Isotopic constraints on the source and transformation of nitrate in groundwater systems

Josephine Emily McSherry

Submitted in accordance with the requirements for the degree of

Doctor of Philosophy

The University of Leeds

School of Earth and Environment

May 2021

The candidate confirms that the work submitted is their own and that appropriate credit has been given where reference has been made to the work of others.

All conclusions are those of the author, and not necessarily those of organisations who supplied data analysed in this thesis.

Acknowledgements

I would like to thank Prof. Jared West and Prof. Simon Bottrell their guidance, support, experience and frequent reassurance throughout this project, it has helped me find my confidence. Thank you to Teresa Honore and Cara Healy for organizing us. I also gratefully acknowledge the academic input of Dr Rob Newton.

I wish to thank Hannah Threadgould, Andrea Lancaster and Sharon Thomas and all of the Environment Agency GWCL team in Yorkshire for their knowledge, help accessing data, placement opportunities and for being videocall companions in early COVID-19 lockdown. I am grateful also to Jamie Duncan for discussing farming practices with me while I was on placement with the Environment Agency. Thanks also to Paul Speight and Mark Morton at Yorkshire Water for kindly sharing data and knowledge, and providing access to Kilham Pumping Station. Thanks to Debbie Wilkinson and Steve Howe at South East Water for their collaboration on the southern catchments. Special thanks go to a kind provider, who will remain anonymous, of inorganic fertiliser samples, which enabled me to analyse and understand my nitrogen inputs.

I am grateful to Dr Prodeo Agbotui and Kirk Handley for introducing me to the beautiful Yorkshire Wolds, being fieldwork facilitators and companions, as well as the source of much knowledge and lively car debates. Thanks to Edd Peacock of Eddfield Airfield and to two other local landowners for allowing us to install and maintain equipment on their land. I would also like to thank the Cohen Lab team, particularly Dr Andy Connelly, Dr Andy Hobson, Dr Bob Jamieson and Fiona Keay. Particular thanks are owed to fellow PhD student, Tim Dixon, for so much lab support, advice with methods and patience.

I would not have made it through this PhD without the support of my cohort - in particular, Anne, Laura, Anya, Sarah, Charley, Gemma, and Danielle. I hope we will be lifelong friends. Thanks also to the Goldney Girls – you lot have always been there. Cheers to my Haddon Road housemates: Liam, Rob, Sam, Callum and Tom for welcoming me to Leeds with boardgames and nonsense. Further thanks are due to Tom for his love and support, and continuing as my sole housemate, even through COVID-19 lockdowns and thesis stress.

Thank you to my parents, Jane and Alan, and Murphy the dog for your moral support throughout – I appreciated knowing you would be on the other end of the phone if it had been a tough day. I have also appreciated the support of Debbie Britton and Des Reid.

I am grateful for NERC Spheres Doctoral Training Programme (grant number NE/L002574/1) and for the Environment Agency for funding this project.

Abstract

Nitrate is a limiting nutrient and is an important additive for agriculture. It is also an environmental risk to surface water and of concern to the water industry. In this study groundwater was sampled over the course of a year from Northern and Southern Province Cretaceous Chalk aquifer catchments in the Yorkshire Wolds and Hampshire, respectively, as well as from the Medway River Terrace Gravels (RTG) aquifer in Kent. Dual stable isotope analysis and major ion concentrations were used to identify nitrate sources and compared to identify to what extent nitrate sources and processes were similar between geologies, aquifer lithology and flow mechanism.

While Chalk aquifers are well-studied due to their strategic importance as drinking water sources, to the author's knowledge dual stable isotope analysis has not been carried out on the Northern Chalk prior to this study. The Medway RTG are little studied in comparison to the Chalk, so this work provides a substantial contribution to understanding of hydrochemistry in this aquifer. Analysis of nitrate temporally and spatially also furthers understanding of nitrate dynamics.

Nitrate often exceeded the legal drinking water limit (PCV) of 11.3 mg/L nitrate-N on the Chalk, especially on the Northern Chalk, compared to no samples on the RTG. Major ion concentrations suggested that anthropogenic pollution had occurred. Nitrate to chloride ratios for all four catchments identified mixing between two end members, likely inorganic fertiliser and manure/slurry. Several samples from the Kilham catchment, however, had a different ratio, possibly the result of highly bioavailable manure/slurry.

Dual stable isotope analysis provided clear evidence of a manure/slurry nitrate source on the Northern Chalk. It was, however, surprisingly rare given that manure and slurry are often applied to fields. Occurrences of manure-type signatures on the Northern Chalk may be due to application of highly bioavailable manure/slurry at these locations or particularly large pollution events. Characteristic heavy-oxygen isotope signatures, representing untransformed nitrate from inorganic fertilisers produced by the Haber-Bosch process, are absent in all groundwater samples. This absence suggests that inorganic fertilisers are being used appropriately in all regions sampled: crops and soil biomass assimilate much of the fertiliser nitrogen. Given the likely relatively short

residence time of groundwater in the RTG, this implies that transformations resulting in this lighter oxygen signature occur primarily in the soil zone rather than in groundwater. Seasonal variation in primarily $\delta^{18}O$, however, possibly resulted from a nitrate source with heavy oxygen (e.g. untransformed inorganic nitrate fertiliser) introduced during recharge. This seasonal variation is possibly due to variation in the amount of nitrate contributed via older and newer groundwaters.

The majority of samples in the Chalk catchments produced signatures in a cluster between $\delta^{15}N$ +4 to +6‰, and $\delta^{18}O$ +0 to +4‰. This near ubiquitous signature suggests dominant nitrogen source and transformation processes are similar across the Chalk, and is likely the result of mixing of several sources, in addition to transformations in the soil zone. Samples with heavier oxygen signatures may contain a proportion of untransformed inorganic fertiliser. This study explored transformation processes in the nitrogen cycle uniting hydrogeochemistry and soil science. The absence of dominant Haber-Bosch heavy oxygen signatures across all catchments demonstrates that nitrate enters the soil nitrogen cycle prior to leaching, supporting previous reports. Loss of heavy oxygen is likely due to nitrate remineralisation as crop debris decomposes or biomass becomes dormant; this is when nitrate is most vulnerable to leaching and provides opportunity for mitigation. Further work should be directed at reducing the amount of nitrate that leaches in this way, during recharge season.

Table of Contents

List of figures

List of tables

Abbreviations

Abbreviation	Definition
‰	Per mille
BGS	British Geological Survey
CFC	Chlorofluorocarbon
δ	Delta notation; the variation between the isotopic ratio of a sample compared to the isotopic ratio of a standard of known composition.
$\delta^{15}N$	The ratio of ^{15}N to ^{14}N
$\delta^{18}O$	The ratio of ^{18}O to ^{16}O
DOC	Dissolved Organic Carbon
ε	Enrichment factor
HB	Haber-Bosch
IGS	Institute of Geological Services (renamed to British Geological Survey in 1984)
IRMS	Isotope Ratio Mass Spectrometer
meq	Milliequivalents
N (AIR)	Standard for nitrogen isotopes in air
NSA	Nitrate Sensitive Area
NUE	Nitrogen Use Efficiency
NVZ	Nitrate Vulnerable Zone
PCV	Prescribed Concentration or Value
RCF	Relative Centrifugal Force
RTG	River Terrace Gravels
sd	Standard deviation
SE	Standard Error
SEC	Specific Electrical Conductivity
SgZ	Safeguard Zone
SPZ	Source Protection Zone
SPZ1	50 day travel time to discharge at the abstraction site.
SPZ2	400 day travel time to discharge at the abstraction site.
SPZ3	Zone within which all groundwater recharge is presumed to discharge at the abstraction site.
SWA	Southern Water Authority (privatised to Southern Water Services in 1989)
TBR	Tipping Bucket Rain gauge
TDS	Total Dissolved Solids

VSMOW	Vienna Standard Mean Ocean Water standard
WFD	Water Framework Directive
WHO	World Health Organisation
WTW	Water Treatment Works
w/v	Weight per volume

Glossary of site names

Three-letter/ short code	Full code name, where different	Type	Catchment
BA2	400G0086-BA2	Public drinking water abstraction	Haisthorpe
BAR	400G0115-BAR	Anaerobic digestion plant, private abstraction	Haisthorpe
BEL	-	Spring	Kilham
BFG	400G0117-BFG	Farm, private abstraction	Haisthorpe
BR2	400G0094-BR2	Public drinking water abstraction	Haisthorpe
BRA	40001257-BRA	Spring	Kilham
BRO	400F0012-BRO	Farm	Kilham
DOF	400G0082-DOF	Farm, observation	Kilham
FWF	400G0110-FWF	Farm, private abstraction	Kilham
HAC	400G0090-HAC	Public drinking water abstraction	Haisthorpe
HAE	400G0091-HAE	Public drinking water abstraction	Haisthorpe
HARA	-	Public drinking water abstraction	Hartlake
HARC	-	Public drinking water abstraction	Hartlake
HAROB1	-	Observation	Hartlake
HAROB3	-	Observation	Hartlake
HARSPF	-	Farm, private abstraction	Hartlake
HOF	400G0116-HOF	Farm, private abstraction	Haisthorpe
HUG	400G0008-HUG	Brewery, private abstraction	Haisthorpe
KIL	400G0093-KIL	Public drinking water abstraction	Kilham
KOB	400F0018-KOB	Observation borehole	Kilham
KSS	49200297-KSS	Spring	Kilham
KWT	40000399-KWT	Observation borehole	Kilham
MGF	400G0074-MGF	Farm, private abstraction	Haisthorpe
MHF	400G0027-MHF	Farm, private abstraction	Kilham
MOF	400G0109-MOF	Farm	Kilham
OCG	400G0107-OCG	Observation borehole	Kilham

Three-letter/ short code	**Full code name, where different**	**Type**	**Catchment**
PTH	400G0022-PTH	Farm, private abstraction	Kilham
ROO	400G0108-ROO	Farm	Kilham
SDF	400G0118-SDF	Farm	Haisthorpe
SHW	400G0106-SHW	Observation borehole	Kilham
SWA	400G0023-SWA	Farm, private abstraction	Kilham
WEA	400G0105-WEA	Observation borehole	Kilham
WES	400G0072-WES	Observation borehole	Kilham
WHF	400G0006-WHF	Farm	Haisthorpe
WIN	400G0112-WIN	Observation borehole	Kilham
WMals	-	Public drinking water abstraction	Woodgarston
WPBH1	-	Farm, private abstraction	Woodgarston
WPBH2	-	Farm, private abstraction	Woodgarston
WPit	-	Public drinking water abstraction	Woodgarston
WWF	400G0119-WWF	Private abstraction	Haisthorpe

Chapter 1 Introduction: Project background and setting

1.1 Rationale

1.1.1 The significance of groundwater

Groundwater is a substantial source of drinking water in the UK, with the Southern and Northern Cretaceous Chalk Provinces being of strategic importance: 20% of all water used in England and Wales is sourced from the Chalk (MacDonald and Allen, 2001). The safety and quality of groundwater is thus vital for human health. Conserving good groundwater quality is also key for environmental purposes as many surface water bodies are groundwater fed and the UK has committed to achieving good qualitative and quantitative status for surface water under the Water Framework Directive (European Commission, 2000a). England has a responsibility to conserve rivers and streams as a priority habitat (Natural Environment and Rural Communities Act 2006) and in particular, the largely groundwater-fed, Chalk streams, as approximately 85% of Chalk streams worldwide occur in the UK (Hickey, 2019). Aquifers are under increasing pressure in terms of quality and quantity to meet current and future water requirements and thus warrant greater scientific understanding to identify appropriate mitigation for anthropogenic activity.

1.1.2 The vulnerability of aquifers to contaminants

Some aquifers are particularly prone to contamination from anthropogenic activity. Catchments with fractured or highly porous bedrock are likely to be vulnerable, as are those with no confining strata because fast transport of pollutants is possible via percolating rainwater, with little opportunity for attenuation. Shallow, thin soils similarly offer less opportunity for attenuation than soils high in organic matter.

This study looks at two lithological aquifer types representing end member behaviour: unconfined Chalk and confined RTG. Chalk aquifers are often highly vulnerable to surface pollution; although matrix permeability is low due to small pore throats, Chalk can be highly fractured, enabling fast flow of solutes to the saturated zone. Low matrix permeability provides potential for pollutants to be stored for extended periods as groundwater migrates slowly down through the unsaturated zone, leading to the long residence time typical of Chalk aquifers. This is also true of the saturated zone, where pollutants can diffuse into matrix water and remain immobile for extensive periods. Where a contaminant is highly conservative this means the pollutant may persist in groundwater long after the event ceases.

River Terrace Gravels (RTG) aquifer is less extensively researched than Chalk as a locally important, rather than strategically important aquifer. As a shallow, alluvial aquifer the RTG may be influenced by river water quality, and as a confined aquifer it does not have a developed unsaturated zone like Chalk. As the aquifer is thin, residence time is short, compared to the Chalk, providing minimal opportunity for attenuation in the aquifer prior to groundwater entering pumping stations. The RTG is a granular flow aquifer, unlike the fracture flow and matrix storage observed in the Chalk. Overlying alluvial deposits, including silts and clay, confine the RTG aquifer, possibly providing some defence against surface pollutants. Parts of the Northern and Southern Province Chalk are also confined, however, of the catchments studied, only the south-eastern edge of the Haisthorpe catchment is overlain by Quaternary deposits and at the feather edge of the cover these deposits will be permeable sands and gravels.

1.1.3 A history of nitrate contamination

Nitrate concentrations have been increasing in groundwater, largely following an increase in ploughed land area, particularly after the Second World War. In some locations, concentrations appear to be plateauing since the millennium but work is still required to understand the problem and facilitate a lasting decrease in groundwater nitrate concentrations. Historically, high nitrate in drinking water has been linked with ill health e.g. methaemoglobinaemia, leading to the World Health Organisation developing a standard of 11.3 mg/L nitrate as nitrogen, which was adopted into UK law.

Where nitrate has contaminated surface water it can contribute to anthropogenic eutrophication, leading to rapid and extensive plant growth. When the plants die the ecosystem degrades, as bacteria proliferate and monopolise dissolved oxygen. Few species flourish in hypoxic water so unsightly algal blooms dominate. In addition to biodiversity loss, a drop in tourism (e.g. from angling or rambling) could also be detrimental to local economies.

Sources and mechanisms of groundwater contamination with nitrate are currently not sufficiently well understood, in addition to the extent of any attenuation (e.g. denitrification) or seasonality. Excessive fertiliser use has previously been blamed for unnaturally high concentrations of nitrate in surface and groundwater, however fertilisers are often required to enable crops to achieve sufficiently high yields and largely appear to fulfil this purpose. This project has brought together geoscience and soil science to explore nitrate sources affecting the Chalk and RTG, and the processes that influence its transport and attenuation. This knowledge will enable implementation of appropriate mitigation, to meet requirements detailed in the Water Framework Directive (WFD) (European Commission, 2000a) and Drinking Water Directive (European Commission, 1998).

1.2 Project aims and objectives

The overall aim of this research project was to improve understanding of the sources and transformations of nitrate in groundwater systems using dual stable isotope analysis. This overall aim has been completed by addressing the following objectives.

1.2.1 Assessment of end members to understand inputs

- Subject four fertilisers and a laboratory grade ammonium nitrate to stable isotope analysis to identify their bulk nitrogen stable isotope ratios, as well as stable isotope ratios of nitrogen and oxygen in nitrate, where applicable.
- Calculate isotopic ratio of nitrogen in ammonium using bulk nitrogen and stable isotope ratios of nitrogen and oxygen in nitrate, where applicable.
- Search published literature for stable isotope signatures for bulk nitrogen, and nitrogen and oxygen in nitrate for manure and slurry.

1.2.2 Characterisation of Northern Chalk groundwater

- Analyse available hydrochemical datasets to characterise groundwater and ascertain the extent to which there is seasonality in major ion concentrations.

- Collect samples and analyse using an acetone dissolution method (Section 3.2.1) for dual stable isotope ratios.
- Assess isotope ratios spatially and temporally in conjunction with hydrochemical information and local knowledge, to identify possible sources of nitrate pollution, and possible transformation mechanisms using a fingerprinting diagram created by Kendall (1998) and developed by Xue et al. (2009) and Nestler et al. (2011) (discussed in detail in Section 2.4.1).

1.2.3 Characterisation of Southern Chalk groundwater

- Subject the catchment to the same analyses defined in Section 1.2.2.

1.2.4 Characterisation of a River Terrace Gravels aquifer

- Subject the catchment to the same analyses defined in Section 1.2.2.

1.2.5 Comparison of the three catchments

- Compare spatial and temporal data from the Northern and Southern Chalk Provinces to assess the extent to which the two catchments are affected by the same nitrate sources and processes.
- Compare spatial and temporal data from the dual porosity Chalk with the River Terrace Gravels intergranular flow aquifer, to address whether the nitrate isotope signatures identified in the Chalk catchments are unique to long residence aquifers or likely to be ubiquitous.

1.2.6 Synthesis of findings from 1.2.1 to 1.2.5 to draw conclusions about nitrate dynamics

- Plot major ion and dual stable isotope data for the three catchments together.
- Assess to what extent the Chalk catchments are different to the River Terrace Gravels, in terms of spatial and temporal differences in nitrate concentrations and isotopic ratios.
- Use these assessments to draw conclusions on the role of nitrate transformation and the dominant location of transformations and increase understanding of nitrate dynamics in agricultural systems.

1.3 Thesis Structure

This thesis is divided into eight chapters and two appendices.

Chapter 1 provides an overview of the project, including background and context, aims and objectives, and the document layout.

Chapter 2 is a review of the current published literature, discussing current understanding of effects of nitrate pollution on human and environmental health, and groundwater vulnerability. It continues with an introduction to dual stable isotope analysis of nitrogen and oxygen in nitrate, and the mass balance equations that may be applied where isotopic signatures of sources are constant. The nitrogen cycle is outlined to aid interpretation of the isotope signatures that might be identified. The chapter closes with examination of conceptual flow models that may apply to the Chalk and River Terrace Gravel catchments studied.

Chapter 3 begins outlining how the groundwater and spring samples were collected and continues by describing methods for preparing samples for dual stable isotope analysis, both those carried out at the University of Leeds and at University of East Anglia. Methods for bulk nitrogen isotope analysis carried out by British Geological Survey are also summarised.

Chapter 4 highlights the importance of fertilisers to agriculture before discussing commonly applied organic and inorganic fertilisers, key reactions and dual stable isotope ratios for nitrogen and oxygen in nitrate from the published literature. Bulk nitrogen and dual stable isotope ratios are also presented for inorganic fertilisers known to be applied in the Yorkshire Wolds and analysed for the purposes of this thesis. To constrain expected isotope ratios for manure/sewage-nitrate, a brief summary of the published literature is presented.

Chapter 5 introduces the geology and characteristics of the Chalk in the Yorkshire Wolds. It then describes the catchments studied for this project, Kilham and Haisthorpe. Long term physiochemical data sets are presented and explored, including nitrate and other major ions. Further analysis includes examination of the ratio of nitrate to chloride, as an additional measure for assessment of nitrate sources and to validate the findings of dual stable isotope analysis. Results of dual stable isotope analysis of nitrogen and oxygen in nitrate are presented and discussed. The isotope data are broken down by site and date to assist in identifying processes that may affect nitrate, including any seasonality.

Chapter 6 addresses two additional catchments that were analysed for dual stable isotopes in nitrate: Woodgarston catchment on the Southern Province Chalk in Hampshire, and Hartlake on the River Terrace Gravels in Kent. Comparable analysis techniques were applied for these catchments as for those on the Northern Province Chalk. First geology, hydrogeology and groundwater vulnerability are outlined, followed by hydrochemistry and dual stable isotope analysis data.

Chapter 7 is a synthesis of the previous three results chapters to compare hydrochemistry, and nitrate sources and processes between the Northern and Southern Province Chalk, and also the Chalk with the RTG. This is followed by qualitative mass balance and the applicability of the fingerprinting diagram to groundwater nitrate.

Chapter 8 provides conclusions and consequences of this project, recommendations for possible mitigation measures to reduce nitrate leaching and suggestions for future work.

Chapter 2 Literature review of nitrate, and geology and hydrogeology of the study catchments

2.1 Nitrate pollution

Nitrate (NO_3) is a limiting nutrient for many plants including wheat, barley and other cereals. Within the optimum range, the addition of N fertilisers to such crops may increase yield five- or six-fold, with a 1 kg application of fertiliser resulting in 20 kg of grain (Addiscott et al., 1991). Applications greater than the optimum range may mean some fertiliser will not be utilised by crops or soil microbes. Because NO_3 is highly water soluble and does not sorb efficiently to soil particles in temperate conditions, the fertiliser can then become vulnerable to leaching into surface and groundwater.

The fertiliser is not considered a pollutant in itself: is it key for ensuring food security. However, NO_3 that is available in the soil after the growing season is vulnerable to leaching and therefore, as Addiscott describes it, “untimely nitrate” in tandem with rainfall or irrigation is often the problem. For instance, autumn fertiliser applications used to be commonplace, as it was believed that winter crops required N over the winter, however Goss et al. (1988) demonstrated that this practice generally just increased the amount of NO_3 that would be leached out of the soil that winter. The practice is now rare, except in the case of winter oilseed rape, where pests such as pigeons may be discouraged if the foliage is suitably thick (Addiscott et al., 1991).

Agricultural fertiliser applications are commonly believed to be the cause of NO_3 leaching into groundwater, however the problem may stem back to the ploughing of permanent grassland after the Second World War when there was a push for the UK to become more self-sufficient. Whitmore et al. (1992) showed that within approximately 25 years of ploughing up pasture, the amount of organic nitrogen in soils dropped from around 10 to 6 tonnes/ha; much of this may have leached as NO_3.

2.1.1 Nitrate and human health

Chronic exposure to NO_3 has been reported to induce methaemoglobinaemia or "blue baby syndrome", with infants having particular susceptibility (Ward et al., 2005). The disease results from the conversion of consumed NO_3 to nitrite (NO_2) in the gastrointestinal tract, which then oxidises haemoglobin to methaemaglobin, making it unable to bind and transport oxygen around the body. The last fatal case in the UK, however was in 1950 (Ewing and Mayon-White, 1951), and cases worldwide are rare, leading some to suggest that negative effects of NO_3 are overstated (e.g. Addiscott et al. 1991) and that water supplies with high NO_3 often contain bacteria, which could also be responsible for observed symptoms of methaemoglobinaemia (Powlson et al., 2008).

Cancers, reproductive effects and thyroid changes have also been reported in relation to NO_3 metabolites (see Ward et al., 2005 for a comprehensive list of reports). Bryan et al. (2012) states that there is no link between dietary NO_3 and NO_2 and stomach cancer, however the authors highlight conflicts of interest. Epidemiological studies exploring NO_3 exposure do not isolate NO_3 from other potential known carcinogens that its presence tends to correlate with, i.e. it may be mistakenly identified as a causative agent. Nevertheless, several publications cite lack of appropriate studies (van Grinsven et al., 2006) and only partial understanding of the potential risks of NO_3 consumption (Levallois and Phaneuf, 1994) as a reason to maintain drinking water within the World Health Organisation (WHO) standard of 50 mg/L NO_3 (11.3 mg/L NO_3-N).

2.1.2 Nitrate in the environment

NO_3, in conjunction with phosphate (PO_4), is responsible for surface water eutrophication. It enables fast growth of riverside and in-channel plants. As the macrophytes die, bacteria feed upon the decaying matter, increase in number and utilise any available oxygen thus reducing water quality. Low oxygen and light levels discourage further macrophyte growth (Hilton et al., 2006) and reduce biodiversity as few organisms can survive in hypoxic conditions (Mainstone and Parr, 2002); in extreme circumstances this may result in ecosystem collapse. In the absence of macrophytes, algae dominate; such algal blooms are unattractive and so may have a negative effect on local quality of life and tourism (Hilton et al., 2006). In addition, decaying organic matter can block water supply pipes, creating water supply issues and potentially expensive repair work (Addiscott et al., 1991).

NO_3 in the water column can also limit growth, affect the immune system or reduce breeding success in affected aquatic organisms (Addiscott et al., 1991). In addition, algae including cyanobacteria, dinoflagellates and diatoms, which are promoted by eutrophication, can produce toxins harmful to humans and other animals (Hilton et al., 2006).

2.1.3 Legislation governing nitrate use

There is legislation in place to reduce NO_3 pollution and mitigate the risk to the environment and human life. The Water Framework Directive (WFD) (European Commission, 2000a) was developed with the objective of achieving good quantitative and qualitative status for all ground and surface water bodies. The Nitrates Directive, 91/676/EEC (European Commission, 2000b), is a key instrument of the WFD and improves quality of water bodies by promoting good farming practice and thus protecting against excessive agricultural NO_3. Under these regulations water bodies should be monitored for NO_3 concentrations of greater than 50 mg/L or concentrations that are on a trajectory to reach 50 mg/L if no action is taken to reverse the trend. Eutrophic conditions should also be monitored for.

Nitrate Vulnerable Zones (NVZ) were introduced in the UK to support the objectives of the WFD and Nitrates Directive. NVZs may be designated when land that contributes to NO_3 pollution drains into NO_3-polluted waters or waters at risk from NO_3 pollution. In England codes of Good Agricultural Practice have been established known as Farming Rules for Water (DEFRA, 2017). These rules limit the periods during which nitrogen fertilisers may be applied, with the aim of reducing N loss during recharge season or rainfall events that result in run-off. Limitations are also placed on the conditions under which organic or inorganic fertilisers may be applied, such as not on to frozen or flooded ground, or where the pollution risk is substantial. In addition manures may not be applied near surface waters or within 50 m of a spring or borehole, and there are specific storage requirements for manure and slurry. Farmers working within NVZs are expected to adopt crop rotations, use winter cover or catch crops to minimise N loss, and have an action plan to ensure that fertiliser applications are appropriate for the crop, with all N inputs considered; manure applications must not be over 170 kg N/ha/year.

DEFRA opened a consultation regarding whether to ban urea fertilisers in November 2020: statutory obligations necessitate a reduction in ammonia of 8% by 2020 and 16% by 2030. Although the aim is to cut ammonia emissions from volatilisation of urea fertiliser, the outcome of this consultation could also affect the amount of nitrogen lost to groundwater. 8% of ammonia emissions are from solid urea fertiliser (DEFRA, 2020c) while 87% of emissions result from agriculture in general (DEFRA, 2020c) so a holistic appraisal of land and livestock management would be beneficial as a longer term solution, both to ammonia emissions and to loss to groundwater. In the absence of a complete overhaul, banning solid urea fertiliser would be the policy that in isolation could bring about the largest reduction in volatilisation (DEFRA, 2020b). However, regarding NO_3 leaching to groundwater, a ban could result in pollution swapping from urea to another more soluble fertiliser such as ammonium nitrate (NH_4NO_3).

2.2 Groundwater vulnerability to nitrate

Groundwater vulnerability is dictated by the surrounding geology, hydrology, hydrogeology and contaminant properties and the interaction between them (Gogu and Dassargues, 2000). The potential for natural attenuation of a contaminant varies greatly according to physical or chemical processes within the soil, vadose or saturated zones. However, these conditions may be bypassed if epikarstic features are present, enabling fast flow of water from the surface to the aquifer. NO_3 is highly soluble and thus is readily transported in water.

N is generally unavailable for use by organisms as N_2 gas stored in the atmosphere, however humans have reportedly doubled available N from that which is accessible via natural N fixation. Anthropogenic sources globally contribute up to 140 Tg N/year to the existing terrestrial base-level N fixation, which is estimated at 90-140 Tg N/year (Vitousek et al., 1997). As much as 70 Tg N/year further may also be mobilised from long term storage by humans via burning biomass, wetland drainage or land conversion (Vitousek and Matson, 1993). NO_3 enters the soil via inorganic fertilisers, sewage, atmospheric deposition or fixation via plants or bacteria (Figure 2.5). Overuse of fertilisers and manures is suspected to contribute significantly to NO_3 concentration in the soil and where plants are not able to take up the NO_3, it can be readily transported to vulnerable groundwater (Allshorn et al., 2007). Little denitrification or degradation of NO_3 takes place unless the soil or rock is under anaerobic conditions, leaving few opportunities for attenuation within highly fractured, unconfined aquifers.

The concentration of NO_3 in the UK groundwater is reportedly rising year on year since recording began in the mid-20th century. For instance, NO_3 concentrations recorded in Etton in Yorkshire were approximately 6-10 mg/L in the 1980s, increasing to 8-12 mg/L in the 2000s (Figure 2.1). Stuart et al. (2007) reported that half of sites analysed from a "large body of groundwater nitrate data" showed 34% of sites exhibited an increase in concentration over time, with an average rise of 0.34 mg/L/year NO_3. This is despite an improvement in land management practices over the past few decades.

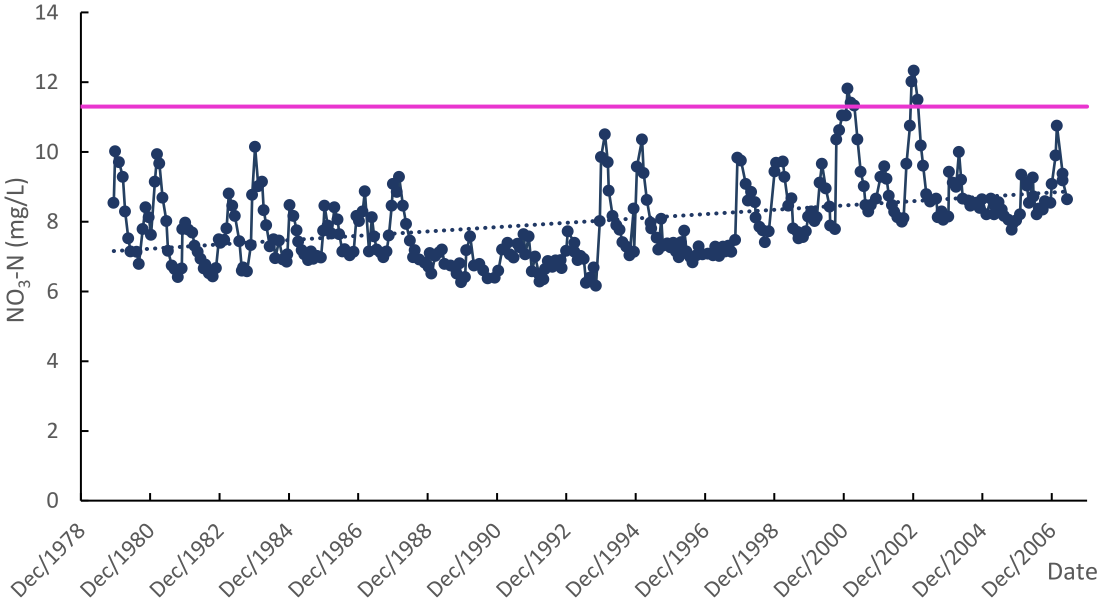

Figure 2.1: NO_3-N concentrations for Etton, Yorkshire from 1980 to 2006. Data courtesy of Yorkshire Water. Etton is approximately 20 km south west of the Northern Chalk catchments investigated in this thesis and introduced in Section 3.1.1. The horizontal pink line marks the legal drinking water limit (PCV) of 11.3 mg/L NO_3-N.

A maximum concentration for drinking water of 11.3 mg/L NO_3-N (50 mg/L NO_3) is stipulated by the WHO; this limit is also adopted by UK law as a Prescribed Concentration or Value (PCV) (Department of Environment, 2000). As abstraction sites approach this legal limit water companies must either blend or treat the water prior to consumption (Knapp, 2005), whereas it may be more financially efficient to reduce NO_3 burdens upon the aquifer in the first place.

Nitrate Sensitive Areas (NSA) were initiated in the 1990s to protect public supply boreholes with concentrations nearing the PCV by providing farmers with financial incentives in return for decreasing applications of fertilisers. In addition to artificial fertilisers on agricultural land, remnants of crops can contribute to the organic N loading in the soil (Kirchmann et al., 2002). In autumn the crops are harvested, but the soil still contains mineralised N and may still be sufficiently warm for microbial degradation to occur. As water becomes more freely available through increased rainfall, microbially-induced nitrification can easily occur and with the lack of plants to utilise the NO_3, it leaches down past the hydrological soil zone into the groundwater during recharge (Kirchmann et al., 2002). Preferential flow in soil can also occur during rainfall, by which water flows from the surface via animal tunnels or fissures. This can lead to NO_3 exiting the zone where plants can access them rapidly and can be particularly problematic if there is heavy rainfall directly after fertiliser application (Lammel, 1990, in Deutsch, 2006).

The last fatal case of methaemoglobinaemia was reported by doctors as being associated with well water after “heavy rainfall following twelve months of exceptional drought” (Addiscott et al., 1991), suggesting increased NO_3 concentrations in the water following recharge initiation. When the water table is high Knapp (2005) hypothesised that groundwater can then incorporate NO_3 that is migrating down through the unsaturated zone. Conversely, Allshorn et al. (2007) carried out tracer tests on the Northern Cretaceous Chalk aquifer that implied NO_3 and other contaminants stored in porewater are incorporated by rainwater that falls during the recharge season, transporting it down to the water table during recharge. Thus, NO_3 was present in percolating water before reaching the water table, invalidating the hypothesis from Knapp (2005), at least at this location. Both theories would explain seasonal variation with high winter peaks in NO_3 concentrations, however the former relies on the water table being close enough to the surface as to reach the high NO_3 zone.

The ability of soil to retain NO_3 is key to assessing the amount of NO_3 available for transportation to the vadose zone and groundwater. Soil becomes vulnerable to NO_3 leaching once NO_3 drains below the rooting depth of plants. It then has the ability to enter groundwater during the next period of downwards water flow (Di and Cameron, 2002). This is controllable to some extent on cropped land as NO_3 application times can be regulated, but is more challenging for grazed land due to animal outputs (Hubbard et al., 2004). Manure may still provide N compounds three years after application, thus providing a persistent and less predictable source of NO_3 (Bergström and Kirchmann, 1999). Ammonia (NH_3) from manure and slurry can also nitrify very rapidly under some conditions. Macdonald et al. (1989) stated NO_3 leached in winter is due to soil N, however this hypothesis would not account for the unnaturally high concentrations of NO_3 recorded in many UK groundwaters, indicating there must be other NO_3 sources such as fertiliser or manure.

