching. The N uptake was assumed to be constant despite soil type and fertilizer management changes. This assumption was a source of error as plant uptake is dependent on soil conditions (Gonzalez-Lopez & Gonzalez-Martinez, 2021). Soil texture can impact N uptake because of its impacts on root growth (Xie et al., 2021).

Changes in fertilizer management can also change N uptake in corn. Delgado et al. (2023) observed an increase of corn N uptake of 106 kg N/ha at an application rate of 132 kg N/ha to 118 kg N/ha at an application rate of 118 kg N/ha. Meanwhile, Abbasi et al. (2020) found that corn crops took up approximately 70-140 kg N/ha with a fertilizer rate of 200 kg N/ha. Based on these findings, corn N uptake depends on much more than fertilizer application rates and can be quite site specific. Therefore, the corn N uptake was assumed to be 104 kg N/ha regardless of fertilizer application since there was no measured data for the sites. This assumption also introduced error to the N index.

Both the inorganic and organic N in the soil increased over the course of a year and as per Delgado et al. (2023) this increase was taken to be a net loss of N. However, the observed increase in N was likely incorrect due to the timing of sampling. The observed data was used in the index but remeasuring soil N yearly after harvest is strongly recommended to ascertain the soil N changes in each site. The soil N was only measured at three of the five sites and was extrapolated to the other sites, this is another potential source of error in the N index. In addition, the N volatilization was assumed to be 7.8% of the total applied fertilizer in all scenarios. This could introduce error as many things control N volatilization that can vary per site including soil pH and temperature and microbial biomes.

The results of the N index are comparable to results found using the NIT-1 index and the Ontario N index. The NIT-1 index showed lower rates of NO_3 leaching in a silty clay loam compared to a sandy clay loam soil (Delgado et al., 2008). This was comparable to the results obtained using the new index. The Ontario N index classifies sandy loams as high risk, silty loams as medium risk, and clay loams as low risk (Reynolds et al., 2016). This relationship was seen for the sandy loam compared to the silty and clay loams. However, the silty loam was deemed a lower risk than clay loams using the newly developed N index. Sogbedji et al. (2001) used the LEACHMN index and found that loamy sand leached more NO_3 than clay loams, however they also found that the model did not accurately predict the amount of NO_3 leached from sandy loam.

It was unexpected for the silty loam sites to retain the most N considering clay loams have higher CEC and lower water permeability than silty loams. This may be attributed to the simulated NO_3 leaching and the change in soil N. The simulated NO_3 leaching was unexpectedly higher in the clay loam compared to the silty loam sites likely due to the soil water characteristic curves used. The change in soil N calculated from 2021 to 2022 at site C was two orders of magnitude lower than the change observed at sites B and D. The soil N at site C was relatively steady increasing only by 11.2 kg N/ha over the year whereas the soil N increased by 220 and

459 kg N/ha at sites B and D, respectively. This difference in soil N may be due to the use of organic fertilizer at site C compared to site B and D. The use of organic fertilizer would increase the microbial activity through the addition of carbon and denitrification would increase and more N would be volatilized, and less N would accumulate in the soil. Alternatively, there was a lab error in the measurements at site C, or the measurements taken were not representative of the field. There was a total of three sample locations per site which would not be representative of the entire field.

Chapter 6 - Summary and conclusions

6.1 Summary

Corn is intensively grown in Canada and uses high inputs of nitrogen (N) fertilizer. Although N inputs to agricultural land is necessary to keep up with global food demand, N losses have negative impacts on the environment, particularly the atmosphere and waterways. Not all N is consumed by the crop; N loss can occur via NO_3 leaching in tile drainage water, N volatilization, and soil processes. Different methods of nutrient management on drained agricultural lands, grown to corn in Quebec, have gained traction over the past few decades to reduce the amount of N losses. One such method is the use of N indices to assess the risk level of N losses at different sites.

The main purpose of this study was to develop an N index for different soil types. The study was conducted on five different corn fields in southern Quebec with three different soil types. Field data were used in DRAINMOD and DRAINMOD-N II models and were also used to calibrate the models. The model NO_3 flux output was then used in conjunction with published data to develop the soil-type-dependent N index.

