Using Spatially Explicit Soil Mapping and Modelling to Understand and Mitigate Nitrate Leaching in an Agricultural Catchment

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Abstract

Diffuse water pollution is a significant environmental management problem associated with nitrate movement from agricultural catchments to groundwater sources. Several factors including agricultural management practices, soil texture and soil depth to the bedrock are responsible for this pollution risk. The Fell Sandstone aquifer which extends across a large part of Northumberland is the lone source for drinking water supply in Berwick upon Tweed and is showing deterioration that is believed to be due to diffuse pollution. Environment Agency monitoring boreholes in the catchment area indicate that nitrate levels in the Fell Sandstone aquifer may exceed the allowable limit for nitrate in drinking water in the next 5 to 15 years. Land use in the catchment is mostly agricultural and fertilizer and manure management accompanied by other agricultural activities are believed to be major contributors to groundwater contamination. In this thesis, high-resolution soil sensing was used to design a better monitoring system for soil nitrate concentration and leaching events in the Fell Sandstone catchment study area. The porous ceramic cups technique was used to extract soil solution below the root zone for three drainage seasons (between autumn 2017 and spring 2020) to monitor nitrate leaching from various soil types, crop rotations and conventional *vs* organically managed fields. The digital soil mapping approach (DSM) was used to understand soil texture and depth to the bedrock variability within the study area. In the results based on the predicted soil texture components, soil texture (clay and sand %) varies within a field in a distance of 300m in the top layer of soil. Soil depth to the bedrock also varies from very shallow (30 cm) to deep (> 120 cm) within the study area. Due to the role of soil texture and depth to the bedrock in nitrate movement, the locations of sandy shallow soil profiles might be hotspots for nitrate leaching. The results further emphasised that the time and amount of drainage volume varied with soil type and soil profile depth. Effect of crop rotations, fertilizer amount and impact of a wet and dry year in terms of drainage was studied. Nitrate leaching from the field after winter wheat followed by potatoes during the first drainage season 2017/2018 was much higher than any other crop rotation in conventionally managed fields and from organically managed winter wheat grown after two years of clover was highest among organic fields. Whereas lowest leaching was recorded from grass fields regardless of the management system. The results reveal no notable difference in leaching from organic and conventionally managed fields. Several strategies are outlined in literature to mitigate the losses of nitrogen from agricultural land. Innovative approaches like nitrification inhibitors and slow-releasing N fertilizer were investigated along with tillage management in field trials in a long term organic and conventional crop rotation and fertility management trial at Nafferton Farm, England. The role of a nitrification inhibitor in reducing nitrate leaching was demonstrated in the field trial but no apparent effect of slow-releasing fertiliser was recorded on leaching but, fertiliser use was improved with slow-releasing fertiliser which could result in less surplus N at the end of the season. A mechanistic nitrogen dynamics model was calibrated and validated with observed soil mineral nitrogen and nitrate leaching data to assess the efficacy of the model in simulating nitrate leaching and to simulate the impact of management practices. This study demonstrated the importance of spatial variability of soil properties, particularly soil texture and soil depth along with other factors, on nitrate leaching. The results can be used to support decisions about management of spatially variable zones within a field for the purpose of controlling nitrate leaching by implementing proven strategies without compromising economic loss. Eventually the outcomes of this thesis can add to the knowledge of understanding the factors causing diffuse nitrate pollution and innovative mitigation strategies to minimise these losses.

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1.1 Identification of the Nitrate Pollution Problem

In the second half of the 20th century, agriculture underwent significant changes (Galloway *et al.*, 2004) and artificial nitrogen fertilisation became a pillar in modern farming (Zufiaurre *et al.*, 2020). During this time, developed countries became large producers of fertilisers and food, implying a dramatic decrease in the number of their farms and an increase in yield (Galloway *et al.*, 2004) and an increase in the use of nitrogen fertilisers to improve crop production (Lord *et al.*, 2002). A four-fold increase was reported in nitrogen (N) inputs from 1950 to 1980 and peak around 1985 with a slow decline afterwards (Robinson and Sutherland, 2002) as shown in **Figure 1. 1**. However, agriculture should continue to grow food and take environmental issues into account at the same time (Wang *et al.*, 2019). Excess supplies of nitrogen can pollute the air, soil and water. One of the most common and harmful impacts of agriculture linked to N fertilisers is the degradation of groundwater quality and pollution of drinking water sources (Schröder *et al.*, 2004). Nitrate leaching is the process by which the nitrate anion moves with soil water down in the soil profile (Padilla *et al.*, 2018). Available nitrate in the arable soil profile in late summer or early winter is leached when crop demand of N is low and soil drainage is taking place. These nitrate losses from the cropping system are directly related to overwintering rainfall, water holding capacity of the soil and the rate and time of fertiliser application (White *et al.*, 1983), in a temperate climate like the UK. Researchers identified several factors contributing to nitrate leaching to groundwater worldwide (Wick *et al.*, 2012).

The principal N contribution to the UK groundwater is derived from diffuse nitrogen pollution sources such as fertilizers, manures, sewage sludge, and farm crop residues (Amin-Hanjani and Todd, 2006; Stuart *et al.*, 2011), which is responsible for the large-scale depletion of the quality of water (Bouraoui and Grizzetti, 2014) and poses a serious problem for the supply of drinking water and contributes to the eutrophication process (Arauzo *et al.*, 2011).

Diffuse nitrogen pollution (DNP), together with gradually controlled point source pollution, has been recognised as a significant threat to water quality (D'Arcy and Frost, 2001). Current studies often consider that farmland contributes the most diffuse nitrogen load due to the inefficient input of chemical fertilisers (Ongley *et al.*, 2010). In comparison, point sources were estimated to contribute < 1 % of the total flux of nitrates to groundwater in the UK (Sutton *et al.*, 2011). To effectively regulate DNP, it is necessary to determine the source, transport route and removal method of nitrogen exports.

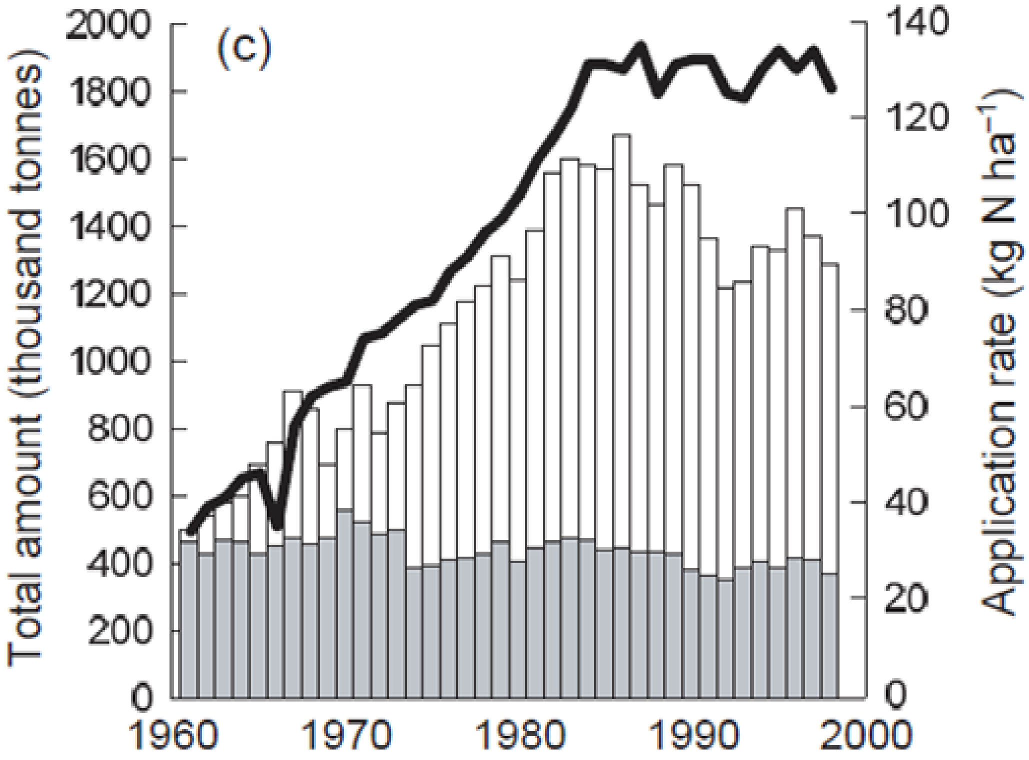


Figure 1. 1 Average nitrogen application rate (line and right axis) to all crops, total amount of nitrogen applied in Britain (open bars and left axis) and phosphate (filled bars) adapted from Robinson and Sutherland (2002).

Excessive concentrations of nitrates in water sources can cause severe long-term environmental concerns and threaten both the economy and human health (Ward, 2009). The health risks are conversion of haemoglobin to methaemoglobin in infants, gastric problems in adults, nitrosamines formation that causes cancer, and a decrease in the functioning of the thyroid gland (Zhai *et al.*, 2017). Several diseases are associated with the ingestion of nitrate contaminated water in epidemiologic studies, including several types of cancers, diabetes, adverse reproductive outcomes, thyroid conditions, and molecular degeneration. There have been a number of inconsistencies in the relationship between maternal exposures to nitrate contaminated water and adverse reproductive outcomes. However, a positive relationship has been reported between drinking water nitrate during pregnancy and central nervous system defects or neural tube defects. Most studies have shown the association of clinical or subclinical hypothyroidism with nitrate consumption. However, there is not enough evidence from epidemiological studies that can prove cancer association with nitrate ingestion (Ward and Brender, 2019). Zhai *et al.* (2017) reported that the health hazards of nitrate concentration from drinking water vary in different age groups in the order infants> children> adult females> adult males.

Eutrophication is a term used to explain the environmental impact of excessive nutrient levels in the water (either aquatic or terrestrial ecosystem). The EC Nitrates Directive describes eutrophication as 'the enrichment of water by nitrogen compounds, causing an accelerated growth of algal and higher forms of plant life to produce an undesirable disturbance to the balance of organisms present in the water and the quality of the water concerned' (Archer, 1994). The higher nutrient levels promote plant growth but can adversely affect ecosystems' productivity and biodiversity, resulting in excessive growth or "blooms" of algae, depletion of oxygen, rendering waters uninhabitable for fish and other animal life (Amin-Hanjani and Todd, 2006). Nitrate reaches surface water either absorbed in drainage or as a result of agricultural surface runoff (Davidson *et al.*, 2012). Due to the massive amounts of additional nitrogen applied as inorganic fertilisers and manure to agricultural fields, agricultural soils represent a notable nitrate input into surface waters compared to semi-natural grasslands and forests where load and export are small (Jansson, 1994). The consequences of eutrophication are not limited to natural habitats and processes alone but also affect human health and well-being directly or indirectly through impacts on human respiratory quality, increased drinking water costs and influences on recreation and habitats (Clark *et al.*, 2017). Understanding essential nitrate pollution determinants such as impacts and magnitude of nitrate leaching, contributing factors, and processes are crucial to help implement mitigation strategies, design regulatory policy, enforcement, and monitoring.

1.2 Understanding the Processes and Factors Involved in Nitrate Leaching

The nitrogen cycle in the soil is an important part of the overall natural N cycle (**Figure 1. 2**). Sources of N that drive the N cycle in soil are fertilizers, manure, and crop residues, due to their chemical conversion from one form to another through fixation, immobilization, nitrification, and denitrification (Atkins, 1976). Biological nitrogen fixation is a highly specialized and complex interaction between higher plants and soil microorganisms to utilize the elemental nitrogen from the atmosphere. For efficient nitrogen input into plants, the process of biological nitrogen fixation has been investigated for a century. However, the actual mechanism of biochemical processes is still unclear. It has been revealed that the host plant dominates in this relationship to regulate biological nitrogen fixation, and the process of fixation is influenced by several environmental factors (Berry *et al.*, 2003).

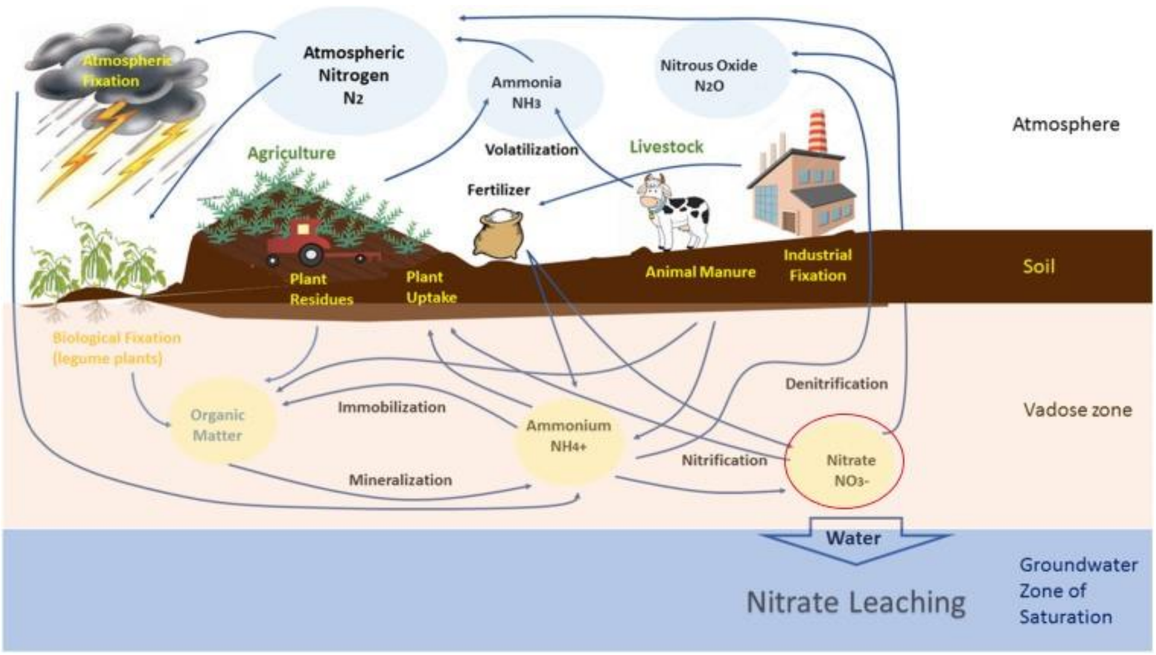


Figure 1. 2 Nitrogen cycle including nitrogen leaching to ground water (Padilla *et al.*, 2018).

The conversion of organic nitrogen to inorganic nitrogen (ammonium and nitrate) by soil microorganisms is known as mineralisation and immobilisation (an opposite process in which microorganisms convert simple forms of N to more complex organic forms) (Jansson, 1994). These two proceed simultaneously in soil. The balance between these two processes decides the amount of N released from soil organic matter (net mineralisation) and available for crop growth or at risk of leaching. Understanding mineralisation is important to ensure that crops efficiently use nitrogen and there are fewer chances of nitrogen pollution through nitrate leaching (Shepherd *et al.*, 1996). In addition to nitrate leaching, ammonia volatilisation from fertilisers and plant tissues and denitrification (N_2 + N_2O) are globally considered the main soil N loss pathways. The amount of N lost as N_2 by fertilisers and manures on agricultural land is seldom quantified because of difficulties in accurately measuring N_2 emissions (Rocha *et al.*, 2020).

In humid temperate climates like the northeast of England, losses of nitrate due to leaching are highest during the autumn-winter months when the amount of water draining from the soil is greater than net evapotranspiration (excess winter drainage). The period of excess winter drainage in these regions usually begins in the autumn when the soil profile reaches field capacity. At this stage, any further rainfall displaces water deeper in the profile resulting in net drainage into the unsaturated zone. This excess water moves down through the soil, displacing the water already in the profile along with dissolved nutrients like nitrogen (Lawniczak *et al.*, 2008).

Arable crops cover more than 4.5 million ha, which is about 30% of agricultural land in the UK, making a significant contribution to the total amount of leached nitrate (Goulding, 2000). It has been reported that agricultural land receives a surplus of 125 kg N ha^{-1} yr^{-1} and that 70-80% of nitrate in English rivers comes from agricultural sources (Neal *et al.*, 2006; Kay *et al.*, 2012). The amount of nitrate lost to the water bodies from an area of land is linked to the type of crops or intensity of livestock farming. Therefore, the concentration of nitrate in water resources (a groundwater or river drinking water source) depends on the balance of agriculture in the catchment (Archer, 1994). The balance between nitrogen input and output is one of the key indicators for sustainable agricultural systems development and also used to estimate leaching of nitrates in groundwater (Dalgaard *et al.*, 2012). The nitrogen balance is calculated in the UK by national agricultural nitrogen surplus 'farm gate', which is defined as the difference between imports of nitrogen and exports from agricultural land. Inputs are fertiliser, livestock feed and waste transported into the agricultural system, and outputs are crops, livestock products, and waste exported from the system. Internally recycled materials (grass, fodder, manure) do not require clear transparency (Lord *et al.*, 2002). Nitrogen balance also depends on whether the agricultural system protects the soil from over-winter leaching, mainly from autumn-sown crops, or if the soil is bare mostly during the winter leaching season (Archer, 1994). However, as the nitrogen balance is a calculated estimation of N leaching, the degree to which the measure is capable of reflecting real nitrate leaching effects is unclear and, therefore, only measures the potential for groundwater contamination (Sieling and Kage, 2006).

Over time, numerous spatially variable and interacting factors, including land-use, vegetation type, climate, soil properties, catchment topography and total nutrient inputs, define the nitrate stocks and fluxes at a farm or catchment level (Nolan and Stoner, 2000; Li *et al.*, 2017). Water moving across the soil or drainage water moving through the soil can both transport nitrate in solution or suspension. In sandy soils, the process of water movement down through the soil is very simple, and water flows down through the soil with a typically uniform wetting front, carrying solutes from the soil profile to groundwater. In soils, such as clays and loams, water normally travels laterally, either over the surface as ‘overland flow' (surface runoff) or through the cracks, channels, and drains collectively known as ‘soil water drainage.'’ (Amin-Hanjani and Todd, 2006). Nitrate is highly mobile and is readily drained in solution when present in the soil. Thus easily draining soils tend to be more leachable than less permeable soils (Ragab *et al.*, 1996). Land used for agricultural purposes will always create some risk when the plant-soil system is uncoupled, especially during periods when there is no crop in the field, or the crop is not growing vigorously.

1.3 Measures Proposed to Mitigate Nitrate Leaching

Since the early 1990s, the European Union has been setting up various guidelines to counter the high nitrogen loads entering groundwater. Because of its importance as the primary aquifer in England and Wales, nitrate movement through unsaturated zones of aquifers has tended to focus on the Chalk aquifers (**Figure 1. 3**) (Buss *et al.*, 2005). The legislation on eutrophication management and nutrient loading in surface and groundwater was introduced in 1991 as the Nitrates directive (ND) (Directive 91/676 / EEC) which was further supplemented by the EU Water Framework Directive (WFD; 2000/60/EC) in 2000. The ND aims to control the leaching of nitrate from diffuse sources (agricultural activities) and the WFD was adopted with the objective of delivering good ecological and chemical status for all water bodies by 2015 through the implementation of Programmes of Measures included in River Basin Management Plans. (Bouraoui and Grizzetti, 2014; Velthof *et al.*, 2014). The Groundwater Directive (2006/118/EC) was introduced as the daughter of the WFD in 2007 (replaces the original Groundwater Directive (80/68//EC)), as it is the most sensitive and largest drinking water source in many regions. Therefore chemical contamination and groundwater deterioration were addressed by the Groundwater Directive (Crowhurst, 2007).

Despite these efforts under the EU WFD, the quality of water in the UK continues to decline, and nitrate concentrations surpass the EU drinking water standard set by the EC Drinking Water Directive (80/778/EEC) of 11.3 mg NO_3-N l^{-1} (50 mg NO_3^- l^{-1}) and show an increasing trend in many rivers and aquifers (Buss *et al.*, 2005; Stuart *et al.*, 2007; Burt *et al.*, 2011).

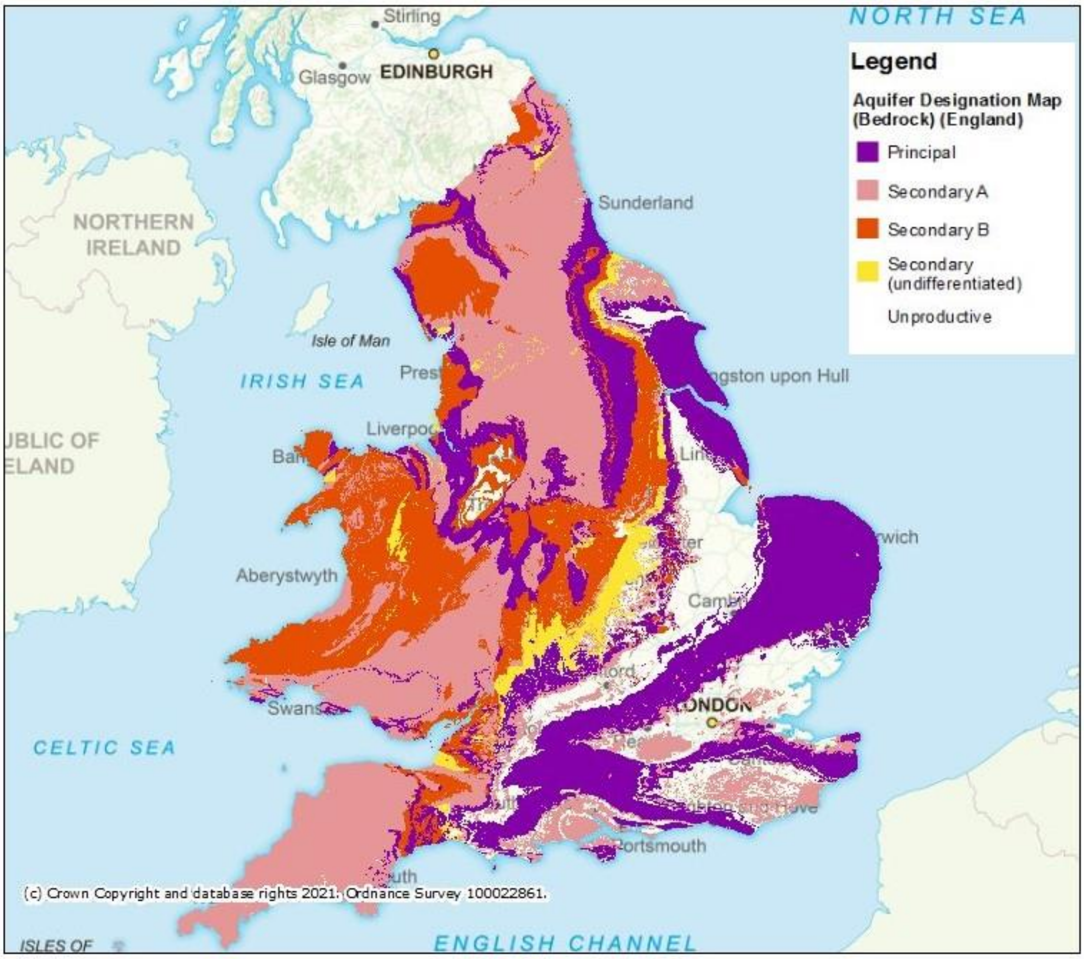


Figure 1. 3 Aquifer designations in England and Wales as principal (with fracture permeability and provide high level of water storage), secondary A (permeable support water supplies at local level), B (less permeable with limited water storage capacity), undifferentiated and Unproductive (low permeability and negligible significance for water supply)[1].

Reducing agricultural nutrient losses is crucial to effective WFD implementation. Many measures can be used to minimise the losses of nitrogen from farming areas to surface and groundwater (Bouraoui and Grizzetti, 2014). Initially, 68 Nitrate Vulnerable Zones (NVZs) were defined by the Environment Agency in England in 1996, covering an area of around 600,000 ha. The NVZ legislation came into force in 1998 (Edwards *et al.*, 2003; Kay *et al.*, 2012). The Nitrates Directive defines nitrate vulnerable zones as the areas of land draining into waters adversely affected by nitrate contamination, including (i) surface freshwaters with elevated nitrate-N concentration (11.3mg l^{-1} threshold), (ii) groundwater with elevated-N concentrations (11.3mg l^{-1} threshold), and (iii) waters affected by eutrophication. In these areas, farmers must comply with the action programmes to improve water quality (Arauzo *et al.*, 2011). The area designated as NVZ was later expanded, and the EA (2017) indicates total NVZ area

[1] http://apps.environment-agency.gov.uk/wiyby/117020.aspx

is 76,000 sq km (of which 33,000 sq km is designated for groundwater protection) that represents 58% of the total land area in England **(Figure 1. 4).**

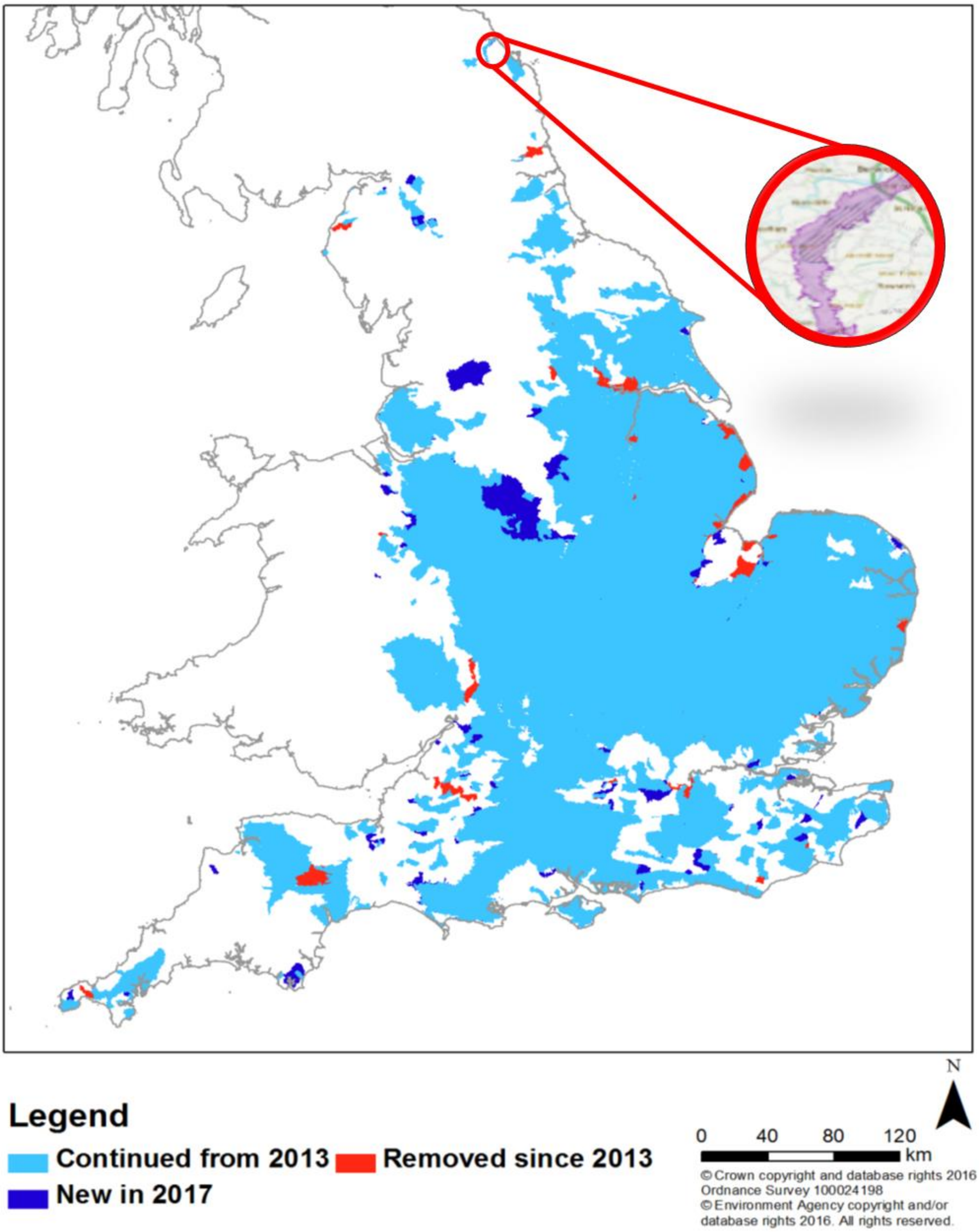


Figure 1. 4 Proposed Nitrate Vulnerable Zones in 2017 (EA, 2017), with the location of the study area in this thesis indicated by pink shading in the inset.

The general purpose of the NVZ regulations was to minimise inputs to catchments and improve application timing to reduce the likelihood of N losses in runoff (Kay *et al.*, 2012). The England Catchment Sensitive Agricultural Delivery Initiative (ECSFDI) is now the principal mechanism for providing farm advice in England on management practices to protect water quality (Kay *et al.*, 2012). By encouraging catchment-sensitive farming, the UK aims to reduce diffuse water pollution (DWP) from agriculture. Farmers in NVZs are expected to implement an action plan to meet Nitrates Directive requirements. This means that farmers must

- limit nitrogen usage to crop needs,
- observe closed times for spreading on land for inorganic and organic nitrogen at risk of runoff,
- use sufficient space for storage to match closed periods and maintain records of nitrogen use.

The N-max limit is a yearly limit on the average quantity of organic and conventional fertilisers that farmers in the NVZs can apply to most crops for a standard yield. The N-max limit for winter wheat and barley are 220 and 180 kg N ha^{-1}, respectively. However, an additional 20 kg N ha^{-1}a can be used for wheat and barley with every tonne increase in the expected yields, or on the fields with shallow soil (except soil over sandstone). In winter oilseed rape, the N-max limit is 250 kg N ha^{-1} with an addition of 30 kg N ha^{-1} if the excepted yield exceeds standard yield by half a tonne. Each year, farmers can apply up to 170 kg N ha^{-1} of livestock manure (both manure deposited directly by livestock and spreading). This is the farm's average loading limit. It is separate from the 250 kg ha^{-1} organic manure field limit[2]. Which means, total nitrogen from all organic manures must not exceed 250 kg ha^{-1} year^{-1}. The field limit excludes livestock manures from grazing animals.

The difference between N input and output is known as N surplus. N surplus has been considered as a predictor of possible nitrogen loss to the environment (De Notaris *et al.*, 2018). No agricultural system can use nitrogen with 100 % efficiency. However, most systems can be improved, resulting in a reduction in the amount of nitrate lost each winter (Archer, 1994). Much work has been done to provide farmers with management recommendations to optimise yields and minimise nitrogen losses from the temperate climate region. Recommended management practises to minimise nitrate leaching include, but are not limited to, optimum fertiliser application to meet crop requirements, not to apply fertilisers if there is a high risk of drainage

[2] Using nitrogen fertilisers in nitrate vulnerable zones - GOV.UK (www.gov.uk)

(Cuttle *et al.*, 2007), crop and soil management practises including tillage, rotations, and the use of catch crops can all have an impact on actual N losses (Hansen *et al.*, 2015). Research has been conducted on the role of catch crops in N leaching reduction, demonstrating their potential as a mitigation method to reduce nitrate leaching from agroecosystems in temperate climate zones over the winter (Tonitto *et al.*, 2006; Tosti *et al.*, 2014; Thapa *et al.*, 2018). To meet agricultural N requirements and increase crop yield and nitrogen use efficiency NUE, many new forms of N fertilisers have been developed (Yuan *et al.*, 2016), including controlled-release fertilisers (Xu *et al.*, 2008), and nitrification inhibitors to improve the N use efficiency (Smith *et al.*, 2007) during the cropping season and reduce the risk of surplus SMN at harvest.

1.4 Role of Digital Soil Mapping and Modelling

Digital soil mapping (DSM) is an approach for developing a geographical reference soil information system with numerical models using laboratory observations and environmental variables data. These maps can help inform soil conservation policies and management practices within the private and scientific sectors. DSMs can be used for detailed spatial scales; the outputs are often reproducible with the assessment of mapping error compared to traditional soil maps (Žížala *et al.*, 2022). The use of machine learning in DSM can produce low cost and time effective maps of spatially variable soil properties (Khanal *et al.*, 2018). Significant advancements in DSM and predictive modelling can improve the representation of soil spatial variability at farm and regional scales. Remote sensing technologies are an advance that has the capacity to deliver more accurate and reliable data for different auxiliary variables than have been previously available across larger spatial regions in DSM. These are, for example; climate variables, terrain variables, and soil surface properties (Žížala *et al.*, 2022)**.**

Nitrogen is an essential nutrient to increase and maintain agricultural production worldwide. However, the overuse of nitrogenous fertilizer with low N use efficiency is usually responsible for diffuse water pollution from cropping systems(Thompson *et al.*, 2007). The transport and losses of N are complex and are influenced by several variables discussed in section 2.2. However, it is difficult to determine the Spatio-temporal influences of these factors on the variability of soil N losses due to the limited number of sampling locations and low sampling frequency. Therefore, numerical models have been developed to simulate the soil nitrogen dynamics and biogeochemical processes of soils (Liao *et al.*, 2021). A list of the most used models are APSIM, DAISY, NDICEA, DNDC, STICS, SUNDIAL, etc. All these models are based on the similar principals to simulate the N biogeochemical processes and plant N uptake. Details on the treatment of these processes differ from one model to another. Distinctive from other N dynamics models, NDICEA is a target oriented model in which expected crop yields are used in the model as a target from which dynamic water and nitrogen requirements are derived. Due to this distinctive feature along with others, NDICEA was used in this study to simulate soil N dynamics.

1.5 Study Objectives

In this study different factors that drive nitrate leaching losses from an agricultural catchment to the Fell Sandstone aquifer were studied. Agricultural management strategies and soil spatial variability were given special attention because of their role in drainage and nitrate movement from agricultural land. The study's objective included assessment of the benefit of using high resolution digital soil maps compared to conventional soil maps to determine soil spatial variability in the study area, and to determine the impact of soil spatial variability on nitrate leaching, as well as assessing already available and innovative recommendations for farmers to minimise nitrate losses to groundwater sources from an agricultural catchment under temperate conditions. Specific objectives of this research include:

- Present a critical literature review that integrates the current understanding of nitrate leaching to groundwater from intensive agriculture and identifies key contributing factors and management strategies to reduce the problem.
- To assess the use of high-resolution digital soil maps compared to conventional soil maps of the study area, intelligent sampling design and point observations for soil nitrate and leaching events across a small but diverse agricultural catchment.
- Investigate the effect of soil spatial variability on nitrate leaching from an agricultural catchment to the Fell Sandstone aquifer
- Investigate the effect of farm management practices on nitrate leaching from an agricultural catchment to the Fell Sandstone aquifer
- Evaluate the role of innovative management strategies in field trials including controlled-release urea and nitrification inhibitors along with tillage method to mitigate nitrate leaching
- Assessment of a calibrated and validated nitrogen dynamics model with different land use to use as a decision-making tool to manage nitrate leaching in the catchment area.

Chapter 2. Literature Review on Nitrate Leaching from Intensive Agriculture System in the Northern Temperate Region

Nitrate leaching from intensive agricultural systems to groundwater is an issue of concern not only for human health but also from an environmental point of view. This diffuse water pollution is associated with many factors e.g. agricultural land use, cropping system, fertiliser type and time of application, and some geological factors such as soil type. The spatial and temporal variability of these factors is also important when estimating total losses of nitrate from agricultural land and implementing any mitigation strategy. Several strategies are already in use in the UK to control groundwater contamination by improving crop nitrogen use efficiency and minimising nitrate leaching, including the use of nitrification inhibitors, controlled-release fertilisers, reduced intensity tillage practices, and the use of cover crops. The long-term effectiveness of these measures can be predicted by using nitrogen dynamic models to simulate the fate and transport of nitrate to groundwater. This review will cover the following topics; nitrate pollution of groundwater in the UK, factors contributing to nitrate leaching (including influence of different land use and geological factors), simulation of nitrate leaching and several strategies (improving N use efficiency during crop growth and drainage season, and optimal manure management) to mitigate nitrate leaching.

2.1 Nitrate Pollution of Groundwater in UK

For several decades, nitrate has been recognised as a significant groundwater contaminant and agricultural land reported in many studies to be the major source of this pollution in the UK (Defra, 2006; Stuart *et al.*, 2007; Wang and Burke, 2017). In the British Geological Survey (BGS) database, the single nitrate-input function obtained in the analysis of Wang *et al.* (2012a) was validated using mean pore-water nitrate concentrations from 300 cored boreholes across the UK (Stuart, 2005). It represents a rapid increase in nitrogen loading of 1.5 kg N ha^{-1} year^{-1} (1955-1975), which was caused by an increase in the use of chemical-based fertilisers. In the UK, nitrate loading peaked in the 1980s and then began to decline due to limitations on the use of fertilisers which were introduced for water resource management. The nitrogen input levels were presumed to be close to those associated with early intensive farming in the mid-1950s, i.e. a constant load rate of 40 kg N ha^{-1} (Wang *et al.*, 2012a; Stuart and Lapworth, 2016). Stuart *et al.* (2011) reported that if no improvements to agricultural practice were made, nitrate leaching increases (ranging from minimal) to a potential doubling of aquifer concentrations by 2100 would be expected.

Mean nitrate concentrations for 2006 across England and Wales were reported using monitoring data (unpublished) from the Environment Agency (Rivett *et al.*, 2007). They demonstrate that many of the high occurrences match with major aquifer outcrops in rural agricultural catchments:

- the Chalk and Lincolnshire Limestones
- parts of the Shropshire Sandstone in the west of England
- Nottinghamshire Sandstones in the East Midlands

The highest nitrate concentrations occur in the areas surrounding the Wash, from the Chalk of South Yorkshire and East Anglia to the Lincolnshire Limestone and the Yorkshire-Nottinghamshire Permo-Triassic Sandstone. These typically correspond to areas of low effective precipitation, with a lower dilution capacity during recharge, together with a large percentage of arable land at high risk of NO_3-N pollution (Foster *et al.*, 1986). The evidence of this hydrological control on nitrate concentration trends in the Chalk of southwest England was demonstrated later by Howden and Burt (2009).

Stuart *et al.* (2007) analysed nitrate data from UK groundwater to report past trends and predict future concentrations. Based on 309 datasets from 191 separate sites, nitrate concentrations were found to increase at an average value of 0.08 mg NO_3-N l^{-1} annually. In 2000, 34% of the sites examined exceeded the EU drinking water standard of 11.3 mg NO_3-N l^{-1}. More NO_3-N literature studies (1985-2014) from the other UK aquifers are reported in **Table 2. 1**. This illustrates the importance of aquifers for the UK's water supply and supports existing concentration trends (Stuart and Lapworth, 2016).

Table 2. 1 Several studies reported NO_3-N concentration in UK groundwater

Location	**Aquifer**	**NO_3^-N conc. range**	**Observations**	**Reference**
East Anglia	Chalk		NO_3-N increasing at 0.05–0.2 mg l^{-1} $year^{-1}$ under arable land since 1965	Carey and Lloyd (1985)
South Dorset	Chalk		100-year trend from 1 to 9 mg l^{-1} NO_3-N	Limbrick (2003)
Dorset and Hampshire	Chalk	30% increase over 30 years Modelled rate: 0.12 mg l^{-1} $year^{-1}$	Low concentrations (up to 5 mg l^{-1} NO_3-N) associated with Salisbury Plain and Cranbourne Chase. Arable and urban with high concentrations.	Roy *et al.* (2007)
East Anglia	Quaternary, Crag, Chalk, Lower Greensand, Lower Cretaceous, Lincolnshire Limestone, Sherwood Sandstone	33% over 11.3 mg l^{-1} as NO_3-N	Concentrations recess to long-term rising baseline in Chalk and to level baseline in Lincolnshire Limestone	Beeson and Cook (2004)
Dumfries	Permian Sandstone	Pre-1950s water 2 mg l^{-1}; modern water 9 mg l^{-1}	Concentration related to % of recent recharge	MacDonald *et al.* (2003)
N E Scotland	Devonian Sandstone, Quater-nary floodplain deposits	<0.05–25.9 mg l^{-1}	Evidence of anthropogenic contamination in the Quaternary floodplain deposits. Low NO_3-N conc. in the sandstone aquifer	MacDonald *et al.* (2014)

2.2 Factors Contributing to Leaching

2.2.1 Influence of land use

Land use for agricultural purposes will always create some risk of surface and subsurface water pollution when the plant-soil system is uncoupled, especially during periods when there is no crop in the field or the crop is not vigorously growing (Defra, 2007). Literature suggests that the potential for NO_3-N leaching will usually follow the order (from low to high risk): forest< cut grassland < grazed pasture < arable cropping < pasture ploughing < vegetables in various land-use systems. However, the actual amount of NO_3-N leached from a given system will depend on soil and environment-related factors, management practices and the form of N used (Di and Cameron, 2002). The leaching of nitrates from agricultural land is a complicated process controlled by many factors as outlined in **section 1.2** and further discussed below. Farmers can easily control factors such as crop type, timing, and rate of fertilizer applications, or tillage practices. Other factors, such as the soil type or rainfall quantity and distribution, cannot be regulated or only with considerable effort (Spiess *et al.*, 2020).

Crop rotation and farming systems

Crops are usually grown in rotation in an arable cropping system. Crop rotation is vital in both organic and conventional farming systems to control weeds and pests. It is a tool to maintain and develop soil fertility with crops as well as livestock production. Legumes in rotation add nitrogen for crops in the system with a limited supply of supplementary nutrients. Carefully planned diverse rotations reduce the incidence of pests and diseases. Due to the complex interactions between different system components, fertility management in organic farming relies on a long-term integrated approach rather than on the more short-term focused approaches common to conventional farming (Watson *et al.*, 2002). The effect of long-term crop rotation was investigated, and leaching was positively related to N inputs and surplus post-harvesting at the rotation level (De Notaris *et al.*, 2018) irrespective of the farming system in several studies (see **Table 2. 2**). The maximum losses are found to be associated with autumn ploughing for winter wheat rotation with no added N fertilisers. High loss of nitrate is associated with grass-clover ley ploughing (Di and Cameron, 2002), However, it is balanced with less loss during arable rotation in an organic system during the subsequent year.

Table 2. 2 Difference of nitrogen inputs and leaching between different cropping systems

N applied (kg N ha^{-1} y^{-1})	Cropping systems	Leaching loss (kg N ha^{-1} y^{-1})	Reference
Ammonium nitrate 200	Cereal rotation: spring wheat	17 - 87	Shepherd and Lord (1996)
Ammonium nitrate 175	Cereal rotation: winter wheat	4 - 45	Shepherd and Lord (1996)
Anhydrous ammonia 200	Continuous maize	11 - 107	Bjorneberg *et al.* (1996)
Anhydrous ammonia 170	Maize -soybean: maize phase	5 - 52	Bjorneberg *et al.* (1996)
None	Maize -soybean: soybean phase	5 - 51	Bjorneberg *et al.* (1996)
Urea + ammonium nitrate 200	No-till maize	8 - 77	Baker and Timmons (1994)
Urea + ammonium nitrate 125	No-till maize	8 - 36	Baker and Timmons (1994)
None	Mixed cropping: autumn ploughing, winter wheat	14 -102	Francis *et al.* (1995)

Data on nitrate leaching was recorded in studies from monitoring carried out on ten field sites in the UK during 1988 to 92 on three commercial organic farms. Nitrate leaching was monitored with porous ceramic cups from the nitrate concentration. The experiments were conducted on a farm with rotations including grass/clover for grazing and conservation, winter and spring wheat/spring oats and potatoes. The average annual losses of NO_3-N calculated from these rotations ranged between 10-21 kg N ha^{-1} yr^{-1} (Philipps and Stopes, 1995).

The sandstone aquifer units are important in terms of groundwater resources and also the issue of nitrate-N losses associated with the aquifer catchments. Wang and Burke (2017) developed a catchment-scale approach to model the long-term trends of nitrate-N concentrations in sandstones (aquifers in the Eden Valley, UK) from agricultural land. They showed that improved grassland and arable land use have a higher load of nitrate than woodland land use. The Sherwood Sandstone, Britain's second-largest aquifer, is facing a threat of high nitrate concentrations due to intense agricultural activities. Six scenarios of land use were analysed by modelling groundwater nitrate concentration simulations. Results from the comparative analysis of scenarios indicate that by 2025 the most significant decrease in the concentration of nitrates (35%)

in public supply ground waters was related to the overall target area covered by forest, while the decrease, based on the implementation of best agricultural practises, did not reduce by more than 20% (Zhang and Hiscock, 2016). Zheng *et al.* (2020) investigated the effect of cultivated farmland and natural vegetation on nitrate leaching from a catchment during an average and wet year. The concentration of NO_3-N in groundwater was recorded at 3.73 mg l^{-1} and 13.33 mg l^{-1} respectively from natural vegetation (NV) and cultivated farmland (FL) under a wheat-maize double cropping system in a normal year. These concentrations increase by 84% and 43% respectively for NV and FL, during a wet year. Other studies also reported that agricultural lands could store a large amount of N that can be leached due to heavy precipitation (Min *et al.*, 2018; Wang *et al.*, 2019).

The effects of the management practices on nitrate-N losses were measured in a four-year long experiment by Eriksen *et al.* (2004). Higher losses were recorded from the crops following ploughing of grass-clover and under grass-clover or barley irrespective of the management system used. However, nitrate-N leaching was reduced compared to the earlier rotation when the winter wheat crop was replaced by spring oats with catch crop in the earlier experimental period (1994–97). The experiment confirmed the overriding importance of grassland N management, particularly the cultivation of the ley in organic crop rotations. In another study, nitrogen losses were highest when maize was produced in a five-year study compared to wheat and soybean. The application rate of fertilisers for each crop was in the range 50-150 kg N ha^{-1} yr^{-1} for maize, 60-90 kg N ha^{-1} yr^{-1} for wheat, and no N fertiliser applied to soybean. This indicates that an increase in the frequency of maize in crop rotations can increase the risk of N loss due to the higher application rates (Congreves *et al.*, 2016).

In an organic system, less use of chemical fertilisers is counterbalanced with the application of animal manure and cultivation of legume-based pasture, which could result in nitrate leaching losses. Studies showed that nitrate leaching in organic farming systems varied from 25kg N ha^{-1} per winter to 70kg N ha^{-1} after ploughing of ley (Di and Cameron, 2002). If the rotational organic farm system is assessed, then nitrate leaching potential is no greater than a conventional farm system. Pandey *et al.* (2018) also reported no significant difference in nitrate leaching from organic and conventionally managed systems in an arable cropping system. This has been suggested that nitrate leaching from an organic system compared to a conventional system is linked with cropping system intensity. Legume based cover crops were used on the organic side, enhancing N input and dry matter production, whereas non-leguminous crops were used on the conventional side. Kristensen *et al.* (1994) recorded that the amount of NO_3-N (31 kg N ha^{-1}) in the soil profile of the organic farm system was similar to (29 kg N ha^{-1}) conventional system. Another study was conducted to investigate the nitrate leaching losses from organic farms (depends on legumes for N) and conventional farms under similar cropping and climatic conditions. These farms were in England, and conventional farms were within Nitrate Sensitive Areas (**section. 1.3**). Nitrate-N losses from the organic ley phase (ploughed in winter) were similar to conventional long-term grass (45 kg N ha^{-1} and 44 kg N ha^{-1} respectively) and from the grass phase of conventional ley-arable rotations (50 kg N ha^{-1}). Nitrate-N losses following arable crops averaged 47 kg N ha^{-1} for the organic system and 58 kg N ha^{-1} for conventional systems. The difference recorded was due to the greater proportion of non-cereal break crops in the latter (Stopes *et al.*, 2002). Under similar cropping, the N losses are similar or slightly smaller from organic farms than those from conventional farms with best practice (Kristensen *et al.*, 1994; Philipps and Stopes, 1995; Di and Cameron, 2002; Stopes *et al.*, 2002).

Fertilisation and manure application

Nitrogen is the primary fertiliser with global environmental impact as a nutrient. Particularly in agricultural settings, soil N is insufficient for healthy non-leguminous crop production, resulting in N fertiliser enhancements, usually ranging from 10% to 200% more N as fertiliser. In general, application of N fertilisers to crops is very cost-effective; that is, the cost of fertiliser is far outweighed by the extra value of the crop obtained. That has encouraged farmers to apply abundant N to ensure high production levels (Kitchen *et al.*, 2008). The introduction and implementation of modern technologies and the expansion of land use management to produce more food per unit of land have been driven by food production for the increasing world population. These new developments and intensified production also involve a greater need for chemical fertiliser nutrients to prevent nitrogen depletion and maintain soil quality and crop productivity (Stewart *et al.*, 2005). Increased fertiliser use contributed to one-third of the increase in cereal production during the 1970s and 1980s worldwide (Bruinsma, 2003). In Rothamsted, England, winter wheat has been consistently cultivated since 1843. For several decades, N fertiliser application with P and K was responsible for up to 82 % of wheat yield, compared to only P and K application, which has an average total value of 64 %. From 1970 to 1995, high-yielding winter wheat continuously received 96 kg of N ha^{-1} (Stewart *et al.*, 2005; Stewart and Roberts, 2012). Nevertheless, this has also produced an input surplus relative to grain/forage product outputs, leaving N at risk of environmental loss (Kitchen *et al.*, 2008).

About 50-80% surplus N applied above the recommendation is believed to be at risk of leaching (Defra, 2007). Townsend *et al.* (1996) discovered that 12-60 mg nitrate-N l^{-1} in groundwater resulted from N fertiliser high application rates to sugar beet fields. Using the ^{15}N technique, Thorburn *et al.* (2003) investigated groundwater nitrate-N concentrations in intensive agricultural areas of northeast Australia. They found that 14-21% of wells were contaminated with nitrate, and about half of them were derived from the application of N fertiliser. Pre-conditions for nitrate leaching into the subsoil or groundwater are high nitrate concentration and free water movement in the soil profile. Residual nitrate can travel downwards constantly and be lost, even if it is not leached during the application season. In the UK, after harvest at the beginning of the autumn, and when the soil is still warm enough to initiate mineralisation and nitrification process, the growing crops can uptake residual NO_3-N but a significant amount will remain in the soil. This nitrate remaining in the soil after harvesting can increase if N application exceeds the optimum rate. The effect of this surplus amount of fertiliser applied to arable crops has been investigated in many studies in temperate regions. The studies showed that around 30-60 kg N ha^{-1} might be present as mineral N in soil at harvest due to an increase in soil microbial activities in the autumn, as evaporation decreases and soil moisture rises, resulting in increased mineralisation of organic nitrogen (Haynes, 1997). Approximately 50-70% of the NO_3-N built up in the soil profile (from mineralisation of organic N and some from the N fertiliser applied) by the end of autumn was found to be susceptible to leaching during winter (Chaney, 1990; Shaffer *et al.*, 1996; Haynes, 1997; Di and Cameron, 2002), which could significantly increase when fertiliser N is applied at a rate of more than 200 kg of N ha^{-1} y^{-1} (Haynes, 1997; Di and Cameron, 2002). Davies and Sylvester-Bradley (1995) found that over 50 years, the annual amount of NO_3-N leached from agricultural land in Britain increased by 36 kg N ha^{-1} and one-third was extracted from residual nitrate.

Another source of nitrogen application is animal manure to the soil, which is a traditional method to maintain soil organic matter (SOM) and plant available N (**Table 2. 3**). Nitrogen is being lost from almost all agricultural systems, but organic manure is especially difficult to use efficiently (Jenkinson, 2001). Mineralisation of organic nitrogen in manure can cause losses of available nitrogen from the soil via leaching, especially during the fallow period (Shrestha *et al.*, 2010).

Table 2. 3 Predicted total N and plant available N in manures and compost at typical application rates (adapted from (Berry *et al.*, 2002)).

Manure	**Application rate (tons)**	**Total N ($kg\ N\ ha^{-1}$)**		**Plant available N ($kg\ N\ ha^{-1}$)**	
Conv. Org.		**Conv.**	**Org.**	**Conv.**	**Org.**
Fresh cattle	25	150	125	**38**	**14**
Stored cattle	25	150	125	**15**	**6**
Cattle slurry	25	75	63	**38**	**22**
Poultry	10	160	-	**80**	**-**
Compost green waste	10	120		**1-8**	

According to the literature, the application of waste effluents on land is the best for both disposal and nutrient cycling. However, it has been shown many times that organic effluents are the source of nutrients for plant growth, but they increase the risk of nitrate leaching as they are rich in N (Cameron *et al.*, 1999; Di and Cameron, 2002). A three-year experiment was conducted to quantify N losses from liquid manure on two different soils (Clay loam and loamy sand). In early autumn, late autumn and early spring, dairy manure was applied in plots under grass and maize at an annual rate of 93 800 $l\ ha^{-1}$ with split applications. Nitrate-N concentrations in drainage water were recorded among application; for grass, the average NO_3-N concentrations remained < 10 $mg\ l^{-1}$ from manure application. Autumn applications of manure on maize show high leaching risks on sandy soils, and on grass it poses minimal leaching effects (Van Es *et al.*, 2006).

Storage of the manure or litter allows flexibility in land application timing. However, poor management of manure storage can increase nitrate leaching (Ershadi *et al.*, 2020). Keeping the storage area small can minimise the volume of water required to wash it down. Poorly designed or inadequately maintained drains and gutters allow rainwater from non-fouled yards and roofs to mix with dirty water and increase volume (Cuttle *et al.*, 2007). Open stockpile (storage outside on ground) is a simple and economic strategy for storing manure (Ogejo and Collins Jr, 2009; Kelly and Westendorf, 2014); however, it can lead to nitrate leaching.

Tillage

Tillage of soils generally stimulates the mineralisation of soil organic matter and can result in a "flush" of mineral N, including nitrate (Balesdent *et al.*, 2000). In a conventional cropping system, the land is usually cultivated between crops to control weeds and improve soil conditions for seed sowing. It is done in the fallow period when there is no crop in the field. Cultivation can increase the mineralisation process if it coincides with the wet season, which can provide conditions for more significant drainage. That is why arable conventional cropping systems are blamed for having a high potential for nitrate leaching (Di and Cameron, 2002). After cultivation, soil microbes come in contact with previously unavailable substrates and increase rates of nitrogen transformations to nitrate (Silgram and Shepherd, 1999). Studies have been conducted looking at tillage effects on N losses and showed that overwinter losses can be reduced up to 25% if intensive tillage is avoided in autumn before the sowing of a spring crop (Thomsen, 2005). This is especially true for sandy loam soils, from which leaching increased with tillage intensity in autumn. The losses recorded ranged from 35 kg N ha^{-1} to 76 kg N ha^{-1} over five years, with the highest level of leaching after autumn ploughing with autumn stubble cultivation and the lowest leaching under reduced tillage without autumn stubble cultivation (Hansen and Djurhuus, 1997).

Tillage has a range of effects on soil processes that can cause nitrate leaching, mainly when it occurs before the intensive water recharge season. When comparing mouldboard plough tillage and no-tillage, the latter preserves root and earthworm channels and can improve soil hydraulic conductivity (Azooz and Arshad, 2001). Reduced soil disturbance can preserve N in aggregates due to reductions in residue decomposition (Dolan *et al.*, 2006). Tillage effects also interact with weather conditions, e.g. amount and timing of rainfall which can affect total precipitation and preferential flow (transportation of water solution through different soil layers by different pathways); these two factors directly decide the concentration of nitrate leaching (Strudley *et al.*, 2008). Tillage may have a more substantial effect on preferential flow. Zero or No-tillage has been demonstrated to decrease nutrient loss via surface water runoff because minimized ploughing ensures continuous macropores and other preferential paths reaching from the soil surface to the subsoil. It is thought that rapid solute fluxes through these preferential paths bypass or short-circuit the biologically active root zone reducing time for degradation of the potentially harmful chemicals before they reach the groundwater (Andreini and Steenhuis, 1990). In contrast, conventional tillage can destroy the soil structure and reduce flow of water through these channels.

2.2.2 Influence of geological factors

Effect of soil type

Soil depth, parent material, texture, and structure are well-known soil physical properties that affect nitrate leaching. Shallow soils are particularly susceptible to nitrate leaching because of the much shorter distance that soil water needs to cover before reaching the saturated zone

(Atkins, 1976). This can lead to exceptionally high leaching during wet winters due to the large volumes of excess winter drainage from coarse-textured soils compared to fine-textured soil because they retain less water before drainage occurs. Coarse soils also have better aeration, which is conducive to nitrification, thereby enhancing the production of nitrates from added fertilisers and mineralised N (Defra, 2007). In comparing heavy and light-textured soils, light-textured sandy soils have more uniform porosity and retain less water. Only a small amount of rainfall is needed for leaching from these soils. On the other hand, clayey soils retain more water and nutrients and favour chemical reactions; more rainfall is needed before leaching nitrate from these soils (Follett and Walker, 2012).

Hansen and Djurhuus (1997) described that the low field capacity of coarse sandy soil could cause rapid and continuous nitrate leaching compared to sandy loam soils with high field capacity. They found annual leaching from coarse sand soils was 68 kg N ha^{-1} $year^{-1}$, which was slightly lower than typical leaching values from such soils in Denmark. On the other hand, average losses of nitrate from sandy loam fields for four years were 63 kg N ha^{-1} $year^{-1}$; much higher than the standard value, which is 40 kg N ha^{-1} $year^{-1}$. They explained that this difference in leaching might be due to mild winters and a comparatively dry crop growth period. Nitrate leaching was considerably different in a study with contrasting soil and climate conditions. Annual average nitrate losses were 56-88 kg N ha^{-1} from sandy soils compared with 4-43 kg N ha^{-1} from loamy soils in an experiment of 8 years. This difference in leaching from sandy soil is explained by the high rate of drainage, which enhances nitrate leaching. In contrast, the loamy soil drainage rate is low and limits the risk of leaching under the same arable cropping system. High drainage meant that most of the available N in the root zone is leached for most of the year and results in lower nitrate concentration left in the soil for a crop (Pandey *et al.*, 2018).

Effect of soil spatial variability

Nitrate leaching can occur in agricultural systems when the soil texture is not taken into account in fertilisation (Cote *et al.*, 2003; Huang *et al.*, 2018; Chen *et al.*, 2020), which affect nitrogen use efficiency (Luce *et al.*, 2011). Soil texture is the property that controls most of the process in soil and has high spatial variability over regions and landscapes (Feng *et al.*, 2020). Numerous experiments were performed to examine the impact of soil spatial heterogeneity on crop production, deep percolation, and nitrate leaching, assuming a homogeneous vertical soil distribution (Salazar *et al.*, 2014; Cordero *et al.*, 2019; Chen *et al.*, 2020). Laboratory soil column experiments have shown that soil texture spatial variability affects crop growth and yield, deep percolation, and nitrate leaching (Feyen *et al.*, 1998; Ritter *et al.*, 2005). Quantifying the dynamics of water and nitrogen due to the spatial variability of soil texture is key to increasing the N use efficiency and reducing losses.

In studies, when fields were divided into yield zones based on measured yield, spatial differences in yield were detected based on spatial variability in soil, even though crop varieties, management practices and fertilisation levels were the same during the growing period (Machado *et al.*, 2002; Brocca *et al.*, 2007; Chen *et al.*, 2020). Soil properties (such as soil texture and nutrients) had moderate spatial variability and affected the dynamics of water and nitrogen during the growing season (Basso *et al.*, 2009; Zhang *et al.*, 2015b), and ultimately gave rise to spatial variability in yield, water use efficiency and fertiliser N use efficiency. Spatial soil texture variation results in different soil water contents. Silt loam and silt clay have higher water and nutrients available, which can lead to higher yields (Fraisse *et al.*, 2001; Chen *et al.*, 2020). Silt loam also has medium saturated hydraulic conductivity to ensure adequate water supply to crops during the growing season (Horne *et al.*, 1992; Vincent *et al.*, 2007). Clay, silt or silt clay impeded the ability of the crop to absorb water and nitrogen from the soil (Fraisse *et al.*, 2001; Feng *et al.*, 2016), though sandy loam or sand with low water holding capacity and high water conductivity allow water to infiltrate swiftly (Chikowo *et al.*, 2004; Chen *et al.*, 2020).

Muschietti-Piana *et al.* (2018) reported that site-specific management of N is an effective way to reduce nitrate leaching, but we should consider the soil properties. Variability in the soil is the main driver of crop production variation, considering no undesirable management effects. Complete spatial soil information is essential for useful site-specific management. With improved precision in soil data, farmers can make more reliable decisions for to target crops, inputs and technologies more efficiently (Li *et al.*, 2019). Results in the literature reported soil variability on different scales, including between fields and within the field (Jin and Jiang, 2002) but available soil maps generally lack the details of the within-field variability of different soil attributes, such as texture, depth to the bedrock, organic matter and pH, and are inadequately precise for site-specific management (Li *et al.*, 2019). The previous studies focused on field-scale soil fertility management and site-specific crop yield management (Fraisse *et al.*, 2001; Tesfahunegn *et al.*, 2011; Iticha and Takele, 2019; Li *et al.*, 2019; Chen *et al.*, 2020). Other processes in soil that are affected by spatial variability in soil texture within a field still need to be understood.

2.3 Simulation of Nitrate Leaching Losses with Modelling

Many literature studies have shown different approaches to tackle nitrate pollution (Thorup-Kristensen *et al.*, 2003; Cuttle *et al.*, 2007; Sharma and Bali, 2017; Shi *et al.*, 2018) (Discussed in **section. 2.4**). In several cases, the focus in literature was on managing the on-ground nitrogen charge from the numerous manageable sources to minimise the incidence of nitrates in groundwater by minimising the leaching of nitrates from the unsaturated zone (Dzurella *et al.*, 2012; Cameira *et al.*, 2019; Huljek *et al.*, 2019). However, a subset of these studies had used models to simulate the fate and transport of nitrate to assess the adequacy and effectiveness of the control measures on groundwater nitrate levels (Almasri *et al.*, 2020). We can test a scientific hypothesis using models and suggest alternative scenarios to minimise nitrate leaching with one or more improved agricultural management practices (Cichota *et al.*, 2013). Many models exist to simulate nitrogen dynamics (see **Table 2. 4**), ranging from simple to complex. Model evaluation is an integral part of the modelling process, comparing measured field data and modelled data (Ramos and Carbonell, 1991). The advantages of using models to simulate nitrate losses from agricultural systems have become the focus of much scientific research (Cherry *et al.*, 2008).

Table 2. 4 Different models and their specification to simulate nitrate leaching

Model	**Description**	***Reference**
NDICEA	NDICEA (Nitrogen Dynamics in Crop Rotations in Ecological Agriculture) explains the dynamics of soil water, mineralization of nitrogen, and dynamics of inorganic nitrogen in relation to weather and crop demand.	Van der Burgt *et al.* (2006)
DNDC	DNDC was originally developed for prediction of trace gas emissions, such as CH_4 and N_2O fluxes from upland agroecosystems	Li *et al.* (1992)
STICS	STICS is crop-soil model has been used to investigate long term effects of crops on nitrate leaching	Brisson *et al.* (1998)
SUNDIAL	SUNDIAL (Simulation of Nitrogen Dynamics In Arable Land) is particularly useful in arable agriculture system to examine the impact of different management strategies on the N cycle	Smith *et al.* (1996)
DAISY	A soil-plant and atmosphere system model. Developed to simulate crop production, soil water dynamics, and nitrogen dynamics under various agricultural management practices	Hansen *et al.* (1990)

*References selected based on the model used first time in the literature.

All the models consider the principal soil N dynamic processes, namely, N application, mineralisation/immobilisation, nitrification, nitrate leaching, denitrification and plant uptake. Details on the treatment of these processes differ from one model to another. Many dynamic processes of soil nitrogen depend on soil water content. Water movement regulates nitrate transportation across the soil profile and to field drains or groundwater. Therefore, every soil nitrogen dynamics model is very highly dependent on an accurate description of the soil water balance and movement of soil water. SUNDIAL simulates water flow as a so-called piston mechanism, with water filling each layer up to its available water holding capacity before drainage, evaporation from the uppermost layer, and bypass flow if rainfall in a specific week reaches a particular value (Wu and McGechan, 1998). At the same time, DNDC uses all factors for the simulation that impact water flow, such as daily rainfall, irrigation, gravitational redistribution, matrix redistribution, plant uptake and surface runoff, infiltration, transpiration, and evaporation. A cascading bucket model describes the percolation of water within the soil profile dependent upon specific soil properties, i.e. field capacity, wilting point, hydraulic conductivity of the saturated layer, and the actual water content of two adjacent soil layers (Li *et al.*, 2006). Fast drainage is a characteristic of DNDC which simulates excess water drainage immediately after field capacity (Brilli *et al.*, 2017). Van der Burgt *et al.* (2006) elaborated the soil water dynamics in the NDICEA model. Where inflows to the topsoil consist of precipitation and irrigation similar to other models, the water contents of each layer may increase with capillary rise, the rate of which depends on the suction properties (pF) of the soil and the depth of the groundwater table. Water in the topsoil above field capacity percolates instantaneously to the subsoil and from the subsoil to deeper layers. Water drained from the subsoil is considered lost from the system. The capillary rise in NDICEA is driven by a matric suction gradient from a soil layer to the groundwater table for each layer. Water transfer into the soil through different layers is calculated based on the cascade model in STICS (Brisson *et al.*, 1998). The crop water uptake calculation in DNDC and STICS depends on the potential demand for transpiration determined by the leaf area index and climate conditions and the uptake capacity determined by soil moisture, root length and distribution in the soil (Li *et al.*, 2014). In NDICEA, calculation of water balance depends on the rooting depth of plant and moisture content in each layer similar to DNDC. However, the water uptake is also determined by the developmental stage of the crop, potential evapotranspiration, and soil pF (Van der Burgt *et al.*, 2006). All the models integrate dynamic simulations driven by weather. DAISY works on a weekly time step, using weather data to drive their submodels of soil water and temperature. NDICEA, STICS, SUNDIAL and DNDC are operating on daily time steps. In operating with weekly rather than a daily time steps, there is some loss of realism and accuracy of model representation, especially concerning rainfall-influenced processes such as high soil wetness, denitrification, drain flows and nitrate leaching, because rainfall occurs in separate events rather than having an average intensity over a weekly cycle.

One of the most critical components of the overall balance represented by the models is removing nitrogen from the soil system by leaching, and the analysis of its environmental implications is the main reason for the models' existence. Solute transport and leaching representation depend on the related model or subroutine of soil water. Regarding the nitrate transfer model, STICS uses a reservoir type model (Brisson *et al.*, 1998), and DNDC simulates using a cascade model. This kind of model does not consider the capillary rise of nitrate with water which is crucial in highly conducting soils with a shallow water-table. The uptake of crop N is modelled as a logistic curve driven by the degree-day in SUNDIAL (measure of heating and cooling) (Gibbons *et al.*, 2005). Different sub-models are used for the simulation of N transformations in DNDC. This includes a relatively complete suite of N transformation reactions in soils, including decomposition, nitrification, denitrification, urea hydrolysis, ammonium-ammonia equilibrium, volatilisation of ammonia, among others (Li *et al.*, 1992; Li, 2000). N is added mainly through inorganic fertiliser and manure as an input to the model. The atmospheric deposition contribution of N is calculated from the daily rainfall data.

By using a crop-dependent coefficient, adding N through biological fixation is empirically calculated in DNDC, but DAISY simulates N dynamics in a way that ignores biological N fixation (Groenendijk *et al.*, 2014). Once NH_4^+ ions are introduced through fertilisation, atmospheric deposition, irrigation or biological fixation into a soil, either assimilation or adsorption will readily fix the ions. Suppose the microbes die and the organic matter decomposes. In that case, the fixed NH_4^+ in the living microbial pool can be released back into the soil liquid phase, and the NH_4^+ fixed on the adsorbents can be released by chemical balance. Nitrifiers can quickly convert the NH_4^+ into NO_3^- release into the soil liquid phase. Although the soil microbes can reuse NO_3^-, the anion has no affinity with the adsorbents of the soil. This creates a better opportunity for NO_3^- to transition to the flow of leaching water. These processes have been linked in DNDC to soil environmental factors and agricultural management practices. Plant uptake and microbe assimilation are subject to both NH_4^+ and NO_3^-. NO_3^- movement in soil solution is simulated as mass flow with water flux and concentration gradient-driven diffusion (Li *et al.*, 2014). Both DAISY and SUNDIAL can simulate nitrate leaching only to deep groundwater because they have no field drain water simulation sub-model (Wu and McGechan, 1998). The flow of nitrogen out of a layer in NDICEA is proportional to water flow and inorganic nitrogen concentration in the layer. For each layer, a nitrogen-leaching factor is introduced to account for preferential water flow and adsorption. The factor values are found by calibration (a built-in function in NDICEA). In the event of capillary rise, the import of nitrogen into topsoil or subsoil is proportional to the concentration of nitrogen in the subsoil and the groundwater, respectively (Van der Burgt *et al.*, 2006).