2.3 Agricultural nitrogen applications

At the beginning of the 20th century Peruvian guano, Chilean saltpetre and sal ammoniac were commonly used for soil fertilisation. They were from limited natural reservoirs and to extract and import them was energetically and financially expensive. Guano is accumulated faeces from birds and bats, and is mined from islands and caves, while Chilean saltpetre is $NaNO_3$ found in arid regions, such as the Atacama Desert in Chile. Sal ammoniac is NH_4Cl that can be extracted from coal. The Haber-Bosch process (discussed in Section 2.5.1) was an attractive discovery as using high temperatures and pressures enabled production of NO_3 from atmospheric N_2 (Erisman et al., 2008). Haber-Bosch NO_3 and NH_4 fertilisers have thus largely replaced application of guano, saltpetre and sal ammoniac and the former are therefore likely to be among the dominant N sources in the study regions. Common inorganic nitrogen fertilisers are discussed in detail in Sections 2.3.1 to 2.3.4. However, where animal agriculture is prominent, manure and slurry will be produced as N-rich waste products. They are applied to the land, both as a method of disposal and to enrich the soil. A conceptual diagram of N inputs with magnitude is presented in Section 2.6.

In 1941 an average of 20 kg/ha fertiliser was used on winter wheat (Figure 2.2) whereas by 1992 an average of 190 kg/ha total fertiliser N was applied to winter wheat as shown in Figure 2.2. Nearly a ten-fold increase in N fertiliser application corresponded to yields around 2.5 times higher (Davies and Sylvester-Bradley, 1995). For 2020 the mean application rate of N across all tillage was 121 kg/ha (Figure 2.3; DEFRA, 2021). However, application rates were far higher for some crops such as winter wheat (in 2019 201 kg/ha for winter wheat for milling; 179 for non-milling winter wheat) (DEFRA, 2020a). Consistency in protein levels for milling wheat is particularly important, thus reduction in N applications for these crops is not currently feasible. Decreases in average N applications have instead been the result of reduced grassland applications, from 109 kg/ha in 1998 to 54 kg/ha in 2019 (DEFRA, 2020a).

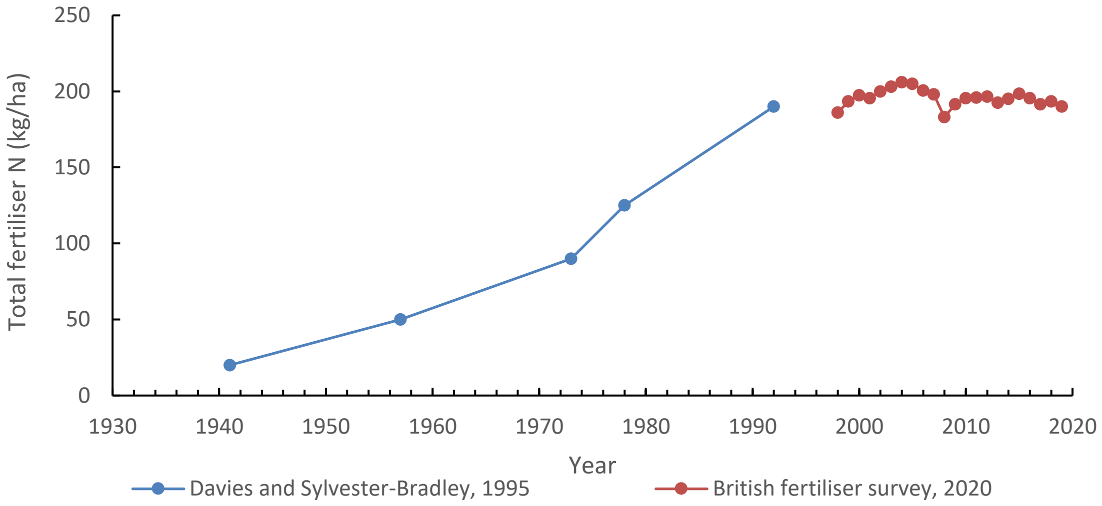

Figure 2.2: Total fertiliser N applied to winter wheat from 1941 to 1992 (Davies and Sylvester-Bradley, 1995) and from 1998 to 2019 (DEFRA, 2020a).

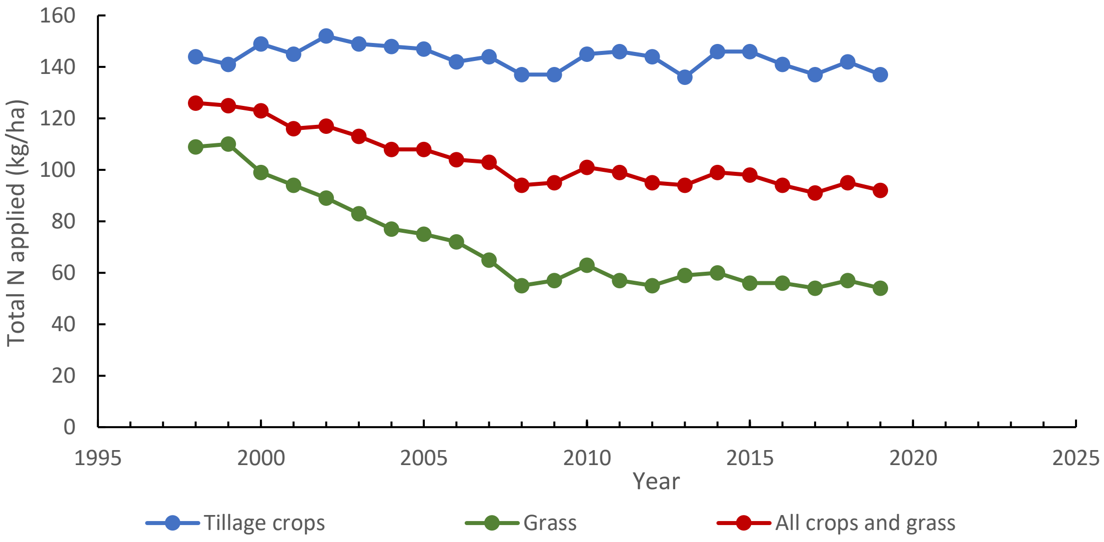

Figure 2.3: Total N use from 1998 to 2019 on tillage crops and grass in Great Britain; dataset from DEFRA (2020a).

2.3.1 Ammonium nitrate

Ammonium nitrate (NH_4NO_3, or commercially, AN) is popular because it contains two forms of N, and 34% N in total. NO_3 can be absorbed quickly by the crop, whereas NH_4 can sorb to soil and will be nitrified over time for gradual use by crops. It is manufactured using anhydrous NH_3 and concentrated HNO_3:

$$HNO_3 + NH_3 \rightarrow NH_4NO_3$$

(2.1)

Both reagents are products of the Haber Bosch process, with NH_3 being oxidised via the Ostwald process to produce HNO_3. Firstly NH_3 is oxidised by heating in the presence of a catalyst and O_2:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

(2.2)

Then NO_2 is produced by a second oxidation:

$$2NO + O_2 \rightarrow 2NO_2$$

(2.3)

HNO_3 can then be produced by reaction in air:

$$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$$

(2.4)

Or NO_2 can be absorbed by water and dilute HNO_3 produced:

$$2NO_2 + 2H_2O \rightarrow 2HNO_3 + H_2$$

(2.5)

Producing HNO_3 using water is less efficient and therefore likely to be far less common in industrial settings, however this method would produce HNO_3 with a lighter $\delta^{18}O$ than via the method using O_2 from air.

Urea ammonium nitrate, a solution of urea (CH_4N_2O) and NH_4NO_3 (commercially known as UAN) is being explored as a safer, less explosive, alternative to NH_4NO_3 (Chambers and Dampney, 2009). UAN however suffers with increased ammonia loss: an “extra c. 20% of urea-N was needed to achieve the same cereal crop yield and quality as from the use of NH_4NO_3.” This could be because urea can easily leach into groundwater. As well as being applied in isolation, NH_4NO_3 is frequently in compound fertilisers as the N source, alongside other significant nutrients, P and K.

2.3.2 Urea fertilisers

Urea, or carbamide, is key in the excretion of N compounds from mammals and in the 1820s Friedrich Woehler discovered that urea could be synthesised. Following this breakthrough, the Bosch-Meiser process was developed in the 1920s, for which the raw materials required are NH_3 and CO_2. As a result, urea is normally manufactured in NH_3 plants as these two reactants are formed as product and by-product of the Haber-Bosch process, respectively. NH_3 and CO_2 react under pressure and heat to form ammonium carbamate (NH_2COONH_4):

$$2NH_3 + CO_2 \rightleftharpoons \mathrm{N}H_2COONH_4$$

(2.6)

Ammonium carbamate is then decomposed to form urea and water:

$$\mathrm{N}H_2COONH_4 \rightleftharpoons \mathrm{C}H_4N_2\mathrm{O} + H_2O$$

(2.7)

The liquid urea can then be solidified into prills or granules.

Urea is reportedly the most commonly used fertiliser worldwide due to its 46% N content (Trenkel, 1997, Zheng et al., 2009, Xiaoyu et al., 2013). Soil bacteria can metabolise urea to NH_4NO_3, also producing HCO_3, making the N available to plants. However a maximum of half of traditional urea applied is captured by plants (Al-Zahrani, 1999, Prasad et al., 1971), thus much leaches into groundwater. As a result, slow-release formulae are being investigated and developed e.g. Fernández-Pérez et al. (2008), Noellsch et al. (2009) and González et al. (2015).

2.3.3 Ammonium phosphates

First available in the 1960s, diammonium phosphate (commercially DAP), $(NH_4)_2HPO_4$, is currently among the most popular P fertilisers and it provides a balance of P (20%) to N (18%). It is formed by reaction of phosphoric acid (H_3PO_4) with NH_3:

$$2NH_3 + H_3PO_4 \rightarrow (NH_4)\ _2HPO_4$$

(2.8)

It is highly soluble and so may be applied either as liquid or granules. As granules dissolve, the area surrounding it becomes temporarily alkaline, which can be damaging to seedlings (IPNI).

For the purposes of this study it may be important to bear in the mind that DAP gradually releases NH_3 when exposed to air at room temperature:

$$(NH_4)\ _2HPO_4 \rightleftharpoons NH_3 + NH_4H_2PO_4 \tag{2.9}$$

Monoammonium phosphate ($NH_4H_2PO_4$) (otherwise called ammonium dihydrogen phosphate) delivers proportionally more P (27%), and 11% N. It is formed by reaction of phosphoric acid with ammonia:

$$NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4 \tag{2.10}$$

As the NH_3 component is smaller, there is a lesser risk to seedlings from increased alkalinity than for diammonium phosphate (IPNI).

2.3.4 Ammonium sulphate

Ammonium sulphate, $(NH_4)_2SO_4$, has been produced as a by-product of coal distillation for around 150 years. It was originally produced with NH_3 from manufacture of coal gas. Later ammonium sulphate was produced as a by-product of coke production: as coal is processed to become coke, NH_3 is removed using sulphuric acid (H_2SO_4). Substantial quantities of ammonium sulphate are also created during nylon production (Boustead, 2005).

In the UK, ammonium sulphate became less popular as sufficient S fell as acid rain; other fertilisers were also a more concentrated source of N as ammonium sulphate is only 21% N. It is now increasing in popularity again as in some regions soils are becoming deficient in S due to declining acid rain inputs.

Ammonium sulphate tends to have an acidifying effect on the soil because of nitrification, therefore it is best applied to alkaline soils. This is an effect of other NH_4 fertilisers, but occurs to a greater extent in ammonium sulphate than NH_4NO_3 because half of NH_4NO_3 does not require nitrification.

2.3.5 Manure and slurry

Manure and slurry are an additional source of nitrogen that can be applied as fertiliser. Manure and slurry spreading is also a method of disposing waste produced by livestock, the volume of which has increased with the intensification of farming and increased meat consumption. Manure is less commonly applied in winter (DEFRA, 2020a) and is not permitted in NVZ (discussed in Section 2.1.3) due to the increased risk of leaching to groundwater during recharge. Under NVZ legislation the equivalent of 170 kg N/ha/year is permitted, a similar magnitude to inorganic fertilisers, however calculating the volume of manure or slurry that equates to is more complex than for manmade fertiliser and requires chemical analysis (AHDB, 2020). Total N varies from 2.6 kg/m^3 in cattle slurry to 30.0 kg/m^3 in turkey litter and is typically applied at a rate of 27 m^3/ha and 6 m^3/ha, respectively (DEFRA, 2020a). Approximately 5-10% of the total N in farmyard manure is available for use by the following crop (AHDB, 2020).

Organic matter and manure also act as nitrogen stores in soil, enabling nutrients to be reserved for the following growing season (Jayasingha et al., 2013). Where it is not leached or harvested from the system, nitrogen may cycle for many seasons, so crops may benefit from previous manure and inorganic fertiliser applications e.g. Powlson et al. (1986). For this reason, farmers must also understand existing soil nutrition.

2.3.5.1 Manure and slurry application

Applying manure and slurry to fields is key for many farmers. As well as fertilising crops, manure spreading avoids the problem of disposing of an existing waste product from animal agriculture. Its application also increases soil organic matter, which can improve the ability of soil to store N and water, as well as improving porosity and soil structure. As an organic material, manure and slurry is far more difficult to predict in terms of N release than artificially produced fertilisers, which makes accurate application problematic, as discussed further in Section 4.1.4. Farmers should test their manure or slurry to identify its composition and therefore determine how much should be applied to the land. Results are highly variable, depending on species, livestock feedstuff, bedding and conditions in the silo, but 5-9.5 kg/t is typical in manure (AHDB, 2020).

AHDB (2017) recommends applying manure to coincide with periods of high crop growth i.e. during late winter to summer, however in Nitrate Vulnerable Zones (NVZs) manures can only be applied from June to October each year to minimise NO_3 leaching into groundwater during recharge season. Shallow soils with low organic matter are particularly vulnerable. During spring and summer, N available from poultry manure to crops is 30-35% of the total applied, compared to 10-15% on shallow soils in autumn (AHDB, 2017). Seasonal variation in N availability is even greater with pig manure, with a spring application being up to 65% available while an autumn application could have as little as 10% of the total N available (AHDB, 2017). Significant NO_3 leaching is observed when manure or slurry is applied in autumn (Goulding et al., 2000), so autumnal applications, particularly of slurry, are discouraged (Smith et al., 2002). High N losses via volatilisation are more likely when applying manures and slurries with higher dry content, as they remain on the soil surface for longer. In addition, applications to dry soils in warm weather are more likely to result in N losses via volatilisation (AHDB, 2017). N losses via leaching, however, become more likely if application is followed by heavy rainfall (Smith et al., 2002). Manure and slurry is also sometimes applied to fields solely as a method of disposal, and therefore application may biased towards fields close to animal housing, and not timed for maximum crop uptake or minimal groundwater leaching. Under these conditions high levels of NH_3 volatilisation is possible (around 40% of available N may be lost this way with standard surface application; AHDB, 2017).

Different types of animal waste have different N availability, which affects the likelihood and extent of N leaching from the soil zone. This is partly due to variation in the carbon to nitrogen ratio (C:N). Soil microorganisms contain approximately 8:1 C:N and respire an additional 16 parts C, therefore a food source would ideally contain 24 C for every N (USDA NRCS, 2011). Variations in this ratio lead to either increased immobilisation of N (>24:1 C:N) or excess N remaining in the soil (<24:1 C:N), depending on whether C or N is the limiting nutrient. Rotted farmyard manure typically has a C:N ratio of approximately 20:1, while chicken manure is normally around 4:1-18:1 (Wortmann and Shapiro, 2012). Therefore, N is more likely to be in excess in the soil, and thus more vulnerable to leaching, following an application of chicken manure than from an equivalent farmyard manure application e.g. Chambers et al. (2000).

2.3.5.2 Soil interactions

Chemoheterotrophic bacteria are largely responsible for decay of organic matter in manure and slurry, oxidising it via dissimilative metabolism. Proteins contained in the waste are broken down into amino acids and then into products such as NO_3 and NH_3.

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3 \leftrightarrow NH_4^+ \tag{2.11}$$

Bacteria can also use NO_3 as a terminal electron acceptor (TEA) to enable denitrifying bacteria to gain energy via respiration under low oxygen conditions. In a slurry lagoon study by Gooddy et al. (2002) high NO_3 and SO_4 were observed near the surface, and with depth the conditions were less oxic and NO_3 concentrations dropped: NO_3 was respired in place of O_2. The authors observed that the aerobic zone was much narrower than usual for a Chalk aquifer, due to the slurry lagoon at the surface. In regions with a deep unsaturated zone these processes are unlikely to occur, due to higher availability of O_2. They also suspected that the denitrifying bacteria originated from the slurry lagoon itself and resided in Chalk fractures, rather than being native to the soil, therefore under normal field conditions these bacterial populations are unlikely to be substantial.

Groundwaters polluted by manure and slurry typically have high SO_4, NO_3 or NH_4, Cl, organic C and HCO_3 (Gooddy et al., 2002). Consulting hydrochemical data in addition to isotopic data can therefore assist in identifying NO_3 sources.

2.3.6 Other nitrogen inputs

Anthropogenic activities have also led to other forms of nitrogen pollution, specifically atmospheric deposition from combustion of fossil fuels and intensive farming. Emissions are in the form of oxidised nitrogen (nitric oxide, nitrogen dioxide and nitric acid) and reduced nitrogen (ammonia and ammonium). Oxidised N emissions in the UK were 312kt N in 1900 and peaked at 787 kt N in 1980-1990 (Fowler et al., 2004). Between 1980 and 2007 emissions of oxidised nitrogen have reduced 50% (Garay-Barayazarra and Puri, 2012). In 1900 reduced nitrogen emissions were around 168 kt N, largely due to coal combustion. This peaked at 263 kt N in 2000, with the primary source switching to agriculture (Fowler et al., 2004).

Deposition of nitrogen from the atmosphere can either occur via gases (dry) or in precipitation (wet). Reduced N deposition was 163 kt N in 1900 compared to 211 kt N in 2000, while oxidised N was 66 kt N in 1900 and 191 kt N in 2000 (Fowler et al., 2004). Despite the substantial decrease in NOx emissions, total N deposition has plateaued at c. 400 kt N/year for the period approx. 1990s to 2010s. NO_3 concentrations in rainfall since the 1980s has only dropped 22%, despite the halving of oxidised nitrogen emissions, which is likely due to decreased exportation of nitrogen (Garay-Barayazarra and Puri, 2012). Dry deposition of reduced nitrogen tends to be highly localised e.g. surrounding areas where there are high emissions from livestock (Garay-Barayazarra and Puri, 2012).

2.3.7 Nitrogen use efficiency

Once fertiliser is applied N retention and availability in the soil for crop use varies depending on atmospheric conditions and soil type. Crop properties then define what proportion of available N is absorbed and utilised for growth. N can be retained as organic matter in soil, or as NH_4 adsorbed to negatively charged surfaces such as clay, whereas NO_3 is highly soluble and highly vulnerable to leaching if crops and soil biomass are unable to utilise it. Chalky and sandy soils have a lower proportion of organic matter compared to other soil-types, and thus have limited N storage. They are therefore prone to low N use efficiency (NUE) and higher leached NO_3 concentrations. Land where soil management is poor and organic matter is depleted will also retain less NO_3 (Hallberg, 1989).

An estimated 33% of applied N is recovered in cereal crops worldwide, as calculated by Raun and Johnson (1999), using:

$$NUE = \frac{total\ cereal\ N\ removed - (Soil\ N + N\ from\ atmosphere)}{fertiliser\ N\ applied} \tag{2.12}$$

This figure, however, varies across the world with NUEs of 42% in developed countries and 29% in developing countries (Raun and Johnson, 1999). Zhang et al. (2015) claimed that improving NUE is “one of the most effective means of increasing crop productivity” without negative environmental impact. They estimated that improvement in NUE from c. 40% to 70% is required for global food security and environmental stewardship. Understanding N sources, their dominant processes in soil and vulnerability to leaching is thus imperative. Reducing N leaching to groundwater could improve existing NUE by increasing N availability to crops, thus helping to address poverty in the face of growing populations and climate change. Hawkesford and Riche (2020) stated that multiple scientific disciplines will be required to improve NUE, principally optimal crop genetics, understanding of local environmental conditions and suitable agronomic management.

2.4 Dual stable isotope analysis of nitrogen and oxygen in nitrate

Isotopes are atoms of the same element (same number of protons and electrons), but with differing numbers of neutrons at their core; this affects the atomic mass. The lighter stable isotope is generally the most common variant and contains an equal number of protons and neutrons, while the heavier isotope contains one or two extra neutrons than protons. Stable isotopes are those that do not decay into other elements, unlike radioactive isotopes. Analysis of the ratio of isotopes in a single element may allow differentiation between sources, however if a second element from the same molecule is also analysed then greater distinction between sources may be achieved.

2.4.1 Stable Isotope Fractionation

Both the heavier and lighter variants of stable isotopes are available for chemical or biological reactions, however the rate of reaction differs between them as less energy is required to break bonds involving the lighter stable isotope. This difference is particularly apparent for elements with low atomic mass. Thus as a reaction progresses, more of the lighter isotope will be utilised than the heavier isotope, resulting in fractionation between the source and the product. This fractionation enables identification and quantification of the processes molecules are derived from.

The ratio of the heavy to light isotopes, expressed as $\delta^{15}N$ or $\delta^{18}O$ in the case of NO_3, relative to a known standard, can be expressed as:

$$\delta\ (‰) = 1000\left(\frac{R_x}{R_s} - 1\right) \tag{2.13}$$

Where *R* is the ratio of the heavy to the light isotope, *x* is the sample and *s* is the standard (Kendall and Caldwell, 1998).

Each source of NO_3 is comprised of O and N with a distinctive isotopic ratio. In isolation, N isotopic ratios are too variable to enable confident conclusions to be drawn as the $^{15}N:^{14}N$ ratios are the result of many reactions and conditions. For instance, Natelhoffer and Fry (1988) found that $\delta^{15}N$ increased with soil depth in forests due to fractionation during decomposition; furthermore, a high volume of leguminous plants resulted in low $\delta^{15}N$ due to increased nitrogen fixation. In addition, there appears to be crossover between ranges for $\delta^{15}N$ values e.g. Cey (1999). Högberg (1997) therefore suggested that stable N isotope ratios should be reviewed alongside another pair of stable isotopes from the same molecule. For NO_3 this would be O. Nestler et al. (2011) concluded that dual stable isotope analysis of NO_3 is an effective tool in assessing its source, enabling production of fingerprinting diagrams as in Figure 2.4, however hydrogeological and physiochemical data should also be consulted. Venkiteswaran et al. (2019) advise collecting additional data such as local $\delta^{15}N$ and $\delta^{18}O$-H_2O values to allow more thorough interpretation of fingerprinting diagrams.

It is imperative that any processes that could occur after NO_3 enters the system investigated, and prior to sampling, are also considered. These include physical, chemical, and biological fractionation transformations, in addition to transport and mixing as these processes could further alter the isotopic ratio of either element. These processes can occur in a predictable manner, and so can be accounted for within the structure of a fingerprinting diagram. Nestler et al. (2011) reviewed source apportionment methods in surface waters and reported that transformation processes warranting the most consideration are nitrification and denitrification (discussed further in Section 2.5).

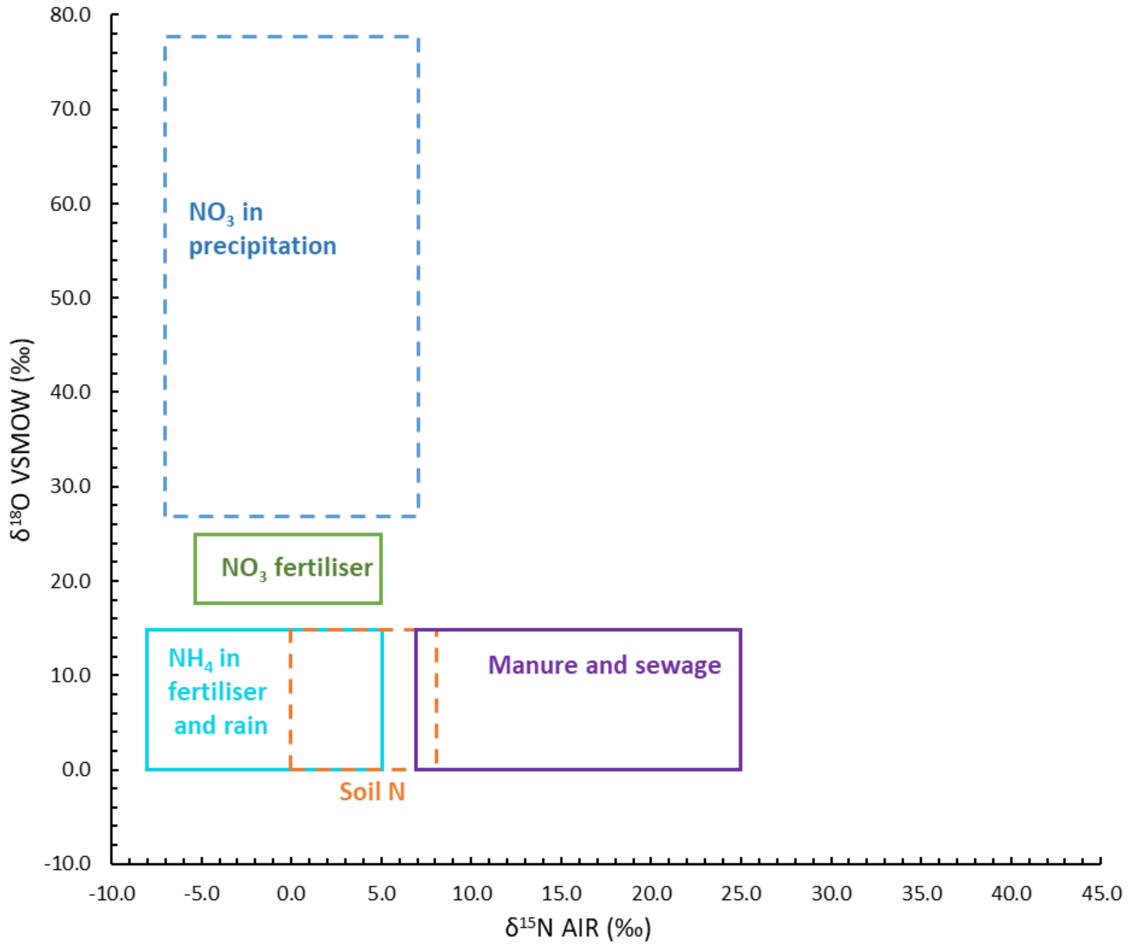

Figure 2.4: Fingerprinting diagram for the dual stable isotope analysis of N and O in NO_3. The boxes estimate δ15N and δ18O values of five possible sources of NO_3. The plot was created by Kendall (1998) and developed by Xue et al. (2009) and Nestler et al. (2011).

2.4.1.1 Equilibrium Fractionation

Equilibrium fractionation involves two or more phases containing the same element attempting to reach equilibrium (Criss, 1999). The effects of this reversible process are generally small but are most significant for elements with low atomic mass, including oxygen and nitrogen. This is in part because the loss or addition of one neutron has a proportionally larger effect on the mass of a light atom than a heavier one. O'Neil (1986) found that equilibrium fractionation effects and covalent bonds are closely correlated, as covalent bonds (including those between O and N in NO_3) are more strongly affected by mass, whereas ionic bonds are less so. Molecules of the same compound but different masses may therefore exhibit variable equilibrium fractionation due to differing physiochemical properties, such as melting point or vapour pressure, with the heavier isotope accruing in the compound, either reactant or product, with the greatest number of bonds (Ryabenko, 2013). Abiotic equilibrium exchange of O between NO_3 and water would likely take millions of years (Kaneko and Poulson, 2013), however biotic processes e.g. incomplete denitrification or the presence of enzymes able to catalyse exchange could increase the speed of reaction.

2.4.2 Isotopic mass balance

Dual isotope data can be input into mass balance calculations to estimate proportional contribution of each NO_3 source to groundwater NO_3 contamination. The equations rely upon the principle of mass conservation and assume that the system is closed and is in isotopic equilibrium. The concept of conservation of mass enables N to “be tracked and accounted for as it is transformed into a variety of chemical forms during N cycling within and among N reservoirs” (Krug and Winstanley, 2002). This is because the mass of a closed system must stay constant over time. The concept can be applied to isotopic analysis in that heavy isotopes identified in the product will equal the sum of heavy isotopes in the reactants, as follows:

$$m_{\Sigma}F_{\Sigma} = m_1F_1 + m_2F_2 + \cdots \tag{2.14}$$

as described in Hayes (2004), where m is the number of moles, F is the fractional isotopic abundance and Σ is the sum of the subsamples. Mass balance calculations can give unique results where the number of elements analysed for their stable isotopes is n+1, where n is the number of inputs. Thus Xue et al. (2009) stated that for NO_3 where N and O are analysed:

$$\delta^{15}N_M = f_1\delta^{15}N_1 + f_2\delta^{15}N_2 + f_3\delta^{15}N_3 \tag{2.15}$$

$$\delta^{18}O_M = f_1\delta^{18}O_1 + f_2\delta^{18}O_2 + f_3\delta^{18}O_3 \tag{2.16}$$

$$1 = f_1 + f_2 + f_3 \tag{2.17}$$

However, the N cycle when applied to agriculture could be described as “leaky” and so the system under investigation may not strictly be described as closed. Understanding of all major sources and sinks of NO_3 is required to assess the O and N isotope ratios collected during dual stable isotope analysis.

2.5 The Nitrogen Cycle

Nestler et al. (2011) asserted that nitrification and denitrification are likely the most important transformation processes in terms of source apportionment in the N cycle. Processes that occur under anoxic conditions are unlikely to be significant to this study as conditions in Chalk soils and groundwater are understood to be primarily oxic. The key processes and nitrogen reservoirs illustrated in Figure 2.5 is described in the following sections.

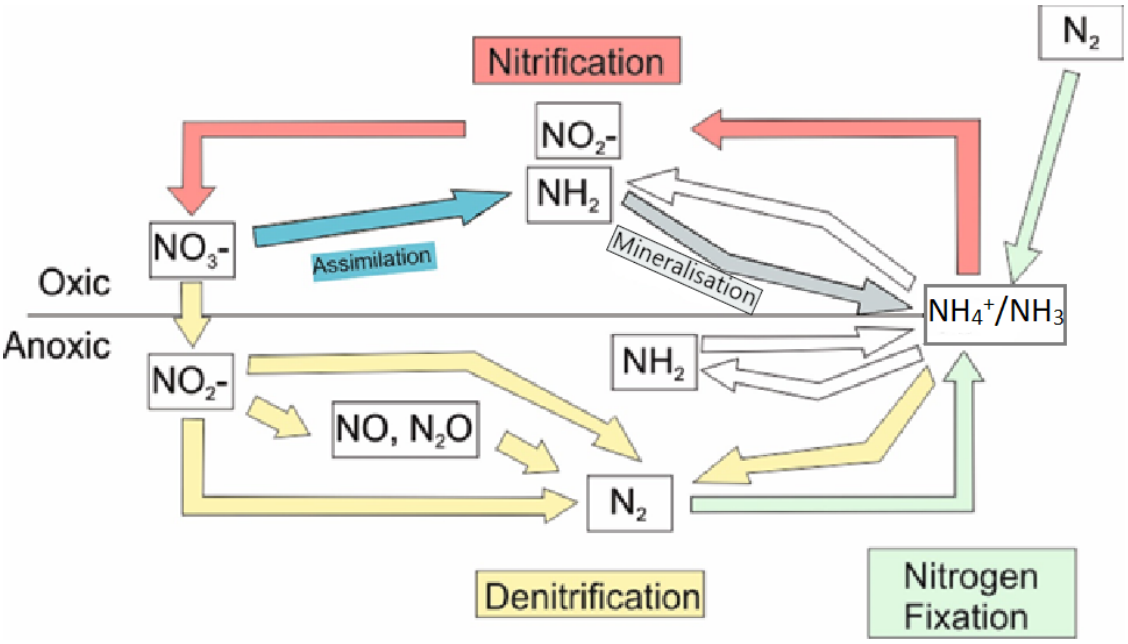

Figure 2.5: Key processes in the N cycle. Nitrogen cycles through various forms in the atmosphere and terrestrially due to both physical and biological processes. Fixation (green) produces a biologically available form, which can then be nitrified (red). NO_3 can then be assimilated into organic molecules (blue). Organic N compounds can then be mineralised (grey) back to NH_4. Under anoxic conditions NO_3 can be denitrified (yellow) either partially to NO or N_2O, or completely to N_2.

2.5.1 Fixation

Atmospheric N_2 is triple bonded and thus cannot be utilised by most microorganisms. On primitive Earth, lightning is thought to have been the primary mechanism for N fixation (Yung and McElroy, 1979). Now however, diazotrophs can fix N_2 to NH_3 or ammonium (NH_4) using nitrogenases. In soil, prokaryotes including *Azotobacter* are responsible for fixation. *Azotobacter* requires pH of 6-9, a C source that is easy to metabolise, and a lack of toxic minerals or organic compounds, in addition to high P and low O. If high levels of N compounds are already present then further fixation will not occur, due to the energetic costs of fixation. Other N-fixing bacteria, such as *Rhizobium*, exist in symbiotic or associative relationships with plants, such as legumes.

N_2 fixation also occurs industrially, via the Haber-Bosch process, which is largely responsible for a doubling of reactive N, as compared to natural systems (Galloway et al., 2002). Unlike biological fixation it requires high temperatures and pressures, 400-500 °C and 15-25 MPa, respectively (Appl, 2006). N and H gases are passed through a series of iron-based catalysts, resulting in around 15% conversion to NH_3, as follows:

$$N_2 + 3H_2 \rightarrow 2NH_3 \tag{2.18}$$

Unconverted gases are recycled and passed through the process again, until up to 97% conversion has been achieved (Appl, 2006).

Diagrams of the N cycle frequently only show NH_4 or NH_3 interchangeably, however their relationship is as follows:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \tag{2.19}$$

At a pH greater than 9 the proportion is around 50%, at a pH of less than 6 there will be negligible NH_3. In soil, N is often lost to the atmosphere as NH_3 gas, while NH_4 can sorb to soil particles and remain relatively stable.