6.2 Conclusions

The soils at the five sites were classified as two silty loams, two sandy loams, and one clay loam. The hydrology of the sites was simulated to obtain the hydrological parameters required to run the NO_3 simulations. The DRAINMOD hydrology simulations performed satisfactorily with indices of agreement (IOA) of 0.58 to0.95 and Kling-Gupta Efficiencies (KGE) of 0.31 to 0.72. DRAINMOD-N II was used to simulate NO_3 fluxes at all five sites. There were sufficient data to calibrate only two of the DRAINMOD-N II simulations. For these two sites DRAINMOD-N II performed satisfactorily with IOA of 0.89 to 0.97 and KGE of 0.45 to 0.8. The soil N was calculated based on field work and the remaining parameters were obtained from literature and agronomists.

Sandy loams were found to leach the most NO_3, followed by clay loams and then silty loams. The clay loam simulation leached more NO_3 than the silty loam because the soil water characteristic curve for the clay loam was generated instead of measured which resulted in a lower wilting point than the silty loam. This showed the importance of the use of measured data and consistency in methodology.

The fertilizer management practice with the lowest risk of N leaching at all three soil types was a single pre-sowing application of 122 kg N/ha of urea and calcium ammonium nitrate (CAN). This was because of the low application rate and the inclusion of urea which provides organic carbon and N which increases rates of denitrification. The fertilizer regime that resulted in the highest amount of leaching was a split application of 180 kg N/ha of diammonium phosphate (DAP) and CAN. The second fertilizer application was followed by consistent heavy rain events which resulted in higher rates of nitrate (NO_3) leaching. Fertilizer type and application timing are major contributors to the risk of NO_3 leaching and must be considered to establish best management practices.

The N index showed that, sandy loams had the highest risk of N losses, followed by clay loams and then silty loams. The results indicate that N management is most important on agricultural fields with sandy loam which agrees with current literature. However, clay loam was deemed a higher risk soil than silty loam despite its higher cation exchange capacity and lower permeability. This was observed because of the simplification of the N losses accounted for in the index and erroneous soil N measurements.

Based on the findings of this research, in order to use a tier three N index accurately, the following information must be compiled for a site: field measurements of soil properties (soil organic and inorganic N, bulk density, particle size distribution, soil water characteristic curves, pH, etc.), detailed field management practices, drainage plans, temperature and precipitation data, N volatilization, and corn grain N. Additionally, a minimum of two years of water table depth, drainage volumes, and NO_3 fluxes are required for proper calibration and validation of computer simulations. It is recommended that farmers and nutrient specialists focus primarily on tier one N indices, as a tier three N index is very data intensive, and if adequate data is not obtained, the findings of a tier three N index have similar applicability as a tier one N index. If the tier one N index flags the site as a high risk, then one should proceed to a tier three index.

6.3 Recommendations for future research

This research highlighted the necessity of obtaining the field measurements for all data necessary for a N index. Based on the results of this study, future research should focus on:

1. Conducting field measurements of daily WTD, drainage volumes, and NO_3 fluxes in drainage water to calibrate and validate the hydrology and NO_3 simulations. This would add credence to the simulated NO_3 leached values and would reduce levels of uncertainty in the N index.
2. Measuring long term soil N trends in different soil types and measure soil N post-harvest each year. A proper measurement of the change in soil N over a year or years would greatly improve the accuracy of the N index developed in this study.
3. Measuring the N volatilization (NO_2-N, NO_x-N and NH_3-N) from fields studied to confirm the assumed values of N volatilization are applicable to artificially drained and shallow water table corn fields.
4. Measuring the corn grain N uptake in different soil types under shallow water table conditions. This would allow for a better understanding of impact of soil type on corn N uptake and would provide standard values for an N index that could be used in Eastern Canada.
5. Analyze the impacts of different types of organic fertilizers on NO_3 leaching in different soil types. Only diluted pig slurry was examined in this study and the impacts of different organic fertilizers is of interest and would be useful to nutrient managers and farmers.