NDICEA model allows the estimation of the effect of crop rotation and manure application on the amount of mineral nitrogen in different phases of the crop rotation (Koopmans and Bokhorst, 2002; Swain *et al.*, 2016). Crop yields are used in the model for target-oriented modelling (distinctive from other models) in which observed or expected crop production is set as a target from which dynamic water and nitrogen requirements are derived. This approach is also found in SUNDIAL. However, crop dynamics are simulated from an initial condition in many published models, which renders results much more sensitive to accumulating errors (Van der Burgt *et al.*, 2006; Swain *et al.*, 2016).

Calibration is an inherent property of modelling philosophy and is used to design plot specific parameters. The calibration function in NDICEA improved model performance in the study by Swain *et al.* (2016) for both the training and validation dataset. In another study, NDICEA model performance was also evaluated with three years of data used for validation. Absolute prediction error was estimated as less than 20 kg N ha $^{-1}$, whereas RMSE values varied between 14 kg N ha $^{-1}$ and 37 kg N ha $^{-1}$ (Van der Burgt *et al.*, 2006). Koopmans and Bokhorst (2002) tested NDICEA performance on eight organic farms using statistical measures and visual performance. The results indicated that the model with modelling efficiency 0.4 fitted observed values of mineral nitrogen for the 30cm topsoil layer. This demonstrates that NDICEA can be used to evaluate nitrate leaching losses due to crop rotation and manure regime using readily available climate data and on-farm data.

2.4 Strategies to Mitigate Losses of Nitrogen via Leaching

Nitrate leaching has many sources and is influenced by many factors, including soils, environmental and management factors, as can be seen from the above discussions. A single magical cure cannot achieve NO_3-N leaching reduction. This requires an integrated approach involving the implementation and adoption of 'best management practises' to maximise plant usage efficiency of N for optimal production while reducing NO_3-N leaching (see **Table 2. 5**). In general, the aim should be to prevent the build-up of high concentrations of mineral N in the soil well above plant demand, particularly towards or during the drainage season (Di and Cameron, 2002).

Table 2. 5 Summary of key strategies to reduce N leaching from soil to water from agriculture system identified in different studies

Category of strategy	Methods
Improving N use efficiency during crop growth	• Fertiliser recommendation system • Precision agriculture approaches to mitigate nitrogen losses • Nitrification inhibitors, urease inhibitors and slow release fertilisers
Reducing N losses during the drainage season	• Use of cover crops • Land cultivation in spring rather than in autumn • Avoid spreading fertiliser and manure to fields at high-risk times
Optimal manure and livestock management	• Improve storage capacity • Reduce overall stocking rates on livestock farms

2.4.1 Improving N use efficiency during crop growth

Fertiliser recommendation system

Evidence is reviewed to show that methods based on Nmin lookup and measurements can provide accurate forecasts of crop N demand under 'normal' soil and weather conditions but are constrained by their inability to compensate for variations in expected yield or mineralisation released N. The greater versatility of the N balance sheet method and (especially) decision support systems based on simulation models can improve reliability of predictions by allowing local soil and weather conditions to be modified (Burns, 2004). The amount of available nitrogen in the fields can vary widely for a crop before any fertiliser application. This variation must be considered to avoid excessive applications of nitrogen. The Soil Nitrogen Supply (SNS) Index for different fields can be estimated by field assessment method. This method uses measurements of available soil mineral nitrogen and nitrogen from the mineralisation of organic matter before applying N as fertilisers or manure. A fertiliser recommendation system (Nutrient Management Guide RB209) is a set of guidelines often prepared by the UK government or advisory organisation to help farmers apply fertilisers in the quantities and at the times that the crop needs them.

Precision agriculture approaches to mitigate nitrogen losses

Precision technologies are used to gather information on spatial and temporal variations in a field to match inputs to site-specific conditions in the field (Diacono *et al.*, 2013). Recently, the use of precision farming techniques, particularly systems that allow for variable rates of N application, have been adopted by many UK farmers. In these systems, decisions about rates of N application are based on an assessment of the crop's N status using a remote sensing technique, usually a recent satellite image of the field, or a real-time sensor (e.g. N-sensor). In this regards, aircraft or satellite sensors may collect the reflected electromagnetic radiation from the canopy in small scales of space and time. The remote sensors can measure variations in growth environments from site to site and have the potential to provide a synoptic view of the entire area (Song *et al.,* 2009). Plant sensors use the light reflectance mechanism from the plant canopy. Active Optical Sensors can work independently of ambient light (Jasper *et al.*, 2009; Holland and Schepers, 2013), whereas Passive Optical Sensors use a separate light source, usually sunlight (Lamb *et al.*, 2002; Holland *et al.*, 2012). Active optical sensor technology is incorporated into commercial sensors that calculate variable rates of nitrogen fertiliser across a field such as Crop- Circle™ (Holland Scientific), Greenseeker™ (Trimble) and the Yara N-Sensor ALS (Active Light Source) (Higgins *et al.*, 2019).

Inadequate soil fertility can be extremely harmful to the productivity of crops. Although soil analysis remains the most reliable method of assessing soil nutritional status, for most farmers, the time needed and expense involved in collecting soil samples from fields in the numbers required to map spatial and temporal variability accurately is cost-prohibitive (McCormick, 2005). Soil sensors can be labour-saving and a valuable management tool provided they are reliable, and the data correctly interpreted, providing more timely results (Sudduth *et al.*, 2017). Hand-held sensors have the advantage of being portable and delivering instant readings, such as soil moisture probes. In-situ sensor networks have also been suggested to allow for a step away from predetermined N recommendations (Defra, 2010) to a more dynamic system that responds to changes in growing conditions in real-time (Shaw *et al.*, 2014). At significantly higher temporal resolution, in-situ sensors can also provide data and thus negate the need for repetitive, expensive sampling throughout the year. Multiple soil properties, including clay content, water content (Pedrera-Parrilla *et al.*, 2016) and salinity, and mobile apparent soil electrical conductivity (ECa) measurements have been commonly used to map soil variability by bulk ECa sensors (Sudduth *et al.*, 2017).

Variable Rate Fertiliser Applicators that can adjust the rates of nutrient application in real-time are now available. The crop is scanned by real-time sensors (enabled using Global Navigation Satellite System technology), and signals are sent directly to the fertiliser applicator, indicating the nutrient requirements at the scanning time. The advantages of variable application rates are most likely to be seen in fields with spatial variability in yield and soil properties (Higgins *et al.*, 2019). In-field variability is a significant source of uncertainty in the decision-making process for crop production. Variability must be interpreted and controlled on a spatial and temporal scale. Innovative experimental methods, proximal and remote sensing and crop simulation models can play an increasing role in evaluating field variability at a relatively low cost to achieve variable N fertilisation (Diacono *et al.*, 2013).

N is applied to the field at varying rates depending on crop need. The concept of soil mapping units can be applied to classify highly variable soils into comparatively distinct management zones. The classification of management zone can be based on the variability of soil fertility parameters (Iticha and Takele, 2019), mineralised N in soil and a constant harvest index (Schellberg and Lock, 2009), and soil electrical conductivity (McCormick *et al.*, 2003). McCormick (2005) found that it is possible to measure ECa cheaply and efficiently, linked to a large number of soil properties. For spatial soil variability surveys and delineating potential site-specific management zones, the application of ECa scanning has tremendous potential. In turn, this would allow a better distribution of resources and long-term management planning. Theoretically, these approaches should result in more efficient use of added N and better crop yields. However, no single method was found efficient to control the nitrogen loss. It was concluded that a combination of two or more methods is the best possible solution to manage nitrogen efficiency (Sharma and Bali, 2017) .

Nitrification inhibitors, urease inhibitors and slow-release fertilisers

Controlled or slow-release fertilisers could mitigate the environmental impact of fertilisers by improving nitrogen use efficiency (Xu *et al.*, 2008). Slow releasing fertilisers are products obtained by reacting most commonly used and cost-effective nitrogenous fertilisers with several aldehydes. These fertilisers release N slowly in soil and facilitate its better uptake and use by crops. These fertilisers are generally prepared by physical encapsulation of fertilisers with an organic or inorganic hydrophobic material that acts as a barrier to control fertiliser activity. The most attractive is insoluble inorganic sulphur because it can control the release of nutrient from fertiliser and neutralise soil alkalinity (Tsai, 1986). However, cracks in the sulphur film on the fertiliser surface are the problem using sulphur as a coating material. So polymers are another

option for coating, although they also have some pollution issues with petroleum-based polymers. Other biopolymers like starch, cellulose, and lignin are being used to improve the efficiency of slow-releasing fertilisers (Shaviv, 2001).
The use of slow-release fertilisers can be beneficial in improving crop nitrogen use efficiency by reducing leaching and volatilisation losses of N and making it available during crop growing season (Nardi *et al.*, 2018). Containerised coastal Douglas-fir seedlings were grown by using soluble fertilisers and slow-releasing fertiliser in different treatments. At the time of out planting, the treatment with slow-releasing fertiliser showed large seedlings with higher foliar nutrient concentration. After four growing seasons, these seedlings had an increase in height, basal stem diameter, and stem volume, up to 19, 21, and 73%, respectively, compared to treatment with conventional fertiliser application (Haase *et al.*, 2006). The higher amount of nitrogenous fertilisers and irrigation applied to the potato on coarse-textured soils result in higher nitrate leaching and low recovery of applied nitrogen from the crop. A 3-year experiment was conducted to compare the effect of single polyolefin coated urea with two rates (140 and 280 kg N ha^{-1}) and split application of non-coated urea. Nitrate leaching at the recommended rate (280 kg N ha^{-1}) was 34 to 49% lower with coated urea than three split applications of non-coated urea. In the third year, leaching from five split applications of non-coated urea was 38% higher than coated. Results suggested that coated urea can reduce leaching and also improve nitrogen recovery during seasons (Zvomuya *et al.*, 2003).

In the UK, the most common slow-release fertilisers on the market are the group of Nitroflo, Nutrisphere, Nitroslow and Polymer/Resin Coated Urea Nutrisphere-N inhibits leaching because leaching occurs after ammoniacal nitrogen is converted to nitrates in the soil. Nutrisphere works to control urea hydrolysis by neutralising urease, as urease is a di-nickel compound and nickel atom has a +5 charge, but Nutrisphere-N has a negative charge of 1800 meq/100g. Nutrisphere-N reacts with the nickel and pulls it out of the urease molecule, which makes urease ineffective. Nutrisphere-N accomplishes this without killing soil microorganisms.

The use of nitrification inhibitors can improve the overall efficiency of fertiliser N use. They can reduce the conversion of ammonium to nitrate during nitrification, and as a result, reduce the risk of the NO_3^- leaching or being denitrified before the crop takes it up (Timmons, 1984). Nitrification inhibitors control the activity of Nitrosomonas bacteria which are responsible for the conversion of NH_4^+ to NO_2^- during nitrification. Their primary purpose is to keep more nitrogen in NH_4^+ form to prevent nitrate losses from leaching. As a result, they can improve fertiliser N use efficiency and decrease groundwater pollution via nitrate leaching (Follett and Walker, 2012). However, the efficacy of nitrification inhibitors in preventing nitrate leaching depends upon the inhibitor used and the cropping system, along with the soil and environmental conditions (Pain *et al.*, 1994).

Nitrapyrin (2-chloro-6-(trichloromethyl)-pyridine) is a chemical nitrification inhibitor that has a selective effect on Nitrosomonas bacteria. It is very persistent in cool soils and provides excellent activity in the fall or winter. When applied in warm soils, measurable activity against Nitrosomonas usually is 6 to 8 weeks compared to 30 weeks or longer when applied to cool soils in the late fall or winter (Trenkel, 1997). DCD (dicyandiamide) is another chemical inhibitor. Depending on the applied N and moisture and temperature of the soil, the ammonium-N in nitrogen fertilizers is stabilized for 6 to 8 weeks through the inhibiting effect of this chemical. When compared to the conventional nitrogen fertilizers applied to the soil, there are more significant amounts of ammonium and less nitrate found when the nitrogen fertilizer used was treated with DCD. DCD applies, particularly to light-textured soils. CMP (1-carbamoyle-3-methylpyrazole) has a bacteriostatic effect on Nitrosomonas bacteria. It can reduce their nitrifying activities for a certain period, thus retarding the conversion of ammonia into nitrite (Trenkel, 1997).

2.4.2 Reducing N losses during the drainage season

Use of cover crops

Catch crops are cover crops that capture excess N from the soil and prevent N leaching losses (Thorup-Kristensen *et al.*, 2003). They are seeded just after the harvesting of the main crop (Herrera *et al.*, 2010). They may be particularly effective after animal manuring when more N is available to capture from the soil (Olesen *et al.*, 2000). In a four year experiment, when ryegrass was used as a catch crop in sandy soil, N leaching was reduced by 39 kg N ha^{-1} $year^{-1}$ and 25 kg N ha^{-1} $year^{-1}$ ploughed in spring and autumn, respectively. For sandy loam soils, the reduction in leaching was found to be 12 kg N ha^{-1} $year^{-1}$ when ploughed in autumn and 16 kg N ha^{-1} $year^{-1}$ when ploughed in spring (Hansen and Djurhuus, 1997).

Table 2. 6 Characteristics of some catch crops that may be suitable for establishment in northern temperate cropping systems

Crop species	Latest possible sowing date[1]	Cold tolerance	Residue characteristics	Key references
Rye (*Secale cereale*)	Early /Later in autumn	Best crop for cool and temperate region	Scavenges 60 % residual N that can be otherwise leached	Shipley *et al.* (1992); Clark (2008)
Annual ryegrass (*Lolium multiflorum*)	From mid-summer to early autumn	In frost conditions show biennial tendency and regrow quickly in late spring	to minimize N tie up, wait few weeks after incorporation	Williams *et al.* (1990); Clark (2008)
Oil radish or Fodder radish (*Raphanus sativus L.)*	Mid-summer	May be killed by heavy frost below -3.9°C	Rapidly capture N and store it in biomass	Clark (2008)
Mustard	Spring/Summer	Winter killing at about -3.9°C	N contents in residue reach 328lb.N/A	Clark (2008)

[1]In an equivalent climatic zone to north eastern England (Mean annual max temp recorded from 1991-2020 is 12.9°C, min temp 5.5°C and max annual rain fall is 793mm (Met office, Climate period: 1991-2020).

The selection of the catch crop species can affect the efficacy of the catch crop in reducing N leaching (Thorup-Kristensen *et al.*, 2003). This selection of species not only depends upon how much a crop can uptake excess N but factors like tolerance to cold weather along with establishment speed, rooting depth and growth rate (Munkholm and Hansen, 2012). As well as considering establishment and N uptake potential, characteristics that will impact the decomposition of the catch crop residue and release nutrients for the following cash crop should be considered. Such factors like C:N ratio, N and lignin contents are also important. Ideally, barley is efficient in capturing N due to its fast growth rate, but it has a high C:N ratio to release N slowly. Brassicas (*Raphanus sativus*) can readily release N as they have a low C:N ratio and can uptake N with the same efficiency as barley (Thorup-Kristensen *et al.*, 2003). It is essential to develop synchrony between N mineralisation from green manure residues and its demand by subsequent cash crops (Crews and Peoples, 2005).

The European Nitrate Directive (91/676/EC) encourages governments to promote catch crops to minimise nitrogen leaching, particularly in fallow periods (Constantin *et al.*, 2012), because the use of cover crops in crop rotation in the fallow period can reduce nitrate leaching to aquifers (Julie *et al.*, 2015). Long term effect of catch crops is much more different than observed in one or two year's experiments. This is due to the higher amount of soil organic matter after 13-24 years which can increase crop N uptake with a change in mineralisation (Constantin *et al.*, 2012). The nitrogen mineralisation process increases over the years if catch crops are in crop rotation with mulching or ploughing (Lewan, 1994). If this mineralisation potential combines with enough precipitation and warm temperatures, there will be more chances of N losses, mostly when soil is left bare (Macdonald *et al.*, 2005). Also, winter catch crops can reduce N leaching during the seepage period (Neumann, 2005). Especially cover crops that are sown earlier can control N losses (Macdonald *et al.*, 2005). These crops can cover the soil in winter and preserve nitrogen in their biomass. Still, soil frost can improve the decomposition of crop residues and increase the concentration of inorganic N in topsoil; however, winter catch crops may reduce N leaching (Aronsson, 2000).

The amount cover crops can reduce N leaching is dependent upon its species and sowing dates along with drainage intensity which is directly related to rainfall and soil properties (Justes *et al.*, 2012).

Precipitation has a vital role in N leaching. Catch crops take up excess N and directly uptake excess moisture in the areas where average annual precipitation is more than the crop demand (North-eastern USA and Northern Europe), thus reducing the downward movement of water and N with water (Thorup-Kristensen *et al.*, 2003). In a study with contrasting growing seasons, catch crops captured N and produced high biomass when precipitation was high. In the dry season, it produced low biomass but efficiency to uptake N and reduce its load to soil was ideal (Cicek *et al.*, 2015). Winter cover crops can change the rate of evapotranspiration, so they directly affect the water budget. Usually, when crops produce dry matter, they lose water to the atmosphere, reducing the quantity of available soil water for leaching. A winter cover crop will use about 60 mm of water to produce 2200 kg of dry matter per hectare. In a climate that has excess winter precipitation, this significantly reduces the nitrate movement (Meisinger *et al.*, 1991).

Land cultivation in spring rather than in autumn

In many parts of the UK, the cropping system is not suitable for cover cropping because the emphasis is on winter-sown crops like winter wheat, winter barley and winter oilseed rape. These crops can play a similar role to a cover crop by taking up any residual N from the previous crop and reducing rates of leaching. However, for spring-sown crops it is best to avoid autumn cultivation leaving the soil bare and instead to use a cover crop during the fallow period. This can reduce nitrate accumulation in the soil due to mineralisation during the autumn and improve the timing of N availability for spring-sown crops. Delayed cultivation can reduce nitrate-N leaching about 2.26 kg N ha^{-1} in arable land without manure (Cuttle *et al.*, 2007). Autumn ploughing of ley phases in the rotation can result in a particularly high risk of N leaching, as the ploughing of the leguminous residues can stimulate rapid mineralisation and the accumulation of nitrate with a high risk of leaching (Silgram *et al.*, 2005); it is better to plough ley arable land in the spring when the crop is ready to establish. A significant effect of tillage was reported by Hansen and Djurhuus (1997) on a sandy loam in a temperate climate region, with leaching from autumn ploughed plots without stubble cultivation being 16 kg N ha^{-1} $year^{-1}$ higher than leaching from spring ploughed plots. The timing of tillage affected nitrogen leaching in another study with almost similar climatic conditions conducted by Stenberg *et al.* (1999). During the autumn, soil mineral nitrogen increased as a result of early tillage. In November, the nitrogen content at 0-90 cm in early ploughed soil averaged 68 kg N ha^{-1}, while it was 39 kg N ha^{-1} when ploughing was postponed until spring. In addition, nitrate leaching was higher in early tillage (autumn) treatments than in late tillage (spring) treatments.

Avoid fertiliser and manure spreading to fields at high-risk times

Fertiliser application time is critical to control the leaching of available NO_3-N from the root zone. A fertiliser is not at risk of leaching if applied during the growing season when drainage is low and crop N demand is high. This condition varies with crops because some crops like potatoes need more nitrogenous fertilisers at the stage when roots are small and the soil has enough water for drainage (Jenkinson, 2001). Concerning the initial application of N fertiliser to winter wheat, Efretuei *et al.* (2016) found no disadvantage in delaying the first N application until the first node detection stage in terms of yield compared to the application of N fertiliser at tillering. It was also observed that delaying the application of N until the early stage of stem elongation had no adverse effect on yield (Bodson *et al.*, 2001).

Manure land application strategy has a significant effect on the quantity of nitrate loss. In particular, the application of manure is restricted in terms of public water well locations and the depth of the water table. According to Sahoo *et al.* (2016), livestock waste should not be used for land application within 15 m of drinking water wells. Application of manure is avoided in many countries at certain times of the year, often immediately before, during, and after heavy rainfall and flooding conditions to control nitrate leaching. Before applying manure, proper considerations must also be given to soil types, for example, coarse-textured soils, broken bedrock and inadequate capacity for holding water (Aga, 2007). Such sites have high leaching potential so that they can cause significant contamination of groundwater (Fraters *et al.*, 1998).

2.4.3 Optimal manure and livestock management

Livestock yards (including barnyards, holding areas, and feedlots) are the significant sources of nitrate contamination. Improper treatment of these storage areas results in loss of waste, which then leaches into the subsurface and induces groundwater nitrate contamination (Sahoo *et al.*, 2016). Manure management from the time of excretion to land application affects the forms and quantities of nitrogen losses. Typical manure management practices include manure management in housing systems, during storage, and land application (Oenema *et al.*, 2014).

Improve storage facilities

Geological composition, soil quality, water table level, and depth to bedrock should be considered in the location of the manure storage facilities. Livestock waste can easily pollute groundwater if a storage facility is situated in areas with shallow soil, coarse-textured permeable soils, over sand and gravel aquifers, where the water table is at or below the surface, or where fractured bedrock is within a few feet of the surface. Therefore, the hydrogeological characteristics of a site must be assessed to ensure that the site is suitable for storage (Sahoo *et al.*, 2016). The safety of groundwater from the leaching of nitrates from manure is of particular concern. Sealed bottom and sides with concrete construction are recommended to avoid leaching (Van der Meer *et al.*, 2008). A basic roof requires an initial investment but is considered an inexpensive method for improving the conditions for storing manure (Tittonell *et al.*, 2010). Usually, the roofed storage includes a concrete base, partial sidewalls and a roof framework. This helps keep the manure dry, decreases or eliminates runoff (especially during rainfall) and thus reduces the risk of leaching nitrate (Ogejo and Collins Jr, 2009; Tittonell *et al.*, 2010).

Nitrate originating from livestock manures, including storage facilities, spreading activities, and deposition during grazing, can be a significant and challenging source to manage. Manure storage facilities on the farm should be adequate to store manure and dirty water. Application of these materials will then be more flexible when there is need for crop uptake and less risk of losses in surface runoff and drainage flow (Cuttle *et al.*, 2007). To avoid direct seepage of liquid from storage material, manure should not be stored on the soil surface. Manure heaps should be sited with facilities for liquid effluent collection on an impermeable concrete base. It is also recommended to avoid application of manure on high-risk areas like near a borehole, on shallow soils, on soils with cracks, or in areas with a network of open drains to wet flushes draining to waterway.

Reduce stocking rates on livestock farms

Late in the autumn, urine returns from grazing animals can cause large amounts of NO_3^- leaching (Silva *et al.*, 1999). This effect can be minimised by removing the stock from the farm earlier in the autumn-winter period and feeding the animals in-house (Di and Cameron, 2002). As a general strategy, reducing the overall stocking rate on livestock farms can reduce chances of nitrate leaching. This is because a major source of nitrate in grazed pastures is urine patches per unit area. Reduced stocking rate can produce fewer excreta and fewer urine patches so there will be less N available in the soil for leaching. The implementation of this method to reduce nitrate leaching from livestock farms is easy but would have serious impacts on profitability (Cuttle *et al.*, 2007). In the same way, if the length of the grazing day or grazing season were reduced particularly in autumn, it can also reduce the urine patch deposits because urine patches of grazing animals act as the hotspot of leaching with high a concentration of nitrogen.

Abandoned yards may pose a significant risk of groundwater nitrate contamination. The manure pack breaks up quickly in these yards due to lack of use, and rainwater can leach through the cracks. The issue can be managed by collecting all the manure and soil mixture from the abandoned feedlot and then distributing it to fields as fertilizer. Later, the field can be planted with crops requiring lots of nitrogen to allow the use of the nitrogen released from the decomposition of the manure (Sahoo *et al.*, 2016). A method of the breakdown of solid manures by using aerobic bacterial metabolism to reduce readily available nitrogen contents with high temperature is recommended. Biological and chemical reactions can increase the temperature up to 70^{o}C, which inactivates pathogens and weed seeds. Mineral N contents in manure reduced from 25% to 10% of total nitrogen, so its losses following application on land are less. Some of the nitrogen in this process is lost to the atmosphere as ammonia and nitrous oxide and some is bound to organic forms (Cuttle *et al.*, 2007).

2.5 Concluding Remarks

Nitrate leaching from agricultural lands to groundwater sources is a global issue with environmental and human health implications. Before resolving the problem, it is essential to understand the factors and their contribution to nitrate leaching. Several studies have been conducted to determine the actual source of this pollution, including fertiliser use and excessive cropping. However, most of the studies focused on one or a maximum of two factors influencing the leaching at a time, while other factors cannot be ignored. This study was designed to monitor the interaction and effects of different factors like agricultural management practices, climate conditions, soil type and depth to the bedrock.

Different management practices have been used to control leaching losses of nitrogen in the literature. These include crop rotation, farming system, fertiliser application etc.; some of them are discussed in ***section 2.4***. Before considering any strategy to mitigate nitrate leaching, a complete understanding is needed for all management practices associated with nitrate leaching (Chapter.4). This might be possible with the modelling approach used in this thesis. We can use different nitrogen dynamic models to understand this relationship e.g. NDICEA (Chapter 6). Moreover, models are also helpful t to explore what changes in agricultural management practice can mitigate leaching losses. Many models have been used for this purpose.

Soil properties are important to understand factors controlling diffuse water pollution in a given area. The conventional soil maps available for the Fell Sandstone area are at a scale that is too small and there is not enough resolution or "granularity" in the information they present, to allow for analysis of factors causing leaching and for implementation of field-specific strategies for mitigation. This study was designed to fill the gap by producing high resolution soil maps for soil texture. Despite extensive literature studies on factors affecting nitrate leaching from agricultural catchments to groundwater, and different management practices to reduce these losses, the effect of land management on leaching are area specific and there are some gaps in knowledge on leaching sources in the Fell Sandstone catchment. It is assumed that the source of this diffuse pollution in the area are agricultural practices however the effect of soil spatial variability has not been studied. Therefore in this thesis, the gap in knowledge on the effect of soil spatial variability is filled and strategies are tested that can be used to mitigate leaching.

All the strategies are reported in studies implemented on the whole field area. Few of them focused on dividing the field into small manageable units based on crop yield and soil available nitrogen for crop use to apply fertiliser N accordingly. Many literature studies have elaborated on the existence of spatial variability within a field. Similarly, spatial variability in the soil can influence the nitrate concentration leached from one unit of the area compared to others. Spatial variability in soil texture can influence nitrate leaching greatly. This been investigated and proved in several studies that coarse soils are more susceptible to nitrate leaching compared to fine-textured soils. This is because of their low field capacity and lesser ability to retain soil water with dissolved nutrients like nitrogen. Therefore, the soil with more sand than clay is more susceptible to leaching. A good understanding of soil texture is vital before estimating nitrate leaching from the area. It is essential to investigate soil spatial variability affecting nitrate leaching on a scale manageable for farmers.

Chapter 3. Digital Soil Mapping and Modelling to Predict Soil Attributes

3.1 Introduction

Mapping soil attributes for land use is not a new concept in soil science. The earliest soil maps were made to identify homogenous areas of inherent soil properties suitable for agricultural purposes in the middle of the 18th century (Miller and Schaetzl, 2014), leading to the emergence of scientific methodology for soil survey and mapping in the first half of the 20th century. Systematic soil mapping depended on auger and pit observations at key locations selected by the surveyor as typical of a particular soil type. Many sample points were needed to understand the continuity and gradual description of fundamental soil properties, such as soil organic matter (SOM), pH, and soil texture, at a fair spatial resolution for agricultural development (Scull *et al.*, 2003). The conventional soil mapping method depended on the surveyor's skill in understanding patterns in the landscape and vegetation to build a conceptual or mental model of the soil variation in a given area. This approach resulted in soil mapping units that were inherently discontinuous and assumed that variation within these units was minimal. During the 21st century, a new approach has been formalized as the digital soil mapping approach (McBratney *et al.*, 2003). Compared to conventional methods, the use of remotely sensed data and machine learning approaches in digital soil mapping can produce low cost and time effective maps of spatially variable soil properties (Khanal *et al.*, 2018). The resulting digital soil maps are efficient and reproducible and provide estimated uncertainty related to the prediction of soil attributes (Arrouays *et al.*, 2020).

Soil is a system that acts as an interface for the hydrosphere, lithosphere, biosphere, and atmosphere. The knowledge of soil spatial variability can play a key role in agricultural development (Yuxin *et al.*, 2017). One of the most important soil properties is soil texture that controls all ongoing processes in soil. It can impose influences on soil functions related to climate, ecology, agricultural management, hydrological modelling and soil pollution control (Montanarella and Vargas, 2012; Feng *et al.*, 2020). The information of variability in soil texture is essential for understanding and managing soil functions of carbon storage, drainage, leaching of nutrients and other groundwater studies (Yakun *et al.*, 2020). Despite its importance, the particle size fraction data is generally not available at the resolution needed for agricultural and environmental management (Dobarco *et al.*, 2017). Soil texture is a property of soil that does not change much with time. Therefore, it can be spatially estimated with geostatistical methods. Soil texture of subsoil layers is as important as topsoil. Depth specific soil texture maps are important for land management according to the textural variability (Ding *et al.*, 2020). The spatially varying soils could be better managed with a precision agriculture approach after classifying the whole field into homogeneous management units (Iticha and Takele, 2019).

Soil scientists have progressively used digital soil mapping (DSM) as a successful sub-discipline. It can be defined as developing a geographical reference soil information system with numerical models using laboratory observations and environmental variables data. Most of the DSM work is based on building a suitable model to relate soil observations with climate, geology, relief, and spatial position. According to Minasny and McBratney (2016), DSM has three basic components: soil information from maps or soil samples, the process of developing statistical models to correlate soil properties with environmental covariates and, output as a predicted soil information system. The auxiliary data or environmental covariates can be extracted from remote sensing, digital elevation models and categorical maps (McBratney *et al.*, 2003). A digital elevation model (DEM) can be used to derive terrain variables that are powerful in predicting soil properties, such as slope, aspect, curvature, topographic position index (TPI) and topographic wetness index (TWI) (Dobos *et al.*, 2001). To develop a numerical model, DSM identifies a correlation between soil properties and covariates.

Kriging was one of the first developed geostatistical methods used to investigate the spatial distribution of soil texture. Kriging uses the observed values and their spatial position to predict non-sampled locations' values (Li *et al.*, 2020). With advances in machine learning and GIS, the prediction covariates have been extended to various environmental variables and remote sensing variables (Hengl *et al.*, 2004b). Development in DSM techniques is associated with developments in machine learning algorithms from simple to complex modelling techniques. There is no single correct approach to predicting the spatial distribution of soil properties under all circumstances. Different machine learning algorithms (MLA) used to investigate the correlation between soil properties are reviewed by Khaledian and Miller (2020). The MLAs commonly used are multiple linear regression (MLR), K-nearest neighbours (KNN), random forest (RF) and artificial neural networks (ANN). It is crucial to examine the limitations and strengths of various algorithms while selecting relevant MLAs for DSM studies. Because the number of hyperparameters has a positive relationship with computation time, algorithms with fewer hyperparameters train faster. As a result, MLR and KNN give results quicker than ANN and RF. If the model's interpretability is essential, such as discovering correlations between covariates and soil properties, MLR and, to a lesser extent, RF would be effective algorithms. For example, when selected covariates show connections not previously identified in soil science, an interpretable model may reveal prospects for exploring soil formation processes (Khaledian and Miller, 2020).

Spatially referenced auxiliary data or environmental covariates can be obtained from geophysical sensing technology using satellite-based, UAV-based, or ground-based platforms deploying various sensors. Electromagnetic (EM) sensors are commonly used to investigate soil heterogeneity by measuring apparent electric conductivity (ECa) (Doolittle and Brevik, 2014) . These sensors can acquire soil information rapidly compared to traditional methods. (Guo *et al.*, 2019).

Soil texture is a fundamental property of the soil and is strongly related to other soil physical properties that affect nitrate movement (Hallaq, 2010). Depending on their texture, soils have varying retentive properties (Gaines and Gaines, 1994). Therefore, as water and dissolved chemicals such as NO_3^- travel through the soil they are influenced by texture. The coarser the soil, like sand, the faster the percolating water movement with dissolved chemicals. Over use of nitrogenous fertilisers on sandy soil can lead to groundwater contamination by nitrogen leaching (Hallaq, 2010). The effect of soil texture and its variability on leaching is explained in *section 2.2.2* in detail. Hence, variability in soil texture within a field is as substantial to determine groundwater quality of a local area as factors like crop and agricultural management at a large scale (Gurevich *et al.*, 2021). Many studies also found the correlation of soil water contents with depth independent of soil texture (Onsoy *et al.*, 2005; Grote *et al.*, 2010). Groundwater nitrate concentrations in the aquifer are typically higher in shallow portions (Gurevich *et al.*, 2021). This association of nitrate leaching with soil texture and soil profile depth emphasises that accurate soil texture and depth estimations are necessary to design various agricultural and environmental management interventions on a field scale to minimise nitrogen losses.

This study used a DUALEM 21S sensor to provide continuous spatial data for shallow and deep ECa of soil. It is a popular EM sensor being used in precision agriculture. Using environmental covariates derived from a DEM combined with point data for soil texture, pH, depth and soil organic matter (SOM), we developed a predictive spatial model of soil variability. Objectives of this study were to

- Incorporate high resolution soil ECa sensing and DEM for digital soil mapping of the study area,
- Evaluate the accuracy of the DSM to predict soil texture variability in relation to depth to the bedrock as an important factor to manage nitrate leaching

3.2 Fieldwork Methodology

3.2.1 Study area

Four farms across the Fell Sandstone aquifer were selected to study variability in soil depth to the bedrock and soil texture that can influence nitrate leaching from agricultural land to groundwater. The study area covers 4.2 km^2 within a catchment of 14.2 km^2 that supplies the Fell Sandstone aquifer, which is affected by nitrate pollution, close to Berwick-upon-Tweed in northern Northumberland in the UK (**Figure 3. 1**). The area includes some woodlands and agricultural lands, including arable crops and long and short-term grass rotations. The mean annual rainfall (1981-2010) is around 589 mm with average annual minimum and maximum temperatures of 6^{o}C and 11.9^{o}C, respectively (office., 2010). The area has slope ranges from less than 1^o to 9.1^o, and the elevation varies from 42.8 to 76.5 m.

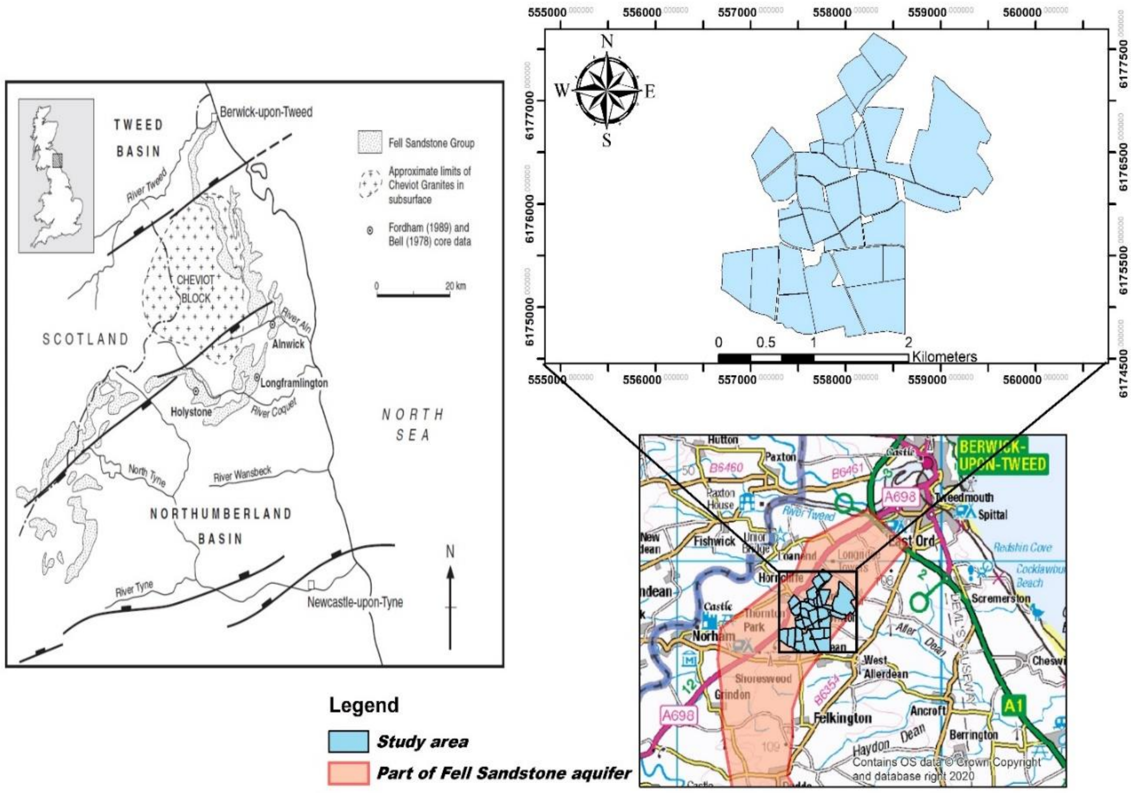


Figure 3. 1 Geographical representation of the Fell Sandstone Aquifer area (left) in north Northumberland, UK after (Turner *et al.*, 1993), and location of the area used in this study.

The soils of the study area as mapped by Jarvis (1984) are dominated by the Nercwys and Salop soil series. The Nercwys association consists of deep, stony, fine loamy soils in drift mainly resulting from Carboniferous sandstones and shales. Sandy soils developed from the sandstone parent material which has resulted in no prominent gleying found in this association above 40 cm depth. The Salop association consists mostly of stagnogley soils of a coarse loamy to a fine loamy texture with slowly permeable subsoils in reddish drift mainly derived from Permo-Triassic rocks. However, along the Northumberland coast, the drift is derived from Carboniferous rather than Permo-Triassic rocks. There is a limited proportion of stagnogleyic argillic brown earth.

3.2.2 Hydrogeology of study area

The northern part of the study area comprises of sandstone while mudstone is the major rock type on the southern side. A part of the area is covered with sand and Diamicton (glacial deposits ranging in size from clay to boulders) as shown in **Figure 3. 2** and **Figure 3. 3**.

The region's sandstone units tend to form ridges, while the intervening mudstone units tend to form low regions in the overall landscape. The Fell Sandstone aquifer is multi-layered being separated by many thick mudstone units. Fractures in the layers also have a significant impact on flow through the Fell Sandstone (Jones *et al.*, 2000). Therefore, groundwater recharge is not only directly to the outcrop of the sandstone units but also considered from runoff towards nearby sandstone units from the intervening lower permeability mudstone unit (Ford *et al.*, 2019; Jeremy and Melissa, 2021).

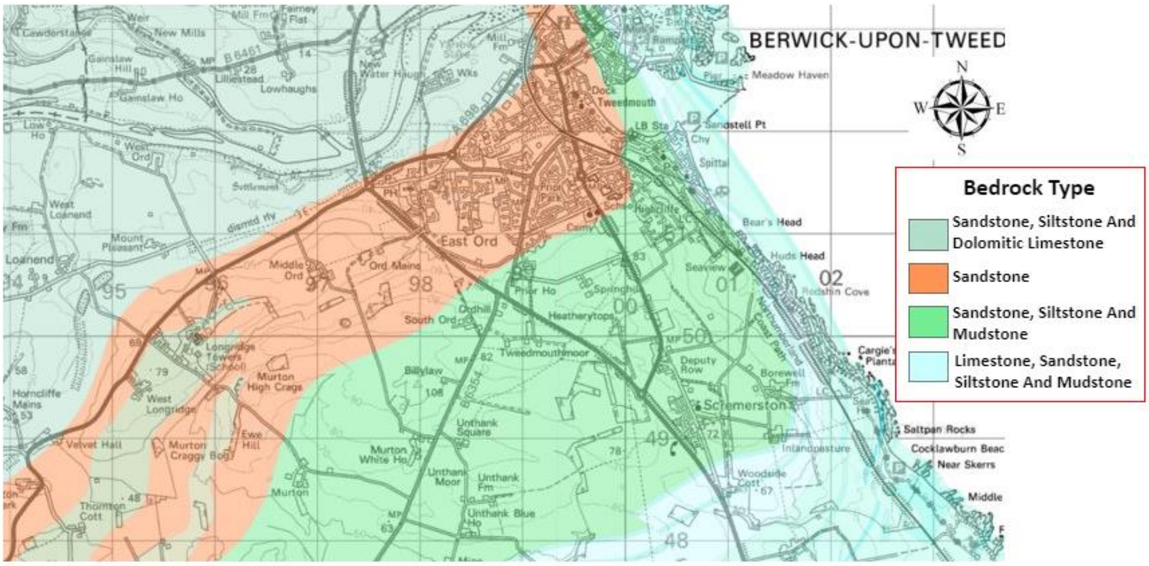


Figure 3. 2 Bedrock geology (solid) of the Fell Sandstone Aquifer area

Figure 3. 3 Superficial deposits (drift) of the Fell Sandstone Aquifer area

Fordham (1989) found that grain size has the main effect on porosity and permeability. Whereas sandstones with coarser grained properties had the maximum porosity and permeability. These sandstone units also have a greater degree of secondary dissolution porosity due to a larger proportion of unstable minerals (Turner *et al.*, 1993). The results from drilling in the area showed that maximum groundwater level is linked with the sandy horizons found at the bottom of the sandstone units (Jones *et al.*, 2000). Due to the effect of porosity and permeability on water movement, the spatial variability of these factors in the Fell Sandstone area is important not only for water recharge but also for the movement of dissolved nutrient from the surface to groundwater.

3.2.3 Geophysical sensor survey

A geophysical survey of the target area has been undertaken from 2016-2017 using DUALEM 21S (www.dualem.com). DUALEM sensors measure apparent electromagnetic conductivity (ECa) of soil and can be used for many types of shallow-earth investigations. They are used in soil mapping and monitoring, archaeology, delineation of conductive contamination, and groundwater and clay exploration. ECa values are generally a good indicator of soil texture. Waine et al., (2000) reported that conductivity greater than 30 mS/m typically represents clay and a conductivity of less than 5 mS/m typically represents sand. In addition, ECa values between 0 and 10 were graded as sandy loam, with values between 10–20 mS/m indicated as clay loam.

The DUALEM 21S has an electromagnetic induction (EMI) transmitter and two pairs of EMI receivers. Together, they form horizontal co-planar geometry (HCP), in a pair of horizontal winding of one receiver with transmitter and perpendicular geometry (PRP) as another pair with the second receiver. The ECa of the soil is represented as the signal responses of the EMI sensor. The dual geometry of the sensor forms 2 arrays of each HPC (at 1and 2 m) and PRP (1.1 and 2.1m). The array of PRP and HCP configurations measure ECa for soil volumes at depths of 0.5 and 1.0 m and 1.6 and 3.2 m, respectively. The investigation's actual depth can differ significantly depending on the true EC. Georeferencing of all these profiles is recorded with a global position system (GPS data logger or external GPS).

For this study the sensor was mounted on a Kubota rtv (rough terrain vehicle) 900. All the fields in the area were scanned in the direction of cultivations or drilling, or the longest transect in the case of grass and pasture, to reduce the number of turns at each end with a swathe working width of about 20m and with a speed of about 5-10Mph. After removing negative values of ECa (due to metal cables, field monitoring installations etc. in general due to anthropogenic coupling), the data were then corrected for the offset between the GPS and the individual channels. Data files created with four measuring depths were used after inversion. We also interpolated EC point values to raster using ordinary kriging with an exponential variogram.

3.2.4 Soil samples and soil analysis

Soil samples were collected during 2017-2018 from 31 locations which were chosen to represent the study area's texture based on ECa mapping. Samples from 22 locations were collected in 2017 from 3 soil layers (0-30, 30-60 and 60-90 cm) or maximum achievable depth and from 9 locations again in 2018. Sampling locations (see **Figure 3. 4**) were selected to cover a range of soil ECa based on the geophysical survey. Due to the effect of the edaphic properties on ECa, the spatial distribution of ECa within the field provides a potential means of mapping the spatial variability of the edaphic properties with an ECa-directed soil sampling. Characterizing spatial variability with ECa-directed soil sampling is based on the assumption that, as ECa correlates with soil properties, spatial ECa information can be used to identify locations representing the range and variability of the soil property or properties (Corwin, 2005).

Out of the total of 31 locations, twenty-six were used to develop the topsoil layer model excluding locations with an organic layer present where soil organic matter was found > 15%. The depth to the 90 cm was achieved only at 21 locations to develop a 60-90 cm soil layer model. A maximum number of samples, 29, were used in developing a model for a 30-60 cm layer. These soil samples were sent to an external lab for texture analysis. Low Laser Scattering (LLS), most commonly known as laser diffraction technique, was used for analysis following the standard method described by Pieri *et al.* (2006). The particle size definitions used in the analysis were Stones >2mm, Sand 2mm to 50μm, Silt 50μm to 2μm and Clay <2μm.

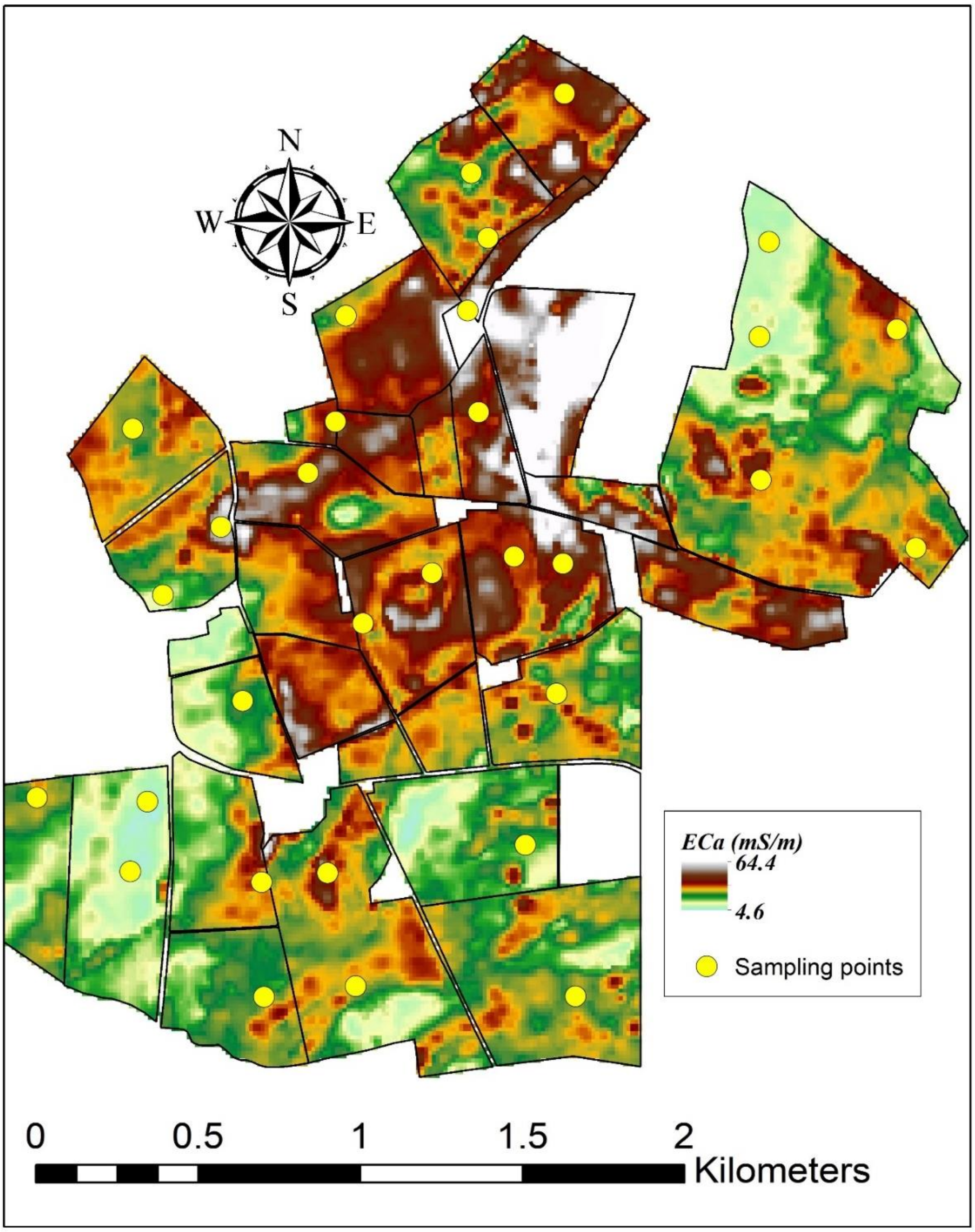


Figure 3. 4 Soil sampling locations for texture analysis in the Fell Sandstone study area shown on the shallow (55cm) ECa base map.

3.2.5 Soil depth survey

To investigate the spatial variation in soil depth, the study area was divided into 465 sampling points shown in **Figure 3. 5**. A simple 120cm peat probe with a strong metal pointed end, and a handheld GPS (to record the grid ref) was used to measure depth manually during the 2019-2020 drainage period when the soil in the field was soft enough. To avoid the possibility that the peat probe hit a stone and wrongly estimate the depth of bedrock, the process was repeated three times from each location before recording a final value. The recorded data was used to predict the whole study area's depth by using the kriging method (**section 3.2.5).** Depth values from the interpolated map were extracted to use as a covariate for modelling purpose to predict soil properties.

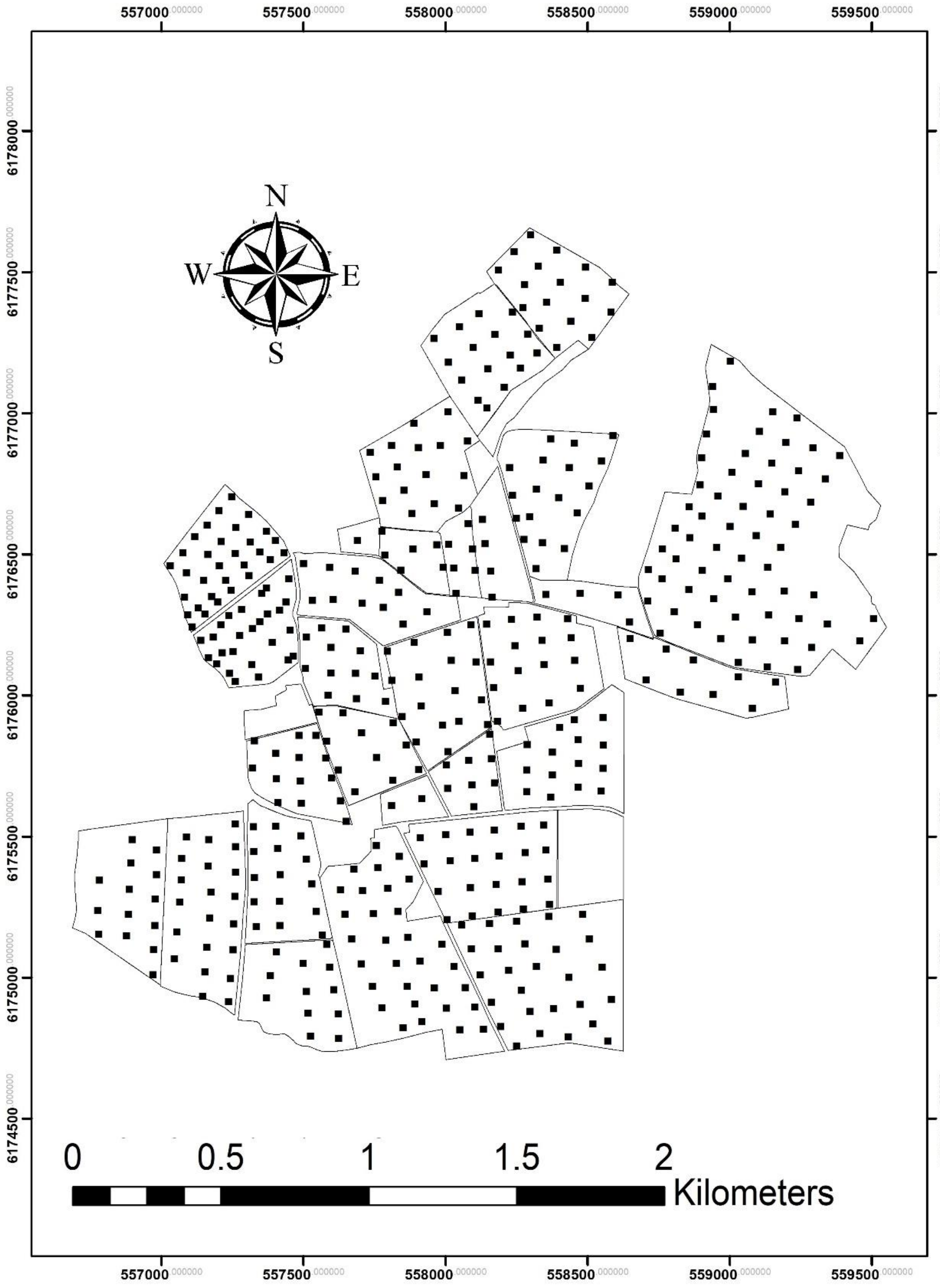


Figure 3. 5 Locations selected for depth measurements from study area

3.2.6 The Digital elevation model (DEM)

LiDAR image was used to derive a high-resolution digital elevation model (E.A, 2017). The LIDAR-derived DEM was produced in VESPER 1.5 software at 2×2 m resolution using a block kriging algorithm that calculated each grid cell's mean elevation value. Terrain analysis and basic hydrological functions were used to produce maps of different topographic variables, including slope, flow accumulation, flow direction, TWI[3], TPI[4], aspect and curvature to check if the DEM represents surface water flow correctly. The TPI provides information regarding the topographic position (valleys, slopes, and ridges) of the soil, which can expose it to different microclimates such as wind, temperature and radiation, and TWI is the predictor for zones of soil saturation. The quality of the terrain parameters is important as it directly affects the spatial model development quality (Hengl *et al.*, 2004a). When these maps were produced with an original DEM of 2 m resolution, they were not clear and had some gaps due to local outliers. That occurred due to a gross error in the data collection process with remote sensing related instruments, or an interpolation algorithm (Hengl *et al.*, 2004a). Smoothing is required for improving the quality of the DEM by reducing the outliers. The statistically sound approach for estimating the neighbouring pixels' central value is to use the spatial dependency structure, i.e. to estimate the central value by kriging (Felicísimo, 1994). First of all, the filtering tool in ArcGIS 10.5 was used to smooth the original DEM map. For interpolation, either spline or kriging can be used, but kriging was adopted because it gives values based on the local trend of elevation, which is more accurate. A local variogram with VESPER 1.5 software was used for block kriging. In Vesper, one can selectively choose the prediction block's size (the area to be used for prediction). This pre-processing of DEM generates a depression free elevation model which was used to extract terrain attributes.

Slope, curvature, Flow direction and Flow accumulation maps were derived from DEM using a spatial analyst tool in ArcGIS 10.5. TPI and TWI were calculated with the following equations

$$\mathrm{TPI} = \mathrm{DEM} - \mu\mathrm{DEM}$$

Where DEM is digital elevation of the area and μDEM represents mean values of DEM

$$\mathrm{TWI} = \ln(\alpha / \tan\beta)$$

[3] Topographic wetness index
[4] Topographic position index

Where α = Flow accumulation of the area and β = local slope (Moore *et al.*, 1993)

3.3 Prediction Methodology

3.3.1 Approach to predicting spatial distribution of soil properties

Interpolation of particle size fractions and soil texture mapping is primarily conducted in stages including basic statistics, spatial analysis, and interpolation with kriging techniques and mapping soil texture. The flow chart in **Figure 3. 6** shows the methods used in this study, performed in a set of steps described as follows:

- Particle size fractions (PSFs) data of 31 sampling locations were collected and analysed for soil texture
- Terrain attributes, remote sensing covariates and depth to the bedrock in **Table 3. 1** associated with the sampling points were derived from the digital elevation model, DUALEM 21S data and measured depth to bedrock
- PSFs were predicted by the selected model with significant covariates from **Table 3. 1** as inputs
- LM was selected for spatial interpolation of PSFs

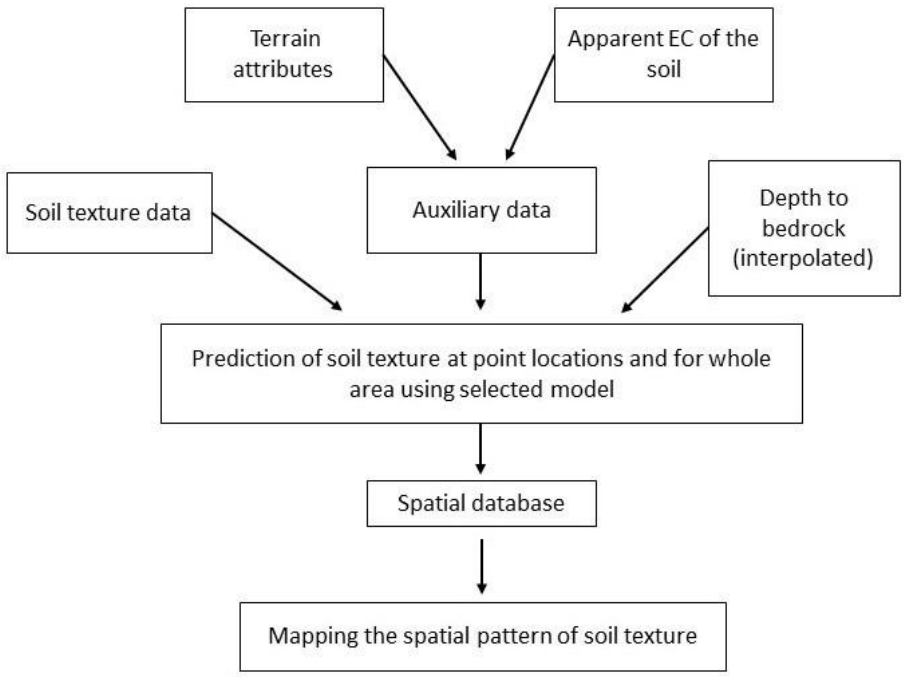


Figure 3. 6 Flow chart of the prediction methodology used in the study for mapping soil texture

3.3.2 Spatial interpolation

Estimation of the targeted values for unvisited locations in spatial prediction, when the prediction is for a whole study area, is referred to as spatial interpolation (Hengl *et al.*, 2004b). Spatial interpolation is a two-step process. The first is to find a suitable model for the prediction of soil properties. The second is to use the selected model to estimate values for unsampled locations. The concept of SCORPAN provides a structure to choose environmental covariates to predict soil properties (McBratney *et al.*, 2003; Feng *et al.*, 2020). After model selection, soil texture for the whole study area was predicted and mapped using GIS 10.5.

SCORPAN = soil, climate, organisms, topography (relief), parent material, age (the time factor) and N for space (spatial position)

For spatial interpolation of the organic layer in the study area, soil sampling locations where organic matter was> 15 % were used to calculate the per cent probability of organic or mineral characteristics. The probability was used to predict the organic top layer's spatial distribution present in the study area.

3.3.3 Model selection and validation

In the model development, soil particle size fractions (sand and clay %) were the dependent variable, and terrain attributes, depth to the bedrock and apparent electric conductivity (ECa) (**Table 3.1**) were the predictors or independent variables. A multiple linear regression model (MLR) was used to predict soil texture components (sand and clay) for three layers of soil, 0-30, 30-60 and 60-90 cm, separately with different covariates used as predictors. MLR is one of the most common and simplest methods used to estimate soil properties and determine the relation between several available covariates and a target variable (Bonfatti *et al.*, 2016; da Silva Chagas *et al.*, 2016; Khaledian and Miller, 2020). JMP Pro software was used for the MLR. We used stepwise regression to resolve the issue of multi-collinearity. In this method, predictors were selected with the highest statistical significance using forwarding selection and backward deletion approaches.

The random forest (RF) model was also used in this study which is currently the most commonly used machine learning algorithm in DSM (Wiesmeier *et al.*, 2011). RF selects a group of observations randomly to form a decision tree from the dataset. Building a decision tree repeatedly forms multiple decision trees by using different sample sets every time. The mean from thousands of such decision trees is used as the final RF prediction (Khaledian and Miller, 2020). The number of trees to grow, the number of covariates randomly selected at each node and the minimum number of sample leaves to capture noise in the training data are the most important hyperparameters for this algorithm.

Table 3. 1 List of variables considered for prediction of soil properties in this study

Source of auxiliary data	Covariates	Description
Terrain attributes	Elevation	Height above sea level
	Slope	Local hillslope gradient
	Topographic wetness index (TWI)	Control of topography on hydrological processes
	Topographic position index (TPI)	Difference between cell elevation and the average cell elevation surrounding it
	Flow direction	Water flow path
	Flow accumulation	Accumulated weight of all cells flowing into each downslope cell
	Basin	Depression in the earth surface
DUALEM sensor data	EM_55 EM_110 EM_160 EM_320	Apparent EC values of soil from four different depth ranges (in cm).
Soil depth	-	Depth to bedrock

For an unbiased evaluation of the predictive ability of the model, it is proposed that the reference dataset be used to create a validation dataset that is independent of the calibration dataset (Snee, 1977). In our study, an inadequate number of samples were available to include an unbiased data set for validation. Therefore, a leave one out cross-validation (LOOCV) method was used to test the predictive models' performance (Picard and Cook, 1984). The LOOCV is the most common type of *n*-fold cross-validation. With the LOOCV method, all but one sampling location are used to calibrate the model, and the remainder are used for validation. This procedure is repeated until all sample points have been used as validation data. For each sampling location, the model was re-fitted, leaving that location out of the calibration data collection. The target variable was then estimated for that location, and the prediction error was determined. Model coefficients were averaged from all iterations in order to compare the model performances. We used root mean square error (RMSE) and the coefficient of determination (R^2). R^2 indicates the degree of variation explained by the model, which is useful to estimate the precision in the relationship between observations and predictions (James *et al.*, 2013b; Lin *et al.*, 2016; Yuxin *et al.*, 2017). RMSE provides a useful measure of accuracy. Prediction models were developed using data from all locations, while goodness-of-fit was expressed for error estimators derived from LOOCV.

3.4 Results

3.4.1 Statistical description of the soil data

Table 3. 2 shows the descriptive statistics of textural components (sand, clay and silt), SOM and pH of the soil in the dataset for the top layer of the soil profile (0-30cm) and the subsoil layers 30-60 cm and 60-90cm. The detailed information of soil properties is reported in **Appendix 1**. The silt and sand ranges were 12-59% and 20-86%, respectively, for topsoil. Clay content varied from 2-27%, with a mean value much less than both sand and silt. The higher maximum value of sand (86%) followed by silt (59%) and clay (27%) indicates the lighter soil texture in the study area. The dominant soil texture was sandy silt loam, as shown in **Figure 3. 7**. There was only one sample of loamy sand and one of sandy texture.

Table 3. 2 Statistical description of soil properties

	Max	Min	Mean	SD	CV	n
0-30 cm						
Sand (%)	86	20	41	14.6	35.4	31
Clay (%)	27	2	14	5.4	40.2	31
Silt (%)	59	12	45	10.5	23.3	31
SOM (g kg^{-1})	47.6	2.5	8.5	10.2	120.5	22
pH	7	5.7	6.2	0.3	5.1	22
30-60 cm						
Sand (%)	71	19	40	12.3	30.2	30
Clay (%)	31	4	17	6.5	38.8	30
Silt (%)	67	22	42	9.2	21.7	30
60-90 cm						
Sand (%)	76	11	41	13.4	32.3	21
Clay (%)	57	5	21	10.3	48.6	21
Silt (%)	53	20	37	8.2	22	21

Note: CV, coefficient of variation; SD, standard deviation

The degree of variation of clay and sand is higher compared to silt in all layers. The coefficient of variance for silt is smaller (21.7%) in the 30-60 cm layer. CV of the clay is highest in the deepest layer of soil (60-90 cm). The standard deviation (SD) of clay is 5.4 to 6.5 and 10.3%, whereas the SD of sand is 14.6, 12.3 and 13.4 %. SOM has the highest CV value, which is 120.5%, indicating that OM varied greatly across the study area.

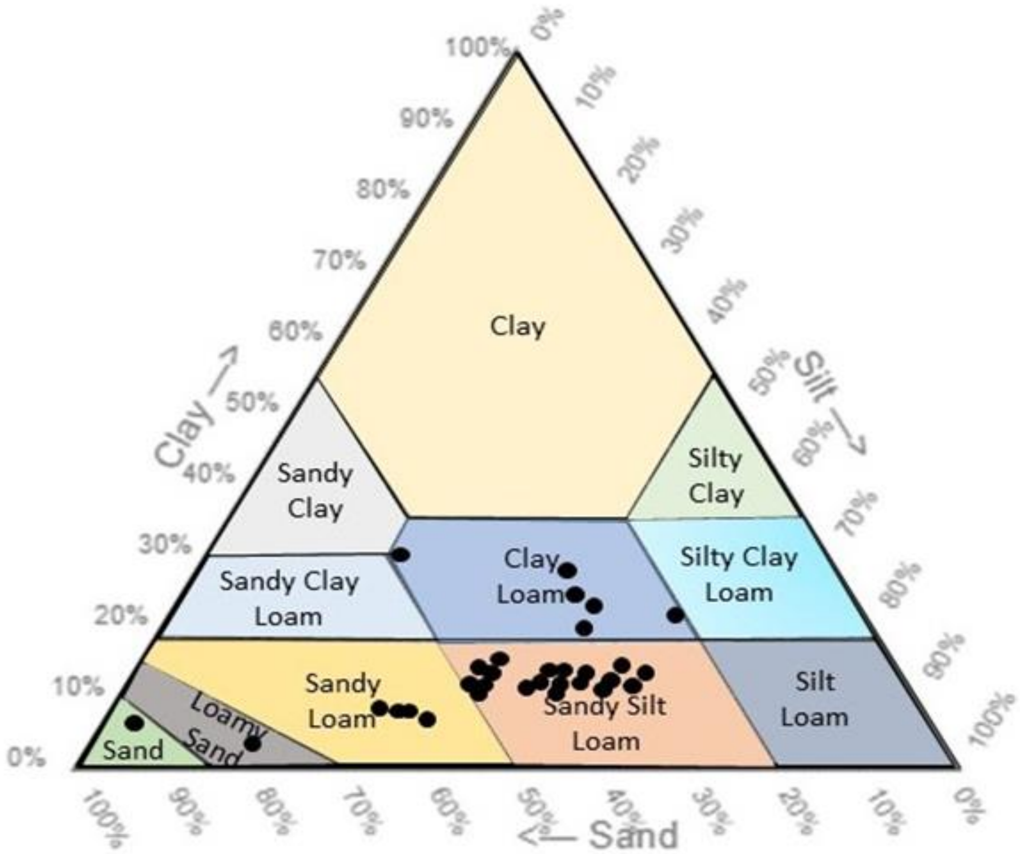


Figure 3. 7 Soil textural class of topsoil at each sampling location

Further distribution of the ranges of soil particles is shown in **Figure 3. 8**. The highest number of samples (14) have clay contents of 10-15% and only one sample has a clay content > 25 %. The sand range is 30-40% for 12 samples observed from the dataset for topsoil. Only one sample has silt % less than 15 % and sand % more than 70%. Silt was the dominant size fraction among the three with maximum values observed between 45-55% in 14 samples. It is observed in the frequency distribution histogram that only the distribution of the clay is similar to a bell shape. At the same time, skewness is apparent in the distribution of sand and silt fractions.

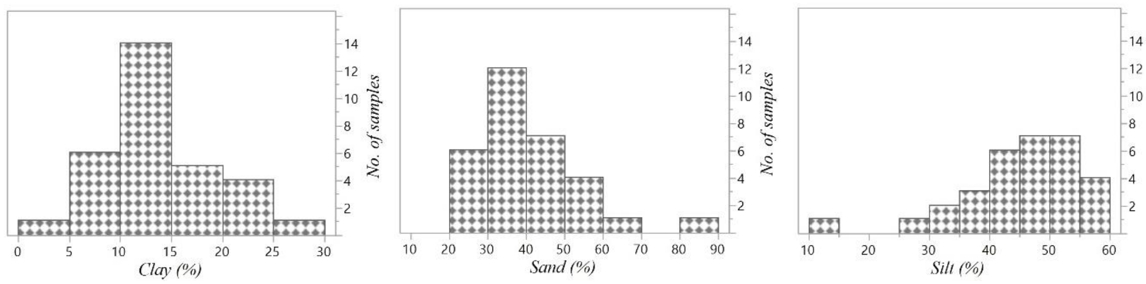


Figure 3. 8 Histogram distribution frequencies of soil textural components in topsoil profile

3.4.2 Statistical description of predictors

Soil apparent electric conductivity varied from 4.9 to 37.7 mS/m for shallow soil profiles (55cm) and 2.4 to 30.4 mS/m for the deep profiles (320cm), as shown in **Table 3. 3**. The highest value of electrical conductivity recorded was 39 mS/m in the second layer of ECa measurement. The mean ECa values ranged between 7.8 (for depth 160cm) to 19.3 (for depth 110 cm), and the mean values for elevation and slope were 53 m and 2.2. Soil depth to the bedrock was spatially variable in the study area ranging from shallow soil profiles (35 cm) to deep profiles (>120cm) with a mean value of 85.4 cm.