Typically ^{15}N constitutes 0.366% of atmospheric N (Dole et al., 1954). In terms of the effect that fixation may have upon the N isotopic ratio, in breaking a triple bond, N_2 molecules comprised of ^{14}N are metabolised in preference to those containing ^{15}N as a result of kinetic isotope effects (Bigeleisen, 1949, Delwiche and Steyn, 1970). Therefore, ^{15}N in the resulting NH_3 compounds is depleted if the reaction is incomplete. This is because the dissociation energy is greater for molecules containing the heavier rather than the lighter isotope.

2.5.2 Volatilisation

Volatilisation is the vaporisation of ammonia, especially from soil following applications of fertiliser such as urea (CH_4N_2O). Urea is a component of manure and slurry and contains two amine groups ($-NH_2$). It can quickly hydrolyse to NH_4, which can bind with the soil and thus is relatively stable. However, NH_4 is in equilibrium with NH_3 and thus much fertiliser N is lost to the atmosphere as NH_3, the balance of which is in large part directed by pH (Galloway and Cowling, 2002).

In terms of isotopic effects, urea containing the lighter N isotopes preferentially hydrolyses to NH_4, and also volatilises to NH_3, leaving heavier isotopes in the substrate (Lee et al., 2011). This has been reported to result in isotopic fractionation of up to +30‰ (Heaton, 1986) but such figures may not be observed in groundwater due to overprinting by ongoing N-cycling in the soil (Wells et al., 2015).

2.5.3 Nitrification

Nitrification is key to agriculture as fertiliser is often applied as NH_4 compounds, products of the Haber-Bosch process. Nitrification is a two-step oxidation process whereby NH_3 is oxidised to NO_2, then NO_2 oxidises to NO_3, as follows:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ \tag{2.20}$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \tag{2.21}$$

By this route, the Haber Bosch process NH_3 is oxidised to produce NO_3. Typically the isotopic ratios for $\delta^{15}N$ in conventionally produced fertilisers fall within −2 to 4‰ (98.5% within this range; mean=0.2‰ *n*=153) (Bateman and Kelly, 2007). In the abiotic conversion of NH_4 to NO_3, all the O used in the industrial process comes from the atmosphere ($\delta^{18}O$ approximately +23.5‰ Vienna Standard Mean Ocean Water, VSMOW) and as a result has a distinctively heavy O signature (as shown in Figure 2.4).

In natural systems, nitrification is carried out in oxic conditions by NH_3-oxidising bacteria and archaea and NO_2-oxidising bacteria. Once converted to NO_3, the molecules become far more vulnerable to leaching, as NH_4 is strongly bound to soil particles whereas NO_3 tends to dissolve into water. The process of nitrification, if incomplete, results in proportionally lighter isotopic ratios in the NO_3 product, while the heavier isotopes are enriched in remaining NH_3 compounds. However, in the corresponding natural process (equations 2.8 and 2.9 above) in the soil zone, one O atom is usually obtained from the atmosphere (Kroopnick and Craig, 1972) and two from water in the soil (Andersson and Hooper, 1983), hence NO_3 produced from NH_4 within the soil tends towards a $\delta^{18}O$ of between −7 and +15‰ VSMOW depending on the region. Only under reduced nitrification conditions, is it possible that all three O atoms are obtained from the atmosphere, which could markedly increase the O isotopic ratio to up to 23.5‰ (Mayer et al., 2001).

In the soil where N is limited, fractionation associated with biotic nitrification is minimal and as a result the isotopic ratio of NO_3-N transformed here would be similar to soil-reduced N (Kendall and Aravena, 2000). Under these conditions the majority of reduced N would be metabolised so no preferential utilisation would be observed. However, if a significant source of soil-zone NH_4 is available, such as after fertiliser application, kinetic fractionation occurs, resulting in an increase in the isotopic ratio of the substrate, and a decrease in the isotopic ratio of the resulting NO_3.

2.5.4 Assimilation, immobilisation by plants and microbes

Several equilibrium and non-equilibrium isotopic fractionations may occur during metabolism by organisms. NO_3 is absorbed by roots primarily via mass-flow and then assimilated in the roots or shoots (Hofman and Cleemput, 2004). Assimilation is required for nutrients to be integrated into the plant. Here the NO_3 is reduced to NO_2 via nitrate reductase, then to NH_4 via nitrite reductase. NH_4 does not require this reduction step, thus requires less energy on behalf of the plant, however it tends to appear in lower concentrations than NO_3 in well-oxygenated soils. NH_4 is usually diffused into the roots via a concentration gradient. NH_4 from both processes can then be converted to glutamine or glutamate. These products are then subject to all number of different processes to produce many other organic compounds within the plant.

The uptake rate of N compounds is primarily driven by demand from the plant (Blom-Zandstra, 1990, King et al., 1992) however above a critical point, it is driven instead by the soil N concentration (Greenwood et al., 1990). If there is very limited NO_3 in the substrate, then no isotopic fractionation will be seen, as all NO_3 is assimilated. Equally, if there is a great excess of NO_3 and assimilation is the limiting factor on rate, then the change in the proportion of $\delta^{15}N$ will be negligible (Robinson, 2001). Thus, effects isotopic fractionation effects on the substrate (here NO_3) are seen for the intermediate case, and will be maximum where around half of the substrate is transformed.

2.5.5 Denitrification

Denitrification is the process by which NO_3 is reduced in place of an O source for respiration, ultimately back to N_2 gas, by denitrifying bacteria:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \tag{2.22}$$

The process only occurs in low O conditions, such as in saturated soils and, if occurring in groundwater, it is usually electron donor limited (Smith et al., 1994). Hydrogen can act as the electron donor and has been proposed as a method of in situ bioremediation (Smith et al., 1994), however it is not without risk as NO is 150 times more potent as greenhouse gas than CO_2 (Powlson, 1993).

Denitrification is distinctive because the isotope ratios fractionate from the original signature with a typical ratio of 2.1:1 for $\delta^{15}N$ versus $\delta^{18}O$, resulting in heavier isotopic ratios in the residual pool of NO_3 (Aravena and Robertson, 1998, Kendall, 1998, Mariotti et al., 1981, Böttcher et al., 1990). While the ratio remains similar, enrichment factors (ε) vary. Enrichment factors of −15.9‰ for ^{15}N and −8.0‰ for ^{18}O, identified by Böttcher et al. (1990) are typical of a groundwater system, despite fractionation being around half that recorded under laboratory conditions: $\varepsilon = -30‰$ for ^{15}N and −16‰ for ^{18}O was reported by Olleros (1983).

2.6 Consideration of the magnitude of N inputs and outputs of the soil and groundwater systems

Figure 2.6 has attempted to quantify the sources (Section 2.3) and processes (Section 2.5) that likely contribute to nitrogen entering vulnerable groundwaters as NO_3 or enabling its storage in the soil zone. Published literature provided a broad range of values, so the figures included originate where possible from the long-running Broadbalk Experiment at Rothamsted (e.g. Sebilo et al., 2013) and DEFRA for consistency.

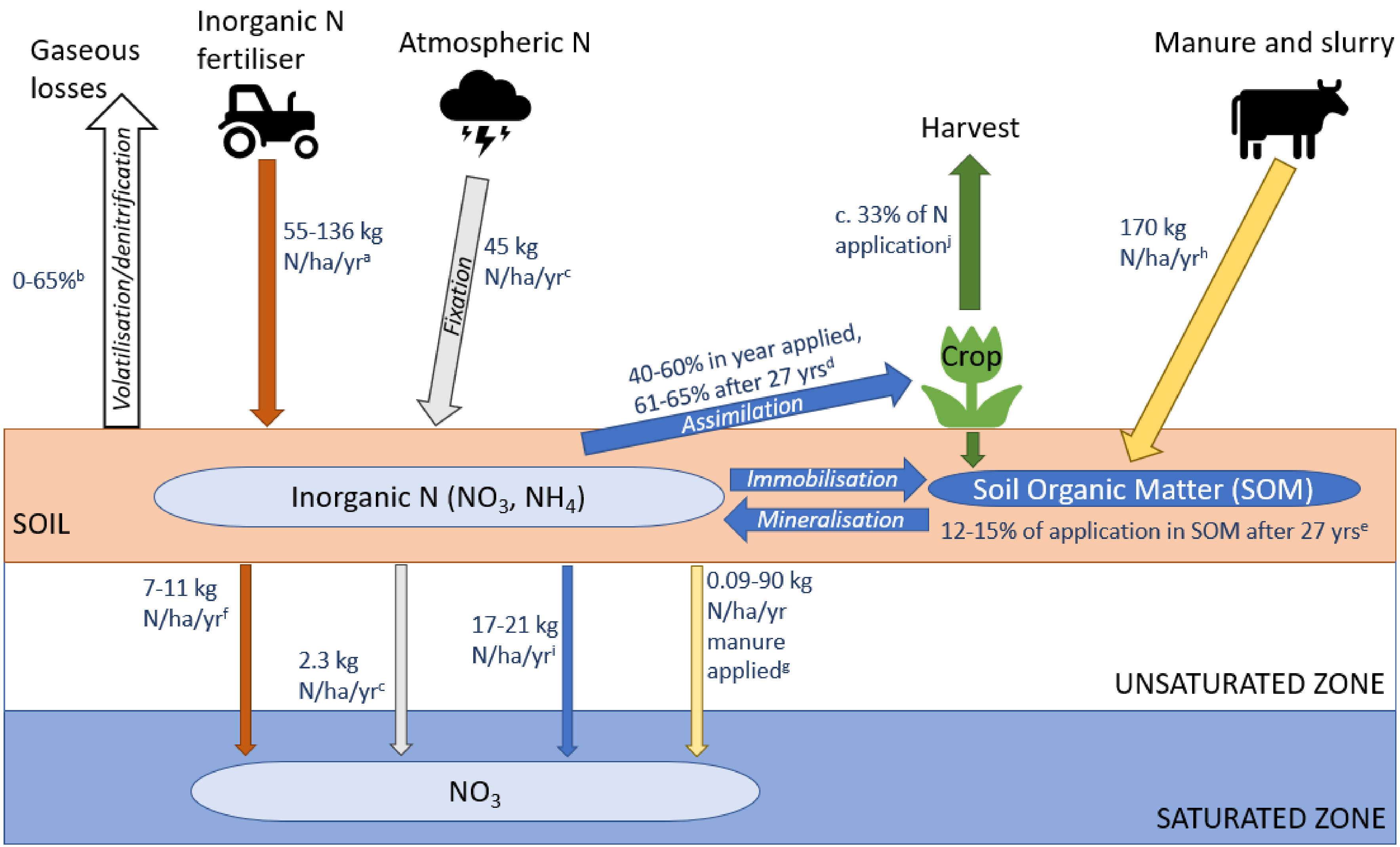

Figure 2.6: Simplified conceptual diagram of N inputs and outputs for soil and groundwater systems, with estimated magnitudes. N may remain in the SOM for many years, so transport of N from surface input to groundwater is not necessarily annual. Data sources listed on the following page.

[a] Mean overall application rate for grass and tillage (55 and 136 kg/ha/yr, respectively), 2016-2020 (DEFRA, 2021).

[b] 0-65% of urea fertiliser applied (urea is especially vulnerable to volatilisation) (Cameron et al., 2013).

[c] 5% of total deposition leached (Goulding et al., 1998).

[d] 40-60% of inorganic N fertiliser applied in same year, 61-65% after 27 years (Sebilo et al., 2013).

[e] 12-15% of inorganic N fertiliser in SOM after 27 years (Sebilo et al., 2013).

[f] 8-12% of inorganic N fertiliser after 27 years (Sebilo et al., 2013).

[g] 0.05-53% of total manure application leached; highly dependent on rainfall (Goulding et al., 2000).

[h] Loading limit for NVZ (DEFRA, 2018).

[i] Mean total N loss when optimal N fertiliser applied (organic and inorganic) 30 kg N/ha/yr (Goulding et al., 2000), with losses from inorganic fertiliser and atmospheric inputs subtracted.

[j] Global nitrogen use efficiency, i.e. the proportion of nitrogen from a fertiliser application that is removed in crops, was calculated as 33% for cereals (Raun and Johnson, 1999).

2.7 Chalk geology and hydrogeology

2.7.1 Northern Province Chalk geology

Chalk is a very fine grained limestone (<10µm), approximately 98% calcium carbonate, with some beds containing marl bands and flints (Hancock, 1975). Marl bands are only a few centimetres thick but can be laterally continuous for many kilometres (Hancock, 1993), whereas flint may be tabular i.e. forming continuous layers or separated into discrete nodules (Mortimore and Wood, 1986).

The Northern Province Cretaceous Chalk spans from its outcrop at Flamborough Head, down the Hull Valley to the River Humber, forming the Yorkshire Wolds. Traditionally, the Northern Chalk has been classified similarly to the more thoroughly researched Southern Chalk: as divided into Lower, Middle and Upper Chalk (e.g. Jukes-Browne, 1880). Wood and Smith (1978) proposed that the Northern Chalk is composed of four formations, Ferriby, Welton, Burnham and Flamborough, in ascending order (Figure 2.7). The lower formations are “remarkably uniform” from Flamborough Head to Lincolnshire (Wood and Smith, 1978); only the boundary between the Burnham and Flamborough Formations appears to be asynchronous throughout the region. Which in terms of the current study, may mean that hydrogeological and geochemical findings in the Kilham catchment are relevant to the wider Northern Province Chalk. Both the Ferriby and Flamborough Formations are free of flint, whereas the Welton contains nodules of flint and several marl bands, and the Burnham tabular and semi-tabular flint, in addition to oyster beds (Wood and Smith, 1978). At the base of the Ferriby Formation is the Red Chalk or Hunstanton Formation, which rests atop the sandstone conglomerate, known as Carstone. There is also the flinty Rowe Formation, atop the Flamborough, however it does not crop out.

While common on the Southern Province Chalk, little “putty-chalk” is observed on the Northern Chalk in contrast, due to its increased hardness as compared its Southern counterpart (Price et al., 1993). This is despite the fact that Ferriby and Welton are found to be softer than the overlying beds. Chalky gravel or rubble is more likely to result from periglacial environments on the Northern Chalk. More generally, the Chalk in Yorkshire contains a wealth of highly variable fracture sets, composed of faults, joints and bedding plane fractures (Bloomfield, 1996).

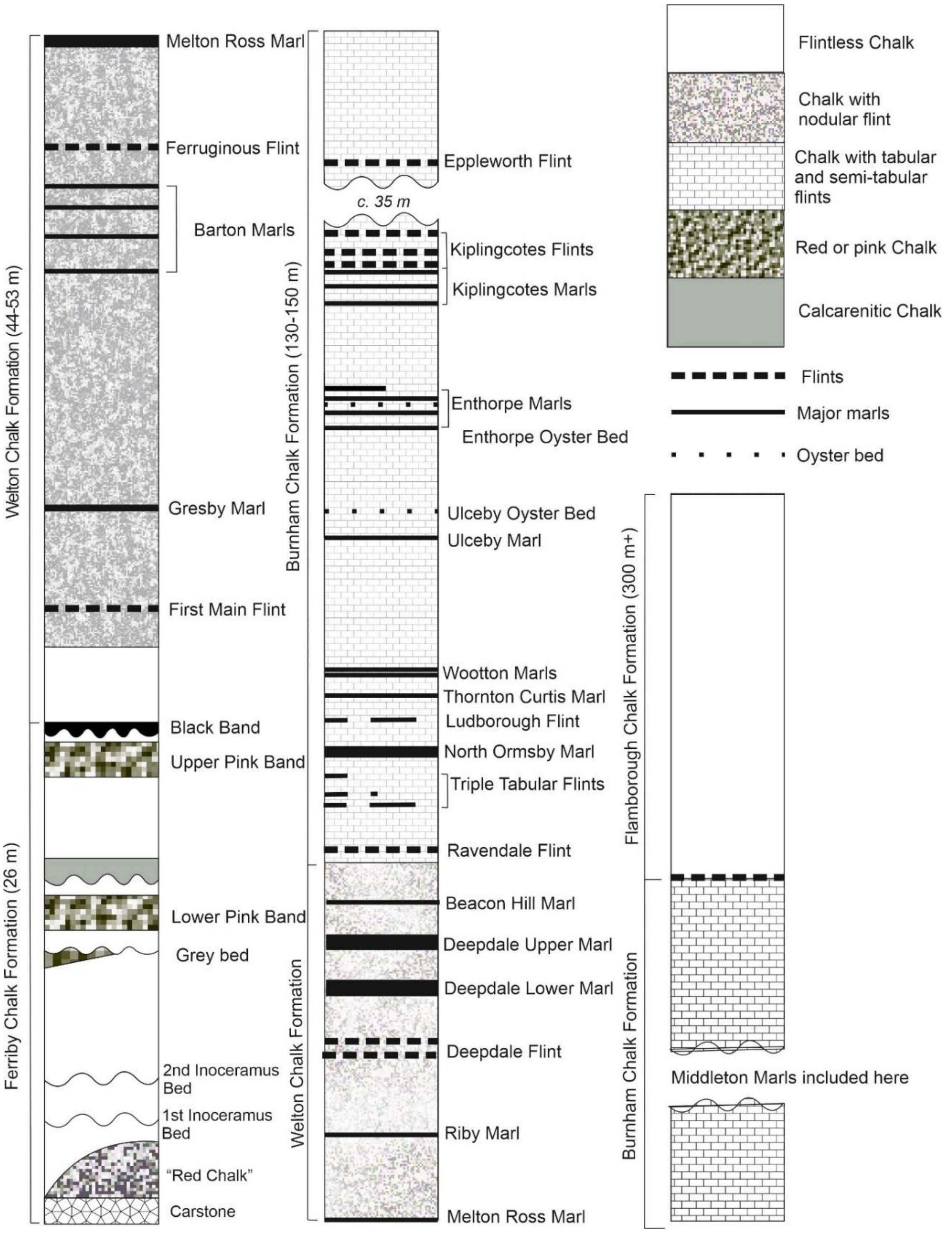

Figure 2.7: Section of the Northern Chalk, from Wood and Smith 1978. The Ferriby Formation marks the base of the Chalk, overlain by the Welton, Burnham and finally the Flamborough Formations.

2.7.2 Southern Province Chalk geology

The Southern Province Cretaceous Chalk consists of the Thames Basin and North Downs, the Hampshire Basin and South Downs, and East Anglia. It overlies the Upper Greensand and is traditionally described as containing three formations: the Upper, Middle and Lower Chalks (e.g. Jukes-Browne, 1880). These have since been further divided (Table 2.1; Bristow et al., 1997). The Upper Chalk correlates approximately to the Flamborough and Burnham Formations of the Northern Chalk Province. The Southern Province is considered more likely to form “putty chalk” where unconsolidated, than the Northern Chalk, as the former is more porous and thus more prone to weathering. Superficial deposits on the Southern Chalk, likely the result of Chalk weathering, include colluvium, and clay with flint, as well as alluvium in the valleys.

Table 2.1: Stratigraphy of the Southern Province Cretaceous Chalk, developed from Bristow et al. (1997) and the BGS GeoIndex (British Geological Survey, 2020).

Formation	Member	Details
Upper Chalk	Portsdown Chalk	White Chalk approx. 60 m thick, with flint bands and many marl seams expect towards the upper boundary; much shell debris at the base.
	Culver Chalk	Soft, white Chalk of 65 to 75 m thick, with flint seams and little marl.
	Newhaven Chalk	Smooth, white Chalks containing marl and flint bands, from 45 to 75 m thick.
	Seaford Chalk	Fine grained Chalk, 50 to 80 m thick, with flint seams; marl largely absent except towards the lower boundary. Crops out in study catchment.
	Lewes Nodular Chalk	Hard, nodular Chalks, interspersed with softer Chalk beds, increasingly at the upper boundary; 35 to 80 m thick. Nodular flint throughout.
Middle Chalk	New Pit Chalk	Blocky, white Chalk, 10 to 50 m thick, with many marl seams and occasional flints towards the upper and lower boundaries in places.
	Holywell Nodular Chalk	Nodular Chalks, generally 25 to 35 m thick, with thin marls and *Mytiloides* debris.
Lower Chalk	Zig Zag Chalk	Off-white to pale grey, blocky; contains marls and marly Chalks towards lower boundary.
	West Melbury Marly Chalk	Marly Chalk off-white to grey in colour with limestone; 15 to 25 m thick. Contains Glauconitic Marl at base, which consists of calcareous sands and silty Chalk.

2.7.3 Chalk hydrogeology

Chalk aquifers are considered to have dual porosity and thus expected to have some rapid bypass flow e.g. Banks et al. (1995), Allen et al. (1997). The Northern Chalk is generally more permeable than the Southern Chalk as a result of its increased hardness, making it more brittle, thus producing cleaner fractures (Allen et al., 1997). Major flow horizons are typically close to the water table or palaeo-water table where substantial dissolution has occurred and bulk permeability may be as high as 200 m/day (Foster, 1974, Younger, 1989). This is in great contrast to the intergranular permeabilities obtained in the laboratory which were approximately 10^{-4} m/day (Price, 1987) and highlights the significance of fracturing to the Chalk as an aquifer.

Matrix hydraulic conductivity of 10^{-4} to 10^{-3} m/day has been reported on the Southern Chalk (Elliot et al., 1999). In Berkshire, tracer tests by Banks et al. (1995) identified water velocities of up to 5.8 km/day through swallow hole systems. This implies karst conduit development where streams sink into unconfined Chalk as they flow off a confining deposit; such sinking streams are not apparent in the study catchment (IGS/SWA, 1979).

The storage potential in the Chalk matrix is low, and the matrix is often near to saturated even within the vadose zone, as a result of small intergranular pore-throats. These can prevent gravity drainage of the matrix (Foster and Milton, 1976). Any large fractures provide opportunity for fast drainage downwards through the unsaturated zone of the unconfined aquifer, as demonstrated by Zaidman et al. (1999) and Allshorn et al. (2007). The specific yield derives primarily from drainage of this fracture space, which typically represents less than 1% of the rock volume. There is limited flow via the matrix, however groundwater may be stored within it for extended periods, which the volume of the Chalk compensating for the low storage potential. Further specifics of Chalk hydrogeology are discussed in Section 2.9.2 and catchment-specific details in Sections 3.1.1 and 3.1.2.

2.7.4 Chalk groundwater vulnerability

The dual porosity of the Chalk makes water movement in the unsaturated zone difficult to predict. It also potentially enables pollutants such as NO_3 to accumulate for extended periods, and the uppermost few metres act “as a buffer” (Zaidman et al., 1999), storing solutes in the matrix until winter rainfall initiates recharge (e.g. Foster and Smith-Carington, 1980). Leaching occurs once the water-retention or field capacity of soils are reached in Autumn, and it does not cease until the soils begin to dry out in the Spring (Powlson, 1993).

The increasing NO_3 concentration in the Chalk groundwater is due to the high specific retention of the chalk matrix and thickness of the unsaturated zone (Wang et al., 2012). Chilton et al. (1997) quoted a rate of increase in NO_3 concentration since 1980 of 0.05 mg/L per year (Gale and Rutter, 2006). Rather than changes to land use, Chilton and his colleagues stated that greater abstraction had led to increased drawdown, resulting in NO_3 being held for an increased period in the vadose zone. This hypothesis is supported by Lawrence et al (1983) who found that NO_3 concentrations were “notably higher” in pore water in the vadose zone than the groundwater.

On the chalk in northern France total NO_3 concentrations have been shown to decrease in the direction of groundwater flow at the boundary between confined and unconfined zones. This is in conjunction with an increase in $\delta^{15}N$ in the remaining NO_3 and Mariotti et al. (1988) concluded this was a result of denitrification. An alternative hypothesis is that the decrease in NO_3 concentration and increase of $\delta^{15}N$ is due to mixing between old, confined water from before intensive agriculture and new water affected by modern agrichemicals (Howard, 1985). Dilution, assimilation by deep-rooted vegetation or bacterial immobilisation may also contribute (Mariotti et al., 1988). $\delta^{15}N$ alone may not be enough to differentiate denitrification from modern and old, confined waters mixing, however analysing $\delta^{18}O$ as well helps to constrain possible conclusions (Böttcher et al., 1990).

2.7.5 Chalk hydrochemistry

Chalk groundwater tends to have specific electrical conductivity (SEC) of approximately 700 µS/cm, and a pH of 7-7.5 (Gale and Rutter, 2006). pH tends to be lower in confined areas, with redox reactions dominating (Elliot et al., 2001). The groundwater is typically dominated by HCO_3 and Ca, but Quaternary cover affects the concentrations of other major ions (Gale and Rutter, 2006). Fresh Chalk groundwaters tend to have total dissolved solids (TDS) of less than 700 mg/L and Cl of less than 40 mg/L. Groundwaters with concentrations over 40 mg/L are likely to have contributions from seawater. Additional Cl is unlikely be from connate water, as higher Li concentrations would be expected, as reported in Southern English connate Chalk groundwater (Elliot et al., 2001).

2.8 River Terrace Gravels geology and hydrogeology

The RTG are far less researched than Chalk aquifers due to their local importance as compared to the national strategic importance of the Chalk. As the Medway RTG catchment investigated in this work is a source within the South East Water supply area, much available knowledge was sought for their purposes and is thus confined to their specific focus area, and more localised than for the Chalk. Much of this local information is included in Section 3.1.3, for consistency.

The River Medway is thought to have developed following uplift in the Palaeogene that led to the Weald anticlinorium (Bridgland, 2003). As the region was not exposed to glaciation in the Quaternary, the terraces are reported to be well-preserved and stratified e.g. Foster and Topley (1865). The RTG formed due to alluvial deposition on the floodplains of the Medway, which consist of broad meadows around Tonbridge (Foster and Topley, 1865). The RTG is underlain by 3 to 4 m of heterogeneous Quaternary Alluvium Deposits comprised of clay, silt, sand and gravels. These overlie Alluvial, sub-alluvial River Terrace Sands and Gravels, which generally consist of well graded sand and gravel (Howe et al 2017). The bedrock is Lower Cretaceous Weald Clay, an aquiclude approximately 240 m thick (Howe et al 2017). It is comprised of shales and mudstones, fine to medium-grain sandstones, limestones with shells, and clay ironstones. A fine to medium grain sandstone, Tunbridge Wells Sand, underlies the Weald Clay. Siltstone, fine mudstone and thin limestone are also present.

Groundwater in the aquifer likely has a short average residence time (approx. 30-40 days; D. Wilkinson, 2018, personal communication; 11 July 2018) in comparison to the Chalk, as a consequence of the RTG being a thin aquifer, of small area and high abstraction, which contrasts with the long residence time Chalk that has otherwise been the focus of this thesis. The RTG aquifer has granular flow (discussed further in Section 2.9.1), unlike the Chalk, which is considered dual porosity. These differences make RTG a useful tool for comparing groundwater NO_3 concentrations and isotope data with those for the

Chalk, thereby enabling greater understanding of the processes affecting NO_3 in groundwaters.

2.9 Potential conceptual flow models

To understand how solutes move within the unsaturated zone to the water table, which marks the top of the saturated zone, conceptual models of water movement must first be developed and understood. The simplest model of water and solute transport in the unsaturated zone is piston flow via the intergranular pore space, whereby water entering from the surface pushes existing water ahead, through the rock matrix, and deeper beneath the ground. In this event, water moves through the unsaturated zone in a uniform manner with little mixing or dispersion of solutes. In karstic systems, groundwater may primarily be transported via fractures. Transport via this mechanism is generally much faster and can lead to very fast passage of water to the aquifer, bypassing the matrix. Any solutes within the water can therefore potentially travel from the surface to the saturated zone (aquifer) relatively quickly.

2.9.1 A potential conceptual flow model for River Terrace Gravels aquifers

The River Terrace Gravels (RTG) is an aquifer of local importance due to its high storage capacity, but is not considered a nationally-significant aquifer and therefore it has been less extensively researched than major aquifers. It is likely to have primarily matrix flow, a thin unsaturated zone where unconfined and a residence time in the order of weeks thanks to high permeability. In a system with classic matrix flow, water may first enter the unsaturated zone as rainfall, typically with very low SEC (<50 µS/cm). In the case of the RTG water from the River Medway may also recharge the Gravels where confining Alluvial clay deposits are absent; typically these deposits are 3-4 m thick (more details in Section 6.7). SEC of river waters are likely to be an order of magnitude or two higher than rainwater, and where there is connection between the river and the aquifer, they are likely to have similar hydrochemistry and the aquifer is likely vulnerable to any pollutants in the river water. There is a dense network of streams and irrigation channels that may also interact with the aquifer (Howe et al., 2017). The Gravels may also be fed by underlying bedrock, Tunbridge Wells Sands, where the Lower Cretaceous Weald Clay aquiclude is not present.

The unsaturated zone is comprised of soil, intermediate and capillary zones and its voids are filled with air and water. When water enters in the soil zone, its SEC increases due to dissolution of solutes that have been applied to, or naturally occur in the soil. Some ions and molecules are highly vulnerable to dissolution in water, such as NO_3, whereas others such as NH_4, more strongly sorb to soil particles. In summer, water is unlikely to travel further into the unsaturated zone due to evapotranspiration, but as the recharge season begins the soil becomes saturated and water can travel below the soil-water zone and into the intermediate zone. For the RTG, it is possible that the root zone may extend directly into the water table in places, so typical soil zone behaviours may be absent. In the intermediate zone capillary and hygroscopic action is present, but surfeit water moves downwards due to gravity into the capillary zone (Todd, 1980). The depth of the capillary zone is inversely proportional to pore size, due to capillary rise; it is effectively saturated due to the capillary effect but it is at less than atmospheric pressure. At the lower limit of the capillary zone is the saturated zone, where water fills all voids.

2.9.2 Potential conceptual flow models for Chalk aquifers

The Chalk is a more complex picture than the RTG and the significance of matrix flow versus other mechanisms has been extensively researched. Following thermonuclear experiments carried out in the mid-1960s, tritium has been used as an environmental tracer. Smith et al. (1970) and Smith and Richards (1972) interpreted that the slow downwards movement of tritium through the Chalk unsaturated zone was due to tritium being transported via matrix flow. Foster (1975) felt that fracture flow may also occur, but that tritium movement was impeded by exchange with fracture water. Darling and Bath (1988) used stable isotope analysis of H and O in water to show water movement on Chalk in Southern England could be “adequately” described by piston flow through the matrix. However, a more complex model was needed to describe a Cambridgeshire Chalk site as annual infiltration from rainfall did not equate to the vertical movement predicted by matrix tritium concentrations, implying a fracture flow component. Variation in flow mechanisms between the two sites were largely attributed to variations in matrix hydraulic conductivity. Similarly, although Barraclough et al. (1994) reported that tracer recovery showed no evidence for bypass flow in the Upper Chalk in Berkshire, England, a “blurring of deuterium signals” implied otherwise, i.e. that there was indeed a fracture flow component. Solutes may not have clear signals, however, as dispersion may be influenced by evapotranspiration in the top 5 m in summer (Wellings and Bell, 1982), and in autumn water may be drawn into the matrix to correct the summer deficit (Foster and Smith-Carington, 1980). Once in the matrix, solutes may not enter more mobile groundwater for a substantial period. This behaviour has been demonstrated by observing tritium concentrations (Geake and Foster, 1989).

Geake and Foster (1989) accepted dual porosity effects (i.e. component of fracture flow) were present for Chalk sites in Cambridge, Dorset and Norfolk. Although matrix porosity was high (0.25-0.45), effective porosity was low, leading to low matrix hydraulic conductivity at less than 5 x 10^{-3}/day (Geake and Foster, 1989). They concluded that while Chalk relies on fractures, fissures or discontinuities for transport through the unsaturated zone, and that molecular diffusion of NO_3 between fractures and matrix is a feasible explanation for slow solute transport evidenced from matrix pore fluid samples. Such exchange is only likely where there is low velocity fracture flow, i.e. where fractures are very small and where the solute has a “high coefficient of aqueous self-diffusion,” allowing the solute to diffuse easily within the water. Under other conditions (where large fractures are active under recharge conditions) water may flow too fast to allow such diffusion to occur. This implies that the dominant flow mechanism varies over the course of the year.

Flow mechanisms also vary depending on the local geology e.g. the Upper Chalk sampled by Wellings and Cooper (1983) had mostly matrix flow in the unsaturated zone, whereas the Middle Chalk they sampled showed mostly flow via fractures. Where Chalk matrix porosity and hydraulic conductivity is relatively high water movement is more likely to be mostly via the matrix (Geake and Foster, 1989). Mechanisms can also change with depth as surface processes may only affect the top few metres and fractures often narrow at depth.

Allshorn et al. (2007) found evidence for rapid bypass flow via the unsaturated zone of the Northern Province Chalk in Yorkshire from quantitative tracer tests from the base of the soil to an underground tunnel at 20-45 m depth using fluorescent dyes: minimum solute velocities of 9.5-19 m/day were recorded in the vadose zone, far greater than the maximum matrix flow velocity of 0.5 m/year that Barraclough et al. (1994) reported for a Southern Province Chalk site. Allshorn modelled fracture flow using the approach of Barker and Foster (1981) and found smaller fractures (apertures 0.3 and 1 mm) led to greater tracer attenuation via diffusion of solute into the matrix, than large fractures (apertures 2.5 and 5 mm), i.e. solutes have a greater opportunity to diffuse into the matrix from smaller fractures than larger ones. Allshorn’s data may also indicate that pipe flow occurs, possibly through channels along fractures widened by dissolution (some of the tracer receptor points in the tunnel emerged at such features). Keim et al. (2012) reached a similar conclusion as modelling of an agricultural site in the Yorkshire Wolds using the HYDRUS model suggested little flow may occur via the Chalk matrix and fracture or channel flow could be the primary conduit of water to the aquifer.

2.10 Summary of a literature review exploring nitrate, and the geology and hydrogeology of the study catchments

As a limiting nutrient, N must be applied to fields to obtain the crop yields growing populations require. The purpose of NO_3 application is for N to become assimilated into the crop, however much is lost from the soil via leaching. A low concentration of NO_3 in the soil occurs via natural fixation, however humans have been introducing greater concentrations into the environment since the discovery of the Haber Bosch process. Where it infiltrates into waterbodies NO_3 is linked to environmental problems, such as eutrophication, and health risks, including methaemoglobinaemia. Due to the potential risk to health, WHO guidelines state that a maximum of 50 mg/L NO_3 is acceptable in drinking water; this has been adopted into UK law. In 2007, Stuart reported concentrations were still increasing in some regions. NO_3 is particularly soluble in water and therefore highly vulnerable to leaching out of the soil and into groundwater, particularly during recharge season. Groundwater vulnerability to NO_3 and other pollutants is, however, affected by geology: a confined aquifer receives some protection, while a highly fractured unsaturated zone may fast-track pollutants to the water table, with little opportunity for mitigation or attenuation.