Chapter 7 - Bibliography

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Appendices

Appendix A: Soil Moisture Curves

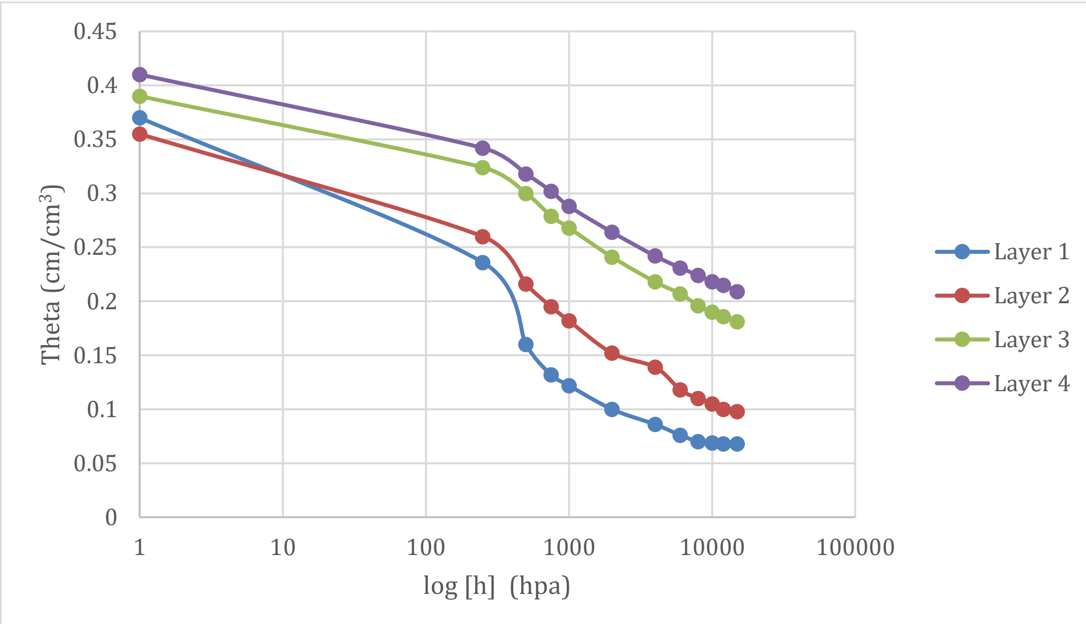

Figure A1. Soil water characteristic curves for Site E, adapted from Bourke (2011)

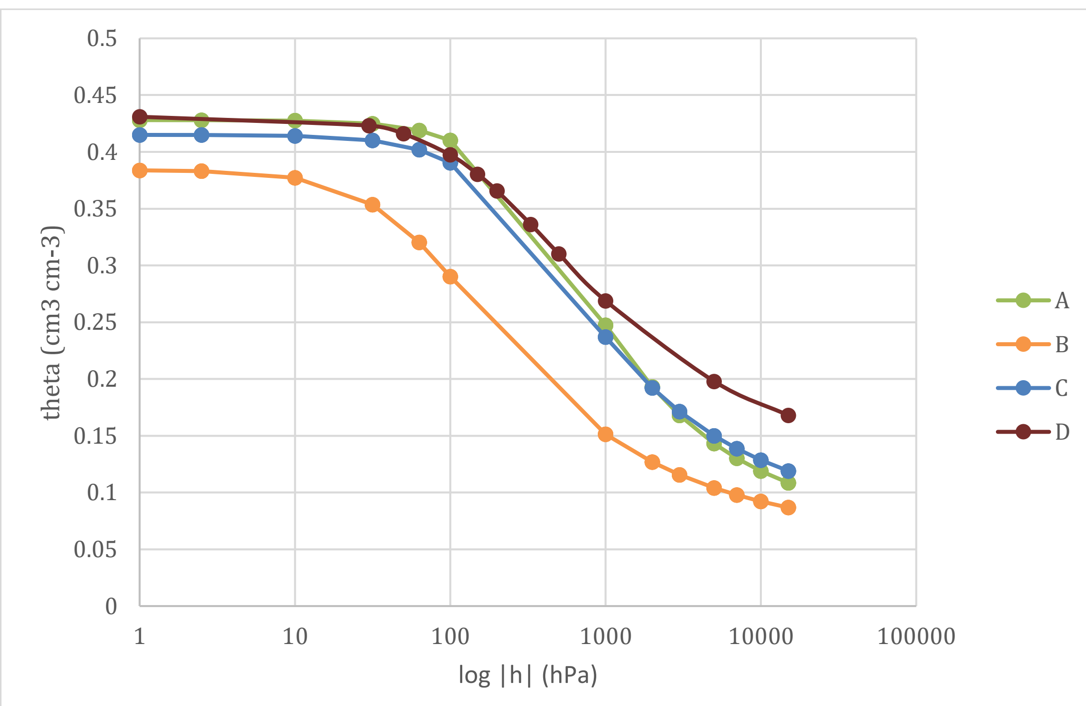

Figure A2. Van Genuchten generated curves for sites A, B, C and D.