Elevation had the lowest CV, 18.4, compared to all other terrain attributes computed from the DEM. In contrast, flow accumulation had the highest CV (319.3) and SD (71.9) among all predictors. The SD for the ECa from all four depths (55, 110, 160 and 320 cm) was <10. The coefficient of variation of ECa increased from 42.5 to 58.7. The CV for TPI, flow accumulation and flow direction were >100.

Table 3. 3. Statistical description of predictors

	Max	**Min**	**Mean**	**SD**	**CV**
ECa (mS/m)					
EM-55	37.7	4.9	16.8	7.2	42.5
EM-110	39	4.9	19.3	5.4	42.9
EM-160	22.9	1.9	7.8	4.6	58.7
EM-320	30.4	2.4	11.2	6.3	56.1
Terrain attributes					
Elevation (m)	75.6	42.8	53	9.8	18.4
Slope (degree)	9.1	0.05	2.2	2.2	99.7
TPI	186.8	1.8	18.3	36.3	197.9
TWI	11.1	3.6	6.9	1.8	25.7
Flow direction	64	1	24.5	25.9	105.7
Flow accumulation	402	0	22.5	71.9	319.3
Basin	75	2	44.7	22.8	50.9
Depth (cm)	>120	35	85.4	27.3	31.9

Note: CV, coefficient of variation; SD, standard deviation

3.4.3 Relative importance of covariates

The relative importance of variables was measured to estimate their importance in the prediction model. In MLR, relative importance was computed from the Log ratio for each model parameter, whereas, for RF, relative importance was measured from the portion of contribution of each variable in prediction. Out of total 12 variables **(Table 3. 1)** used to develop the model, eight had significant effects for predicting topsoil clay in MLR and five in RF as shown in **Figure 3. 9** and **Figure 3. 10**. Seven variables were significant in predicting topsoil sand in MLR. We used the highest related auxiliary variables to predict soil fractions. Elevation was found to have relative importance 17% and 9.6% in MLR and RF, respectively, for topsoil sand. Elevation plays an important role in predicting PSFs for all depths of soil in both models.

Shallow and deep soil ECa also contribute to prediction. Shallow ECa (EM55) had a relative importance of 19.4 and 17.2 % t in LM but had only 10 and 8.9% importance in RF for predicting topsoil clay and sand. The ECa from 110 cm depth (EM110) was significant in predicting both sand and clay for all layers in MLR, whereas EM320 was significant only in the prediction of sand in the 60-90cm layer and topsoil clay in MLR.

The degree of slope is another important covariate in predicting particle size fractions for all soil layers in both models. This is because the slope gradient influences the rate of surface runoff and the rate of surface erosion. Depth to the bedrock was significant only in predicting topsoil sand in RF. The TPI was important only for predicting topsoil clay in MLR and sand in RF.

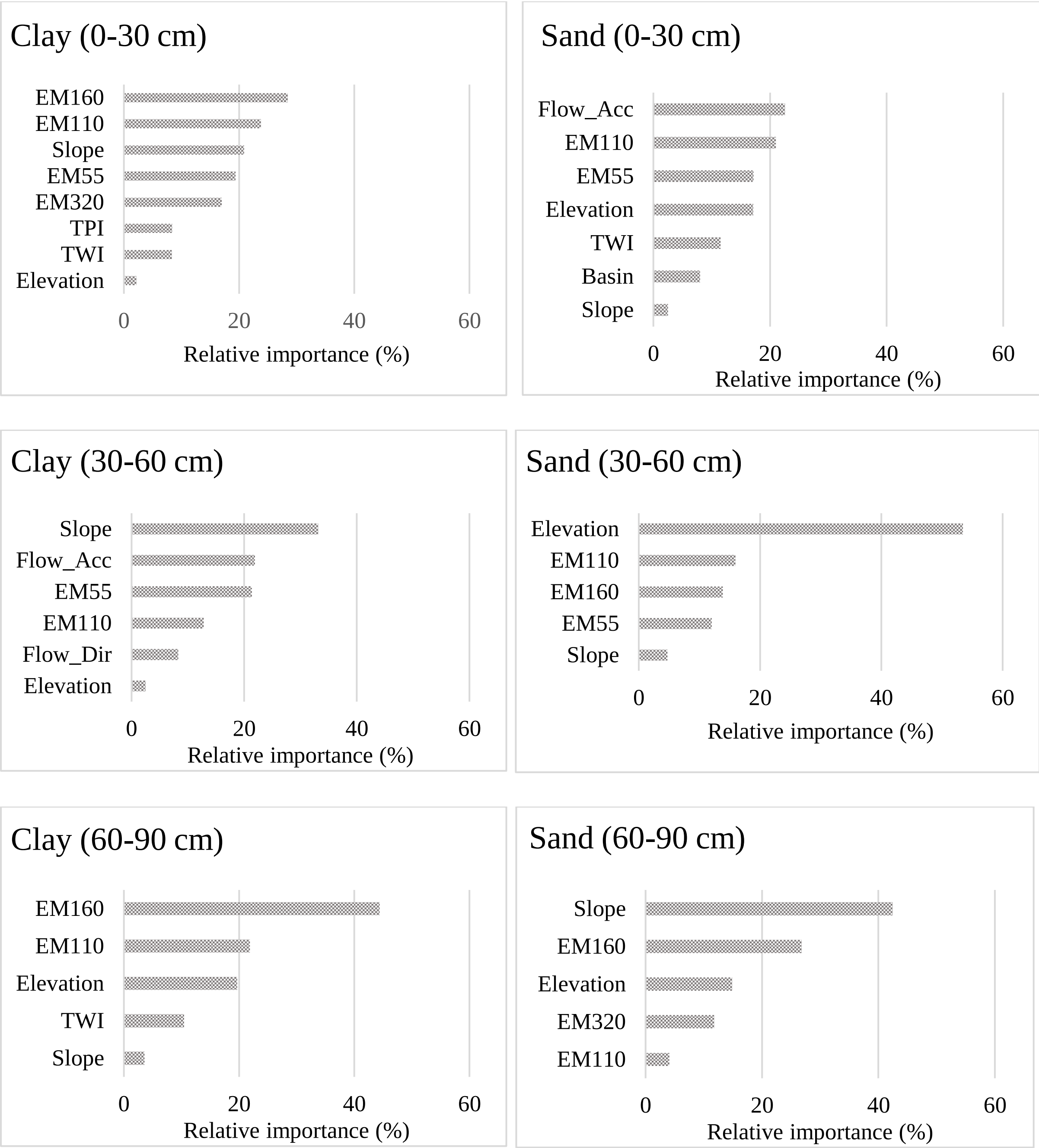


Figure 3. 9 Relative importance of covariates in predicting soil particle size fractions in MLR**,** Where TPI: Topographic position index, TWI: Topographic wetness index, Flow_Acc: Flow accumulation and EM's: Apparent EC values of soil from four different depth ranges.

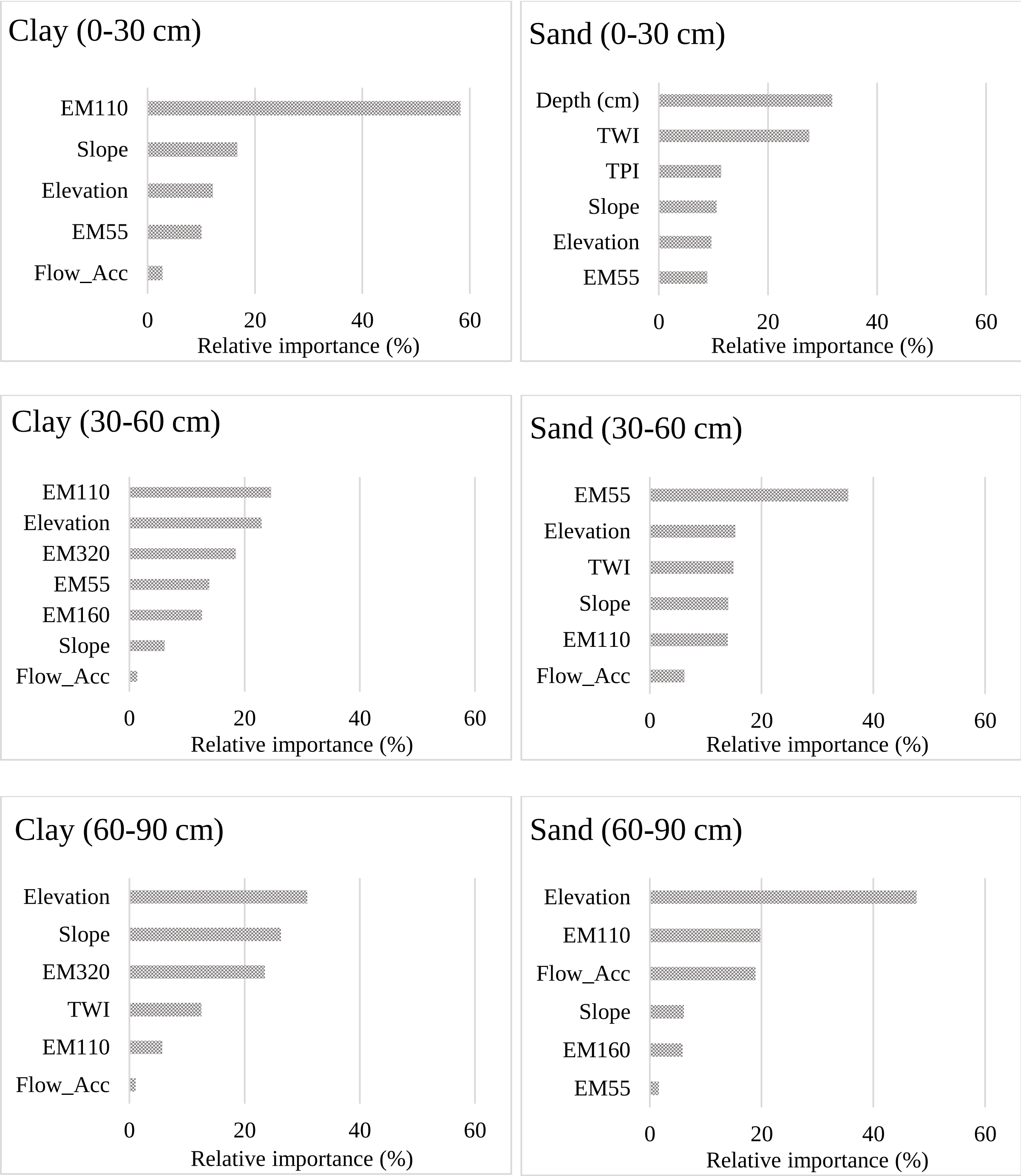


Figure 3. 10 Relative importance of covariates in predicting soil particle size fractions in RF**,** Where TPI: Topographic position index, TWI: Topographic wetness index, Flow_Acc: Flow accumulation and EM's: Apparent EC values of soil from four different depth ranges.

3.4.4 Comparison of Linear model and random forest

MLR and RF performance is shown in **Table 3. 4** in terms of R^2 and RMSE. Both models were used to predict soil clay and sand contents. The silt was predicted with the difference method (100 – (sand % + clay %)) by using predicted values of sand and clay (Ließ *et al.*, 2012). Some of the sampling locations have an organic layer with >15% OM. So, the prediction of soil texture with the same organic and mineral soil model showed R^2 values close to zero. To avoid this problem, the organic layer's data points were excluded from the data set used for modelling the topsoil layer. According to comparing the two models, the R^2 of MLR for % sand from three soil depth ranges (0-30, 30-60 and 60-90 cm) were 0.5, 0.5 and 0.4, respectively. For RF, the R^2 values for sand are 0.3, 0.4 and 0.2 for the three layers. There was an increase of 66% in R^2 of MLR compared to RF for topsoil sand prediction.

Table 3. 4 Performance of MLR and RF (averaged from all iterations of LOOCV)

Soil texture fraction	**LM**		**RF**	
(0-30 cm)	**R2**	**RMSE**	**R2**	**RMSE**
Clay (%)	0.4	4.3	0.3	4.1
Sand (%)	0.5	9.0	0.3	8.6
(30-60 cm)				
Clay (%)	0.4	5.7	0.2	5.3
Sand (%)	0.5	8.3	0.4	7.5
(60-90 cm)				
Clay (%)	0.4	8.9	0.1	9.3
Sand (%)	0.4	11.9	0.2	11.6

Note: R^2, Coefficient of determination; RMSE, Root mean square error

The RMSE for sand was higher compared to clay in both modelling approaches for all soil layers. The RMSE is 4.3, 5.7 and 8.9 % for clay in MLR and 4.1, 5.3 and 9.3 in RF. The RMSE is 9, 8.3 and 11.9 % for sand in MLR and 8.6, 7.5 and 11.6 in RF. There was a 4%, 9% and 2% decrease in RMSE values of RF compared to MLR for sand prediction from 0-30, 30-60 and 60-90 cm layers.

MLR always performs better than RF when measured as R^2. The **Figure 3. 11** and **Figure 3. 12** further visually compare the performance of the two models. The figures represent the linear relation between actually measured (y-axis) and predicted (x-axis) sand and clay contents for three soil layers used in the study (0-30, 30-60 and 60-90 cm) for both models.

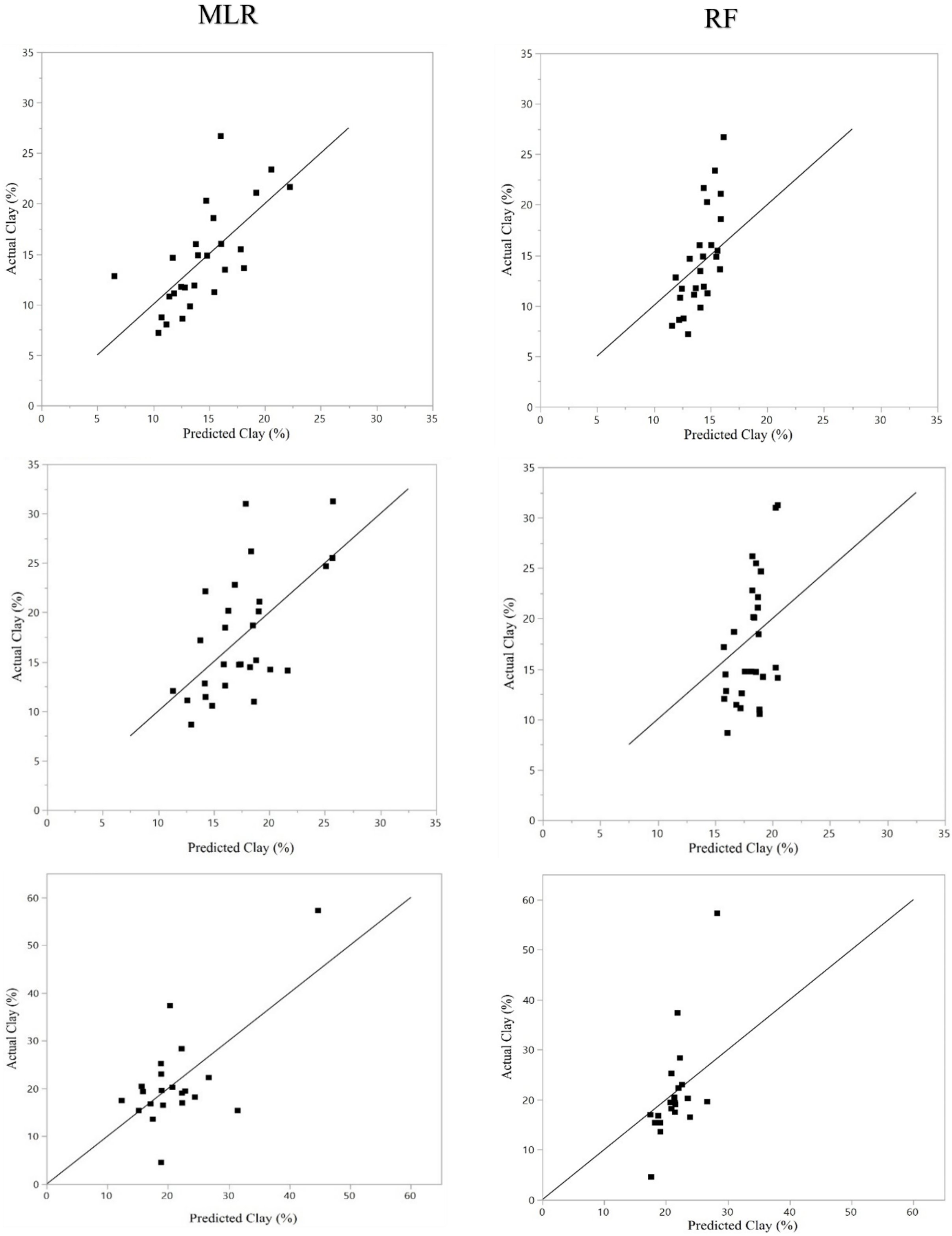


Figure 3. 11 Comparisons of MLR and RF in terms of observed vs. predicted Clay (%) in three soil layers (0-30, 30-60 and 60-90 cm) from top to bottom. The line is 1:1 line.

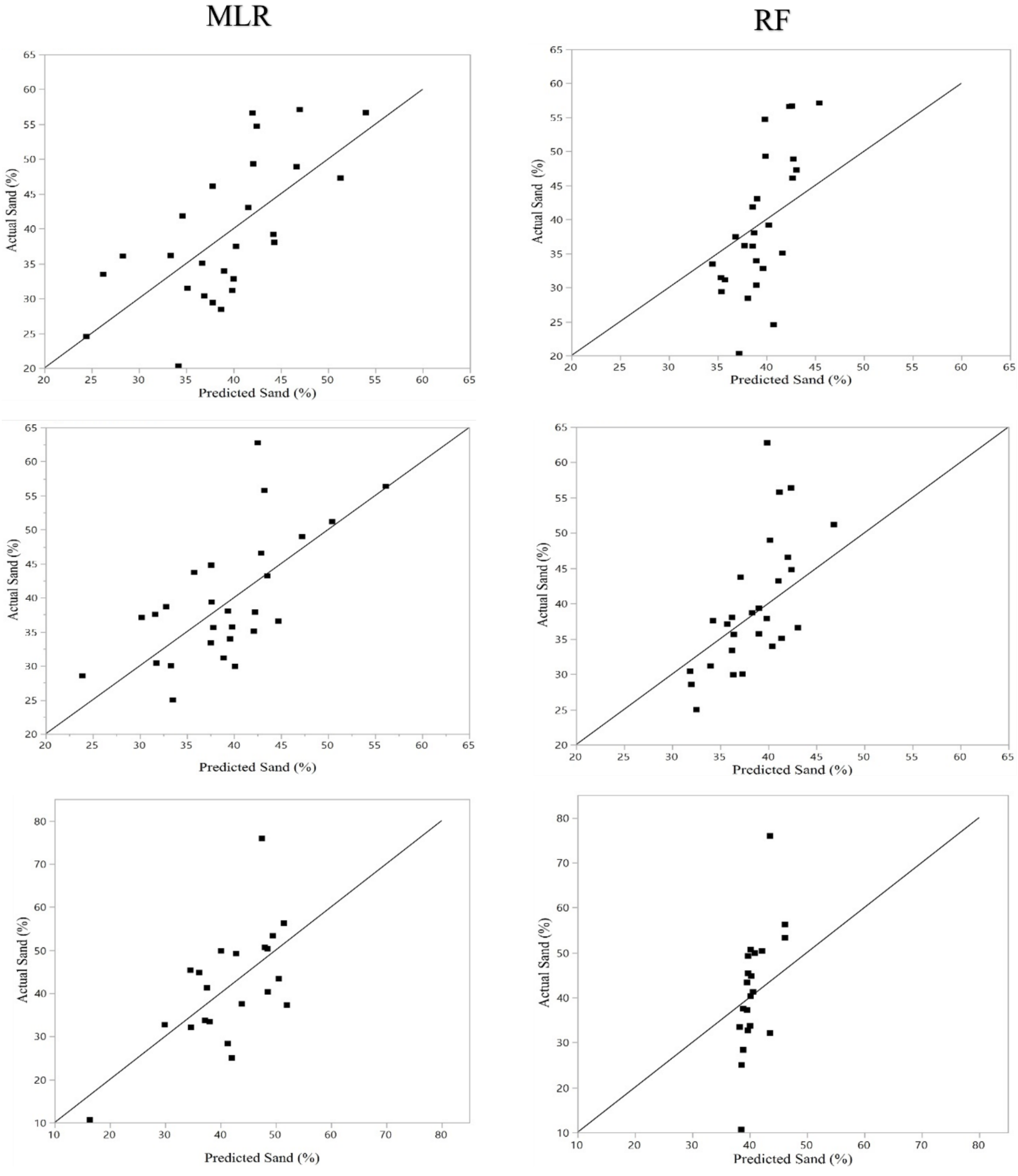


Figure 3. 12 Comparisons of MLR and RF in terms of observed vs. predicted Sand (%) in three soil layers (0-30, 30-60 and 60-90 cm) from top to bottom. The line is 1:1 line.

3.4.5 Mapping soil properties

Maps of soil particle size fractions predicted using MLR, show that the distribution of sand and clay is different in each layer. Clay fraction ranges 2-48% in the top layer. The maximum fraction of clay was recorded in the deepest soil samples (60-90 cm) which was 5-50%. The sand fraction range was 10-86 % in three layers.

In the study area, soil depths were spatially variable ranging from shallow to deep (30 to >120 cm) as shown in **Figure 3. 13** depending on the landforms. Soils on convex slopes were shallower compared to flat or gently sloping areas, where soils were deeper. The north part of the study area has a shallow soil profile. The area with a shallow soil profile (< 45cm) was excluded from the spatial distribution of sand and clay map of 30-60 cm depth due to the presence of bedrock within the lower limit (60 cm) of the layer. A further area was excluded again for mapping spatial soil particle fractions in the 60-90 cm soil layer where soil depth was < 75 cm.

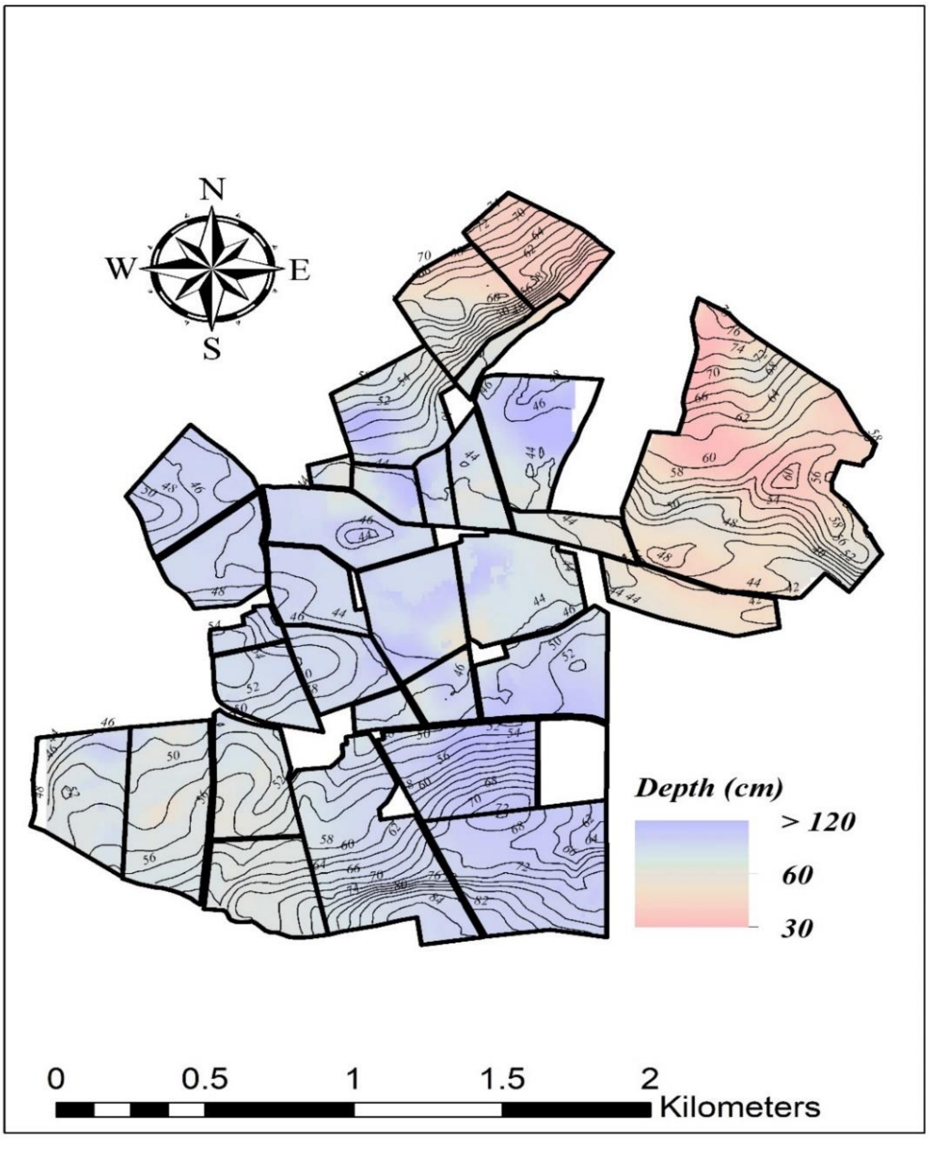


Figure 3. 13. Spatial variability in depth to the bedrock (superimposed on elevation contour lines) from study area produced with interpolation of depth measured from 465 locations.

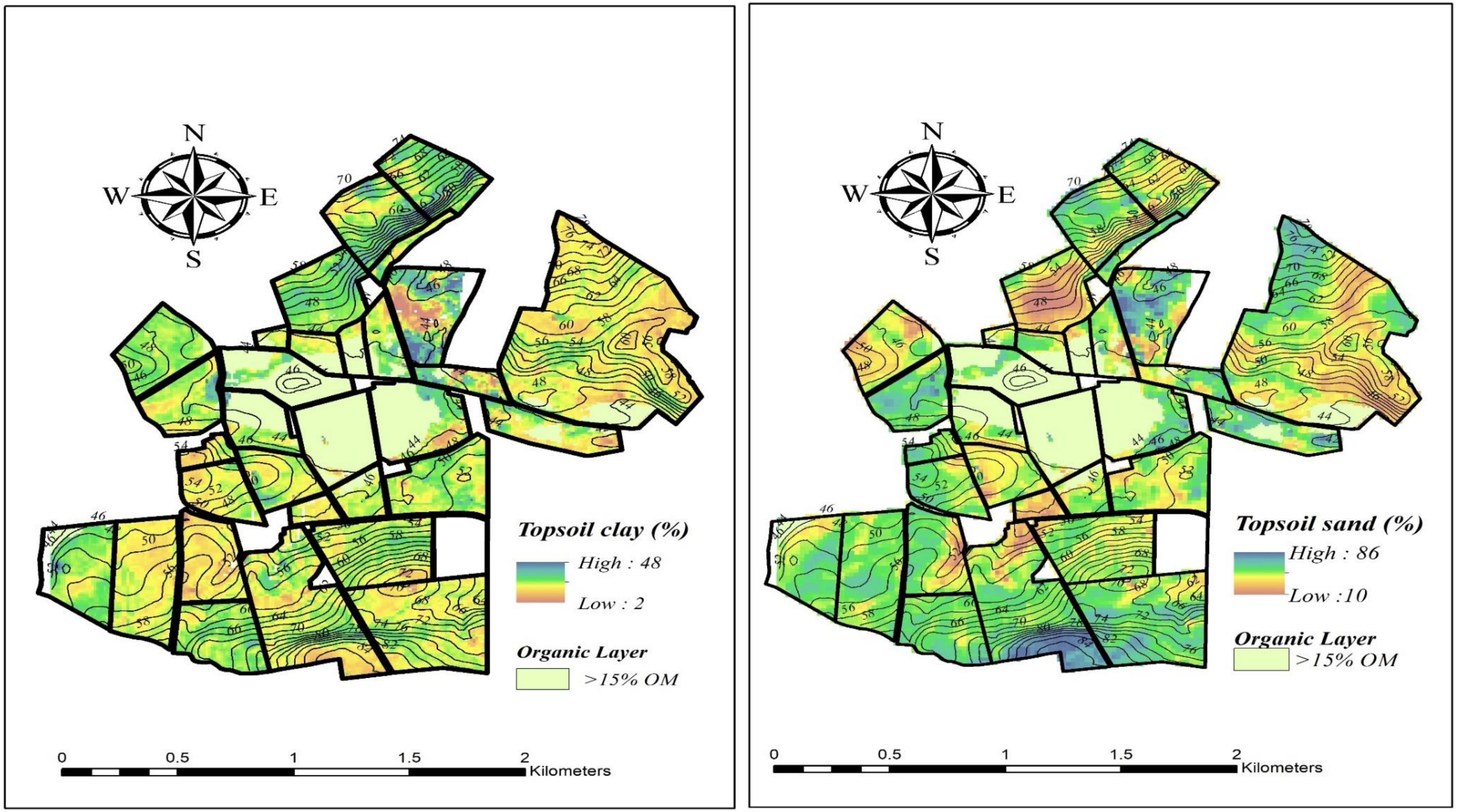


Figure 3. 14a. Map of organic layer, clay % and sand % in topsoil (0-30 cm) superimposed on elevation contour lines.

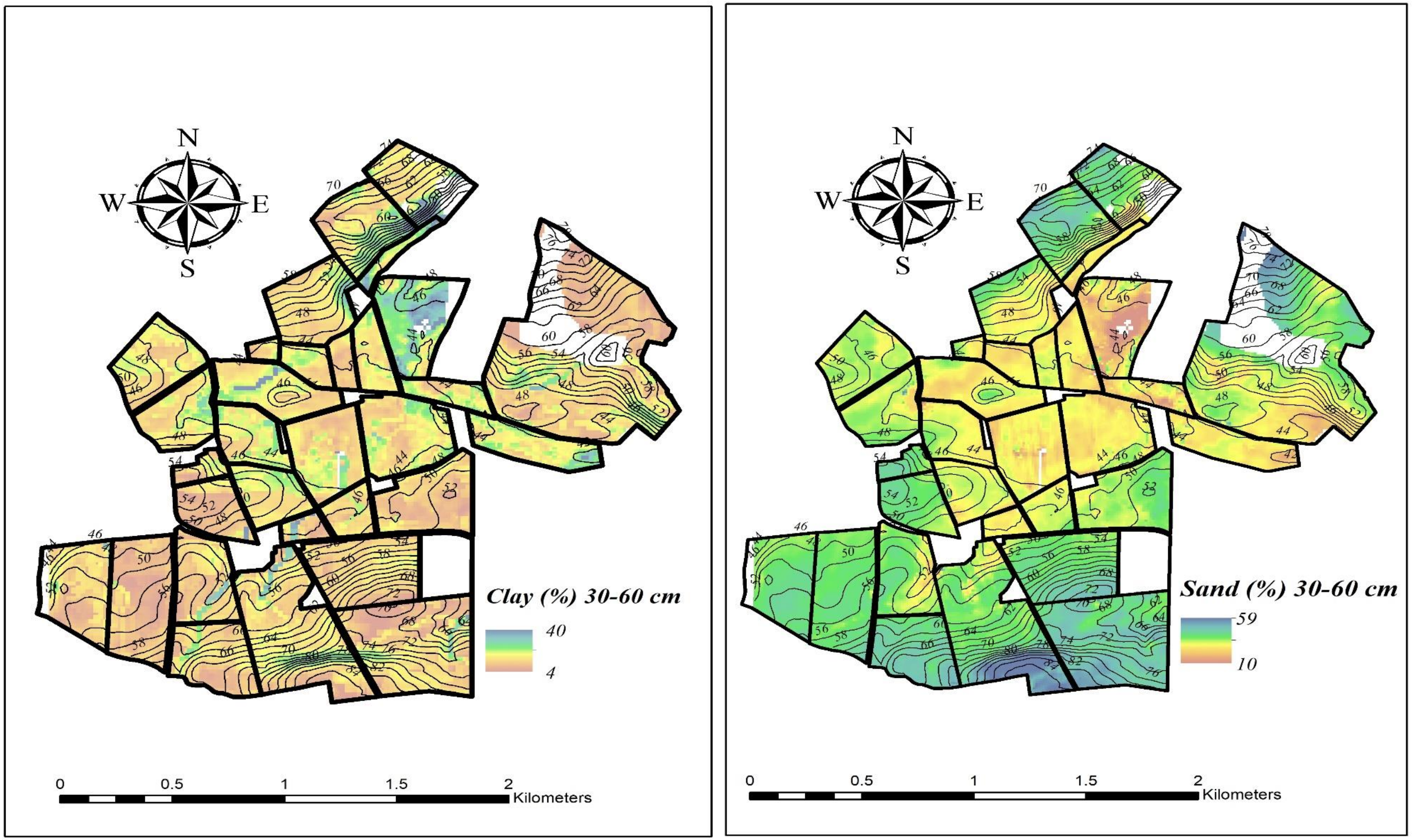


Figure 3. 14b. Map of clay % and sand % in 30-60 cm (excluded area where depth < 45 cm) soil layer superimposed on elevation contour lines.

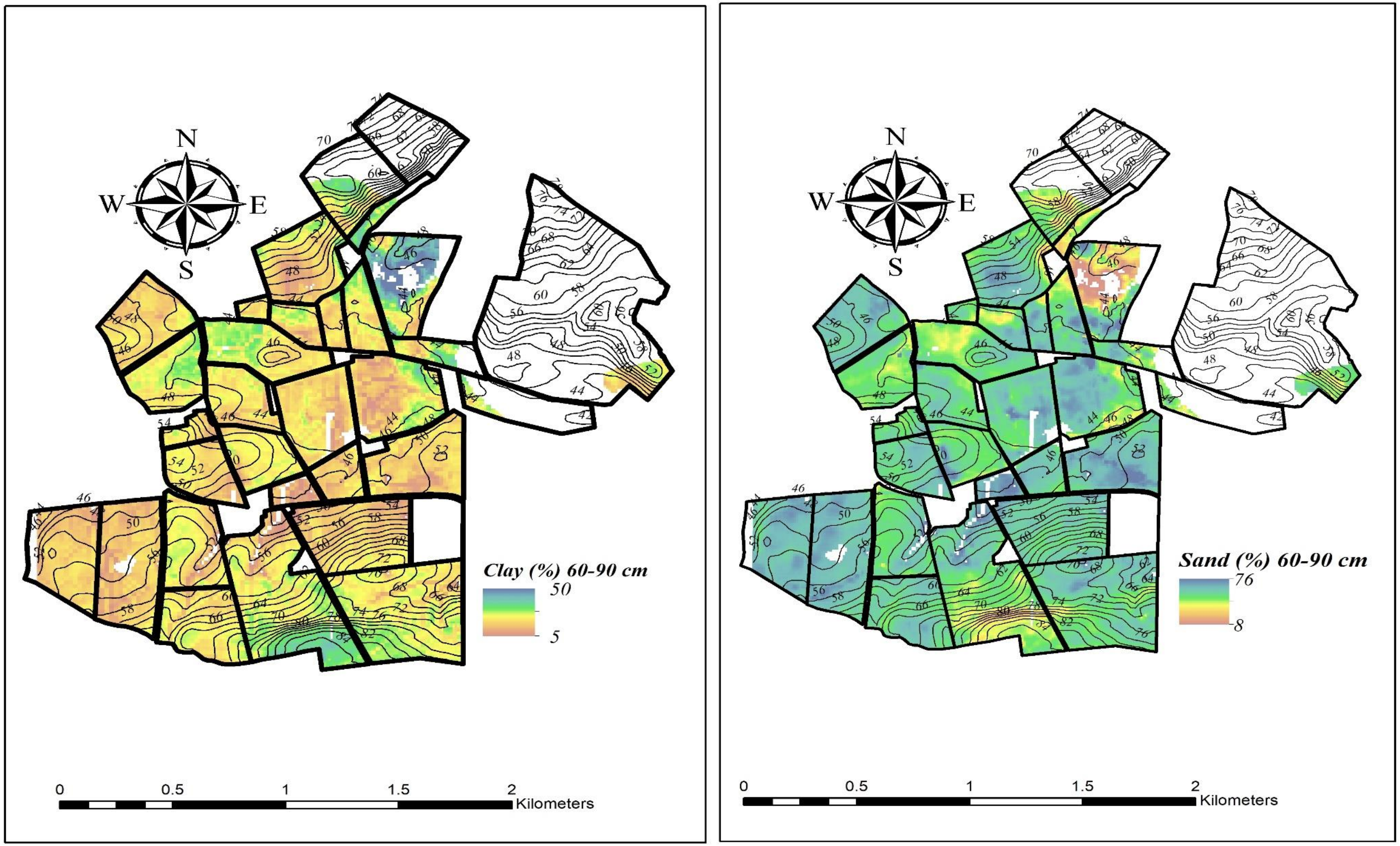


Figure 3. 14c. Map of clay % and sand % in 60-90 cm soil layer (excluded area where depth < 75 cm) superimposed on elevation contour lines.

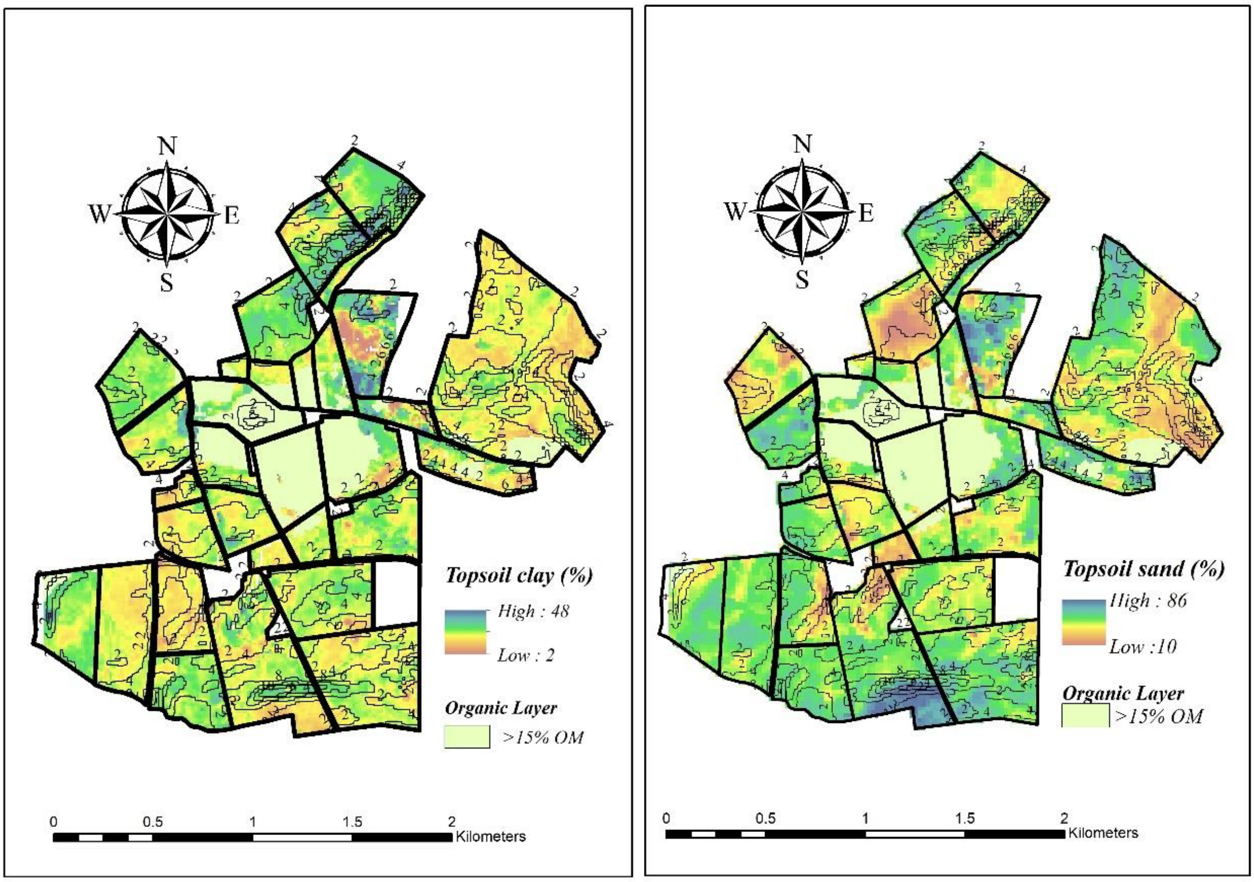


Figure 3. 15. Topsoil predictions (Clay and Sand (%)) on the degree of slope contour lines.

Areas of higher elevation in the map were observed to have higher sand contents (**Figure 3. 14a**). In other words, sand content increases with elevation. However, a different trend was observed in clay contents, and they decrease with elevation. At higher elevation in the study area, sand content varies between 51 and 86 %, whereas clay fraction ranges from 2 to 9 % in the same areas. Sand and clay fractions in the topsoil layer ranges between 29-50% and 4-19% respectively for most of the study area. Maximum sand content was observed at higher elevations due to finer particles' movement from the surface as a result of soil erosion and, likely, through eluviation down the soil profile. This shallow flow did not influence the deep soil layers so less effect of elevation can be seen in deeper layers. The higher sand/clay ratio can also be explained by steeper slopes (**Figure 3. 15**).

3.5 Discussion

In the study, DEM-derived variables and EMI data were integrated with field data collected to develop a model for predicting soil particle size fractions (sand and clay). The comparison of two models, MLR and RF, is reported in **Table 3. 4**. We used the LOOCV approach to evaluate the performance of MLR and RF. The distinction between the leaving one out cross-validation and data splitting validation methods is that the splitting is replicated in cross-validation, making it more effective than data splitting (Brus *et al.*, 2011). If sampling numbers are less and no extra sample is available for validation, leave one out cross-validation of the soil map is suggested, which is clearly preferable to keeping the map unvalidated (Brus *et al.*, 2011). LOOCV is in contrast to the validation set approach, in which the training set is usually around half the size of the original data set. Consequently, the LOOCV alternative does not overestimate the test error rate as much as the validation set approach does. Secondly, the validation approach, can yield different outcomes when performed consistently due to the randomness in the training/validation set splits, while performing LOOCV several times often produces the same results. There is no randomness in the training/validation set splits (James *et al.*, 2013a).

The RF method performed significantly better in the topsoil than the lower layers (except 30-60 cm sand). So many others have published similar findings (Henderson *et al.*, 2005; Vasques *et al.*, 2010; Ugbaje and Reuter, 2013; Akpa *et al.*, 2014). This could be primarily the result of the environmental variables used (Adhikari *et al.*, 2013) or the density of sampling numbers which decrease down the profile (Akpa *et al.*, 2014). In terms of predictive accuracy, sand content had the highest RMSE values at all depths in both the models. This pattern corroborates findings from other studies using RF (Buchanan *et al.*, 2012; Akpa *et al.*, 2014). The RMSE values ranged from 19.26 to 19.67 % for sand, from 11.77 to 12.22 % for silt, and from 13.11 to 13.59 % for clay reported by Akpa *et al.* (2014) were higher than those obtained in the present study. The MLR model performed better in all layers showing a moderate correlation between sand and clay contents, and covariates; the R^2 value for predicting sand was 0.5 and for clay was 0.4 for 0-30 cm soil layer. This means that the regressions explain 50% and 40% of the sand and clay variances, respectively. The R^2 values are similar to those reported by Chagas *et al.* (2016) who used the MLR model for surface soil texture (0-20 cm), but better than 0.32 for sand and 0.36 for clay reported by Liao *et al.* (2013) who used MLR. They attributed this low performance to the variability in landscape and low density of sampling numbers.

The better modelling efficiency in the current study is due to the use of the EMI sensor data as a covariate, as suggested in a number of studies (Cook *et al.*, 1996; Rawlins *et al.*, 2009; Akpa *et al.*, 2014). EMI data was found to be significant in predicting clay and sand contents at all depths of the soil profile. The importance of ECa to reflect soil texture has been reported by others (Waine *et al.*, 2000; Schmidhalter *et al.*, 2001; Domsch and Giebel, 2004).

The RMSE values in MLR for sand are 9, 8.3, and 11.9%, and for clay, RMSE values are 4.3, 5.7, and 8.9 from the 0-30, 30-60, and 60-90 cm layers, respectively. Shahriari *et al.* (2019) reported RMSE of 17.45 and 8.89% for sand and clay, respectively. Another study reported, RMSE values for sand, silt, and clay of 21.4, 17.45, and 6.02 % respectively (Pahlavan-Rad and Akbarimoghaddam, 2018). The RMSE illustrates how much the model could be wrong in the prediction. A model with higher RMSE might over or underestimate the clay and sand % and ultimately could predict the wrong textural class compared to the actual. The dominant texture class in topsoil was sandy silt loam (SSL) in the original data shown in the textural triangle (**Figure 3. 7**) with the maximum number of samples (19). The textural classes calculated from the predicted soil particles have a similar pattern as in the original data (**Figure 3. 16**). The predicted particles represent SSL instead of originally observed sandy loam at one location, which is due to the model underestimating sand contents. One sample of loamy sand and sandy and 3 from sandy silt loam texture from the original dataset has been removed as they were in the area of organic topsoil.

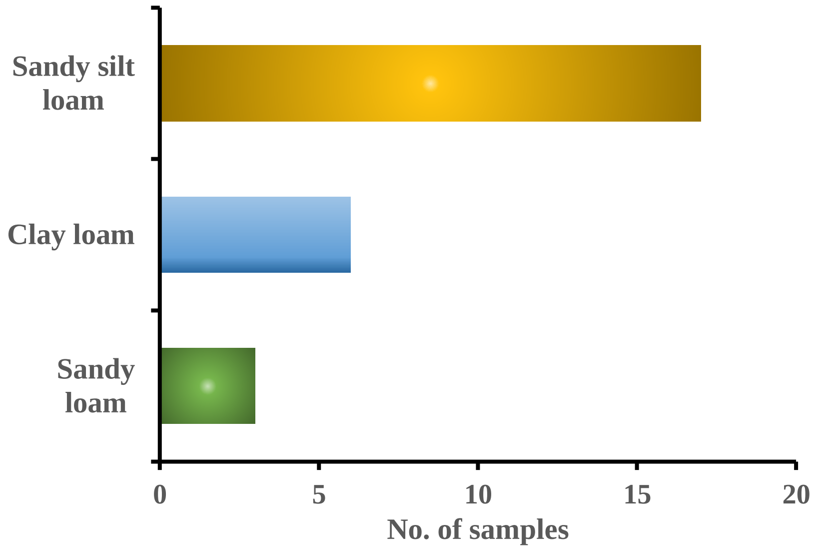


Figure 3. 16 Soil textural classes predicted from sand and clay contents obtains from MLR

There was a significant influence of terrain attributes on the spatial distribution of fractions of the particle size. The importance of terrain attributes in predicting soil properties, especially PSF, has been documented in studies (Thompson *et al.*, 2006; Ließ *et al.*, 2012). The relation between elevation and clay in MLR and slope and sand in MLR and RF is not strong (**Figure 3. 9** and **Figure 3. 10**) in the topsoil profile. However, we also used less important variables because sometimes poorly correlated variables can improve the modelling efficiency to predict soil properties (Bishop and McBratney, 2001; Dematte *et al.*, 2009; Shahriari *et al.*, 2019).

Figure 3. 14a shows the variability of sand and clay % with elevation. We found a maximum sand % in the study area with higher elevation and higher clay contents in depressions. The importance of elevation in topsoil fractions can be attributed to its effect on clay and sand distribution, as reported in other studies (Pahlavan-Rad and Akbarimoghaddam, 2018). Elevation

can influence gravity and water flow, removing fine particles such as clay from higher elevations leaving behind coarse particles (sand). Feng *et al.* (2020) observed relatively high sand content at higher elevations than low-relief neighbouring areas. This relation of sand and elevation with a convex and concave curvature concept has been explained in other studies (Gessler *et al.,* 2000; Ließ *et al.*, 2012). Higher sand/clay ratios can be expected in areas with convex compared to concave curvature due to the removal of fine particles from highly exposed convex areas and their accumulation in concave areas. **Figure 3. 15** Shows the effect of slope gradient on soil particles distribution. In the areas where the slope is steep and water accumulates more, fine fractions are accumulated in these areas. This is due to the erosion and transport of fine particles, which are dominant processes on hillsides, while valley bottoms are typically depositional areas (Gallant and Dowling, 2003).

Soil depth to the bedrock varied across the study area, as shown in **Figure 3. 13**. We found a shallow soil profile on higher elevations than plain areas with a deeper soil profile (> 1m). Sand contents decreased from surface to deep soil layers from 86 to 76%. On the other hand, the maximum values of clay content increased slightly from the top layer (48%) to the bottom layer (50%) of soil. The shallow areas' sandy soil represents the underlying sandstone geology with glacial till deposits covering part of the Fell Sandstone outcrop. The decrease in sand and increase in clay contents down the profile is due to the influence of the factors like surface runoff of light particles from elevated areas to the depression and the eluviation of clay particles down the profile.

3.6 Conclusion

Conventional soil mapping is less reliable than digital soil mapping when spatial variability in soil texture is important. There are fewer chances of reproducibility and modification in conventional soil survey maps based on a person's knowledge and understanding of spatial variability in soil type. On the other hand, DSMs can be reproduced with different modelling approaches and are more reliable in predicting soil spatial variability based on soil-forming factors. Secondly, conventional soil mapping is time-consuming and labour intensive work. About 150-300 soil auger samples would be required in conventional soil mapping to understand soil texture continuity from the study area (4.5 km^2) (Kempen *et al.*, 2012). In contrast, we selected only 31 sampling locations for texture analysis, which has saved time for sampling and analysis. Therefore, DSM is a more efficient and less laborious way to map an area's soil type. However, several studies reported low modelling efficiency in mapping soil texture using just DEM derived terrain attributes as predictors and fewer soil samples. Further improvement in mapping soil texture using the DSM approach is possible with electromagnetic induction data as covariates. We did not find the significance of soil profile depth in predicting soil texture. However, spatial variability in depth is also an important factor in locating the hotspots for nitrate leaching in the study area based on soil texture variability.

A spatial map of soil texture is important to understand variability in the study area and determine the more susceptible locations within the field to minimize nitrate leaching. The available national soil survey map (1:250,000) of England and Wales (Jarvis, 1984) broadly reported coarse to fine loamy soil type in the study area. This classification of soil texture is not enough to explain the effect of texture on nitrate leaching in this catchment. According to the predicted soil texture components, within a distance of 300m, sand and clay contents vary from 56 to 28 % and 8-18%, respectively, in the top layer of soil. The wider range in the sand and clay contents represents soil spatial variability in the study area. Soil profile depth is also observed to be spatially variable. The information of variability in soil profile depth is important while managing the land because areas with more sand and shallow depth to the bedrock, as we monitored in part of the study area, might contribute more in leaching nitrate to the underlying Fell Sand Stone aquifer than deep clay soils. These areas with shallow profile and sandy texture are hotspots and could be easily managed using different strategies on a micro-scale to minimize leaching compared to field scale.

Chapter 4. Effects of Farm Management Practices and Soil Spatial Variability on Nitrate Leaching in the Fell Sandstone Study Area

4.1 Introduction

Nitrogen (N) is an important nutrient in agricultural ecosystems, but it is also a major environmental pollutant (Zhang *et al.*, 2015a). Edaphic and climatic variables, agricultural management practices, and anthropogenic activities significantly impact N pollution (Huang *et al.*, 2017). N loss and transformation in agricultural systems are complicated and influenced by various factors (Salazar *et al.*, 2009) such as land use, soil type, soil thickness etc. Land-use practices can alter nitrate-N (NO_3-N) inputs from the surface, recharge sources and mechanisms (Wilson, 2015). The increased farming intensity and higher NO_3^- leaching from agricultural systems were associated with growing groundwater NO_3^- levels in numerous cases (e.g., (Suthar *et al.*, 2009; Exner *et al.*, 2010; Huang *et al.*, 2011; Zhang *et al.*, 2013; Ahada and Suthar, 2018).

NO_3^- is a water-soluble ion; excess NO_3^- is easily transported through the soil profile by percolating water and accumulates in the aquifers. The location of an aquifer, rainfall and irrigation, organic matter content, and other soil chemical features influence the fate of NO_3-N in agricultural catchments (van Duijvenboden and Loch, 1983). Soil physical properties, such as hydraulic conductivity, water holding capacity, texture, soil structure, thickness, and pore characteristics, influence water flow and NO_3-N leaching from the root zone to the aquifer. Due to the soil porosity, soil water travels downward more quickly in sandy soils than clayey soils, causing NO_3-N to move to deeper levels. In soils with a higher water holding capacity, NO_3^- leaching is less likely to occur (Knox and Moody, 1991).

The combined impacts of the soil N cycle and soil hydrological processes result in NO_3^--N leaching (Osaka *et al.*, 2010; Zhang *et al.*, 2018). The soil NO_3-N pool available for leaching is directly determined by the soil N cycle, particularly the nitrification process (Osaka *et al.*, 2010). Soil hydrology influences NO_3-N leaching in two ways:

(i) from a biochemical perspective, soil water reduces the soil air-filled pore space, affecting the redox reaction of soil N and changing the soil NO_3-N content available for leaching by denitrification (Stoliker *et al.*, 2016; Mekala and Nambi, 2017).

(ii) from a physical point of view, soil water flow is a major driving force in NO_3-N leaching (Donner *et al.*, 2002).

As a result, to understand NO_3-N leaching, knowledge of both the soil-N cycle and soil hydrology must be acquired appropriately.

Improving water and nitrogen use efficiency to reduce water and nitrogen losses are recommended to improve the sustainability of agricultural practices (Luo *et al.*, 2014; Adegbeye *et al.*, 2020). Even if sufficient efforts to limit NO_3-N leaching are performed, once it pollutes the aquifers, they will remain contaminated for decades (WHO, 2007). The EU Water Framework Directive states that required measures must be adopted to decrease NO_3-N leaching through the soil profile and prevent pollution in aquifers (O'Shea and Wade, 2009). However, identifying areas at risk of NO_3^- contamination is a crucial step in deciding on the best alternative management techniques for aquifer protection (Masetti *et al.*, 2008). Previous research has reported the spatio-temporal fluctuations of NO_3-N leaching flux at various geographic (farm and regional) scales (e.g.,(Baram *et al.*, 2016a; Dwivedi *et al.*, 2018). To define the spatio-temporal fluctuations of NO_3-N leaching, the concepts of hot spots and moments were used (Kurunc *et al.*, 2011; Dwivedi *et al.*, 2018). Hot spots of NO_3-N leaching were typically related to coarse-textured soils, shallow water tables, and converging topography, and hot moments were generally observed after rainy events and N fertiliser application (Kurunc *et al.*, 2011; Baram *et al.*, 2016b).

Groundwater nitrate concentrations in the UK were reported to be rising at an average of 0.34 mg NO_3^- l^{-1} annually for the 191 sites based on 309 datasets analysed by Stuart *et al.* (2007). The Lincolnshire Limestone aquifer had the highest average trend (0.96 mg NO_3^- l^{-1}annually); Chalk and Permo-Triassic sandstone aquifers had average trends of 0.38 mg NO_3^- l^{-1} and 0.44 mg NO_3^- l^{-1}, respectively. The Fell Sandstone formation is used in three main areas of England, as the ground source for the supply of public water. The largest is near Berwick, where it serves as the only source of public water supply, and since the early 1900s, a string of abstraction wells have extended southward from Berwick Tweed mouth at Dock Road to the outlying rural hamlet of Felkington to serve Berwick upon Tweed's increasing water needs (Markou, 2013). The Environment Agency categorise the Fell Sandstone aquifer as a Principal aquifer (**Figure 1.3**). Fell Sandstone is the only source of water supply (Northumbrian Water abstract public water supplies) to the town of Berwick upon Tweed and the surrounding area (Jeremy and Melissa, 2021). The Nitrate-N concentration in most of the Northumbrian Water (NW) abstraction boreholes and Environment Agency observation boreholes exceeded the drinking water limit of 50 mg l^{-1} (increase in the nitrate concentration begins 1996 to 2007 from different observation boreholes in the area) as Nitrate. Diffuse agricultural pollution is assumed to be the major source of nitrate in the Fell Sandstone aquifer, although point sources such as manure heaps may play a role. Land use is mainly agricultural, with farmers growing arable crops under both conventional and organic practices, and some livestock grazing. Superficial geology in the area is spatially variable, comprising areas of exposed sandstone bedrock, and areas with thin glacial till.

The aquifer is vulnerable to contamination from the surface and is currently designated as a Nitrate Vulnerable Zone. Therefore, the aims of this study were to investigate i) the effect of agricultural practices, particularly crop type, autumn ploughing, and fertilisation, in organic and conventional farming systems, on NO_3-N leaching, ii) the effect of soil texture variability and depth to the bedrock on drainage volume and NO_3-N leaching and, iii) the influence of wet and normal years in terms of rainfall on NO_3-N leaching.

4.2 Methodology

4.2.1 Site description and monitoring locations

The study was conducted on four farms near Berwick upon Tweed (*Chapter 3*) in northern Northumberland, the UK to monitor nitrate leaching from agricultural catchment to the Fell Sandstone aquifer. The study area covers 4.2 km^2 within a catchment affected by nitrate pollution. The soil in the study area from three layers (0-30, 30-60 and 60-90 cm) varies in texture from sandy to clay loam with soil depth to the bedrock in the range from 30 to >120 cm. To monitor NO_3-N leaching initially, 24 locations were selected in the first drainage season (2017/2018) based on the variability in soil apparent electric conductivity (ECa). **Figure 4. 1** shows the locations of monitoring points in different fields. A subset of 8 locations was selected for sample collection for the next two years based on soil type, depth to the bedrock and NO_3-N concentration in soil solution observed during 2017/2018.

Data about the land use for both organic and conventional farming was collected through interviews with the local farmers and is summarised in **Table 4. 1**. During the first drainage season, nine (809, 811, 813, 815, 816, 817, 818, 834 and 835) sites were selected from an organic farm and fifteen from the conventional farming system. For the monitoring in 2018/2019 and 2019/2020, six locations were selected from the conventional farming system and two from the organic system. The crop rotation in the organic farming system consisted of winter/spring cereals alternating with annual clover leys and in the conventional farming typical arable rotations of winter/spring cereals or oilseed rape with some other crops included (e.g. potatoes).

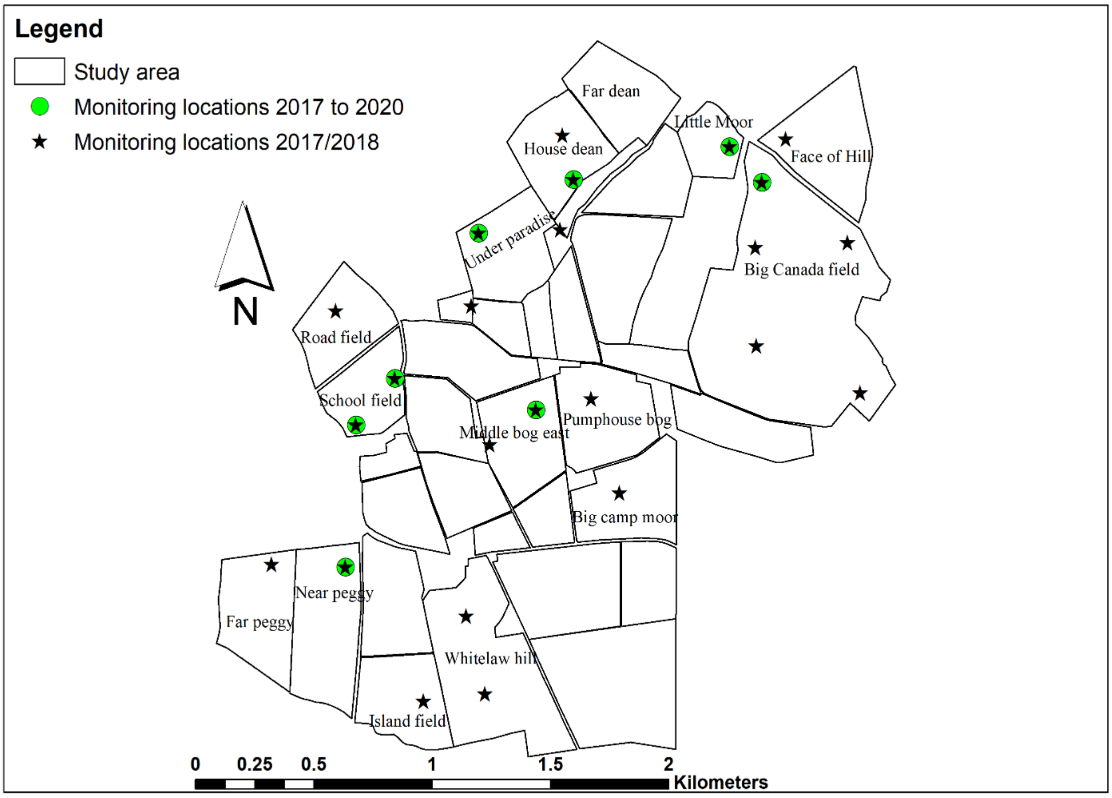


Figure 4. 1 Map of the study area fields indicating locations monitored for nitrate leaching during the first drainage season (2017/2018) and a subset of fewer locations that were monitored for three drainage seasons (from 2017 to 2020).

Table 4. 1 Details of the cropping sequence and nitrogen inputs during the monitoring period from 2017 to 2018 at the 24 sites and eight sites from 2017 to 2020, and previous crops.

Site ID	Previous crop	Crop 2017/2018	Nitrogen input (2017/2018)	Crop 2018/2019	Nitrogen input (2018/2019)	Crop 2019/2020	Nitrogen input (2019/2020)
809	Spring wheat (harvested 24.09.2017)	Spring barley (drilled 07.04.2018)					
811	Spring barley (harvested 01.09.2017)	Spring barley (drilled 20.04.2018)	poultry manure (22.04.2018)				
813	Clover (ploughed 06.09.2017)	Winter wheat (14.10.2017)					
815	Clover (drilled 23.05.2017)	Clover					
816	Clover (drilled 27.06.2016)						
817 and 818	Spring triticale (harvested 15.10.2017)	Clover (drilled 30.05.2018)		Clover		Clover/Spring oats	
819	Winter barley	Winter oilseed rape (drilled 22.08.2017)	180 kg N ha^{-1}				
820	Winter wheat	Winter wheat	Urea (200 kg N ha^{-1})	Fallow		Fallow	
821,822, 823, 824 and 825	Peas	Winter wheat (drilled 06.09.2017)	180 kg N ha^{-1}	Winter wheat (drilled 19.09.2018)	185 kg N ha^{-1}	Winter oilseed rape (drilled 28.08.2019)	210 kg N ha^{-1}

826,827 and 828	Grass	Grass	Cattle FYM (22.2 t/ha)	Grass		Grass	
829	Spring barley (harvested 05.09.2017)	Winter barley/stubble turnip	AN & Cattle FYM (188 kg N ha^{-1}, 22.2 t ha^{-1})				
830	Grass	Grass		Grass		Grass	
831	Potatoes (harvested 10.10.2017)	Winter wheat (drilled 22.10.2017)	240 kg N ha^{-1}				
832 and 833	Winter wheat (harvested 15.08.2017)	Potatoes (drilled 28.03.2018)	250 kg N ha^{-1}	Winter wheat (drilled 24.09.2018)	230 kg N ha^{-1}	Winter wheat (drilled 22.09.2019)	250 kg N ha^{-1}
834	Spring oats (harvested 13.09.2017)	Clover (drilled 23.05.2018)		Clover		Clover/spring barley	
835	Clover (ploughed Feb-2018)	Spring barley (drilled 29.03.2018)					

4.3 Sampling Soil Solution with Porous Ceramic Cups

Ceramic cup samplers are commonly used in agriculture to collect soil solution samples for NO_3-N analysis. The method of preparation and installation followed in the study is described in detail by Curley *et al.* (2010). SDEC SPS 200 sampling tubes were used in this study, measuring 110 cm in length and 31 mm in diameter. Cups were first rinsed with deionized water three times before field installation and then put in a container of deionized water for cleaning purposes, and a vacuum was applied. Three days later, the cups were drained and washed with diluted 1 M hydrochloric acid before rinsing with deionized water again. In the area, a gouge auger with a diameter equal to the cup was used to ensure good hydraulic contact between ambient soil and the sampler (Lord and Shepherd, 1993; Weihermüller *et al.*, 2007). Vertical auger holes were drilled in the soil for porous cup installation to a depth of 90 cm or an achievable depth. A paste of fine silica sand and water was prepared and poured into the bottom of the hole to make good contact between the soil and the ceramic cup. The cup was then inserted into the hole and firmly pressed into the sand/water mixture. Moistened bentonite clay was then applied to the top 10 cm between the tube and the surrounding soil to avoid preferential flow of water down to the sampling area. Immediately after installation, suction of 80 kPa was applied using a hand pump through an insertion tube bung (**Figure 4. 2**) and left for a week for soil moisture recharge and the first sample was then discarded.

Figure 4. 2 Porous ceramic cup in the field

Soil water samples were collected during the drainage season for three years (2017-2020). Twenty-four porous cups were installed in the first year (one at each location) and during the second and third years, 16 porous cups were installed at eight locations (8 x 2 with a distance of 1 m between the cups). On each sampling occasion a suction of 80 kPa was applied to each porous cup using the bung and the hand pump and left for 2 to 4 hours. The bung was then removed, a 5 mm collection tube was inserted down the pipe and then partly pulled to prevent adhesion to the ceramic surface. The tubing was connected to a conical flask from which the hand pump was attached by a double holed bung, providing a vacuum. Water was then drawn up the collecting tube and into the conical flask using the suction pump until the porous cup was drained. The sample volume was recorded and then moved into a numbered storage container. Bottled samples were frozen at -20^{o}C until analysis for nitrate concentration. Samples were then sent to Environment Agency for nitrate concentration analysis using the Discrete Analyser following the procedure in **Appendix 2**.

4.3.1 Soil moisture characteristics

Intact soil cores were collected from selected locations (**Figure 4. 3**) from 8 to 14 February 2019. Three replicated soil cores were collected from each depth representing 0-30, 30-60 and 60-90 cm soil layers. Each sample was taken by gently hammering a core into the soil with the core-top 1–2 cm below the soil surface; then the core was extracted after removing surrounding soil from the core using a trowel. Extra and loose soil at the two sides of the core was peeled off using a knife before tightly packing the core with plastic lids.

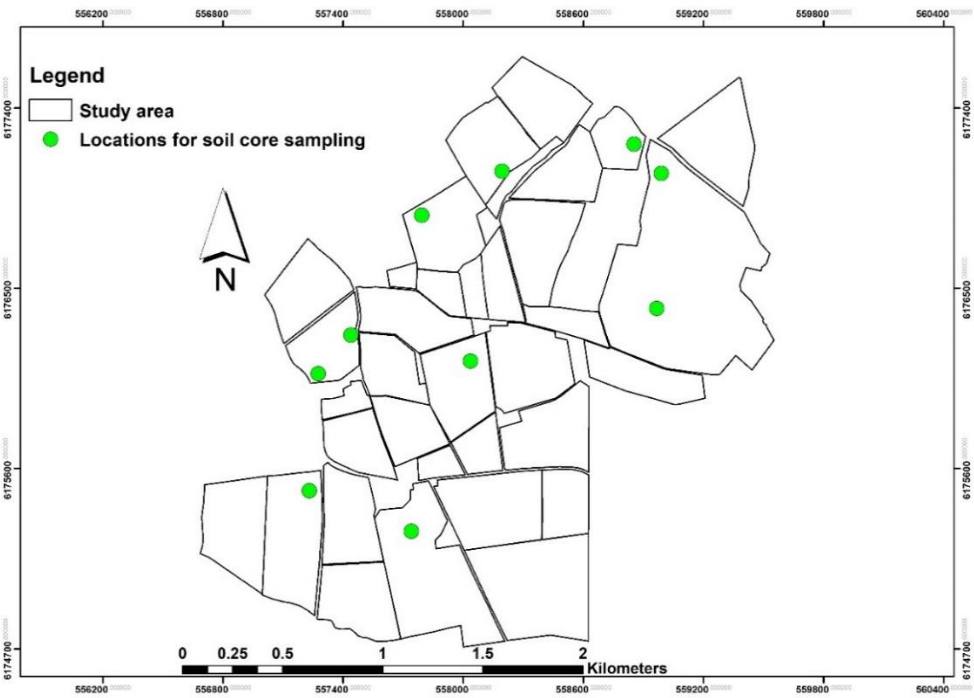


Figure 4. 3 Locations in the study area used to install soil moisture sensors and core sampling for soil moisture characterisation

The soil cores were transported to an external laboratory for determination of soil moisture characteristics following the pressure plate protocol attached in **Appendix 3**.