Isotope analysis of NO_3-N has been applied to estimate NO_3 sources since the 1970s (e.g. Kohl et al. 1971), however, using O isotopes in conjunction with the N enables differentiation between atmospheric NO_3 and several other NO_3 sources. A fingerprinting diagram to aid source identification was created by

Kendall (1998) and developed by Xue et al. (2009) and Nestler et al. (2011). The authors stated that the diagram cannot distinguish nitrate that has undergone transformations, which potentially limits its applicability to groundwaters with long residence times. Understanding key processes of the N cycle is thus vital in identifying potential transformations. Careful interpretation of data is key: Kendall and Caldwell (1998) stated that isotope analysis should be used in conjunction with additional data e.g. physiochemical analysis, and an understanding of the watershed.

This chapter has highlighted the key processes and reservoirs in the N cycle that are likely to affect the geologies explored in this thesis. Volatilisation is likely responsible for NH_3 losses from soils, leaving a glut of heavy N in the soil, while assimilation and nitrification also likely have considerable effects on N and O isotopic ratios. Denitrification is expected to have a minimal role given it requires low-O or anoxic conditions, however it can be represented within the dual isotope fingerprinting diagram where necessary.

Chapter 3 Methodology for assessing nitrate sources and processes

3.1 Groundwater sampling procedure

Samples were collected from pumped and observation boreholes, and from springs over a hydrological year. Collection was carried out by the Environment Agency (EA) and South East Water (SEW). Sampling methods varied according to sample type. Pumped boreholes should ideally be purged and the sample taken directly from the rising main, but where this is not possible, for instance on private farm sites, samples should be collected from a freshly filled header tank. Bailers were used to sample from springs, and often from observation boreholes, as the depth to the unsaturated zone frequently made pumping infeasible. Samples were analysed for major ion concentrations and the stable isotope composition of the nitrogen and oxygen in nitrate. Samples were typically filtered on collection, stored in two 500 mL polyethylene terephthalate bottles and frozen on return from the field.

3.1.1 Northern Chalk study catchments

3.1.1.1 Geology of the Kilham and Haisthorpe catchments

The Kilham and Haisthorpe catchments are on the Northern Province Cretaceous Chalk in the Yorkshire Wolds. At Kilham, the Flamborough Formation crops out, flanked to the west by Burnham Formation. To the south-east, the Flamborough slopes gently towards the coast, and is covered with impermeable superficial deposits of boulder clay and chalky gravel deposited during the Quaternary. To the north, near Kilham these are around 10 m deep and increase to over 20 m at the most southern edge of the Hull Valley (Gale and Rutter, 2006). Although not currently well defined, a network of buried channels exist in the Chalk beneath and infilled by Quaternary deposits, possibly a result of interglacial processes or subaerial erosion. In addition, these surface layers of Chalk have been subject to cryoturbation, solifluction and modern weathering resulting in extensive fragmentation and development of secondary porosity; in the extreme the Chalk has been reduced to a putty-like material with no structure and reduced permeability (Younger, 1989).

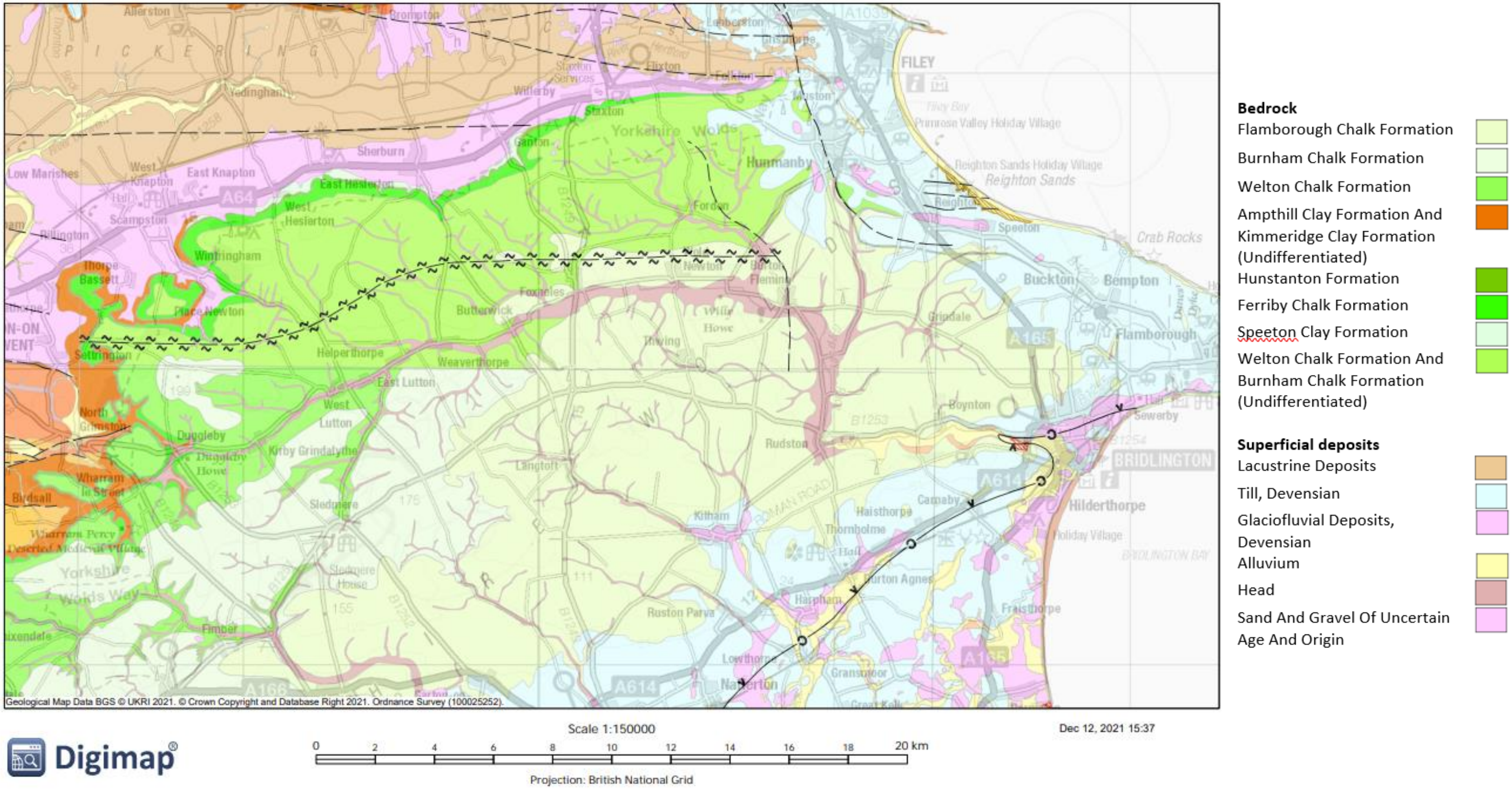

Figure 3.1: Bedrock and superficial geology of the Yorkshire Wolds. Geological Map Data BGS © UKRI 2021. © Crown Copyright and Database Right 2021. Ordnance Survey (100025252).

3.1.1.2 Hydrogeology of the Kilham and Haisthorpe catchments

In the Yorkshire Wolds surface waters are uncommon, with the Gypsey Race being an exception (Hayfield and Wagner, 1995). Once perennial (Dakyns and Fox-Strangways, 1885), the Gypsey Race is now a winterbourne stream (Hayfield and Wagner, 1995). The water table largely mimics the surface topography, dividing either side of the peak of the Chalk escarpment, with springs developing where the base of the Wolds slopes meet the confining Quaternary superficial deposits of the Hull Valley. North and west of these superficial deposits, the aquifer is unconfined, thus the Kilham and Haisthorpe catchments are predominantly unconfined. The unsaturated zone is over 120 m thick on the escarpment, while it is typically less than 10 m in valleys (Gale and Rutter, 2006). In the unconfined zone hydraulic head is subject to a seasonal variation of up to 30 m, whereas such variability has not been observed in the confined zone. A "consistent" hydraulic gradient has been described from the escarpment to the coast at Flamborough suggesting that at least a proportion of groundwater discharges into the sea (Foster and Milton, 1976 in Gale and Rutter, 2006).

The Chalk has dual porosity, which in the Yorkshire Wolds results in highly varied transmissivity of approx. 1250 m^2/day (geometric mean) and a range 1-10000 m^2/day, (Gale and Rutter, 2006). The bulk of flow occurs through fractures within 40 m of the water table, which likely developed due to dissolution during the Holocene (Gale and Rutter, 2006). Tracer tests have shown that surface water is able to travel quickly to the aquifer via such fractures (Zaidman et al., 1999); velocities were too high for matrix alone to be responsible (Allshorn et al., 2007). At Etton pumping station, approximately 20 km south west of the study catchments, transmissivity was found to vary between 1000 m^2/day and 2200 m^2/day during pumping tests with just a 7 m change in groundwater level during abstraction (Gale and Rutter, 2006). This demonstrates that there are preferential, highly weathered, horizons, which are responsible for much of the transmissivity.

The porosity of the Chalk in the Yorkshire Wolds has been shown to decrease with depth from a mean of 35.4% in the Flamborough/Burnham Chalk to 20.6% in the Ferriby formation (Gale and Rutter, 2006). This pattern is a consequence of diagenetic processes, including solution transfer diagenesis and mechanical compaction, acting upon varying grain size and composition (Bloomfield, 1997).

3.1.1.3 Groundwater vulnerability in the Kilham and Haisthorpe catchments

The Northern Chalk is unconfined across the Wolds, but is confined by impermeable Quaternary superficial deposits in the east of the Haisthorpe catchments, providing partial protection from surface pollution. The artesian regions, e.g. around Kilham, also show some resilience to pollutants due to the upward flow of groundwater, however abstraction in this area may reverse the movement of groundwater, potentially enabling recharge and the drawing in of pollutants (Gale and Rutter, 2006).

On the Yorkshire Wolds the soil is permeable and thin, and so is highly susceptible to NO_3 (Holman et al., 2005). The ability of the soil to retain NO_3 is key to assessing the concentration of NO_3 that will be available for transportation to the vadose zone and groundwater. The Wolds are dominated by two soil types: lithomorphic in the steeper regions and brown calcareous in the shallower eastern areas. Clay and sand deposits on dip slopes can slow drainage (Smedley et al., 2004). The Yorkshire Wolds are dominated by arable agriculture, and intensive pig and poultry farming are common, so the high penetrability of the region to pollutants such as NO_3, is of particular concern. Thin and permeable soils have a limited ability to retain NO_3 so during recharge NO_3 passes below the zone of influence for roots and into the unsaturated zone. The aquifer is particularly vulnerable to pollutants from the surface due to the thick and highly fractured unsaturated zone: tracer tests have identified rapid bypass flow which can fast-track solutes to the saturated zone (Zaidman et al., 1999). Zaidman et al. (op. cit.) also observed that the matrix at experimental field sites remained saturated for the majority of the year, as has been reported previously e.g. (Foster and Smith-Carington, 1980).

According to Knapp (2005), of 218 groundwater sources utilised by Yorkshire Water, 137 have been shut since the 1970s. Although some closures were a result of decreased yield, or unacceptable water quality in terms of mineral content, around 40% were due to human activities including fertilisers, pesticides and hydrocarbons. The Nitrate Vulnerable Zone (NVZ) scheme that the Kilham catchment currently falls into is part of the Nitrate Sensitive Area (NSA) strategy; however the NVZ provides less stringent guidelines than the NSAs, which tend to apply to much smaller scale, such as a single farm. NVZs restrict the times at which fertilizers can be applied, in addition to limiting where organic manure can be stored and when it can be spread on the land.

Opportunities for NO_3 attenuation are understood to be limited as denitrification is not anticipated to occur in significant amounts in the Chalk groundwater in Yorkshire as it is understood to remain oxic, nevertheless the possible presence of a 2.1:1 of $\delta^{15}N$ to $\delta^{18}O$ signal will be monitored for, as this trend has been shown to signify denitrification is occurring (Böttcher et al., 1990).

3.1.1.4 Descriptions of the Kilham and Haisthorpe catchments on the Northern Province Chalk

The catchments monitored are largely within safeguard zones (SgZs)[1] on the Northern Province Cretaceous Chalk on the Yorkshire Wolds in North Eastern England. Groundwater in the SgZs flows from the top of the escarpment in a south easterly direction to feed four pumping stations at Kilham, Haisthorpe, Bridlington and Burton Agnes (Figure 3.2, Figure 3.3). They are dominated by agricultural activities including arable and livestock (primarily pigs and chickens) and therefore inorganic fertiliser and manures are likely to represent the primary NO_3 sources in groundwater. Other possible sources could include leaking septic tanks, wastewater treatment works and atmospheric pollution.

The sites consisted of five Yorkshire Water drinking water abstraction sites, one wastewater treatment works and 24 privately or Environment Agency owned boreholes that included 18 farms, one at the roadside, one churchyard, one anaerobic digestion plant, and a brewery (details in Table 3.1). All samples from Haisthorpe, Bridlington and Burton Agnes catchments, hereafter abbreviated to “Haisthorpe” for clarity, were taken from pumped wells, however in the Kilham catchment four sample sites were springs and eight were unpumped observation wells. Throughout this thesis sites will be referenced using the three-letter code

---

[1] SgZs are areas established by the Environment Agency and water companies where extra pollution control measures are necessary to protect public water supplies. They are usually based on Source Protection Zone 2 (SPZ2). SPZs utilise groundwater modelling, with modifications based on local knowledge (Environment Agency, 2019b). SPZ boundaries may change following new information or with groundwater conditions. SPZ2 is the area within which there is a maximum 400 day travel time to the public water source.

that follows the Environment Agency Unique Reference Number in “Site name” column in Table 3.1.

Table 3.1: Sample site details for Kilham, Haisthorpe, Bridlington and Burton Agnes SgZs. The sites are referenced throughout the text using the three-letter code at the end of the full site name. Information regarding superficial deposits obtained from Environment Agency software, Easimap (Environment Agency, 2019a).

Site name	Land use	Date installed	Depth (m)	Notes
400G0115 -**BAR**	Anaerobic digestion plant	-	-	Overlain by superficial deposits (Devensian till)
400G0094 -**BR2**	Public drinking water abstraction	-	-	Long-term monitoring Overlain by superficial deposits (Devensian till)
400G0086 -**BA2**	Public drinking water abstraction	1938	30.8	Long-term monitoring Overlain by Quaternary superficial deposits
400G0117 -**BFG**	Farm	1951	25.25	
400G0090 -**HAC**	Public drinking water abstraction	1955	76.3	Long-term monitoring Overlain by superficial deposits (Devensian till)
400G0091 -**HAE**	Public drinking water abstraction	-	-	Long-term monitoring Overlain by superficial deposits (Devensian till)
400G0116 -**HOF**	Farm	-	-	Overlain by superficial deposits (Holocene, HEAD)
400G0008 -**HUG**	Brewery		129	Long-term monitoring
400G0074 -**MGF**	Arable farm	1951	12.19	Long-term monitoring Overlain by superficial deposits (Holocene, Head)
400G0118 -**SDF**	Farm	c. 1951	17.8	
400G0006 -**WHF**	Farm	30/04/1994	63	Long-term monitoring
400G0119 -**WWF**	Farm	26/05/2008	130	
400G0112 -**WIN**	Near churchyard; possible paddock	Pre-1952	unknown	Observation borehole
BEL	Arable	-	-	Spring South of Kilham catchment
40001257-**BRA**	In buffer zone behind layby	-	-	Spring South of Kilham catchment

Site name	**Land use**	**Date installed**	**Depth (m)**	**Notes**
400F0012 -**BRO**	Possible chicken farm	1978?	85 m	Fracture close to surface?
400G0082 -**DOF**	Pig farm	Unknown	70 m	
400G0110 -**FWF**	Intensive poultry farm	2010s	unknown	Newly dug
400G0093 -**KIL**	Public drinking water abstraction	Unknown	unknown	
400F0018 -**KOB**	Roadside, next to arable	c. May/Jun 1979	20 m	Observation borehole
49200297-**KSS**	Residential	-	-	Spring
49200298-**KSP**	Duck pond, residential	-	-	Spring
400G0027 -**MHF**	Mixed farm	07/10/1984	50 m	Private abstraction Water struck at 30 m; transmissivity=429m^2/day (middle) T=1262m^2/day (late)
400G0109 -**MOF**	Intensive poultry farm	Unknown	90 m	
400G0107 -**OCG**	Arable farm	pre-Oct 1951	23.55 m	In 1951, pump was disused
400G0108 -**ROO**	Farm	-	-	
400G0106 -**SHW**	Farm	12/09/1984	100 m	"Water strike at 91 m"
400G0023 -**SWA**	Arable farm	05/11/1996	130 m	Private abstraction "major fissure at 125 m"
400G0105 -**WEA**	Roadside, next to arable	13/01/1971	45.72 m	Observation borehole “Good return of water” at 29.0-31.7 m
400G0072 -**WES**	Arable	20/06/1980	65 m	Observation borehole "Fissure zone at 59.8 m" "water apparent by 35.0 m"
40000399-**KWT**	Waste water treatment works	Unknown	unknown	Observation borehole
400G0022 -**PTH**	Mixed farming	Pre-Oct 83	90 m	Private abstraction

In the Haisthorpe catchments, samples were collected for dual stable isotope analysis in November 2017, February or March 2018, and November 2018, which took place at the University of East Anglia via the denitrification method (Sigman et al., 2001, Casciotti et al., 2002). In the Kilham catchment samples for isotopic analysis were collected every two months, resulting in five samples per site, and analysed by the University of Leeds via the acetone dissolution method (Huber et al., 2011).

Hydrographs analysed by Agbotui (2019) showed the Chalk in the Kilham catchment to be highly transmissive, as only the observation borehole directly adjacent to Kilham pumping station responds to abstraction. Tracer tests have been carried out in the Kilham catchment, revealing high groundwater flow velocities and complex hydrogeological conditions (Ward et al., 1998). Bacteriophage tracers injected upgradient of Kilham pumping station were not identified at Kilham, despite being observed at a shallow downgradient borehole on a near straight line between Kilham and the injection site. This implies that flow paths in the catchment are complex. Single borehole tests supported the theory of a complex fracture network, showing that while most local boreholes have a single flow horizon, it is not always a shared horizon (assuming a 2.2° dip to the South-East).

Ward et al. (1998) suggested that there is a fault perpendicular to the Langtoft valley (6 km north-west of, and up the hydraulic gradient from, Kilham), resulting in a discontinuity in the bed where the majority of groundwater flow occurs. The effect on flow is not clear, but it is a potential barrier to flow. This work was developed by Agbotui (2019) and Agbotui et al. (2020), who confirmed the presence of discrete flow horizons, largely close to the water table, reducing in frequency with depth. Permeability also reduced with depth, suggesting slower flow at depth results in less extensive fractures.

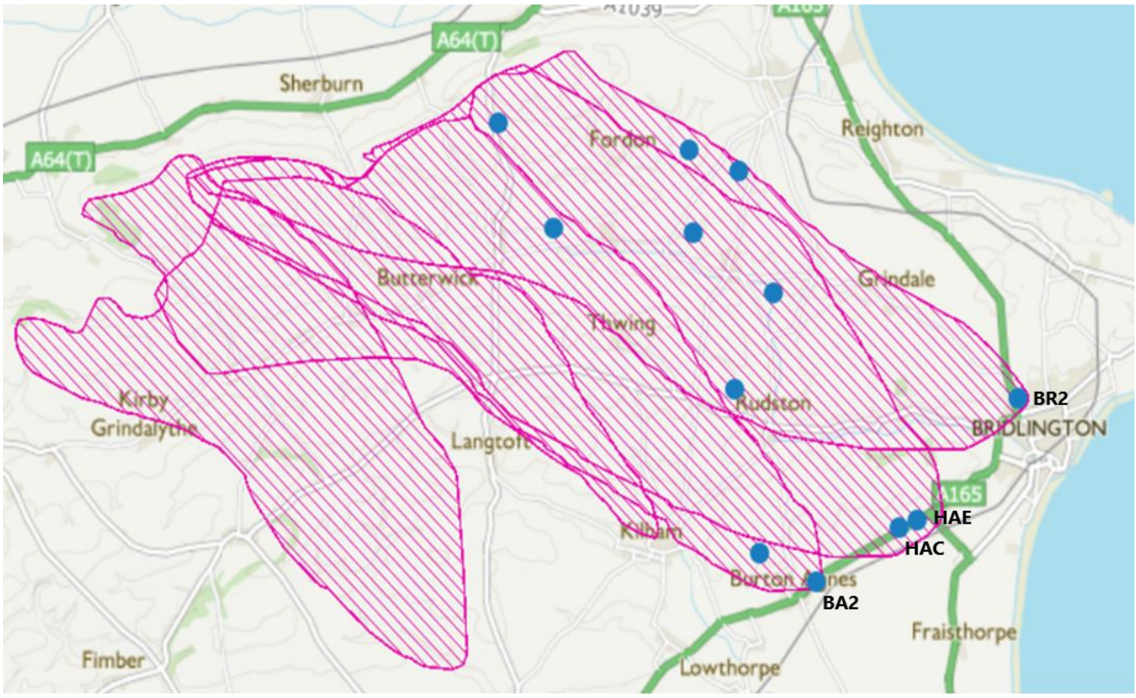

Figure 3.2: Map of sites sampled in Haisthorpe, Bridlington and Burton Agnes, hereafter collectively "Haisthorpe", catchments (blue points) and SgZs (pink polygons). Public abstraction wells associated with each SgZ are labelled with their three letter code. BA2=Burton Agnes SgZ, HAC and HAE=Haisthorpe, BR2=Bridlington.

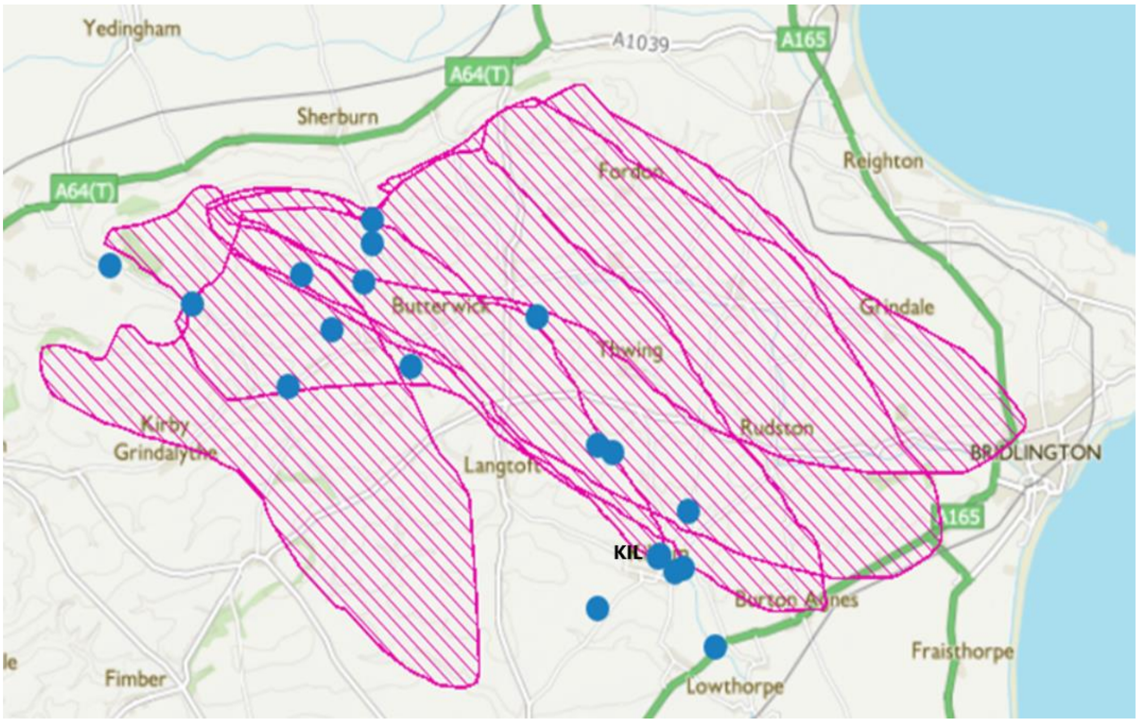

Figure 3.3: Map of sites sampled in Kilham catchment (blue points) and SgZs (pink polygons). The public abstraction well at Kilham is labelled with the three letter code KIL.

3.1.2 Southern Chalk study catchment

3.1.2.1 Geology of the Woodgarston catchment

The Hampshire basin, where the Woodgarston catchment is located, was affected by Alpine tectonics and therefore has a more complex structure than the Northern Province Chalk introduced in the previous section (Thomas, 1961). In Hampshire the beds traditionally defined as the Upper Chalk crop out and the stratigraphic thickness is up to 400 m, but typically in areas of outcrop substantial parts are lost to erosion (Wilkinson et al., 2017). The formation contains large folds and faults, within the greater anticlinal structure. The Chalk beds dip to the South of the fold-axis through Hampshire under Palaeogene cover, and to the North of the fold-axis into the London Basin (Allen and Crane, 2019). The region was never glaciated, however it was affected by periglaciation. The Hampshire basin is typical of Chalk downland in that it has steep escarpments and gentle dip slopes, with seasonal streams and dry valleys containing alluvium (Allen et al., 1997).

3.1.2.2 Hydrogeology of the Woodgarston catchment

In Hampshire, the Candover catchment matrix hydraulic conductivity was found to be a couple of orders of magnitude smaller than borehole packer tests, and Southern Water Authority identified that the highly permeable zones were at fractures (Allen et al., 1997). In Hampshire, transmissivity can range from 0.55 to 29,000 m^2/day, and results may be skewed as high-yield sites were tested to inform river augmentation projects, however 1000 m^2/d is thought to be common in valleys (Allen et al., 1997). High transmissivities are most likely in the Upper Chalk, and in valleys more so than interfluves due to its extensive fracturing (Allen et al., 1997, Allen and Crane, 2019). Boreholes drilled in valleys typically have more consistent yields than those on interfluves, demonstrating that local topography has an effect on transmissivity and storage co-efficient (Allen et al., 1997). In regions confined by Palaeogene cover the aquifer has a storage coefficient of as low as $7x10^{-5}$, whereas specific yield in the unconfined areas can be as high as 0.06 (Allen et al., 1997). Marl and flint beds enable dissolution to occur, creating flow horizons. Accordingly, the majority of flow has been found to occur in uppermost 30 m of Chalk in Alresford, Hampshire (Headworth, 1978, Allen et al., 1997). This is a similar variation with depth as observed on the Northern Province Chalk, in addition to deeper horizons e.g. Agbotui (2019). Southern Water Authority (1979) found the marls at the top of the Middle Chalk tend to give the formation lower permeability. However, in the Alre catchment substantial fracture flow has been observed in the Middle Chalk. Boreholes in the Lower Chalk tend to have low specific capacity due to a lack of dissolution and frequent marl (Allen et al., 1997). Transmissivity values of less than 500 m^2/day are common on the Lower Chalk (Stuart and Smedley, 2009). Giles and Lowings, 1990, believed the units were not connected, however the two are now considered to be in hydraulic connectivity in some locations (Allen and Crane, 2019). In the south-east of the Hampshire Basin the Upper Greensand is subject to abstraction (Stuart and Smedley, 2009).

Beneath the zone of high transmissivity there is some evidence that the rest of the aquifer provides “upwards leakage” (Headworth, 1978). Pumping tests carried out in the Candover catchment suggested that the aquifer was “multi-layered” (Headworth et al., 1982): the top 6 m was highly-transmissive but it overlay Chalk which mostly had low transmissivity and storage capacity. The Alre catchment was however found to have different characteristics to Candover. These differences imply that the region is highly variable, so local investigations may not be reflective of other areas within the Hampshire Chalk.

3.1.2.3 Groundwater vulnerability in the Southern Chalk catchment

The Southern Chalk aquifers are at risk from overexploitation, particularly around London, where the water table dropped up to 70 m following initiation of abstraction (Water Resources Board, 1972). Abstraction reduction schemes have largely mitigated this drop in groundwater level in London, however abstraction is still linked with low river flow in surrounding regions e.g. Chilterns. In addition, future-proofing water supplies is a challenge as Thames Water are reliant on the Chalk aquifer for 90% of their groundwater, populations are anticipated to increase in the South East, and development of new sources is complex. In Hampshire human populations are lower, but resource pressures still exist from neighbouring towns and industry, and water quality is at risk from agricultural activities. The Rivers Test and Itchen are popular for fishing, and therefore baseflow quality and quantity are valued (Stuart and Smedley, 2009).

Vulnerability varies across the Hampshire basin and also with depth. Palaeogene cover is low permeability so where it is thick in the basin recharge may be minimal (Allen and Crane, 2019). At the edge of Palaeogene cover streams run off and continue as surface water before sinking into the unconfined Chalk (MacDonald et al., 1998, Allen and Crane, 2019). Sinkholes and solutionally enhanced features are the consequence of this at the south of the River Itchen catchment. The Lower and Middle Chalks tend to be marlier and are linked with lower transmissivity than the Upper Chalk (Allen and Crane, 2019). The Upper Chalk may also be more likely to develop secondary hydraulic conductivity via fractures than the Lower or Middle Chalks (Entec, 2002 in Allen and Crane, 2019). More highly transmissive zones also exist where the Chalk has been weathered at the palaeo and current water tables (Allen and Crane, 2019).

3.1.2.4 Hydrochemistry of the Southern Chalk

Stuart and Smedley (2009) reported that the Hampshire Basin has groundwater quality typical of Chalk groundwater, dominated by Ca and HCO_3. Hydrochemical changes occur dependant on groundwater residence time. Palaeogene cover gives the confined aquifer water a different composition to unconfined aquifer waters; in the former, concentrations of many ions are relatively high, including magnesium, potassium and sulphate and several minor ions. In addition, 14% of waters in the region contain relatively high concentrations of dissolved sodium due to cation exchange with Ca or Mg for Na (Edmunds et al., 1987). Some mixing is thought to occur between modern water and connate water stored in lower permeability lithologies (Edmunds et al., 1987), which could increase the concentration of Na and Cl ions in the groundwater. Connate water still being present in the deeper Chalk matrix demonstrates how slowly diffusion occurs between fractures and the matrix in some places.

A previous study sampled the Woodgarston water treatment works (WTW), where WPBH1 and WPBH2 are located, and reported NO_3 concentration of 2.48 mg/L NO_3 (0.56 mg/l N NO_3-N)[2] (Elliot et al., 1999). The study also recorded a of

---

[2] In Elliot et al. (1999) data were quoted as being in µmol/L, however it is assumed that this was a mistake and the data are actually in mmol/L, otherwise the data are around 1000 times too small and would be lower than rainfall concentrations. Samples were likely taken in mid-1990s so the data are unlikely to be from historical, less polluted waters.

pH 7.0, 19.1 mg/L Cl, 323.4 mg/L HCO_3, 7.7 mg/L SO_4, 8.5 mg/L Na, 1.6 mg/L K and 117.8 mg/L Ca (Elliot et al., 1999)[3].

3.1.2.5 Description of the Woodgarston catchment on the Southern Province Chalk

Four sites were sampled in the Woodgarston catchment (Table 3.2) to analyse the O and N stable isotopes in NO_3 (acetone dissolution method and dual stable isotope analysis as described in Chapter 3). Two sites are part of the Woodgarston WTW and two are privately owned boreholes. Samples were taken on a quarterly basis from November 2018 until August 2019. Long term hydrochemistry data are available for all four sites from the Environment Agency (Environment Agency, 2020) and unpublished data from South East Water. All four boreholes are pumped, but with varying regularity and therefore each was purged before samples were taken.

Table 3.2: Details of sample sites in the Woodgarston catchment, with date borehole drilled and borehole depth, where known.

Site name	Land use	Date installed	Depth (m)
WMals	Farm	Unknown	Unknown
WPit	Farm	Unknown	Unknown
WPBH1	Public drinking water abstraction	1928	142.5
WPBH2	Public drinking water abstraction	1974	152.4

The Woodgarston catchment is on the northern edge of the Hampshire Basin. It is traditionally agricultural, with few changes other than declining woodland seen since 1877 (Wilkinson et al., 2017). The region is primarily improved grassland for grazing and crops including cereals, oil seed rape, field beans, peas and linseed (Hampshire County Council, 2007). Some pigs and poultry are also reared, and a dairy farm is reported to be 400 m from the Woodgarston WTW (Wilkinson et al., 2017, Stuart and Smedley, 2009). In the valleys there are watercress beds, some abandoned, in addition to water meadows (Stuart and

---

[3] As described in [1] data were reported by Elliot et al., (1999) in µmol/L, however it is assumed that this was a mistake and the data are actually in mmol/L, otherwise the data are around 1000 times too small and would be lower than rainfall concentrations.

Smedley, 2009). In recent years small vineyards have also been planted (Hampshire County Council, 2004).

The Upper Chalk (Newhaven, Seaford, Lewes Nodular Chalk) crops out in the study area, with London Clay and the Bracklesham Group confining the Chalk at the north of the sample sites (Stuart and Smedley, 2009). In the Woodgarston catchment the Chalk is unconfined or peripherally confined as it is on the boundary of the Clay and the Chalk (Allen and Crane, 2019). This makes it more vulnerable to surface pollution than confined regions of the Hampshire Basin (Younger and Elliot, 1995). A section from the Woodgarston WTW showed superficial cover at the site is 11 m thick clay with flint, which thins towards its edges (Wilkinson et al., 2017).

The population in the Hampshire Basin is generally low and the land is largely agricultural, however a wealth of hydrogeological research and river augmentation projects have been carried out, to better understand and supply water to neighbouring urban and industrial areas. Surrounding the Woodgarston catchment, there are the Rivers Test, Itchen and Loddon (Figure 3.4). Flow is largely southwards towards the Itchen and Test rivers (IGS/SWA, 1979), but in North Hampshire, flow is likely northwards towards the Loddon. Contours from IGS/SWA (1979) suggest that groundwater at three sample sites (WPit, WPBH1 and WPBH2) drains into the Loddon, while groundwater at one site, WMals, is on the other side of the groundwater divide and drains into the Itchen and Test. The water table largely follows the surface topography, but with a thicker unsaturated zone beneath hills than valleys (Allen and Crane, 2019). The Woodgarston catchment is largely unconfined and Palaeogene deposits are patchy, so specific yields at the higher end of the range are more likely applicable.