Appendix B: Nitrogen Balance

Table B1. Nitrogen balance and N index values for a fertilizer application of 120 kg N/ha.

Site	TN soil kg N/ha	Inorganic N kg N/ha	Organic N kg N/ha	N uptake by corn kg N/ha	N off gassed kg N/ha	N leaching (DRAINMOD) kg N/ha	Fertilizer applied kg N/ha	N losses kg N/ha	N index
A	11.20	0.997	10.20	104.0	9.36	24.33	120.0	-28.89	0.806
B	459.2	6.275	452.9	104.0	9.36	57.96	120.0	-510.52	0.190
C	11.20	0.997	10.20	104.0	9.36	13.77	120.0	-18.33	0.867
D	220.3	2.690	217.6	104.0	9.36	36.53	120.0	-250.15	0.324
E	459.2	6.275	452.9	104.0	9.36	2.13	120.0	-454.69	0.209

Table B2. Nitrogen balance and N index values for a fertilizer application of 122 kg N/ha.

Site	TN soil kg N/ha	Inorganic N kg N/ha	Organic N kg N/ha	N uptake by corn kg N/ha	N off gassed kg N/ha	N leaching (DRAINMOD) kg N/ha	Fertilizer applied kg N/ha	N losses kg N/ha	N index
A	11.20	0.997	10.20	104.0	9.52	22.93	122.0	-25.65	0.826
B	459.2	6.275	452.9	104.0	9.52	52.39	122.0	-503.11	0.195
C	11.20	0.997	10.20	104.0	9.52	11.6	122.0	-14.32	0.895
D	220.3	2.690	217.6	104.0	9.52	32.6	122.0	-244.38	0.333
E	459.2	6.275	452.9	104.0	9.52	2.09	122.0	-452.81	0.212

Table B3. Nitrogen balance and N index values for a fertilizer application of 127 kg N/ha.

Site	TN soil kg N/ha	Inorganic N kg N/ha	Organic N kg N/ha	N uptake by corn kg N/ha	N off gassed kg N/ha	N leaching (DRAINMOD) kg N/ha	Fertilizer applied kg N/ha	N losses kg N/ha	N index
A	11.20	0.997	10.20	104.0	9.91	23.46	127.0	-21.57	0.855
B	459.2	6.275	452.9	104.0	9.91	55.08	127.0	-501.19	0.202
C	11.20	0.997	10.20	104.0	9.91	11.68	127.0	-9.79	0.928
D	220.3	2.690	217.6	104.0	9.91	34.38	127.0	-241.55	0.345
E	459.2	6.275	452.9	104.0	9.91	2.1	127.0	-448.21	0.221

Table B4. Nitrogen balance and N index values for a fertilizer application of 180 kg N/ha.

Site	TN soil	Inorganic N	Organic N	N uptake by corn	N off gassed	N leaching (DRAINMOD)	Fertilizer applied	N losses	N index
	kg N/ha	kg N/ha	kg N/ha	kg N/ha	kg N/ha	kg N/ha	kg N/ha	kg N/ha	
A	11.20	0.997	10.20	104.0	14.04	33.77	180.0	16.99	1.104
B	459.2	6.275	452.9	104.0	14.04	82.12	180.0	-479.36	0.273
C	11.20	0.997	10.20	104.0	14.04	17.66	180.0	33.10	1.225
D	220.3	2.690	217.6	104.0	14.04	55.13	180.0	-213.43	0.458
E	459.2	6.275	452.9	104.0	14.04	2.27	180.0	-399.51	0.311

Table B5. Nitrogen balance and N index values for a fertilizer application of 222 kg N/ha.

Site	TN soil	Inorganic N	Organic N	N uptake by corn	N off gassed	N leaching (DRAINMOD)	Fertilizer applied	N losses	N index
	kg N/ha	kg N/ha	kg N/ha	kg N/ha	kg N/ha	kg N/ha	kg N/ha	kg N/ha	
A	11.20	0.997	10.20	104.0	17.32	24.58	222.0	64.90	1.413
B	459.2	6.275	452.9	104.0	17.32	58.67	222.0	-417.19	0.347
C	11.20	0.997	10.20	104.0	17.32	21.41	222.0	68.07	1.442
D	220.3	2.690	217.6	104.0	17.32	36.33	222.0	-155.91	0.587
E	459.2	6.275	452.9	104.0	17.32	2.11	222.0	-360.63	0.381