4.3.2 Drainage estimation and nitrate leaching calculation

Cumulative drainage was calculated for the hydrological (rainfall begins after 1st Oct to re-charge groundwater reserves) years 2017/2018, 2018/2019 and 2019/2020 using daily meteorological data and estimated actual evapotranspiration. The field capacity (FC) values for each soil layer (0-30, 30-60 and 60-90 cm) was calculated at 0.1 bar (10kPa) and permanent wilting point (PWP) at 15 bar (1500kPa). Available water contents were then calculated between FC and PWP to initiate the drainage model (complete results in **Appendix 4)**. Daily rainfall and potential evapotranspiration (ETp) data were received from the Environment Agency. Crop evapotranspiration (ETc) was calculated using crop coefficient (Kc) values derived from FAO-56 for the initial, mid, and end growth stages for crops.

Vertical drainage was calculated using data for inputs (rainfall and irrigation in mm), outputs (actual evapotranspiration in mm), soil moisture deficit (SMD) and available water content, using a simple water balance approach. The model was initiated to calculate water balance six months (April-2017) before the first hydrological year (Oct-2017) to avoid any uncertainty in the drainage estimation. Coefficient (Ka) for the actual evapotranspiration (ETa), was computed as 1 as long as the SMD on the previous day was less than half of the AWC, after which Ka starts decreasing. Crop evapotranspiration (ETc) and actual evapotranspiration (ETa) were calculated as

$$ETc = Kc \times ETp$$

$$ETa = Ka \times ETc$$

The trapezoidal rule was used to measure NO_3-N loss for each drainage season. The area under the plot of NO_3-N concentrations (mg l^{-1}) against cumulative drainage (mm) is the loss in kg NO_3-N ha^{-1}. The trapezia from successive sampling concentrations (C1, C2 mg l^{-1}) and drainage volume (V1, V2 mm) was used in the following equation,

Nitrate-N Leached (kg NO_3-N ha^{-1}) $= 0.5 \times (C1 + C2) \times (V1 - V2) \div 100$

4.3.3 Statistical analysis

A multiple linear regression (MLR) analysis was performed to model the relation between the factors (soil depth, topsoil sand%, soil organic matter and drainage volume) and NO_3-N leaching. The analysis was performed using the lm package in R software (Team, 2021b). The *P*-

values were reported in the results to represent the significance of factors on the response variable (NO_3-N).

4.4 Results

4.4.1 Weather conditions and soil drainage during the monitoring period

Daily rainfall and potential evapotranspiration (ETp) from April 2017 to September 2020 is depicted in **Figure 4. 4.** The total annual rainfall in each hydrological year was recorded as 621.1 mm, 714 mm and 594.2 mm for 2017/18, 2018/2019 and 2019/2020 respectively. The annual rainfall during 2019/2020 was similar to recorded mean annual rainfall (1981-2010) which was around 589 mm (*Chapter 3*). Compared to the mean annual rainfall, 2018/2019 was a wet hydrological year with 21% more rainfall. The increasing and decreasing trend in the daily ETp was similar for all three hydrological years during the experimental period.

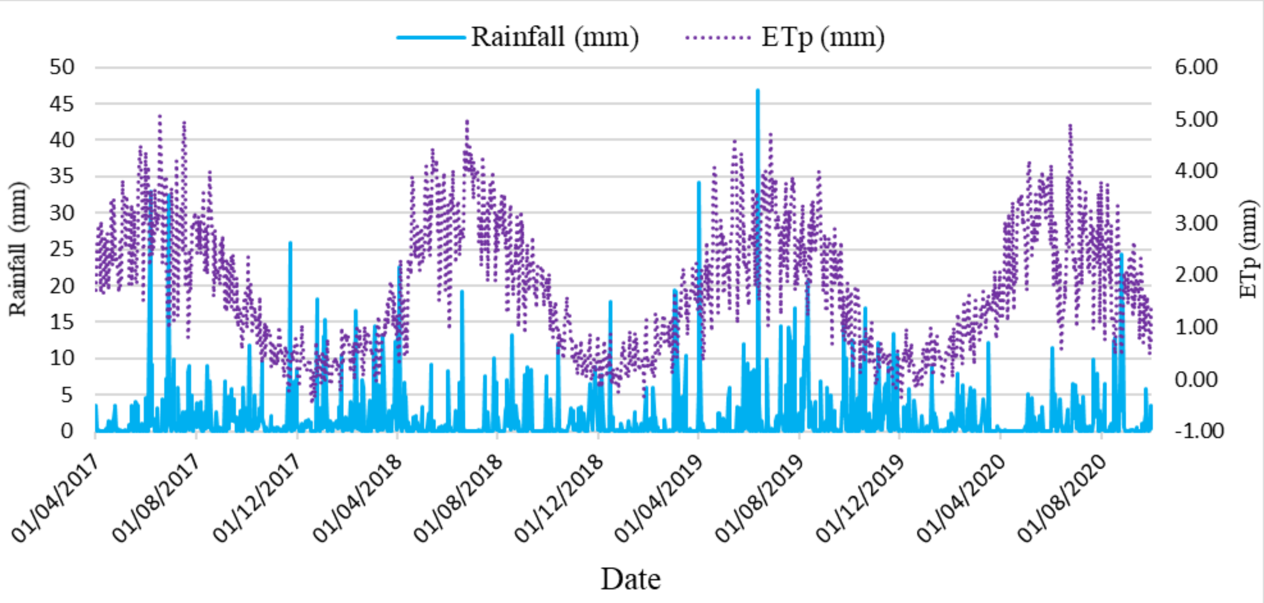


Figure 4. 4 Daily rainfall (mm) and daily potential evapotranspiration (mm) from April-2017 to September-2020 (end of hydrological year 2020) in the Fell Sandstone study area

Plant available water contents (AWC) at field capacity from maximum achievable soil thickness and different soil textures are shown in **Table 4. 2**. The half of AWC was used as the threshold level for plants to take up water from the soil without restriction. These values of AWC and threshold levels were then used to calculate drainage volume. Deep soil with less sand % held more water, ranging from 69 to 306 mm, compared to the medium and shallow soils. Maximum AWC was determined from location 817, where 138 mm out of a total of 306 mm was observed from the topsoil layer with 33% sand and 11.8 % clay contents. AWC from site 820 was 54% less than 817 with similar soil thickness but the topsoil sand % at 820 was 46%. The AWC from the locations with medium soil thickness (60 cm) ranged from 42 to 51 mm. The locations 829 and 832 with similar soil texture and profile depth were determined to hold 42 mm of water. Whereas the soil from location 834 had a higher AWC having lower sand contents compared to 829 and more clay contents than 832.

Table 4. 2 Available water contents (mm), threshold level of soil water (limit after which ETa < ETp), soil thickness and soil texture from ten locations selected for soil moisture characterisation

Site ID	Soil profile thickness	Soil texture	Available water contents (AWC) at field capacity	Threshold level for soil moisture deficit (SMD)
	cm		mm	mm
809	0-30	SASILO	75	37
	30-60	CLLO		
	60-90	SACLLO		
817	0-30	SASILO	306	153
	30-60	SASILO		
	60-90	SALO		
820	0-30	SASILO	138	70
	30-60	SALO		
	60-90	CLLO		
821	0-30	SALO	66	33
823	0-30	SASILO	69	34
	30-60	CLLO		
	60-90	SASILO		
827	0-30	CLLO	27	14
829	0-30	SASILO	42	21
	30-60	CLLO		
832	0-30	SASILO	42	21
	30-60	CLLO		
833	0-30	SASILO	81	40
	30-60	SILO		
	60-90	SASILO		
834	0-30	SASILO	51	25
	30-60	SASILO		

SASILO = Sandy silty loam, CLLO = Clay loam, SACLLO = Sandy clay loam, SALO = Sandy loam, SILO = Silty loam

Daily drainage (mm) was calculated for each hydrological year during the experiment. Drainage values vary in different soil types and soil profile depths. **Figure 4. 5** represents daily drainage (mm) during hydrological years from eight locations monitored for three seasons. The highest cumulative drainage was estimated during 2019/2020. Overall cumulative drainage was lowest from all the sites during the 2018/2019 hydrological year despite the maximum rainfall (714 mm). However, total rainfall during the drainage months (Oct to mid-April) was recorded 426.3 mm in 2017/2018 and a minimum of 317 mm in 2018/2019 therefore, 2017/2018 was a wet winter with the highest rainfall during drainage months. Drainage was lower at locations 817 and 820 (36 and 189 mm in 2018/2019) during three years of monitoring because the soil was much drier with maximum SMD at these sites (**Appendix 5**), so that more rainfall was needed to restart drainage. Effect of land use on actual evapotranspiration (ETa) and soil moisture deficit (SMD) was more obvious than on drainage (**Appendix 6**).

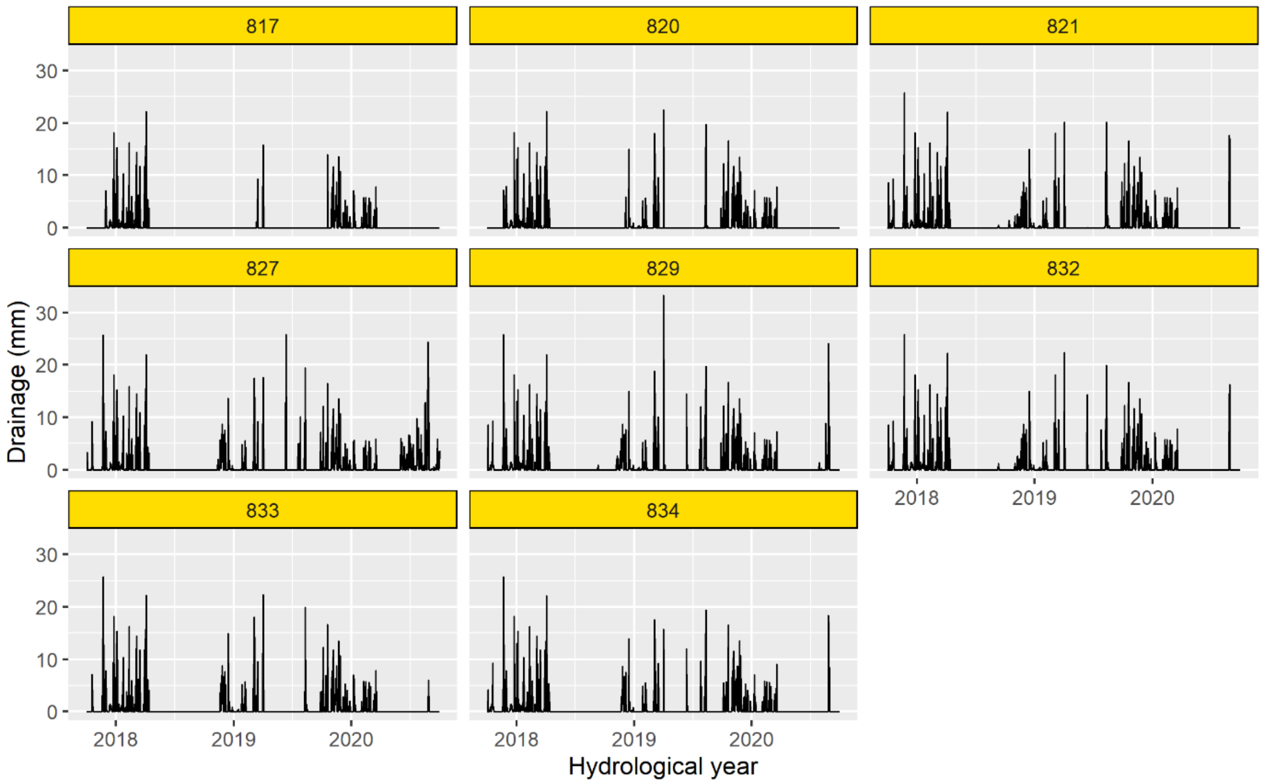
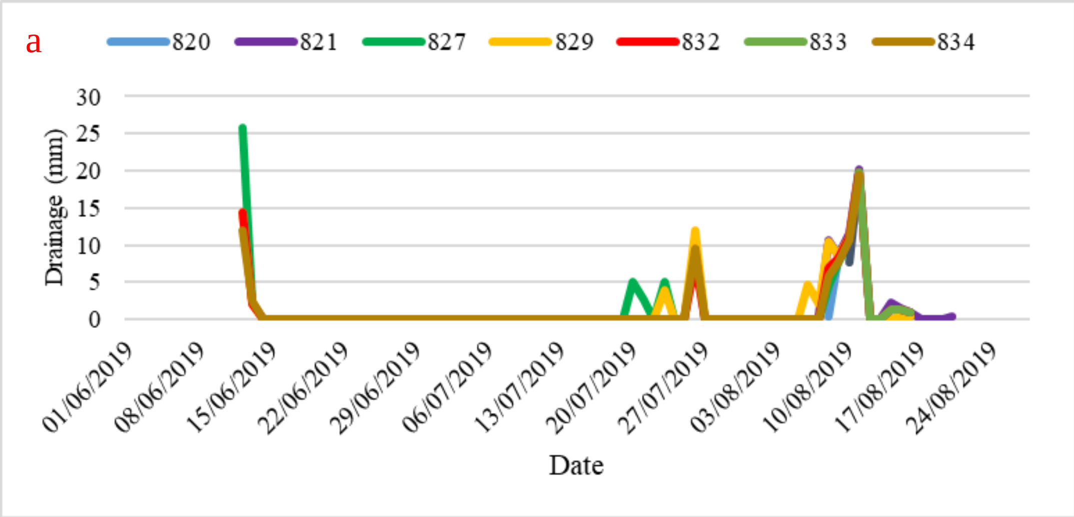


Figure 4. 5 Drainage (mm/day) during the hydrological years starting from October-September in 2017/2018, 2018/2019 and 2019/2020 for the eight locations monitored for three drainage seasons

Drainage during the summer months (i.e. outside normal drainage season) was also observed in 2018/2019 and 2019/2020 hydrological years from some locations as shown in **Figure 4. 6**. After a day or two of heavy rainfall in early June 2019, the maximum amount of drainage 25.7 mm was observed from the shallow soil profile (827) and locations 832 and 834 (60 cm soil profile depth). More rainfall in early August 2019 caused drainage in almost all the locations except 817. Some summer drainage was also estimated during 2019/2020 particularly in August from 827, 829, 832 and 834 sites. However, continuous drainage from 827 was modelled throughout the summer (June to August 2020) with maximum values, 24.4 mm/day at the end of August.



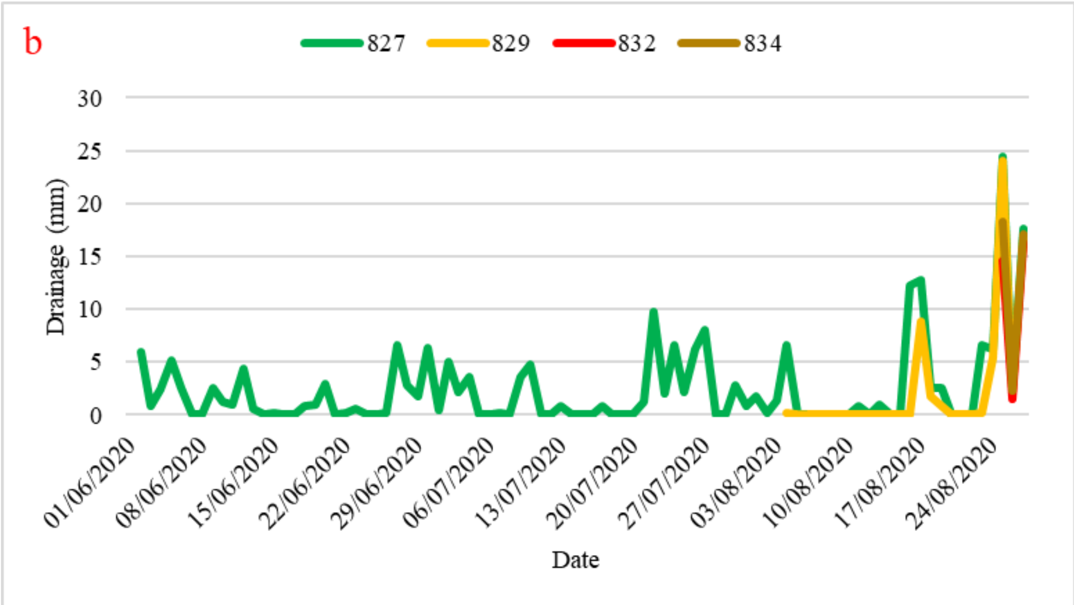


Figure 4. 6 Daily drainage (mm) determined from seven locations during summer-2019 (a) and from four locations during summer- 2020 (b).

4.4.2 Nitrate-N losses from different locations during the three drainage seasons

NO_3-N concentrations vary in soil solution collected from different locations (**Figure 4. 7**) with different soil types, land use and N input during the 2017/2018 drainage season. The maximum amount of NO_3-N leaching was estimated from locations 832 and 833 (139.4 and 128.9 kg ha^{-1}). This field had been left fallow over the drainage season after winter wheat harvesting in

2017. After this amount, the maximum NO_3-N lost via leaching in 2017/2018 was estimated at 96.9 kg ha^{-1} from the organically managed winter wheat sown after two years of clover (813). The minimum amount of NO_3-N lost due to leaching was estimated from grass fields, ranging from 2.5 to 6.5 kg N ha^{-1}during three years of monitoring.

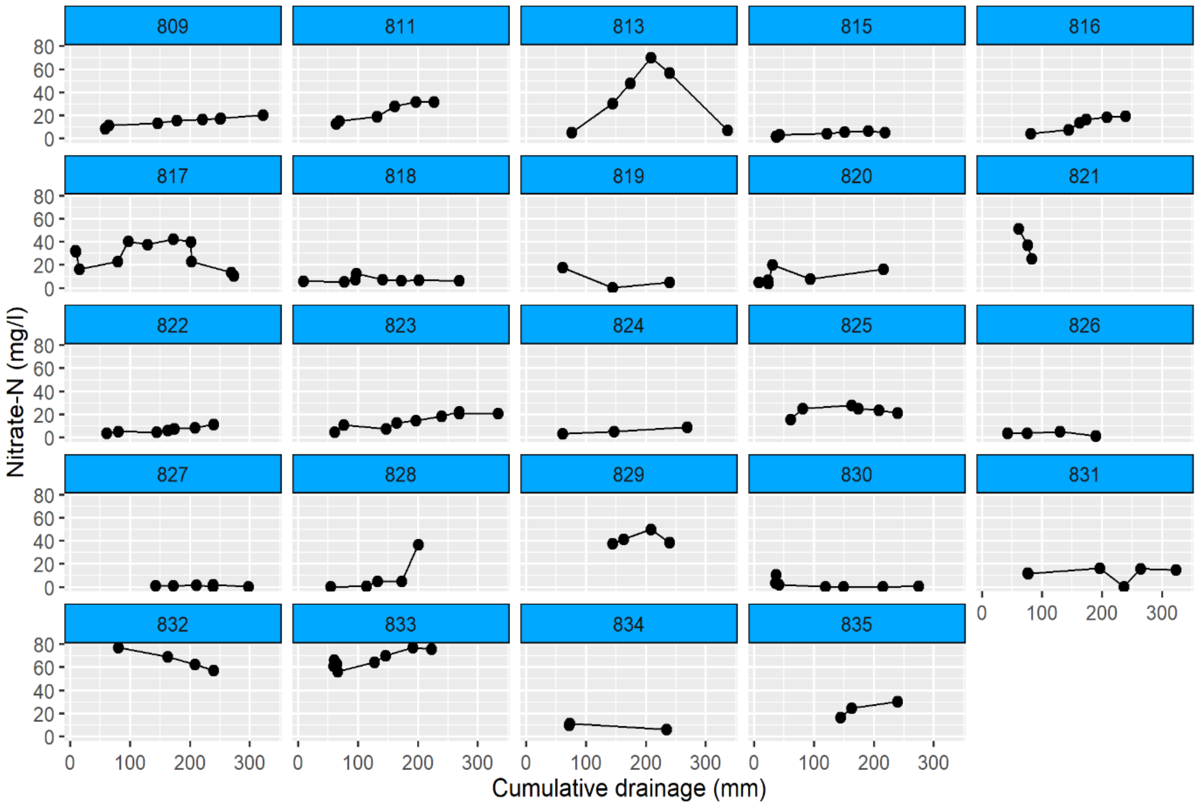


Figure 4. 7 Nitrate-N (NO_3-N) concentration in soil solution against cumulative drainage (mm) during 2017/2018, used to determine NO_3-N (kg ha^{-1}) leaching from twenty four locations. (No values obtained on dates when water extraction was not possible from ceramic cups)

Monitoring of fewer locations during the 2018/2019 and 2019/2020 drainage seasons also demonstrated variation in NO_3-N concentration in soil solution and leaching as shown in **Table 4. 3.** During both the drainage years, maximum NO_3-N leaching was observed from 833. Winter wheat was drilled in this particular field in September 2018 after potato harvesting. Rates of N application were relatively high with the 2018 crop of potatoes receiving a total of 250 kg N ha^{-1} and the 2019 crop of wheat receiving 230 kg N ha^{-1} (**Table 4.1**). The leaching losses from 820 vary greatly from 2018/2019 to 2019/2020. For this particular location, porous cups were installed at the fallow side of the field in both the drainage seasons. However, the difference in NO_3-N is due to the low numbers of soil solution samples collected during 2019/2020 (porous cups removed for a farmer to prepare the field for Brussels sprouts planting).

The *P –values* of multiple linear regression (MLR) are shown in **Table 4. 3**, despite numerical differences, no statistical significance of any of the factors, soil profile depth (cm), soil organic matter, cumulative drainage volume (mm) and topsoil sand % was found on NO_3-N leaching with *P –values* >0.05.

Table 4. 3 Mean NO_3-N (kg ha^{-1}) and standard deviation (SD) during drainage season 2018/2019 and 2019/2020 from eight locations. P-values represents the results of multiple linear regression (MLR) including topsoil sand, depth and drainage as predictors.

Site ID	NO_3-N leaching in kg ha^{-1} (2018/2019)	NO_3-N leaching in kg ha^{-1} (2019/2020)
817	5.50 (0.2)	3.34 (1.0)
820	74.73 (39.7)	2.41 (0.5)
821	8.14 (1.1)	13.68 (3.3)
827	19.20 (0.4)	11.20 (1.7)
829	11.70 (4.2)	72.10 (14.4)
832	25.12 (4.1)	56.58 (3.8)
833	110.52 (1.8)	105.30 (16.4)
834	22.63 (4.2)	22.63 (6.5)
P-Value		
Soil Profile depth	0.197	
Topsoil sand (%)	0.192	
Soil Organic matter (%)	0.286	
Drainage volume	0.314	

Out of the total of 24 locations monitored during the first year, nine sites (in three fields) were chosen to evaluate the effect of soil texture variability and soil profile depth as shown in **Figure 4. 8**. The amount of NO_3-N leached from five locations (821, 822, 823, 824 and 825) in the Big Canada field were respectively 24.5, 12.9, 42.0, 13.6 and 48.8 kg ha^{-1}. The topsoil texture of site 821 was sandy loam with a shallow soil profile. The concentration of NO_3-N (mg l^{-1}) in the soil solution from this particular site was always higher than any other location in the same field, however, the total leaching losses calculated were apparently lower due to fewer soil solution samples available for N concentration analysis from this site. Another site with fewer samples was 824, the only location where the soil was a deep clay loam (0-90 cm), the NO_3-N concentration from this site never exceeded 10 mg l^{-1}. However, both of these locations were excluded from the MLR due to fewer samples. The maximum NO_3-N leaching was recorded from 825 which had a more sandy soil texture (0-60 cm soil profile).

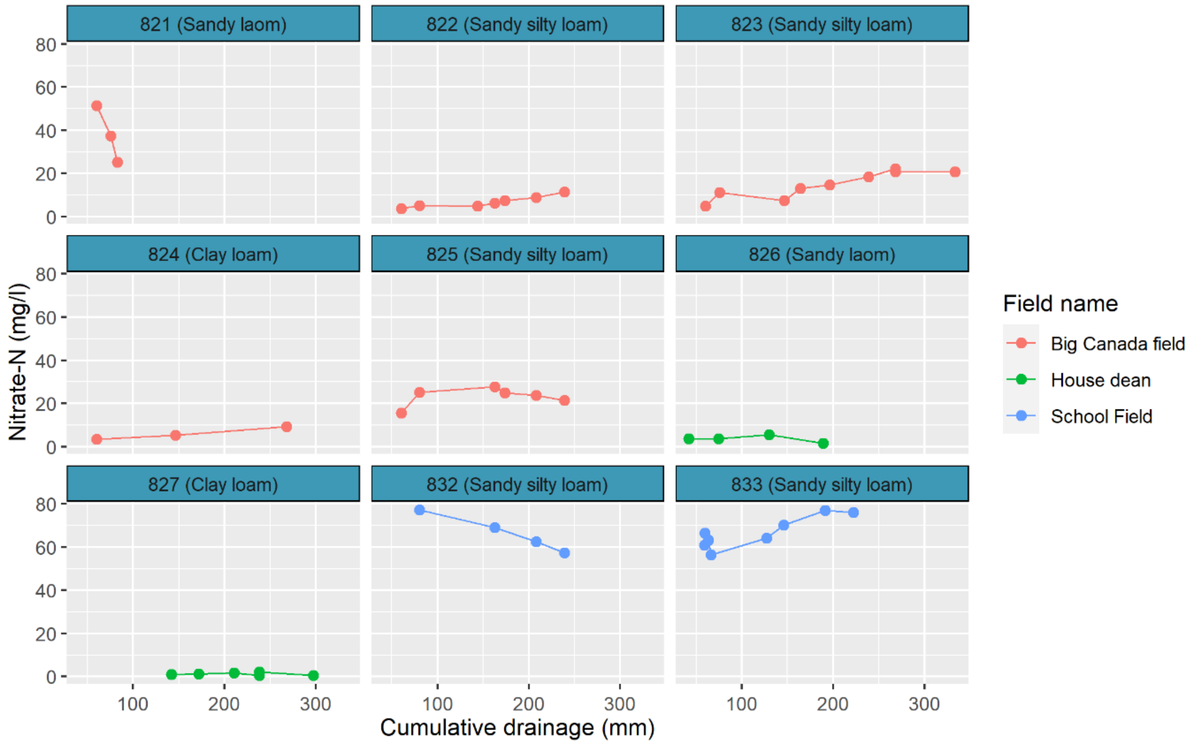


Figure 4. 8 Nitrate-N (mg l^{-1}) concentration in soil solution against cumulative drainage from locations in three fields (selected for similar land use for two or more locations), different top-soil texture and soil profile depth

4.4.3 Nitrogen leaching and land use

The average amount of NO_3-N (kg ha^{-1}) from different land-use ranged from 5.12 to 98.04 kg ha^{-1} during the drainage season 2017/2018 as shown in **Figure 4. 9**. The land use was separated based on organic and conventional agricultural practices. Maximum N losses were recorded from the field left fallow (conventionally managed) for potato cultivation after winter wheat harvesting in August 2017 (832 and 833). The minimum amount of NO_3-N leaching was measured from grassland and winter oilseed rape (WOSR) during the 2017/2018 drainage season. The minimum losses from WOSR might be due to the early sowing of the crop and root developed to uptake available N from the soil.

The maximum average losses of NO_3-N (kg ha^{-1}) during 2018/2019 monitoring were estimated from fallow fields (conventionally managed). The average NO_3-N leaching losses from clover were 60% less in 2018/2019 compared to 2017/2018. This reduction might be due to well-established clover (sown in May 2018) at the time of winter drainage. The NO_3-N was further reduced by 8% in 2019/2020 compared to 2018/2019 from clover.

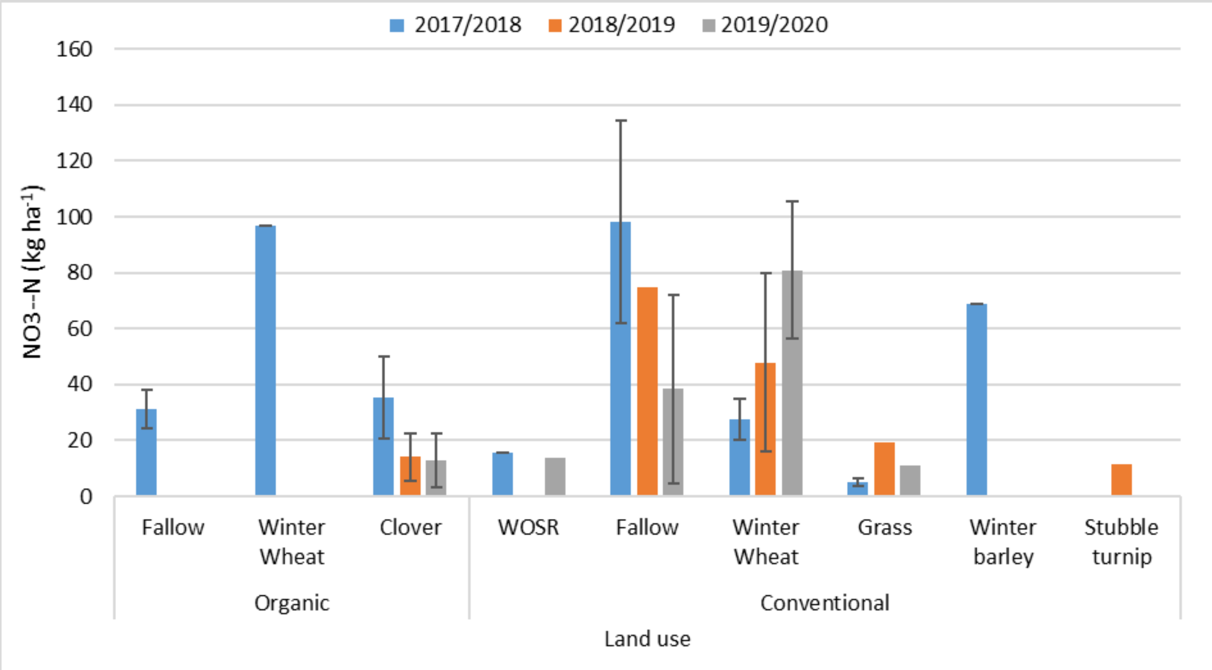


Figure 4. 9 Average NO_3-N (kg ha^{-1}) from organic and conventional management during three drainage seasons of monitoring. X-axis labels indicate crop growing during the drainage season. The error bars represent the standard error of means.

4.5 Discussion

The study was designed to evaluate the effect of different factors on NO_3-N leaching from an agricultural catchment. Different methods can be used to estimate NO_3-N losses from the soil, including soil core sampling, soil solution sampling using porous cups and sampling drainage water using a lysimeter. When porous ceramic cups, lysimeter, and the soil core sampling technique were compared, the total amount of NO_3^- leached during winter from three methods, was not significantly different (Webster *et al.*, 1993). The method of soil solution sampling from porous cups was used in this study to determine NO_3-N in soil solution and to estimate NO_3-N losses via leaching. Porous ceramic cups are easy to install and use directly in situ for collecting soil solution. Because no large soil holes or extraction methods are necessary, therefore costs are comparatively low (Wang *et al.*, 2012b).

The study found that sites, soil properties, and preceding crops all played a role in soil NO_3-N concentration and leaching. During the 2017/2018 drainage season total rainfall was highest (426.3 mm), representing 34% and 26% more than the rainfall in drainage seasons 2018/2019 and 2019/2020 respectively. Due to the heavy rainfall periods, summer drainage was also observed from some locations during the three years of water balance calculation. But, due to no

NO_3-N concentrations being measured during summer it was not possible to estimate corresponding leaching losses. The amount of NO_3-N leaching measured during the wet winter (2017/2018) was lower compared to an average drainage season (2018/2019). The reason for lower N concentrations and leaching over the winter could be due to accelerated denitrification caused by temporary anaerobic conditions in saturated soil. High nitrate concentrations in soil solution and high soil moisture content, which is likely to occur during the winter season, dictate the potential denitrification rate (Blombäck *et al.*, 2003; Martínková *et al.*, 2011). Cardenas *et al.* (2019) reported peak emissions from denitrification ranged from 300 to 800 g N_2O-N ha^{-1} d^{-1} coinciding with the rainfall events from the UK soils from five different locations.

The soil profile depth varied from very shallow 30 cm (821 and 827) to > 90 cm and affected NO_3-N leaching as shown in **Figure 4. 8**. The AWC increased with increasing depth and reached a maximum from the sites with a soil profile depth of 90 cm and medium values from the 60 cm soil profile. However other factors like soil texture and evapotranspiration by crops also influenced the AWC. Soil available water contents (AWC) from the sites varied from 27 to 306 mm. Where depth was equal, texture was also an important factor determining AWC and leaching. A sandy loam texture can lead to less water retention and increased water infiltration as well as NO_3-N leaching (Acutis *et al.*, 2000). Water filled capacity (WFC) has also been proven to be a significant explicative variable by Richter et al. (1998) and Webster et al. (2003). Because of the varying available water and nutrient holding capacity of the soil, spatial heterogeneity of soil properties is likely to have induced heterogeneous NO_3-N leaching (Li *et al.*, 2017).

Despite no statistical significance, the maximum amount of NO_3-N leaching was observed from the sites with more sand content compared to clayey soils as shown in **Table 4. 3** and **Figure 4. 8**. This supports previous research by Nieder *et al.* (1995) and Beaudoin *et al.* (2005). From 1986 to 1988, the first authors examined 205 plots in Germany and calculated losses ranging from 16 kg N ha^{-1} $year^{-1}$ in clayey or loamy soils to 63 kg N ha^{-1} $year^{-1}$ in sandy soils. In the latter study, the authors reported 16 kg N ha^{-1} $year^{-1}$ in deep loamy soils and 50 kg N ha^{-1} $year^{-1}$ in shallow sandy soils.

Leaching varied between soil types, soil profile depth and cropping sequence. However, the concentration of NO_3-N as well as overall leaching losses were substantially higher from site 833 (**Table 4. 3**) during three drainage seasons irrespective of crop type and weather conditions. The increased N leaching from this location is most likely related to a higher initial soil organic matter concentration (18.5%) compared to any other site monitored for three drainage seasons, which leads to a higher rate of soil N mineralization (Olesen *et al.*, 2007). The findings corroborate the results of Jabloun *et al.* (2015) who investigated NO_3-N leaching losses from three years studies and found the highest leaching from the field with the highest initial soil organic matter in a temperate region.

The effect of early harvesting and sowing of spring crops (cereals, potatoes) also affected the amount of NO_3-N leaching. The sites, 832 and 833 were left fallow throughout the drainage season after early harvesting of winter wheat in 2017 which resulted in high amounts of leaching (139.4 and 128.9 kg N ha^{-1} respectively). The leaching losses from these sites was also higher (56.6 and 105.3 kg N ha^{-1}) during the 2019/2020 drainage season when winter wheat was harvested in early August 2019 and the field was left fallow until the next planting of winter wheat in late September 2019. Early harvesting followed by later winter cereal planting may result in a prolonged period of bare soil in autumn, increasing the risk of N leaching (Patil *et al.*, 2012). This can be further exacerbated by increased autumn temperatures that enhance soil organic matter turnover, which potentially increases the soil mineral N and the risk of N leaching (Børgesen and Olesen, 2011).

The NO_3-N losses from the fields (809, 811, 813, 832, and 833) were higher in the 2017/2018 drainage season when the fields were fallow over winter or the crop was sown late in winter 2017, compared to the fields (821, 822, 823, 824, 825, and 831) with early crop drilling of the next winter crop as shown in **Table 4. 1**. This is because the planting date determines the length of the fallow period as well as the timing and length of crop growth. Vos and van der Putten (1997) in the Netherlands ascribed this effect mostly to significant rainfall events, and hence drainage, happening before the complete establishment of late-sown crops.

The effect of wetter winter (2017/2018) on late sown crops was also prominent in the current study. This impact may be especially strong following the incorporation of a substantial amount of N in organic materials, such as grass-clover (Berntsen *et al.*, 2006). One of the reasons is early incorporation of clover with high leaching risks such as excess winter rainfall can result in NO_3-N leaching losses of mineralised N (Thorup-Kristensen and Dresbøll, 2010). Conditions that promote high rates of mineralisation of residues should be avoided to reduce N leaching losses. Management strategies that improve N uptake in autumn, on the other hand, should be preferred. Several management methods, including early winter cereal sowing and late-season tillage, have been investigated to attain this goal in the temperate region (Myrbeck *et al.*, 2012; Biernat *et al.*, 2020). The minimum amount of NO_3-N leaching was estimated from winter oilseed rape (WOSR) among all other winter cereals (**Figure 4. 9**). The difference might be due to the quick development of the root system in WOSR after seedling emergence, and mineral

N is efficiently taken from the soil and integrated into the plant biomass. The WOSR has a high N demand and absorbs the maximum amount of available N in autumn in temperate climates as documented by Bouchet *et al.* (2016).

The mean amount of leached NO_3-N during 2017/2018 from organic and conventional farming were 40.0 kg N ha^{-1} and 37.7 kg N ha^{-1} (**Figure 4. 9**). Over the next two drainage periods (2018/2019 and 2019/2020), the average leaching of N from organic rotations was 13.5 kg N ha^{-1} and. from conventional rotations, the average losses over two drainage seasons were higher at 42.9 kg N ha^{-1}. In the organic farming system during the first drainage season where clover was ploughed in autumn 2017 followed by winter wheat leaching (96.9 kg N ha^{-1}) reached a maximum. The results revealed that the transition from clover to the subsequent winter crop is the most critical phase in terms of NO_3-N leaching loads in organic farming. However, ploughing of the field in September enhances the turnover of soil organic matter, which increases N mineralization and the availability of soil mineral N, according to the field studies by Chatskikh and Olesen (2007) and Chatskikh *et al.* (2008). Overall, a minimum amount of average NO_3-N lost via leaching was 7.6 kg N ha^{-1} from grassland over the three drainage monitoring seasons. The effect of grass is most likely due to the lower soil disturbance and ultimately lower amount of organic N mineralised in winter compared to other crop sequences (Catt *et al.*, 1998) during the same three years.

Previous crops and autumn field management appeared to be important determinants of N leaching and nitrate concentration in soil solution. Soil cover during the three years of monitoring included clover, winter cereals, grass and bare soil following cultivation of winter cereals. The application of N fertilisers or manure was usually at the end or after the monitoring period, therefore no direct effect of N input was found in this study. However, soil N mineralisation post-harvest is determined by any residual fertiliser, as well as mineralization of N from the soil organic matter and crop residues. The effect of mineralisation of clover residues incorporated (813) during 2017/2018 was more obvious. Crop type, yield, and N fertiliser rate all influence soil N mineralisation (Shepherd and Lord, 1996) and eventually, N leaching.

The losses after stubble turnip (829) during 2019/2020 were estimated as 72.10 kg N ha^{-1} (**Table 4. 3**). More NO_3-N leaching may have occurred after the removal of porous pots due to the high N accumulation in stubble turnip which undergoes mineralisation when ploughed before spring barley cultivation. High N mineralisation from stubble turnip was also observed by Cottney *et al.* (2021) when stubble turnip was destroyed and incorporated for spring barley cultivation. The maximum amount of mineralised N from stubble turnip is susceptible to leaching before being taken up by spring barley. Another reason for higher NO_3-N concentration in soil solution from the stubble turnip crop might be due to the outwintering of sheep as there could be an effect of sheep manure on this NO_3-N concentration and ultimately higher leaching losses.

4.6 Conclusion

This study was conducted to fill the important gap to understand the impact of land use, soil texture and soil depth to the bedrock variability in the Fell Sandstone agricultural catchment and influence of wet and normal year in terms of rainfall, on NO_3-N leaching. The study results showed that NO_3-N (kg ha^{-1}) leaching losses were mainly affected by management factors, depth to the bedrock and soil organic matter. The locations with more sandy shallow soil profiles are detected as hotspots for NO_3-N leaching. The estimated leaching losses in this study are from NO_3-N concentrations collected during the winter drainage period. But, during summer drainage was also estimated from some locations that might contribute to annual NO_3-N leaching losses.

There were no statistically significant differences in average losses between the organic and conventional fields monitored. At all the organic farming sites, clover crops reduced leaching and the duration of the fallow period increased NO_3-N leaching losses from conventional farming. Nitrate leaching losses from crop rotations were found to be highly dependent on field management practices in the autumn and previous crops. The maximum amount of nitrate leaching was found from organically managed winter wheat drilled after clover incorporation and from fields left fallow for longer periods during autumn-winter in conventional farming. The minimum amount of NO_3-N was lost from grassland and the next lowest was from clover. The N leaching losses from the winter wheat crop rotation were also modified by the early and late crop sowing. The key risk factors related to agricultural practices included high rates of N use, grazing stubble turnip, ploughing in a ley before fallow; soil properties including soil organic matter and soil texture were found influencing factors of NO_3-N leaching. The influence of these risk factors can be minimised by management practices such as, keeping the shallow sandy soil in grass, avoiding ploughing the field in autumn to avoid longer fallow periods, and avoid outwintering on stubble turnip.

Chapter 5. Investigating Innovations to Mitigate Nitrate Leaching from Cropping Systems

5.1 Introduction

Farmers and the agricultural industry worldwide are constantly facing major challenges and opportunities to improve the efficiency of their nutrient inputs in crop production, particularly nitrogen (N). Fertiliser N has been and will remain essential for human nutrition, clothes, and bioenergy supply. However, ammonia and nitrous oxide emissions and nitrate-N (NO_3-N) losses to surface and groundwater supplies are risks linked with fertiliser N use that must be appropriately managed to help fulfil larger community expectations (Snyder, 2017). When nitrates leave the soil in drainage water, a natural phenomenon called nitrate leaching occurs. Since NO_3^- is soluble and mobile, it is not a concern in the root zone, but it pollutes the environment when it leaves the root zone and reaches groundwater and other freshwater bodies (Khan *et al.*, 2017).

Tillage has a variety of effects on NO_3-N leaching from agricultural land, all of which are different (Addiscott and Dexter, 1994; Strudley *et al.*, 2008). No-tillage, in comparison to conventional tillage, increases hydraulic conductivity by preserving root or earthworm preferential-flow channels (Azooz and Arshad, 2001; Palmer *et al.*, 2011); increases soil organic nitrogen (ON) due to reduced decomposition caused by minimising soil disturbance and protecting ON within aggregates (Zibilske and Bradford, 2007); increases soil water content. As a result, tillage has a variety of impacts on soil processes that can affect NO_3-N leaching. Due to larger saturated hydraulic conductivities and improved preferential flow with no-tillage, there is more NO_3-N leaching from no-tillage compared to conventional tillage (Meisinger *et al.*, 2015).

There are specialised N fertilisers on the market that have a physical coating on the granules or chemical compounds added to the fertiliser that slows nitrogen transformation in the soil. Both technologies restrict the amount of N released into the soil to ensure sufficient crop uptake for an extended period (Golden *et al.*, 2011; Maharjan *et al.*, 2017). These products can improve crop N uptake and grain yield while reducing N losses due to improved soil N retention. Controlling the conversion of ammonium to nitrate may help maintain more N on soil colloids (Maharjan *et al.*, 2017).

Chemical additives to N fertilizers are used to restrict one of the following two processes: either the urease activity that causes urea hydrolysis (urease inhibitor) or the nitrification process at the first step when NH_3 is oxidized to nitrite (nitrification inhibitor), as shown in **Figure 5. 1**.

As N fertilizers, such as urea, ammonium nitrate and ammonium sulfate, are added, a microbial mechanism known as nitrification converts much of the ammonium (in N fertilizers) into highly mobile NO_3^- in less than 2-3 weeks. The bulk of nitrogen is lost by leaching or denitrification before it can be used by plants, resulting in a low nitrogen use efficiency (NUE). Nitrification inhibitors (NIs) can prevent *Nitrosomonas sp.* from completing the first step of nitrification (conversion of NH_4^+ to nitrite NO_2^-) and delay the nitrification process. Inhibiting nitrification by using NI can promote the retention of soil N in the less mobile NH_4^+ form, which can help minimize NO_3^- leaching (Zerulla *et al.*, 2001). According to Qiao *et al.* (2015)'s global meta-analysis, NIs can reduce annual NO_3^- leaching by 38-56 %, although they are less effective in sandy soils than clayey soils.

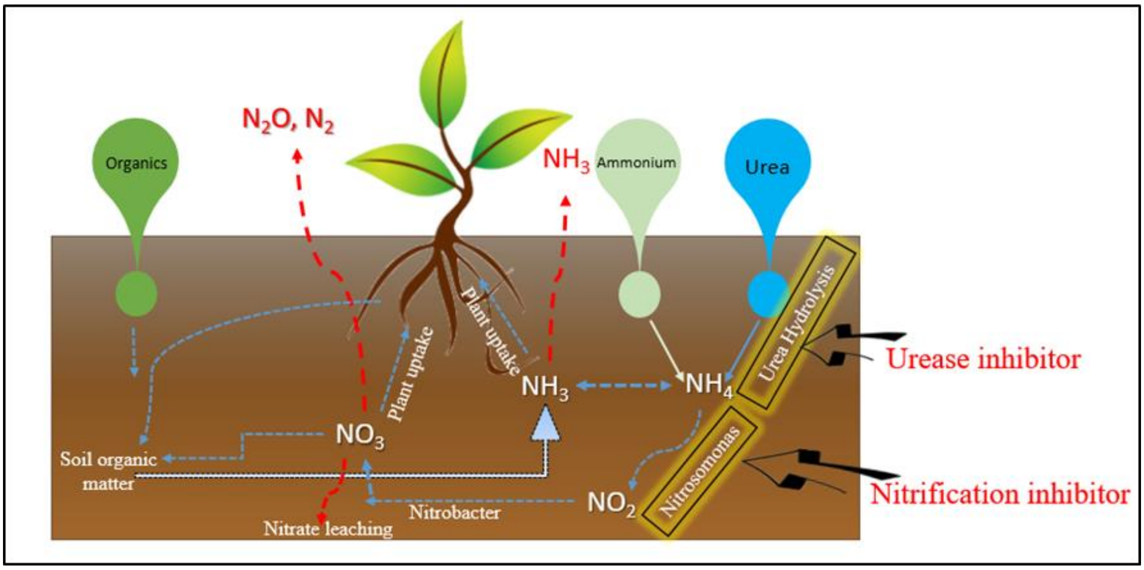


Figure 5. 1 Mode of action of chemical additives (Urease and nitrification inhibitor) in nitrogen cycle to reduce nitrate leaching

Several compounds have been tested as nitrification inhibitors; only a few are commercially available, with the most common being dicyandiamide (DCD) and 3, 4 dimethyl pyrazole phosphate (DMPP) (Bronson *et al.*, 1992; Chiodini *et al.*, 2019). DMPP inhibits NO_3^- conversion from NH_4^+. As a result, even at very low DMPP application concentrations (0.5–1.5 kg DMPP ha^{-1}), N_2O emissions from nitrification and NO_3-N leaching are reduced for 4 to 10 weeks (Tindaon *et al.*, 2012). However, the amount of N released by these modified products is influenced by soil moisture and temperature (Haderlein *et al.*, 2001).

Another approach is coating urea with a polymer (NutriSphere-N). Nutrisphere is a branched polymer with a long chain and a strong negative charge (1800 meq 100 g^{-1}). Nutrisphere is a 30-40 mer long-chain polymer structure coating designed to attract multivalent nickel cations, copper and iron present in the soil and influence nitrogen loss. Nutrisphere coats the fertilizer molecule when added to it. It binds to positively charged cations like nickel in the soil, making these cations unavailable to form the urease enzyme. The hydrolysis of urea or nitrate into ammonia ceases when the urease enzyme is absent (Heiniger *et al.*, 2013). Nutrisphere does not harm soil bacteria, earthworms, and other soil life when used with urea fertilizer. In the soil, the Nutrisphere-N polymer breaks down into carbon, oxygen, hydrogen, and calcium. Since the molecule is too large to be taken up by the plant, there are no residues in the harvested crop[5].

A DMPP based nitrification inhibitor (BASF product, Vizura) is a formulation for liquid manure (slurry). DMPP can reduce the N losses from nitrification and denitrification pathways due to its effect on minimising soil N accumulation. DMPP can delay the oxidation of NH_4^+ and its conversion to NO_3^- (which then accumulate in soil) by inhibiting the ammonium monooxygenase enzyme's activity (Ruser and Schulz, 2015). In a lysimeter study Vizura was used on grass/clover (Nair *et al.*, 2020) and in mesocosms (Kong *et al.*, 2017); investigations showed that treating above-ground biomass of grass/clover with DMPP reduced N_2O emissions, most likely by restricting nitrite and nitrate supply for denitrification associated with residue. DMPP also had no negative effects on soil microorganisms (Kong *et al.*, 2016), earthworm feeding behaviour (Kong *et al.*, 2017), or residue mineralization (Duan *et al.*, 2017). As a result, we hypothesised that Vizura application on grass/clover prior to incorporation could have an impact on the NO_3-N leaching.

This study was conducted to monitor the efficiency of polymer coated urea (NutriSphere-N®) and a DMPP based nitrification inhibitor (Vizura®) to improve crop nitrogen use efficiency and minimise N leaching. The aims of the study were:

i. To assess the efficiency of a nitrification inhibitor (DMPP, Vizura®) in reducing nitrate leaching from autumn ploughed leys
ii. To assess the effect of minimum tillage compared to conventional tillage on nitrate leaching under winter wheat
iii. To assess the effect of NutriSphere-N® on soil nitrogen dynamics and potato yields

[5] NutriSphere-N® | Products | Verdesian Life Sciences

5.2 General Methodology

5.2.1 Site description

Field sampling and experiments were conducted from November 2018 to September 2019 at Newcastle University's Nafferton Farm, Northumberland, UK (**Figure 5. 2**). A detailed description of experiment is reported in Cooper *et al.* (2011).

Nafferton farm soils are mapped as part of the Brickfield association, which is dominated by Stagnogley characteristics. The underlying geology is greyish till derived from Carboniferous shale and sandstone (Payton *et al.*, 1990), which is seasonally moist, slowly permeable, acidic loamy to clayey soil with low fertility (www.landis.org.uk). The mean annual rainfall (2014-2018) is around 734 mm with average annual minimum and maximum temperatures of 6^{o}C and 12.8^{o}C, respectively, recorded on the weather station at the farm.

This experimental site was approximately 60 miles to the South of the Fell Sandstone study site. Both sites are at a similar altitude but annual rainfall is typically 20% higher at Nafferton where soils are deeper and have a higher clay content.

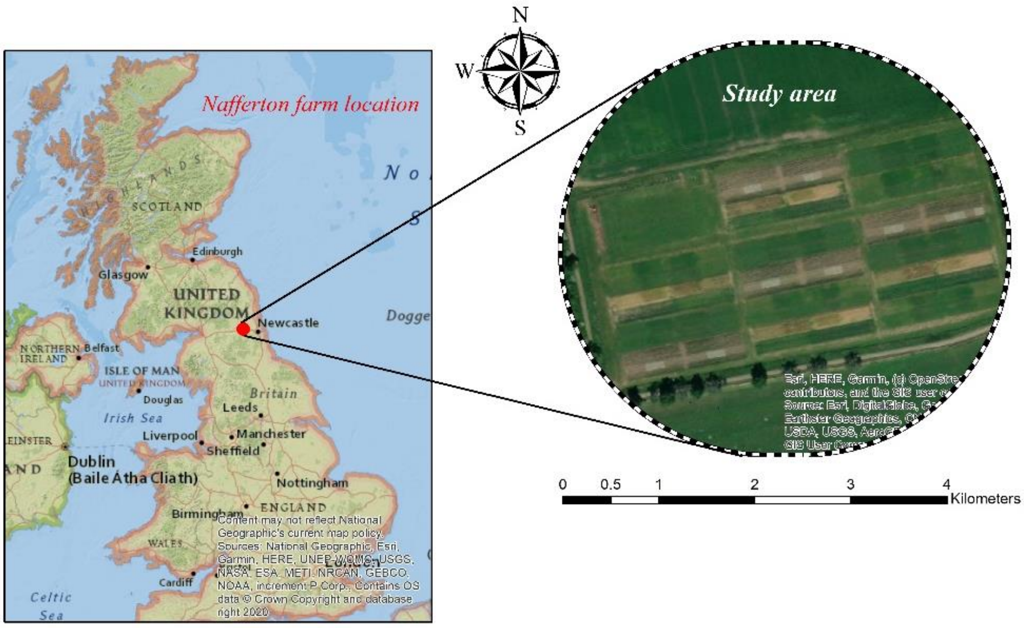


Figure 5. 2 Location of the Nafferton Factorial Systems Comparison trial (Nafferton farm), 12 miles west of Newcastle upon Tyne in north-east England, and the field area used in the study.

5.2.2 Field trial design

The experiment was conducted on the Nafferton Factorial Systems Comparison Trial (NFSC), which was established in 2003 to focus on low-input, sustainable and organic approaches to crop management. It is made up of a series of four field experiments within four replicate blocks. These four experiments were initially designed in a way to compare organic and conventional farming systems. The original design of the NFSC consisted of 4 experiments with similar designs; each has two main plots (12m x 96m) representing either a conventional or an organic crop rotation. The crop rotation from 2017-2019 is illustrated in **Table 5. 1**. The design of one of the blocks as an example within the trial in 2019 is shown in **Figure 5. 3**.

The crop rotation plots are divided into two crop protection subplots (12 m x 48 m) that follow either organic or conventional crop protection (weed, insect and disease control) practices, as shown in **Figure 5. 3**. Finally, each subplot is split into two fertility management sub-sub plots (12 m x 24 m), which follow either organic fertility management (ORGFM) in which composted dairy manure is applied according to the recommended rate of nitrogen for each crop and conventional fertility management (CONFM) in which inorganic NPK fertilizers are applied as recommended in the AHDB Nutrient Management Guide (RB209) (AHDB, 2019). A Delta-T Devices, Type M2-ENCL weather station, is located near block 3 of the experiment. Weather data: maximum and minimum air and soil temperature, relative humidity, wind speed, rainfall and radiation are recorded hourly. All data are downloaded regularly from the weather station and stored in an Excel spreadsheet.

Table 5. 1 Sequence of crops in the organic (ORG) and conventional (CON) rotations in the NFSC trial from 2017 to 2019

	2017	2018	2019	
CON rotation	GC*	GC	w-wheat	**Experiment 1** **Tillage trial**
ORG rotation	GC	GC	S-wheat	
CON rotation	w-wheat	W-barley	Potato Potato	**Experiment 4** **Original**
ORG rotation	Potato Brassica	Peas/Beans	Cabbage Potato	
CON rotation	W-barley	GC	GC	**Experiment 2** **Fertility input trial**
ORG rotation	GC	GC	GC	
CON rotation	Spelt/rye Spelt/rye	Potato Potato	w-barley	**Experiment 3** **Tillage Hybrid trial**
ORG rotation	Peas/Beans	Brassica Potato	S-barley	

***GC = Grass/clover**

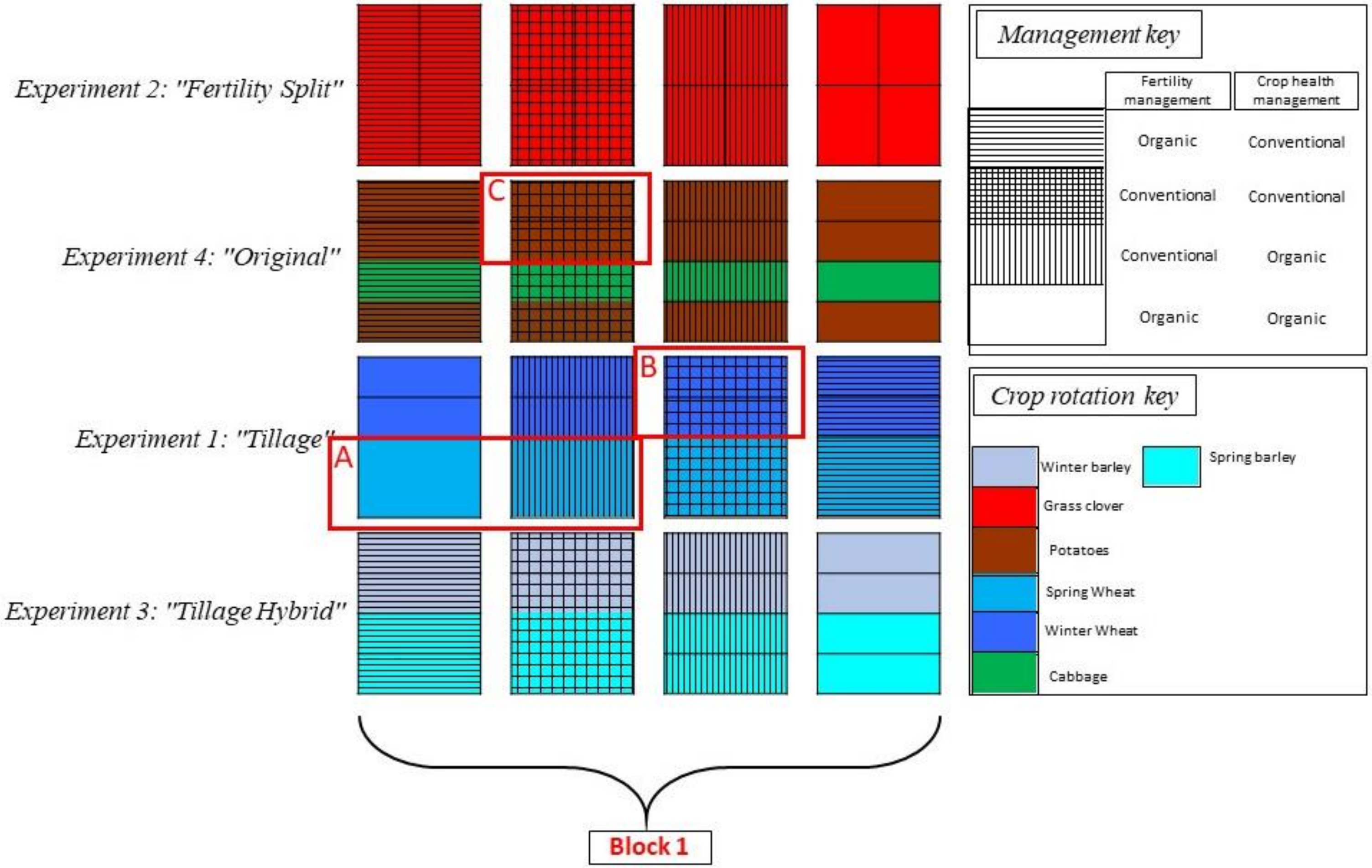


Figure 5. 3 The organisation of treatments within the NFSC's blocks. As an example, the Figure depicted Block 1 in 2019. The main plot is vertically subdivided into two crop protection (organic and conventional) subplots and further subdivided into two fertility management subplots. (Managements are shown in the separate keys)

5.2.3 Soil and soil solution sampling

Soil solution samples were collected from experiments A and B (**Figure 5. 3**) using the porous ceramic cup sampler. The porous cups installation and sample collection method are described in ***chapter 4, section 4.2.2***. The porous cups in experiments A and B were installed on 6th November 2018. A 3cm diameter manual soil auger was used to collect initial soil samples to assess the soil mineral N concentration for all blocks before installing porous cups. Four soil cores were collected to a depth of 50 cm in each plot, and each was divided into two layers (0-30 and 30-50 cm). It was the maximum depth that the manual soil auger could reach. A single composite sample for each layer was placed into plastic bags for each plot and stored in a freezer at -20 °C.

After the porous cups installation, soil samples were collected weekly from the 0-30 cm layer. Three cores were collected (from different locations around the plot) and mixed to form one sample from each treatment plot and stored at -20 °C for later extraction of soil mineral N (SMN). Soil solution samples for nitrate-N measurement were also collected from the porous pots every week over the winter 2018/2019 and stored at -20 °C until later analysis.

Soil samples from each experimental plot (A, B and C) were collected from topsoil before the start of the experiment for initial characterisation of soil chemical properties. All the soil samples were oven-dried (105^{o}C) and stored in plastic bags for later analysis.

5.2.4 Characterization of initial soil chemical properties

For total carbon (C) and nitrogen (N), an agate mortar was used to grind a subsample of roughly 0.100 g of dry soil to a fine powder, which was then analysed. The Leco CN-2000 dry combustion analyser was used in this study. The analyser worked on a dry combustion principle, with C detection by infrared and N detection by thermal conductivity described by Wright and Bailey (2001). The oxygen used in the combustion process was delivered in two ways, both of which could be controlled: a lance flow directly over the sample and a background purge. As a result, the furnace conditions might be changed. Standard weights (i.e., 0.1500 g) of a Leco EDTA calibrator containing 95.7 g N kg^{-1} and 410 g C kg^{-1} were used to calibrate the instrument. The analytical procedure described by Mclean (1983) was used for soil pH determination in H_2O (1:2.5 soil: solution).

The standard laboratory method was used for measuring the plant available phosphorous (P) content of soil using Olsen's extracting (0.5M sodium bicarbonate ($NaHCO_3$) solution at pH 8.5) (M.R. Carter, 2007). When a P indicator solution (ammonium molybdate and ascorbic acid) was added to the extract, the colour change was analysed on a spectrophotometer and compared to a set of standards (2, 4, 6, 8 and 10 ppm) for known P concentrations to calculate the amount of P in the extracted solution. The phosphorus in the solution was converted to phosphorus in the soil. To determine the potassium (K) contents of soil, the standard laboratory method of shaking the soil with an extraction solution was used. We used 1M ammonium nitrate solution for K extraction. The added ammonium ions were exchanged with the potassium ions on the clay and organic matter. The concentration of potassium ions released into the solution was then measured using the flame photometer. Before soil extracts, standards of known concentrations (5, 10, 15, 20 and 25 ppm) and a blank were used to calibrate the flame photometer and draw the standard curve.

5.2.5 Soil mineral nitrogen determination

Before analysis, soil samples from all the experimental blocks were taken out of the freezer and stored at 4°C overnight. After thawing, all soil samples were thoroughly mixed inside the bag and then sieved through a 4mm sieve size. A subsample (5g) from each bag of the sieved soil was used to determine gravimetric water content. The moist soil was weighed into a known-weight container, dried in a fan oven at 105°C for 24 hours, and then reweighed. The gravimetric water content of the soil was then calculated as a percentage of the oven-dry soil mass.

Soil mineral nitrogen (SMN) was determined using the standard extraction method described by Keeney and Nelson (1982). In a 125 ml acid-washed plastic bottle, 10 g of moist soil was placed, followed by 100 ml of 2M KCl. The bottles were shaken for one hour at 250 rpm on an IKA KS 260B shaker. After shaking, the samples were allowed to settle for about 30 minutes. The soil extract was then filtered into plastic vials using Whatman No. 42 filter paper. A blank extraction in each batch was used to account for the possibility of contamination of the filter paper or the extraction procedure. The blank extraction followed the same procedure as the samples. The nitrate and ammonium concentrations obtained were subtracted from any measured ammonium or nitrate concentrations in the blank sample. All extracts were checked to ensure that they were free of sediments and were colourless, making them ideal for colorimetric nitrate and ammonium determinations. Until the time of analysis, the extracts were kept frozen at -20 °C.

5.2.6 Determination of SMN using an Auto analyser

The nitrate and ammonium concentrations in the sample matrix (soil extracts and water samples) were measured. Concentrations of NO_3-N and NH_4-N in the sample matrix were measured using a Brann+Luebbe Autoanalyzer 3 and the hydrazine reduction method for NO_3-N and the salicylate method for NH_4-N (Swain *et al.*, 2016).

Around 5 ml of the sample was needed for the nitrate and ammonium content analysis. For ammonium, the auto analyser's working concentration range is 0- 8 mg N l^{-1}, and for nitrate, it is 0-40 mg N l^{-1}. The analyser uses a continuous flow system that automatically takes samples from the sample tray and automatically separates them with air bubbles inside the continuous flow system to avoid cross-contamination. After reagents reacted during the process, colour develops in the sample. The absorbance is shown on a chart recorder as a peak for nitrate and ammonium concentration, displayed automatically as mg l^{-1}.

Table 5. 2 lists all of the reagents used in this method. The 1000 ppm stocks for NO_3-N and NH_4-N were diluted to make 100 ppm standards. Working standards of NO_3-N (2, 4, 6, 8 and 10ppm) and NH_4-N (1, 2, 3, 4 and 5ppm) were made by diluting the 100 ppm standard using *2.0 M* KCl (for soil extracts) and water (for water samples). All the reagents were prepared once at the start of the analysis. After that, only those were prepared again, which were entirely used during the setting up procedure of the analyser, except the colour reagent, which needs to be prepared fresh every week. The nitrate and ammonium concentrations were determined following the method explained by Carter (1993). In this method, at 37 °C, at pH 9.5, nitrate is reduced to nitrite using hydrazine in an alkaline solution with a copper catalyst, and the sample is then reacted with sulphanilamide and N-1-Naphthylethylenediamine to form azo Chromophore (a pink compound), which can be measured colorimetrically at 550 nm. The detection limit for nitrate is 0.006 mg l^{-1}. For ammonium concentration, the sample is treated with salicylate and hypochlorite; this reacts to form a green colour compound (indophenol) that is colorimetrically measured at 667 nm. The detection limit for ammonium is 0.003 mg l^{-1}. The final concentrations of NO_3-N and NH_4-N were converted to mg kg^{-1} of dry soil.

Table 5. 2 Reagent used for Nitrate-N and Ammonium-N analysis using the Auto analyser

Reagents for Nitrate –N	**Reagents for Ammonium –N**
Colour reagent	Buffer
Sodium Hydroxide	Sodium salicylate
Phosphoric acid	DCL solution
Hydrazine sulphate	Ammonium standards
Nitrate standards	

Samples with known concentrations (1, 2, 3, 4 and 5 ppm) for NH_4-N and (2, 4, 6, 8, and10 ppm) for NO_3-N were tested in each auto analyser batch to see whether there was some drift in measuring the concentrations. Since no drift occurred, no correction for NO_3-N and NH_4-N concentrations were needed when using known samples.

The recovery efficiency of the concentrations of NH_4^+ and NO_3^- added in a known sample was used to assess the precision of the method for determining NH_4^+ and NO_3^- concentrations. A sample with a known concentration was added to the blank (2 *M* KCl). To assess recovery quality by comparing the observed concentration to the known concentration, three measured concentrations were averaged and used to calculate % recovery as shown in **Table 5. 3**.

Table 5. 3 Recovery of nitrate and ammonium from known concentrations using Auto analyser

Known concentrations	Measured concentrations			% Recovery
	1	2	3	
NO_3-N (mg l^{-1})				
10 (Day-1)	9.7	9.6	10.1	98.00
10 (Day-2)	9.9	9.7	9.9	98.33
10 (Day-3)	10.1	9.9	9.9	99.67
10 (Day-4)	9.7	9.9	9.6	97.33
NH_4-N (mg l^{-1})				
4 (Day-1)	4.1	3.9	3.9	99.17
4 (Day-2)	4.0	3.9	3.9	98.33
4 (Day-3)	3.5	3.8	3.6	90.83
4 (Day-4)	3.9	3.7	3.7	94.17

A known soil standard was also used to check the extraction and analysis method's accuracy and performance. Collected field soil was sieved (4 mm sieve size), homogenised, air-dried, and stored. Between 10-11 g of air-dried standard soil was extracted in each extraction batch in the same way as the samples. **Table 5. 4** shows the findings for seven extraction batches, demonstrating that the extraction procedure and method of determination are both robust and reliable.