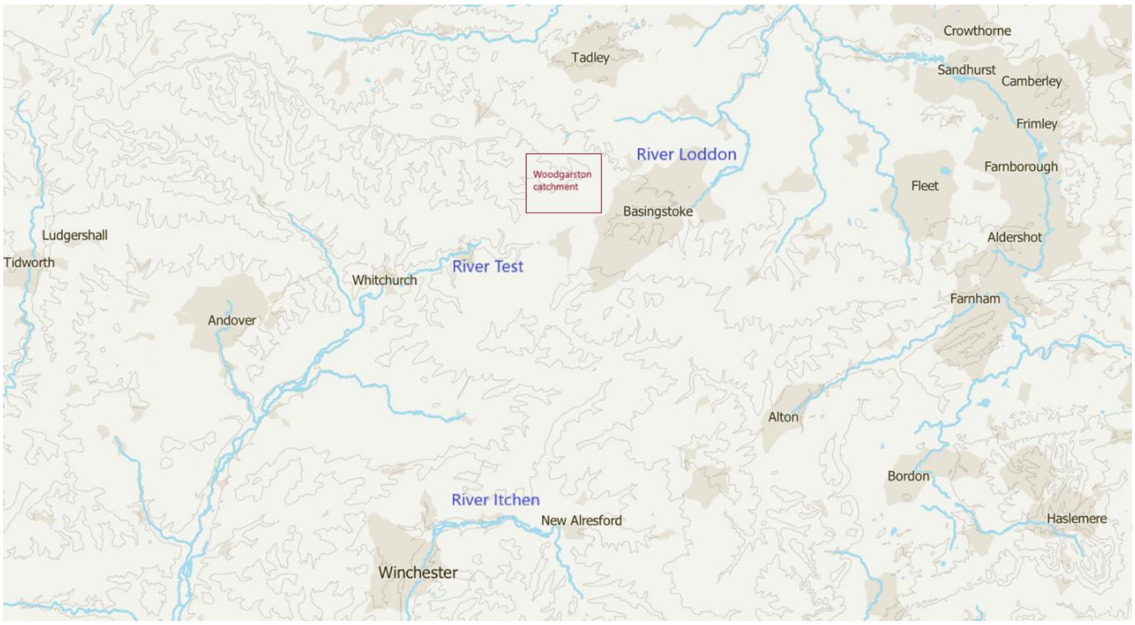

Figure 3.4: Approximate location of Woodgarston, including the three rivers that drain the catchment: the Itchen, Loddon and Test. The red box marks the approximate location of the four study boreholes.

South East Water report that the water treatment works (WTW) at Woodgarston is near the watershed, and groundwater divide, between the River Test and Itchen catchments, and River Loddon catchment (Wilkinson et al., 2017). Groundwater is understood to flow from north-west to south-east across the region. The two production boreholes sampled in this study abstract from the Upper Chalk (geology described in Table 2.1). Long term data demonstrated a link between abstraction and groundwater levels, in addition to rainfall and groundwater levels with one to two month delay. Groundwater levels at Woodgarston tend to peak in March or April, as is typical of a Chalk aquifer (Wilkinson et al., 2017).

At Woodgarston WTW South East Water already resort to blending water to mitigate for high NO_3 concentrations: 20-50% of borehole samples are over the legal drinking water limit or Prescribed Concentration or Value (PCV) (Wilkinson et al., 2017). According to Water Framework Directive standards (European Commission, 2000a) the groundwater hydrochemistry of the nearby Rivers Itchen and Test catchments is considered to be poor due to high NO_3 (Stuart and Smedley, 2009). Woodgarston WTW is on an interfluve north of the River Test and WPBH1 and 2 are production boreholes contained within it. A Source Protection Zone (SPZ; described in Section 3.1.1.2) has been defined for the WTW (Figure 3.5). The direction of groundwater flow through the SPZ is from south west to north east. Although private abstraction boreholes, WMals and WPit, are slightly outside SPZ3 (zone within which all groundwater recharge is presumed to discharge at abstraction site), they are close to the boundary of the steady state SPZ[4] (Figure 3.5). WPBH1 has not been used for abstraction since 2010 due to its high NO_3 concentrations; it first breached the PCV in May 2007. It is now only run for 15-30 minute intervals to enable water quality samples to be taken.

There are various potential nitrogen sources nearby, primarily agricultural. There are two known dairy farms within 1 km of the WTW, one of which contains an in-use clay-lined slurry pit. Wilkinson et al. (2017) stated that the pit was not compliant with Nitrate Vulnerable Zone (NVZ) regulations, but improvements have been made. Manure heaps are also present at least at one site, and leaching is possible via adjacent road drains. Potential diffuse NO_3 sources include general use of artificial fertilisers and manure spreading. Non-agricultural sources include a small amount of septic tank discharge (Wilkinson et al., 2017).

---

[4] A steady state SPZ assumes no changes to hydrogeological conditions, however these change seasonally. Under some conditions all or most groundwater from WMals and WPit may discharge at WPBH1 and WPBH2.

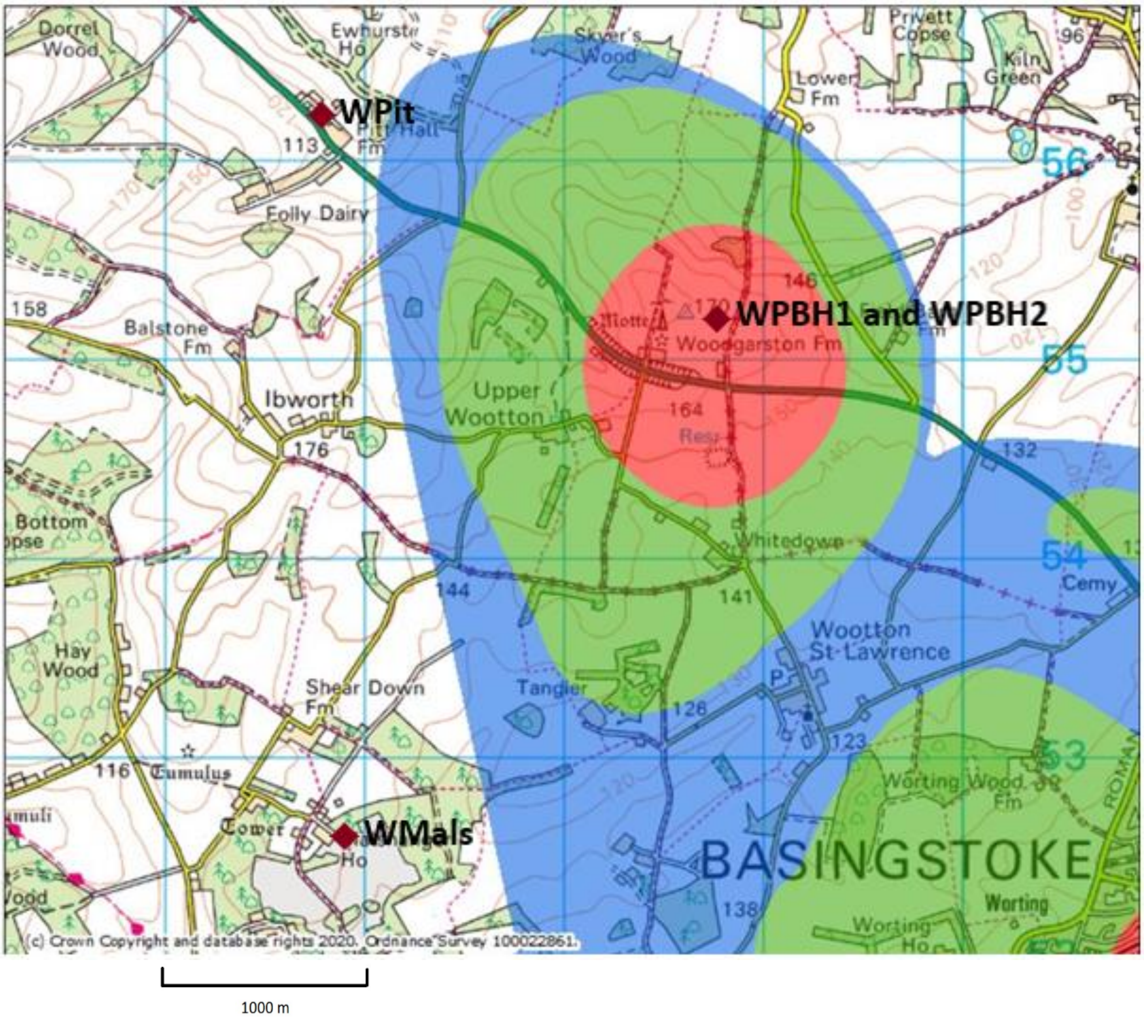

Figure 3.5: Groundwater Source Protection Zones (SPZ) for the Woodgarston WTW. Red = SPZ1 (50 day travel time to abstraction site), Green = SPZ2 (400 day travel time to abstraction site), Blue = SPZ 3 (zone within which all groundwater recharge is presumed to discharge at the abstraction site.) (DEFRA Magic Map; contains Ordnance Survey data.)

3.1.3 The Medway River Terrace Gravels catchment

While the Chalk aquifers are of nationally strategic importance for UK drinking water supplies, the Medway River Terrace Gravels (RTG) are considered locally important. This means that the RTG are less extensively researched than the Chalk and information is less readily available.

3.1.3.1 Geology of the River Terrace Gravels catchment

The Hartlake catchment on the River Medway in Kent (Figure 3.6) is underlain by floodplain deposits that accumulated during the Quaternary period, firstly by 3 to 4 m of heterogeneous Quaternary Alluvium Deposits consisting of clay, silt, sand and gravels. These overlie Alluvial, sub-alluvial River Terrace Sands and Gravels, which generally consist of well graded sand and gravel (Howe et al 2017).

The bedrock is Lower Cretaceous Weald Clay, an aquiclude approximately 240 m thick (Howe et al 2017). It is comprised of shales and mudstones, fine to medium-grain sandstones, limestones with shells, and clay ironstones. A fine to medium grain sandstone, Tunbridge Wells Sand, underlies the Weald Clay. Siltstone, fine mudstone and thin limestone are also present in this formation.

Figure 3.6: Location of the Hartlake catchment, both in the UK and on a local scale. Contains OS data © Crown copyright and Database right 2021.

3.1.3.2 Hydrogeology of the Hartlake catchment on the River Terrace Gravels

The Environment Agency defined the RTG as “permeable layers capable of supporting water supplies at a local rather than strategic scale, and in some cases forming an important source of base flow to rivers” (Howe et al., 2017). Hydraulic conductivity was recorded as 1 x 10^{-4} to 1 x 10^{-1} m/sec (Dynamco, 1992 in Howe et al., 2017) and transmissivity was calculated by as ranging from 482 to 994 m^2/day (Howe et al., 2017). RTG aquifers have a large kinematic porosity as compared to the Chalk aquifers; although data are not publicly available for the Hartlake catchment, Birks et al. (2013) estimate a kinematic porosity of 20% for a RTG aquifer in London. Pumping tests were carried out 5 km from Hartlake, at

Tonbridge, from which transmissivity was calculated as 157 m^2/day to 256 m^2/day and storativity as between 2.0×10^{-6} and 4.55×10^{-6}. A storativity of this magnitude implies that the aquifer is confined, otherwise a much larger figure would be observed. The RTG connects with the River Medway in some locations, and therefore the Medway recharges the groundwater under certain conditions, including floods (Howe et al., 2017). Groundwater may also flow from the Tunbridge Wells Sands into the RTG.

As asserted in Section 2.8, groundwater in the RTG aquifer likely has a short average residence time (approx. 30-40 days; D. Wilkinson, 2018, personal communication; 11 July 2018) in comparison to the Chalk, as a consequence of the RTG being a thin aquifer, of small area and high abstraction. This contrasts with the long residence time Chalk that is otherwise the focus of this thesis. The RTG aquifer has granular flow, unlike the Chalk, which is considered dual porosity. These differences make RTG a useful tool for comparing groundwater NO_3 concentrations and isotope data with those for the Chalk, thereby enabling greater understanding of the processes affecting NO_3 in groundwaters.

3.1.3.3 Groundwater vulnerability of the Hartlake catchment on the River Terrace Gravels aquifer

The RTG surrounding the Hartlake catchment are largely agricultural. The lower elevation, wetter fields are primarily used for grazing and the higher, drier, ground is mainly arable with orchards on south-facing slopes (Howe et al., 2017). Groundwater NO_3 sources are therefore likely to include inorganic fertilisers, manure and slurry. To the north west the area becomes more suburban, making sewage and pollution potential NO_3 sources. The area has been quarried for gravel and the resulting pits have been allowed to flood to become lakes. The connectivity of the lakes with the aquifer is unproven, however given the water table is very shallow, it is likely that the lakes and the groundwater are hydraulically connected.

Overlying Alluvium offers some protection to the aquifer against contamination, as it is clayey and silty and therefore not highly permeable. However, the thickness of the Alluvium may vary and therefore permeability across the catchment could fluctuate, meaning it may not serve as an aquitard across the entirety of Hartlake. Soils primarily consist of clay, fine silt and fine loam, with few stones (Howe et al., 2017). South East Water have, however reported high concentrations of Fe and Mn, which imply anoxic conditions may prevail in some locations (Howe et al., 2017).

3.1.3.4 Hartlake catchment site descriptions

Four sites in the Hartlake catchment (Figure 3.7) were sampled quarterly from November 2018 until August 2019 for dual stable isotope analysis as described in Section 3.3.1. In Hartlake abstraction is from the highly permeable and porous RTG and the pumping station is protected by a groundwater SgZ (explanation in Section 3.1.1.4), the boundaries of which are heavily influenced by the presence of the River Medway. Two of the boreholes are pumped for public abstraction, and two are for farm use (Table 3.3); all boreholes were purged prior to sampling. The sites were chosen for analysis as two have very low NO_3 concentrations in comparison to the others. South East Water also provided long term data for Cl and SO_4 concentrations for the two production wells.

In the study catchment the River Terrace Gravels are between 2.5 and 4.8 m thick, and span around 7 km^2 of flood plain (Howe et al., 2017). Unlike other gravels in the region, they are heterogeneous and comprise higher proportions of ironstone and subangular sandstone, in addition to intermittent bands of clay and silt (Dynamco, 1994). As the Hartlake RTG aquifer is covered by thin superficial deposits, a proportion of recharge likely comes from rainfall seepage.

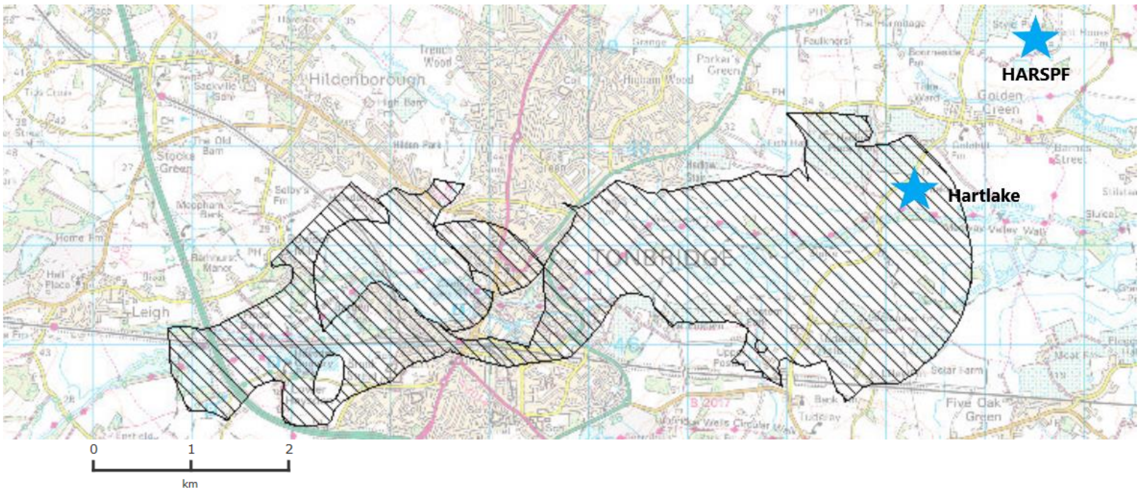

Figure 3.7: Map showing the safeguard zone for Hartlake. The approximate locations of the Hartlake public abstraction and HARSPF are marked with blue stars. Map produced by MAGIC on 14 May, 2021. © Crown Copyright and database rights 2021. Ordnance Survey 100022861.

Table 3.3: Borehole sites sampled in the Hartlake catchment with dates drilled and depth, where known. The total depth of borehole HARSPF is considered "doubtful" in the borehole log; data and descriptions are based on well drilling in 1866.

Site name	Date installed	Depth (m BGL)	Notes
Hartlake production borehole 1 (**HARA**)	1974	5.4	
Hartlake production borehole 3 (**HARC**)	1974	6.6	Refurbished at unknown date
Hartlake observation borehole 1 (**HAROB1**)	Unknown	9	
Hartlake observation borehole 3 (**HAROB3**)	Unknown	9	
HARSPF Private abstraction	1866	253 m claimed pre-1890, but doubtful. 111 m reported in 1964.	Borehole logs BGS ID: 610016 BGS Reference: TQ64NW9 British National Grid (27700) : 564640,149020 Reported artesian once drilled through Grinstead Clay (1964).

Water abstracted from the catchment has been reported to have high concentrations of Mn and Fe, most likely from sandstone and ironstone within the RTG aquifer itself (Howe et al., 2017). Mn and Fe in solution implies anoxic conditions within the soil zone or aquifer as these ions are reduced into solution during anaerobic respiration, but more frequently once NO_3 has already been utilised (DiChristina, 1992, Achtnich et al., 1995).

An additional site, HARSPF (as shown in Figure 3.7), is also included in this chapter as longer-term hydrochemical datasets were available via Environment Agency (2020). Lithology data are summarised in Table 3.4. Although HARSPF is much deeper than the four Hartlake sites, and unconfined, the sites share geology.

Table 3.4: Reported geology at HARSPF (UKRI, 1964). The total depth of the borehole is considered "doubtful" in the borehole log; data and descriptions are based on well drilling in 1866.

Unit name	Thickness (m)	Depth (m)
Palaeogene deposits (RTG)	3.28	3.28
Weald Clay	88.04	91.31
Upper Tunbridge Wells Sand	15.24	106.55
Grinstead Clay	14.94	121.49
Lower Tunbridge Wells Sand	34.14	152.58
Wadhurst	38.71	191.29
Ashdown Beds	61.72	253.01

3.2 Data ownership

Data from various sources are compiled within this thesis, descriptions of which are summarised in Table 3.5.

Dual stable isotope analysis datasets produced for this thesis can be found at https://doi.org/10.5285/aead7506-6523-4b5e-8591-9c895dd03d62, hosted at the National Geoscience Data Centre (NGDC) repository (McSherry, 2022).

Table 3.5: Sources and ownership of data contained within this thesis.

Location	Data description	Sample dates	Analyses undertaken	Methods	Source/Owner
Kilham; occasional Haisthorpe sample	Isotope analyses	11/2015-04/2016; ad hoc sampling until 11/2018	Dual stable isotope analysis of N and O in NO_3	Extraction via acetone dissolution method; analysis via pyrolysis (Section 3.3.1)	University of Leeds, in partnership with Environment Agency
Kilham	Major ion concentrations, pH, SEC	05/2000-02/2019	Ca, Cl, HCO_3, K, Mg, Na, NO_3, SO_4, pH, SEC at 25°C	Various, carried out by external accredited laboratories	Environment Agency, Yorkshire Water
Yorkshire; Driffield, Bridlington, High Mowthorpe	Long-term rainfall	2009-2019	Rainfall gauging at Driffield, Bridlington, High Mowthorpe	Tipping bucket rain gauge with paired storage gauge	Environment Agency
Kilham (KOB, ROO, SHW, WEA, WES)	Groundwater levels	2006-2018	Groundwater levels (mAOD)	Borehole logger or dip meter	Environment Agency
Haisthorpe	Isotope analyses	11/2017-11/2018	Dual stable isotope analysis of N and O in NO_3	Extraction via denitrifier method; analysis via IRMS (Section 3.3.2)	University of East Anglia, on behalf of Environment Agency
Haisthorpe	Major ion concentrations, pH, SEC	11/2000-01/2019	Ca, Cl, HCO_3, K, Mg, Na, NO_3, SO_4, pH, SEC at 25°C	Various, carried out by external accredited laboratory	Environment Agency, Yorkshire Water
Woodgarston	Isotope analyses	11/2018-08/2019	Dual stable isotope analysis of N and O in NO_3	Extraction via acetone dissolution method; analysis via pyrolysis (Section 3.3.1)	University of Leeds, in partnership with South East Water
Woodgarston	Major ion concentrations	01/1997-07/2020	Cl, NH_3, NO_3, SO_4	Various	South East Water

Location	Data description	Sample dates	Analyses undertaken	Methods	Source/Owner
WPit at Woodgarston	Major ion concentrations, pH, SEC	05/2014-11/2019	Ca, Cl, HCO_3, K, Mg, Na, NO_3, SO_4	Various	Environment Agency
Hartlake	Isotope analyses	11/2018-08/2019	Dual stable isotope analysis of N and O in NO_3	Extraction via acetone dissolution method; analysis via pyrolysis (Section 3.3.1)	University of Leeds, in partnership with South East Water
Hartlake	Major ion concentrations	05/2015-04/2020	Cl, NO_3, SO_4	Various	South East Water
HARSPF	Major ion concentrations, pH, SEC	05/2007-04/2019	Ca, Cl, HCO_3, K, Mg, Na, NO_3, pH, SO_4, SEC at 25°C	Various	Environment Agency
N/A	Bulk N isotope analyses of fertiliser	N/A	Isotope analysis of bulk N in fertiliser samples	Extraction via $AgNO_3$ method; analysis via combustion (Section 3.4)	British Geological Survey, on behalf of University of Leeds
N/A	Isotope analyses of NO_3 fertilisers	N/A	Dual stable isotope analysis of N and O in NO_3	Extraction via acetone dissolution method; analysis via pyrolysis (Section 3.3.1)	University of Leeds

3.3 Dual stable isotope analysis methodology

Data resulting from two methods for isolation of NO_3 from samples are included in this thesis. Analysis carried out at the University of Leeds utilised the acetone dissolution method (Huber et al., 2011), while analysis at the University of East Anglia, on behalf of the Environment Agency, used the denitrifier method (Sigman et al., 2001, Casciotti et al., 2002). The methods produce directly comparable results as both are corrected to international scales: Vienna Standard Mean Ocean Water (VSMOW) for oxygen and, as ^{15}N in air remains close to constant at 0.366‰ (Junk and Svec, 1958), N_{AIR} for nitrogen. Other methods considered, but not chosen, included the ion-exchange method (e.g. Chang et al. (1999), Silva et al. (2000)) and the cadmium reduction method (McIlvin and Altabet, 2005). The former entails using cation and anion-exchange columns to isolate NO_3. NO_3 is extracted from the resulting solution using silver oxide to form silver nitrate. Although not a feasible method for seawater or soil extracts, it can be useful for concentrating NO_3 from dilute samples. It is however, time consuming and therefore less suitable for this study than the acetone dissolution method. The latter method utilises cadmium and reduces NO_3 to nitrite (NO_2), then sodium azide reduced to nitrous oxide. Although sensitive and suitable for saline water, it involves use of toxic chemicals, which is an unnecessary risk for this study.

3.3.1 Acetone dissolution method for isolating nitrate from freshwater samples

Acetone dissolves inorganic compounds to differing degrees enabling isolation of NO_3 from freshwater samples. For instance, magnesium nitrate and calcium nitrate are highly soluble, whereas barium nitrate ($BaNO_3$) is near insoluble. NO_3 recovery from this procedure is around two-thirds (Huber et al., 2011). Some potential error is introduced in that some sulphate and carbonate compounds have no data for their solubility in acetone. Huber et al. (2011) concluded that due to the low solubility of such compounds in water, which decrease in aqueous acetone, in pure acetone they can be considered insoluble. In their study, river water samples high in sulphate and carbonate were analysed successfully with the method.

Based on Huber's results, the method results in a uniform enrichment of $\delta^{15}N$ of 0.2‰ from the original salt, and good reproducibility to 0.1‰. Thus,

$$\delta^{15}N = \delta^{15}N_{measured} - 0.2‰$$

(3.1)

Huber reported that the blank (Milli-Q water) contributed no N so the enrichment was likely an isotopic fractionation resulting from only two-thirds of the NO_3 being recovered during the extraction. The fractionation was thought to be caused by “incomplete precipitation of the $BaNO_3$ from the ternary solvent” resulting in enrichment of the solid phase with ^{15}N. The oxygen isotope data were found to be more variable: while Huber’s measured values for standards IAEA-N3 and internal KNO_3 were within 0.2-0.4‰ of the anticipated values, results for USGS-34 were 2.4‰ higher than the published values. This variation could be the result of blank contribution (co-precipitation of O-containing compounds e.g. sulphate or carbonate) and/or the absorption of water to the surface of the $BaNO_3$. Huber et al. found a maximum of 3‰ error from blank contribution “if the difference between $\delta^{18}O_{blank}$ and $\delta\ ^{18}O_{nitrate}$ is 100%.” The method assumes that a set of samples will have a similar blank contribution, therefore effective comparison will still be possible. Another possible cause of the enrichment from expected $\delta^{18}O$ values is incorporation of oxygen from water to $BaNO_3$ during the final evaporation process, which Huber corrected for by:

$$\delta^{18}O_{nitrate} = 1.027\ x\ \delta^{18}O_{measured} +\ 0.1\%$$

(3.2)

A concern was the effect of dissolved organic carbon (DOC) on oxygen isotopic analysis. Huber et al. (2011) concluded that DOC contributed 3.7-5.6% to the $\delta^{18}O$ signature of a natural river water sample. Groundwater samples are likely to have lower DOC than river samples.

3.3.1.1 Procedure for nitrate extraction via the acetone dissolution method

As summarised in Figure 3.8, samples were filtered through 0.45 µm hydrophilic filters, ideally at the time of sampling, but in some cases when the samples were defrosted for analysis. The samples were stored frozen to limit microbial activity and thus avoid any transformations involving N and O isotopes.

Aliquots of 25-30 µmol NO_3 were pipetted into 50 mL centrifuge tubes. Where a 50 ml centrifuge tube was not sufficient capacity for 27.5 µmol total NO_3, then the sample were pre-concentrated by freeze-drying the 27.5 µmol samples in appropriately sized Nalgene bottles, then dissolving the resulting solid in 10 mL Milli-Q water and decanting into a 50 mL centrifuge tube.

The samples were freeze-dried in the centrifuge tubes, lid removed and the opening covered with parafilm, punctured with a couple of holes to enable evaporation of the water component. The resulting salts were suspended in 350 µL 1 M sodium iodide using a vortex shaker for one minute, after which 20 mL of acetone (CHROMASOLVE for HPLC >99.8%, Sigma-Aldrich, Munich, Germany) was added to the centrifuge tube using a mechanical pipette. 10 ml of n-hexane was then added, and the tube inverted several times to enable gentle mixing; the samples were then refrigerated overnight so solids settled.

The following day samples were centrifuged at RCF 3220 g for ten minutes, then the supernatant pipetted into new, labelled, 50 mL centrifuge tubes and the solid component discarded. 750 µL of 0.1 M $BaNO_3$ in acetone was added to each sample. The samples were then returned to the refrigerator overnight so precipitated $BaNO_3$ could settle.

$BaNO_3$ was isolated by centrifuging at RCF 3220 g for ten minutes, then decanting supernatant into a waste container. $BaNO_3$ was dried in open tubes in a 60 °C oven overnight. Solid $BaNO_3$ was dissolved in 240 ul Milli-Q water and divided equally between four silver 4 x 6 mm capsules. A desiccator containing silica gel was then used for 4-5 days to dry the open capsules.

After, the capsules were sealed by folding them into a small pellet using forceps. NO_3 recovery is around two-thirds, thus 4-5 µmol NO_3 remains in each capsule at the end of the extraction process.

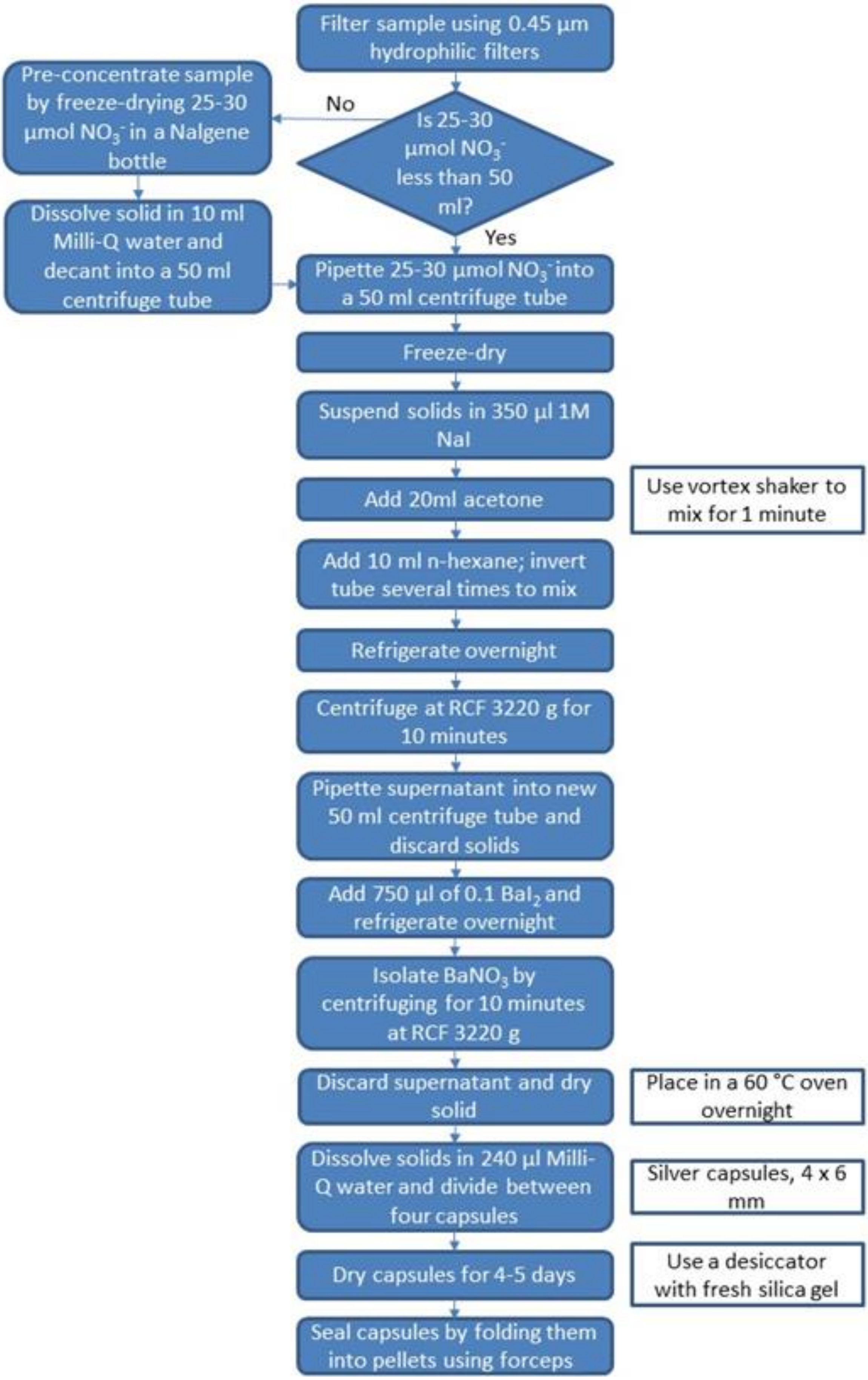

Figure 3.8: Procedure for NO_3 extraction from freshwater samples, developed by Huber et al. (2011).

3.3.1.2 Procedure for dual stable isotope analysis of extracted nitrate

The samples were subjected to pyrolysis at 1450 °C in an Elementar Pyrocube to convert the NO_3 into CO and N_2 gases. The gases were then passed through water and carbon dioxide absorption traps and transferred individually to an Isoprime continuous flow isotope ratio mass spectrometer (IRMS). Isotopic ratios are reported according to international standards, with calibration standards IAEA-NO_3 and USGS-34 (values reported in Table 3.6) in addition to internal laboratory $BaNO_3$ check standards.

Table 3.6: Actual statistics, and statistics observed in analyses for this study, for international standards IAEA-NO_3 (n=99) and USGS-34 (n=99). Actual values reported from Gonfiantini (1984), Böhlke and Coplen (1995), Böhlke et al. (2003) and Brand et al. (2009).

International standard	**IAEA-NO_3**		**USGS-34**	
	$\delta^{15}N$	**$\delta^{18}O$**	**$\delta^{15}N$**	**$\delta^{18}O$**
Actual +/- sd (‰)	4.7 +/- 0.2	25.6 +/- 0.4	-1.8 +/- 0.1	-27.8 +/- 0.37
Observed mean (‰)	4.69	26.39	-1.80	-27.08
Observed median (‰)	4.69	25.82	-1.82	-27.48
Observed interquartile range	0.13	2.07	0.10	2.12
Observed sd	0.12	2.07	0.083	1.75

3.3.1.3 Data quality control and method precision

Dual stable isotope data were assessed to ensure the ratio of peak heights for CO and N were consistent and at a ratio of approximately 3 to 1, as higher ratios imply contamination from an additional source of O. ^{13}C was also monitored to ensure that it remained consistent, as variations in the $\delta^{13}C$ of CO could indicate contamination of C (and potentially O) from a source such as natural organic matter, or fractionation of CO during gas preparation.

Long-term standard error (SE) for the acetone dissolution method (Section 3.3.1) was small for both $\delta^{15}N$ and $\delta^{18}O$: 0.060 and 0.237, respectively. SE for $\delta^{18}O$ was approximately four times the SE for $\delta^{15}N$, possibly relating to the greater complexity of the chemical processing involved in converting NO_3-O into CO-O in comparison to conversion of NO_3-N into N_2. To calculate the long-term standard error a single trial KNO_3 solution was prepared. It was then extracted and analysed periodically in triplicate. Standard deviations were pooled to estimate long-term standard error.