Table 5. 4 Concentration of NO_3-N (mg kg^{-1}) and NH_4-N (mg kg^{-1}) in standard soil replicates

Extraction batch	**NO_3-N (mg kg^{-1})**	**NH_4-N (mg kg^{-1})**
Standard soil- Batch 1	39.68	8.40
Standard soil- Batch 2	47.13	12.08
Standard soil- Batch 3	43.42	10.26
Standard soil- Batch 4	45.37	9.66
Standard soil- Batch 5	44.36	8.69
Standard soil- Batch 6	43.53	9.77
Standard soil- Batch 7	41.15	9.87
Mean	43.52	9.82
SE Mean	0.36	0.17

5.2.7 Estimation of evapotranspiration and drainage

The Penman-Monteith equation proposed by Allan *et al.* (1998), was used to estimate crop evapotranspiration. The reference evapotranspiration (ETo) was first calculated using only climate factors for a standard crop (grass), and soil properties were kept constant over time. The crop coefficients (Kc) were then used to adjust ETo to evaluate the potential crop ET (ETc) in mm day^{-1} for winter wheat during the drainage season 2018/19. The Nafferton Farm weather station provided all of the weather data. Daily maximum and minimum temperatures (°C), rainfall (mm day^{-1}), mean daily wind speed (m s^{-1}), solar radiation in KW m^{-2} (converted to MJ m^{-2} day^{-1} following the equation, KW m^{-2} 86.4 = MJm^{-2} day^{-1}) (Allan *et al.*, 1998) and average daily humidity (%) were all used as input weather parameters to calculate ETo.

$$ETo = \frac{0.408\Delta(Rn - G) + \gamma \frac{900}{T + 273} u_2(e_s - e_a)}{\Delta + \gamma(1 + 0.34u_2)}$$

Where ETo is the reference evapotranspiration (mm day^{-1}), Rn is net radiation at the crop surface (MJ m^{-2} day^{-1}), G is soil heat flux density (MJ m^{-2} day^{-1}) the value was ignored for daily records therefore G=0, T is average daily air temperature at two meters height (°C), u_2 is wind speed at two meter height (m s^{-1}), e_s is saturation vapour pressure (kPa), e_a is actual vapour pressure deficit (kPa), e_s - e_a is saturation vapour pressure deficit (kPa), Δ is slope of the vapour pressure curve (kPa °C^{-1}), γ is psychrometric constant (kPa °C^{-1}). These input parameters (slope and saturation vapour pressure) were calculated by using the equations,

$$\Delta = \frac{4098\left[0.6108exp\left(\frac{17.27T}{T+237.3}\right)\right]}{(T+237.3)^2}$$

Where Δ slope of the vapour pressure curve and T is air temperature.

$$e_s = \frac{e^0(Tmax) + e^0(Tmin)}{2}$$

Where e_s is saturation vapour pressure, e^0 is saturation vapour pressure at air temperature.

The γ psychrometric constant value of 0.067 was used during the calculation.

Daily rainfall was recorded on the weather station at Nafferton farm. Evapotranspiration was calculated using the Penman-Monteith equation, and available water contents at field capacity were reported by Almadni (2014), obtained from the pressure plate (0.05 bar) from similar experimental fields. The average soil water content in the 0-90 cm profile was 279 mm at field capacity.

Daily meteorological data and calculated evapotranspiration and average available water contents at soil field capacity (cm^3 cm^{-3}) and soil moisture deficit (SMD) were used to measure cumulative drainage. The cumulative drainage over the trial was calculated as described in Chapter 4. The trapezoidal rule was used to measure nitrate loss over the trial duration. The area under the plot of NO_3-N concentrations (mg l^{-1}) against drainage (mm) is nitrate loss in kg NO_3-N ha^{-1}. The trapezia from successive sampling concentrations (C1, C2 mg/l) and drainage volume (V1, V2 mm) were used in the following equation,

Nitrate Leached (kg NO_3-N ha^{-1}) = 0.5 x (C1 + C2) x (V1 - V2) ÷ 100

5.2.8 Statistical analysis

In all scenarios, the data were analyzed using linear mixed-effects models (Pinheiro and Bates, 2000) with the fixed effect of treatment factors, e.g. fertilizer management, tillage and nitrification inhibitor, and random effect of blocks and sampling dates to generate ANOVA *P*-values for key effects including fertilizer management (FM) and nitrification inhibitor (NI) for experiment A, effect of tillage practices (Minimum tillage and conventional tillage) in experiment B and effect of fertilizer management (Urea and NutriSphere-N)in experiment C and all interactions using the R software (nlme package) (Team, 2021a). To follow the normal data distribution criterion, the normality of the residuals of all models was tested using qqnorm, and data were transformed using square root or log where necessary. Tukey contrasts in the multcomp package's general linear hypothesis testing (glht) function were used to test differences among interaction means (Pinheiro *et al.*, 2021).

5.3 Experiment A: Assessment of a Nitrification Inhibitor to Reduce N Leaching from Autumn Ploughed Leys in a Long Term Field Trial

5.3.1 Experimental design

All activities within this study took place in the southern half of Experiment 1 of the trial, shown as experiment **A** in **Figure 5. 3**. The experiment was used to monitor nitrogen (N) leaching during the 2018/2019 drainage season following mouldboard ploughing of a three year grass/clover ley. In autumn 2018, all fertility management sub-sub plots (COMP and NPK) were divided in half, creating eight sub-sub-sub plots (12 m x 12 m) in each replicated block (**Figure 5. 4**)

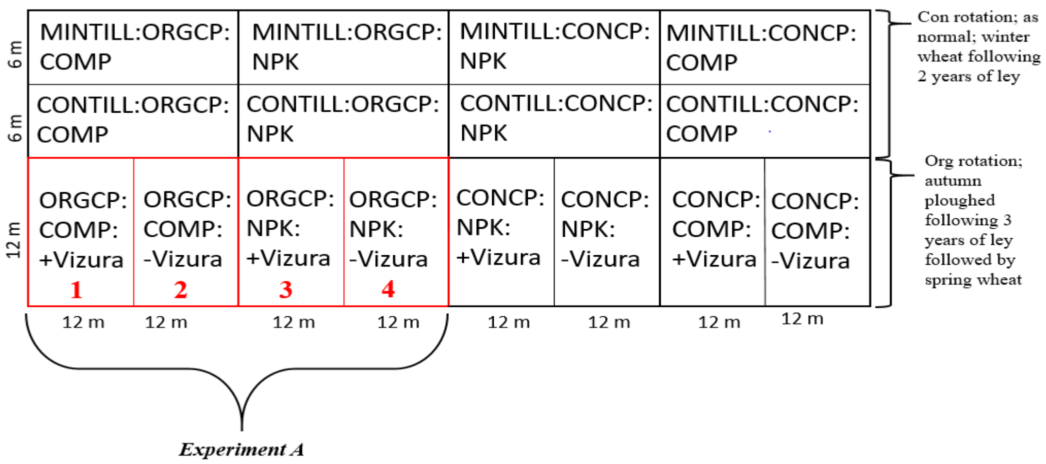


Figure 5. 4 Detailed illustration of treatments in Block 1 of Experiment 1 of the trial. Plots monitored for nitrogen leaching and SMN in 2018/19 drainage season (numbered 1, 2, 3 and 4). Note: plots are not drawn to scale

*MINTILL= minimum tillage, CONTILL=conventional moulboard ploughing, ORGCP=organic crop protection, CONCP=conventional crop protection, COMP=compost and NPK=chemical fertilisers

DMPP-based product Vizura® was sprayed (1 kg ha^{-1}) on the grass/clover ley before ploughing in autumn (22/10/2018) on half of these plots (indicated as +Vizura) on the ORG CP side. Nitrogen (N) leaching was monitored in plots 1, 2, 3 and 4 in **Figure 5. 4** to evaluate the Vizura® application's effect. Comparing the mean leaching from plots 1 & 3 compared to plots 2 & 4 allowed us to assess the efficacy of Vizura® in reducing N leaching post ploughing of a ley.

Due to the impact of NPK fertiliser on clover contents in leys, we know that the % clover in the COMP treatments is consistently higher than the NPK plots. Therefore assessment of leaching from plot 2 compared to plot 4 will provide interesting additional information on the impact of clover content on N leaching. These plots were autumn ploughed, and spring wheat was drilled on 16/04/2019. Spring wheat was managed as follows:

- COMP plots – no added fertilisers
- NPK plots – 120 kg N ha^{-1} as ammonium nitrate

To evaluate the effect of Vizura® applied in autumn on spring wheat, the aboveground plant biomass of spring wheat was collected manually from all experimental plots (from 1 m^2) at the final harvest. Subsamples of the aboveground biomass were used to calculate the dry weight.

5.4 Experiment B: Effect of Minimum and Conventional Tillage on Nitrate Leaching

5.4.1 Experiment design

In the conventional (CON) crop rotation plots in Experiment 1 in **Figure 5. 3**, the trial was slightly modified to test the effects of autumn ploughing of a previous three-year grass/clover ley on N leaching compared to minimum tillage. In 2012 minimum tillage was introduced as an additional factor into Experiment 1. The conventional crop rotation main plot was split into two longitudinal subplots (each 6 m x 96 m) with minimum tillage practices implemented in the northern half of the plot and conventional mouldboard ploughing used in the southern half of the plot. All the activities reported in this section took place in experiment B in **Figure 5. 5**.

The plots labelled MINTILL: CONCP in **Figure 5. 5** were sprayed with glyphosate in autumn 2018 and direct drilled to winter wheat on 25/10/2018 using a combined seed drill. Those labelled CONTILL: CONCP were sprayed with glyphosate and then mouldboard ploughed (~25 cm depth) and planted with winter wheat using a combined seed drill. Monitoring of N leaching in plots labelled 5 and 6 in **Figure 5. 5** in all four replicates (a total of 8 plots) was conducted in the 2018/19 winter drainage season (see section 5.2.3). No other chemicals for crop protection or nutrients were applied during the drainage period.

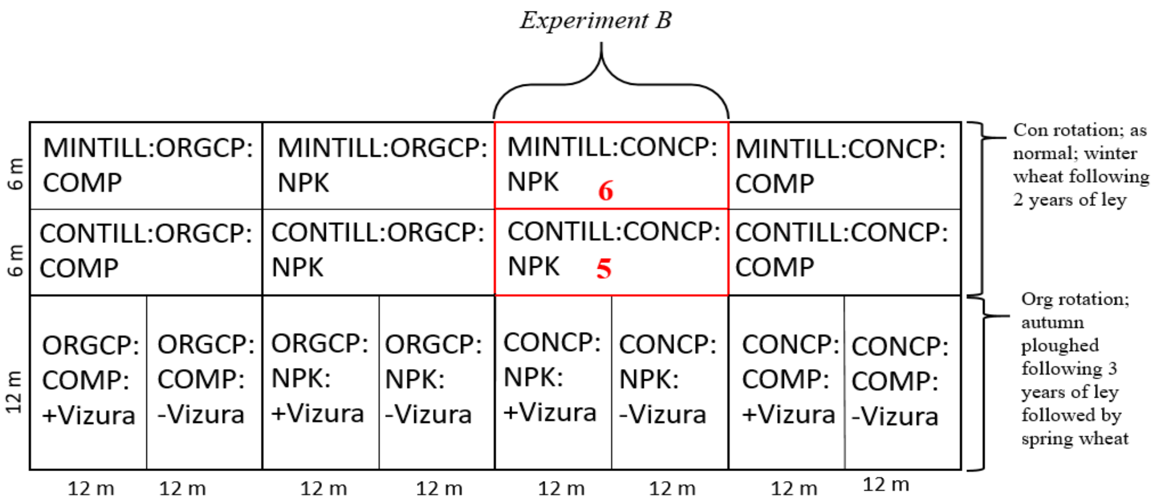


Figure 5. 5 Detailed illustration of treatments in Block 1 of Experiment 1 of the trial. Plots monitored for N leaching and SMN in 2018/19 drainage season to compare minimum vs conventional tillage

*MINTILL= minimum tillage, CONTILL=conventional moulboard ploughing, ORGCP=organic crop protection, CONCP=conventional crop protection, COMP=compost and NPK=chemical fertilisers

Topsoil samples (0-30 cm) were collected to estimate soil nitrogen dynamics and the proportion of nitrate: ammonium and soil solution samples for mineral N analysis taken from the field by using porous pots over winter 2018-19 (*see section 5.2.3*).

5.5 Experiment C: Impact of Nutrisphere on Soil N Dynamics and Potato Yield

5.5.1 Experiment design and sample collection

Experiment 4 (as shown in **Table 5. 1**) was used to study the impact of NutriSphere-N® on soil nitrogen dynamics and crop yield. Treatments were focused on the fully conventional subset of plots within the conventional rotation. These plots were split into three sub-plots; full details are shown in **Figure 5. 6**. The plot size was 12 m x 8 m. Note that **Figure 5. 6** illustrates just one replicate block, and there were four of these in the experiment, so a total of 12 plots were monitored in the study.

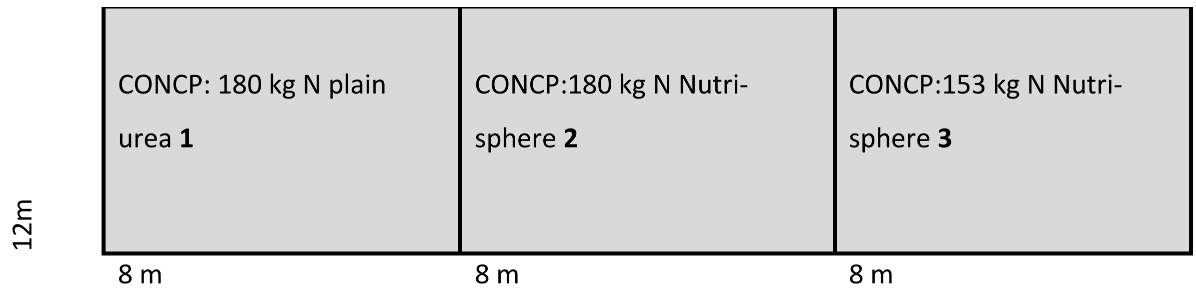


Figure 5. 6 Illustration of treatments for NutriSphere-N® trial in Experiment 4, Block 1 of the trial. The subset of plots representing the CON rotation. Plots monitored for soil N dynamics and potato yield in the 2019 cropping season

*CONCP=conventional crop protection

The N rate is based on the AHDB Nutrient Management Guide (RB209) for a deep clayey soil following winter barley in a low rainfall area (considering the Northeast UK's very dry conditions during the 2018/19 winter). Whereas, in plot 3, the NutriSphere-N® (NS) applied at the rate of 153 kg of N ha^{-1} (85% of total N recommended in RB209). This reduced application was based on the product manufacturer recommendation using 85% of the standard rate of application, which would bring immediate commercial benefit and equal to normal crop yield (Verdesian). The application was full placement before drilling. The potato crop was managed during the experiment, as shown in **Table 5. 5**.

Table 5. 5 Detailed management practices and application dates

Management practice	Description
Fertilizer input	180 kg of N ha^{-1} as Urea and Nutrisphere and, 153kg N ha^{-1} as NutriSphere-N® (24/04/2019); broadcast and incorporated into the soil
Planting date	02/05/2019
Herbicides	Praxim 3l ha^{-1} (21/05/2019), Wicket 3l ha^{-1} (21/05/2019) Laser 2.25 l ha^{-1} (27/06/2019), Reglone 3l ha^{-1} (10/09/2019)
Fungicides	Shirlan 300 ml ha^{-1} (18/06/2019 and 18/07/2019) Mancozeb 1.7kg ha^{-1} (10/07/2019)
Harvesting	23/10/2019

Soil samples were collected using a manual soil augur biweekly from the topsoil (0-30 cm) soil layer to observe SMN (after fertiliser application) during the potato growing season from May to September 2019. All the soil samples were stored at -20 °C in a freezer for later analysis. To monitor the fertiliser response, plant above and below-ground biomass at two growth stages (during tuber development and senescence) and final potato yield were collected. Subsamples of the aboveground biomass, root and tuber fresh weight were used to determine dry weights. Tubers were left for four weeks in the ground before final harvesting for the skin maturation process after defoliation. The final yield was assessed by using the harvested potatoes from two middle rows from $4m^2$ of each plot.

5.6 Results

5.6.1 Experiment A

Soil chemical properties

The soil properties reported in **Table 5. 6** were used to evaluate the chemical status of soil collected from experimental plots. The values are the means of results (for each soil parameter). The pH of conventionally fertility managed plots (NPK) was 5.9, slightly lower than 6.4 recorded from organically managed plots (COMP). The soil organic carbon (SOC) concentration in COMP plots was noted ~27% more than NPK plots (11.9 g kg^{-1}). Topsoil nitrogen (N) concentration was also higher (approximately 15%) in COMP plots compared to NPK. The N concentration in NPK was 1.09 g kg^{-1}, whereas in COMP plots were 1.25 g kg^{-1}. The mean value of extracted phosphorus (P) concentration was 17.8 mg kg^{-1} from COMP plots. On the other side, P concentration from NPK plots was 8.0 mg kg^{-1}. Soil potassium (K) concentration determined by using extraction method was recorded a bit higher (91.1 mg kg^{-1}) in NPK plots than in COMP plots where K concentration was 87.6mg kg^{-1}.

Table 5. 6 Topsoil (0-30 cm) properties of conventional (NPK) and organic fertility management (COMP) plots selected to monitor the effect of nitrification inhibitor.

Soil Parameter	NPK	COMP	P-value
Soil pH (H_2O)	5.9 (0.1)	6.4 (0.1)	0.06
Soil C (g kg^{-1})	11.9 (1.6)	15.1 (1.2)	0.34
Soil N (g kg^{-1})	1.09 (0.1)	1.25 (0.1)	0.49
Soil P (mg kg^{-1})	8.0 (0.3)	17.8 (3.0)	0.05
Soil K (mg kg^{-1})	91.1 (8.4)	87.6 (4.2)	0.71

Values are the means of four replicated blocks (n=4) and standard error (SE) of means

Weather pattern during the experiment

The weather pattern during the trial is shown in **Figure 5. 7**. The drainage season 2018/2019 was dry with 140.20 mm of total rain from Nov 2018 to Feb 2019 compared to the previous year when rainfall between Nov 2017 and Feb 2018 was 248.4 mm. Monthly rainfall during the study was the highest (75 mm) in November 2018 and lowest (14 mm) in February 2019. The highest monthly average temperature was 7.59°C in Nov 2018 and a minimum of 3.14°C in Jan 2019, which was the coldest month during this study.

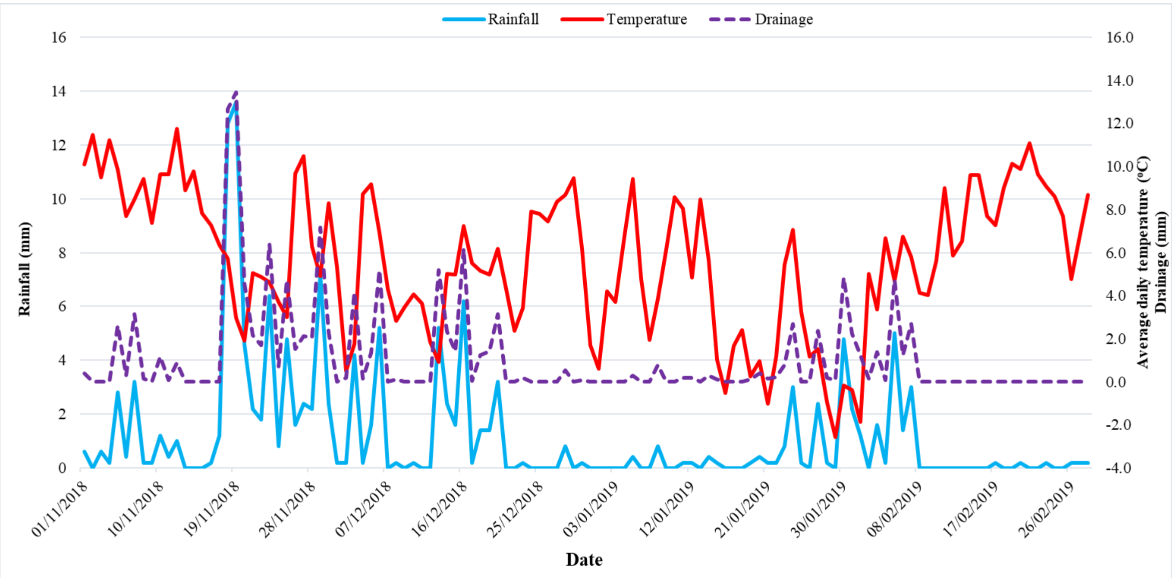


Figure 5. 7 Daily rainfall (mm) and average daily temperature (°C) recorded from the weather station at Nafferton farm and daily drainage (mm) calculated during the study period using daily water balance

There was a continuous decrease in monthly average temperature from Nov 2018 to Jan 2019; after that, the temperature was elevated to 6.9 ^{o}C in Feb 2019. Monthly total drainage starts rising in Nov 2018 (45 mm) after the period of maximum rainfall.

Effect of Vizura on topsoil mineral N dynamics

Mean SMN from organically (COMP) and conventionally (NPK) managed fertility plots is reported in **Table 5. 7**. The COMP plots had the highest mean NO_3-N (47.56 kg ha^{-1}) compared to all other treatments. The minimum nitrate value was measured (32.49 kg ha^{-1}) in the plots where NPK was used to fulfil crop nutrient demand and Vizura® was sprayed before ploughing in autumn 2018. The NO_3-N in INPK plots was 24% less than in the NPK plots and ~8 % less in ICOMP plots compared to the COMP. Note that the values in **Table 5. 7** are the means of four replicated blocks (n=4) for ICOMP, NPK and INPK treatments, except for COMP (n=3) due to the outlier values excluded (almost three times higher than other values on the same sampling date).

The main and interactive effects of historical fertility management (FM) and nitrification inhibitor (I) Vizura® on nitrate-N and ammonium-N are depicted in **Table 5. 7**. FM's effect was not significant on either soil mineral nitrogen form (NO_3-N and NH_4-N) with *P* = 0.1533 and *P* = 0.3161, respectively. We found a significant effect of Vizura® (I) on NO_3^--N (*P* <0.05). There was no significant effect of the treatments used in the study (FM and I) on soil NH_4-N contents.

Table 5. 7 Mean (SE) NO_3-N and NH_4-N (kg ha^{-1}) in topsoil from replicated blocks during the drainage season from Nov 2018 to Feb 2019 with ANOVA results for main and interactive effects (*P*-value) of fertility management (FM) and nitrification inhibitor (I) Vizura®

Factor	**NO_3-N (kg ha^{-1})**	**NH_4-N (kg ha^{-1})**
Main effect means		
+Vizura	38.18 (2.77)	2.64 (0.67)
- Vizura	44.96 (2.40)	2.39 (0.59)
COMP	45.45 (2.73)	3.15 (0.70)
NPK	37.74 (2.29)	1.97 (0.52)
Interaction means		
NPK+Vizura (INPK)	32.49 (3.31)b	1.78 (0.71)a
NPK (NPK)	43.01 (2.98)ab	2.16 (0.76)a
Compost (COMP)	47.56 (3.37)a	2.69 (0.81)a
Compost + Vizura (ICOMP)	43.87 (3.76)ab	3.49 (1.01)a
ANOVA (*P-Value*)		
Historical fertility management (FM)	0.1536	0.3152
Inhibitor (I)	0.0225	0.6840
Sampling date (D)	0.0020	0.5474
I X FM	0.0315	0.1227
I X FM X D	< 0.001	0.2139

To investigate the soil nitrate-N concentration in topsoil, the detailed change in the concentration of NO_3-N in kg ha^{-1} on different sampling dates is shown in **Figure 5. 8** from all experimental plots. The pattern in decrease and increase of the concentrations over time were similar in all four treatments (COMP, ICOMP, NPK and INPK). Overall, NO_3-N was lower in NPK plots (dominated by grass prior to incorporation) with Vizura application as shown **Figure 5. 8**. The NO_3-N was higher in COMP plots (dominated by legumes) with Vizura application compared to NPK.

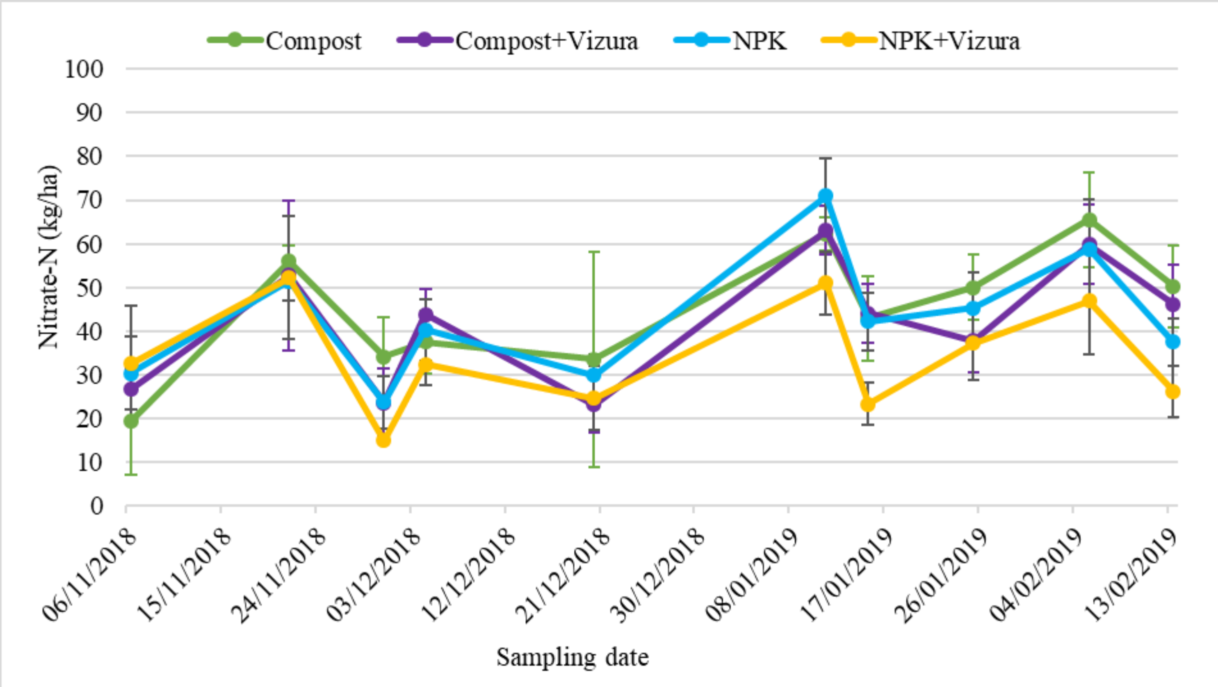


Figure 5. 8 Detailed topsoil nitrate-N (kg ha^{-1}) changes over the study time from compost and NPK plots with Vizura application (ICOMP, INPK) and without (COMP, NPK) Vizura application (error bars represent standard error).

In initial soil samples, the NO_3-N concentration was almost similar in both the NPK treatments (NPK and INPK) as shown in **Figure 5. 8**. From the 3rd sampling date (after 35 days of Vizura application), soil nitrate-N in INPK treatment were always lower than in NPK. However, the overall increase and decrease in the peak values were similar in both treatments throughout the experiment. At the end of the experiment, NO_3-N in the soil of INPK was 26.1 kg ha^{-1} (30% less) and 37.5 kg ha^{-1} in NPK plots.

Table 5. 8 Nitrate-N losses (kg ha^{-1}) in leachate during the drainage season

Fertility management	***Vizura***	***NO_3-N leaching (kg ha^{-1})***
NPK	+Vizura	24.80
	-Vizura	42.94
	ANOVA *P-value*	0.001
Compost	-Vizura	18.40
	+Vizura	20.35
	ANOVA *P-value*	0.362

Nitrate-N concentration (mg l^{-1}) from soil solution samples collected using porous cups were plotted against cumulative drainage to estimate the actual NO_3-N leaching (kg ha^{-1}) losses from all treatment plots. The cumulative drainage starts at zero and was 22.7 mm at the start of the sampling period and 113.5 mm at the end, as shown in **Figure 5. 9**. A maximum of 42.94 kg ha^{-1} of NO_3-N was leached from the NPK plot over the 2018/19 drainage season (**Table 5. 8**). Other treatments leached 24.80, 18.4 and 20.35 kg NO_3-N ha^{-1} for INPK, COMP and ICOMP plots respectively. During this period, the nitrogen leaching losses accounted for 30%, 44%, 54%, and 48% of total N losses during the 2018/19 drainage season.

At the end of sampling season, the concentration of NO_3-N (mg l^{-1}) was 8% lower in INPK plots than in the NPK treatments and 6% more in the ICOMP treatments than the COMP treatments. The effect of Vizura® was not as prominent in ICOMP plots as in INPK plots. The concentration of NO_3-N (mg l^{-1}) in soil solution was higher in ICOMP plots for most of the time, which results in slightly higher leaching from ICOMP (20.3 kg ha^{-1}) than from COMP (18.4 kg ha^{-1}) plots.

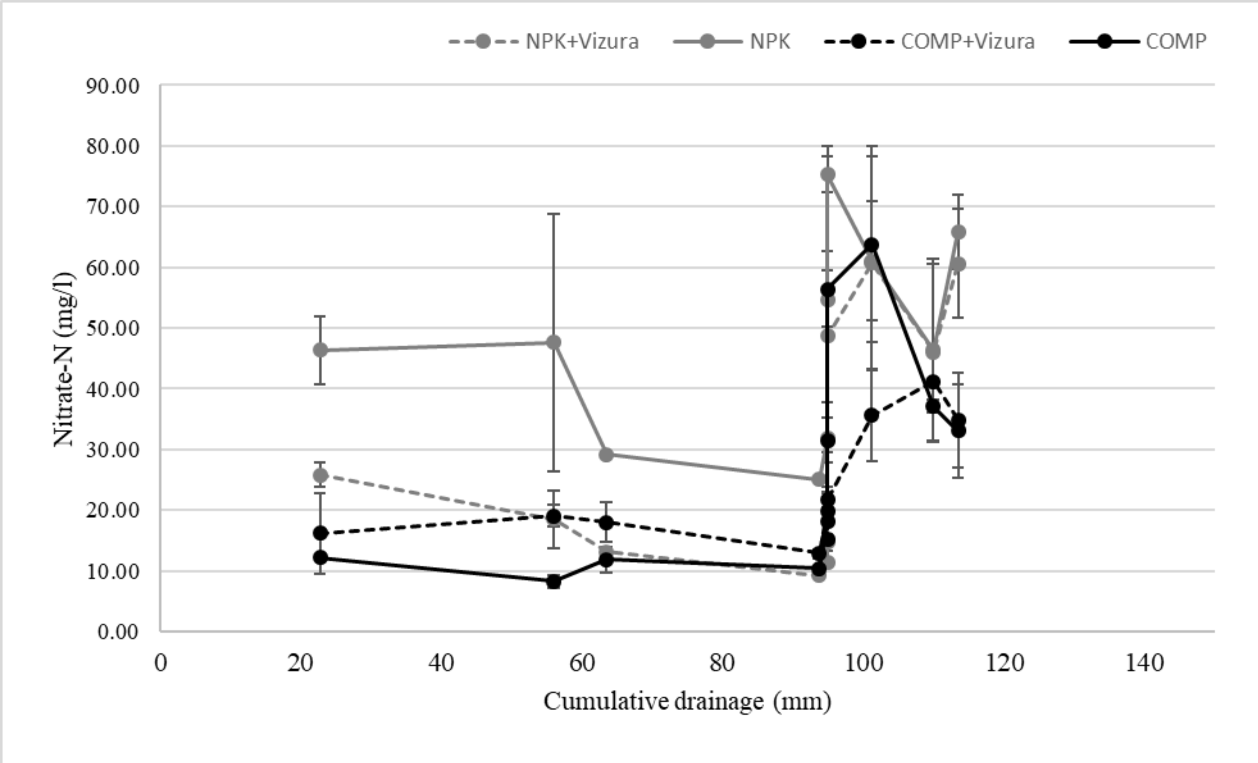


Figure 5. 9 Nitrate-N concentration (mg l^{-1}) in soil solution collected from porous cups against calculated cumulative drainage (mm) over the drainage season 2018/19. The area under plot is Nitrate-N loss in leaching.

Effect of Vizura on spring wheat crop

Following application of Vizura treatments in the 2018/19 drainage season, growth of spring wheat and levels of SMN were monitored (**Table 5. 9**). No significant NI and FM effect was found on soil nitrate-N and ammonium-N concentrations during the growing season (P >0.05).

The agronomic effect of Vizura® on spring wheat was recorded from plant biomass samples collected before harvesting. The *P- values* for the main and interactive effects of NI and FM were always >0.05 representing no significant effect of any factor on the agronomic response of spring wheat.

Table 5. 9 Mean (± SE) of SMN during growing season 2019 (July-Sep) and agronomic parameters of spring wheat with ANOVA results as main and interactive effects (*P*-value) of fertility management (FM) and nitrification inhibitor (I) Vizura

Variables	**NPK (NPK)**	**NPK+Vizura (INPK)**	**Compost (COMP)**	**Compost + Vizura (ICOMP)**
NO_3-N (kg ha^{-1})	5.7 ± 1.5	3.6 ± 1.0	6.6 ± 1.6	4.9 ± 1.2
NH_4-N (kg ha^{-1})	19.8 ± 2.3	21.8 ± 3.4	25.1 ± 4.0	24.9 ± 3.5
Agronomic Response				
Straw fresh weight (g m^{-2})	153.0 ± 28.8	159.8 ± 19.9	129.9 ± 11.9	105.3 ± 38.1
Straw dry weight (g m^{-2})	78.6 ± 11.3	84.8 ± 8.2	74.3 ± 7.6	61.0 ± 16.4
Ear fresh weight (g m^{-2})	105.6 ± 25.5	102.9 ± 12.8	92.1 ± 10.5	76.0 ± 17.2
Ear dry weight (g m^{-2})	90.1 ± 21.5	88.8 ± 10.4	79.8 ± 9.9	66.8 ± 13.6
ANOVA *P-Values*				
Parameters	Straw fresh weight (g m^{-2})	Straw dry weight (g m^{-2})	Ear fresh weight (g m^{-2})	Ear dry weight (g m^{-2})
Historical fertility management (FM)	0.2195	0.3234	0.3237	0.3228
Inhibitor (I)	0.7621	0.7792	0.638	0.6586
I X FM	0.5174	0.5594	0.6413	0.6556

5.6.2 Experiment B

Soil chemical properties

Topsoil samples were collected from 0-30 cm layers of both tillage plots (Conventional and minimum tillage) and analysed for the chemical properties at the beginning of the experiment. The mean soil pH values from experimental plots with conventional tillage (CT) and minimum tillage (MT) were 6.5 (0.2) and 5.9 (0.1), respectively (**Table 5. 10**). Soil carbon (C) in the soil samples representing MT was 16.9 (1.1) g kg^{-1}, 22% more than soil C contents recorded in CT plots (13.8 (0.8) g kg^{-1}). Soil organic nitrogen (N) concentrations did not vary between both the tillage systems, i.e. 1.21 (0.1) and 1.36 (0.1) g kg^{-1} in CT and MT plots, respectively. Tillage has influenced the available phosphorus (P) and potassium (K) concentrations in soil. The available P in MT plots was 28.9 (5.8) mg ka^{-1} of soil, which is ~210% more than the available P in CT plots. In the same way, the exchangeable K in MT plots was noted ~45% more than in CT plots.

Table 5. 10 Soil chemical properties of topsoil (0-30 cm) layer from conventional tillage (Conv. Till) and minimum tillage (Min. Till) plots. Each value represents the mean on four replicated blocks with standard error (SE)

Soil Parameter	Conv. Till	Min. Till	P-Value
Soil pH (H_2O)	6.5 (0.2)	5.9 (0.1)	0.122
Soil C (g kg^{-1})	13.8 (0.8)	16.9 (1.1)	0.200
Soil N (g kg^{-1})	1.21 (0.1)	1.36 (0.1)	0.399
Soil P (mg kg^{-1})	9.3 (2.6)	28.9 (5.8)	0.054
Soil K (mg kg^{-1})	105.7 (15.5)	153.9 (12.9)	0.188

Conventional vs Minimum tillage effect on soil mineral nitrogen

The means of soil mineral nitrogen (nitrate-N and ammonium-N) measured during the 2018-19 drainage season are represented in **Figure 5. 10**. The mean nitrate-N concentration was 34.4 kg N ha^{-1} in conventional tillage (CT) plots and 36.4 kg N ha^{-1} in minimum tillage (MT) plots. No significant difference was found in the nitrate-N (kg ha^{-1}) contents from conventional and minimum tillage plots with P= 0.171. The NH_4-N was almost the same (4.76 and 4.96 kg ha^{-1}) in CT and MT plots, respectively (P= 0.222).

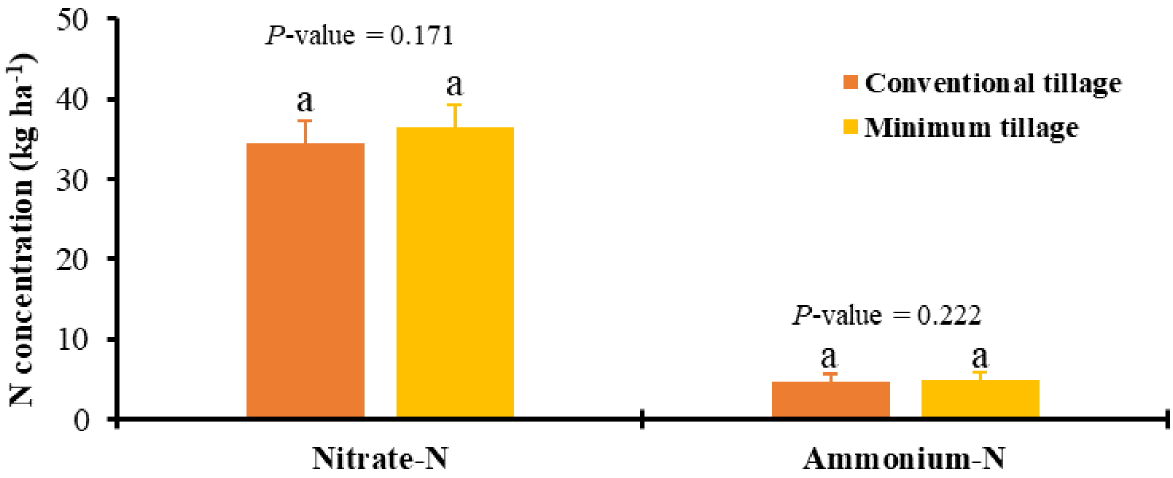


Figure 5. 10 Means of four replicated blocks (n=4) with error bars representing standard error of means (SE) of soil mineral nitrogen from conventional and minimum tillage over the 2018/19 drainage season. *P*-values of main effect of treatments.

The amounts of nitrate-N and ammonium-N measured in the topsoil layer during this study are depicted in **Figure 5. 11**. NH_4-N was always <10 kg ha^{-1} in conventional tillage throughout the study, except for a slight increase (14.7 kg ha^{-1}) in the middle of January 2019. Almost similar trends were noted in the NH_4-N contents in plots where winter wheat was direct drilled (minimum) tillage. The NO_3-N: NH_4-N ratios in CT and MT were 20:3 and 13:4 at the start of sampling (21st November 2018), respectively. Compared to CT, the amount of NO_3-N was higher in MT, with a 90 % rise in the last soil sample.

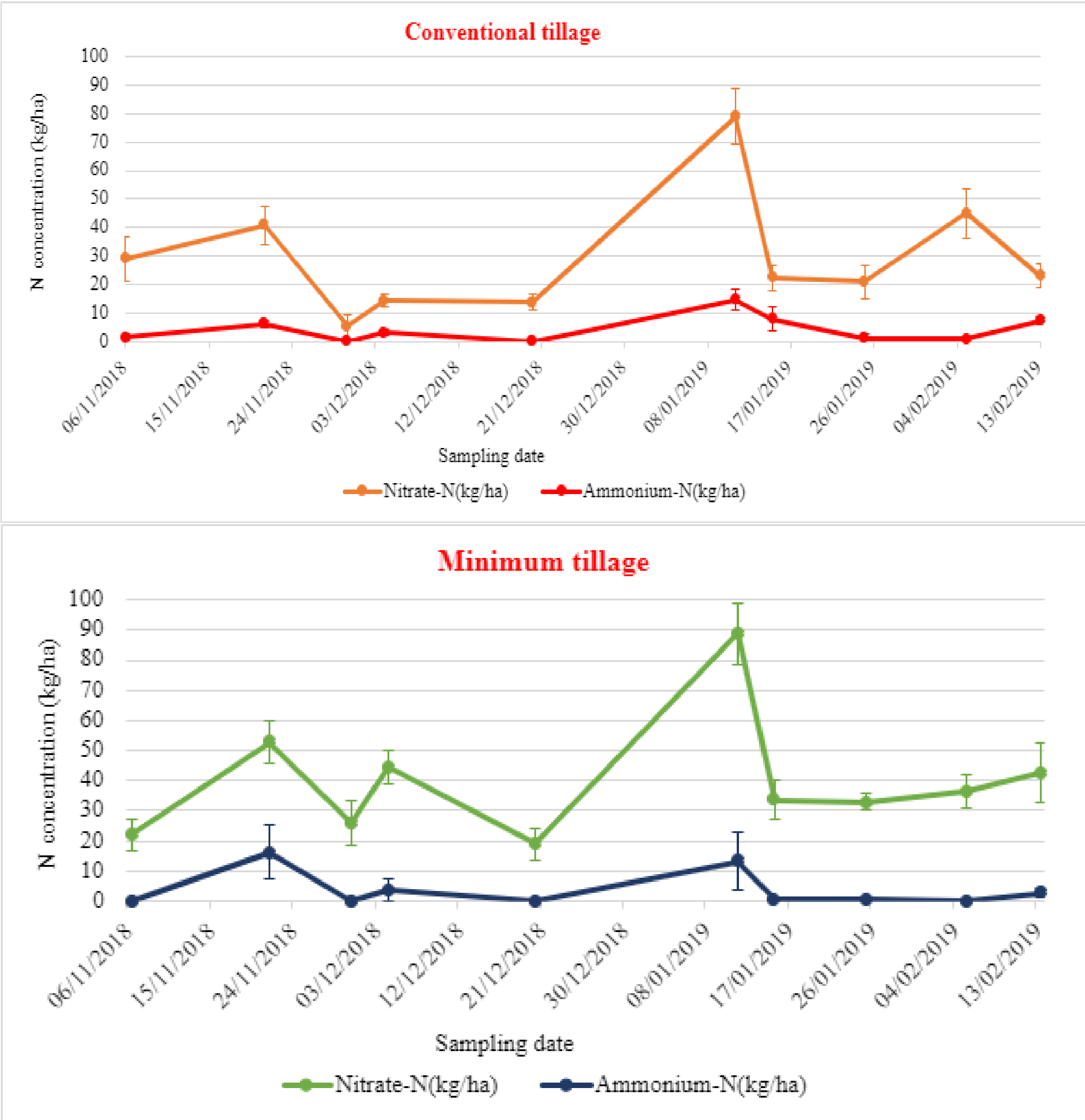


Figure 5. 11 Nitrate-N and ammonium-N in the topsoil (0-30 cm) from conventional tillage (CT) and minimum tillage (MT) plots during the drainage season. Each value represents the mean of four replicated blocks (n=4) with error bars depicting standard error (SE)

Effects of tillage system on nitrate leaching over the 2018/2019 drainage season

The NO_3-N leaching losses from both tillage systems (CT and MT) were measured using nitrate-N concentrations (mg l^{-1}) and cumulative drainage, as shown in **Figure 5. 12**. Nitrate-N lost via leaching from MT was 70.6 kg ha^{-1} and from CT it was 10.4 kg ha^{-1}. The mean NO_3-N (mg l^{-1}) concentration from the beginning of the experiment was numerically higher (62 mg l^{-1}) in MT plots. The concentration of NO_3-N (mg l^{-1}) in the soil solution was lower throughout the experiment therefore, leaching losses from conventional till plots were lower than minimum tillage. The concentration was similar in both treatments only at one point when cumulative drainage was 108 mm and mean NO_3-N in MT plots was 11 mg l^{-1} compared to 9.6 mg l^{-1} in CT plots. The highest NO_3-N concentrations in MT were noted in November when 62, 87 and 75 mg l^{-1} was recorded; this resulted in a high chance of leaching due to heavy rainfall events.

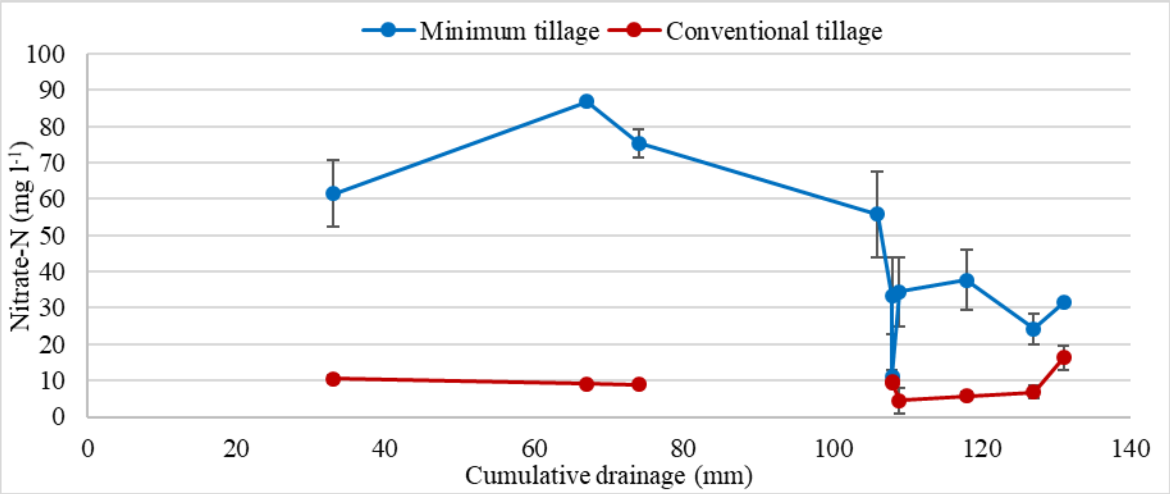


Figure 5. 12 Nitrate-N concentration (mg/l) in soil solution against cumulative drainage (mm) over the drainage season from conventional tillage (CT) and minimum tillage (MT). The area under plot is Nitrate-N loss due to leaching. A gap in the line indicates that there was no sample in the porous cup on that date.

5.6.3 Experiment C

Soil Chemical properties

Initial soil samples were taken from all four replicates from the fully conventional plots (conventional crop protection and fertility management) in experiment 4 (**Figure 5. 3**) and used to determine the chemical properties of the soil. Topsoil (0-30 cm) pH in H_2O was moderately acidic with an average value of 5.6 (0.04) (see **Table 5. 11**).

Table 5. 11 Soil analysis immediately prior to fertiliser application to the fully conventional plots (CONVFM). C and N are total values by Dumas combustion; P is Olsen's; K is ammonium nitrate-extractable. Values are the means of four replicated blocks with standard error (SE)

Soil properties	CONVFM
Soil pH (H_2O)	5.6 (0.04)
Soil C (g kg^{-1})	15.2 (0.33)
Soil N (g kg^{-1})	1.30 (0.06)
Soil P (mg kg^{-1})	6.55 (0.97)
Soil K (mg kg^{-1})	136.9 (9.18)

Soil organic carbon and nitrogen were 15.2 (0.33) and 1.30 (0.06) g kg^{-1}, respectively. Soil available potassium (K) concentration was 136.9 (9.18) mg kg^{-1} (K index=1) and Olsen's P was 6.55 (0.97) mg kg^{-1} (P index= 0).

Effect of fertilizer treatment on soil mineral nitrogen dynamics

The effects of N source on soil NO_3-N and NH_4-N contents in the 0-30 cm soil layer across the growing season are shown in **Figure 5. 13**. The bar graphs represent the average nitrate-N and ammonium-N values, excluding the outliers from replicated blocks. The mean values of nitrate-N were 62.16, 49.28, and 45.38 kg ha^{-1} and 37.67, 37.04 and 31.25 kg ha^{-1} ammonium-N from urea, NutriSphere-N® (NS), and 85% NutriSphere-N® treated plots. Despite the difference between means, no statistically significant effects were found due to N treatment on soil NO_3-N during potato growth (*p*-value= 0.9204). The effect of fertilizer management on NH_4-N contents was also not significant (*p*-value = 0.5443).

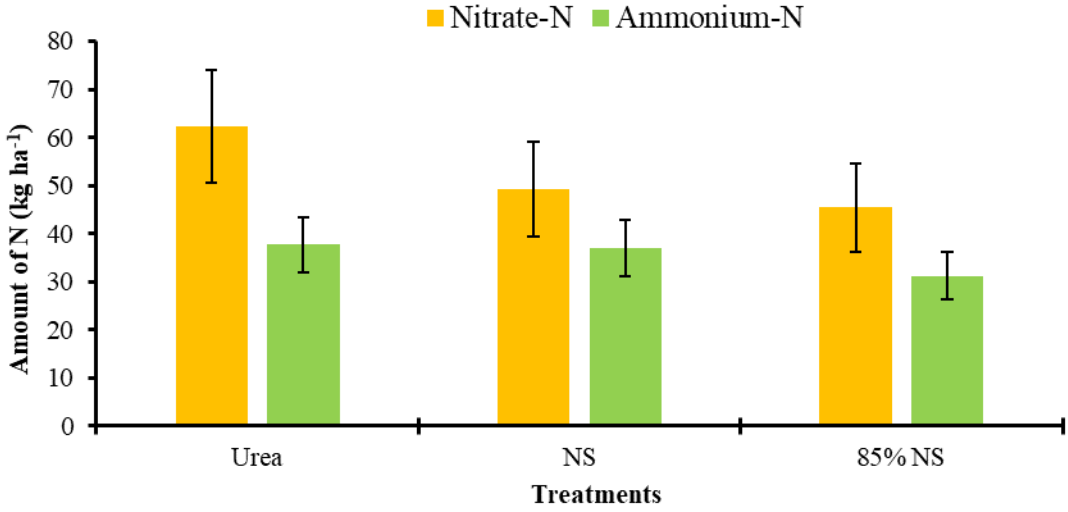
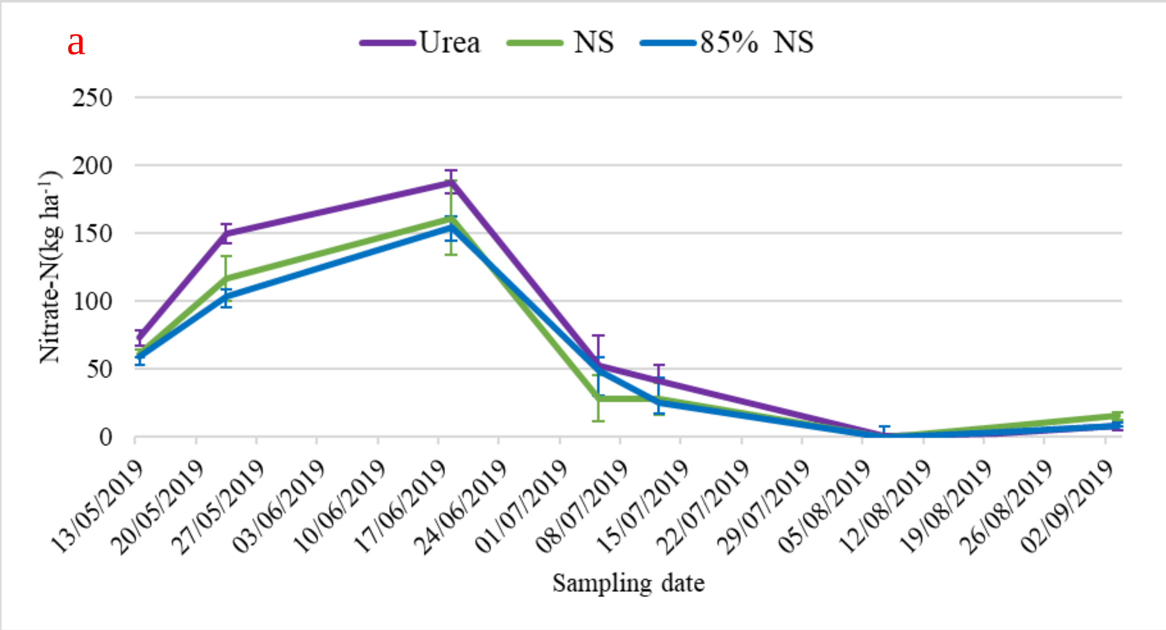


Figure 5. 13 Effect of fertilizer source on the average amount of nitrate-N and ammonium-N measured from mid-May to start-September at 0-30 cm depth during potato growth. Standard error (error bars) of means were calculated from all replicates.

Detailed SMN dynamics over the study period are shown in **Figure 5. 14**. Eighteen days after fertilizer application, the amount of nitrogen (N) as nitrate in soil was 73.08, 61.28 and 58.79 kg ha^{-1} for urea, NS and 85% NS treated plots respectively. However, 28 days after application, soil nitrate was 149.4, 116.7 and 103.4 kg of NO_3-N ha^{-1} respectively for urea, NS and 85% NS treatments. After 29 days, NO_3-N contents in all three treated plots reached maximum values (187.64, 161.37 and 154.46 kg ha^{-1} from urea, NS and 85% NS treated plots, respectively) then started declining. NH_4-N contents reached a maximum 28 days after fertilizer application in all treatments. After that, NH_4-N remained similar in all treatments, as shown by the trend lines throughout experiment in **Figure 5. 14 b.**



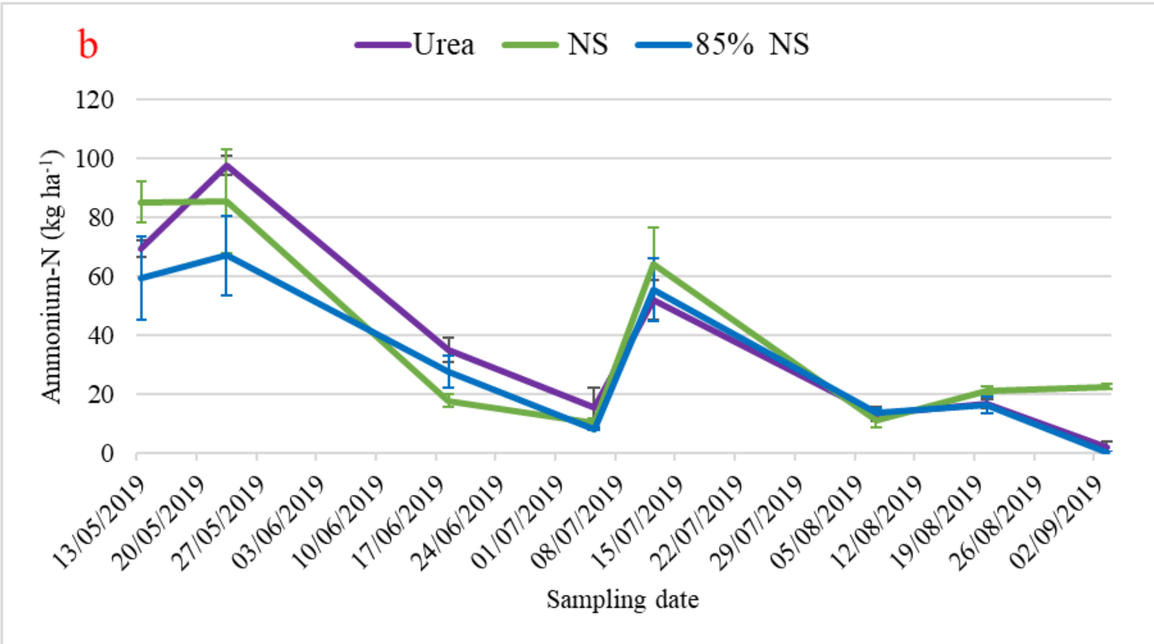


Figure 5. 14 Changes during the study period for soil mineral nitrogen: Nitrate-N (a) and Ammonium-N (b) in urea, NutriSphere-N® (NS) and 85% Nutrisphere (85% NS) treated plots.

Agronomic response to slow releasing fertilizer

The agronomic responses to fertilisers are shown in **Table 5. 12**. No statistically significant effect of any fertiliser treatment was found for either crop growth stage. Despite no statistical significance (*P >0.05*), the means of tuber fresh and dry weights at tuber development stage were numerically different with the highest mean tuber dry weight noted from urea treated plots and minimum from 85% NutriSphere-N® plots (85%NS). This numerical difference due to fertiliser treatment on tuber yield was not visible at the senescence stage. No significant difference among the means of aboveground biomass and root weights (fresh and dry) was found.

Table 5. 12 Means for dependent variables at two growth stages as influenced by N source and N rate with standard errors (SE) of mean

Source of N	**Aboveground biomass**		**Belowground**			
	Fresh weight	**Dry weight**	**Root fresh weight**	**Root dry weight**	**Tubers fresh weight**	**Tubers dry weight**
	(kg m^{-2})	(kg m^{-2})	(g m^{-2})	(g m^{-2})	(g m^{-2})	(g m^{-2})
Tuber development stage						
Urea	2.44 (0.38)	0.27 (0.05)	400.1 (26.97)	53.2 (2.56)	2052.1 (286.45)	369.9 (49.00)
NS	2.15 (0.35)	0.24 (0.03)	378.2 (74.14)	53.8 (10.59)	1502.6 (152.72)	266.1 (29.45)
85% NS	2.29 (0.16)	0.26 (0.01)	374.5 (66.65)	54.5 (9.91)	1362.5 (201.02)	253.4 (39.69)
ANOVA P-values	0.812	0.847	0.948	0.994	0.118	0.135
Senescence stage						
Urea	2.23 (0.45)	0.28 (0.06)	455.7 (61.56)	65.8 (8.51)	3490.4 (265.52)	694.2 (34.97)
NS	2.13 (0.18)	0.28 (0.22)	420.1 (34.53)	63.7 (5.50)	3821.1 (305.13)	744.1 (66.90)
85% NS	2.09 (0.15)	0.27 (0.25)	462.9 (8.01)	63.3 (1.81)	3517.4 (100.29)	704.8 (31.37)
ANOVA P-values	0.939	0.974	0.740	0.953	0.578	0.740

5.7 Discussion

5.7.1 Experiment A

DMPP has already been described as one of the most effective nitrification inhibitors in studies (Linzmeier *et al.*, 2001; Hatch *et al.*, 2005). The present study was conducted to investigate the effect of application of a DMPP based nitrification inhibitor (Vizura®) to a grass-clover ley before incorporation, on topsoil (0-30 cm) mineral N dynamics and nitrate leaching. Because of its high performance, low mobility in soil, and a more prolonged period of activity than other NIs (Azam *et al.*, 2001; Chaves *et al.*, 2006), DMPP was chosen as the NI for this experiment.

The DMPP starts inhibiting nitrification and reduced NO_3-N contents after 35 days of application and continued even after three months as shown in **Figure 5. 8**. The nitrification inhibition by DMPP has been observed to last from 42 day (Duan *et al.*, 2017), to up to 95 days when applied on grass/clover. The potential amount of nitrified N was predicted to be reached after 200 days of application in a linear regression by Chaves *et al.* (2006). Therefore, the risk of nitrate leaching will be decreased over the complete winter season following DMPP application.

The losses of nitrate-N in both the fertility treatments was lower in plots where DMPP based nitrification inhibitor (Vizura®) was applied. Application of Vizura® reduced NO_3-N leaching by ~ 72% from NPK plots as shown in **Figure 5. 9**. Leaching losses from NPK plots were 42.9 kg of NO_3-N ha^{-1}, and from INPK plots, the losses were 24.8 kg of NO_3-N ha^{-1}. However, the nitrification inhibitor did not work well in reducing leaching losses from the soil with a history of organic fertility management, as the reduction in nitrate leaching was only 10 % compared to non Vizura®. This difference in performance is explained and, in line with the study by Zhu *et al.* (2019), might be due to the adsorption capacity of the soil. They used an agricultural soil collected from a temperate climate region from the UK with high soil organic carbon (C) contents (27.4 g kg^{-1}) to test the effect of DMPP in comparison with low carbon contents soil (9.1 g kg^{-1}) and found poor efficiency of DMPP associated with higher soil organic C. We observed slightly higher C contents in COMP plots (**Table 5. 6**). DMPPs effectiveness is negatively associated with SOM content due to its adsorption on soil colloids (McGeough *et al.*, 2016; Volpi *et al.*, 2017). On the other hand, SOM provides energy to heterotrophic microbes that degrade DMPP, reducing DMPP's ability to inhibit ammonia oxidation (Barth *et al.*, 2001). To improve the effectiveness of DMPP in COMP plots, a higher rate of application may be recommended. The potential of DMPP to reduce nitrate leaching was also reported by Chaves *et al.* (2006) when the NI was sprayed before crop residues' incorporation in soil with almost similar chemical properties (pH of 6.5 and soil C 15 g kg^{-1}).

No significant effect of NI was observed in the agronomic response of spring wheat in 2019. The lack of plant response to nitrification inhibitors could be because many plants prefer nitrate since it is more easily delivered with water mass flow to the roots. In the current study, SMN (nitrate-N and ammonium-N) results during summer-2019 represents more soil ammonium-N (kg ha^{-1}) compared to nitrate-N as shown in **Appendix 7** irrespective of plots with or without DMPP application. Nitrification inhibitors only increased crop yields in soils with low N fertility and significant sensitivity to mineral N losses (Malzer *et al.*, 1989; Chaves *et al.*, 2006).

The findings showed that treating grass/clover with DMPP before incorporation can alter soil N dynamics and reduce the risk of NO_3-N leaching over the winter period, as hypothesized. The results are in accordance with other studies on the potential of DMPP in reducing leaching of NO_3-N from grass/clover in a lab and field experiments (Wu *et al.*, 2007; Chiodini *et al.*, 2019). So far, no toxicological or ecotoxicological adverse effects have been discovered in any of these assays. As a result, neither DMPP-containing fertilizers nor liquid DMPP formulations as urea ammonium nitrate solution or slurry additives need to be labelled as hazardous substances (Zerulla *et al.*, 2001). The probability of DMPP being leached into groundwater appears to be extremely low. More study, however, is needed. No DMPP concentrations above the detection limit of 0.5 g l^{-1} were observed in the leachate in lysimetric studies performed at the Jülich Research Centre over three years (Fettweis *et al.*, 2001).

5.7.2 Experiment B

Reduced tillage practices are often used to improve soil health and nutrient status. The purpose of the current study was to investigate the effect of long term conventional and minimum tillage practices on soil nitrogen dynamics in topsoil (0-30 cm) when winter wheat was direct drilled following two years of ley in comparison with deep ploughed, plots. There were no significant differences in the soil nitrate and ammonium concentrations due to tillage treatments, as shown in **Figure 5. 10**. Despite the absence of statistically significant differences, data indicated in the trends in **Figure 5. 11** higher NO_3-N contents in minimum tilled (MT) plots compared to conventional tillage (CT). Soil nitrate levels were consistently higher in MT plots compared to CT with NO_3-N values 29 % more, 209 % more and 37 % more after 26, 40 and 55 days respectively following wheat planting. The increased accumulation of crop residues near the soil surface with minimum tillage reported in a study evaluating the effect of 6 years of tillage practices, was associated with increased SOM content and resulted in higher N (Salinas-Garcia *et al.*, 2001).

Figure 5. 12 represents the NO_3-N concentration (mg l^{-1}) in soil solution. The NO_3-N concentration in plots where winter wheat was direct drilled (MT) was higher throughout the drainage

season than the CT plots. The total leaching losses from MT were ~ 7 times higher (70.6 kg of N ha^{-1}) than for the CT plots (10.4 kg of N ha^{-1}), which could be due to the higher infiltration rates in MT plots, allowing soluble nutrients to move into the soil profile through water infiltration into macropores. The infiltration rate has not been measured in the current study but Aulakh and Malhi (2005) found a similar effect of MT on infiltration rate. Conservation tillage causes less disturbance in soil structure and leads to macropores in direct contact with the soil surface. As a result, these macropores, therefore, provide a route for water to flow to the maximum depth of the soil profile, leading to more nitrate leaching in the case of no-tillage than in the deep tillage practices, which disrupt the soil structure and impedes water flow (Khan *et al.*, 2017).

Tillage has a variety of impacts on the agricultural system e.g., soil tillage is found as one of the most significant factors influencing crop yield, soil physical properties, and eventually NO_3^- movement through the soil profile (Halvorson *et al.*, 2001). The results found the significant effect of minimum tillage on topsoil NO_3-N contents and NO_3-N leaching from soil. Minimum tillage can enhance nutrient availability, can improve soil physical and chemical properties and infiltration rates (Khan *et al.*, 2017) and also provide the route for rapid drainage water movement (Kanwar *et al.*, 1985) and cause dissolved NO_3-N leaching from the root zone. Therefore, it is not recommended to use minimum tillage is a system where there are maximum chances of excess N availability.

5.7.3 Experiment C

The key to improving yield without increasing the amount of N fertiliser used is to improve the nitrogen use efficiency (NUE) of fertilisers. New fertiliser additives such as NutriSphere-N® that improve nitrogen uptake or reduce nitrogen losses have the potential to increase the NUE. The NutriSphere-N® coating sticks to positively charged cations like nickel in the soil, making these cations unavailable to form the urease enzyme. The hydrolysis of urea into ammonia ceases when the urease enzyme is absent. The NutriSphere-N's (NS) effectiveness is less vulnerable to environmental or management factors because it inhibits the primary pathway for N conversion in the soil (Heiniger *et al.*, 2013). The current study was designed to improve the NUE of potatoes by using NutriSphere-N (coated urea) in full and reduced rates compared to non-treated urea, to reduce the risks of N losses from residues post-harvest.

For all fertiliser treatments, NO_3-N concentrations in topsoil increased linearly from Day 0 of sampling to Day 35, while NH_4-N concentrations decreased linearly from Day 0 to Day 52 as shown in **Figure 5. 14**. The NO_3-N concentrations were higher compared to NS and 85%NS plots. The results showed that within two months of fertiliser application, the soils treated with urea and 85% NS had very little ammonium-N left. However, the ammonium-N left in NS plots was higher which could be due to later ammonium release from urea that was inhibited during the cropping season (because NS is a urease inhibitor) and NS stops further inhibiting at the end of the season. This residual ammonium-N could be nitrified during autumn and susceptible to leaching over winter if nitrified (Vogeler *et al.*, 2020), because residual fertiliser N uptake by crops has been found to be negligible (Thomsen *et al.*, 2003; Petersen *et al.*, 2010)

The effects of NutriSphere-N® (NS) at a recommended rate of N and 85% of the recommended rate (85% NS) compared to Urea (U) on potato yield were not significant. However, at the tuber development stage the tuber yield was higher in the plots with plain urea application **Table 5. 12**, indicating that NS was inhibiting N supply to plants at this stage which increased by senescence stage. Despite the numerical significance, no statistical significance of NS was found at two growth stages (*P*-Value > 0.05) possibly due to high variability in the sampling method. The final yield of potatoes was 37.8, 41.2 and 38.1 t ha^{-1} from U, NS and 85% NS treatments. No prominent effect of NS was found on potato yield, but NS improved the nitrogen use efficiency of potatoes which was a maximum for 85%NS (46) and minimum for U (38). According to previous studies, slow-release nitrogen fertilizers do always lead to higher crop yields (Wiatrak, 2014). Plant dry matter and grain yields of winter wheat did not differ significantly between coated and uncoated urea, according to Man *et al.* (2011). Spring wheat and rice yields were not higher with Nutrisphere-N than urea in results reported by Franzen *et al.* (2011). However, Heiniger *et al.* (2013) found a significant increase in maize yield and improved NUE with NutriSphere-N® application.

5.8 Conclusion

The current study aimed to investigate the efficiency of different strategies to minimize nitrate leaching to groundwater without compromising crop yield. Among all available options, three approaches were tested, including the nitrification inhibitor (Vizura®), slow-releasing coated fertilizer (NutriSphere-N®) source and tillage management. Vizura® had a significant effect in reducing nitrate leaching in one drainage season; however, the effect is more prominent from conventional fertility management plots. The influence of Vizura® was also visible in reducing overall nitrate-N concentration in autumn ploughed ley plots. Vizura® could be used in the fields in the Fell Sandstone catchment area with similar land management practices (autumn ploughing of grass/clover) before winter wheat drilling to minimise NO_3-N leaching losses.

NutriSphere-N® inhibited N supply early in the season that reduced the tuber yield determined during the tuber development stage in plots where NS was applied (100% and 85%). The use of NutriSphere-N® resulted in a similar response for final yield as from the plots where plain urea with the same rate was applied, which has been proved in the literature that NutriSphere-N® efficiency does not result in increases in yield but the nitrogen use efficiency of potatoes has been improved in the plots where 85% NS is used. Also, the use of a lower rate of N than recommended did not affect the yield negatively, as suggested by the manufacturer. Therefore, a reduced rate of N as NutriSphere-N® (85%) can be used to minimize the risks of nitrogen losses during crop growth without any significant reduction in yield.

The results indicated that both the innovations were effective in reducing nitrate-N availability from grass/clover residues (Vizura®), reduced chances of residual fertiliser's N post-harvest by improving crop NUE (NutriSphere-N®) particularly when used at a lower N rate, and ultimately can minimise N leaching chances during winter from a temperate climate.

Chapter 6. Calibration and Validation of a N Dynamics Model in the Fell Sandstone Catchment

6.1 Introduction

Fertilizer nitrogen (N) management is hard to achieve to fulfil both production and environmental goals because cropping system N dynamics are based on complex interactions that are difficult to monitor and predict (Norton, 2008). In the context of mitigating groundwater nitrate (NO_3^-) pollution, assessing and predicting leaching of NO_3^- from soil to groundwater is difficult. To simulate NO_3^- transport, numerical models have been developed and are widely used (Yang and Wang, 2010). They can be used to develop and test a hypothesis and build a management-focused decision support system to improve productivity, profitability, and environmental quality (Udvardi *et al.*, 2021). The assessment of credibility of a model's results is important before using a model as a decision support system. The models' quality and complexity will directly impact the modelling results' credibility (Krause *et al.*, 2007; Collins and McGonigle, 2008). The following aspects should be therefore considered in good models:

- Weather-driven processes and meteorological conditions (e.g., precipitation, air temperature, solar radiation, and wind speed) influence water quantity and quality.
- Source of nitrogen.
- Complex soil-water interfaces for water flow and solute fluxes considering natural events and human activities.

Empirical models are derived from observed relations (statistical and mathematical) and are easier to run and require less data, but they have limited modelling flexibility in conditions with unclear limitations (Giltrap *et al.*, 2020). Process-based models are more realistic when knowledge of flow pathways, distributed state variables, and/or physical limitations is required. For example, recognising the implications of climatic non-stationarity or responses among diverse Earth system processes. In these cases, process-based models outperform other models (Fatichi *et al.*, 2016), and simulate the multiple impacts of biophysical processes and management strategies. Process-based models' outputs are always uncertain due to their complexity and the absence of some site-specific characteristics such as microbial activity, which can be reduced by calibration and validation (Giltrap *et al.*, 2020).

Cropping systems models combine individual component models that focus on certain biophysical aspects (e.g., water balance, crop growth and soil N mineralisation). Models based on site-specific inputs and processes indicating major nitrogen dynamics can be used to assess the current cropping system and evaluate alternative systems, thereby accelerating farmer learning. Those models published in the literature (as discussed in *Chapter 2.*), that attempt to improve scientific knowledge of system functioning are not always suitable for practice (Koopmans and Bokhorst, 2002). Almost all of the models (see *Table 2.4*) include N application, mineralisation/immobilisation, nitrification, and nitrate leaching, denitrification, and plant absorption as the major soil N dynamic processes. The management of these processes varies depending on the model. Scientific rigour must be linked with an application-oriented philosophy in model building, as in the case of the NDICEA model, to contribute to an informed decision-making process (Jones *et al.*, 2003; Keating *et al.*, 2003; Van der Burgt *et al.*, 2006).

The NDICEA model was developed to represent the dynamics of water, organic matter, and inorganic nitrogen in well-drained mineral soils so that fertilization strategies could be evaluated using data on initial states, parameters, and driving variables that was relatively easy to come by (Van der Burgt *et al.*, 2006). NDICEA applies an internal method as input for crop yield data, which reduces the probability of inaccuracies in soil mineral nitrogen. In NDICEA, the crop nitrogen uptake is quantified by taking into account the nitrogen concentration in the crop products including roots and residues, nitrogen concentration in the soil water, water uptake, and soil moisture contents (Kersebaum *et al.*, 2007). NDICEA is a useful tool for field-scale visualizing of N dynamics, despite model limitations that do not fully explain biological aspects of the results. NDICEA provides a safe environment for experimentation in which to practice making real-world decisions to learn about complex relationships and interactions. All of these factors could help farmers and advisors improve N efficiency on the farms (Swain *et al.*, 2016).

This study was designed to assess the credibility of NDICEA as a tool for farmers to use for nitrate-N leaching management in the study catchment with measurable soil properties and land management data. The study aimed to: (1) calibrate NDICEA for predicting soil inorganic N from selected locations in the study catchment; (2) evaluate the performance of site-specific calibrated NDICEA for the drainage years 2017/2018 and 2018/2019 with the measured data of leaching; (3) investigate the effect of different environmental input parameters, variable soil types and grass on nitrate leaching using NDICEA.

6.2 Material and Methods

6.2.1 Study sites description

The data used in the study were collected from eight locations across the Fell Sandstone groundwater catchment in Berwick upon Tweed. Details of the study are explained in *Chapter 3 and Chapter 4***.** The eight locations selected for site-specific modelling are shown in **Figure 6. 1**. Six out of eight are under conventional crop management with use of mineral fertilizers, whereas two sites, 817 and 834, are under organic management. The topsoil type for 827 and 821 was clay loam and sandy loam, and for all other six locations, the soil type was sandy silty loam. Soil organic matter varies from 2.5% at site 834 to 18.1% at site 834. Detail on soil information is in **Appendix 8**.

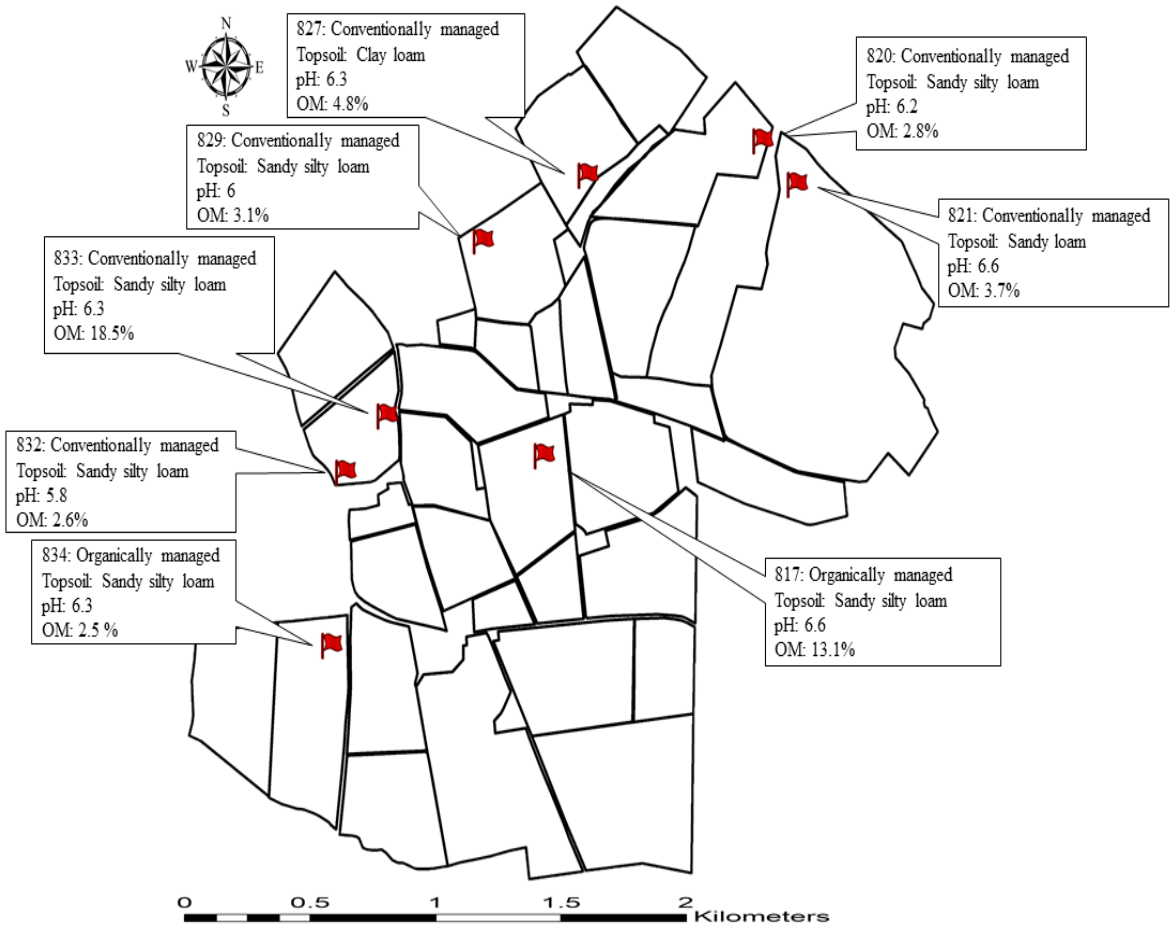


Figure 6. 1 Location of eight sites in the study area, topsoil type, pH and organic matter % for each site

The detailed crop rotations used for modelling are shown in **Table 6. 1**. The use of clover as a cover crop is practised on both organic field locations with oats and barley. Only one location (827) in all the sites was under grass throughout the experimental period. Site 832 and 833 follow a winter wheat/potatoes rotation. Complete management information from 2017 to 2020, including fertilisers' type and amount are given in **Appendix 8**.

Table 6. 1 Crop type on eight sites (including two organic and six conventional) from 2017-2020

Site ID	*Crop type 2017*	*Crop type 2018*	*Crop type 2019*	*Crop type 2020*
817 ORG	Triticale/Clover	Clover	Clover	Oats
820 CON	WW	Fallow	Fallow	Sprouts
821 CON	WW	WW	WW	WOSR
827 CON	Grass	Grass	Grass	Grass
829 CON	S.barley	W.barley/ turnip	S.barley	W.barley/ turnip
832 CON	WW	Potatoes	WW	WW
833 CON	WW	Potatoes	WW	WW
834 ORG	Oats	Clover	Clover	Barley

ORG = Organic

CON = Conventional

WW = Winter wheat & WOSR = winter oilseed rape

6.2.2 Soil sampling and analysis

Soil samples from the eight locations were collected from topsoil (0-30 cm) and subsoil (30-maximum achievable depth) at the start of the experiment (autumn, 2017) for soil assessment of properties, including texture, organic matter % and pH (analysis procedures explained in *Chapter 3 and Chapter 5*). For soil mineral N dynamics (SMN), topsoil (0–30 cm) samples (3 replicates from each location) were collected using a 3cm diameter manual soil auger at the time of soil solution sampling (Chapter 4) during the 2019-2020 drainage season. For each sampling occasion, a single composite sample was placed into a plastic bag for each location and stored in a freezer at -20 °C.

Soil mineral N was extracted using 2 M KCl as described in *Chapter 5, section 5.2.5.* Concentrations of NO_3-N and NH_4-N in KCl extracts were measured using a Brann+Luebbe Autoanalyzer 3 and the hydrazine reduction method for nitrate and the salicylate technique for ammonia (see *Chapter 5, section 5.2.5*).

6.2.3 NDICEA model

The goal of NDICEA (Nitrogen Dynamics in Crop rotations in Ecological Agriculture) is to improve farmers' and extension agents' experience learning by reconstructing the dynamics of water, carbon, organic/inorganic nitrogen (from soil organic matter and organic inputs such as manure and compost) and fresh organic matter in soil under agricultural systems taking into consideration the impacts of weather, irrigation, and soil type. The crop yield and crop quality parameters, such as dry matter and NPK levels, are the basis for crop uptake estimates in the NDICEA model. The model uses a daily time step and user-defined soil and crop parameters, as well as site-specific weather data (rainfall, temperature, and evapotranspiration) (Van der Burgt *et al.*, 2006). The NDICEA model is comprised of three sub-models explained in **Figure 6. 2** detail in **Appendix 9**.

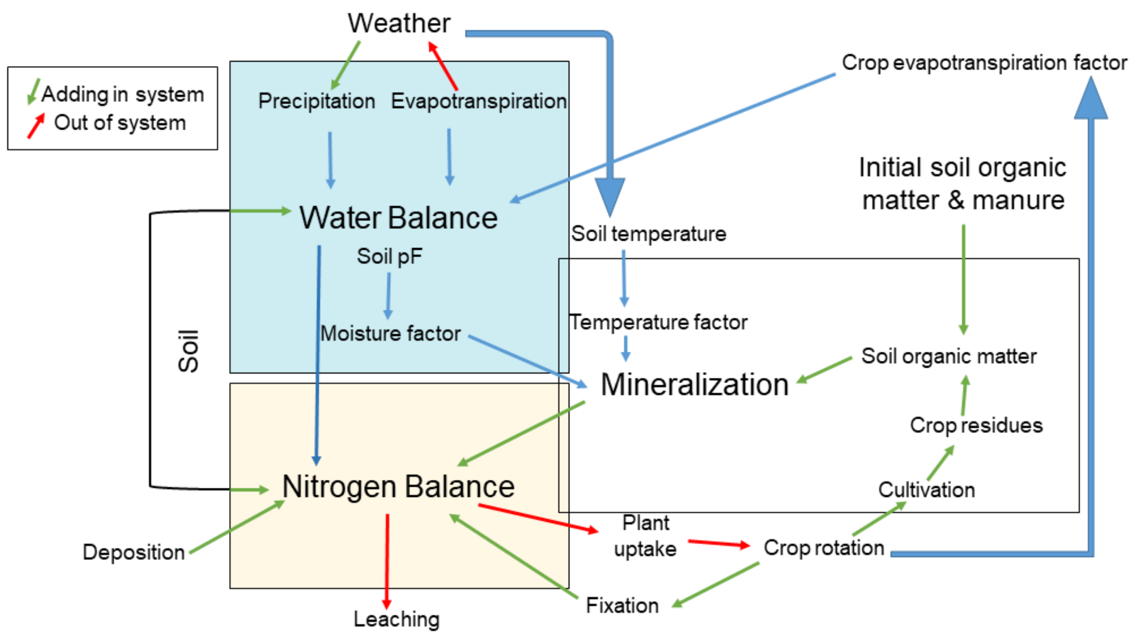


Figure 6. 2 Schematic structure of model (modified from *NDICEA 4.23 Model description manual)*

The dynamics of soil water are calculated in the first component (water balance), which takes into account rainfall, irrigation, evapotranspiration, and capillary rise (or its inverse, percolation). In the second component, a modified one-parameter carbon dissimilation model and a nitrogen mineralization model, which take into account soil temperature, soil moisture content, soil pH, and organic matter, estimate the decomposition of organic matter and mineralization of organic N from the initial soil organic matter stock and continuous additions of crop residues and organic manure. Soil inorganic nitrogen dynamics are calculated in the third model component (Nitrogen balance) using nitrogen input from mineralization, atmospheric deposition, irrigation, fertilizers, capillary rise, and biological fixation, and nitrogen loss through crop uptake, denitrification and leaching.

6.2.4 Model setup

Default values for NDICEA's 46 parameters are given to set up the model for simulation purposes. The necessary input data for NDICEA is summarised in **Table 6. 2**. Measured soil properties including soil type, soil profile depth, and pH, organic matter, are used to set the scenarios for eight locations. NDICEA has some limitations e.g. limited availability for soil types to select from the model's built-in options and limitations on soil hydrological properties. The model works on a pre-set pedotransfer function to estimate daily water balance and does not allow the user to specify soil hydrological properties. In limited availability of soil type, % of mineral soil components (sand, silt and clay %) was used to select a soil type for modelling (**Table 6. 4**) using the soil texture triangle from the UK Centre for Ecology and Hydrology (https://cosmos.ceh.ac.uk/soil).

Table 6. 2 List of input and output data for NDICEA

Inputs	**Outputs (Graph)**
Weather data (Daily average temperature, rainfall, evapotranspiration, irrigation and N contents in irrigation water)	Cumulative available N (reset to zero with each crop) Course of soil mineral N (also show entered measured mineral N values) N leaching below soil layers (cumulative for sowing of one crop to sowing of next crop, reset to zero with each crop) Cumulative denitrification from topsoil layer (reset to zero at 1^{st} January) Precipitation pF of topsoil Mineralised N from different source Changes in OM in the top layer
Soil data (soil type of top and subsoil, initial value of OM contents, thickness of soil layer, initial soil pH, highest and lowest groundwater levels)	
Crop data (Expected or observed yield, crop sowing and harvesting dates)	**Outputs (Table)** Mineral balance RMSE values per soil layer for the comparison between measured and calculated N-mineral values Average deviation between measured and calculated value of mineral N
Fertilisers data (Type of fertiliser, application time and method, amount)	

Data for model initiation from 2017 to 2020 on crop type, planting and harvesting dates, fertilizers (type, time of application and available N), and crop yield was collected from the farmers on datasheets. Some information on yield was provided ; where the information on yield was not available, yield reported for a specific crop in national statistics from DEFRA (Defra, 2019) or model default values were used.

The three main components of the model: organic matter, soil N and water dynamics, are strongly affected by weather (Van der Burgt *et al.*, 2006). Therefore, it is preferred to use site-specific weather data for modelling purposes. The Environment Agency provided the daily rainfall and evapotranspiration data, and the daily air temperature was recorded by a farmer near the study area.

6.2.5 Model calibration and validation

A model is a good representation of reality only if it can be used to accurately predict, within a calibrated and validated range, a particular phenomenon with acceptable accuracy and precision (Van der Burgt *et al.*, 2006). In this study, SMN from topsoil (0-30 cm) for three dates during 2019/2020 were used to calibrate the model. The soil parameters adjusted during calibration are listed in **Table 6. 3**.

The *t* statistic can be used to show a significant difference between simulated and measured values within a small sample set. The statistical parameters used in the study including root mean square error (RMSE), coefficient of determination (CD), mean difference (M), relative error (E) and modelling efficiency (EF). RMSE (***Equation 1***) is a commonly used statistical approach to evaluate model performance when individual replicates of SMN at each time point are not available. The lower limit of RMSE and M (***Equation 3***) is zero (when measured and simulated values are the same) whereas, a RMSE of 20 kg N ha^{-1} is considered a reasonable result for models simulating N leaching in the field (Van der Burgt *et al.*, 2006).

Table 6. 3 Parameters with defaults values (pre-calibration) adjusted during calibration

Soil parameters	Default values	Description
Protection factor (PF)	0.66-0.86	PF adjust the decomposition rate of OM, incorporate soil texture, structure and soil OM contents
Nitrogen leaching factor (NLF) Topsoil Subsoil	 0.85 0.85	NLF is used to determine what fraction of the nitrogen present in the relevant layer (topsoil and subsoil) is transported with the leaching water
Apparent age of OM (years) Humus Decomposed OM Fresh OM	 24 4 1.4	Apparent age is the single factor with which the decay of organic matter (OM) can be described.
MWO topsoil	0.75	The maximum water uptake out of topsoil (MWO) restricted by plant available water and soil pF.
C/N microorganism	6.5	C/N ratio of microorganisms, can impact the assimilation rate of N
As/Ds microorganism	0.4	The ratio of microorganism's assimilation (As) (organic carbon used as organic building material) and dissimilation (Ds) organic carbon burnt to CO_2.
Nitrogen fixation barrier	15	Threshold values of mineral N in topsoil above which potential N fixation is reduced
Denitrification factor	0.10	The denitrification factor is account for the influence of nitrate distribution and hot spots (locations close to decomposing OM) in the soil.

RMSE, E (***Equation 4***) and M quantify the difference and coincidence between measured and model-simulated values. The EF (***Equation 5***) compares the model's efficiency compared to simply describing data as the mean of the observations. Values can be either positive or negative, with a maximum value of 1 indicating that the measured and predicted values are the same. Positive EF values indicate that the model-simulated values are better than the observed mean, whilst less than zero EF values suggest that the model-simulated values are worse. The CD (***Equation 2***) indicates the total variance in the data, which is explained by the predicted data. The lowest value CD can be 0, indicating that the mean of observations better describes the data than the model. In contrast, CD equals one if the measured and simulated values are the same. The CD values greater than one show that the model better describes the measured data than the mean of measurements (Loague and Green, 1991). All these statistical parameters were calculated using the equations 1 to equation 5 below.

Equation 1. $$RMSE = \frac{100}{\bar{O}} \times \frac{\sqrt{\sum_{i=1}^{n}(O_i - P_i)^2}}{n}$$

Equation 2. $$CD = \frac{\sum_{i=1}^{n}(O_i - \bar{O})^2}{\sum_{i=1}^{n}(P_i - \bar{O})^2}$$

Equation 3. $$M = \frac{\sum_{i=1}^{n}(O_i - P_i)}{n}$$

Equation 4. $$E = \frac{100}{\bar{O}} \frac{\sum_{i=1}^{n}(O_i - P_i)}{n}$$

Equation 5. $$EF = \frac{\sum_{i=1}^{n}(O_i - \bar{O})^2 - \sum_{i=1}^{n}(P_i - \bar{O})^2}{\sum_{i=1}^{n}(O_i - \bar{O})^2}$$

Where $\boldsymbol{O_i}$ are the observed values; $\boldsymbol{P_i}$ are the predicted values, $\boldsymbol{n}$ is the number of soil mineral nitrogen samples, $\boldsymbol{\bar{O}}$ is mean of observed values.

The model's performance before and after calibration was assessed by using basic statistical approaches first. Then all soil parameters in the model were tested using a *t-test* (two-tailed) to see if there was a significant difference between the pre-calibrated results and the calibrated ones.

The calibrated model with adjusted soil parameters was used for validation purposes. The nitrate leaching values estimated for the eight locations (see *Chapter 4*) were used (during the 2017/2019 drainage seasons) to validate the model. Model performance was assessed in the simulation of nitrate leaching using the statistical tests for simulated and measured data, described above including RMSE, M, E and CD.

6.2.6 Sensitivity analysis

Sensitivity analysis, a basic approach for evaluating the behaviour of simulation models, helps demonstrate which model inputs have a significant impact on the model outputs. The sensitivity analysis of the NDICEA model was used in this study to evaluate which input parameters affect nitrate leaching. Soil type, daily air temperature, rainfall, and organic matter were among the parameters used for sensitivity analysis due to the importance of these parameters in N mineralisation and nitrate-N leaching. All of the target input parameters were checked one at a time, with the other parameters being kept at their original values.

Out of all eight scenarios, three were selected for sensitivity analysis of organic matter (OM) and environmental input parameters. These three scenarios were selected to cover a range of OM, soil types, and agricultural management, e.g. organic and conventional system. Daily air temperature and OM were tested by increasing the target input parameter by a factor of ± 1, i.e. ±1 °C and ±1%, respectively, and daily rainfall was changed by a factor of 10 (± 10%).

Due to the lack of precise soil texture representation in the model, all sites where model performance in the validation was acceptable were used to test the sensitivity of N leaching to a change in soil type. The sensitivity analysis was conducted by selecting a soil type that was one category more coarse (better draining) and one category less coarse (more poorly drained), as shown in **Table 6. 4**. The sensitivity study results were reported as a per cent change in nitrate leaching over a single simulation period, from 2017 to 2018, relative to the calibrated model simulation. To evaluate the effect of soil spatial variability on N leaching, loam was used as a standard soil type with 90 cm soil depth at all the sites. Land use was found an important factor influencing N leaching (*Chapter 4*) and minimum N leaching was estimated from grass fields; therefore, grass was used for all the locations and N leaching was compared with the original land use (see **Table 6. 1**).

Table 6. 4 Topsoil types measured from soil analysis, soil type used for model initiation due to limited availability of soil types in NDICEA and two nearest soil types for sensitivity analysis.

Scenario	*Original soil type*	*Soil type used in NDICEA*	*Coarse soil type*	*Fine soil type*
817	Sandy silty loam	Silt loam	Loam	Silt
820	Sandy silty loam	Loam	Sandy loam	Silt loam
827	Clay loam	Clay loam	Sandy clay loam	Silt loam
829	Sandy silty loam	Loam	Sandy loam	Silt loam
834	Sandy silty loam	Loam	Sandy loam	Silt loam
821	Sandy loam	Sandy loam	-	-
832	Sandy silty loam	Loam	-	-
833	Sandy silty loam	Loam	-	-

6.3 Results

6.3.1 Model parameters changed in calibration

The default values for eleven soil parameters, as shown in **Table 6. 5**, were adjusted during calibration in the NDICEA model to increase the correlation between the simulated and observed SMN values. These parameters have an impact on the rates of decomposition, N leaching, N fixation, and denitrification as shown in **Table 6. 3**.

The default value of the protection factor (PF) was 0.86 for most of the sites. PF is a measure of the decay rate, with a low value suggesting a slow rate of decay. The PF varied from 0.51 to 1.25 after calibration. The nitrogen leaching factors (topsoil and subsoil) are used to adjust N flow out of a soil layer to account for both preferential flow and adsorption. The default values for both the leaching factors were the same (0.85) and ranged between 0.50 to 1.03 for topsoil and 0.56 to 0.98 for subsoil after calibration.

The apparent age of humus is decreased for all scenarios except one (24.46 years for 817) from the default value of 24 years. The minimum value of apparent age of humus was 15.64 years for two sites, 820 and 827. In contrast to humus, the apparent age of decomposed and fresh organic matter (OM) increased from default values 4 years and 1.4 years, respectively, in all the scenarios. The apparent age of decomposed OM increased to a maximum value of 9.7 years, and the apparent age of fresh OM was increased to an age of 2.2 years.

Another soil parameter, maximum water uptake (MWO) out of the topsoil which depends on soil pF and plant available water, decreased from a default value of 0.75 to 0.60 for site 820 and increased for all other scenarios up to the maximum value of 0.93. Changes in soil microbial community function indicated by a change in the assimilation (carbon incorporation in soil) and dissimilation (carbon loss through respiration) were indicated by a reduction in the ratio of AS/Dis from 0.4 to a minimum value of 0.31. The C/N ratio increased in all scenarios and was approximately equal to the default value of 6.5 for one site. The nitrogen fixation barrier reduced from 15 to the minimum value of 11, indicating a reduction of N contribution to the available soil N pool from fixation. The N fixation barrier represents the threshold value for soil inorganic N levels in the topsoil at which legume N fixation is thought to be negatively affected (Van der Burgt *et al.*, 2006; Swain *et al.*, 2016). The denitrification factor (DF) was adjusted from 0.10 to the minimum value of 0.03 and the maximum of 0.12.

Table 6. 5 Soil parameters changed from default values (in parenthesis) to final values post-calibration used in validation

scenarios	Protection factor	Topsoil N leaching factor	Humus (year)	Decomposed OM (year)	fresh OM (year)	Subsoil N leaching factor	MWO top-soil	C/N MO	As/Ds MO	N fixa-tion bar-rier	Denitrification factor
817	0.78 (0.82)	1.03 (0.85)	24.46 (24)	7.52 (4)	2.1 (1.4)	0.86 (0.85)	0.85 (0.75)	6.48 (6.5)	0.38 (0.4)	13 (15)	0.09 (0.10)
820	0.51 (0.86)	0.71 (0.85)	15.64 (24)	6.68 (4)	1.7 (1.4)	0.56 (0.85)	0.60 (0.75)	7.28 (6.5)	0.36 (0.4)	11 (15)	0.09 (0.10)
821	0.91 (0.81)	0.89 (0.85)	19.4 (24)	7.94 (4)	1.5 (1.4)	0.88 (0.85)	0.93 (0.75)	7.02 (6.5)	0.31 (0.4)	11 (15)	0.09 (0.10)
827	0.51 (0.66)	0.65 (0.85)	15.64 (24)	5.62 (4)	2.2 (1.4)	0.61 (0.85)	0.81 (0.75)	7.32 (6.5)	0.37 (0.4)	13 (15)	0.11 (0.10)
829	1.2 (0.86)	0.73 (0.85)	23.28 (24)	9.66 (4)	2.1 (1.4)	0.89 (0.85)	0.88 (0.75)	8.05 (6.5)	0.32 (0.4)	14 (15)	0.12 (0.10)
832	1.25 (0.86)	1.1 (0.85)	17.82 (24)	7.55 (4)	2 (1.4)	0.92 (0.85)	0.81 (0.75)	7.47 (6.5)	0.38 (0.4)	11 (15)	0.09 (0.10)
833	1 (0.86)	0.5 (0.85)	20.16 (24)	6.34 (4)	1.9 (1.4)	0.98 (0.85)	0.84 (0.75)	7.48 (6.5)	0.32 (0.4)	13 (15)	0.03 (0.10)
834	0.87 (0.86)	0.66 (0.85)	18.38 (24)	9.07 (4)	2 (1.4)	0.73 (0.85)	0.87 (0.75)	8.22 (6.5)	0.33 (0.4)	17 (15)	0.06 (0.10)

6.3.2 Model performance before and after calibration

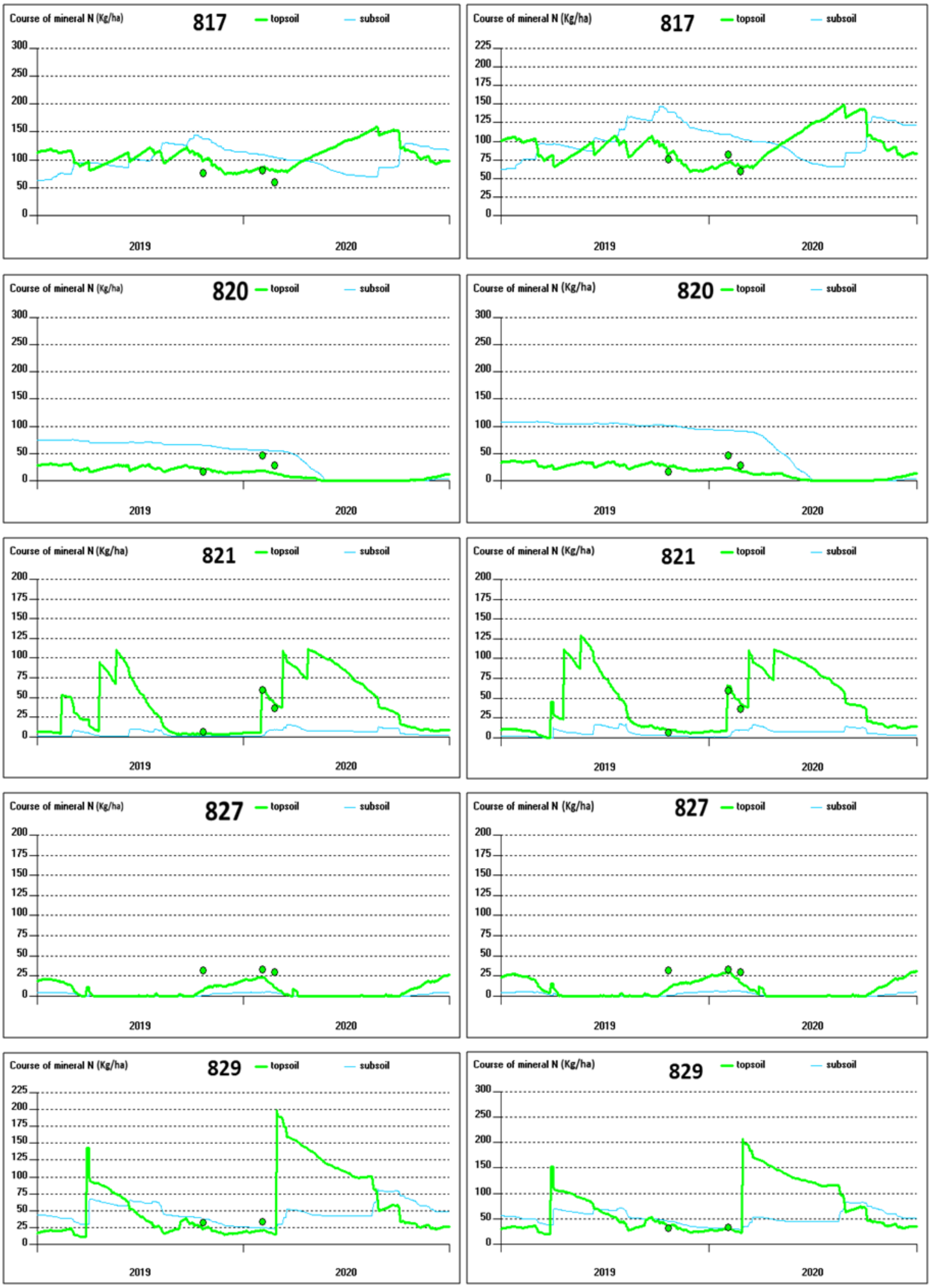
The performance of NDICEA based on statistical tests was assessed before and after calibration for eight locations, as shown in **Table 6. 6**. The model performance improved after calibration for almost all the scenarios, but the difference was not statistically significant. Overall, calibration improved the RMSE in six scenarios. The RMSE for scenarios 827, 832 and 833 were 25.89, 20.77and 43.99 kg N ha^{-1} which was higher than the acceptable limit (20 kg N ha^{-1}) before calibration. The RMSE for all these scenarios improved after calibration but 827 and 833 were still higher than 20 kg N ha^{-1}. The RMSE slightly increased for two sites (820 and 821) after calibration but was still lower than the acceptable limit. The maximum RMSE (43.99 kg N ha^{-1}) was noted in scenario 833, which improved to 31.23 kg N ha^{-1} post-calibration.

The coefficient of determination (CD) improved after calibration in all the cases. However, no statistical significance was noted (P=0.08). CD was greater than 1 (2.36, 1.08, 8.11 and 1.67) for half of the scenarios indicating that the model better describes the measured data than the mean of actual measurements. Modelling efficiency (EF) improved in the calibrated model but was still negative in most scenarios. There was also no significant difference between the mean difference (M; P = 0.167); however, the individual M values improved for all the scenarios after calibration. Relative error (E) also showed improvement without any statistical significance, but was 5.88 for 821, indicating that model overestimated the measured values only for this site after calibration.

Table 6. 6 Statistical performance of model before and after calibration. *t-test* compares the pre- and post-calibration values of the model performance for all scenarios.

Scenario	**817**	**820**	**821**	**827**	**829**	**832**	**833**	**834**	**817**	**820**	**821**	**827**	**829**	**832**	**833**	**834**	**t-test**
	Before calibration								**After calibration**								
RMSE	9.13	3.80	3.40	25.89	14.31	20.77	43.99	17.84	1.83	9.89	4.76	24.11	4.31	12.98	31.23	13.11	NS
CD	0.36	0.05	0.80	0.003	0.002	4.24	0.17	0.66	2.36	1.08	0.86	0.004	0.03	8.11	0.35	1.67	NS
M	-13.9	9.50	-1.03	17.97	10.95	28.80	40.07	8.17	0.63	4.57	-3.53	13.23	0.35	19.13	27.30	1.80	NS
E	-18.38	26.04	-14.64	56.15	22.81	148.86	60.71	30.25	0.83	4.79	-5.88	41.35	0.73	130.45	41.36	6.67	NS
EF	<0	<0	0.97	<0	<0	<0	<0	<0	0.32	<0	0.94	<0	<0	<0	<0	<0	NS

Before calibration **After calibration**



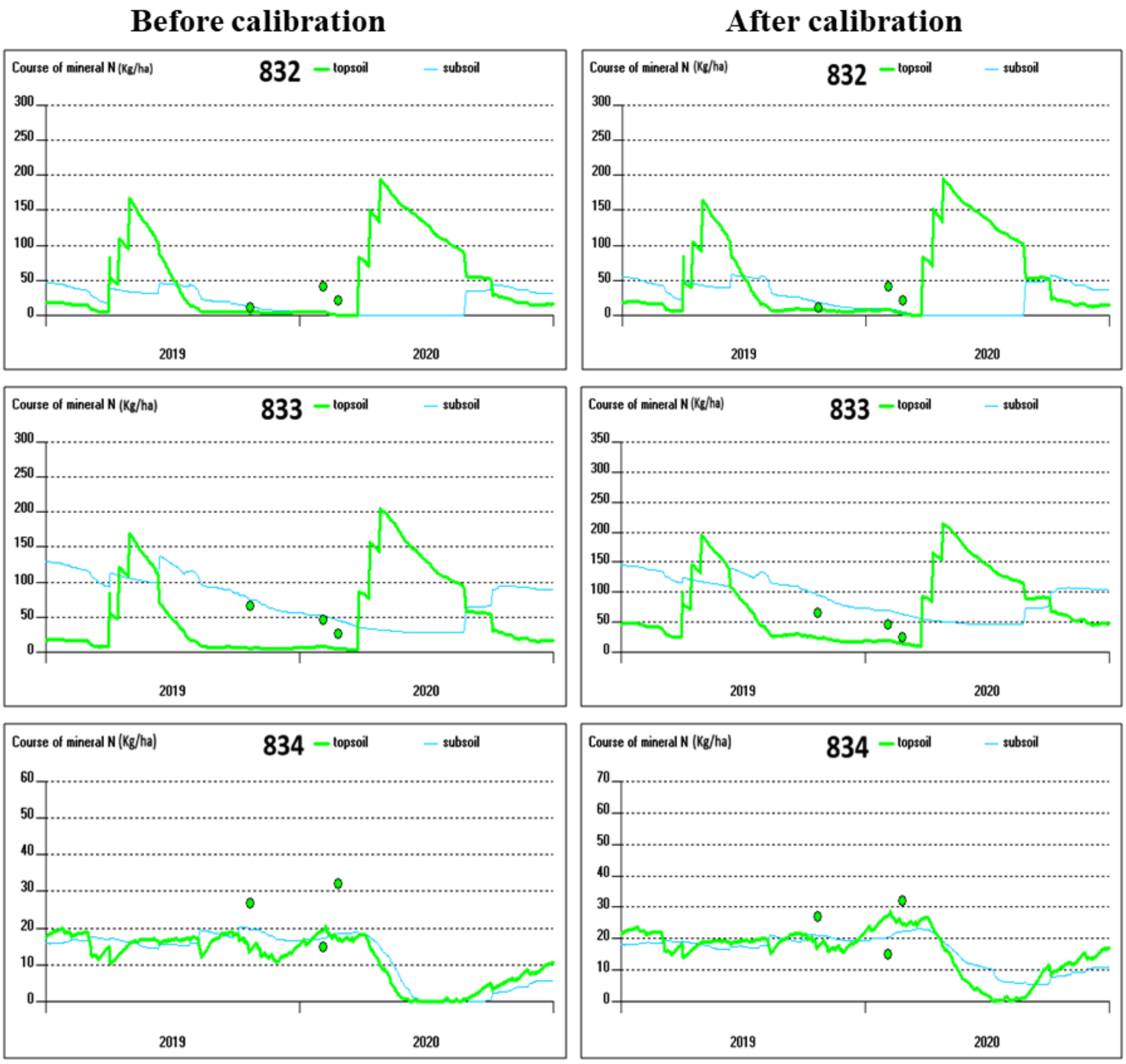


Figure 6. 3 Simulated (drawn thick line) and observed (symbols) dynamics of the inorganic nitrogen in kg ha^{-1} in the topsoil (0 –30 cm) layer during 2019/2020.

The performance of NDICEA is represented in **Figure 6. 3** before and after calibration comparing soil inorganic N (kg N ha^{-1}) in the topsoil (0-30 cm) layer during the 2019/2020 drainage season. Overall, the calibration process decreased the difference between simulated and measured soil inorganic N by adjusting soil parameters presented in **Table 6. 5**. However, this difference is more visible in scenarios 817, 829 and 834 and less prominent in 821 and 827. The model performance as RMSE is also more visible in the same three scenarios in **Table 6. 6**.

6.3.3 Nitrogen leaching prediction following model validation

The calibrated model was used for validation purposes. Estimated values for N leaching from the 2017/2018 and 2018/2019 drainage seasons were compared against model predictions to assess model performance. **Table 6. 7** shows the model's statistical performance as RMSE, M, E and CD. The RMSE were 13.3, 20.2, 15.9, 19.8 and 11.3 kg N ha^{-1} for 817, 820, 827, 829 and 834, respectively. The RMSE for scenario 821 was 69.3 kg N ha^{-1}, for 832 and 833 were 67.2 and 38.9 kg N ha^{-1} indicating that model predictions of N leaching were worse at these two sites. The observed N leaching was highest from these two sites (832 and 833) for both drainage seasons. Scenarios 817 and 834 were organically managed fields and represent good model predictions with RMSE 13.3 and 11.3 kg N ha^{-1}. The coefficient of determination (CD) for sites 817, 820, 827, 829 and 832 is > 1, indicating that model predicted N leaching better than the mean of measured leaching. However, the mean error (M) for 832 and 833 was calculated as 49.2 and 71.5, respectively, representing the worst performance of the model. The CD reaches the minimum limit < 0 for site 833. The modelling efficiency (EF) values were positive for sites 817, 827 and 829, indicating that the model predicted leaching values for these three sites are better than average of observed means. Overall model performance indicated that the model simulated N leaching with the RMSE in the acceptable limit (<20 kg ha^{-1}) for four and slightly higher (20.2 kg N ha^{-1}) for one site, out of eight locations, and failed to match the observed leaching where N leaching was > 100 kg ha^{-1} (832 and 833).

Table 6. 7 Statistical performance of NDICEA for validation purposes using the calibrated model to simulate N leaching in comparison with measured N leaching during the 2017/2018 and 2018/2019 drainage seasons

Scenario	***Statistical parameters***			
	RMSE	**CD**	**M**	**EF**
817	13.3	1.4	2.0	0.96
820	20.2	8.9	7.5	<0
821	69.3	0.5	11.1	<0
827	15.9	6.2	1.9	0.44
829	19.8	38.8	-8.4	0.78
832	67.2	1.3	49.2	<0
833	38.9	0.0	71.5	<0
834	11.3	0.2	4.5	<0

6.3.4 Sensitivity analysis for nitrogen leaching

Three scenarios were used to test model sensitivity to initial soil organic matter and environmental parameters (rainfall and temperature) in simulated nitrogen leaching and five for sensitivity analysis of soil type for the 2017/2018 drainage season due to the maximum N leaching data available for this year. The model simulation showed low sensitivity to daily rainfall change and higher sensitivity to daily air temperature change (**Figure 6. 4**). Simulated nitrogen leaching changed from -2% to +1% for site 817, -5% to +3% for 820 and -8% to +3% for 827 with 10% change in daily rainfall. Scenario 827, initially with high soil organic matter % (OM), showed no sensitivity in simulation with a 1% increase and decrease in OM. Whereas, -20% to +19% change was recorded in model simulation with change in OM at site 820 and -28% to +30% at site 827. The model simulation was recorded as highly sensitive to a 1°C change in daily air temperature. The location with a shallow soil profile (827) showed - 37% to +37% change in N leaching. For sites 820 and 817, the % change due to change in daily air temperature ranged from -3% to +4% and -11% to +11%, respectively.

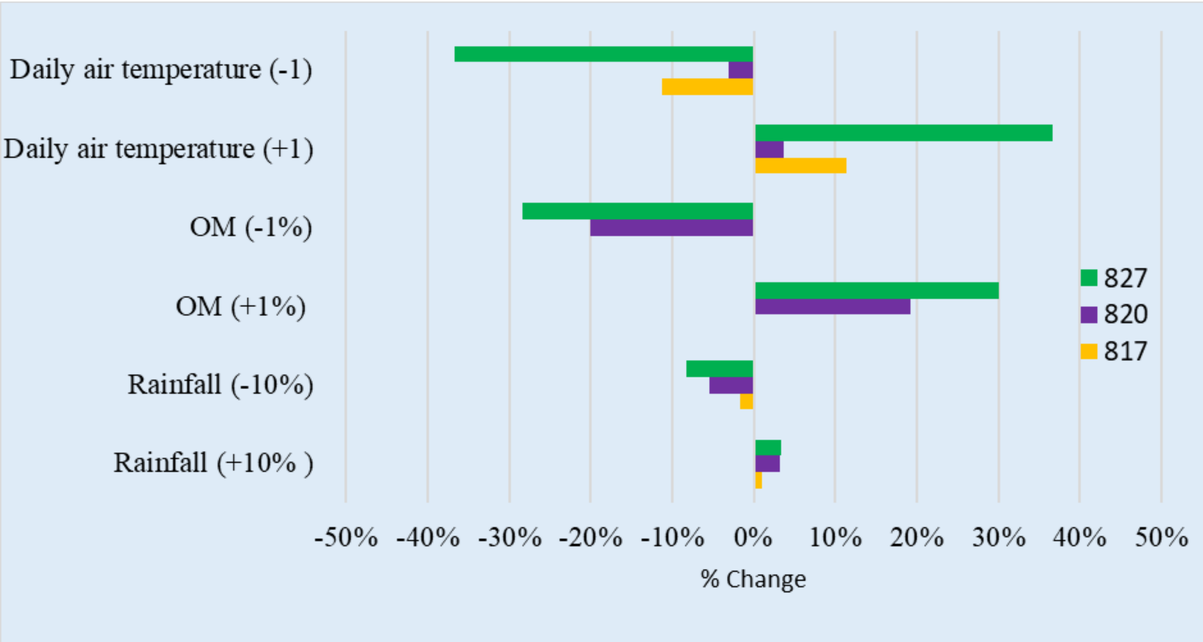


Figure 6. 4 Model sensitivity to changes in organic matter %, daily air temperature and precipitation for simulated of N leaching during the 2017/2018 drainage season (% change).

The modelling sites for which the performance was categorised as good based on RMSE (**Table 6. 7**), were used for model sensitivity to soil type, comparing a less well drained and better soil (**Figure 6. 5**). The model showed no sensitivity to soil type in simulating N leaching at 817 and 834 (organically managed). An increase of 2% in simulated N leaching was recorded at site 820 when the soil type was changed to a better drained soil type (sandy loam) and a decrease of 0.43% when changed to a less well drained soil type (silt loam). Maximum change from -3% to +3% was noted when the loamy soil type (scenario 829) was changed to sandy loam (+3%) and silt loam (-3%).

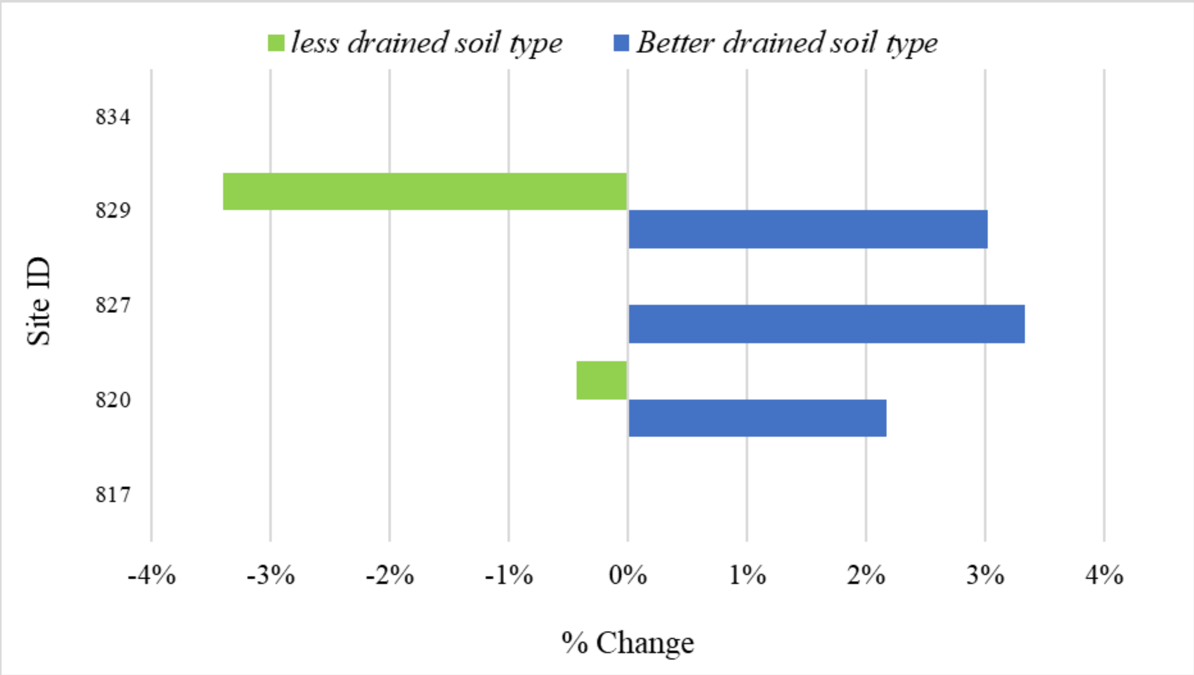


Figure 6. 5 Model sensitivity to more coarse and fine soil type compared to original soil type in simulation of nitrogen leaching

The amount of N leaching (kg ha^{-1}) simulated by NDICEA during the drainage seasons (Oct to March) for three years (2017/2020) was changed with change in soil type and soil depth as shown in **Table 6. 8**. N leaching (kg ha^{-1}) was increased with increased depth for the sites 821 during three drainage seasons and from 832 during 2017/2018 and 2019/2020. The amount of N leaching (kg ha^{-1}) reduced with increased depth and loamy soil from the sites 820, 827, 829 during three drainage seasons and from 834 during 2018/2019 and 2019/2020. No change in the amount of N leaching (kg ha^{-1}) from site 817 was observed due to no change in soil profile depth from the original depth.

Table 6. 8 Change in N leaching (kg ha^{-1}) using standard soil type (Loam) and soil profile depth 90 cm for all the locations compared to the leaching with variable soil types and soil depth and N leaching (kg ha^{-1}) from grass compared to the original land use in **Table 6. 1**

Site	N leaching (kg ha^{-1}) 2017/2018			N leaching (kg ha^{-1}) 2018/2019			N leaching (kg ha^{-1}) 2019/2020		
	STD soil & depth	Spatially variable	Grass	STD soil & depth	Spatially variable	Grass	STD soil & depth	spatially variable	Grass
817	68.8	68.8	9.8	10.7	10.7	4.1	152.2	152.2	5.7
820	67.8	70.7	0.7	50.7	51.6	1.7	56.0	56.3	0.5
821	76.8	74.3	15.5	28.6	19.4	12.7	35.3	31.9	13.4
827	5.2	12.9	12.9	3.2	11.6	11.6	4.7	14.1	14.1
829	118.4	127.1	11.7	58.8	70.1	8.0	77.3	84.9	31.3
832	64	60.5	15.8	105.1	112.5	10.1	51.5	31.2	20.2
833	64.6	64.6	5.1	95.2	93.5	2.4	66.9	67.4	2.5
834	30.0	22.5	2.0	12.2	14.6	0.9	36.6	38.9	1.2

6.4 Discussion

6.4.1 Model performance after site-specific calibration

The model performed well for most sites to predict soil mineral nitrogen (N) before calibration irrespective of the type of N inputs (inorganic fertilisers or organic source as FYM) and varying soil types at each location. These findings support Koopmans and Bokhorst (2002); they found a strong correlation between simulated and measured inorganic nitrogen (N) in topsoil using uncalibrated data sets from farms with varying soil types and fertiliser application. However, researchers suggested that calibration would be useful to improve the modelling efficiency where measured soil organic matter and soil N data is available (Van der Burgt *et al.*, 2006; Smith *et al.*, 2016). **Table 6. 6** summarises the statistical performance of NDICEA before and after calibration. A site-specific calibration approach is used in this study. Mean values for the calibrated parameters can also be used for model evaluation when soils were collected from the same field, as reported by Swain *et al.* (2016), who used mean values for each soil parameter for final calibration of NDICEA and validated the model to simulate soil mineral N. The model calibration in this study with the means for the adjusted soil parameters increased RMSE statistically significant ($p < 0.05$) compared to individual calibrated parameters for each scenario. The soil samples in the current study were from different fields and represent different soil types therefore, a site-specific calibration was used. The importance of site-specific calibration of NDICEA is also advised, when the model was used to predict soil inorganic N dynamics, and experimental data vary considerably (Van der Burgt *et al.*, 2006) which is true in the current study. The model performance with adjusted parameters was not significant, this might be due to the lack of soil mineral N samples used for calibration, or model estimation of water balance might be different than the estimated drainage used to calculate N leaching. However, the calibrated model performed well in predicting N leaching with RMSE < 20 kg ha^{-1}. Therefore, individual values for the soil parameters were used post-calibration for validation, as shown in **Table 6. 5**.

The importance of adjustment of SOM parameters to improve model fitness for SMN simulation, was documented by Swain *et al.* (2016), who calibrated and validated NDICEA on UK soils. In order to improve the simulation, NDICEA changes values for soil parameters related to N leaching, N fixation, decomposition and denitrification during the calibration process. The topsoil N leaching factor (NLF) decreased from default values in six scenarios and increased for 817 and 832. The NLF increased to increase simulation of N leaching and decrease N accumulation at these two sites. Soil parameters such as apparent age of humus decreased in all the scenarios, which will increase the N mineralisation except 817, where the apparent age of humus decreased. At this particular location (817), the model adjusted the apparent age of humus to decrease N mineralisation, as the model was overestimating soil inorganic N with higher negative relative error (E) before calibration. An increase in the mineralisation in all other locations was adjusted with an increase in the apparent ages of decomposed and fresh OM and an increase in the C: N ratio of microorganisms (C: N increased minimum for site 817).

SOM can significantly control the results of a nitrogen dynamics simulation. This cannot be verified because no data on changes in SOM was available. More clarity on the soil N dynamics would have been acquired if data had been available and incorporated in the calibration procedure with soil inorganic N, as reported by Van der Burgt *et al.* (2006). The model simulation of soil inorganic N for site 827 was poor (RMSE > 20 kg N ha^{-1}) post-calibration, which might be due to the continuous addition of soil organic N at site 827 from green manure application. The researchers reported similar findings of poor NDICEA performance for sites with high crop residues and green manure applications and recommended using SOM data in the calibration process to better track the organic N pool.

6.4.2 Simulation of nitrogen leaching in NDICEA and sensitivity analysis

The NDICEA performance in predicting mineral N leaching was poor for sites 832 and 833 (RMSE > 20 kg N ha^{-1}). This might be due to the lack of management information for these two sites, as the information used in the model simulation only included the conventional source of N and the farmer might also use the organic source of N which is not added in the simulation. Another reason might be the model simulations are limited as the measured N leaching for these two sites was higher for both the drainage seasons. Overall, the model performed well as RMSE for most sites was < 20 kg N ha^{-1}. However, the model performed particularly well for sites 817 and 834, where organic management was followed. This difference in model performance between organic and conventionally managed sites might be because NDICEA simulates the complete availability of mineral-N additions on the day they are applied. Poor fits have previously been documented when conventional fertiliser is used (Swain *et al.*, 2016). As a result, when conventional fertiliser is applied, prominent expected peaks in SMN occur. In practice, fertiliser distribution across the soil profile does not occur immediately after application (Norman *et al.*, 1987), as the model predicts.

Model sensitivity was tested for four input parameters that can have an impact on N mineralisation and N leaching. Sensitivity analysis reflected that the model was highly sensitive to change in initial SOM, which resulted in a change in N leaching simulation of up to +30% at site 827 with a 1% change in SOM (**Figure 6. 4**). NDICEA showed no sensitivity to change in SOM for site 817, which might be due to higher initial SOM than the other two sites tested for sensitivity analysis. Another important factor for which NDICEA showed maximum sensitivity was daily air temperature (^oC). An increase in the model simulation for N leaching was observed with a 1^oC increase in daily air temperature. The temperature change can alter soil N mineralisation due to changes in microbial activity, responsible for N transformation. Other studies have found an increase in gross N transformation rates as temperature rises, mainly related to increased microbial activity due to high temperatures. It was found that under high temperature conditions microbes' ability to consume NH_4^+ (through nitrification or immobilisation) was higher than gross N mineralization, whereas under low temperature conditions it was the opposite (Andersen and Jensen, 2001; Sharma and Kumar, 2021).

Model sensitivity was also tested to change soil types to more coarse-textured (better drained) and fine-textured soil (less drained) for five scenarios. The change in N leaching is because soil texture with more sand (coarse soil type) have high porosity and permeability, allowing for efficient NO_3^- transport and leaching. Conversely, fine texture soils, with good soil structure and nutrient retention, accumulated more NO_3^- (Yang and Tang, 2012). As, in the case of 827 (shallow soil profile depth, 30cm), when soil type changed to a better drained condition compared to the original clay loam, a greater increase in the N leaching was found than the decrease when changing to a less drained soil. Su *et al.* (2014) also found high NO_3^- accumulation in loamy soil, intermediate in sandy loam and lowest in loamy sand. However, model sensitivity to soil type was not similar for all the scenarios, e.g. model showed no sensitivity to soil types for sites 834 and 817. This might be due to the presence of loamy subsoil at both sites. So, any increase in N leaching from topsoil with changing soil type does not impact the total N leaching out of the subsoil (out of system).

The model was also used to evaluate the effect of soil spatial variability compared to a standard soil type and soil profile depth as shown in **Table 6. 8**. The amount of N leaching decreased with increase in soil depth to 90 cm from most of the sites, but from the site 821 (shallow sandy loam) was increased with increase in soil depth and loamy soil type. This increase in the amount of N leaching might be due to increased amounts of mineralised N from soil organic matter which increased with increasing depth. This variation in N leaching simulated by NDICEA further depicted the importance of soil variability in N leaching. The amount of N leaching was reduced from all the sites with grass as land use compared to any other land use, therefore, at the sites with higher N leaching particularly with shallow soils, the losses can be minimised by growing grass.

6.5 Conclusion

The performance of NDICEA to simulate soil inorganic N improved post-calibration for most of the sites. After analysing site-specific and average calibration parameters, site-specific calibration is used due to significant differences and variable soil types and management practices for all the locations. Improvement in model simulation after site-specific calibration was not proved statistically. However, the model performed well in all the scenarios except for those with high initial OM or the sites where OM was continuously added as manure, which proved the importance of SOM for calibration as recommended in the literature. Model performance for predicted N leaching for two sites was not satisfactory.

NDICEA showed sensitivity to environmental input parameters. The maximum change in N leaching was observed with a change in daily air temperature. Model sensitivity to these input parameters elaborates the importance of the use of location-specific environmental data for modelling. Model sensitivity to soil type is unclear, which may be due to limitations of model input soil types. However, the model performed well with limited soil types due to true representation of measured soil type with available soil types. The change in simulated N leaching from a standard soil type and soil profile depth represents the importance of soil variability on N leaching. With some limitations on soil types used for model setup, overall model performance for simulation of N leaching was acceptable for most of the sites. The results could improve for the sites where model performance was not satisfactory, if complete management information is available for simulation purposes.

Overall model performance was satisfactory for N leaching simulation if complete management information is available. Model calibration did not significantly improve the model performance therefore NDICEA can be used by farmers in the catchment area as a tool to track N dynamics in crop rotations without local calibration and can be used as a decision-making tool to manage the field in a way to minimise N losses via leaching.

Chapter 7. General Discussion and Conclusions

Nitrate (NO_3^-) leaching losses from the soil into the groundwater represent not only a loss of soil fertility but also a threat to the environment and human health (Di and Cameron, 2002; Andrews *et al.*, 2007; Goulding *et al.*, 2008). Climate, soil properties, and land use are all the factors that influence NO_3^- leaching losses from the soil (Cameron *et al.*, 2013). In modern agricultural systems, 10-30 % of fertiliser nitrogen (N) is lost, although the fate of N in the subsurface environment is determined by many biochemical and bio-physicochemical processes. Precise knowledge of nitrate-N (NO_3-N) leaching to the groundwater bodies has remained a challenging problem due to the complex interaction between land use activities, fertiliser N management, rainfall, irrigation management, soil N dynamics, and soil properties (Meisinger *et al.*, 2006; Bijay and Craswell, 2021). NO_3-N is also produced in significant amounts by organic waste produced by farm animals and sewage produced by cities, and it can enter groundwater bodies (Bijay and Craswell, 2021). Furthermore, if the supply and demand for nitrogen are not in synchronization, leaching and gaseous losses of N might occur, especially after ley cultivation (Patil *et al.*, 2010). Groundwater NO_3^- concentrations in many UK aquifers are constantly increasing and exceeding legal drinking water standards (UKWIR, 2003). The NO_3^- concentrations in the groundwater of the UK are rising at an average rate of 0.34 mg NO_3^- l^{-1} $year^{-1}$ (Stuart *et al.*, 2007). To manage the diffuse water pollution from agricultural catchments to groundwater sources, the government has already set up the "Farming rules for water" to protect the water resources. These rules are applicable to all the farmers in the Nitrate vulnerable zone (NVZs) (Chapter.1) about how to manage the rate and timing of N fertilisers and manure. There are projects like "Sustainable farming incentive pilot" to encourage farmers in the NVZs to manage their land in an environmentally sustainable way. The current study integrated the impact of key factors on NO_3-N leaching to protect the groundwater in the study area and help farmers to better manage their land in an environmentally sustainable way with management like tillage type and time, use of less susceptible crops, and N additives.

This thesis was carried out to investigate and understand the effects of agricultural land use, soil properties and rainfall (average and wet year) on NO_3-N leaching from an agricultural catchment to the Fell Sandstone aquifer during three drainage seasons (the autumn-winter period when evaporation is low and drainage is high). The specific objectives of this study were: i) to produce high-resolution digital soil maps to determine the soil spatial variability in the study area and assess the relative benefits of using digital soil maps compared to conventional soil maps, ii) to investigate the influence of different factors including land use, soil texture and soil profile depth and rainfall on nitrate leaching from an agricultural catchment, iii) to determine the impact of innovations including a Nitrification inhibitor and a Urease inhibitor to mitigate N leaching and improve crop nitrogen use efficiency, and iv) to calibrate and validate a N dynamics model and elaborate how well the model can predict NO_3-N leaching using measurable soil properties and land management data, and its potential use as a decision making tool for farmers about land management in a way to minimise N leaching.

The current study was designed with the above-mentioned linked objectives. In the findings of this thesis, the results indicated that the soil is spatially variable within a short distance (within a field) for both soil texture and depth to the bedrock. It was also demonstrated that both of these factors (soil texture and depth) along with other factors, can alter NO_3-N leaching significantly. In the investigation of innovative mitigation strategies to control N leaching, the nitrification inhibitor was found to be effective to inhibit nitrification and minimise NO_3-N leaching, and the urease inhibitor also showed improved nitrogen use efficiency of potatoes. A nitrogen dynamic model (NDICEA) was calibrated and validated to predict NO_3-N leaching based on site-specific soil and management information. NDICEA is a tool to simulate changes in soil N dynamics and losses from the soil profile. It therefore, can be used to guide management decisions on agricultural land (crop rotations, N input time and amount, straw incorporation/removal).

7.1 Digital Soil Maps are Useful in Understanding Soil Spatial Variability

Soil maps are important to illustrate the spatial variability of soil properties to help decision making to implement land management practices in the area. The conventional soil mapping approach is time and labour intensive and generates data with minimum chances of reliability compared to digital soil mapping, a reliable and reproducible method. For the study area, the conventional soil map (1:250,000) categorised the soil in two soil associations mainly coarse loamy to fine loamy by Jarvis (1984). This thesis indicated that the soil in the area fell into three different soil textural classes according to the UK textural triangle (mainly Sandy silty loam, Clay loam and Sandy loam) and the topsoil sand % ranged from 10 to 86% (Chapter 3.), indicating a high degree of the spatial variability in soil texture. The use of electromagnetic induction was important to map soil textural variability. Soil electric conductivity (ECa) measured by electromagnetic induction improved the prediction of soil properties in the current study (Figure 3.7) when used in geostatistical modelling, due to the strong correlation of ECa with the soil mineral particle size classes (sand and clay %). Therefore ECa is an important covariate in digital soil mapping (Siqueira *et al.*, 2016). Soil depth to the bedrock also varied and ranged from 30 to >120 cm across the study area. A spatial map of soil texture and depth to bedrock was produced (Chapter 3.) to understand heterogeneity in the research area and identify the more susceptible spots within the field.

The movement of water through the soil, and thus the transport of dissolved compounds like NO_3-N, is influenced by texture and soil profile depth. Moreover, soil available water was correlated with texture and profile depth. A shallow soil type with more sand % compared to silt and clay % held less water. However, soil types with a deep profile and more silt and clay % held more water at field capacity. Due to the variation in the water holding capacity of a soil type at a specific depth, the cumulative drainage and ultimately NO_3-N leaching also varied from site to site in the study area. The faster movement of drainage water and dissolved NO_3-N through shallow coarser soils, such as sands compared to clayey soil, potentially contaminating groundwater supplies. The probability of any of these events is greatly dependent on soil texture (Hallaq, 2010). This thesis demonstrated the effects of soil texture and soil profile depth variability on NO_3-N leaching. Nitrate leaching below the root zone and NO_3-N concentration in the soil solution was found most frequently in shallow sandy soils, while it was less common in deep clay soils (Figure 4.7, Chapter 4.) (Cameron *et al.*, 2013).

7.2 Factors Affecting NO_3-N Leaching and Mitigation Strategies

Precipitation was found to be important in controlling NO_3-N leaching in this thesis, particularly winter rainfall, because NO_3-N leaching from the soil system depends on the amount of percolating water which increases with an increasing amount of rainfall from similar soil types. With the increased winter rainfall, less NO_3-N (kg ha^{-1}) leaching and NO_3-N concentration (mg l^{-1}) in the soil solution was found in the current study (Chapter 4.) attributed by other studies (Beaudoin *et al.*, 2005; Martínková *et al.*, 2011). This may have been due to both the dilution and denitrification of NO_3-N, which is enhanced with an excess amount of water.

Crop type also had a significant effect on NO_3-N leaching from both organic and conventional farming. NO_3-N leaching losses are influenced not only by the type of crops grown before the leaching season but also by post-harvest crop management practices in cropping systems. The amount of NO_3-N leaching is affected by the timing of crop ploughing and the duration of fallow time in the autumn. The ploughing of clovers in autumn before winter wheat sowing maximised the losses, probably by increasing the soil organic matter turnover and the amount of mineral N in the topsoil in organic farming. Whereas in conventional farming, the results in this thesis indicated that, when a crop is ploughed too early (e.g. winter wheat), such as in early autumn, and the field is then left fallow, there is plenty of time for mineralization to occur, resulting in increased NO_3-N leaching losses in the winter. The maximum amount of NO_3-N leached during the first monitoring year (2017/2018) was from fallow fields after winter wheat and the minimum amount was recorded from the fields where the soil was covered with clover crop (sown in summer and well-established root system for N uptake). With a short time for mineralization to occur, late ploughing resulted in less leaching (Di and Cameron, 2002) (Chapter 4). Soil tillage type is another significant factor influencing NO_3-N movement from the soil profile (Halvorson *et al.*, 2001). This thesis showed the influence of conventional and no-tillage on NO_3-N leaching and NO_3-N concentration in soil solution collected below the root zone (Chapter 5.). NO_3-N (mg l^{-1}) in the soil solution was higher in the no-tillage system where winter wheat was direct drilled after two years of grass-clover ley. The maximum amount of NO_3-N (kg ha^{-1}) was also leached from no-tillage plots which may be due to the impact of macropores on increased water movement and dissolved NO_3-N from the soil profile. (Kanwar *et al.*, 1985; Khan *et al.*, 2017).

To mitigate NO_3-N leaching from the agricultural sources including N input as fertilisers and plant residues, two innovative products were investigated in this thesis. To overcome the N mineralisation rate and enhanced NO_3-N leaching from a crop residue (following the incorporation of grass-clover in autumn ploughing), DMPP based nitrification inhibitor (Vizura®) was used. Vizura® significantly reduced the nitrification process from crop residues incorporated in organically (compost) and conventional (NPK) managed plots. The nitrification process was not directly measured but, topsoil mineral N (SMN) was monitored to estimate the N availability as NO_3-N. Vizura® is a DMPP (3, 4 dimethyl pyrazole phosphate) product that inhibits NO_3^- conversion from NH_4^+, and ultimately NO_3-N leaching with the soil water (Linzmeier *et al.*, 2001; Tindaon *et al.*, 2012). The amount of NO_3-N in the topsoil was reduced significantly (*P=<0.05*) with nitrification inhibitor and ultimately NO_3-N losses via leaching in winter from organic and conventional fertilisers managed plots (chapter 5.). Another fertiliser amendment that can help to reduce NO_3-N losses caused by excess availability of N from fertilisers is NutriSphere-N® (Urease inhibitor). NutriSphere-N® can restrict urea hydrolysis (Heiniger *et al.*, 2013) and release N in soil according to the plant needs. NutriSphere-N® showed improvement in potatoes nitrogen use efficiency (NUE) in the current study (**Table 5. 10,** Chapter 5.).

7.3 Importance of N Dynamic Modelling to Mitigate N Leaching

NDICEA is an important tool for estimating the amount of nitrogen supply and loss in crop rotations. In NDICEA, one has the choice of using default values for input parameters to initiate the simulation process. The findings suggest that NDICEA can be effectively used to simulate N dynamics employing readily available data (daily climatic data, soil data and crop yields) (Koopmans and Bokhorst, 2002). In the current study, site-specific input parameters of soil and land use were used to set up the model based on specific soil conditions (due to variability in the soil type and maximum depth in the study area) recommended by Van der Burgt *et al.* (2006).

Calibration and validation of the NDICEA model in this thesis demonstrated the credibility and reliability of NDICEA as a decision support tool for farmers to help make decisions on how to manage their land in a way to minimise NO_3-N leaching with measurable soil properties and land management data and also to test the effect of alternative management. Simulation models such as NDICEA, may overestimate or underestimate the decomposition and N contents at initial settings. As a result, calibration was required to improve the models' accuracy in estimating these processes (Ferreira do Nascimento *et al.*, 2011) for UK conditions where measured values (crop NPK, soil N, and organic matter) are available (Smith *et al.*, 2016). Topsoil mineral N (SMN) values were available and used to calibrate NDICEA in the current study. The calibration process did not improve the model performance significantly (Chapter 6.). As a result, the model can be utilized to evaluate the two processes (decomposition and N release) that control soil N availability without calibration. The improvement in modelling efficiency in predicting SMN pre and post-calibration was not prominent possibly due to the low number of samples used for calibration (Swain *et al.*, 2016), or lack of data on tracking soil organic matter (SOM) changes, which is an essential parameter for N dynamics simulation due to its importance in N availability in the soil system (Van der Burgt *et al.*, 2006).