3.3.2 Denitrifier method for dual stable isotope analysis of nitrate

Denitrifying bacteria obtain C and energy from a variety of organic and inorganic compounds. They can convert NO_3 to atmospheric N, however *Pseudomonas chlororaphis* lacks the nitrous oxide reductase enzyme required for complete denitrification (Greenberg and Becker (1977), Christensen and Tiedje (1988), Højberg et al. (1994)), and thus incomplete denitrification occurs, resulting in nitrous oxide, which can be analysed by IRMS. A strain of *Pseudomonas chlororaphis*, *P. aureofaciens,* enables isotopic analysis of O as well as N, as it incorporates less O from water into the nitrous oxide product than *P. chlororaphis*.

The method has precision of 0.2‰ (1 sd) at NO_3 concentrations as low as 1 µM, however there can be a relatively large NO_3 contribution from blanks dependant on the bacterial strain, of up to 10%, meaning significant corrections must be applied after isotopic analysis. It can be an effective method for NO_3 in seawater down to natural (uncontaminated seawater) abundance levels (Sigman et al., 2001). Assuming conversion of NO_3 to nitrous oxide is complete then no fractionation of N will occur. The effect on the O signature is not so simple however: only one in six oxygen atoms from the NO_3 sample will be present in the resultant nitrous oxide (Sigman et al., 2001). O isotopic ratios can however be calculated if no variation in fractionation occurs.

3.3.2.1 Overview of the denitrifier method procedure

The denitrifier cultures were prepared by propagating *P. aureofaciens* on tryptic soy agar, containing potassium nitrate and ammonium sulphate, at room temperature, while 400 mL of a mixture of tryptic soy broth, 10mM potassium nitrate, 1 mM ammonium sulphate and 1 mL/L of antifoaming agent was dispensed into media bottles and autoclaved. Ammonium sulphate was added to both the agar and broth to safeguard against the bacteria assimilating the sample nitrate. 5 mL of the broth was inoculated by a single colony from the agar and placed overnight on a reciprocal shaker to enable growth. This starter tube was then used to inoculate the 400 mL broth, after which it was grown on a reciprocal shaker for 6-10 days.

Prior to addition of the water sample the culture was concentrated by splitting it into 40 mL aliquots and centrifuging for 10 minutes at 18 °C, 7500 g. The supernatant medium was then decanted, and the cells re-suspended in 4 mL of the medium. The cells were then divided between 20 mL headspace vials, and capped by silicone septa. The nitrous oxide formed by the potassium nitrate included in the broth and agar was purged with N_2 gas, while maintaining anaerobic conditions. A volume of water sample to give a final sample of 10-20 nmol N was then injected into each vial, and the vial was inverted and incubated overnight to enable the partial denitrification to take place.

Once a complete conversion to nitrous oxide had occurred, the bacteria were lysed by the addition of sodium hydroxide, which also scavenges carbon dioxide. The nitrous oxide was then removed from the vial using a helium carrier gas, purified, and then isotope analysis carried out using an IRMS. Isotopic ratios are calculated according to international standards, with calibration standard IAEA-NO3 ($\delta^{15}N$ = +4.7‰ AIR, sd 0.2; $\delta^{18}O$ =+25.6‰ VSMOW, sd 0.4) (Gonfiantini, 1984, Hut, 1987, Böhlke and Coplen, 1995).

Given the complex reactions of O in the samples, corrections were carried out for O according to equations presented in Casciotti et al. (2002):

$$m = s + b \tag{3.1}$$

$$\delta^{18}O_m m = (\delta^{18}O_s + \epsilon)s(1 - x) + \delta^{18}O_{H_2O} sx + \delta^{18}O_b b \tag{3.2}$$

For a description of the parameters, see Table 3.7.

Table 3.7: Description of symbols used in Equations 3.1 and 3.2, derived by Casciotti et al. (2002).

Symbol	Description
m	total amount of nitrous oxide-N in the sample
s	amount of sample NO_3-N added
b	amount of N from the blank
x	fraction of oxygen atoms in the nitrous oxide that derived from exchange with water during denitrification
$\delta^{18}O_m$	measured $\delta^{18}O$ value (vs V-SMOW)
$\delta^{18}O_s$	true $\delta^{18}O$ of the sample NO_3 (vs V-SMOW)
$\delta^{18}O_{H_2O}$	oxygen isotopic composition of the water
$\delta^{18}O_b$	oxygen isotopic composition of the blank
ϵ	net isotopic fractionation caused by the removal of oxygen atoms in the reduction of NO_3 to N_2O

3.4 Isotope analysis of four inorganic nitrogen fertilisers

Four fertilisers (Table 3.8) were isotopically analysed to determine the isotopic signatures of some of the N-containing compounds that have been applied close to the catchments of interest, in an effort to gain a greater understanding of the processes that occur once these compounds enter the soil and prior to groundwater sampling. A control sample, laboratory ammonium nitrate (NH_4NO_3), was also analysed as an example of NO_3 definitely produced via the Haber-Bosch process.

Table 3.8: Fertilisers and a laboratory grade NH_4NO_3 tested for N isotopic signatures, and O in NO_3 where possible.

Fertiliser	Formula	% N
Diammonium phosphate (DAP)	$(NH_4)_2HPO_4$	18
Ammonium sulphate (AS)	$(NH_4)_2SO_4$	21
Ammonium nitrate (Nitram)	NH_4NO_3	34.5
50:50 Ammonium sulphate: ammonium nitrate (Double Top)	$(NH_4)_2SO_4$ + NH_4NO_3	27
Laboratory ammonium nitrate	NH_4NO_3	34.5

Fertiliser samples were stored in sealed plastic bags prior to testing, to limit contact with air and thus reduce the potential for NH_3 volatilisation (discussed in Section 2.3.3). Approximately 5 g of each fertiliser and the laboratory standard NH_4NO_3 was ground up using a quartz pestle and mortar. The pestle and mortar were cleaned between samples using ethanol and tissue and stubborn deposits were removed using clean quartz sand. All moisture was then removed from the samples by placing them in an open jar in a desiccating cabinet filled with fresh silica gel for several days. In an initial experiment, fertilisers were heated to remove water, but given the absence of solids after the acetone dissolution stage of the NO_3 extraction, it is inferred this caused NH_4 to volatilise. Furthermore, Kimura (2013) stated that freeze-drying fertilisers was not appropriate, so desiccation was chosen. All samples were then isotopically analysed for total N at the National Environmental Isotope Facility at the British Geological Survey, via combustion using an elemental analyser (Flash/EA) coupled to a ThermoFinnigan Delta Plus XL IRMS via a ConFlo III interface. The samples were calibrated against N1 ($\delta^{15}N$ 0.43‰) and N2 ($\delta^{15}N$ 20.41‰) standards. BGS reported that within the analysis N1 $\delta^{15}N$ (AIR) ranged between 0.23 and 0.56‰ and N2 $\delta^{15}N$ (AIR) ranged from 20.00 to 20.95‰.

The samples from the initial experiment were considered to provide signatures for NO_3-N and O (as only NH_4 was volatilised), and therefore were subject to dual stable isotope analysis of the N and O in NO_3 as described in Section 2.3. Unheated samples were subsequently used to provide bulk N signatures including NH_4-N, which allowed the signature of NH_4-N to be determined, given that for the NO_3-N was known.

For Double Top, Nitram and laboratory NH_4NO_3 a small amount of each sample was dissolved in Milli-Q water and subjected to the method detailed in Section 3.2.1 (Huber et al., 2011) to isolate NO_3 from the NH_4. This was to enable analysis of NO_3 and bulk N compositions separately, thus allowing estimation of the N isotopic signature in NH_4.

3.5 Planned analysis of nitrate in rainfall

To further constrain this study *in-situ* ion exchange columns for collecting NO_3 in rainfall were developed and installed in the Yorkshire Wolds to assess the isotopic composition of wet deposition (discussed in Section 2.3.6). However, due to a lack of laboratory access during COVID-19 the columns were not analysed. Methods are included here for completeness.

The method for extracting low concentrations of NO_3 from freshwater was developed by Silva et al. (2000) and adapted in this study for use with ion exchange columns in the field. The adapted method (as described in Figure 3.9) avoided complex or hazardous preservation techniques, as the resin conserves

NO_3, bypassing the need for collection of rainfall samples on an event basis to avoid sample degradation. Furthermore the method avoids transport of large volumes of low-NO_3 samples between field and laboratory, while concentrating samples for simpler analysis. Anion resin, AG1-X8 (Bio-Rad), was chosen due to its affinity for NO_3. The resin must adsorb NO_3 completely with minimal competition from other anions, while still exchanging NO_3 when elution is required. Incomplete adsorption or elution could lead to fractionation of the N or O isotopes.

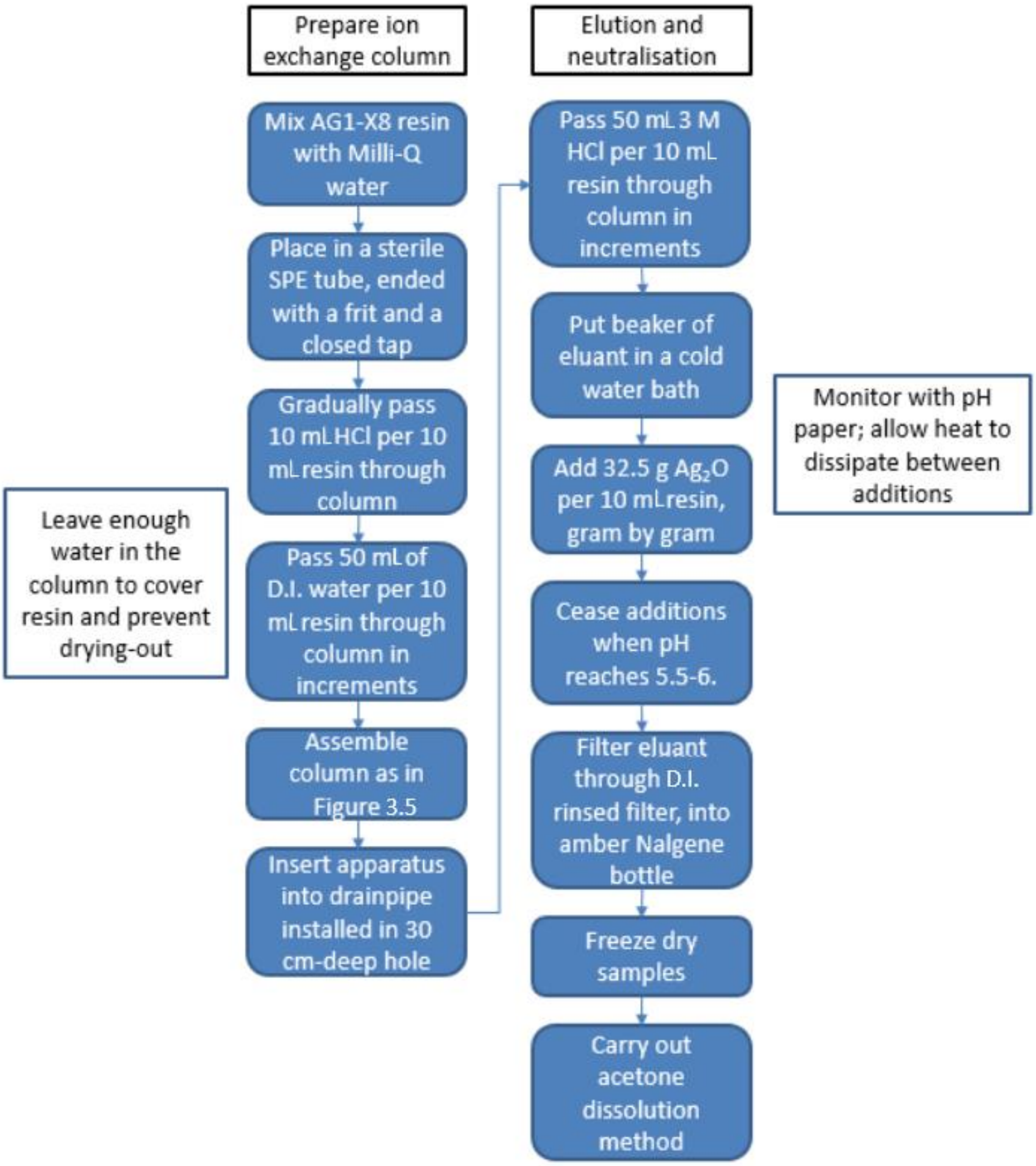

Figure 3.9: Procedure for preparing ion exchange columns, eluting from the column and neutralisation of the eluant in preparation for NO_3 extraction.

Cl, SO_4 and HCO_3 were most likely to interfere with NO_3 adsorption as they tend to be the most concentrated anions in natural water (Hem, 1992). Mean concentrations for Thorganby in 2019 were 29.1 mg/L for Cl and 0.48 mg/L for SO_4 (Braban, 1985-2019). Local HCO_3 concentrations were not available. AG1-X8 resin has a lower selectivity for both Cl and HCO_3 than NO_3 (Table 3.9). HCO_3 has approximately ten times lower selectivity than NO_3 (Table 3.9) and therefore was not likely to interfere with NO_3 adsorption. Silva et al. (2000) stated that as a divalent molecule SO_4 is likely to have a higher relative selectivity than NO_3, however experiments showed that for N, SO_4 adsorption caused no isotopic fractionation even when the sum of NO_3 and SO_4 concentrations exceeded the capacity of the column. However, Silva et al. (2000) did not test for isotopic fractionation of O, so to ensure competition did not limit NO_3 adsorption in this study, the column contained 27 mL AG1-X8 resin: sufficient capacity for the maximum observed masses of NO_3, Cl and SO_4 (3.0 mg/L, 52.50 mg/L and 8.9 mg/L, respectively, in Thorganby and High Muffles (Braban, 1985-2019)).

Table 3.9: Relative Selectivity of Various Counterions Relative Selectivity (edited from Bio-Rad AG ® 1, AG MP-1 and AG 2 Strong Anion Exchange Resin Instruction Manual, 2000). Ions in bold are considered to be of particular relevance to this study.

Counterion	Relative Selectivity for AG 1 and AG MP-1 Resins
Hydroxide (OH^-)	1.0
Benzene sulfonate ($C_6H_5O_3S^-$)	500
Salicylate ($C_7H_5O_3^-$)	450
Citrate ($C_6H_5O_7^{3-}$)	220
Iodide (I^-)	175
Phenate ($C_6H_5O^-$)	110
Bisulphate (HSO_4^-)	**85**
Chlorate (ClO_3^-)	74
Nitrate (NO_3^-)	**65**
Bromide (Br^-)	50
Cyanide (CN^-)	28
Bisulphite (HSO_3^-)	27
Bromate (BrO_3^-)	27
Nitrite (NO_2^-)	24
Chloride (Cl^-)	**22**
Bicarbonate (HCO_3^-)	**6.0**
Iodate (IO_3^-)	5.5
Hydrogen phosphate (HPO_4^-)	5.0
Formate (CHO_2^-)	4.6
Acetate ($C_2H_3O_2^-$)	3.2
Propionate ($C_3H_5O_2^-$)	2.6
Fluoride (F^-)	1.6

Silva et al. (2000) prepared anion columns by passing 3 M HCl through the resin, as a precaution to ensure that only Cl occupied exchange sites. Deionised water was passed through the resin to remove any excess Cl, followed by the sample. The column with adsorbed NO_3 sample was then returned to the lab for analysis. Silva et al. found that NO_3 stored refrigerated on the column for one month had identical nitrogen isotope ratios to the KNO_3 used to make the original NO_3 solution, and samples stored on columns for between three and 24 months "showed good agreement" with samples analysed immediately, with no correlation between divergence from the expected $\delta^{15}N$ and storage time. It should be noted that only $\delta^{15}N$ was analysed by Silva et al. (2000) for the purposes of investigating fractionation potential, and as a result $\delta^{18}O$ should be interpreted with caution, particularly as the findings of Huber et al. (2011) imply that O isotope ratios tend to have more variability and less predictability.

To elute the rainfall NO_3 3 M hydrochloric acid was passed through column and into glass beakers. The resulting NO_3 solution was placed in a cold water bath and neutralised by adding silver oxide a gram at a time, stirring and crushing the solids to ensure all silver oxide was available to react. Heat was allowed to dissipate before the next addition and no vapour was produced. This process neutralised hydrochloric acid, precipitated Cl and produced silver nitrate:

$$HCl + HNO_3 + \ Ag_2O \ \rightarrow AgCl_{(s)} + Ag^{+}_{(aq)} + NO^{-}_{3\,(aq)} + H_2O \tag{3.3}$$

At all stages Silva advised that light contact with the silver oxide was restricted due to its photosensitivity. pH paper was used to monitor the mixture, and silver oxide additions ceased when the pH reached 5.5-6. The eluant was then filtered through deionised water-rinsed Whatman No. 1 filters to remove silver chloride precipitate, and stored in a Nalgene bottle covered in foil to avoid photo degradation of the dissolved silver nitrate. Silva et al. carried out isotope analysis on the N and O in NO_3 separately, via combustion.

To reduce the expense of the method, the silver chloride waste was regenerated to silver oxide by boiling it in potassium hydroxide overnight, three times. The fresh silver oxide was then dissolved in nitric acid and then decanted, separating any unconverted silver chloride. The silver oxide was then precipitated with further potassium hydroxide, before being filtered and rinsed, as described above (Silva et al., 2000).

For this study, the Silva method has been adapted as described in Figure 3.9, so prepared columns were stationed in the field in a larger collection column to enable rain water collection. Several studies have adopted a similar approach for assessing NO_3 concentrations in throughfall e.g. Simkin et al. (2004), Fenn et al. (2002) and Van Dam et al. (1991) and NO_3 isotope composition in throughfall and rainfall (Garten Jr, 1992). This study necessitated that samples were at atmospheric temperatures for three months while in the field, before being refrigerated on return to the laboratory.

The column was assembled as described in Figure 3.9 and presented in Figure 3.10; polyester floss in a separate SPE tube topped the resin tube to exclude organic matter, as in e.g. Simkin et al. (2004), and two lengths of tubing were attached in series beneath the tap, with the top length swan-necked to enable sample passage to the collection vessel without a vacuum forming and thus the resin becoming dry. An additional SPE tube was added during summer months to provide greater storage capacity. These apparatus were inserted inside a 1.5 m length of 15 cm diameter drainpipe, providing protection from the elements. On installation in the field, the drainpipe was placed vertically in a 30 cm deep hole (Figure 3.10).

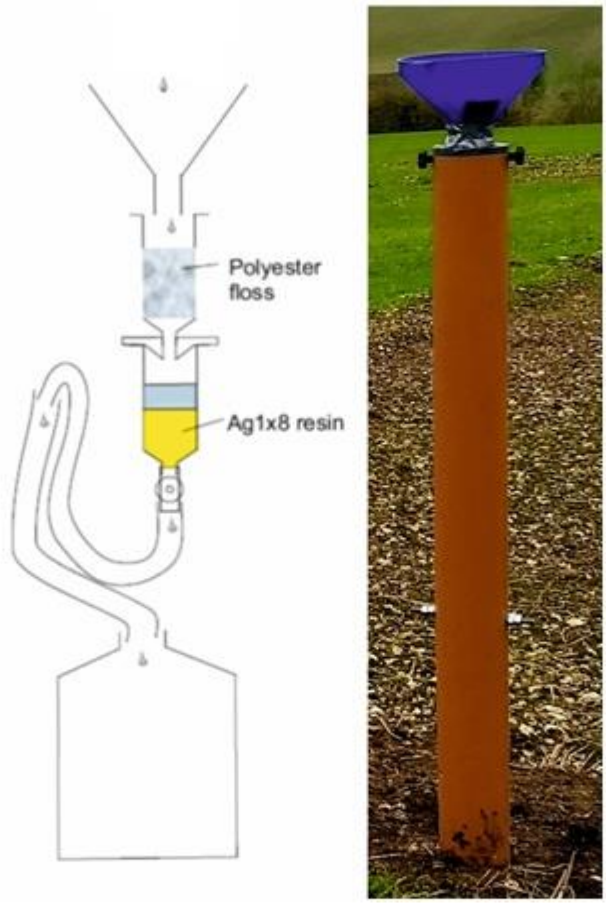

Figure 3.10: Schematic of ion-exchange column (left), with column *in situ* (right). Rainwater entered via the funnel and polyester floss excluded organic matter. SPE tubing was swan-necked to avoid drying out the Ag1x8 resin as rainwater passed into collection vessel.

The collection vessel was exchanged on every field visit and the volume of rainfall measured to allow estimation of NO_3 mass in the resin, and for easier comparison with the paired TBR. On some occasions, it was not possible to change the vessel before it overflowed, so TBR data was relied upon for calculating NO_3 in the resin. Rainfall data was obtained monthly from the Environment Agency (daily data for

Filey, High Mowthorpe, Bridlington and Driffield) and Weathercast.com (15 minute data for High Mowthorpe) to validate the data collected by the column and TBR.

Data were obtained from the UKEAP: Precip-Net project (Braban, 1985-2019) for Thorganby and High Muffles and analysed in order to infer the NO_3 concentration of rainfall in rural Yorkshire. This figure was then used to estimate the size of the rainfall collection funnels, and for approximating the amount of NO_3 in the eluted solution. The overall median of the median NO_3-N concentrations for the individual sampling dates, 0.366 mg/L, was chosen as an approximate rainfall NO_3 concentration. The highest NO_3 concentrations were observed at the lowest average daily depths of rainfall, however all median concentrations were between 0 and 1 mg/L NO_3-N and concentrations dropped rapidly to between 0.2 and 0.4 mg/L NO_3-N, as daily rainfall depths increased. Assuming a NO_3-N concentration of 0.366 mg/L per 1 mm of rainfall, and given that a funnel with a 22 cm diameter would collect 38 mL water per 1 mm rainfall, 958 to 1149 mL would be needed for a 25 to 30 µmol sample for the mass spectrometer, if elution isolated 100% of the NO_3.

3.5.1 Preparation of the rainfall samples for IRMS

This study employed the acetone dissolution method (Huber et al., 2011) described in Section 3.1.1, enabling dual stable isotope analysis. Thus the samples were frozen, caps taken off the Nalgene bottles containing the silver nitrate samples and replaced with Parafilm (Figure 3.9). Several holes were punched in the Parafilm and the samples were freeze-dried. Deionised water was then used to transfer the sample to a 50 mL centrifuge tube ready for the acetone dissolution method.

3.6 Summary of methodologies applied in this study

Groundwater samples were collected by the Environment Agency and South East Water. The majority of samples were analysed at the University of Leeds, using the acetone dissolution method (Huber et al., 2011) for NO_3 extraction and dual stable isotope analysis via pyrolysis. Some samples from the Environment Agency were analysed by the University of East Anglia using the denitrifier method (Sigman et al., 2001, Casciotti et al., 2002) for NO_3 extraction and stable isotope analysis via combustion.

Four fertilisers and one laboratory control were subject to NO_3 extraction via the acetone dissolution method (Huber et al., 2011) at the University of Leeds. They were stored in a desiccator prior to analysis. Dual stable isotope analysis using pyrolysis was carried out at the University of Leeds and bulk N isotope analysis using combustion was carried out by the British Geological Society at Keyworth.

Analysis of rainwater NO_3 was planned following collection of field samples via a bespoke ion exchange column. Data from these analyses were intended to further constrain the dual isotope fingerprinting diagram, however due to a lack of laboratory access during COVID-19 analysis was regrettably abandoned.

Chapter 4 End-member quantification

There are many key factors to crop growth, one of which is the presence of mineral nutrients in the soil. These nutrients include N, PO_4, K, SO_4, Ca and Mg amongst others. If crops are not able to absorb sufficient amounts from the soil then crop growth may be limited. It has long been understood that soil must recover between crops to allow maximum growth, however farmers may continue using the same field and apply fertilisers to replenish the soil with key limiting nutrients.

N is key for good crop yield in non-leguminous plants, in addition to crop quality. N can increase stem and leaf growth due to higher chlorophyll and protein production, and with larger leaves more photosynthesis can occur. In cereal crops, more tillers may grow with N-rich substrate, leading to more leaves and greater yield. N can also support flower development in cereals, therefore increasing grain yield, but the effect of N on crop quality is more complicated. It is valuable to bread flour where a protein-rich grain is needed, but not for brewing barley where low protein content is preferable (Addiscott et al., 1991).

At the beginning of the 20th century fertilisers came from limited natural reservoirs, making them expensive (discussed in further detail in Section 2.3). However, following industrialisation of the Haber Bosch process ammonia become more readily available for lower cost. In conjunction with a driver for self-sufficiency in the UK following World War Two, this led to greater usage of inorganic fertilisers. Commonly applied nitrogen fertilisers are discussed in Section 2.3.1 to 2.3.4.

The aim of this chapter was to constrain feasible end-members in order to better understand NO_3 sources present in groundwater signatures. Prior to this study accurate isotopic signatures for artificial NO_3 fertilisers applied to study catchments were not available, to the author’s knowledge. Thus inorganic NO_3 fertilisers applied in Yorkshire were subject to dual stable isotope analysis and are presented here. For end-members where analysis was not possible within the scope of this study, isotopic data from the published literature is summarised. More tightly constrained end-members allow key reactions and processes to be identified and assist in building a picture of N inputs to groundwater and any potential for NO_3 attenuation.

4.1 Isotopic analyses obtained from previous studies

This section aims to assess the isotopic signatures of agricultural N sources, and O signatures where applicable, from the published literature where direct analysis of end-members was not possible. This is to evaluate the validity of the existing dual isotope fingerprinting diagram presented in Section 2.3 (Kendall, 1998, Nestler et al., 2011) and to aid understanding of N transformation processes that may be occurring within the material, soil zone or groundwater system. These data can be used alongside results in this study to create a more robust understanding of the NO_3 fingerprinting diagram and its applications.

4.1.1 Bulk fertiliser nitrogen isotopic signatures from the published literature

Bateman and Kelly (2007) found that most (98.5%) synthetic N fertilisers had $\delta^{15}N$ of less than +4‰, and 80% within the range −2 to +2‰ (Table 4.1). All $\delta^{15}N$ presented in Table 4.1 are within the range anticipated by the fingerprinting diagram for artificial N fertilisers (−5.9 to +2.6‰). Bateman and Kelly (2007) identified a greater range of signatures for synthetic urea than noted for other inorganic fertiliser types. The lightest $\delta^{15}N$, −5.9‰, was only recorded for one manufacturer and therefore could reflect a difference in their production technique. Using solely bulk N signatures does not enable differentiation between NH_4 and NO_3 fertilisers.

Table 4.1: Stable isotope signatures recorded in previous published studies for bulk N in synthetic N fertilisers. NPK is the generic name for fertilisers containing nitrogen, phosphorus and potassium.

Fertiliser	$\delta^{15}N$ (‰)	Country	Reference
NH_4NO_3	−0.7 to +2.5	Spain	Vitòria et al 2004
NH_4NO_3	−1.4 to +2.6	UK	Bateman
NPK	−0.7 to −0.3	UK	Bateman and Kelly 2007
Urea	−5.9 to −0.8	UK	Bateman and Kelly 2007
Urea	−1.1	Spain	Vitòria et al 2004

4.1.2 Fertiliser nitrate isotopic signatures from the published literature

N signatures for NO_3 fertilisers (Table 4.2) are largely similar to those recorded for bulk N (Table 4.1), with a slightly greater range for $\delta^{15}N$ of −6 to +6‰. Recent studies have explored dual stable isotope analysis of oxygen, as well as N, in NO_3 to allow great differentiation between sources; for NO_3 fertilisers $\delta^{18}O$ ranges from +17 to +25‰ (Table 4.2). Most fertiliser NO_3 is manufactured via the Haber-Bosch process (described in Section 2.3), which uses O_2 from the atmosphere to synthesise NO_3. As a result, most $\delta^{18}O$ for manufactured NO_3 fertiliser are similar to those found in the atmosphere, approximately +23.5‰ (Kroopnick and Craig, 1972).

Table 4.2: Isotopic ratios of N and O for fertiliser NO_3, as analysed in previous studies.

$\delta^{18}O$ (‰)	$\delta^{15}N$ (‰)	Country	Reference
-	−1 to +4	Canada	Cey (1999)
-	+0.5 to +5	Various	Bedard-Haughn et al. (2003)
+17 to +25	−6 to +6	Various	Xue et al. (2009)
+25.1	+5.6	Spain	Vitòria et al. (2004)

4.1.3 Ammonium-N isotopic signatures from the published literature

$\delta^{15}N$-NH_4 fertiliser signatures identified in published literature range between −6 to +6.6‰ (Table 4.3). Ammonium sulphate N isotopic signatures may vary to a greater degree than other N fertilisers as 60% of ammonium sulphate is a by-product of several manufacturing processes other than Haber Bosch e.g. nylon and plastic production, hydrometallurgy (Hagen, 1990). The fingerprinting diagram constrains $\delta^{15}N$ of nitrified NH_4 fertiliser as −8 to +5‰; which would not encompass the range of data from Bateman and Kelly (2007) or Xue et al. (2009) assuming no change to $\delta^{15}N$ during nitrification.

Table 4.3: $\delta^{15}N$ of NH_4 fertilisers from the published literature.

$\delta^{15}N$ (‰)	Country	Reference
−6 to +6	Various	Xue et al. (2009)
−5 to +4.5	Various	Bedard-Haughn et al. (2003)
-0.3 to 0	Spain	Vitòria et al. (2004) (NH_4SO_4)
+6.6	UK	Bateman and Kelly (2007) (NH_4SO_4)
−0.5	USA, South Africa	Heaton (1986)

4.1.4 Manure and slurry isotopic signatures from the published literature

Manure and slurry have more variable isotope signatures compared to artificial fertilisers (Table 4.4). This is because signatures depend largely upon the animals' feed. Feed sources used to be fairly local and constant, however now they are highly changeable as the feed market is now global, and decisions are now dependent upon price. $\delta^{15}N$ of marine protein is different to that of terrestrially sourced protein, and terrestrial proteins will vary depending on soil moisture and climate. It is, however, possible to identify the country of origin for pig meat (e.g. Kim et al. 2013), and therefore there is likely some conformity in pig manure too.

Table 4.4: $\delta^{15}N$ and $\delta^{18}O$ (where available) for manure and slurry samples. Some studies included the $\delta^{15}N$ and $\delta^{18}O$ of the NO_3 produced when organic matter oxidised.

Type of organic material	$\delta^{15}N$ (‰) (AIR)	$\delta^{18}O$ (‰) (VSMOW)	Study country	Reference
Decomposition of barnyard "animal waste"	+10 to +22 (following oxidation to NO_3)	-	Texas, USA	(Kreitler, 1975), Kreitler (1979)
"Animal or sewage waste"	+8 to +22 (with one sample at −0.2 to −2).	-	USA, South Africa	Heaton (1986), review paper
Poultry manure	+7.9 to +8.6	-	Canada	Wassenaar (1995)
Groundwater nitrate from poultry manure	+8 to +16	+2 to +5		
Farmyard manure	+3.5 to +16.2	-	UK	Bateman and Kelly (2007)
Chicken manure pellets	+4.8 to +8.4			
Groundwater contaminated by pig manure	+8 to +15	-	Spain	Vitòria et al. (2004)
Manure NO_3	+5 to +25		Various	Xue et al. (2009), review paper
NO_3 from nitrification, including manure		0 to +15		
Manure NO_3	+7 to +25	When nitrified: 0 to +15	Various	Nestler et al. (2011), using data from Kendall (1998) and Xue et al. (2009)

Manure is applied as a primary fertiliser in Osona, North-East Spain, with artificial fertilisers playing a minimal role in comparison to England (Vitòria et al., 2008). This region of Spain produces large quantities of manure, which requires disposal, due to intensive animal agriculture: the region supports one million pigs. Vitòria et al. (2008) found that when manure and slurry is stored in a pit isotopic fractionation of N occurs. Storage was a maximum of 4 months, but $\delta^{15}N\text{-}NH_4$ changed from +8 to +15‰ following volatilisation (Vitòria et al., 2004). If the pit was uncovered then the pit may be subject to evaporation, which would lead to an increase in $\delta^{18}O$ in any NO_3 present. When applied to a field, manure and slurry is subject to urea hydrolysis and NH_3 volatilisation and thus it is likely that $\delta^{15}N\text{-}NH_4$ could continue to get heavier (Letolle, 1980). Nestler et al. (2011) similarly identified that $\delta^{15}N\text{-}NO_3$ was higher from fields where pig manure was applied, as opposed to artificial fertilisers.

Vitòria et al. (2008) assumed that $\delta^{15}N\text{-}NH_4$ had the same $\delta^{15}N$ as newly mineralised NO_3 because in oxic conditions they found residual NH_4 (following volatilisation) was completely nitrified, therefore no fractionation could occur. However, the $\delta^{18}O$ during chemolithoautotrophic nitrification will likely be dictated by:

$$\delta^{18}O_{NO_3} = 2/3\delta^{18}O_{H_2O} + 1/3\delta^{18}O_{O_2} \tag{4.1}$$

This assumes no further fractionation is occurring (Mayer et al., 2001). Equation 4.12 states that when nitrified the resulting NO_3 will contain two thirds O from water and one third atmospheric O; this should be reflected in the isotopic signature. However, using additional stable isotope analysis (Cl and C) Vitòria et al. (2008) showed, qualitatively, that subsequent denitrification occurred, resulting in further O isotopic fractionations. In this case study, denitrification was likely associated to autotrophic pyrite oxidation; this process is unlikely influential in the catchments in this study as pyrite is likely absent from the soil in study catchments.

4.2 Fertilisers known to be in current use

Although fertilisers that are currently applied are not necessarily the same as those applied historically, and therefore do not fully encompass those circulating in the groundwater sampled for this study, it is helpful to identify common fertilisers to guide interpretations of results. This is particularly true of inorganic N fertilisers, where products are largely manufactured using the Haber-Bosch process, and signatures are likely to be similar for a wide range of fertilisers.

4.2.1 Fertilisers in use in the Yorkshire Wolds on the Northern Province Chalk

Four samples of N fertilisers were supplied by a Yorkshire farmer for analysis of their N and O isotopic composition (Table 3.8). A second farmer confirmed that he used three N-containing liquid fertilisers (Table 4.5). Thus it can be confirmed that both NH_4 and NO_3 fertilisers, in addition to urea, are in current use on the Northern Province Cretaceous Chalk.

Table 4.5: N-containing fertilisers applied at a farm in the Yorkshire Wolds. NPK is the generic name for fertilisers containing nitrogen, phosphorus and potassium.