Independent validation of NDICEA was performed in this study to evaluate the model performance in predicting NO_3-N leaching during the drainage season 2017/2018 and 2018/2019. The calibrated model performance was compared with the measured NO_3-N leaching (Chapter 4.). Overall results of the thesis showed that, model performance was satisfactory in simulations except for the few locations where data on observed NO_3-N leaching was insufficient for comparison (Table 6.4, Chapter 6.). In the sensitivity analysis of NDICEA, the model was sensitive to different factors in the order of daily air temperature > SOM > daily rainfall> soil type, when predicting NO_3-N. The maximum change in the model prediction was found for an increase in temperature due to its effect on N transformation and N availability (Sharma and Kumar, 2021). Increased temperature leads to N mineralization; excess N can leach down below the crop root zone, especially during the winter in temperate regions (Patil *et al.*, 2010).

This thesis found that the NDICEA model can be a useful tool to simulate the mineralisation process in the soil and N availability, and can be used to guide decisions on green manure crops and fertiliser selection, timing, and application, not only when the nitrogen becomes accessible in the soil but also what happens to that nitrogen (i.e. uptake by plants, or loss via leaching) (Bokhorst and Oomen, 1997), and can be used to gain insight into N and organic matter dynamics (Koopmans and Bokhorst, 2002).

7.4 Conclusion and Future Work

Due to the continuous increase in the concentration of NO_3-N (mg l^{-1}) in the drinking water of the Fell Sandstone aquifer, the knowledge and understanding of driving factors and impact of mitigation strategies are important before implementation of any land-use change and management strategy to minimise this pollution. This thesis addressed the gap in understanding about the influence of the factors like soil texture, depth to the bedrock and land use in the catchment area on leaching. Compared to the previously available conventional soil maps, soil spatial variability was noted by producing high-resolution soil maps with the digital soil mapping approach of the study area. Soil spatial variability is important due to the impact of soil texture and depth on drainage volume and in the leaching losses of NO_3-N. The effect of variable soil type was important with change in model simulated N leaching compared to a standard soil. The findings of the impact of soil on leaching are based on site-specific monitoring and modelling. However, the information produced on soil spatial variability in high-resolution digital soil maps and a map of depth to the bedrock could be used as input parameters to simulate the impact of soil variability on NO_3-N leaching on a catchment scale using an N dynamics model. In this study, hotspots for NO_3-N leaching were identified as shallow sandy sites but, a catchment scale model could be used to further elaborate the locations of these hotspots.

Several studies have investigated the impact of agricultural land use on NO_3-N leaching including organic and conventional farming. A fallow, autumn ploughed field and a field with late sown crops and residue incorporation were more susceptible to leaching losses, likely due to less uptake of soil available N compared to fields with well-established winter cover crops. All these factors associated with agricultural management practices were found to be driving factors increasing leaching losses of NO_3-N. Mitigation strategies including land management changes (avoid autumn ploughing, avoid long fallow periods and change in crop rotations), along with N fertilisers amendments, can be used. The use of Vizura® and NutriSphere-N® were tested in this study in a long term field trial and found effective in reducing NO_3-N leaching and improving nitrogen use efficiency. The mitigation strategies were investigated only for one drainage season (Vizura®) applied on grass-clover and monitored during the winter, and one cropping season (only investigated the impact of NutriSphere-N® on potatoes). Further studies are needed to verify that these products perform in the same way with different soil types and crop rotations, under varying environmental conditions.

The NDICEA model, proved to be a useful tool for simulating nitrogen dynamics in a crop rotation with some limitations. Because the model showed no statistical improvement after calibration for site-specific soil and land management data, local farmers in the area can use the NDICEA without calibration to gain insight into choice and rate of N source before applying fertiliser to their land, and they can modify their crop rotations in a way that reduces NO_3-N leaching losses.

The mitigation strategies used in this study can be effective to minimise leaching losses of N. However, due to the high soil spatial variability, it is recommended to implement a site-specific strategy which is possible by using a spatial map of nitrate leaching to locate the hotspots in the area.

References

Acutis, M., Ducco, G. and Grignani, C. (2000) 'Stochastic Use of the LEACHN Model to Forecast Nitrate Leaching in Different Maize Cropping Systems', *European Journal of Agronomy*, 13(2), pp. 191-206.

Addiscott, T.M. and Dexter, A.R. (1994) 'Tillage and Crop Residue Management Effects on Losses of Chemicals from Soils', *Soil and Tillage Research*, 30(2), pp. 125-168.

Adegbeye, M.J., Reddy, P.R., Obaisi, A.I., Elghandour, M.M.M.Y., Oyebamiji, K.J., Salem, A.Z.M., Morakinyo-Fasipe, O.T., Cipriano-Salazar, M. and Camacho-Díaz, L.M. (2020) 'Sustainable Agriculture Options for Production, Greenhouse Gasses and Pollution Alleviation, and Nutrient Recycling in Emerging and Transitional Nations - An Overview', *Journal of Cleaner Production*, 242, p. 118319.

Adhikari, K., Kheir, R., Greve, M.B., Bøcher, P.K., Malone, B.P., Minasny, B., McBratney, A.B. and Greve, M.H. (2013) 'High-Resolution 3-D Mapping of Soil Texture in Denmark', *Soil Science Society of America Journal*, 77(3), pp. 860-876.

Aga, D.S. (2007) *Fate of Pharmaceuticals in the Environment and in Water Treatment Systems*. CRC Press.

Ahada, C.P.S. and Suthar, S. (2018) 'Groundwater Nitrate Contamination and Associated Human Health Risk Assessment in Southern Districts of Punjab, India', *Environmental Science and Pollution Research*, 25(25), pp. 25336-25347.

AHDB (2019) 'The Nutrient Management Guide (RB209), Section 4 Arable crops'. Agriculture and Horticulture Development Board.

Akpa, S.I.C., Odeh, I.O.A., Bishop, T.F.A. and Hartemink, A.E. (2014) 'Digital Mapping of Soil Particle-Size Fractions for Nigeria', *Soil Science Society of America Journal*, 78(6), pp. 1953-1966.

Allan, R., Pereira, L. and Smith, M. (1998) *Crop Evapotranspiration-Guidelines for Computing Crop Water Requirements-FAO Irrigation and Drainage Paper 56*. Rome: FAO.

Almadni, M.A. (2014) *Impact of Agricultural Management on Risks of Nitrate Leaching in Crop Rotations with Potatoes and Cereals*. Newcastle University.

Almasri, M.N., Judeh, T.G. and Shadeed, S.M. (2020) 'Identification of the Nitrogen Sources in the Eocene Aquifer Area (Palestine)', *Water*, 12(4), p. 1121.

Amin-Hanjani, S. and Todd, R. (2006) 'Catchment-Sensitive Farming: Tackling Diffuse Water Pollution From Agriculture In England - Policies And Drivers', in *Water and Agriculture: Sustainability, Markets and Policies*. pp. 337-356.

Andersen, M.K. and Jensen, L.S. (2001) 'Low Soil Temperature Effects on Short-term Gross N Mineralisation–Immobilisation Turnover after Incorporation of a Green Manure', *Soil Biology and Biochemistry*, 33(4), pp. 511-521.

Andreini, M.S. and Steenhuis, T.S. (1990) 'Preferential Paths of Flow under Conventional and Conservation Tillage', *Geoderma*, 46(1-3), pp. 85-102.

Andrews, M., Scholefield, D., Abberton, M.T., McKenzie, B.A., Hodge, S. and Raven, J.A. (2007) 'Use of White Clover as an Alternative to Nitrogen Fertiliser for Dairy Pastures in Nitrate Vulnerable Zones in the UK: Productivity, Environmental Impact and Economic Considerations', *Annals of Applied Biology*, 151(1), pp. 11-23.

Arauzo, M., Valladolid, M. and Martínez-Bastida, J. (2011) 'Spatio-Temporal Dynamics of Nitrogen in River-Alluvial Aquifer Systems Affected by Diffuse Pollution from Agricultural Sources: Implications for the Implementation of the Nitrates Directive', *Journal of Hydrology - J HYDROL*, 411.

Archer, J. (1994) 'Policies to Reduce Nitrogen Loss to Water from Agriculture in the United Kingdom', *Marine Pollution Bulletin*, 29(6-12), pp. 444-449.

Aronsson, H. (2000) *Nitrogen Turnover and Leaching in Cropping Systems with Ryegrass Catch Crops*. Doctoral thesis. Acta Universitatis Agriculturae Sueciae.

Arrouays, D., McBratney, A., Bouma, J., Libohova, Z., Richer-de-Forges, A.C., Morgan, C.L., Roudier, P., Poggio, L. and Mulder, V.L. (2020) 'Impressions of Digital Soil Maps: The Good, the Not so Good, and Making them ever Better', *Geoderma Regional*, 20, p. e00255.

Atkins, S.F. (1976) *Nitrogen Leaching from Fertilizers: Lysimeter Trials: Published Results from Europe and USA*.

Aulakh, M.S. and Malhi, S.S. (2005) 'Interactions of Nitrogen with Other Nutrients and Water: Effect on Crop Yield and Quality, Nutrient Use Efficiency, Carbon Sequestration, and Environmental Pollution', in *Advances in Agronomy*. Academic Press, pp. 341-409.

Azam, F., Benckiser, G., Müller, C. and Ottow, J. (2001) 'Release, Movement and Recovery of 3,4-Dimethylpyrazole Phosphate (DMPP), Ammonium, and Nitrate from Stabilized Nitrogen Fertilizer Granules in a Silty Clay Soil under Laboratory Conditions', *Biology and Fertility of Soils*, 34(2), pp. 118-125.

Azooz, R.H. and Arshad, M.A. (2001) 'Soil Water Drying and Recharge Rates as Affected by Tillage under Continuous Barley and Barley-Canola Cropping Systems in Northwestern Canada', *Canadian Journal of Soil Science*, 81(1), pp. 45-52.

Baker, J.L. and Timmons, D.R. (1994) 'Fertilizer Management Effects on Leaching of Labeled Nitrogen for No-till Corn in Field Lysimeters', *Journal of environmental quality*, 23(2), pp. 305-310.

Balesdent, J., Chenu, C. and Balabane, M. (2000) 'Relationship of Soil Organic Matter Dynamics to Physical Protection and Tillage', *Soil and tillage research*, 53(3-4), pp. 215-230.

Baram, S., Couvreur, V., Harter, T., Read, M., Brown, P.H., Hopmans, J.W. and Smart, D.R. (2016a) 'Assessment of Orchard N Losses to Groundwater with a Vadose Zone Monitoring Network', *Agricultural Water Management*, 172, pp. 83-95.

Baram, S., Couvreur, V., Harter, T., Read, M., Brown, P.H., Kandelous, M., Smart, D.R. and Hopmans, J.W. (2016b) 'Estimating Nitrate Leaching to Groundwater from Orchards: Comparing Crop Nitrogen Excess, Deep Vadose Zone Data-Driven Estimates, and HYDRUS Modeling', *Vadose Zone Journal*, 15(11), p. 2016.07.0061.

Barth, G., von Tucher, S. and Schmidhalter, U. (2001) 'Influence of Soil Parameters on the Effect of 3,4-Dimethylpyrazole-Phosphate as a Nitrification Inhibitor', *Biology and Fertility of Soils*, 34(2), pp. 98-102.

Basso, B., Cammarano, D., Chen, D., Cafiero, G., Amato, M., Bitella, G., Rossi, R. and Basso, F. (2009) 'Landscape Position and Precipitation Effects on Spatial Variability of Wheat Yield and Grain Protein in Southern Italy', *Journal of Agronomy and Crop Science*, 195(4), pp. 301-312.

Beaudoin, N., Saad, J.K., Van Laethem, C., Machet, J.M., Maucorps, J. and Mary, B. (2005) 'Nitrate Leaching in Intensive Agriculture in Northern France: Effect of Farming Practices, Soils and Crop Rotations', *Agriculture, Ecosystems & Environment*, 111(1), pp. 292-310.

Beeson, S. and Cook, M.C. (2004) 'Nitrate in Groundwater: A Water Company Perspective', *Quarterly Journal of Engineering Geology and Hydrogeology*, 37(4), pp. 261-270.

Berntsen, J., Grant, R., Olesen, J.E., Kristensen, I.S., Vinther, F.P., Mølgaard, J.P. and Petersen, B.M. (2006) 'Nitrogen Cycling in Organic Farming Systems with Rotational Grass–Clover and Arable Crops', *Soil Use and Management*, 22(2), pp. 197-208.

Berry, P.M., Stockdale, E.A., Sylvester-Bradley, R., Philipps, L., Smith, K.A., Lord, E.I., Watson, C.A. and Fortune, S. (2003) 'N, P and K Budgets for Crop Rotations on Nine Organic Farms in the UK', *Soil Use and Management*, 19(2), pp. 112-118.

Berry, P.M., Sylvester-Bradley, R., Philipps, L., Hatch, D.J., Cuttle, S.P., Rayns, F.W. and Gosling, P. (2002) 'Is the Productivity of Organic Farms Restricted by the Supply of Available Nitrogen?', *Soil Use and Management*, 18, pp. 248-255.

Biernat, L., Taube, F., Vogeler, I., Reinsch, T., Kluß, C. and Loges, R. (2020) 'Is Organic Agriculture in Line with the EU-Nitrate Directive? On-Farm Nitrate Leaching from Organic and Conventional Arable Crop Rotations', *Agriculture, Ecosystems & Environment*, 298, p. 106964.

Bijay, S. and Craswell, E. (2021) 'Fertilizers and Nitrate Pollution of Surface and Ground Water: An Increasingly Pervasive Global Problem', *SN Applied Sciences*, 3(4), p. 518.

Bishop, T.F.A. and McBratney, A.B. (2001) 'A comparison of Prediction Methods for the Creation of Field-Extent Soil Property Maps', *Geoderma*, 103(1-2), pp. 149-160.

Bjorneberg, D.L., Kanwar, R.S. and Melvin, S.W. (1996) 'Seasonal Changes in Flow and Nitrate-N loss from Subsurface Drains', *Transactions of the ASAE*, 39(3), pp. 961-967.

Blombäck, K., Eckersten, H., Lewan, E. and Aronsson, H. (2003) 'Simulations of Soil Carbon and Nitrogen Dynamics During Seven Years in a Catch Crop Experiment', *Agricultural Systems*, 76(1), pp. 95-114.

Bodson, B., Vancutsem, F. and Falisse, A. (2001) 'Timing of Nitrogen Application to Improve Quality, Reduce Lodging and Minimise Disease Risks for Hybrid and Inbred Wheat', *Aspects of Applied Biology*, (64), pp. 193-200.

Bokhorst, J.G. and Oomen, G.J.M. (1997) 'Fine-Tuning of the N Fertilization in Biological Agriculture using the N-DICEA Model ', *Meststoffen*, pp. 40-46.

Bonfatti, B.R., Hartemink, A.E., Giasson, E., Tornquist, C.G. and Adhikari, K. (2016) 'Digital Mapping of Soil Carbon in a Viticultural Region of Southern Brazil', *Geoderma*, 261, pp. 204-221.

Børgesen, C.D. and Olesen, J.E. (2011) 'A Probabilistic Assessment of Climate Change Impacts on Yield and Nitrogen Leaching from Winter Wheat in Denmark', *Nat. Hazards Earth Syst. Sci.*, 11(9), pp. 2541-2553.

Bouchet, A., Laperche, A., Bissuel-Belaygue, C., Snowdon, R., Nesi, N. and Stahl, A. (2016) 'Nitrogen use Efficiency in Rapeseed. A Review', *Agronomy for Sustainable Development*, 36(2), p. 38.

Bouraoui, F. and Grizzetti, B. (2014) 'Modelling Mitigation Options To Reduce Diffuse Nitrogen Water Pollution From Agriculture', *Science of The Total Environment*, 468-469, pp. 1267-1277.

Brilli, L., Bechini, L., Bindi, M., Carozzi, M., Cavalli, D., Conant, R., Dorich, C.D., Doro, L., Ehrhardt, F., Farina, R., Ferrise, R., Fitton, N., Francaviglia, R., Grace, P., Iocola, I., Klumpp, K., Léonard, J., Martin, R., Massad, R.S., Recous, S., Seddaiu, G., Sharp, J., Smith, P., Smith, W.N., Soussana, J.F. and Bellocchi, G. (2017) 'Review and Analysis of Strengths and Weaknesses of Agro-Ecosystem Models for Simulating C and N Fluxes', *Science of the Total Environment*, 598, pp. 445-470.

Brisson, N., Mary, B., Ripoche, D., Jeuffroy, M.H., Ruget, F., Nicoullaud, B., Gate, P., Devienne-Barret, F., Antonioletti, R. and Durr, C. (1998) 'STICS: A Generic Model for the Simulation of Crops and their Water and Nitrogen Balances. I. Theory and Parameterization Applied to Wheat and Corn', *Agronomy*, 18, pp. 311 - 346.

Brocca, L., Morbidelli, R., Melone, F. and Moramarco, T. (2007) 'Soil Moisture Spatial Variability in Experimental Areas of Central Italy', *Journal of Hydrology*, 333(2-4), pp. 356-373.

Bronson, K.F., Mosier, A.R. and Bishnoi, S.R. (1992) 'Nitrous Oxide Emissions in Irrigated Corn as Affected by Nitrification Inhibitors', *Soil Science Society of America Journal*, 56(1), pp. 161-165.

Bruinsma, J. (2003) *World agriculture: Towards 2015/2030: An fao perspective*. Earthscan.

Brus, D.J., Kempen, B. and Heuvelink, G.B.M. (2011) 'Sampling for Validation of Digital Soil Maps', *European Journal of Soil Science*, 62(3), pp. 394-407.

Buchanan, S., Triantafilis, J., Odeh, I.O.A. and Subansinghe, R. (2012) 'Digital Soil Mapping of Compositional Particle-Size Fractions (PSFs) using Proximal and Remotely Sensed Ancillary Data.', *Geophysics*, 77(4), pp. 201-211.

Burns, L.G. (2004) *International Symposium Towards Ecologically Sound Fertilisation Strategies for Field Vegetable Production 700*.

Burt, T.P., Howden, N.J.K., Worrall, F., Whelan, M.J. and Bieroza, M. (2011) 'Nitrate in United Kingdom Rivers: Policy and its Outcomes since 1970', *Environmental Science and Technology*, 45(1), pp. 175-181.

Buss, S.R., Rivett, M.O., Morgan, P. and Bemment, C.D. (2005) *Attenuation of Nitrate in the Subsurface Environment* (SC030155/2).

Cameira, M.R., Rolim, J., Valente, F., Faro, A., Dragosits, U. and Cordovil, C.M. (2019) 'Spatial Distribution and Uncertainties of Nitrogen Budgets for Agriculture in the Tagus River Basin in Portugal–Implications for Effectiveness of Mitigation Measures', *Land Use Policy*, 84, pp. 278-293.

Cameron, K.C., Di, H.J. and McLaren, R.G. (1999) 'Comparison of Nitrogen Leaching Losses from Different forms and Rates of Organic Wastes, Fertilisers and Animal Urine Applied to Templeton Soil Lysimeters', *Best Soil Management Practices for Production. Massey University, Palmerston North, New Zealand*, pp. 241-249.

Cameron, K.C., Di, H.J. and Moir, J.L. (2013) 'Nitrogen Losses from the Soil/Plant System: A Review', *Annals of Applied Biology*, 162(2), pp. 145-173.

Cardenas, L.M., Bhogal, A., Chadwick, D.R., McGeough, K., Misselbrook, T., Rees, R.M., Thorman, R.E., Watson, C.J., Williams, J.R., Smith, K.A. and Calvet, S. (2019) 'Nitrogen use efficiency and nitrous oxide emissions from five UK fertilised grasslands', *Sci Total Environ*, 661, pp. 696-710.

Carey, M.A. and Lloyd, J.W. (1985) 'Modelling Non-Point Sources of Nitrate Pollution of Groundwater in the Great Ouse Chalk, UK', *Journal of Hydrology*, 78(1-2), pp. 83-106.

Carter, M.R. (1993) *Soil Sampling and Methods of Analysis*. Boca Raton: Lewis Publishers.

Catt, J.A., Howse, K.R., Christian, D.G., Lane, P.W., Harris, G.L. and Goss, M.J. (1998) 'Strategies to Decrease Nitrate Leaching in the Brimstone Farm Experiment, Oxfordshire, UK, 1988–1993: the Effects of Winter Cover Crops and Unfertilised Grass Leys', *Plant and Soil*, 203(1), pp. 57-69.

Chagas, C., de Carvalho Junior, W., Bhering, S.B. and Calderano Filho, B. (2016) 'Spatial Prediction of Soil Surface Texture in a Semiarid Region using Random Forest and Multiple Linear Regressions', *CATENA*, 139, pp. 232-240.

Chaney, K. (1990) 'Effect of Nitrogen Fertilizer Rate on Soil Nitrate Nitrogen Content after Harvesting Winter Wheat', *Journal of Agricultural Science, Cambridge*, 114(2), pp. 171-176.

Chatskikh, D. and Olesen, J.E. (2007) 'Soil Tillage Enhanced CO2 and N2O Emissions from Loamy Sand Soil under Spring Barley', *Soil and Tillage Research*, 97(1), pp. 5-18.

Chatskikh, D., Olesen, J.E., Hansen, E.M., Elsgaard, L. and Petersen, B.M. (2008) 'Effects of Reduced Tillage on Net Greenhouse Gas Fluxes from Loamy Sand Soil under Winter Crops in Denmark', *Agriculture, Ecosystems & Environment*, 128(1), pp. 117-126.

Chaves, B., Opoku, A., De Neve, S., Boeckx, P., Van Cleemput, O. and Hofman, G. (2006) 'Influence of DCD and DMPP on Soil N Dynamics after Incorporation of Vegetable Crop Residues', *Biology and Fertility of Soils*, 43(1), pp. 62-68.

Chen, S., Du, T., Wang, S., Parsons, D., Wu, D., Guo, X. and Li, D. (2020) 'Evaluation and simulation of spatial variability of soil property effects on deep percolation and nitrate

leaching within a large-scale field in arid Northwest China', *Science of The Total Environment*, p. 139324.
Cherry, K.A., Shepherd, M., Withers, P.J.A. and Mooney, S.J. (2008) 'Assessing the Effectiveness of Actions to Mitigate Nutrient Loss from Agriculture: A Review of Methods', *Science of the Total Environment*, 406(1-2), pp. 1-23.
Chikowo, R., Mapfumo, P., Nyamugafata, P. and Giller, K.E. (2004) 'Mineral N Dynamics, Leaching and Nitrous Oxide Losses under Maize Following Two-Year Improved Fallows on a Sandy Loam Soil in Zimbabwe', *Plant and soil*, 259(1-2), pp. 315-330.
Chiodini, M.E., Perego, A., Carozzi, M. and Acutis, M. (2019) 'The Nitrification Inhibitor Vizura® Reduces N2O Emissions When Added to Digestate before Injection under Irrigated Maize in the Po Valley (Northern Italy)', *Agronomy*, 9(8), p. 431.
Cicek, H., Martens, J.R.T., Bamford, K.C. and Entz, M.H. (2015) 'Late-Season Catch Crops Reduce Nitrate Leaching Risk after Grazed Green Manures but Release N Slower than Wheat Demand', *Agriculture, ecosystems & environment*, 202, pp. 31-41.
Cichota, R., Snow, V.O. and Vogeler, I. (2013) 'Modelling Nitrogen Leaching from Overlapping Urine Patches', *Environmental Modelling & Software*, 41, pp. 15-26.
Clark, A. (2008) *Managing Cover Crops Profitably*. Third Edition edn. Diane Publishing.
Clark, C.M., Bell, M.D., Boyd, J.W., Compton, J.E., Davidson, E.A., Davis, C., Fenn, M.E., Geiser, L., Jones, L. and Blett, T.F. (2017) 'Nitrogen-Induced Terrestrial Eutrophication: Cascading Effects and Impacts on Ecosystem Services', *Ecosphere*, 8(7).
Collins, A.L. and McGonigle, D.F. (2008) 'Monitoring and Modelling Diffuse Pollution from Agriculture for Policy Support: UK and European Experience', *Environmental Science & Policy*, 11(2), pp. 97-101.
Congreves, K.A., Dutta, B., Grant, B.B., Smith, W.N., Desjardins, R.L. and Wagner-Riddle, C. (2016) 'How Does Climate Variability Influence Nitrogen Loss in Temperate Agroecosystems Under Contrasting Management Systems?', *Agriculture, Ecosystems & Environment*, 227, pp. 33-41.
Constantin, J., Beaudoin, N., Launay, M., Duval, J. and Mary, B. (2012) 'Long-Term Nitrogen Dynamics in Various Catch Crop Scenarios: Test and Simulations with STICS Model in a Temperate Climate', *Agriculture, Ecosystems & Environment*, 147, pp. 36-46.
Cook, S.E., Corner, R.J., Groves, P.R. and Grealish, G.J. (1996) 'Use of Airborne Gamma Radiometric Data for Soil Mapping', *Soil Research*, 34(1), pp. 183-194.
Cooper, J., Sanderson, R., Cakmak, I., Ozturk, L., Shotton, P., Carmichael, A., Haghighi, R.S., Tetard-Jones, C., Volakakis, N., Eyre, M. and Leifert, C. (2011) 'Effect of Organic and Conventional Crop Rotation, Fertilization, and Crop Protection Practices on Metal Contents in Wheat (Triticum aestivum).', *J Agric Food Chem.* .
Cordero, E., Longchamps, L., Khosla, R. and Sacco, D. (2019) 'Spatial Management Strategies for Nitrogen in Maize Production Based on Soil and Crop Data', *Science of The Total Environment*, 697, p. 133854.
Corwin, D.L. (2005) 'Geospatial Measurements Of Apparent Soil Electrical Conductivity For Characterizing Soil Spatial Variability', in Javier Alvarez-Benedi, R.M.-C. (ed.) *Soil-Water-Solute Process Characterization*. 1st edn. CRC Press, Boca Raton, FL, pp. 639-672.
Cote, C.M., Bristow, K.L., Charlesworth, P.B., Cook, F.J. and Thorburn, P.J. (2003) 'Analysis Of Soil Wetting And Solute Transport In Subsurface Trickle Irrigation', *Irrigation Science*, 22(3-4), pp. 143-156.
Cottney, P., Williams, P.N., White, E. and Black, L. (2021) 'Investigation Of The Effect Of Slurry, Combined With Inorganic N Rate And Timing, On The Yield Of Spring Barley Post Cover Crop Of Stubble Turnips', *Agronomy*, 11(2), p. 232.

Crews, T.E. and Peoples, M.B. (2005) 'Can The Synchrony Of Nitrogen Supply And Crop Demand Be Improved In Legume And Fertilizer-Based Agroecosystems? A Review', *Nutrient cycling in Agroecosystems*, 72(2), pp. 101-120.

Crowhurst, G. (2007) 'Groundwater Daughter Directive: A UK Perspective', *European Energy and Environmental Law Review*, 16(7), pp. 203-210.

Curley, E.M., O'Flynn, M.G. and McDonnell, K.P. (2010) 'Porous Ceramic Cups: Preparation And Installation Of Samplers For Measuring Nitrate Leaching', *International Journal of Soil Science*, 5(1), pp. 19-25.

Cuttle, S.P., Macleod, C.J.A., Chadwick, D.R., Scholefield, D., Haygarth, P.M., Newell-Price, P., Harris, D., Shepherd, M.A., Chambers, B.J. and Humphrey, R. (2007) 'An Inventory of Methods to Control Diffuse Water Pollution From Agriculture (DWPA)', *User Manual (DEFRA Project ES0203), UK, 113p*.

D'Arcy, B. and Frost, A. (2001) 'The Role of Best Management Practices in Alleviating Water Quality Problems Associated with Diffuse Pollution', *Science of the Total Environment*, 265(1-3), pp. 359-367.

da Silva Chagas, C., de Carvalho Junior, W., Bhering, S.B. and Calderano Filho, B. (2016) 'Spatial Prediction Of Soil Surface Texture In A Semiarid Region Using Random Forest And Multiple Linear Regressions', *Catena*, 139, pp. 232-240.

Dalgaard, T., Bienkowski, J.F., Bleeker, A., Dragosits, U., Drouet, J.L., Durand, P., Frumau, A., Hutchings, N.J., Kedziora, A., Magliulo, V., Olesen, J.E., Theobald, M.R., Maury, O., Akkal, N. and Cellier, P. (2012) 'Farm Nitrogen Balances in six European landscapes as an Indicator for Nitrogen losses and Basis for Improved Management', *Biogeosciences*, 9(12), pp. 5303-5321.

Davidson, K., Gowen, R.J., Tett, P., Bresnan, E., Harrison, P.J., McKinney, A., Milligan, S., Mills, D.K., Silke, J. and Crooks, A. (2012) 'Harmful Algal Blooms: How Strong is the Evidence that Nutrient Ratios and Forms Influence their Occurrence?', *Estuarine, Coastal and Shelf Science*, 115, pp. 399-413.

Davies, D.B. and Sylvester-Bradley, R. (1995) 'The Contribution Of Fertiliser Nitrogen To Leachable Nitrogen In The UK: A Review', *Journal of the Science of Food and Agriculture*, 68(4), pp. 399-406.

De Notaris, C., Rasmussen, J., Sørensen, P. and Olesen, J.E. (2018) 'Nitrogen Leaching: A Crop Rotation Perspective on the Effect of N Surplus, Field Management and Use of Catch Crops', *Agriculture, Ecosystems & Environment*, 255, pp. 1-11.

Defra (2006) *Nitrates in water – the current status in England, ADAS Report to Defra – Supporting Paper D1 for the Consultation on Implementation of the Nitrates Directive in England*. Defra, London.

Defra (2007) *Diffuse nitrate pollution from agriculture-Strategies for reducing nitrate leaching*.

Defra (2010) 'Fertiliser manual RB209. Fertiliser recommendations for Agricultural and Horticultural crops', *Food and Rural Affairs, London, UK.*

Defra (2019) *Farming Statistics Provisional crop areas, yields and livestock populations*

At June 2019 - United Kingdom. United Kingdom: Defra. [Online]. Available at: https://www.gov.uk/government/statistics/farming-statistics-provisional-crop-areas-yields-and-livestock-populations-at-1-june-2019-united-kingdom.

Dematte, J.A.M., Fioriob, P.R. and Ben-Dor, E. (2009) 'Estimation of Soil Properties by Orbital and Laboratory Reflectance Means and its Relation with Soil Classification', *The open Remote sensing journal*, 2(1), pp. 12-23.

Di, H.J. and Cameron, K.C. (2002) 'Nitrate Leaching In Temperate Agroecosystems: Sources, Factors And Mitigating Strategies', *Nutrient Cycling in Agroecosystems*, 64(3), pp. 237-256.

Diacono, M., Rubino, P. and Montemurro, F. (2013) 'Precision Nitrogen Management Of Wheat. A Review', *Agronomy for Sustainable Development*, 33(1), pp. 219-241.
Ding, X., Zhao, Z., Yang, Q., Chen, L., Tian, Q., Li, X. and Meng, F. (2020) 'Model Prediction Of Depth-Specific Soil Texture Distributions With Artificial Neural Network: A Case Study In Yunfu, A Typical Area Of Udults Zone, South China', *Computers and Electronics in Agriculture*, 169, p. 105217.
Dobarco, M.R., Arrouays, D., Lagacherie, P., Ciampalini, R. and Saby, N.P. (2017) 'Prediction Of Topsoil Texture For Region Centre (France) Applying Model Ensemble Methods', *Geoderma*, 298, pp. 67-77.
Dobos, E., Montanarella, L., Nègre, T. and Micheli, E. (2001) 'A Regional Scale Soil Mapping Approach Using Integrated Avhrr And Dem Data', *International Journal of Applied Earth Observation and Geoinformation*, 3(1), pp. 30-42.
Dolan, M.S., Clapp, C.E., Allmaras, R.R., Baker, J.M. and Molina, J.A.E. (2006) 'Soil Organic Carbon And Nitrogen In A Minnesota Soil As Related To Tillage, Residue And Nitrogen Management', *Soil and Tillage Research*, 89(2), pp. 221-231.
Domsch, H. and Giebel, A. (2004) 'Estimation of Soil Textural Features from Soil Electrical Conductivity Recorded Using the EM38', *Precision Agriculture*, 5(4), pp. 389-409.
Donner, S.D., Coe, M.T., Lenters, J.D., Twine, T.E. and Foley, J.A. (2002) 'Modeling The Impact Of Hydrological Changes On Nitrate Transport In The Mississippi River Basin From 1955 To 1994', *Global Biogeochemical Cycles*, 16(3), pp. 16-1-16-19.
Doolittle, J.A. and Brevik, E.C. (2014) 'The use of electromagnetic induction techniques in soils studies', *Geoderma*, 223, pp. 33-45.
Duan, Y.F., Kong, X.W., Schramm, A., Labouriau, R., Eriksen, J. and Petersen, S.O. (2017) 'Microbial N Transformations and N2O Emission after Simulated Grassland Cultivation: Effects of the Nitrification Inhibitor 3,4-Dimethylpyrazole Phosphate (DMPP)', *Appl Environ Microbiol*, 83(1).
Dwivedi, D., Arora, B., Steefel, C.I., Dafflon, B. and Versteeg, R. (2018) 'Hot Spots and Hot Moments of Nitrogen in a Riparian Corridor', *Water Resources Research*, 54(1), pp. 205-222.
Dzurella, K.N., Medellin-Azuara, J., Jensen, V.B., King, A.M., De La Mora, N., Fryjoff-Hung, A., Rosenstock, T.S., Harter, T., Howitt, R. and Hollander, A.D. (2012) *Nitrogen Source Reduction To Protect Groundwater Quality*.
E.A (2017) *LIDAR Composite DTM 2017-2m*. Available at: https://data.gov.uk/dataset/002d24f0-0056-4176-b55e-171ba7f0e0d5/lidar-composite-dtm-2017-2m.
EA (2017) *Implementation of the Nitrate Pollution Prevention Regulations 2015 in England* (HOEV151604/R). Horizon House, Deanery Road, Bristol BS1 5AH: Agency, E.
Edwards, A.C., Sinclair, A.H. and Domburg, P. (2003) 'Identification, Designation and Formulation of an Action Plan for a Nitrate Vulnerable Zone: A Case Study of the Ythan Catchment, NE Scotland', *European journal of agronomy*, 20(1-2), pp. 165-172.
Efretuei, A., Gooding, M., White, E., Spink, J. and Hackett, R. (2016) 'Effect Of Nitrogen Fertilizer Application Timing On Nitrogen Use Efficiency And Grain Yield Of Winter Wheat In Ireland', *Irish Journal of Agricultural and Food Research*, 55(1), pp. 63-73.
Eriksen, J., Askegaard, M. and Kristensen, K. (2004) 'Nitrate Leaching From An Organic Dairy Crop Rotation: The Effects Of Manure Type, Nitrogen Input And Improved Crop Rotation', *Soil Use and Management*, 20(1), pp. 48-54.
Ershadi, S.Z., Dias, G., Heidari, M.D. and Pelletier, N. (2020) 'Improving Nitrogen Use Efficiency In Crop-Livestock Systems: A Review Of Mitigation Technologies And Management Strategies, And Their Potential Applicability For Egg Supply Chains', *Journal of Cleaner Production*, p. 121671.

Exner, M.E., Perea-Estrada, H. and Spalding, R.F. (2010) 'Long-Term Response of Groundwater Nitrate Concentrations to Management Regulations in Nebraska's Central Platte Valley', *TheScientificWorldJOURNAL*, 10, p. 701538.

Fatichi, S., Vivoni, E.R., Ogden, F.L., Ivanov, V.Y., Mirus, B., Gochis, D., Downer, C.W., Camporese, M., Davison, J.H., Ebel, B., Jones, N., Kim, J., Mascaro, G., Niswonger, R., Restrepo, P., Rigon, R., Shen, C., Sulis, M. and Tarboton, D. (2016) 'An Overview Of Current Applications, Challenges, And Future Trends In Distributed Process-Based Models In Hydrology', *Journal of Hydrology*, 537, pp. 45-60.

Felicísimo, A.M. (1994) 'Parametric statistical method for error detection in digital elevation models', *ISPRS Journal of Photogrammetry and Remote Sensing*, 49(4), pp. 29-33.

Feng, G., Zhang, Y., Chen, Y., Li, Q., Chen, F., Gao, Q. and Mi, G. (2016) 'Effects of Nitrogen Application on Root Length and Grain Yield of Rain-Fed Maize under Different Soil Types', *Agronomy Journal*, 108(4), pp. 1656-1665.

Feng, L., Gan-Lin, Z., Xiaodong, S., Decheng, L., Yuguo, Z., Jinling, Y., Huayong, W. and Fei, Y. (2020) 'High-Resolution And Three-Dimensional Mapping Of Soil Texture Of China', *Geoderma*, 361, p. 114061.

Ferreira do Nascimento, A., de Sá Mendonça, E., Leite, L.F.C. and Neves, J.C.L. (2011) 'Calibration Of The Century, Apsim And Indexa Models Of Decomposition And Non-Mineralization Of Plant Residues In The Humid Tropics', *Brazilian Journal of Soil Science*, 35(3), pp. 917-928.

Fettweis, U., Mittelstaedt, W., Schimansky, C. and Führ, F. (2001) 'Lysimeter Studies On The Translocation Of The 14c-Labelled Nitrification Inhibitor 3,4-Dimethylpyrazole-Phosphate In A Gleyic Ambisol.', *Biol Fertil Soils*.

Feyen, J., Jacques, D., Timmerman, A. and Vanderborght, J. (1998) 'Modelling Water Flow And Solute Transport In Heterogeneous Soils: A Review Of Recent Approaches', *Journal of Agricultural Engineering Research*, 70(3), pp. 231-256.

Follett, R.F. and Walker, D.J. (2012) *Ground Water Quality Concers About Nitrogen*. Elsevier.

Ford, J.R., Wakefield, O.J.W. and Kearsey, T. (2019) *Geological Characterisation And Cross-Section Study Of The Fell Sandstone Formation In The Berwick-Upon-Tweed Area, Northumberland* (British Geological Survey Commissioned Report CR/18/130).

Foster, S.S.D., Bridge, L.R., Geake, A.K., Lawrence, A.R. and Parker, J.M. (1986) 'The Groundwater Nitrate Problem: A Summary Of Research On The Impact Of Agricultural Land-Use Practices On Groundwater Quality Between 1976 And 1985', *British Geological Survey Hydrogeological Report*, 86(2), p. 1986.

Fraisse, C.W., Sudduth, K.A. and Kitchen, N.R. (2001) 'Calibration Of The Ceres–Maize Model For Simulating Site–Specific Crop Development And Yield On Claypan Soils', *Applied Engineering in Agriculture*, 17(4), p. 547.

Francis, G.S., Haynes, R.J. and Williams, P.H. (1995) 'Effects Of The Timing Of Ploughing-In Temporary Leguminous Pastures And Two Winter Cover Crops On Nitrogen Mineralization, Nitrate Leaching And Spring Wheat Growth', *The Journal of Agricultural Science*, 124(1), pp. 1-9.

Franzen, D., Goos, R.J., Norman, R.J., Walker, T.W., Roberts, T.L., Slaton, N.A., Endres, G., Ashley, R., Staricka, J. and Lukach, J. (2011) 'Field and Laboratory Studies Comparing Nutrisphere-Nitrogen Urea with Urea in North Dakota, Arkansas, and Mississippi', *Journal of Plant Nutrition*, 34(8), pp. 1198-1222.

Fraters, D., Boumans, L.J.M., van Drecht, G., de Haan, T. and Wim, D. (1998) 'Nitrogen Monitoring In Groundwater In The Sandy Regions Of The Netherlands', *Environmental pollution*, 102(1), pp. 479-485.

Gaines, T.P. and Gaines, S.T. (1994) 'Soil texture effect on nitrate leaching in soil percolates', *Communications in Soil Science and Plant Analysis*, 25(13-14), pp. 2561-2570.

Gallant, J.C. and Dowling, T.I. (2003) 'A Multiresolution Index Of Valley Bottom Flatness For Mapping Depositional Areas', *Water resources research*, 39(12).
Galloway, J., Dentener, F., Boyer, E., Howarth, R., Seitzinger, S., Asner, G., Cleveland, C., Green, P., Holland, E., Karl, D., Michaels, A., Porter, J., Townsend, A.R. and Vöosmarty, C. (2004) 'Nitrogen Cycles: Past, Present, and Future', *Biogeochemistry*, 70, pp. 153-226.
Gessler, P.E., Chadwick, O.A., Chamran, F., Althouse, L. and Holmes, K. (2000) 'Modeling Soil–Landscape And Ecosystem Properties Using Terrain Attributes', *Soil Science Society of America Journal*, 64(6), pp. 2046-2056.
Gibbons, J.M., Sparkes, D.L., Wilson, P. and Ramsden, S.J. (2005) 'Modelling Optimal Strategies For Decreasing Nitrate Loss With Variation In Weather–A Farm-Level Approach', *Agricultural Systems*, 83(2), pp. 113-134.
Giltrap, D., Yeluripati, J., Smith, P., Fitton, N., Smith, W., Grant, B., Dorich, C.D., Deng, J., Topp, C.F.E., Abdalla, M., Liáng, L.L. and Snow, V. (2020) 'Global Research Alliance N_2O Chamber Methodology Guidelines: Summary Of Modeling Approaches', *Journal of Environmental Quality*, 49(5), pp. 1168-1185.
Golden, B., Slaton, N., Norman, R., Gbur, E. and Wilson, C. (2011) 'Nitrogen Release from Environmentally Smart Nitrogen Fertilizer as Influenced by Soil Series, Temperature, Moisture, and Incubation Method', *Communications in Soil Science and Plant Analysis*, 42(15), pp. 1809-1824.
Goulding, K. (2000) 'Nitrate Leaching from Arable and Horticultural Land', *Soil use and management*, 16, pp. 145-151.
Goulding, K., Jarvis, S. and Whitmore, A. (2008) 'Optimizing Nutrient Management For Farm Systems', *Philosophical Transactions of the Royal Society B: Biological Sciences*, 363(1491), pp. 667-680.
Groenendijk, P., Heinen, M., Klammler, G., Fank, J., Kupfersberger, H., Pisinaras, V., Gemitzi, A., Peña-Haro, S., García-Prats, A. and Pulido-Velazquez, M. (2014) 'Performance Assessment Of Nitrate Leaching Models For Highly Vulnerable Soils Used In Low-Input Farming Based On Lysimeter Data', *Science of the total environment*, 499, pp. 463-480.
Grote, K., Anger, C., Kelly, B., Hubbard, S. and Rubin, Y. (2010) 'Characterization of Soil Water Content Variability and Soil Texture using GPR Groundwave Techniques', *Journal of Environmental and Engineering Geophysics*, 15, pp. 93-110.
Guo, Y., Zhou, Y., Zhou, L., Liu, T., Wang, L., Cheng, Y., He, J. and Zheng, G. (2019) 'Using proximal sensor data for soil salinity management and mapping', *Journal of Integrative Agriculture*, 18(2), pp. 340-349.
Gurevich, H., Baram, S. and Harter, T. (2021) 'Measuring nitrate leaching across the critical zone at the field to farm scale', *Vadose Zone Journal*, n/a(n/a), p. e20094.
Haase, D.L., Rose, R. and Trobaugh, J. (2006) 'Field Performance Of Three Stock Sizes Of Douglas-Fir Container Seedlings Grown With Slow-Release Fertilizer In The Nursery Growing Medium', *New Forests*, 31(1), pp. 1-24.
Haderlein, L., Jensen, T.L., Dowbenko, R.E. and Blaylock, A.D. (2001) 'Controlled Release Urea As A Nitrogen Source For Spring Wheat In Western Canada: Yield, Grain N Content, And N Use Efficiency.', *The Scientific World Journal*, (1 Suppl 2), pp. 114–121. .
Hallaq, A. (2010) 'The Impact Of Soil Texture On Nitrates Leaching Into Groundwater In The North Governorate, Gaza Strip', *Journal of the Social Sciences*, 38, pp. 11-35.
Halvorson, A., Wienhold, B. and Black, A. (2001) 'Tillage and Nitrogen Fertilization Influence Grain and Soil Nitrogen in an Annual Cropping System', *Agronomy Journal*, 93.
Hansen, E.M. and Djurhuus, J. (1997) 'Nitrate Leaching As Influenced By Soil Tillage And Catch Crop', *Soil and Tillage Research*, 41(3-4), pp. 203-219.

Hansen, E.M., Munkholm, L.J., Olesen, J.E. and Melander, B. (2015) 'Nitrate Leaching, Yields and Carbon Sequestration after Noninversion Tillage, Catch Crops, and Straw Retention', *Journal of Environmental Quality*, 44(3), pp. 868-881.

Hansen, S., Jensen, H.E., Nielsen, N.E. and Svendsen, H. (1990) 'DAISY: Soil plant atmosphere system model. NPO Report No. A 10. The National Agency for Environmental Protection, Copenhagen'.

Hatch, D., Trindade, H., Cardenas, L., Carneiro, J., Hawkins, J., Scholefield, D. and Chadwick, D. (2005) 'Laboratory Study Of The Effects Of Two Nitrification Inhibitors On Greenhouse Gas Emissions From A Slurry-Treated Arable Soil: Impact Of Diurnal Temperature Cycle', *Biology and Fertility of Soils*, 41(4), pp. 225-232.

Haynes, R.J. (1997) *Leaching Of Nitrate From New Zealand Agricultural Soils*.

Heiniger, R.W., Smith, T.A. and Wiatrak, P. (2013) 'The impact of the polymer coating NutriSphere-N®; in increasing nitrogen use efficiency and corn yield', *American Journal of Agricultural and Biological Sciences*, 9(1).

Henderson, B.L., Bui, E.N., Moran, C.J. and Simon, D.A.P. (2005) 'Australia-Wide Predictions Of Soil Properties Using Decision Trees', *Geoderma*, 124(3), pp. 383-398.

Hengl, T., Gruber, S. and Shrestha, D.P. (2004a) 'Reduction of errors in digital terrain parameters used in soil-landscape modelling', *International Journal of Applied Earth Observation and Geoinformation*, 5(2), pp. 97-112.

Hengl, T., Heuvelink, G.B.M. and Stein, A. (2004b) 'A Generic Framework For Spatial Prediction Of Soil Variables Based On Regression-Kriging', *Geoderma*, 120(1-2), pp. 75-93.

Herrera, J.M., Feil, B., Stamp, P. and Liedgens, M. (2010) 'Root Growth And Nitrate-Nitrogen Leaching Of Catch Crops Following Spring Wheat', *Journal of environmental quality*, 39(3), pp. 845-854.

Higgins, S., Schellberg, J. and Bailey, J.S. (2019) 'Improving Productivity And Increasing The Efficiency Of Soil Nutrient Management On Grassland Farms In The UK And Ireland Using Precision Agriculture Technology', *European Journal of Agronomy*, 106, pp. 67-74.

Holland, K.H., Lamb, D.W. and Schepers, J.S. (2012) 'Radiometry Of Proximal Active Optical Sensors (Aos) For Agricultural Sensing', *IEEE Journal of Selected Topics in Applied Earth Observations and Remote Sensing*, 5(6), pp. 1793-1802.

Holland, K.H. and Schepers, J.S. (2013) 'Use Of A Virtual-Reference Concept To Interpret Active Crop Canopy Sensor Data', *Precision Agriculture*, 14(1), pp. 71-85.

Horne, D.J., Ross, C.W. and Hughes, K.A. (1992) 'Ten Years Of A Maize/Oats Rotation Under Three Tillage Systems On A Silt Loam In New Zealand. 1. A Comparison Of Some Soil Properties', *Soil and Tillage Research*, 22(1-2), pp. 131-143.

Howden, N.J.K. and Burt, T.P. (2009) 'Statistical Analysis Of Nitrate Concentrations From The Rivers Frome And Piddle (Dorset, Uk) For The Period 1965–2007', *Ecohydrology: Ecosystems, Land and Water Process Interactions, Ecohydrogeomorphology*, 2(1), pp. 55-65.

Huang, J., Xu, J., Liu, X., Liu, J. and Wang, L. (2011) 'Spatial Distribution Pattern Analysis Of Groundwater Nitrate Nitrogen Pollution In Shandong Intensive Farming Regions Of China Using Neural Network Method', *Mathematical and Computer Modelling*, 54(3), pp. 995-1004.

Huang, P., Zhang, J., Zhu, A., Li, X., Ma, D., Xin, X., Zhang, C., Wu, S.F., Garland, G. and Pereira, E.I.P. (2018) 'Nitrate Accumulation And Leaching Potential Reduced By Coupled Water And Nitrogen Management In The Huang-Huai-Hai Plain', *Science of the Total Environment*, 610, pp. 1020-1028.

Huang, T., Ju, X. and Yang, H. (2017) 'Nitrate Leaching In A Winter Wheat-Summer Maize Rotation On A Calcareous Soil As Affected By Nitrogen And Straw Management', *Scientific Reports*, 7(1), p. 42247.

Huljek, L., Perković, D. and Kovač, Z. (2019) 'Nitrate Contamination Risk Of The Zagreb Aquifer', *Journal of Maps*, 15(2), pp. 570-577.

Iticha, B. and Takele, C. (2019) 'Digital Soil Mapping For Site-Specific Management of Soils', *Geoderma*, 351, pp. 85-91.

Jabloun, M., Schelde, K., Tao, F. and Olesen, J.E. (2015) 'Effect Of Temperature And Precipitation On Nitrate Leaching From Organic Cereal Cropping Systems In Denmark', *European Journal of Agronomy*, 62, pp. 55-64.

James, G., Witten, D., Hastie, T. and Tibshirani, R. (2013a) *An Introduction to Statistical Learning* 1edn. Springer-Verlag New York.

James, G., Witten, D., Hastie, T. and Tibshirani, R. (2013b) 'Linear Regression', in *An Introduction to Statistical Learning with Applications in R*. Springer, pp. 59-126.

Jansson, P.E. (1994) *Nitrate: Processes, Patterns and Management* John Wiley & Sons, Ltd.

Jarvis, R.A. (1984) *Soils and Their Use in Northern England. Harpenden: [Soil Survey of England and Wales]*. Print. Bulletin (Soil Survey of England and Wales) ; No.10.

Jasper, J., Reusch, S. and Link, A. (2009) 'Active Sensing Of The N Status Of Wheat Using Optimized Wavelength Combination: Impact Of Seed Rate, Variety And Growth Stage', *Precision agriculture*. pp. 23-30.

Jenkinson, D.S. (2001) 'The Impact Of Humans On The Nitrogen Cycle, With Focus On Temperate Arable Agriculture', *Plant and Soil*, 228(1), pp. 3-15.

Jeremy, P.L.D. and Melissa, S. (2021) 'Groundwater Nitrate and Sustainability studies in the Fell Sandstone Aquifer, Northumberland', *Joseph London*.

Jin, J. and Jiang, C. (2002) 'Spatial Variability Of Soil Nutrients And Site-Specific Nutrient Management In The P.R China', *Computers and Electronics in Agriculture*, 36(2-3), pp. 165-172.

Jones, H.K., Morris, B.L., Cheney, C., Brewerton, L.J., Merrin, P.D., Lewis, M., Macdonald, A., Coleby, L.M., Talbot, J.C., McKenzie, A., Bird, M.J., Cunningham, J.E., Robinson, V., Waters, C., Barclay, W., Ellison, R., Goode, A., Hamblin, R., Hopson, P. and Sumbler, M. (2000) *The physical properties of minor aquifers in England and Wales*.

Jones, J.W., Hoogenboom, G., Porter, C.H., Boote, K.J., Batchelor, W.D., Hunt, L.A., Wilkens, P.W., Singh, U., Gijsman, A.J. and Ritchie, J.T. (2003) 'The DSSAT Cropping System Model', *European Journal of Agronomy*, 18(3), pp. 235-265.

Julie, C., Christine, L.B. and Eric, J. (2015) 'Large-Scale Assessment of Optimal Emergence and Destruction Dates for Cover Crops to Reduce Nitrate Leaching in Temperate Conditions using the STICS Soil–Crop Model', *European Journal of Agronomy*, 69, pp. 75-87.

Justes, E., Beaudoin, N., Bertuzzi, P., Charles, R., Constantin, J., Dürr, C., Hermon, C., Joannon, A., Bas, C.l. and Mary, B. (2012) *Proceedings-International Fertiliser Society*. International Fertiliser Society.

Kanwar, R.S., Baker, L.J. and Laflen, M.J. (1985) 'Nitrate Movement Through the Soil Profile in Relation to Tillage System and Fertilizer Application Method', *Transactions of the ASAE*, 28(6), pp. 1802-1807.

Kay, P., Grayson, R., Phillips, M., Stanley, K., Dodsworth, A., Hanson, A., Walker, A., Foulger, M., McDonnell, I. and Taylor, S. (2012) 'The Effectiveness of Agricultural Stewardship for Improving Water Quality at the Catchment Scale: Experiences from an NVZ and ECSFDI Watershed', *Journal of Hydrology*, 422-423, pp. 10-16.

Keating, B.A., Carberry, P.S., Hammer, G.L., Probert, M.E., Robertson, M.J., Holzworth, D., Huth, N.I., Hargreaves, J.N.G., Meinke, H., Hochman, Z., McLean, G., Verburg, K., Snow, V., Dimes, J.P., Silburn, M., Wang, E., Brown, S., Bristow, K.L., Asseng, S., Chapman, S., McCown, R.L., Freebairn, D.M. and Smith, C.J. (2003) 'An Overview Of Apsim, A Model Designed For Farming Systems Simulation', *European Journal of Agronomy*, 18(3), pp. 267-288.

Keeney, D.R. and Nelson, D.W. (1982) 'Nitrogen - Inorganic Forms', in A.L., M., R.H. and Keeney, D.R. (ed.) *Methods of Soil Analysis part 2: Chemical and microbiological properties*. 2nd edn. Madison: WI: American Society of Agronomy, pp. 643-698.

Kelly, F. and Westendorf, M. (2014) *Storing Manure on Small Horse and Livestock Farms*.

Kempen, B., Brus, D.J., Stoorvogel, J.J., Heuvelink, G.B.M. and de Vries, F. (2012) 'Efficiency Comparison of Conventional and Digital Soil Mapping for Updating Soil Maps', *Soil Science Society of America Journal*, 76(6), pp. 2097-2115.

Kersebaum, K.C., Hecker, J.M., Mirschel, W. and Wegehenkel, M. (2007) *Modelling water and nutrient dynamics in soil–crop systems*. Dordrecht, 2007//. Springer Netherlands.

Khaledian, Y. and Miller, B.A. (2020) 'Selecting Appropriate Machine Learning Methods For Digital Soil Mapping', *Applied Mathematical Modelling*, 81, pp. 401-418.

Khan, S., Shah, A., Nawaz, M. and Khan, M. (2017) 'Impact Of Different Tillage Practices On Soil Physical Properties, Nitrate Leaching And Yield Attributes Of Maize (Zea Mays L.)', *Journal of soil science and plant nutrition*, 17.

Khanal, S., Fulton, J., Klopfenstein, A., Douridas, N. and Shearer, S. (2018) 'Integration Of High Resolution Remotely Sensed Data And Machine Learning Techniques For Spatial Prediction Of Soil Properties And Corn Yield', *Computers And Electronics In Agriculture*, 153, pp. 213-225.

Kitchen, N.R., Goulding, K.W.T. and Shanahan, J.F. (2008) 'Proven Practices And Innovative Technologies For On-Farm Crop Nitrogen Management', in *Nitrogen in the Environment*. Elsevier, pp. 483-517.

Knox, E. and Moody, D.W. (1991) 'Influence of Hydrology, Soil Properties, and Agricultural Land Use on Nitrogen in Groundwater', in *Managing Nitrogen for Groundwater Quality and Farm Profitability*. pp. 19-57-6.

Kong, X., Duan, Y., Schramm, A., Eriksen, J., Holmstrup, M., Larsen, T., Bol, R. and Petersen, S.O. (2017) 'Mitigating N_2O Emissions From Clover Residues By 3,4-Dimethylpyrazole Phosphate (Dmpp) Without Adverse Effects On The Earthworm Lumbricus Terrestris', *Soil Biology and Biochemistry*, 104, pp. 95-107.

Kong, X., Duan, Y., Schramm, A., Eriksen, J. and Petersen, S.O. (2016) '3,4-Dimethylpyrazole Phosphate (DMPP) Reduces Activity Of Ammonia Oxidizers Without Adverse Effects On Non-Target Soil Microorganisms And Functions', *Applied Soil Ecology*, 105, pp. 67-75.

Koopmans, C.J. and Bokhorst, J. (2002) 'Nitrogen Mineralisation In Organic Farming Systems: A Test Of The NDICEA Model', *Agronomie*, 22, pp. 855-862.

Krause, S., Heathwaite, A.L., Miller, F., Hulme, P. and Crowe, A. (2007) 'Groundwater-Dependent Wetlands In The Uk And Ireland: Controls, Functioning And Assessing The Likelihood Of Damage From Human Activities', *Water Resources Management*, 21(12), pp. 2015-2025.

Kristensen, S.P., Mathiasen, J., Lassen, J., Madsen, H.B. and Reenberg, A. (1994) 'A Comparison Of The Leachable Inorganic Nitrogen Content In Organic And Conventional Farming Systems', *Acta Agriculturae Scandinavica B-Plant Soil Sciences*, 44(1), pp. 19-27.

Kurunc, A., Ersahin, S., Uz, B.Y., Sonmez, N.K., Uz, I., Kaman, H., Bacalan, G.E. and Emekli, Y. (2011) 'Identification Of Nitrate Leaching Hot Spots In A Large Area With Contrasting Soil Texture And Management', *Agricultural Water Management*, 98(6), pp. 1013-1019.

Lamb, D.W., Steyn-Ross, M., Schaare, P., Hanna, M.M., Silvester, W. and Steyn-Ross, A. (2002) 'Estimating Leaf Nitrogen Concentration In Ryegrass (Lolium Spp.) Pasture Using The Chlorophyll Red-Edge: Theoretical Modelling And Experimental Observations', *International Journal of Remote Sensing*, 23(18), pp. 3619-3648.

Lawniczak, A.E., Zbierska, J. and Kupiec, J. (2008) 'Changes of Nutrient Concentrations in Water Sensitive to Nitrate Pollution from Agricultural Sources in the Samica Steszewska River Catchment', *Annals of Warsaw University of Life Sciences-SGGW. Land Reclamation*, 40.

Lewan, E. (1994) 'Effects Of A Catch Crop On Leaching Of Nitrogen From A Sandy Soil: Simulations And Measurements', *Plant and Soil*, 166(1), pp. 137-152.

Li, C., Farahbakhshazad, N., Jaynes, D.B., Dinnes, D.L., Salas, W. and McLaughlin, D. (2006) 'Modeling Nitrate Leaching With A Biogeochemical Model Modified Based On Observations In A Row-Crop Field In Iowa', *Ecological modelling*, 196(1-2), pp. 116-130.

Li, C., Frolking, S. and Frolking, T.A. (1992) 'A Model Of Nitrous Oxide Evolution From Soil Driven By Rainfall Events: 1. Model Structure And Sensitivity', *Journal of Geophysical Research: Atmospheres*, 97(D9), pp. 9759-9776.

Li, C.S. (2000) 'Modeling Trace Gas Emissions From Agricultural Ecosystems', in *Methane emissions from major rice ecosystems in asia*. Springer, pp. 259-276.

Li, H., Wang, L., Qiu, J., Li, C., Gao, M. and Gao, C. (2014) 'Calibration Of DNDC Model For Nitrate Leaching From An Intensively Cultivated Region Of Northern China', *Geoderma*, 223, pp. 108-118.

Li, J., Wan, H. and Shang, S. (2020) 'Comparison Of Interpolation Methods For Mapping Layered Soil Particle-Size Fractions And Texture In An Arid Oasis', *CATENA*, 190, p. 104514.

Li, T., Hao, X. and Kang, S. (2017) 'Spatial Variability Of Grape Yield And Its Association With Soil Water Depletion Within A Vineyard Of Arid Northwest China', *Agricultural Water Management*, 179, pp. 158-166.

Li, Z., Taylor, J., Frewer, L., Zhao, C., Yang, G., Liu, Z., Gaulton, R., Wicks, D., Mortimer, H. and Cheng, X. (2019) 'A Comparative Review On The State And Advancement Of Site-Specific Crop Management In The UK And China', *Frontiers of Agricultural Science and Engineering*, (6(2)), pp. 116-136.

Liao, K., Lv, L., Lai, X. and Zhu, Q. (2021) 'Toward A Framework For The Multimodel Ensemble Prediction Of Soil Nitrogen Losses', *Ecological Modelling*, 456, p. 109675.

Liao, K., Xu, S., Wu, J. and Zhu, Q. (2013) 'Spatial Estimation Of Surface Soil Texture Using Remote Sensing Data', *Soil Science and Plant Nutrition*, 59(4), pp. 488-500.

Ließ, M., Glaser, B. and Huwe, B. (2012) 'Uncertainty In The Spatial Prediction Of Soil Texture: Comparison Of Regression Tree And Random Forest Models', *Geoderma*, 170, pp. 70-79.

Limbrick, K.J. (2003) 'Baseline Nitrate Concentration In Groundwater Of The Chalk In South Dorset, UK', *Science of the Total Environment*, 314, pp. 89-98.

Lin, C., Wu, Z., Ma, R. and Su, Z. (2016) 'Detection Of Sensitive Soil Properties Related To Non-Point Phosphorus Pollution By Integrated Models of SEDD and PLOAD', *Ecological Indicators*, 60, pp. 483-494.

Linzmeier, W., Gutser, R. and Schmidhalter, U. (2001) 'Nitrous Oxide Emission From Soil And From A Nitrogen-15-Labelled Fertilizer With The New Nitrification Inhibitor 3,4-Dimethylpyrazole Phosphate (DMPP)', *Biology and Fertility of Soils*, 34, pp. 103-108.

Loague, K. and Green, R.E. (1991) 'Statistical And Graphical Methods For Evaluating Solute Transport Models: Overview And Application', *Journal of Contaminant Hydrology*, 7(1), pp. 51-73.

Lord, E.I., Anthony, S.G. and Goodlass, G. (2002) 'Agricultural Nitrogen Balance and Water Quality in the UK', *Soil Use and Management*, 18(4), pp. 363-369.

Lord, E.I. and Shepherd, M.A. (1993) 'Developments In The Use Of Porous Ceramic Cups For Measuring Nitrate Leaching', *Journal of Soil Science*, 44(3), pp. 435-449.

Luce, M.S., Whalen, J.K., Ziadi, N. and Zebarth, B.J. (2011) 'Nitrogen Dynamics And Indices To Predict Soil Nitrogen Supply In Humid Temperate Soils', in *Advances in agronomy*. Elsevier, pp. 55-102.
Luo, L., Wang, Y. and Qin, L. (2014) 'Incentives For Promoting Agricultural Clean Production Technologies In China', *Journal of Cleaner Production*, 74, pp. 54-61.
M.R. Carter, E.G.G. (2007) *Soil Sampling And Methods Of Analysis* 2nd edn. CRC Press.
Macdonald, A.J., Poulton, P.R., Howe, M.T., Goulding, K.W.T. and Powlson, D.S. (2005) 'The Use Of Cover Crops In Cereal-Based Cropping Systems To Control Nitrate Leaching In SE England', *Plant and Soil*, 273(1-2), pp. 355-373.
MacDonald, A.M., Darling, W.G., Ball, D.F. and Oster, H. (2003) 'Identifying Trends In Groundwater Quality Using Residence Time Indicators: An Example From The Permian Aquifer Of Dumfries, Scotland', *Hydrogeology Journal*, 11(4), pp. 504-517.
MacDonald, A.M., Lapworth, D.J., Hughes, A.G., Auton, C.A., Maurice, L., Finlayson, A. and Gooddy, D.C. (2014) 'Groundwater, Flooding And Hydrological Functioning In The Findhorn Floodplain, Scotland', *Hydrology Research*, 45(6), pp. 755-773.
Machado, S., Bynum, E.D., Archer, T.L., Bordovsky, J., Rosenow, D.T., Peterson, C., Bronson, K., Nesmith, D.M., Lascano, R.J. and Wilson, L.T. (2002) 'Spatial And Temporal Variability Of Sorghum Grain Yield: Influence Of Soil, Water, Pests, And Diseases Relationships', *Precision Agriculture*, 3(4), pp. 389-406.
Maharjan, B., Ferguson, R.B. and Slater, G.P. (2017) 'Irrigated Corn Productivity as Influenced by Nitrogen Source, Rate, and Climatic Conditions', *Agronomy Journal*, 109(6), pp. 2957-2965.
Malzer, G.L., Kelling, K.A., Schmitt, M.A., Hoeft, R.G. and Randall, G.W. (1989) 'Performance Of Dicyandiamide In The North Central States', *Communications in Soil Science and Plant Analysis*, 20(19-20), pp. 2001-2022.
Man, J.G., Zhou, J., Wang, D., Yu, Z.W., Zhang, M., Hu, Z.Y. and Hou, X.T. (2011) 'Effects of sulfur plus resin-coated controlled release urea fertilizer on winter wheat dry matter accumulation and allocation and grain yield', *Ying Yong Sheng Tai Xue Bao*, 22(5), pp. 1175-82.
Markou, A. (2013) *System Dynamics study of the Fell Sandstone aquifer*. School of Civil Engineering and Geosciences, Newcastle University.
Martínková, M., Hesse, C., Krysanova, V., Vetter, T. and Hanel, M. (2011) 'Potential Impact Of Climate Change On Nitrate Load From The Jizera Catchment (Czech Republic)', *Physics and Chemistry of the Earth, Parts A/B/C*, 36(13), pp. 673-683.
Masetti, M., Poli, S., Sterlacchini, S., Beretta, G.P. and Facchi, A. (2008) 'Spatial And Statistical Assessment Of Factors Influencing Nitrate Contamination In Groundwater', *Journal of Environmental Management*, 86(1), pp. 272-281.
McBratney, A.B., Mendonça Santos, M.L. and Minasny, B. (2003) 'On Digital Soil Mapping', *Geoderma*, 117(1-2), pp. 3-52.
McCormick, S. (2005) *The Nature And Causes Of Spatial Variability In Forage Grass Production In Cool Temperate Climes*. Queen's University of Belfast;.
McCormick, S., Bailey, J.S., Jordan, C. and Higgins, A.J. (2003) 'A Potential Role For Soil Electrical Conductivity Mapping In The Site-Specific Management Of Grassland', *Precision Agriculture Proceedings*, pp. 393-397.
McGeough, K.L., Watson, C.J., Müller, C., Laughlin, R.J. and Chadwick, D.R. (2016) 'Evidence That The Efficacy Of The Nitrification Inhibitor Dicyandiamide (Dcd) Is Affected By Soil Properties In Uk Soils', *Soil Biology and Biochemistry*, 94, pp. 222-232.
Mclean, E.O. (1983) 'Soil pH and Lime Requirement', in *Methods of Soil Analysis*. pp. 199-224.

Meisinger, J.J., Delgado, J.A. and Alva, A.K. (2006) 'Nitrogen Leaching Management', *Encyclopedia of Soils in the Environment*, (2), pp. 1122-1124.

Meisinger, J.J., Hargrove, W.L., Mikkelsen, R.L., Williams, J.R. and Benson, V.W. (1991) 'Effects Of Cover Crops On Groundwater Quality', *Cover crops for clean water*, pp. 57-68.

Meisinger, J.J., Palmer, R.E. and Timlin, D.J. (2015) 'Effects Of Tillage Practices On Drainage And Nitrate Leaching From Winter Wheat In The Northern Atlantic Coastal-Plain USA', *Soil and Tillage Research*, 151, pp. 18-27.

Mekala, C. and Nambi, I.M. (2017) 'Understanding The Hydrologic Control Of N Cycle: Effect Of Water Filled Pore Space On Heterotrophic Nitrification, Denitrification And Dissimilatory Nitrate Reduction To Ammonium Mechanisms In Unsaturated Soils', *Journal of Contaminant Hydrology*, 202, pp. 11-22.

Miller, B.A. and Schaetzl, R.J. (2014) 'The Historical Role Of Base Maps In Soil Geography', *Geoderma*, 230, pp. 329-339.

Min, L., Shen, Y., Pei, H. and Wang, P. (2018) 'Water Movement And Solute Transport In Deep Vadose Zone Under Four Irrigated Agricultural Land-Use Types In The North China Plain', *Journal of Hydrology*, 559, pp. 510-522.

Minasny, B. and McBratney, A.B. (2016) 'Digital Soil Mapping: A Brief History And Some Lessons', *Geoderma*, 264, pp. 301-311.

Montanarella, L. and Vargas, R. (2012) 'Global governance of soil resources as a necessary condition for sustainable development', *Current Opinion in Environmental Sustainability*, 4(5), pp. 559-564.

Moore, I.D., Gessler, P.E., Nielsen, G.A. and Peterson, G.A. (1993) 'Soil Attribute Prediction Using Terrain Analysis', *Soil Science Society of America Journal*, 57.