Brand name	Type of fertiliser	% weight N (w/v)
Chafer 4-12-12	Liquid NPK, containing ammonium polyphosphate	Ammoniacal 3.6 Ureic 0.5
Chafer 6-11-12	Liquid NPK, containing ammonium polyphosphate	Ammoniacal 3.3 Ureic 2.7
Chafer N30.3+10.8 SO_3	Liquid, containing NH_4NO_3	Nitric 6.6 Ammoniacal 10.4 Ureic 13.3

4.2.2 Fertilisers in use in Woodgarston on the Southern Province Chalk

Farmers in the Woodgarston catchment confirmed that they applied NH_4NO_3 and urea, in addition to granular and liquid inorganic fertiliser formulations (Howe, 2019). In terms of organic fertilisers they applied biosolid/digested cake, compost, farmyard manure, sewage sludge, whole digestate and poultry litter. Most farms surveyed also grazed animals for 6 months per year or all year round. Estimated N applications are presented in Table 4.6.

Table 4.6: N applications for a group of farmers in the Woodgarston catchment for cropping years ending August 2017 and August 2018 (Howe, 2019).

Crop	2017 mean N application (kg/ha)	2018 mean N application (kg/ha)
Herb	210	155
Spring barley	140	125
Spring oat	120	80
Winter barley	180	170
Winter oat	0	106.5
Oil seed rape	181	220
Winter wheat	220	201.75

4.2.3 Fertilisers in use in Hartlake on the River Terrace Gravels

Less site-specific information was available for the Hartlake catchment, however using the AGRI-insight survey (an audit of 2000 arable farms of >10 ha in Great Britain) and iMAP analysis (iMAP software evaluates inputted agricultural data), South East Water have presented general activities that may be carried out in the Hartlake catchment (Howe et al., 2017). The AGRI-insight survey was carried out across Great Britain, with 18.7% of the farms being in South East England. South East Water highlighted the following N sources could lead to groundwater NO_3 contamination in Hartlake:

- Manure, directly from livestock, as crop fertiliser or as leachate from silos.
- Inorganic N, as pellets or spray (foliate feed).
- “Green manure” as clover cover crops.
- N-fixation crops, such as peas.
- Seaweed based soluble fertilisers for arable crops and top fruit.
- Liquid or solid NPK (generic name for fertilisers containing nitrogen, phosphorus and potassium) for arable and top fruit.

4.3 Fertiliser application regimes

The amount of N that a field receives via human application varies year on year, making estimation of fertiliser applications across a catchment challenging. Firstly it depends on soil type and depth, as well as on the crops grown the previous year. For instance, the Chalk has shallow soils with little organic matter, therefore N uptake efficiency is approximately 55% (AHDB, 2017) and more N may need to be applied for a given yield. By comparison, medium depth, clayey, silty or organic and peaty soils have a 60% efficiency, while light sandy soils have 70% efficiency (AHDB, 2017). Previous leguminous crops may enrich the soil with N, or if a significant amount of crop debris is returned to the soil after harvest. Secondly, weather affects the N application regime, for instance heavy rain may lead to an increased amount of soil N leaching into groundwater, less N remaining in the soil and therefore larger N applications.

There are limits in the amount of N that can be applied to fields in order to improve crop yields. Other nutrients such as K, P and S may be limiting factors to crop growth. In Nitrate Vulnerable Zones (NVZ) there are maximum permitted applications (N-max limit) per year (Table 4.7). There are, however, caveats to the maximum permitted N applications, including if the crop yield is higher than the standard crop yield.

Limits also exist for manure, however the picture is more complex as manure and slurry are waste products that require timely disposal. Restrictions apply as an average across the holding and therefore some fields may receive frequent, high manure applications and be flooded with available N that can't be utilised, while other areas will receive very little, due to the additional fuel necessary to spread the waste further afield.

Table 4.7: The maximum amount of N permitted (N-max limit) in Nitrate Vulnerable Zones (NVZ) per crop type. Adapted from DEFRA (2018).

Crop	N-max limit (kg N/ha/year)
Autumn or early winter-sown wheat	220
Spring-sown wheat	180
Winter barley	180
Spring barley	150
Winter oilseed rape	250 (with max. 30 in closed season)
Sugar beet	120
Potatoes	270
Forage maize	150
Field beans	0
Peas	0
Grass	300
Asparagus, carrot, radish, swede	180
Celery, courgette, dwarf bean, lettuce, onions, parsnip, runner bean, sweetcorn, turnip	280
Beetroot, brussel sprout, cabbage, calabrese, cauliflower, leek	370

4.4 Planned quantification of nitrate in rainfall

Dual stable isotope analysis of rainfall NO_3 was planned, but practical difficulties in completing sample analysis during COVID-19 required this element of the project to be abandoned. Given its small percentage contribution to groundwater NO_3 signatures (0.53 mg/L NO_3-N in rainfall recorded at Thorganby in Yorkshire, Irwin et al, 2002) the influence of rainfall NO_3 on groundwater NO_3 signatures was likely small and thus the impact of the loss of this analysis is considered minor. The NO_3 to Cl ratio was instead applied as a desk-based solution to further constrain NO_3 sources and associated processes (described in further detail in Section 5.4.3).

4.5 Results of stable isotope analysis of fertiliser samples

4.5.1 Bulk N isotope analysis of fertiliser samples

The fertiliser samples and laboratory standard had isotopic signatures typical of industrially manufactured N, including fertiliser ($\delta^{15}N$ −0.21 to 3.09‰) (Table 4.8). The laboratory standard had the heaviest N signature at 3.09‰ which was heavier than analysed in the previous studies discussed in Section 4.1.1. However, it is still well within the constraints for NO_3 fertiliser in the fingerprinting diagram created by Kendall (1998), as discussed in Section 2.3. The laboratory $\delta^{15}N$-NH_4NO_3 were also still within the range specified by Bateman and Kelly (2007) of −2 to +4‰. Results are presented in Figure 4.1.

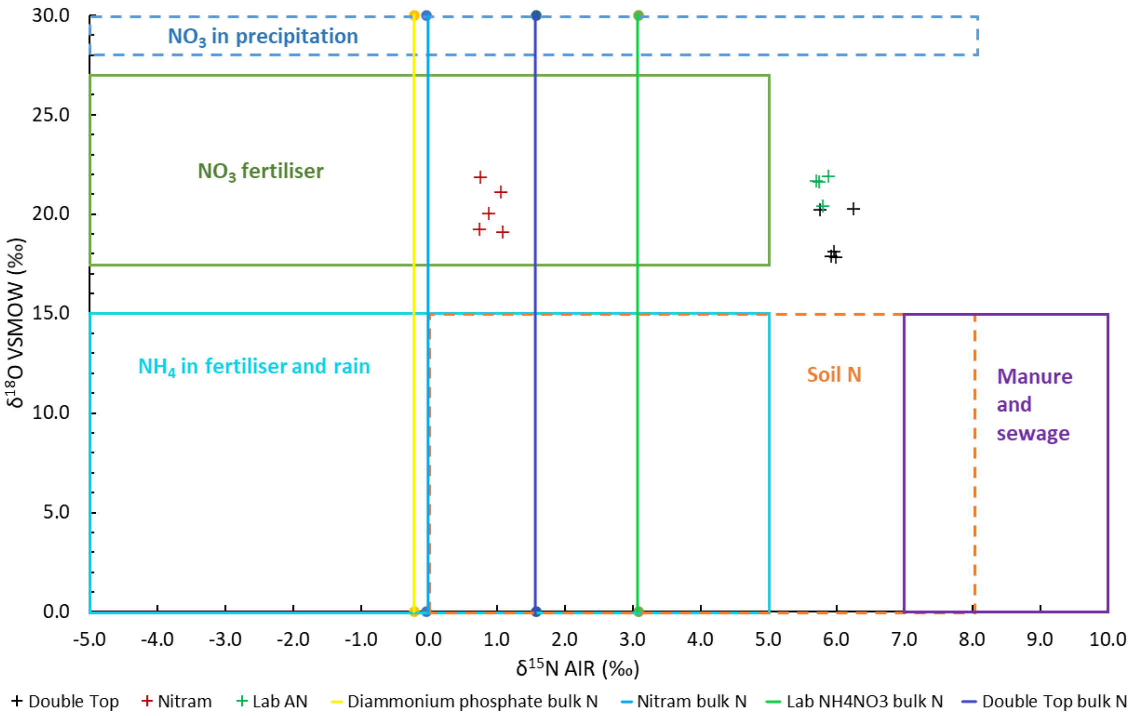

Figure 4.1: Fingerprinting diagram of dual stable isotope results for N and O in fertiliser NO_3 and bulk N (Table 4.10). Bulk N analyses have no $\delta^{18}O$ thus $\delta^{15}N$ of fertilisers are represented as vertical lines on the plot.

Table 4.8: Bulk N stable isotope analysis for four fertiliser samples and a laboratory standard NH_4NO_3.

Fertiliser	$\delta^{15}N$ (‰ AIR)	Mean $\delta^{15}N$ (‰ AIR)	Standard deviation
Diammonium phosphate (n=2)	−0.36	−0.21	0.21
	−0.06		
Ammonium sulphate (n=2)	1.34	1.22	0.18
	1.09		
50:50 Ammonium sulphate: NH_4NO_3 (Double Top) (n=2)	1.71	1.58	0.18
	1.45		
NH_4NO_3 (Nitram) (n=2)	0.06	−0.04	0.15
	−0.15		
Laboratory NH_4NO_3 (n=2)	3.08	3.09	0.01
	3.09		

4.5.2 Nitrate-N dual stable isotope analysis of fertiliser samples

The two NO_3-containing fertilisers and the laboratory NH_4NO_3 showed similar $\delta^{18}O$ signatures (+18.87 to +21.40‰; Table 4.9, Figure 4.1), which are consistent with NO_3 production via the Haber-Bosch process and the studies presented in Section 4.2.2. There were two distinct groups for $\delta^{15}N$ (+0.90‰ and +5.78 to +5.98‰; Table 4.9). The $\delta^{15}N$ for Double Top and the laboratory NH_4NO_3 is heavier than the fingerprinting diagram depicts (Figure 4.1), however, similar or larger signatures have been observed in previous studies (Section 4.2.2).

Table 4.9: Dual stable isotope results for Double Top, Nitram and laboratory NH_4NO_3. There was poor sd for some analyses, however $\delta^{18}O$ is within the range that is expected for NO_3 fertilisers produced via the Haber-Bosch process. Each fertiliser was analysed in triplicate.

Fertiliser	$\delta^{18}O$ (‰)	sd	$\delta^{15}N$ (‰)	sd
50:50 Ammonium sulphate: NH_4NO_3 (Double Top)	+18.87	1.27	+5.98	0.18
NH_4NO_3 (Nitram)	+20.27	1.20	+0.90	0.16
Laboratory NH_4NO_3	+21.40	0.67	+5.78	0.08

4.5.3 Calculation of ammonium-N isotope signatures in fertiliser samples

The bulk N and NO_3-N isotope ratios in Sections 4.5.1 and 4.5.2 were used to estimate the composition of NH_4-N, taking into account the ratio of NH_4 to NO_3 in each sample (Table 4.10). The $\delta^{15}N$ of NH_4-N was between −0.98‰ and +1.22‰ (Table 4.10) and the data are within the data range observed in previous studies (−6.0 to 6.6‰, Section 4.1.3). Given Equation 4.12, and assuming $\delta^{18}O_{atmos}$ of +23.5‰ (Kroopnick and Craig, 1972), and $\delta^{18}O$-H_2O of −7.5‰ (Darling et al., 2003) during natural nitrification of NH_4 fertilisers in the soil zone, the resulting $\delta^{18}O$-NO_3 would be around +8.5‰.

Table 4.10: Isotopic ratios for bulk N, NO_3-N of inorganic N fertilisers, and an estimation of NH_4-N calculated using bulk N and $\delta^{15}N$-NO_3.

Fertiliser	Formula	% N	$\delta^{15}N$-NO_3 (‰ AIR)	Bulk N (‰)	$\delta^{15}N$-NH_4 (‰)	NH_4:NO_3
Diammonium phosphate	$(NH_4)_2HPO_4$	18	n/a	−0.21	−0.21	n/a
Ammonium sulphate	$(NH_4)_2SO_4$	21	n/a	1.22	1.22	n/a
Ammonium nitrate (Nitram)	NH_4NO_3	34.5	0.90	−0.04	-0.98	1:1
50:50 Ammonium sulphate: ammonium nitrate (Double Top)	$(NH_4)_2SO_4$ + NH_4NO_3	27	5.98	1.58	0.11	3:1
Laboratory ammonium nitrate	NH_4NO_3	34.5	5.78	3.09	0.40	1:1

4.6 Summary of end-member quantification

This chapter demonstrates that fertilisers known to be applied in the primary study area, the Yorkshire Wolds, are largely representative of N fertilisers analysed in previous studies. As commonly used fertilisers, these results are likely to also be representative of current agricultural inputs in general. Bulk $\delta^{15}N$ ranged from −0.21 to +3.09‰; NO_3, where applicable, ranged from +0.90 to +5.98‰ for $\delta^{15}N$, and +18.87 and +21.40‰ for $\delta^{18}O$. The NH_4-N component was calculated to be between −0.98 and +1.22‰ for $\delta^{15}N$. Lab NH_4NO_3 and Double Top had $\delta^{15}N$ signatures greater than those accounted for in the fingerprinting diagram (discussed in Chapter 2, Section 2.3). The difference is approximately 1‰ and thus is unlikely to affect the study greatly. Ascertaining the isotopic signatures of N fertilisers applied enables clearer understanding of inputs and therefore more accurate interpretation of the outputs: groundwater NO_3 isotopic signatures.

Limitations lie in that fertilisers analysed in the present day do not necessarily reflect land management strategies and materials used when water in a long residence time aquifer first entered the system. Nevertheless, most fertilisers are manufactured via the Haber-Bosch process and so although formulations may change, NH_3 and NO_3 synthesis is likely to have stayed the same since post-Second World War. Dating groundwater may assist in understanding relevant inputs further. A more significant constraint on understanding is that although soil inputs are known, N transformations that occur in soil before water infiltrates to the groundwater are more complex to identify and quantify. This concept will be developed further in Chapters 5, 6 and 7.

Chapter 5 Assessing nitrate sources and processes in groundwater from the Northern Province Chalk

This chapter introduces the geology and hydrogeological framework of the study catchments in the Yorkshire Wolds, England, and the Northern Province Cretaceous Chalk aquifer that they overlie. The Northern Chalk aquifer is a nationally important source of drinking water and thus ensuring that the quality of this water source remains high is a priority. As the catchments studied in this chapter are largely unconfined, and due to the fractured nature of the Chalk, the aquifer is vulnerable to pollution, including nitrate. Despite this vulnerability the Northern Province Chalk is little studied in comparison to some catchments on the Southern Province Chalk. This is especially true of the Haisthorpe catchments, on which there is little mention in the published literature. To the author's knowledge, dual stable isotope analysis of nitrate has never been executed in the catchments investigated in this chapter.

Nitrate concentrations in the aquifer can be high, often approaching or exceeding the legal drinking water limit of 11.3 mg/L NO_3-N, as observed in Etton (discussed in Section 2.2). Sources of groundwater nitrate have previously been assumed to be agricultural as farming is the primary industry in the region. This chapter explores the extent to which this assumption is correct using firstly hydrochemical data, followed by dual stable isotope analysis to identify likely nitrate sources and key processes. This enhanced understanding will enable more informed strategies to be developed for both land management and nitrate mitigation, as discussed towards the end of the chapter.

5.1 Sampling regime

Groundwater samples were collected from boreholes and springs to analyse NO_3 and other major ion concentrations and for NO_3 dual stable isotope analysis, as described in Section 0. Throughout this thesis sites are referenced using the three-letter code that follows the Environment Agency Unique Reference Number in "Site name" column in Table 3.1.

Additional hydrochemical data are analysed in this chapter to supplement hydrochemical and isotopic data collected for this study. The sources of these data are summarised in Table 3.5.

5.2 Hydrochemistry of the Kilham and Haisthorpe catchments

For both the Kilham and Haisthorpe catchments pH centred around 7.5, however there is notable variation (6.07-8.18; Figures 5.1 to 5.4). The range in Haisthorpe is less (6.56-7.91) than for Kilham (6.07-8.18). The pH expected for Chalk groundwater is typically 7.0-7.5 (Gale and Rutter, 2006), so the observed figures broadly correspond with this. Broadly, specific electrical conductivity (SEC) data in this study align to that of typical Chalk groundwater too; the Kilham catchment had a median SEC of 611 µS/cm and the Haisthorpe catchments of 617 µS/cm. Chalk groundwater tends to have SEC of approximately 700 µS/cm (Gale and Rutter, 2006). There was a substantial range in SEC, however: the Kilham catchment ranged from 104 to 2144 µS/cm (Figure 5.5, Figure 5.6) and the Haisthorpe catchments from 314 to 818 µS/cm (Figure 5.7, Figure 5.8). The lowest concentrations are likely due to human or instrument error, as 104 µS/cm is more similar to rainwater SEC than Chalk groundwater e.g. DEFRA (2020d). If troughs in SEC observed of c. 100 µS/cm were genuinely due to rainwater infiltration they would likely be observed more frequently and following storms/heavy rainfall events, which was not the case.

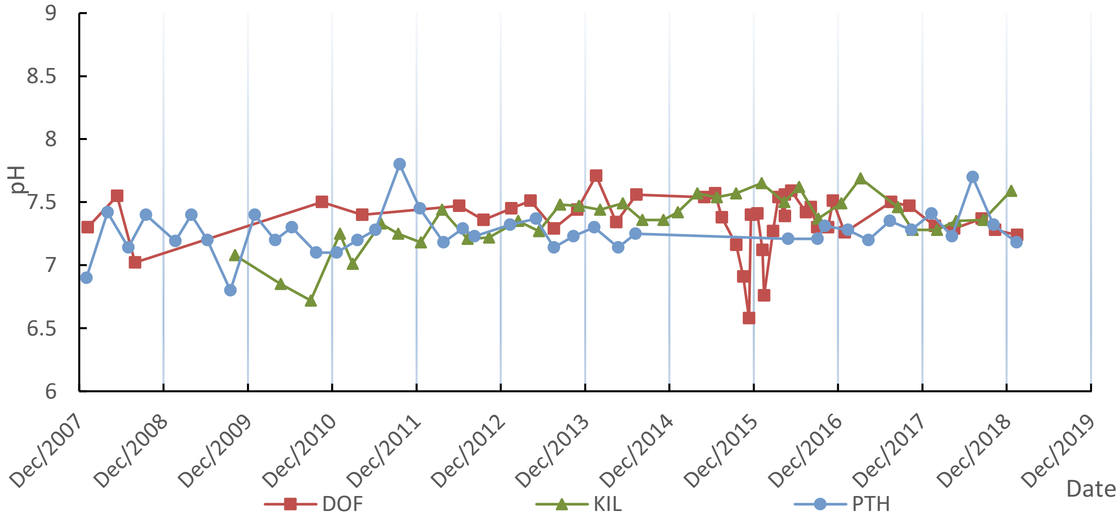

Figure 5.1: pH *in-situ* at sites in the Kilham catchment subject to long-term monitoring. Gridlines mark 31st December. Data from the Environment Agency (2020).

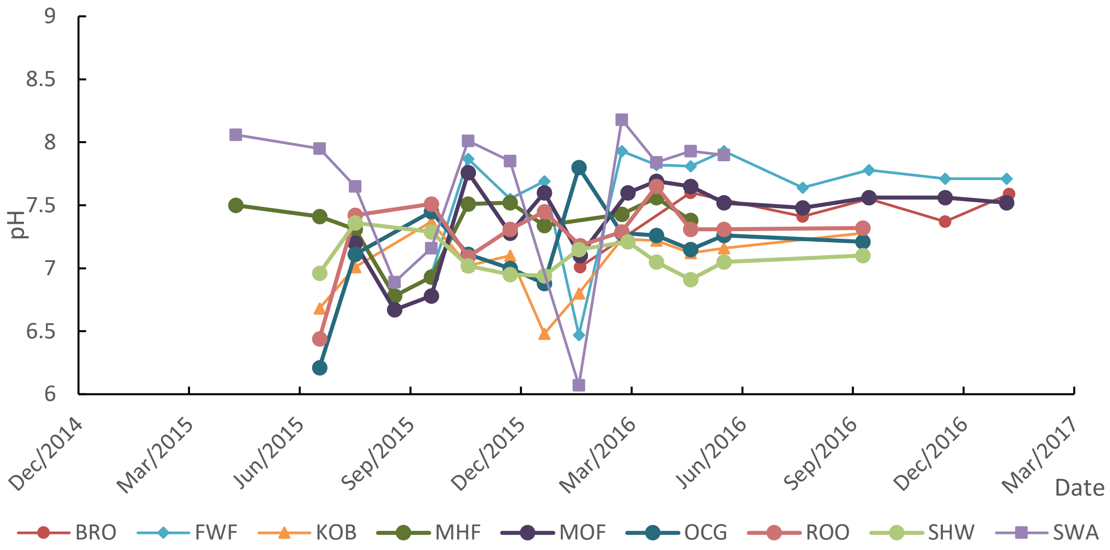

Figure 5.2: pH *in-situ* at sample sites in the Kilham catchment monitored for this study from 2015 until 2017. Data from the Environment Agency (2020).

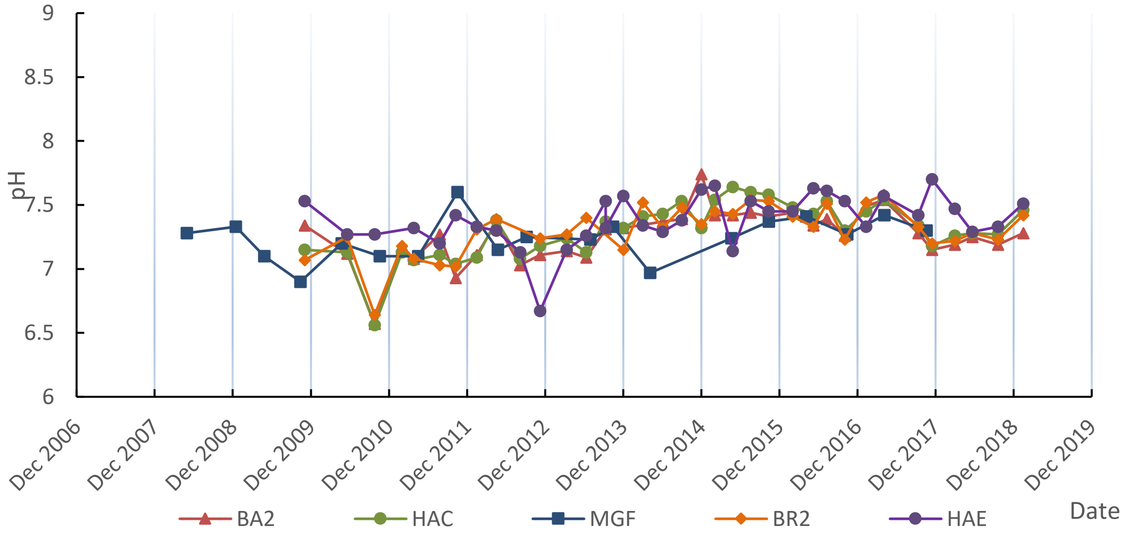

Figure 5.3: pH *in-situ* for sites subject to long-term monitoring in the Haisthorpe catchment. Gridlines mark 31st December. Data from the Environment Agency (2020).

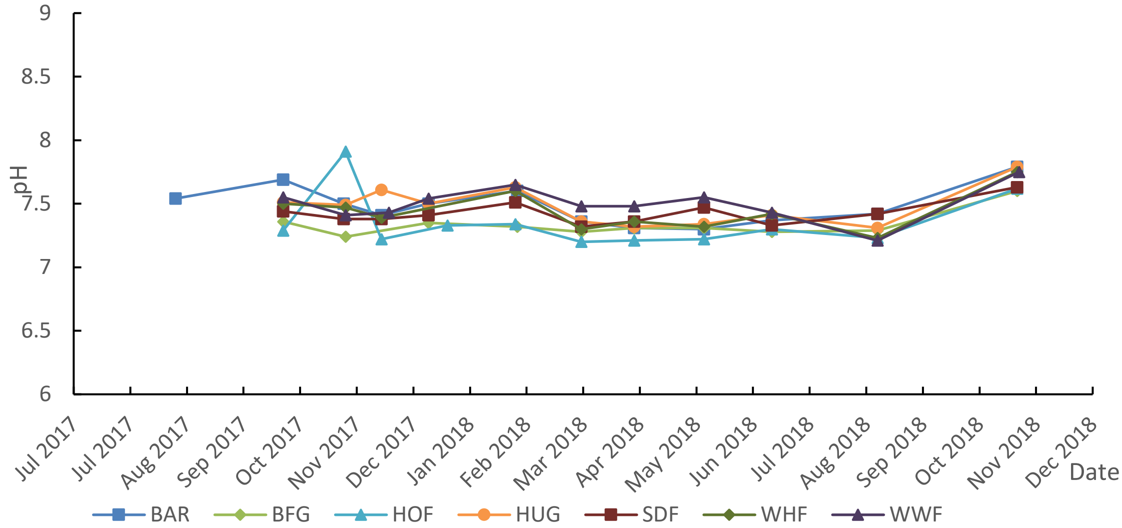

Figure 5.4: pH *in-situ* for sites in the Haisthorpe catchment monitored for the present study. Data from the Environment Agency (2020).

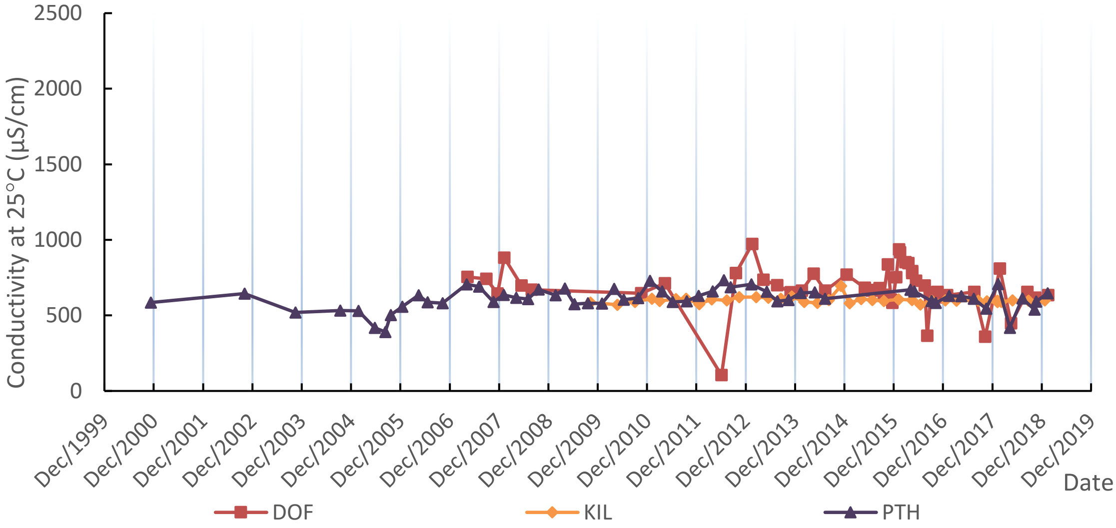

Figure 5.5: SEC at 25°C for long-term monitoring sites in the Kilham catchment. Gridlines mark 31st December. Data from the Environment Agency (2020).

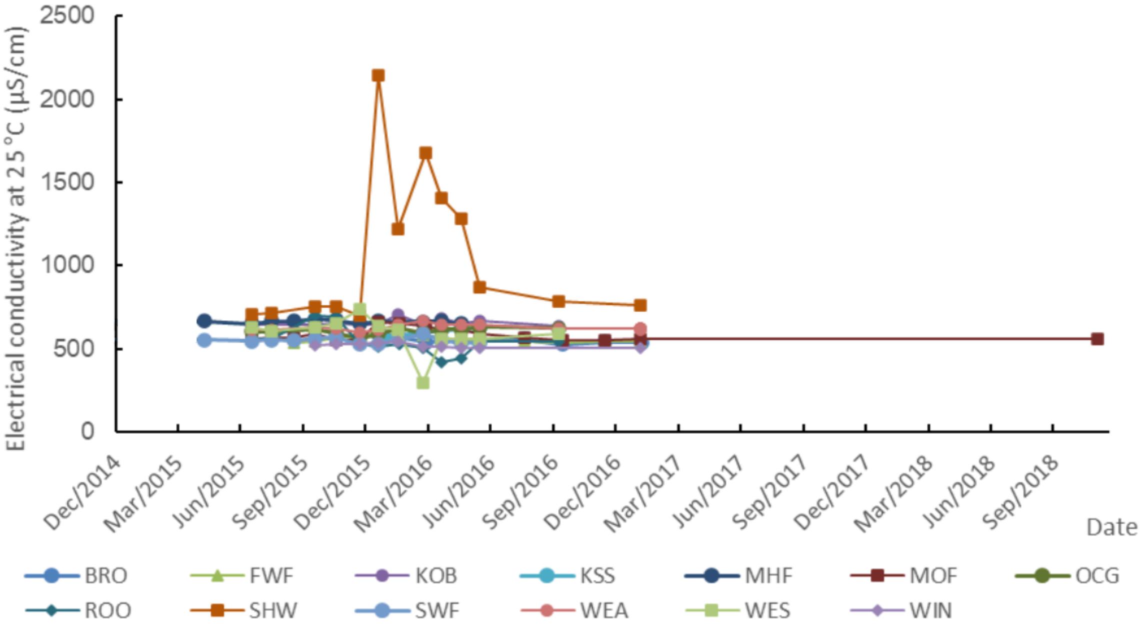

Figure 5.6: SEC at 25°C for sample sites monitored for this study in the Kilham catchment. Data from the Environment Agency (2020).

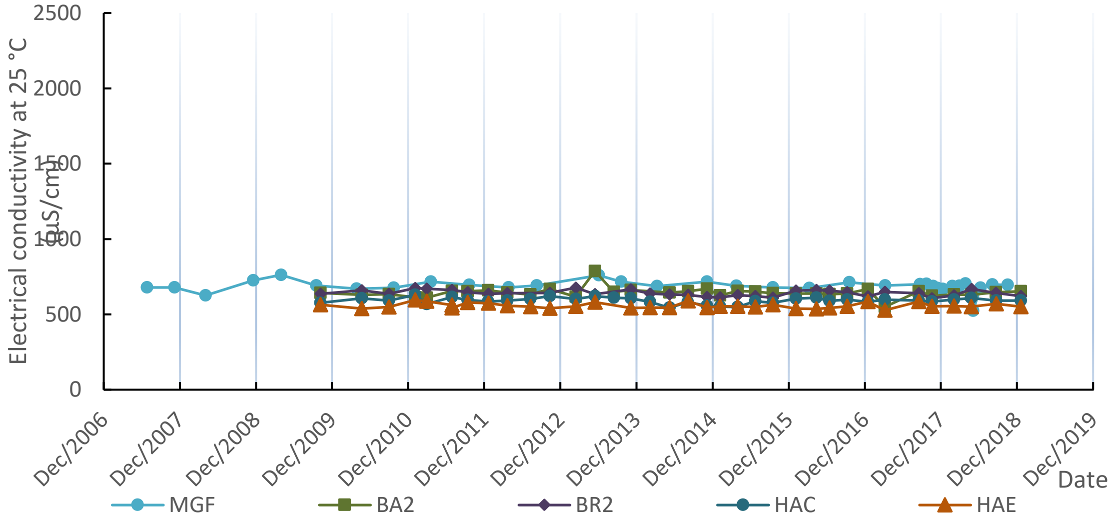

Figure 5.7: SEC at 25°C for sample sites subject to long-term monitoring in the Haisthorpe catchments. Data from the Environment Agency (2020).

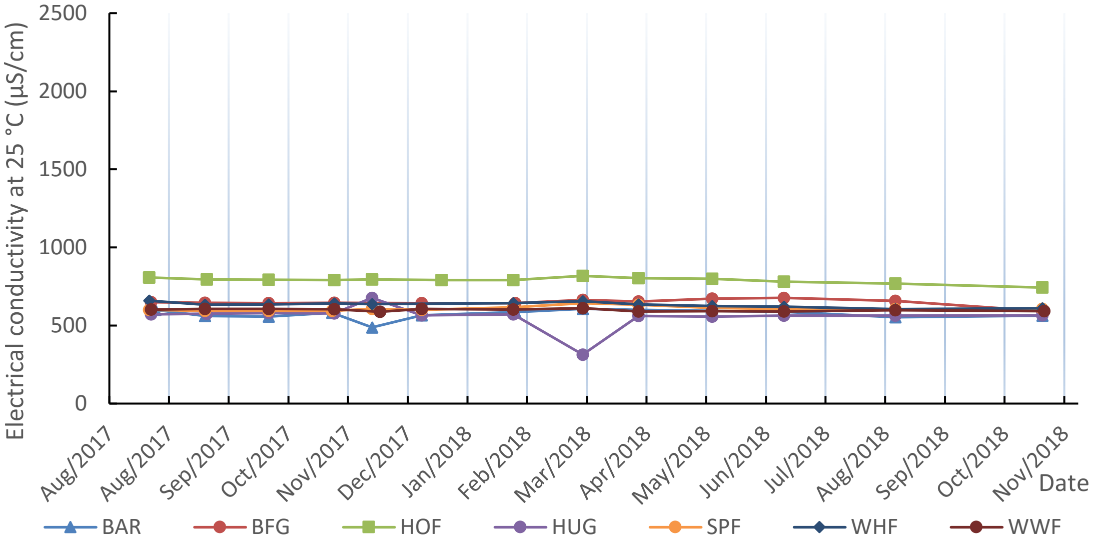

Figure 5.8: SEC at 25°C for sample sites monitored for this study in the Haisthorpe catchments. Data from the Environment Agency (2020).

Groundwater major ion chemistry in the Kilham and Haisthorpe catchments are broadly similar (Figure 5.9, Figure 5.10), reflecting their similar geologies and processes. HCO_3 and Ca concentrations dominated, as is expected in Chalk groundwater, and are similar between Kilham (181-366 mg/L HCO_3, 54.3-191 mg/L Ca) and Haisthorpe (165-310 mg/L HCO_3, 86.6-139 mg/L Ca) catchments, with greater variation in Kilham.