Munkholm, L.J. and Hansen, E.M. (2012) 'Catch Crop Biomass Production, Nitrogen Uptake And Root Development Under Different Tillage Systems', *Soil Use and Management*, 28(4), pp. 517-529.

Muschietti-Piana, M., Cipriotti, P.A., Urricariet, S., Peralta, N.R. and Niborski, M. (2018) 'Using Site-Specific Nitrogen Management In Rainfed Corn To Reduce The Risk Of Nitrate Leaching', *Agricultural Water Management*, 199, pp. 61-70.

Myrbeck, Å., Stenberg, M. and Rydberg, T. (2012) 'Establishment Of Winter Wheat—Strategies For Reducing The Risk Of Nitrogen Leaching In A Cool-Temperate Region', *Soil and Tillage Research*, 120, pp. 25-31.

Nair, D., Baral, K.R., Abalos, D., Strobel, B.W. and Petersen, S.O. (2020) 'Nitrate Leaching And Nitrous Oxide Emissions From Maize After Grass-Clover On A Coarse Sandy Soil: Mitigation Potentials Of 3,4-Dimethylpyrazole Phosphate (DMPP)', *J Environ Manage*, 260, p. 110165.

Nardi, P., Neri, U., Di Matteo, G., Trinchera, A., Napoli, R., Farina, R., Subbarao, G.V. and Benedetti, A. (2018) 'Nitrogen Release From Slow-Release Fertilizers In Soils With Different Microbial Activities', *Pedosphere*, 28(2), pp. 332-340.

Neal, C., Jarvie, H.P., Neal, M., Hill, L. and Wickham, H. (2006) 'Nitrate Concentrations in River Waters of the Upper Thames and its Tributaries', *Science of the Total Environment*, 365(1-3), pp. 15-32.

Nieder, R., Kersebaum, K.C. and Richter, J. (1995) 'Significance Of Nitrate Leaching And Long Term N Immobilization After Deepening The Plough Layers For The N Regime Of Arable Soils In N.W. Germany', *Plant and Soil*, 173(1), pp. 167-175.

Nolan, B.T. and Stoner, J.D. (2000) 'Nutrients in Groundwaters of the Conterminous United States, 1992-1995', *Environmental Science and Technology*, 34(7), pp. 1156-1165.

Norman, R.J., Kurtz, L.T. and Stevenson, F.J. (1987) 'Distribution and Recovery of Nitrogen-15-labeled Liquid Anhydrous Ammonia Among Various Soil Fractions', *Soil Science Society of America Journal*, 51(1), pp. 235-241.

Norton, J.M. (2008) 'Nitrification in Agricultural Soils', in *Nitrogen in Agricultural Systems*. pp. 173-199.
O'Shea, L. and Wade, A. (2009) 'Controlling Nitrate Pollution: An Integrated Approach', *Land Use Policy*, 26(3), pp. 799-808.
Oenema, O., Ju, X., de Klein, C., Alfaro, M., del Prado, A., Lesschen, J.P., Zheng, X., Velthof, G.L., Ma, L. and Gao, B. (2014) 'Reducing Nitrous Oxide Emissions From The Global Food System', *Current Opinion in Environmental Sustainability*, 9, pp. 55-64.
office., M. (2010) *UK Climate Averages*. Available at: https://www.metoffice.gov.uk/research/climate/maps-and-data/uk-climate-averages/gcyt62suu (Accessed: December 31, 2020).
Ogejo, J.A. and Collins Jr, E.R. (2009) *Storing And Handling Poultry Litter*. Virginia Polytechnic Institute and State University. Fact sheet: College of Agriculture and Life Sciences. [Online]. Available at: https://vtechworks.lib.vt.edu/bitstream/handle/10919/48469/442-054_pdf.pdf?sequence=1&isAllowed=y.
Olesen, J.E., Askegaard, M. and Rasmussen, I.A. (2000) 'Design Of An Organic Farming Crop-Rotation Experiment', *Acta Agriculturae Scandinavica, Section B-Plant Soil Science*, 50(1), pp. 13-21.
Olesen, J.E., Hansen, E.M., Askegaard, M. and Rasmussen, I.A. (2007) 'The Value Of Catch Crops And Organic Manures For Spring Barley In Organic Arable Farming', *Field Crops Research*, 100(2), pp. 168-178.
Ongley, E.D., Xiaolan, Z. and Tao, Y. (2010) 'Current Status of Agricultural and Rural Non-Point Source Pollution Assessment in China', *Environmental Pollution*, 158(5), pp. 1159-1168.
Onsoy, Y.S., Harter, T., Ginn, T.R. and Horwath, W.R. (2005) 'Spatial Variability and Transport of Nitrate in a Deep Alluvial Vadose Zone', *Vadose Zone Journal*, 4(1), pp. 41-54.
Osaka, K., Ohte, N., Koba, K., Yoshimizu, C., Katsuyama, M., Tani, M., Tayasu, I. and Nagata, T. (2010) 'Hydrological Influences On Spatiotemporal Variations Of δ15N and δ18O Of Nitrate In A Forested Headwater Catchment In Central Japan: Denitrification Plays A Critical Role In Groundwater', *Journal of Geophysical Research: Biogeosciences*, 115(G2).
Padilla, F.M., Gallardo, M. and Manzano-Agugliaro, F. (2018) 'Global Trends in Nitrate leaching Research in the 1960–2017 Period', *Science of The Total Environment*, 643, pp. 400-413.
Pahlavan-Rad, M.R. and Akbarimoghaddam, A. (2018) 'Spatial Variability Of Soil Texture Fractions And Ph In A Flood Plain (Case Study From Eastern Iran)', *Catena*, 160, pp. 275-281.
Pain, B.F., Misselbrook, T.H. and Rees, Y.J. (1994) 'Effects Of Nitrification Inhibitor And Acid Addition To Cattle Slurry On Nitrogen Losses And Herbage Yields', *Grass and forage science*, 49(2), pp. 209-215.
Palmer, R.E., .Hill, R.L., Meisinger, J.J. and Magette, W.L. (2011) 'Undisturbed Soil-Columns for Lysimetry: II. Miscible Displacement and Field Evaluation', *Applied Engineering in Agriculture*, 27(3), pp. 391-400.
Pandey, A., Li, F., Askegaard, M., Rasmussen, I.A. and Olesen, J.E. (2018) 'Nitrogen Balances In Organic And Conventional Arable Crop Rotations And Their Relations To Nitrogen Yield And Nitrate Leaching Losses', *Agriculture, ecosystems & environment*, 265, pp. 350-362.
Patil, R.H., Laegdsmand, M., Olesen, J.E. and Porter, J.R. (2010) 'Effect Of Soil Warming And Rainfall Patterns On Soil N Cycling In Northern Europe', *Agriculture, Ecosystems & Environment*, 139(1), pp. 195-205.

Patil, R.H., Laegdsmand, M., Olesen, J.E. and Porter, J.R. (2012) 'Sensitivity Of Crop Yield And N Losses In Winter Wheat To Changes In Mean And Variability Of Temperature And Precipitation In Denmark Using The FASSET Model', *Acta Agriculturae Scandinavica, Section B — Soil & Plant Science*, 62(4), pp. 335-351.

Payton, R.W., Palmer, R.C., Hodgson, J.M., Survey, S. and Centre, L.R. (1990) *Soils of the Alnwick and Rothbury District*. National Soil Resources Institute.

Pedrera-Parrilla, A., Brevik, E.C., Giráldez, J.V. and Vanderlinden, K. (2016) 'Temporal Stability Of Electrical Conductivity In A Sandy Soil', *International Agrophysics*, 30(3), pp. 349-357.

Petersen, J., Thomsen, I.K., Mattsson, L., Hansen, E.M. and Christensen, B.T. (2010) 'Grain Yield And Crop N Offtake In Response To Residual Fertilizer N In Long-Term Field Experiments', *Soil Use and Management*, 26(4), pp. 455-464.

Philipps, L. and Stopes, C. (1995) 'The Impact Of Rotational Practice On Nitrate Leaching Losses In Organic Farming Systems In The United Kingdom', *Biological Agriculture & Horticulture*, 11(1-4), pp. 123-134.

Picard, R.R. and Cook, R.D. (1984) 'Cross-Validation of Regression Models', *Journal of the American Statistical Association*, 79(387), pp. 575-583.

Pieri, L., Bittelli, M. and Pisa, P.R. (2006) 'Laser diffraction, transmission electron microscopy and image analysis to evaluate a bimodal Gaussian model for particle size distribution in soils', *Geoderma*, 135, pp. 118-132.

Pinheiro, J., Bates, D., DebRoy, S., Sarkar, D. and Team, R.C. (2021) 'nlme: Linear and Nonlinear Mixed Effects Models'.

Pinheiro, J.C. and Bates, D.M. (2000) *Mixed-Effects Models in S and S-PLUS*. 1 edn. Springer, New York, NY.

Qiao, C., Liu, L., Hu, S., Compton, J.E., Greaver, T.L. and Li, Q. (2015) 'How Inhibiting Nitrification Affects Nitrogen Cycle And Reduces Environmental Impacts Of Anthropogenic Nitrogen Input', *Global Change Biology*, 21(3), pp. 1249-1257.

Ragab, R., Cooper, D.M., Harris, G.L. and Catt, J.A. (1996) 'Simulating Nitrate Leaching under Winter Wheat Grown on a Structured Clay soil Considering Bypass Flow', *Journal of Hydrology*, 182(1-4), pp. 157-173.

Ramos, C. and Carbonell, E.A. (1991) 'Nitrate Leaching And Soil Moisture Prediction With The LEACHM Model', *Fertilizer Research*, 27(2-3), pp. 171-180.

Rawlins, B.G., Marchant, B.P., Smyth, D., Scheib, C., Lark, R.M. and Jordan, C. (2009) 'Airborne Radiometric Survey Data And A DTM As Covariates For Regional Scale Mapping Of Soil Organic Carbon Across Northern Ireland', *European Journal of Soil Science*, 60(1), pp. 44-54.

Ritter, A., Muñoz-Carpena, R., Regalado, C.M., Javaux, M. and Vanclooster, M. (2005) 'Using TDR and Inverse Modeling To Characterize Solute Transport In A Layered Agricultural Volcanic Soil', *Vadose Zone Journal*, 4(2), pp. 300-309.

Rivett, M.O., Smith, J.W.N., Buss, S.R. and Morgan, P. (2007) 'Nitrate Occurrence And Attenuation In The Major Aquifers Of England And Wales', *Quarterly Journal of Engineering Geology and Hydrogeology*, 40(4), pp. 335-352.

Robinson, R.A. and Sutherland, W.J. (2002) 'Post-war Changes in Arable Farming and Biodiversity in Great Britain', *Journal of Applied Ecology*, 39(1), pp. 157-176.

Rocha, K.F., de Souza, M., Almeida, D.S., Chadwick, D.R., Jones, D.L., Mooney, S.J. and Rosolem, C.A. (2020) 'Cover Crops Affect the Partial Nitrogen Balance in a Maize-Forage Cropping System', *Geoderma*, 360.

Roy, S., Speed, C., Bennie, J., Swift, R. and Wallace, P. (2007) 'Identifying The Significant Factors That Influence Temporal And Spatial Trends In Nitrate Concentrations In The

Dorset And Hampshire Basin Chalk Aquifer Of Southern England', *Quarterly journal of engineering geology and hydrogeology*, 40(4), pp. 377-392.
Ruser, R. and Schulz, R. (2015) 'The Effect Of Nitrification Inhibitors On The Nitrous Oxide (N2O) Release From Agricultural Soils—A Review', *Journal of Plant Nutrition and Soil Science*, 178(2), pp. 171-188.
Sahoo, P.K., Kim, K. and Powell, M.A. (2016) 'Managing Groundwater Nitrate Contamination From Livestock Farms: Implication For Nitrate Management Guidelines', *Current Pollution Reports*, 2(3), pp. 178-187.
Salazar, O., Vargas, J., Nájera, F., Seguel, O. and Casanova, M. (2014) 'Monitoring Of Nitrate Leaching During Flush Flooding Events In A Coarse-Textured Floodplain Soil', *Agricultural Water Management*, 146, pp. 218-227.
Salazar, O., Wesström, I., Youssef, M.A., Skaggs, R.W. and Joel, A. (2009) 'Evaluation of the DRAINMOD–N II Model For Predicting Nitrogen Losses In A Loamy Sand Under Cultivation In South-East Sweden', *Agricultural Water Management*, 96(2), pp. 267-281.
Salinas-Garcia, J.R., Báez-González, A.D., Tiscareño-López, M. and Rosales-Robles, E. (2001) 'Residue Removal And Tillage Interaction Effects On Soil Properties Under Rain-Fed Corn Production In Central Mexico', *Soil and Tillage Research*, 59(1), pp. 67-79.
Schellberg, J. and Lock, R. (2009) 'A Site-Specific Slurry Application Technique On Grassland And On Arable Crops', *Bioresource technology*, 100(1), pp. 280-286.
Schmidhalter, U., Zintel, A. and Neudecker, E. (2001) *3rd. Europ. Conference Precision Agriculture*.
Schröder, J., Scholefield, D., Cabral, F. and Hofman, G. (2004) 'The Effects of Nutrient Losses from Agriculture on Ground and Surface Water Quality: the Position of Science in Developing Indicators for Regulation', *Environmental Science & Policy*, 7(1), pp. 15-23.
Scull, P., Franklin, J., Chadwick, O.A. and McArthur, D. (2003) 'Predictive soil mapping: a review', *Progress in Physical Geography*, 27(2), pp. 171-197.
Shaffer, M.J., Hall, M.D., Wylie, B.K. and Wagner, D.G. (1996) 'NLEAP/GIS Approach For Identifying And Mitigating Regional Nitrate-Nitrogen Leaching', *Applications of GIS to the modeling of non-point source pollutants in the vadose zone*, 48, pp. 283-294-4.
Shahriari, M., Delbari, M., Afrasiab, P. and Pahlavan-Rad, M.R. (2019) 'Predicting Regional Spatial Distribution Of Soil Texture In Floodplains Using Remote Sensing Data: A Case Of Southeastern Iran', *Catena*, 182, p. 104149.
Sharma, L.K. and Bali, S.K. (2017) 'A Review Of Methods To Improve Nitrogen Use Efficiency In Agriculture', *Sustainability*, 10(1), pp. 1-23.
Sharma, N. and Kumar, S. (2021) 'Nitrogen Transformation Rates In The Himalayan Soils At Different Temperature And Elevation Conditions', *Journal of Soils and Sediments*, 21(1), pp. 13-26.
Shaviv, A. (2001) 'Advances In Controlled-Release Fertilizers', *Advances in Agronomy*, 71, pp. 1-49.
Shaw, R., Williams, A.P., Miller, A. and Jones, D.L. (2014) *Developing An In Situ Sensor For Real Time Monitoring Of Soil Nitrate Concentration*. Bangor University.
Shepherd, M.A. and Lord, E.I. (1996) 'Nitrate Leaching From A Sandy Soil: The Effect Of Previous Crop And Post-Harvest Soil Management In An Arable Rotation', *The Journal of Agricultural Science*, 127(2), pp. 215-229.
Shepherd, M.A., Stockdale, E.A., Powlson, D.S. and Jarvis, S.C. (1996) 'The Influence of Organic Nitrogen Mineralization on the Management of Agricultural Systems in the UK', *Soil Use and Management*, 12(2), pp. 76-85.
Shi, N., Zhang, Y., Li, Y., Luo, J., Gao, X., Jing, Y. and Bo, L. (2018) 'Water pollution risk from nitrate migration in the soil profile as affected by fertilization in a wheat-maize rotation system', *Agricultural Water Management*, 210, pp. 124-129.

Shipley, P.R., Messinger, J.J. and Decker, A.M. (1992) 'Conserving Residual Corn Fertilizer Nitrogen With Winter Cover Crops', *Agronomy Journal*, 84(5), pp. 869-876.
Shrestha, R.K., Cooperband, L.R. and MacGuidwin, A.E. (2010) 'Strategies To Reduce Nitrate Leaching Into Groundwater In Potato Grown In Sandy Soils: Case Study From North Central USA', *American Journal of Potato Research*, 87(3), pp. 229-244.
Sieling, K. and Kage, H. (2006) 'N Balance as an Indicator of N Leaching in an Oilseed Rape-Winter Wheat-Winter Barley Rotation', *Agriculture, ecosystems & environment*, 115(1-4), pp. 261-269.
Silgram, M. and Shepherd, M.A. (1999) 'The effects of cultivation on soil nitrogen mineralization', in *Advances in agronomy*. Elsevier, pp. 267-311.
Silgram, M., Williams, A., Waring, R., Neumann, I., Hughes, A., Mansour, M. and Besien, T. (2005) 'Effectiveness Of The Nitrate Sensitive Areas Scheme In Reducing Groundwater Concentrations In England', *Quarterly Journal of Engineering Geology and Hydrogeology*, 38(2), pp. 117-127.
Silva, R.G., Cameron, K.C., Di, H.J. and Hendry, T. (1999) 'A Lysimeter Study Of The Impact Of Cow Urine, Dairy Shed Effluent, And Nitrogen Fertiliser On Nitrate Leaching', *Australian Journal of Soil Research*, 37(2), pp. 357-369.
Siqueira, G.M., Dafonte, J.D., González, A.P., Vázquez, E.V., Armesto, M.V. and Filho, O.G. (2016) 'Spatial Soil Sampling Design Using Apparent Soil Electrical Conductivity Measurements', *Soil and Plant Nutrition*, 4, pp. 459-473.
Smith, J.U., Bradbury, N.J. and Addiscott, T.M. (1996) 'SUNDIAL: a PC-Based System For Simulating Nitrogen Dynamics In Arable Land', *Agronomy Journal*, 88(1), pp. 38-43.
Smith, L.G., Tarsitano, D., Topp, C.F.E., Jones, S.K., Gerrard, C.L., Pearce, B.D., Williams, A.G. and Watson, C.A. (2016) 'Predicting The Effect Of Rotation Design On N, P, K Balances On Organic Farms Using the NDICEA Model', *Renewable Agriculture and Food Systems*, 31(5), pp. 471-484.
Smith, P., Martino, D., Cai, Z., Gwary, D., Janzen, H., Kumar, P., McCarl, B., Ogle, S., O'Mara, F. and Rice, C. (2007) 'Policy and Technological Constraints to Implementation of Greenhouse Gas Mitigation Options in Agriculture', *Agriculture, Ecosystems & Environment*, 118(1-4), pp. 6-28.
Snee, R.D. (1977) 'Validation of Regression Models: Methods and Examples', *Technometrics*, 19(4), pp. 415-428.
Snyder, C.S. (2017) 'Enhanced Nitrogen Fertiliser Technologies Support The '4r' Concept To Optimise Crop Production And Minimise Environmental Losses', *Soil Research*, 55(6), pp. 463-472.
Song, X., Wang, J., Huang, W., Liu, L., Yan, G. and Pu, R. (2009) 'The Delineation Of Agricultural Management Zones With High Resolution Remotely Sensed Data', *Precision Agriculture*, 10(6), pp. 471-487.
Spiess, E., Humphrys, C., Richner, W., Schneider, M.K., Piepho, H., Chervet, A. and Prasuhn, V. (2020) 'Does No-Tillage Decrease Nitrate Leaching Compared To Ploughing Under A Long-Term Crop Rotation In Switzerland?', *Soil and Tillage Research*, 199, p. 104590.
Stenberg, M., Aronsson, H., Lindén, B., Rydberg, T. and Gustafson, A. (1999) 'Soil Mineral Nitrogen And Nitrate Leaching Losses In Soil Tillage Systems Combined With A Catch Crop', *Soil and Tillage Research*, 50(2), pp. 115-125.
Stewart, W.M., Dibb, D.W., Johnston, A.E. and Smyth, T.J. (2005) 'The Contribution Of Commercial Fertilizer Nutrients To Food Production', *Agronomy Journal*, 97(1), pp. 1-6.
Stewart, W.M. and Roberts, T.L. (2012) 'Food Security And The Role Of Fertilizer In Supporting It', *Procedia Engineering*, 46, pp. 76-82.
Stoliker, D.L., Repert, D.A., Smith, R.L., Song, B., LeBlanc, D.R., McCobb, T.D., Conaway, C.H., Hyun, S.P., Koh, D., Moon, H.S. and Kent, D.B. (2016) 'Hydrologic Controls on

Nitrogen Cycling Processes and Functional Gene Abundance in Sediments of a Groundwater Flow-Through Lake', *Environmental Science & Technology*, 50(7), pp. 3649-3657.
Stopes, C., Lord, E.I., Philipps, L. and Woodward, L. (2002) 'Nitrate leaching from organic farms and conventional farms following best practice', *Soil Use and Management*, 18(s1), pp. 256-263.
Strudley, M.W., Green, T.R. and Ascough, J.C. (2008) 'Tillage effects on soil hydraulic properties in space and time: State of the science', *Soil and Tillage Research*, 99(1), pp. 4-48.
Stuart, M., Gooddy, D., Bloomfield, J. and Williams, A.T. (2011) 'A Review of the Impact of Climate Change on Future Nitrate Concentrations in Groundwater of the UK', *Science of The Total Environment*, 409(15), pp. 2859-2873.
Stuart, M.E. (2005) *Development Of Nitrate Profiles Database*. [Online]. Available at: http://nora.nerc.ac.uk/id/eprint/11103.
Stuart, M.E., Chilton, P.J., Kinniburgh, D.G. and Cooper, D.M. (2007) 'Screening For Long-Term Trends In Groundwater Nitrate Monitoring Data', *Quarterly Journal of Engineering Geology and Hydrogeology*, 40(4), p. 361.
Stuart, M.E. and Lapworth, D.J. (2016) 'Macronutrient Status Of UK Groundwater: Nitrogen, Phosphorus And Organic Carbon', *Science of The Total Environment*, 572, pp. 1543-1560.
Su, Y., Yang, X. and Yang, R. (2014) 'Effect Of Soil Texture In Unsaturated Zone On Soil Nitrate Accumulation And Groundwater Nitrate Contamination In A Marginal Oasis In The Middle Of Heihe River Basin', *Huan jing ke xue= Huanjing kexue*, 35(10), pp. 3683-3691.
Sudduth, K.A., Kitchen, N.R. and Drummond, S.T. (2017) 'Inversion Of Soil Electrical Conductivity Data To Estimate Layered Soil Properties', *Advances in Animal Biosciences*, 8(2), p. 433.
Suthar, S., Bishnoi, P., Singh, S., Mutiyar, P.K., Nema, A.K. and Patil, N.S. (2009) 'Nitrate Contamination In Groundwater Of Some Rural Areas Of Rajasthan, India', *Journal of Hazardous Materials*, 171(1), pp. 189-199.
Sutton, M.A., Howard, C.M., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H. and Grizzetti, B. (2011) *The European Nitrogen Assessment: Sources, Effects and Policy Perspectives*. Cambridge: Cambridge University Press.
Swain, E.Y., Almadni, M., Leifert, C., Stockdale, E.A. and Cooper, J.M. (2016) 'NDICEA Calibration And Validation On A Northern UK Soil', *Organic Agriculture*, 6(4), pp. 267-280.
Team, J.P.a.D.B.a.S.D.a.D.S.a.R.C. (2021a) 'nlme}: Linear and Nonlinear Mixed Effects Models', R package version 3.1-152.
Team, R.D.C. (2021b) *R: A Language and Environment for Statistical Computing* [Computer program].
Tesfahunegn, G.B., Tamene, L. and Vlek, P.L.G. (2011) 'Catchment-Scale Spatial Variability Of Soil Properties And Implications On Site-Specific Soil Management In Northern Ethiopia', *Soil and Tillage Research*, 117, pp. 124-139.
Thapa, R., Mirsky, S.B. and Tully, K.L. (2018) 'Cover Crops Reduce Nitrate Leaching in Agroecosystems: A Global Meta-Analysis', *Journal of environmental quality*, 47(6), pp. 1400-1411.
Thompson, J.A., Pena-Yewtukhiw, E.M. and Grove, J.H. (2006) 'Soil–Landscape Modeling Across A Physiographic Region: Topographic Patterns And Model Transportability', *Geoderma*, 133(1), pp. 57-70.
Thompson, R.B., Martínez-Gaitan, C., Gallardo, M., Giménez, C. and Fernández, M.D. (2007) 'Identification Of Irrigation And N Management Practices That Contribute To Nitrate

Leaching Loss From An Intensive Vegetable Production System By Use Of A Comprehensive Survey', *Agricultural Water Management*, 89(3), pp. 261-274.

Thomsen, I.K. (2005) 'Crop N Utilization And Leaching Losses As Affected By Time And Method Of Application Of Farmyard Manure', *European Journal of Agronomy*, 22(1), pp. 1-9.

Thomsen, I.K., Djurhuus, J. and Christensen, B.T. (2003) 'Long Continued Applications Of N Fertilizer To Cereals On Sandy Loam: Grain And Straw Response To Residual N', *Soil Use and Management*, 19(1), pp. 57-64.

Thorburn, P.J., Biggs, J.S., Weier, K.L. and Keating, B.A. (2003) 'Nitrate In Groundwaters Of Intensive Agricultural Areas In Coastal Northeastern Australia', *Agriculture, ecosystems & environment*, 94(1), pp. 49-58.

Thorup-Kristensen, K. and Dresbøll, D.B. (2010) 'Incorporation Time Of Nitrogen Catch Crops Influences The N Effect For The Succeeding Crop', *Soil Use and Management*, 26(1), pp. 27-35.

Thorup-Kristensen, K., Magid, J. and Jensen, L.S. (2003) 'Catch Crops And Green Manures As Biological Tools In Nitrogen Management In Temperate Zones', *Advances in agronomy*, 79(79), pp. 227-302.

Timmons, D.R. (1984) 'Nitrate Leaching As Influenced By Water Application Level And Nitrification Inhibitors', *Journal of environmental quality*, 13(2), pp. 305-309.

Tindaon, F., Benckiser, G. and Ottow, J.C.G. (2012) 'Evaluation Of Ecological Doses Of The Nitrification Inhibitors 3,4-Dimethylpyrazole Phosphate (DMPP) and 4-chloromethylpyrazole (ClMP) in Comparison To Dicyandiamide (DCD) in their Effects On Dehydrogenase And Dimethyl Sulfoxide Reductase Activity In Soils', *Biology and Fertility of Soils*, 48(6), pp. 643-650.

Tittonell, P., Rufino, M.C., Janssen, B.H. and Giller, K.E. (2010) 'Carbon And Nutrient Losses During Manure Storage Under Traditional And Improved Practices In Smallholder Crop-Livestock Systems—Evidence From Kenya', *Plant and soil*, 328(1-2), pp. 253-269.

Tonitto, C., David, M.B. and Drinkwater, L.E. (2006) 'Replacing Bare Fallows with Cover Crops in Fertilizer-Intensive Cropping Systems: A Meta-Analysis of Crop Yield and N Dynamics', *Agriculture, Ecosystems & Environment*, 112(1), pp. 58-72.

Tosti, G., Benincasa, P., Farneselli, M., Tei, F. and Guiducci, M. (2014) 'Barley–Hairy Vetch Mixture As Cover Crop For Green Manuring And The Mitigation Of N Leaching Risk', *European Journal of Agronomy*, 54, pp. 34-39.

Townsend, M.A., Sleezer, R.O. and Macko, S.A. (1996) 'Effects Of Agricultural Practices And Vadose Zone Stratigraphy On Nitrate Concentration In Ground Water In Kansas, USA', *Water Science and Technology*, 33(4-5), pp. 219-226.

Trenkel, M.E. (1997) *Controlled-Release And Stabilized Fertilizers In Agriculture*. International Fertilizer Industry Association Paris.

Tsai, B.S.E. (1986) *Continuous Spouted Bed Process For Sulphur-Coating Urea*. University of British Columbia.

Turner, B.R., Younger, P.L. and Fordham, C.E. (1993) 'Fell Sandstone Lithostratigraphy South-West Of Berwick-Upon-Tweed: Implications For The Regional Development Of The Fell Sandstone', *Proceedings of the Yorkshire Geological Society*, 49(4), p. 269.

Udvardi, M., Below, F.E., Castellano, M.J., Eagle, A.J., Giller, K.E., Ladha, J.K., Liu, X., Maaz, T.M., Nova-Franco, B., Raghuram, N., Robertson, G.P., Roy, S., Saha, M., Schmidt, S., Tegeder, M., York, L.M. and Peters, J.W. (2021) 'A Research Road Map for Responsible Use of Agricultural Nitrogen', *Frontiers in Sustainable Food Systems*, 5, p. 165.

Ugbaje, S.U. and Reuter, H.I. (2013) 'Functional Digital Soil Mapping For The Prediction Of Available Water Capacity In Nigeria Using Legacy Data', *Vadose Zone Journal*, 12(4).

UKWIR (2003) *Implications Of Changing Groundwater Quality For Water Resources And The Uk Water Industry. Phase 2: Trend Detection Methodology And Improved Monitoring And Assessment Programmes* (03/WR/09/06).

Van der Burgt, G.J.H.M., Oomen, G.J.M., Habets, A.S.J. and Rossing, W.A.H. (2006) 'The NDICEA Model, A Tool To Improve Nitrogen Use Efficiency In Cropping Systems', *Nutrient Cycling in Agroecosystems*, 74(3), pp. 275-294.

Van der Meer, H.G., Sommer, S.G., Smith, K., Matsunaka, T. and Ong, H.K. (2008) 'Guidelines For Sustainable Manure Management In Asian Livestock Production Systems', in Vienna: International Atomic Energy Agency, pp. 1-118.

van Duijvenboden, W. and Loch, J.P.G. (1983) 'Nitrate in the Netherlands: a serious threat to groundwater', *Aqua London*, 2, pp. 59-60.

Van Es, H.M., Sogbedji, J.M. and Schindelbeck, R.R. (2006) 'Effect of manure application timing, crop, and soil type on nitrate leaching', *Journal of environmental quality*, 35(2), pp. 670-679.

Vasques, G.M., Grunwald, S., Comerford, N.B. and Sickman, J.O. (2010) 'Regional Modelling Of Soil Carbon At Multiple Depths Within A Subtropical Watershed', *Geoderma*, 156(3), pp. 326-336.

Velthof, G.L., Lesschen, J.P., Webb, J., Pietrzak, S., Miatkowski, Z., Pinto, M., Kros, J. and Oenema, O. (2014) 'The Impact Of The Nitrates Directive On Nitrogen Emissions From Agriculture In The Eu-27 During 2000–2008', *Science of The Total Environment*, 468-469, pp. 1225-1233.

Verdesian *NutriSphere-N® - UK, Technical sheet* (Accessed: 03/04/2021).

Vincent, A., Benoit, P., Pot, V., Madrigal, I., Delgado-Moreno, L. and Labat, C. (2007) 'Impact Of Different Land Uses On The Migration Of Two Herbicides In A Silt Loam Soil: Unsaturated Soil Column Displacement Studies', *European journal of soil science*, 58(1), pp. 320-328.

Vogeler, I., Thomsen, I.K., Jensen, J.L. and Hansen, E.M. (2020) 'Marginal Nitrate Leaching Around The Recommended Nitrogen Fertilizer Rate In Winter Cereals', *Soil Use and Management*, n/a(n/a).

Volpi, I., Laville, P., Bonari, E., di Nasso, N.N. and Bosco, S. (2017) 'Improving The Management Of Mineral Fertilizers For Nitrous Oxide Mitigation: The Effect Of Nitrogen Fertilizer Type, Urease And Nitrification Inhibitors In Two Different Textured Soils', *Geoderma*, 307, pp. 181-188.

Vos, J. and van der Putten, P.E.L. (1997) 'Field Observations On Nitrogen Catch Crops. I. Potential And Actual Growth And Nitrogen Accumulation In Relation To Sowing Date And Crop Species', *Plant and Soil*, 195(2), pp. 299-309.

Waine, T.W., Blackmore, B.S. and Godwin, R.J. (2000) 'Mapping Available Water Content And Estimating Soil Textural Class Using Electro-Magnetic Induction', *Proc. EurAgEng*.

Wang, L. and Burke, S.P. (2017) 'A catchment-scale method to simulating the impact of historical nitrate loading from agricultural land on the nitrate-concentration trends in the sandstone aquifers in the Eden Valley, UK', *Science of the Total Environment*, 579, pp. 133-148.

Wang, L., Stuart, M.E., Bloomfield, J.P., Butcher, A.S., Gooddy, D.C., McKenzie, A.A., Lewis, M.A. and Williams, A.T. (2012a) 'Prediction Of The Arrival Of Peak Nitrate Concentrations At The Water Table At The Regional Scale In Great Britain', *Hydrological Processes*, 26(2), pp. 226-239.

Wang, Q., Cameron, K., Buchan, G., Zhao, L., Zhang, E.H., Smith, N. and Carrick, S. (2012b) 'Comparison Of Lysimeters And Porous Ceramic Cups For Measuring Nitrate Leaching In Different Soil Types', *New Zealand Journal of Agricultural Research*, 55(4), pp. 333-345.

Wang, S., Wei, S., Liang, H., Zheng, W., Li, X., Hu, C., Currell, M.J., Zhou, F. and Min, L. (2019) 'Nitrogen stock and leaching rates in a thick vadose zone below areas of long-term nitrogen fertilizer application in the North China Plain: A future groundwater quality threat', *Journal of Hydrology*, 576, pp. 28-40.

Ward, M.H. (2009) 'Too Much of a Good Thing? Nitrate from Nitrogen Fertilizers and Cancer: President's Cancer. Panel-October 21, 2008', *Reviews on environmental health*, 24(4), p. 357.

Ward, M.H. and Brender, J.D. (2019) 'Drinking Water Nitrate and Human Health', in *Encyclopedia of Environmental Health*. pp. 173-186.

Watson, C.A., Atkinson, D., Gosling, P., Jackson, L.R. and Rayns, F.W. (2002) 'Managing Soil Fertility In Organic Farming Systems', *Soil use and management*, 18, pp. 239-247.

Webster, C.P., Shepherd, M.A., Goulding, K.W.T. and Lord, E. (1993) 'Comparisons Of Methods For Measuring The Leaching Of Mineral Nitrogen From Arable Land', *Journal of Soil Science*, 44(1), pp. 49-62.

Weihermüller, L., Siemens, J., Deurer, M., Knoblauch, S., Rupp, H., Göttlein, A. and Pütz, T. (2007) 'In Situ Soil Water Extraction: A Review', *Journal of environmental quality*, 36(6), pp. 1735-1748.

White, R.E., Wellings, S.R. and Bell, J.P. (1983) 'Seasonal Variations in Nitrate leaching in Structured Clay Soils under Mixed Land Use', *Agricultural Water Management*, 7(4), pp. 391-410.

WHO (2007) 'Nitrate and Nitrite in Drinking-water. Background Document for Development of WHO Guidelines for Drinking-water Quality', *World Health Organization, Geneva (2007)*.

Wiatrak, P. (2014) 'Evaluation of Nitrogen Application Methods and Rates with Nutrisphere-N on Corn in Southeastern Coastal Plains', *American Journal of Agricultural and Biological Sciences*, 9(1), pp. 109-118.

Wick, K., Heumesser, C. and Schmid, E. (2012) 'Groundwater Nitrate Contamination: Factors and Indicators', *Journal of Environmental Management*, 111, pp. 178-186.

Wiesmeier, M., Barthold, F., Blank, B. and Kögel-Knabner, I. (2011) 'Digital Mapping Of Soil Organic Matter Stocks Using Random Forest Modeling In A Semi-Arid Steppe Ecosystem', *Plant and soil*, 340(1-2), pp. 7-24.

Williams, W.A., Graves, W.L. and Cassman, K.G. (1990) 'Nitrogen Fixation By Irrigated Berseem Clover Versus Soil Nitrogen Supply', *Journal of agronomy and Crop Science*, 164(3), pp. 202-207.

Wilson, C.O. (2015) 'Land Use/Land Cover Water Quality Nexus: Quantifying Anthropogenic Influences On Surface Water Quality', *Environmental Monitoring and Assessment*, 187(7), p. 424.

Wright, A.F. and Bailey, J.S. (2001) 'Organic Carbon, Total Carbon, And Total Nitrogen Determinations In Soils Of Variable Calcium Carbonate Contents Using A Leco Cn-2000 Dry Combustion Analyzer', *Communications in Soil Science and Plant Analysis*, 32(19-20), pp. 3243-3258.

Wu, L. and McGechan, M.B. (1998) 'A Review Of Carbon And Nitrogen Processes In Four Soil Nitrogen Dynamics Models', *Journal of agricultural engineering research*, 69(4), pp. 279-305.

Wu, S.F., Wu, L.H., Shi, Q.W., Wang, Z.Q., Chen, X.Y. and Li, Y.S. (2007) 'Effects Of A New Nitrification Inhibitor 3,4-Dimethylpyrazole Phosphate (DMPP) on Nitrate And Potassium Leaching In Two Soils', *J Environ Sci (China)*, 19(7), pp. 841-7.

Xu, M., Li, D., Li, J., Qin, D., Kazuyuki, Y. and Hosen, Y. (2008) 'Effects of Organic Manure Application with Chemical Fertilizers on Nutrient Absorption and Yield of Rice in Hunan of Southern China', *Agricultural Sciences in China*, 7(10), pp. 1245-1252.

Yakun, Z., Wenjun, J., Daniel, D.S., Tahmid Huq, E., Hongyi, L., Zhou, S., A, V.I. and Asim, B. (2020) 'Three-Dimensional Digital Soil Mapping Of Multiple Soil Properties At A Field-Scale Using Regression Kriging', *Geoderma*, 366, p. 114253.

Yang, K. and Tang, Z. (2012) 'Nitrogen Distribution In Deep Soil Of Farmland In Beijing', *Soil and Fertilizer Sciences in China*, 3.

Yang, Y.S. and Wang, L. (2010) 'A Review of Modelling Tools for Implementation of the EU Water Framework Directive in Handling Diffuse Water Pollution', *Water Resources Management*, 24(9), pp. 1819-1843.

Yuan, Z., Ata-Ul-Karim, S.T., Cao, Q., Lu, Z., Cao, W., Zhu, Y. and Liu, X. (2016) 'Indicators for Diagnosing Nitrogen Status of Rice Based on Chlorophyll Meter Readings', *Field Crops Research*, 185, pp. 12-20.

Yuxin, M., Budiman, M. and Chunfa, W. (2017) 'Mapping Key Soil Properties To Support Agricultural Production In Eastern China', *Geoderma Regional*, 10, pp. 144-153.

Zerulla, W., Barth, T., Dressel, J., Erhardt, K., Horchler von Locquenghien, K., Pasda, G., Rädle, M. and Wissemeier, A. (2001) '3,4-Dimethylpyrazole phosphate (DMPP) – A New Nitrification Inhibitor For Agriculture And Horticulture', *Biology and Fertility of Soils*, 34(2), pp. 79-84.

Zhai, Y., Zhao, X., Teng, Y., Li, X., Zhang, J., Wu, J. and Zuo, R. (2017) 'Groundwater Nitrate Pollution and Human Health Risk Assessment by using HHRA Model in an Agricultural Area, NE China', *Ecotoxicology and Environmental Safety*, 137, pp. 130-142.

Zhang, H. and Hiscock, K.M. (2016) 'Modelling Response Of Groundwater Nitrate Concentration In Public Supply Wells To Land-Use Change', *Quarterly Journal of Engineering Geology and Hydrogeology*, 49(2), pp. 170-182.

Zhang, H., Xu, W.L. and Hiscock, K.M. (2013) 'Application of MT3DMS and Geographic Information System to Evaluation of Groundwater Contamination in the Sherwood Sandstone Aquifer, UK', *Water, Air, & Soil Pollution*, 224(2), p. 1438.

Zhang, W., Li, Y., Zhu, B., Zheng, X., Liu, C., Tang, J., Su, F., Zhang, C., Ju, X. and Deng, J. (2018) 'A Process-Oriented Hydro-Biogeochemical Model Enabling Simulation Of Gaseous Carbon And Nitrogen Emissions And Hydrologic Nitrogen Losses From A Subtropical Catchment', *Science of The Total Environment*, 616-617, pp. 305-317.

Zhang, X., Davidson, E.A., Mauzerall, D.L., Searchinger, T.D., Dumas, P. and Shen, Y. (2015a) 'Managing Nitrogen For Sustainable Development', *Nature*, 528(7580), pp. 51-59.

Zhang, Y., Wang, H., Liu, S., Lei, Q., Liu, J., He, J., Zhai, L., Ren, T. and Liu, H. (2015b) 'Identifying Critical Nitrogen Application Rate For Maize Yield And Nitrate Leaching In A Haplic Luvisol Soil Using The DNDC Model', *Science of the Total Environment*, 514, pp. 388-398.

Zheng, W., Wang, S., Tan, K. and Lei, Y. (2020) 'Nitrate Accumulation And Leaching Potential Is Controlled By Land-Use And Extreme Precipitation In A Headwater Catchment In The North China Plain', *Science of The Total Environment*, 707, p. 136168.

Zhu, G., Ju, X., Zhang, J., Müller, C., Rees, R.M., Thorman, R.E. and Sylvester-Bradley, R. (2019) 'Effects Of The Nitrification Inhibitor DMPP (3,4-dimethylpyrazole phosphate) on Gross N Transformation Rates And N2o Emissions', *Biology and Fertility of Soils*, 55(6), pp. 603-615.

Zibilske, L.M. and Bradford, J.M. (2007) 'Soil Aggregation, Aggregate Carbon and Nitrogen, and Moisture Retention Induced by Conservation Tillage', *Soil Science Society of America Journal*, 71(3), pp. 793-802.

Žížala, D., Minařík, R., Skála, J., Beitlerová, H., Juřicová, A., Reyes Rojas, J., Penížek, V. and Zádorová, T. (2022) 'High-resolution agriculture soil property maps from digital soil mapping methods, Czech Republic', *CATENA*, 212, p. 106024.

Zufiaurre, R., Martín-Ramos, P. and Cuchí, J.A. (2020) 'Nitrates in Groundwater of Small Shallow Aquifers in the Western Side of Hoya de Huesca (NE Spain)', *Agronomy*, 10(1), p. 22.

Zvomuya, F., Rosen, C.J., Russelle, M.P. and Gupta, S.C. (2003) 'Nitrate Leaching And Nitrogen Recovery Following Application Of Polyolefin-Coated Urea To Potato', *Journal of Environmental quality*, 32(2), pp. 480-489.

Appendices

Note: Raw data collected in this study can be accessed from the Newcastle University data repositories,

- NDICEA model calibration and validation https://doi.org/10.25405/data.ncl.20424741.v1
- Nafferton Trial https://doi.org/10.25405/data.ncl.20424753.v1
- Nitrate monitoring Berwick https://doi.org/10.25405/data.ncl.20424771.v1

Appendix 1. Environmental covariates, apparent electric conductivity (EM) from four depth and soil texture

Location	Elevation	Slope	TWI	TPI	Flow_ direction	Flow_ accumulation	Basin	EM 55	EM 110	EM 160	EM 320	0_30 (cm) Sand	0_30 (cm) Clay	0_30 (cm) Silt	30_60 (cm) Sand	30_60 (cm) Clay	30_60 (cm) Silt	60_90 (cm) Sand	60_90 (cm) Clay	60_90 (cm) Silt	Depth (cm)	Soil class (topsoil)
809	53.87	2.91	6.04	7.02	64	6	63	21.6	29.91	8.34	13.61	36.08	13.44	50.48	38.68	21.07	40.25	50.65	20.45	28.9	120	Sandy silt loam
811	66.29	4.14	6.18	1.80	64	11	63	16.08	21.51	6.66	10.14	31.14	14.84	54.02	33.94	20.09	45.97	33.42	19.04	47.54	120	Sandy silt loam
813	65.76	4.13	4.39	3.27	64	1	71	14.36	18.99	4.77	8.21	29.39	26.68	43.93	35.07	26.18	38.75	37.5	28.33	34.17	80	Clay loam
815	48.65	1.56	7.22	9.47	32	11	60	15.49	18.52	6.23	10.3	28.41	18.56	53.03	35.62	18.44	45.94	37.24	19.38	43.38	120	Clay loam
816	42.91	0.05	8.16	91.60	32	0	38	19.62	23.2	8.61	12.9	86.17	1.55	12.28	67.67	10.73	21.6	56.25	15.39	28.36	120	Sandy
817	42.76	0.07	7.86	186.83	2	0	55	19.33	22.14	8.97	13.15	33.93	11.88	54.19	43.71	10.52	45.77	53.29	13.58	33.13	120	Sandy silt loam
818	43.30	0.41	7.48	10.36	64	3	61	19.8	24.15	9.19	13.41	27.2	16.54	56.26	37.09	14.7	48.21	50.32	16.79	32.89	90	Sandy silt loam
821	75.60	1.59	7.49	3.79	4	15	19	6.49	5	2.39	2.44	56.65	8.01	35.34	56.36	12.03	31.61				35	Sandy laom
822	59.14	1.17	9.16	7.62	4	61	21	20.34	25.38	10.17	15.56	35.05	14.63	50.32	31.15	20.14	48.71				60	Sandy silt loam
823	50.97	9.08	3.63	3.66	8	2	44	17.53	23.52	7.93	12.57	33.45	13.59	52.96	30	24.67	45.33	32.66	16.49	50.85	85	Sandy silt loam
824	48.72	1.09	11.10	6.67	8	402	19	16.25	16.41	9.17	11.89	24.52	21.64	53.84	33.35	25.48	41.17	33.68	23.01	43.31	120	Clay loam
825	64.37	2.86	5.90	4.54	2	5	19	6.81	5.11	2.97	3.01	48.88	10.78	40.34	51.17	17.16	31.67				55	Sandy silt loam
826	62.54	1.17	8.77	3.76	1	41	14	12.69	12.89	5.89	7.2	57.09	8.58	34.33	48.97	11.43	39.6				40	Sandy laom
827	49.61	7.77	4.63	3.01	2	5	17	13.21	14.08	6.28	8.78	31.44	23.37	45.19							45	Clay loam

828	45.22	0.35	6.25	7.59	4	0	17	37.7	39.01	22.96	30.43	43.04	15.98	40.98	28.53	31.23	40.24	10.65	57.26	32.09	80	Sandy silt loam
829	55.49	3.10	6.32	5.07	4	9	25	14.92	17.08	6.28	8.84	46.09	16	37.91	37.88	22.78	39.34	49.85	20.26	29.89	75	Sandy silt loam
830	43.27	0.49	8.40	17.06	4	11	25	25.33	28.36	13.08	17.72	44.73	12.98	42.29	30.4	15.13	54.47	41.23	16.99	41.78	75	Sandy silt loam
831	46.00	0.87	6.43	9.70	1	2	37	14.47	15.62	6.23	8.92	30.35	20.27	49.38	29.9	22.12	47.98	40.29	19.61	40.1	90	Clay loam
832	47.35	2.97	5.68	5.17	64	4	47	8.29	6.02	4.49	4.58	39.18	11.68	49.14	39.35	18.67	41.98	44.76	19.45	35.79	65	Sandy silt loam
833	42.96	0.23	7.76	22.53	1	2	50	29.97	31.07	16.89	23.98	27.04	13.79	59.17	18.82	14.1	67.08	32.07	15.39	52.54	120	Sandy silt loam
834	48.00	1.46	8.72	7.92	64	49	70	4.99	5.21	1.91	2.5	38.03	12.8	49.17	38.03	12.8	49.17	43.33	17.5	39.17	90	Sandy silt loam
835	48.31	2.14	5.11	8.93	32	1	69	14.61	18.14	4.23	7.64	36.14	15.44	48.42	35.69	14.73	49.58				60	Sandy silt loam
1	65.47	3.42	5.99	2.71	2	7	2	21.63	26.57	9.4	14.85	20.3	21.07	58.63	62.76	10.96	26.28				55	Clay loam
3	44.01	0.29	8.91	55.61	16	11	33	22.16	24.17	11.21	15.59	56.59	9.8	33.61	24.97	30.99	44.04	24.99	37.36	37.65	80	Sandy laom
4	43.24	0.27	8.69	39.93	16	8	60	23.41	26.07	11.22	16.85	76.64	3.39	19.97	71.29	3.86	24.85	75.93	4.55	19.52	120	Loamy sand
5	42.83	0.13	10.13	11.25	4	17	25	24.23	23.37	14.58	19.07	47.27	11.08	41.65	37.55	14.2	48.25				60	Sandy silt loam
6	64.19	5.09	5.06	3.01	64	4	72	10.19	13.87	2.82	4.7	37.46	14.86	47.68	46.54	14.45	39.01	28.32	25.23	46.45	75	Sandy silt loam
7	74.01	3.32	5.56	2.70	64	4	74	13.88	19.35	5	8.37	49.3	8.73	41.97	36.56	12.57	50.87	49.21	18.2	32.59	120	Sandy silt loam
8	53.84	3.21	5.59	7.14	32	4	71	16.68	21.81	6.67	9.85	41.82	11.21	46.97	44.78	14.73	40.49				70	Sandy silt loam
9	51.988	1.811	5.278	10.738	32	1	75	6.26	6.01	2.42	3.14	54.7	7.17	38.13	55.76	8.63	35.61				50	Sandy laom
10	53.07	0.79	6.119	7.911	4	1	71	13.68	16.17	4.96	7.64	32.8	11.72	55.48	43.2	11.09	45.71				70	Sandy silt loam

Appendix 2. Method Summary for the Determination of Alkalinity, Ammonia, Chloride, Nitrite, Orthophosphate, Silicate and Total Oxidised Nitrogen by Discrete Analysis

Determinand: Alkalinity (methyl orange) expressed as mg/L $CaCO_3$**,** Ammonia reported as Ammoniacal Nitrogen as N**,** Soluble Chloride**,** Reactive phosphorus (generally that in the form of orthophosphate)**,** Nitrite ion**,** Silicate**,** Total Oxidised Nitrogen**,** Nitrate (obtained by calculation)

Matrix: Freshwater (Surface and Groundwater), treated and untreated sewage effluents and trades to controlled waters and sewer. Leachates prepared and Land

Instrumentation: Discrete Analyser

Principle:

Alkalinity

The reagent used is methyl orange buffered with potassium hydrogen phthalate. Reduction in the red acid component of the indicator by carbonate/bicarbonates present in the sample is measured as a decrease in absorbance at 550nm.

Ammonia

Ammonia reacts with salicylate and dichloroisocyanurate in the presence of sodium nitroprusside to form a blue colour, the intensity of which is proportional to the amount of ammonia present. Sodium citrate is added to mask possible interference from cations. The colour produced is measured at 660nm.

Chloride

Chloride reacts with mercuric thiocyanate forming a mercuric chloride complex. Released thiocyanate reacts with iron (III) forming a red ferric thiocyanate complex. The intensity of colour produced, measured at 510nm, is proportional to the chloride concentration.

Nitrite

Nitrite ions, when reacted with a reagent containing sulphanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride, in the presence of acid, produce a highly coloured azo dye that is measured photometrically at 540nm.

Orthophosphate

Orthophosphate reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex which, when reduced with ascorbic acid produces an intense blue colour, the absorbance of which is measured at 880nm.

Silicate

Silicates in solution react with molybdate under acidic conditions to form a silicomolybdate complex. The complex is reduced by ascorbic acid to silicomolybdate blue. Interference by phosphate can be overcome by the addition of tartaric acid. The resultant compound is measured spectrophotometrically at 760nm. Molybdate reactive silicon includes mainly monomeric and dimeric silic acids and silicate.

TON

Nitrate is reduced to nitrite with hydrazine sulphate. The nitrite ions produced, together with those already present, are determined by diazotisation with sulphanilamide and coupling with

N-(1-naphthyl)-ethylenediamine dihydrochloride. The coloured azo-dye absorbance is measured at 540nm.

Nitrate

Nitrate is determined by subtracting nitrite from TON. The calculation is performed by StarLims

Range of Application: Normal Range

Determinand	**Range (mg/L)**
Alkalinity	0 – 100
Ammonia	0 – 2
Chloride	0 – 200
Nitrite	0 – 1
Orthophosphate	0 – 2
Silicate	0 – 20
TON	0 – 20

The above ranges are on undiluted samples. The range of application can be extended by dilution of the sample.

High Range

Determinand	**Range (mg/L)**
Ammonia	0 – 50
Chloride	0 – 1000
Nitrite	0 – 10
Orthophosphate	0 – 10
TON	0 – 50

The above ranges are on undiluted samples. The range of application can be extended by dilution of the sample.

Container: 1000ml PET bottle

Storage/Preservation:

Interferences: All the tests are subject to interference from highly coloured or turbid samples. Where this is present samples are diluted sufficiently to eliminate this interference and the minimum reporting value raised where applicable. The following are details of interference specific to each test.

Alkalinity: Certain oxidising reagents may bleach the methyl orange producing falsely high results.

Ammonia: Magnesium may interfere by forming a precipitate of magnesium hydroxide. The use of tri-sodium citrate as a complexing agent prevents this interference at levels normally encountered in non-saline samples.

Chloride: Positive bias may occur where cyanide, thiocyanate or other halides are present.

Nitrite: Amines, oxidising agents, chloramines, thiosulphate, hexametaphosphate, alkalis and ferric iron may interfere.

Orthophosphate: Silica can form a blue complex at the wavelength used. However, this is not generally a problem since a concentration of around 4000ppm is required to produce a 1ppm error in phosphate result. Ferric iron concentrations exceeding 50mg/L may give a negative bias. Pre-treatment of samples with sodium bisulpate can eliminate this.

Silicate: Phosphate may interfere, however, this is overcome by the use of tartaric acid.

TON: Non identified.

Within Laboratory Quality Control & Performance Criteria:

Precision Targets = Better than 5% RSD

Bias Targets = Better than 10% RSD

External Quality Control: Aquacheck

Appendix 3. Pressure plates for soil moisture release

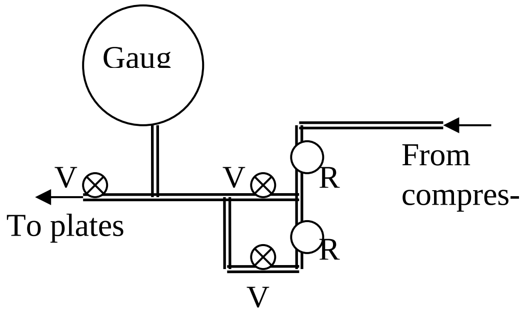
Sampling

Usually, soil in undisturbed cores. Wet up to saturated.

Equipment

- Pressure plates and regulators, compressor
- Balance 0.001g
- beakers,

Setting up pressure plates



1. Wet up plate. Wet from below by connecting reservoir to outlet tube. Ideally, leave overnight at zero tension.
2. Place samples on wet plate.
3. Close pressure vessel, ensure nuts are tightened evenly (tighten opposite pairs in sequence). **Warning! High pressures applied to improperly sealed vessel may be dangerous!**
4. Close valve V3, switch on compressor and allow to come up to pressure.
5. Coarse adjust: with valve V1 open, V2 shut, adjust regulator R1 to give about 3psi over the desired pressure
6. Fine adjust: Close valve V1, open V2; R2 is now supplied with slight overpressure. Adjust R2 to give exact reading. (Note: regulators work by releasing slight overpressure. A small difference between pressures set at R1, R2 gives a slow leak of air from the compressor, and slower response when pressurising the plate vessel.)
7. Open V3 to apply pressure to plate in vessel. Pressure will slowly rise back to level set.

Releasing pressure

Do not try to open the pressure vessel while pressurised!

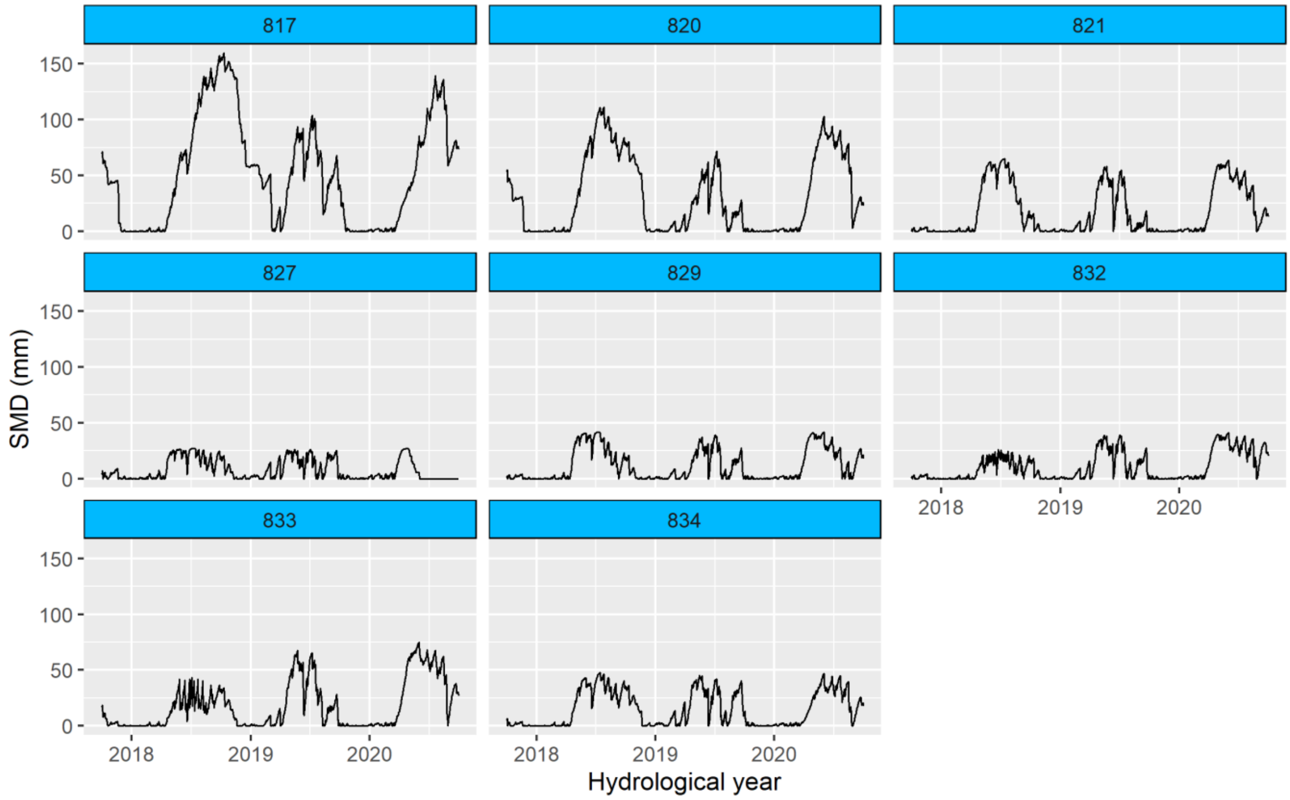
1. Shut off air from compressor at compressor tank.
2. Release pressure by adjusting R2 down.

When gauge reads zero, open pressure vessel by slackening nuts in opposite pairs in sequence.

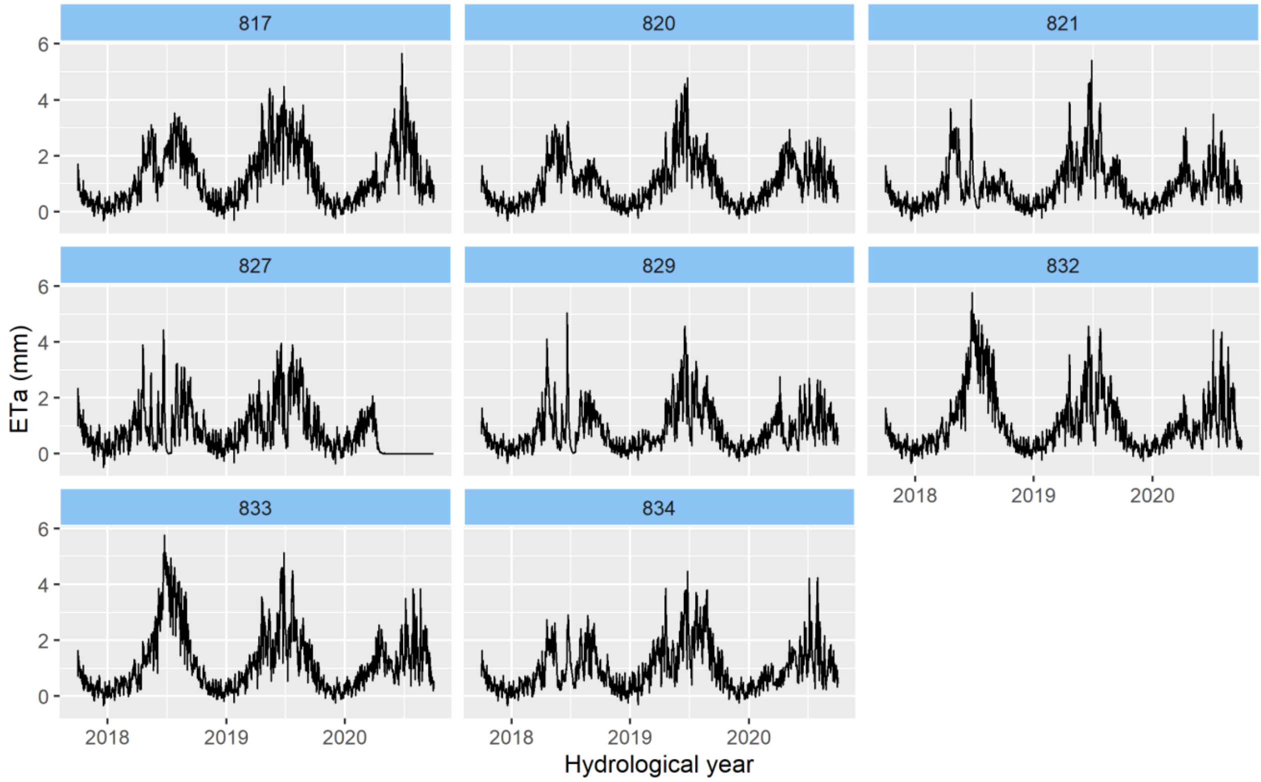
Appendix 4. Soil Moisture Characteristics

Location ID	0.1 Bar	15 Bar	Available water contents (AWC)	Volume mm in 30 cm	AWC (mm)
817	0.49	0.01	0.48	138	306
817	0.45	0.21	0.24	72	
817	0.43	0.11	0.32	96	
820	0.35	0.20	0.15	45	138
820	0.34	0.18	0.16	48	
820	0.22	0.06	0.15	45	
821	0.32	0.10	0.22	66	66
827	0.34	0.25	0.09	27	27
829	0.34	0.27	0.08	21	42
829	0.31	0.24	0.07	21	
832	0.38	0.31	0.07	21	42
832	0.33	0.26	0.07	21	
833	0.51	0.45	0.07	21	81
833	0.66	0.56	0.09	30	
833	0.62	0.52	0.10	30	
834	0.36	0.28	0.08	24	51
834	0.36	0.27	0.09	27	
809	0.42	0.34	0.09	27	75
809	0.36	0.26	0.09	27	
809	0.29	0.21	0.07	21	
823	0.32	0.24	0.08	24	69
823	0.36	0.29	0.07	21	
823	0.37	0.29	0.08	24	

Appendix 5. Soil moisture deficit (SMD) in mm from eight location during three hydrological years (from 2017 to 2020)



Appendix 6. Actual evapotranspiration (ETa) in mm/day from eight location during three hydrological years (from 2017 to 2020)



Appendix 7. Detail description of soil Nitrate-N (kg ha^{-1}) and Ammonium-N (kg ha^{-1}) with standard error (SE) on three sampling dates during summer 2019

Date	**COMP**	**COMP+Vizura**	**NPK**	**NPK+Vizura**
	Nitrate-N (kg ha^{-1})			
05/07/2019	4.73 (3.9)	7.62 (4.9)	7.40 (5.7)	1.73 (1.6)
20/08/2019	6.88 (7.0)	2.42 (1.8)	4.80 (4.3)	3.06 (3.9)
03/09/2019	8.33 (6.1)	4.79 (3.9)	5.09 (6.5)	6.06 (3.9)
	Ammonium-N (kg ha^{-1})			
05/07/2019	12.92 (3.3)	14.21 (6.0)	11.20 (2.3)	10.01 (2.7)
20/08/2019	22.18 (5.7)	26.61 (1.0)	20.69 (1.5)	20.11 (1.8)
03/09/2019	40.06 (3.2)	33.91 (5.5)	26.71 (3.1)	35.29 (2.4)

Appendix 8. Soil profile depth, soil types and land management information at the sites used in NDICEA

Location ID	Soil thick-ness (cm)	Soil type	Cropping 2017/2018	Nitrogen-in-put 2017/2018	Cropping 2018/2019	Nitrogen-in-put 2017/2018	Cropping 2019/2020	Nitrogen-input 2017/2018
817	0-30 30-60 60-90	SAS-ILO SAS-ILO SALO	White clover		White clover		White clo-ver/Spring oats	
820	0-30 30-60 60-90	SAS-ILO SALO CLLO	Winter wheat	Urea (200 kg N/ha)	Fallow		Fallow/ Sprouts	
821	0-30	SALO	Winter wheat	Urea (180 kg N/ha)	Winter wheat	Urea (185 kg N/ha)	Winter oilseed rape	Urea (210 kg N/ha)
827	0-30	CLLO	Grass	Cattle FYM(22.2 t/ha	Grass	Cattle FYM(22.2 t/ha)*	Grass	Cattle FYM(22.2 t/ha)*
829	0-30 30-60	SAS-ILO CLLO	Winter barley, Stubble turnip	AN & Cattle FYM (188 kg N/ha, 22.2 t/ha)	Spring barley*	Ammonium nitrate (127.6 kg N/ha)*	Winter bar-ley*	AN & Cattle FYM (188 kg N/ha, 22.2 t/ha)*

832	0-30 30-60	SAS-ILO CLLO	Potatoes	Urea (250 kg N /ha)	Winter wheat	Urea (230 kg N /ha)	Winter wheat	Urea (250 kg N /ha)
833	0-30 30-60 60-90	SAS-ILO SILO SAS-ILO	Potatoes	Urea (250 kg N /ha)	Winter wheat	Urea (230 kg N /ha)	Winter wheat	Urea (250 kg N /ha)
834	0-30 30-60	SAS-ILO SAS-ILO	Red clover		Red clover		Red clover /Spring barley	

* Data assumed for model setup (based on land management history)

AN= Ammonium nitrate

SASILO = Sandy silty loam, CLLO = Clay loam, SACLLO = Sandy clay loam, SALO = Sandy loam, SILO = Silty loam

Appendix 9. NDICEA soil water and nitrogen dynamics calculations

1. *Calculation of water balance*

The topsoil layer receives water from rain, irrigation, and capillary rise. The topsoil evaporates without crop, evaporates with crop, and leaches to the second layer. The second soil layer output is crop evaporation, capillary rise, and leaching (i.e. outside the system). The inputs are leaching from top layer and capillary rise from groundwater. The model assumes a daily rebalancing of water. In the case of excessive rainfall, it is assumed that enough water flushes out within a day to restore field capacity (pF = 2). Higher pF values can occur if extraction (evaporation) exceeds precipitation and replenishment due to capillary rise is too slow (which is not true in this study due to deep groundwater). The capillary rise creates a lower pF if the soil layer is close to the groundwater.

Actual water uptake from a layer decreases when soil pF increases from 2.7 to 4.2.

The proportion of root biomass in topsoil and subsoil determines water uptake partitioning. The rooting depth is assumed to increase linearly from zero at sowing to a maximum at full cover, after which it remains constant. A linear reduction in root biomass with depth. The remaining water is assumed to be taken up from the subsoil if the rooting depth exceeds the topsoil thickness. The crop takes up more water from topsoil when the subsurface pF exceeds 2.7, regardless of rooting depth. In bare soil, there is no rooting depth and just topsoil evaporation occurs.

2. *Calculation of nitrogen balance*

Nitrogen deposition (independent of rainfall due to even distributed over the year), nitrate in irrigation water, mineral part of nitrogenous fertilisers, nitrogen from breakdown of all organic matter types, and capillary rise from the second soil layer supply nitrogen to topsoil. Crop uptake, denitrification, N-immobilisation (decomposition of organic matter with insufficient nitrogen), fertiliser volatilization, and leaching to the second soil layer comprise the removal of N from the topsoil layer. The second soil layer supply includes leaching from the topsoil, possibly N via breakdown of organic materials, and capillary rise from subsoil. The removal from subsoil includes drainage, capillary rise, crop uptake, leaching, and denitrification. Ammonia volatilization removes nitrogen from applied manure. With organic manure, this volatilization is expected to be immediate. Volatilized nitrogen is not added to the topsoil layer and subsequently removed, but first "from the manure" before being added back to the soil. With artificial fertilisers, this process takes several days, allowing the soil to fully utilise the nitrogen before volatilization removes it.

3. *Mineral nitrogen leaching*

After calculating N uptake by crop/crops (two crops at the same time) and other N movements, the final step estimates nitrogen leaching. The Nitrogen Leaching Factor determines how much nitrogen from the relevant layer is transported by the leaching water.