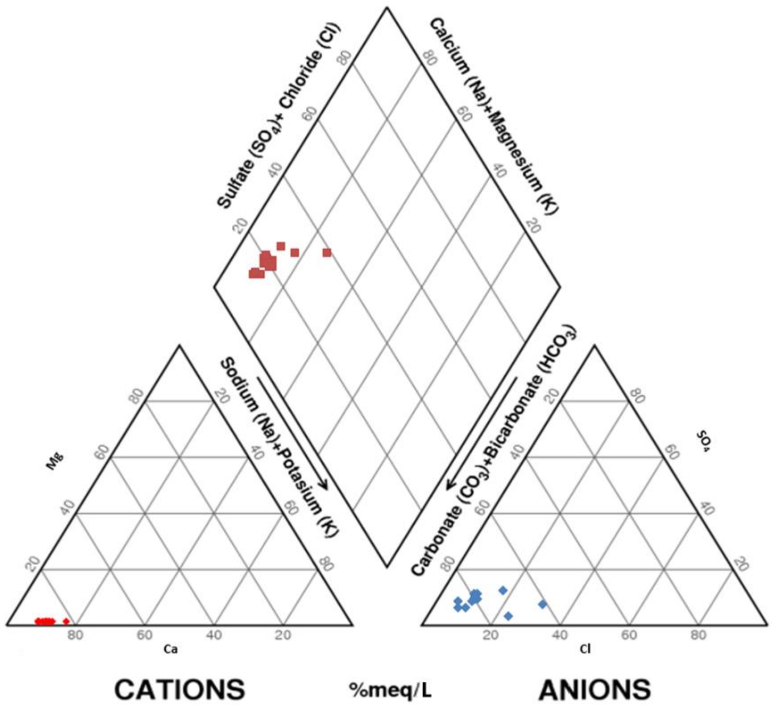

Figure 5.9: Piper plot using the mean ion concentrations for the Kilham catchment sample sites, from May 2000 to Feb 2019. There is less than 3% error in charge balance calculations. Data from the Environment Agency (2020).

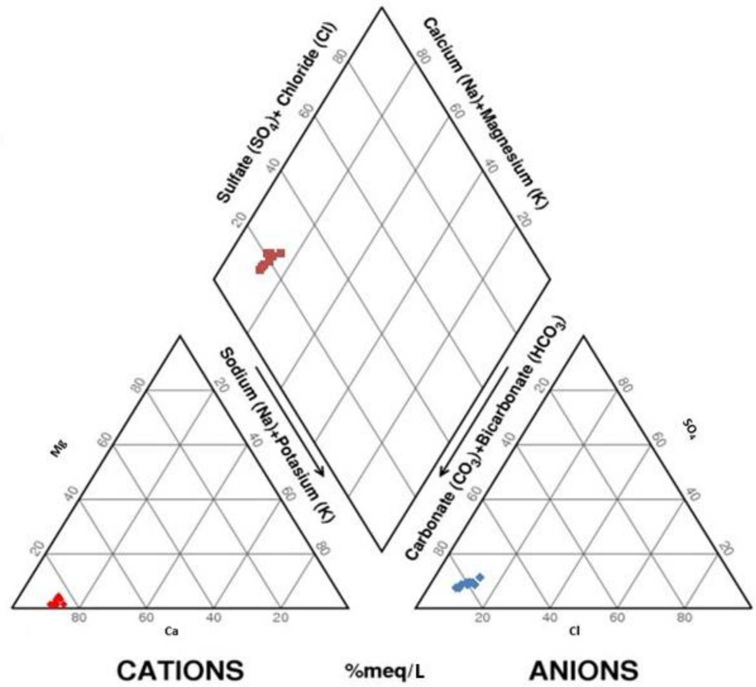

Figure 5.10: Piper plot of mean ion concentrations for sample sites in the Haisthorpe catchments, for 2000 to 2019, where data were available. There is less than 3% error in charge balance calculations. Data from the Environment Agency (2020).

5.2.1 Nitrate concentrations in the Kilham and Haisthorpe catchments

NO_3 concentrations from both the current study and long-term Environment Agency data are presented in Table 5.1. Concentrations range from 3.04 to 46.0 mg/L NO_3-N, however concentrations were typically between 8 and 16 mg/L NO_3-N. The majority of sites sampled exhibited NO_3 concentrations that were above the legal drinking water limit at some point during the studied periods (Table 5.1). Seven sites consistently had NO_3 concentrations beneath the limit, five of which are the most south easterly sites sampled (BA2, HAE, HAC, BR2 and BAR) and two were the most northerly (SHW and WIN). FWF, in the Kilham catchment, had very low NO_3 concentrations when it was first dug in 2015, however it then increased in concentration rapidly, likely as the borehole became more highly developed. DOF showed the most variation in NO_3 concentration, from 13.1 to 46.0 mg/L (Table 5.1, Figure 5.12).

Table 5.1: Minimum, mean and maximum NO_3-N concentrations for sites sampled in the Kilham and Haisthorpe catchments. The sampling period varied thus is included in brackets, and NO_3 values greater than the legal drinking water limit of 11.3 mg/L NO_3-N in bold red. The sites are referenced throughout the text using the three letter code at the end of the full site name. Data from the Environment Agency, Yorkshire Water, and Agbotui (2019).

Site name (dates monitored)		**NO_3-N concentration (mg/L)**		**Site name** (dates monitored)		**NO_3-N concentration (mg/L)**
400G0115-BAR (24/08/17-13/11/18) *n=13*	Min	8.7		**400G0094-BR2** (04/11/09-15/01/19) *n=34*	Min	9.9
	Mean	9.9			Mean	10.5
	Max	10.7			Max	11.3
400G0086-BA2 (04/11/09-15/01/19) *n=35*	Min	8.3		**400G0117-BFG** (22/07/17-13/11/18) *n=12*	Min	**14.4**
	Mean	9.0			Mean	**15.4**
	Max	9.6			Max	**17.3**
400G0090-HAC (04/11/09-15/01/19) *n=36*	Min	6.7		**400G0091-HAE** (04/11/09-15/01/19 *n=36*	Min	7.3
	Mean	7.6			Mean	8.3
	Max	8.2			Max	8.8
400G0116-HOF (21/08/17-13/11/18) *n=13*	Min	**14.2**		**400G0008-HUG** (22/08/17-31/11/18) *n=16*	Min	**13.7**
	Mean	**15.1**			Mean	**14.2**
	Max	**16.1**			Max	**14.7**
400G0074-MGF (26/07/07-13/11/18 *n=33*	Min	**14.3**		**400G0118-SDF** (21/07/17-13/11/18) *n=13*	Min	**13.0**
	Mean	**15.5**			Mean	**14.0**
	Max	**16.9**			Max	**17.0**
400G0006-WHF (21/08/17-13/11/18) *n=13*	Min	**14.1**		**400G0119-WWF** (22/08/17-14/11/18) *n=13*	Min	**11.6**
	Mean	**15.2**			Mean	**12.4**
	Max	**16.2**			Max	**13.0**
400G0112-WIN (14/10/2015-24/01/2017) *n=10*	Min	7.8		**400G0093-KIL** (04/11/2009-16/01/2019) *n=35*	Min	**12.3**
	Mean	8.3			Mean	**13.7**
	Max	9.8			Max	**14.3**
Spring BEL (17/02/2017-19/01/2018) *n=8*	Min	8.1		**400F0018-KOB** (17/05/2000-29/09/2016) *n=62*	Min	11.1
	Mean	**13.5**			Mean	**15.0**
	Max	**14.2**			Max	**16.2**
Spring 40001257-BRA (17/02/2017-19/01/2018) *n=9*	Min	5.66		**Spring 49200297-KSS** (22/01/2016-08/06/2016) *n=4*	Min	**13.1**
	Mean	**11.9**			Mean	**13.4**
	Max	**12.2**			Max	**13.5**
400F0012-BRO (17/05/2000-26/01/2017) *n=82*	Min	10.2		**Spring 49200298-KSP** (22/01/2016) *n=1*	Min	**13.8**
	Mean	**11.6**			Mean	**13.8**
	Max	**13.7**			Max	**13.8**
400G0082-DOF (10/05/2007-11/02/2019) *n=47*	Min	**13.1**		**400G0027-MHF** (25/09/2001-12/05/2016) *n=12*	Min	**13.5**
	Mean	**24.9**			Mean	**14.4**
	Max	**46.0**			Max	**15.0**

Site name (dates monitored)		**NO_3-N concentration (mg/L)**		**Site name** (dates monitored)		**NO_3-N concentration (mg/L)**
400G0110-FWF (14/09/2015-24/01/2017) *n=14*	Min	3.04		**400G0109-MOF** (15/07/2015-14/11/2017) *n=17*	Min	**12.0**
	Mean	**11.5**			Mean	**15.7**
	Max	**13.8**			Max	**24.0**
400G0107-OCG (15/07/2015-29/09/2016) *n=13*	Min	8.62		**400G0105-WEA** (15/07/2015-21/01/2017) *n=20*	Min	**13.6**
	Mean	**13.5**			Mean	**15.0**
	Max	**16.0**			Max	**16.8**
400G0108-ROO (15/07/2015-29/09/2016) *n=13*	Min	7.56		**400G0072-WES** (15/07/2015-29/09/2016) *n=13*	Min	10.8
	Mean	10.0			Mean	**12.7**
	Max	**11.7**			Max	**13.7**
400G0106-SHW (15/07/2015-25/01/2017) *n=14*	Min	4.38		**40000399-KWT** (04/01/2016-06/10/2017) *n=41*	Min	**13.6**
	Mean	4.76			Mean	**14.1**
	Max	5.33			Max	**14.6**
400G0023-SWA (11/08/2000-08/06/2016) *n=14*	Min	10.1		**400G0022-PTH** (07/12/2000-08/02/2019) *n=56*	Min	10.0
	Mean	**11.7**			Mean	**13.4**
	Max	**12.2**			Max	**19.3**

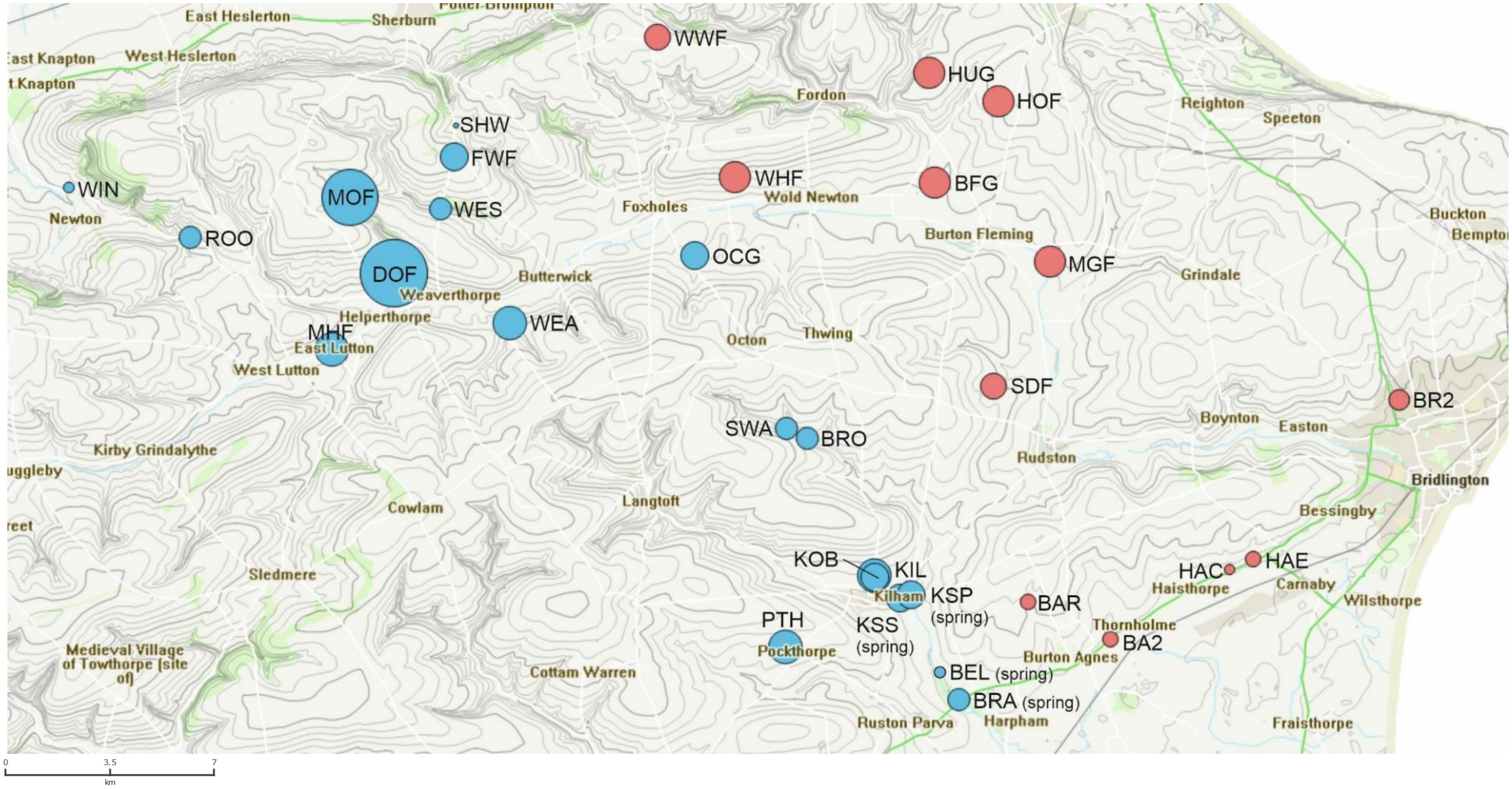

Figure 5.11: Map of NO_3-N concentrations in the Haisthorpe (red) and Kilham (blue) catchments, for November 2017, or January to April 2016 respectively, depending on data availability (except for BEL (spring) where the presented concentration is from March 2017). Circles increase in size with increasing NO_3-N concentrations(min= 4.5 mg/L NO_3-N, max=27.0 mg/L NO_3-N).

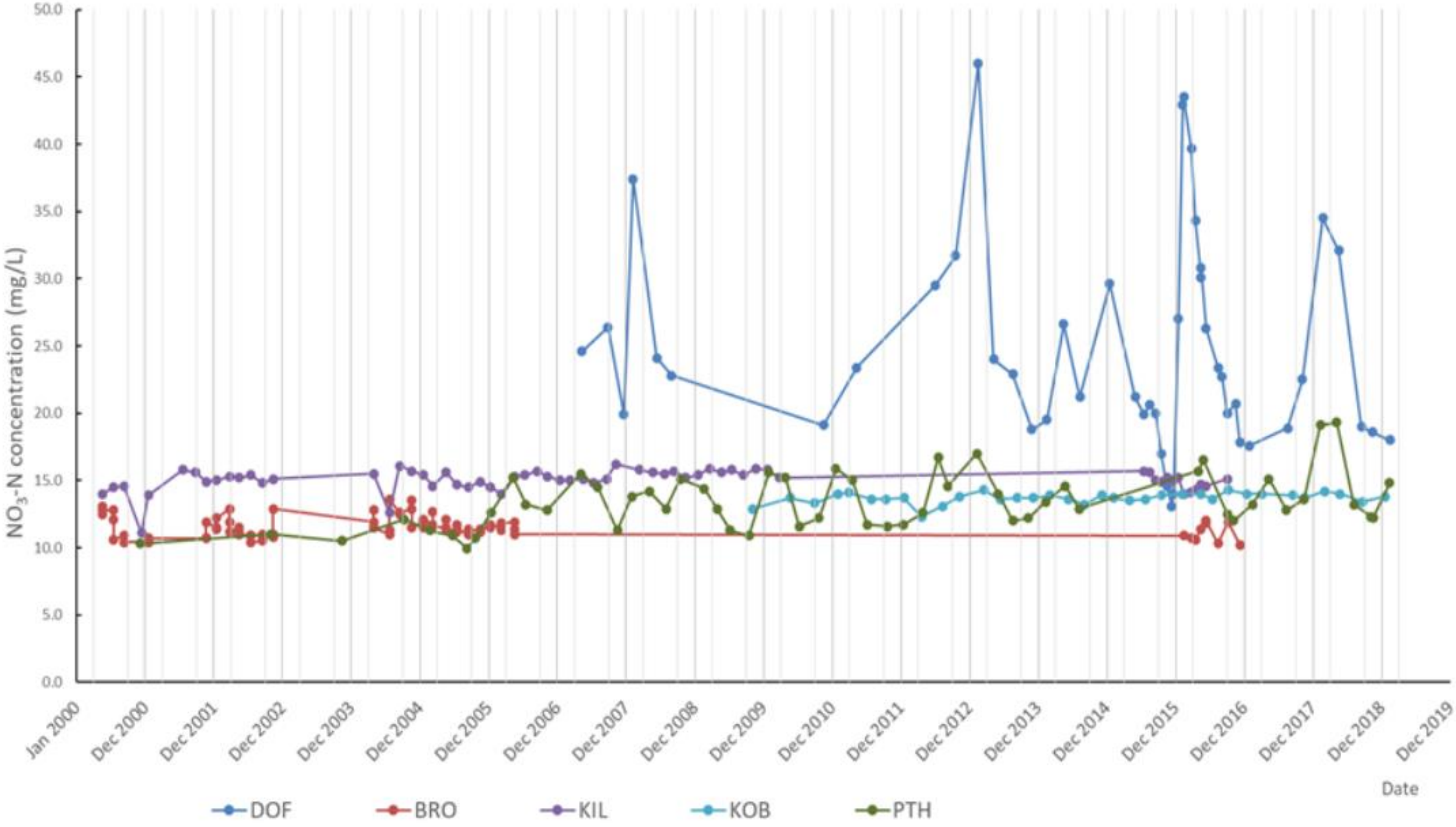

Figure 5.12: NO_3-N concentrations from 2000 to 2018 for sites in the Kilham catchment that have undergone long-term monitoring. Dark grey gridline = 31st December; light grey gridlines = 3 months either side of 31st December i.e. 31st March or 30th September. Data from the Environment Agency (2020).

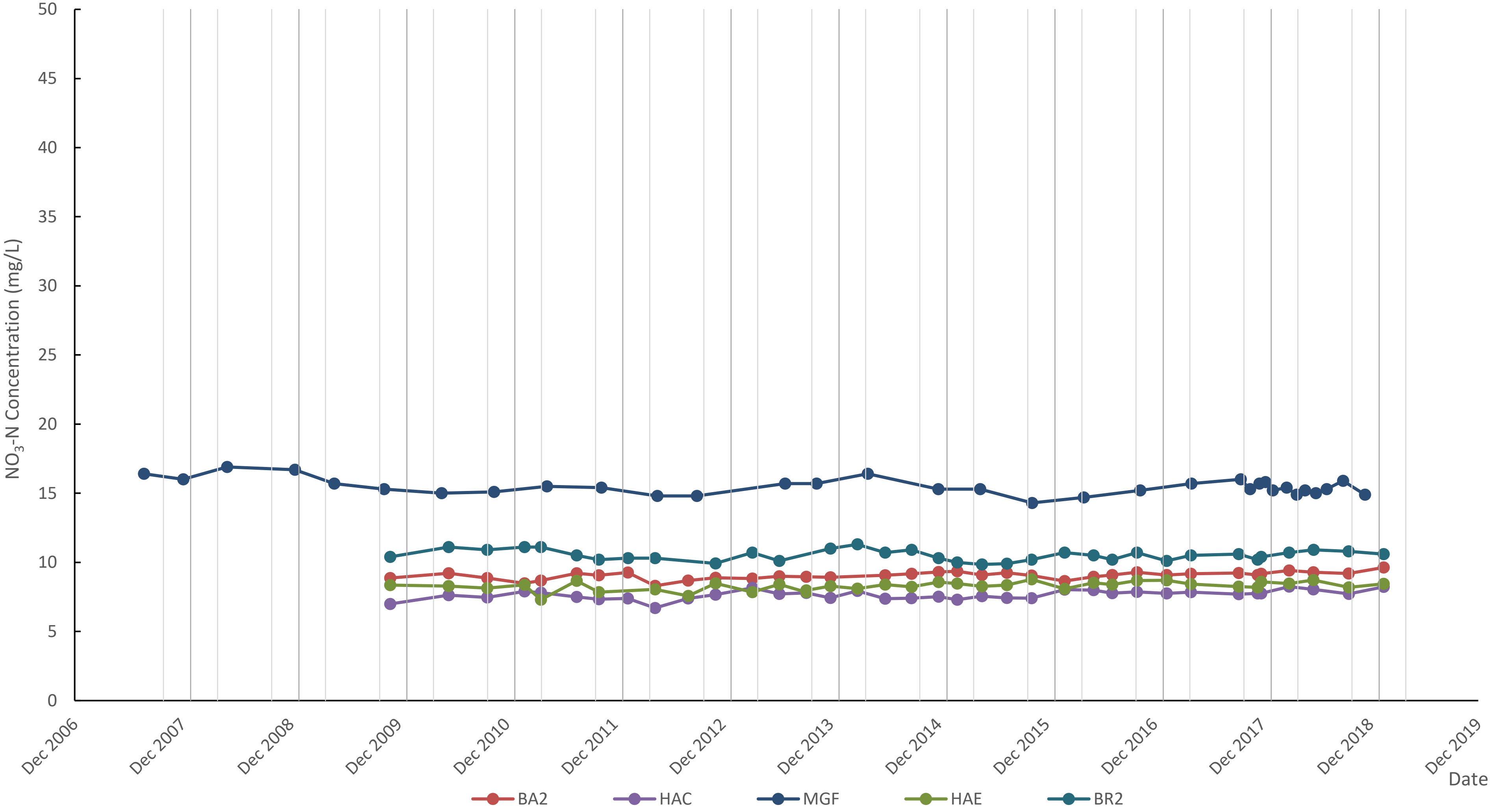

Figure 5.13: NO_3-N concentrations from 2007 to 2019 for sites in the Haisthorpe catchment that have undergone long-term monitoring. Dark grey gridline = 31st December; light grey gridlines = 3 months either side of 31st December i.e. 31st March or 30th September. Data from the Environment Agency (2020).

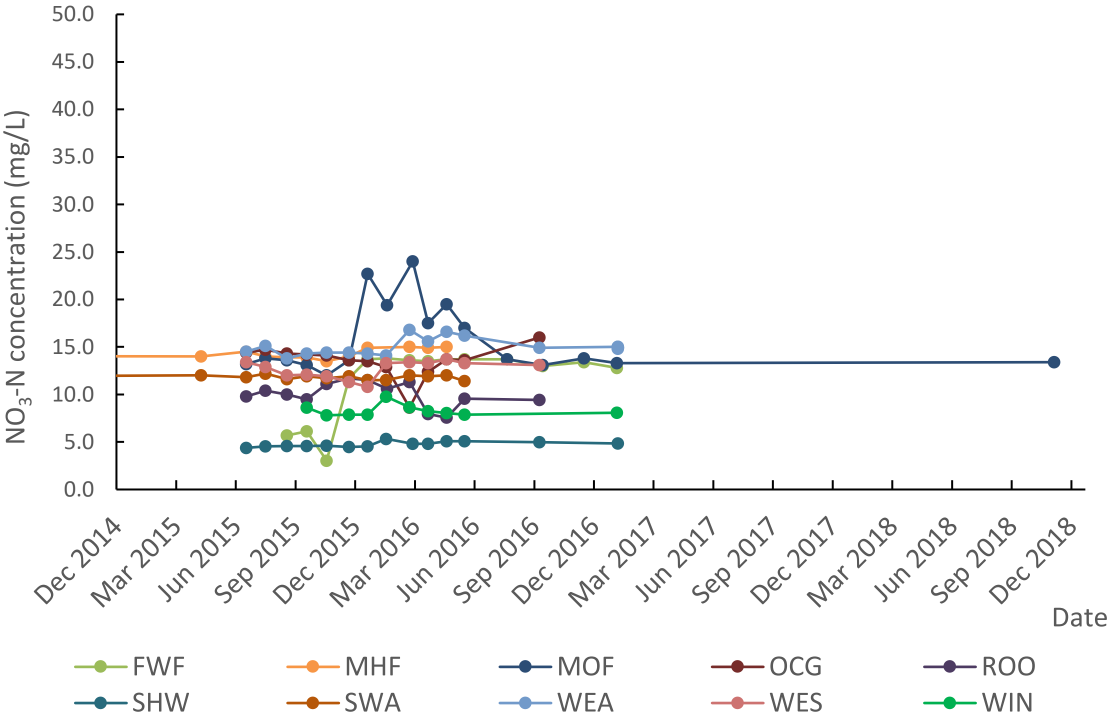

Figure 5.14: NO_3-N concentrations for sites in the Kilham catchment that were sampled for this study. Data from the Environment Agency (2020).

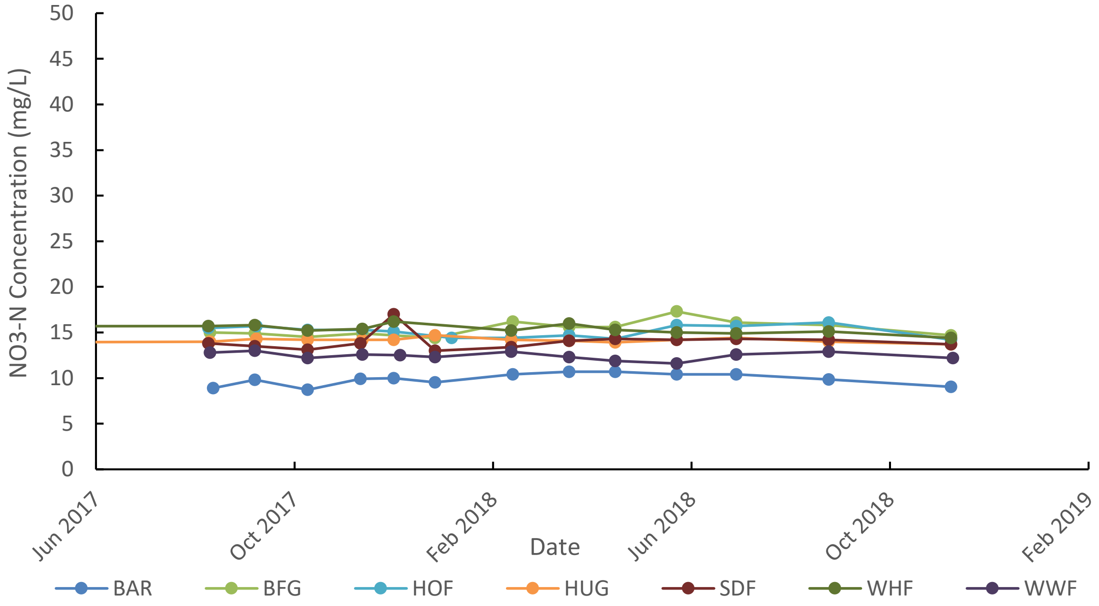

Figure 5.15: NO_3-N concentrations for sites in the Haisthorpe catchment that were sampled for this study. Data from the Environment Agency (2020).

5.2.2 Idiosyncratic hydrochemistry observed in the Kilham catchment

Some sample sites exhibited hydrochemistry that was different to that expected of Chalk groundwater, or to the typical character of the Kilham and Haisthorpe catchments discussed in Section 5.3. Sample sites where this was most notable were DOF and SHW, with FWF demonstrating a change over time; all three of which are in the Kilham catchment. Hydrochemistry appeared more stable in the Haisthorpe catchment.

Figure 5.16 shows major ions plotted against time at DOF, where the highest HCO_3 concentration in the catchment was recorded (366 mg/L, in November 2015). This occurred just prior to a spike in Cl, SO_4, NO_3, Na and K. There were similar patterns in 2008 and 2013 (Figure 5.16). SHW also had high HCO_3 concentrations and the highest Ca concentrations, between December 2015 and Jun 2016 (Figure 5.17). Possible seasonal variation in major ion concentrations were observed at SHW (Figure 5.17) with increases in several ion concentrations from December to May, during recharge season, and stabilising by June. Similar observations were made for several sites (Environment Agency, 2020). At SHW the seasonal change in concentration was particularly apparent for Na and Cl.

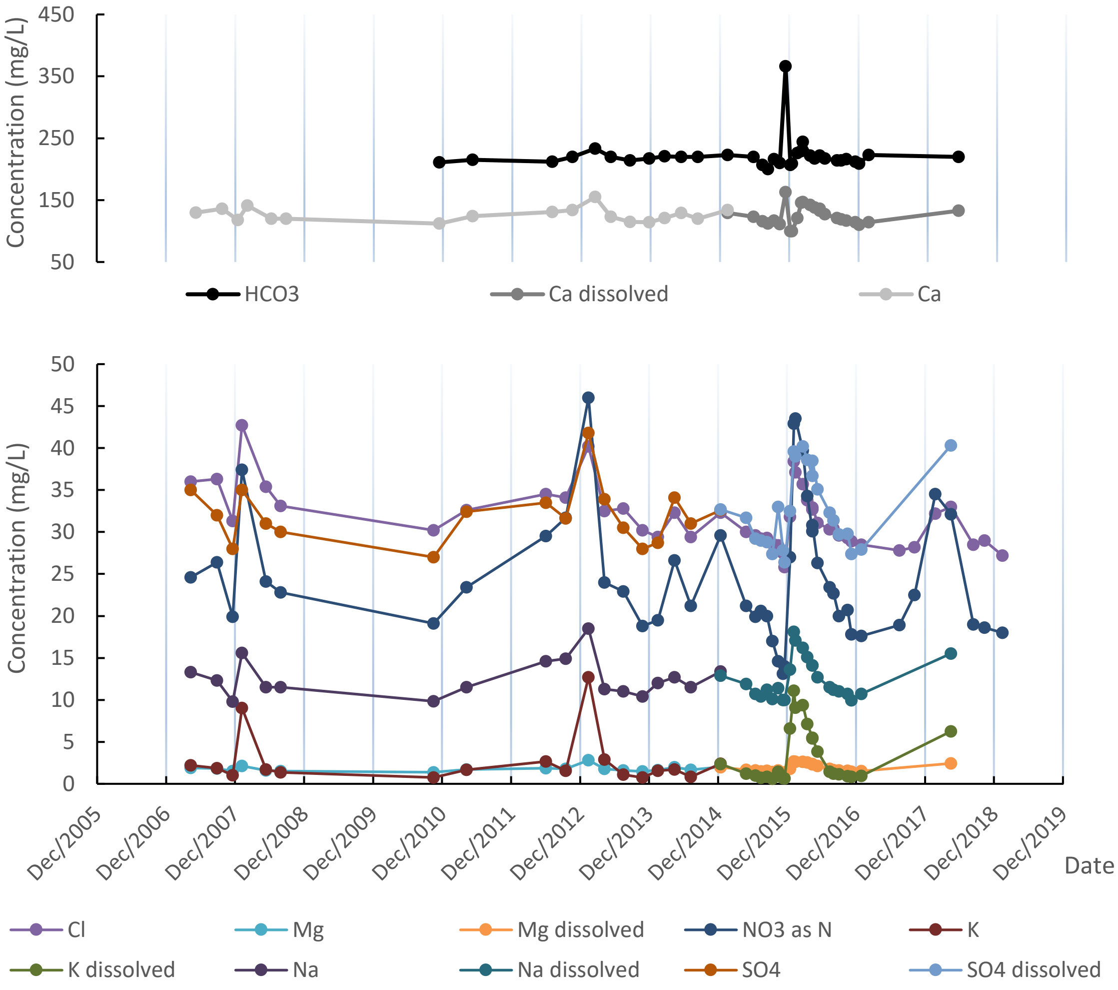

Figure 5.16: Major ions at DOF from May 2007 to February 2019. [Note: Ca and HCO_3 concentrations presented on separate plot to aid clarity]. Major gridline = 31st December. Data from the Environment Agency (2020).

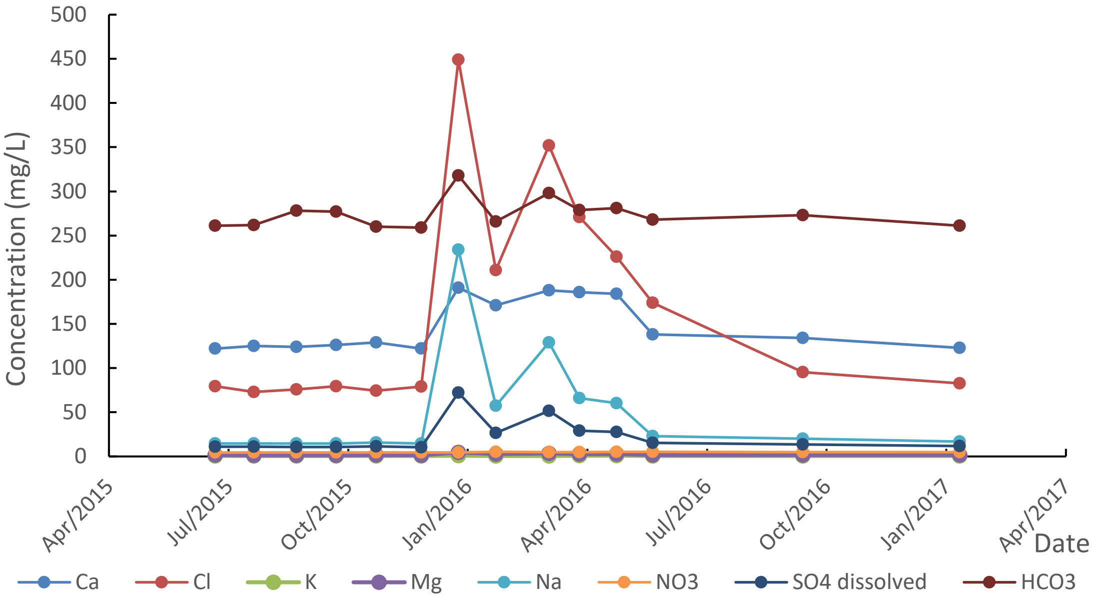

Figure 5.17: Hydrochemistry at SHW in the Kilham catchment from 2015 to 2017. Data from the Environment Agency (2020).

At FWF, which was newly drilled in 2015, initial HCO_3 and Ca concentrations were 229-237 mg/L and 54.3-65.5 mg/L, respectively (Figure 5.18). As the borehole developed, HCO_3 concentrations decreased and stabilised to 192-200 mg/L while Ca increased and stabilised to 94.2-100 mg/L. NO_3-N concentrations at this borehole were initially very low (3.0-6.1 mg/L) but over the same period increased to 12.8-13.8 mg/L (Figure 5.18).

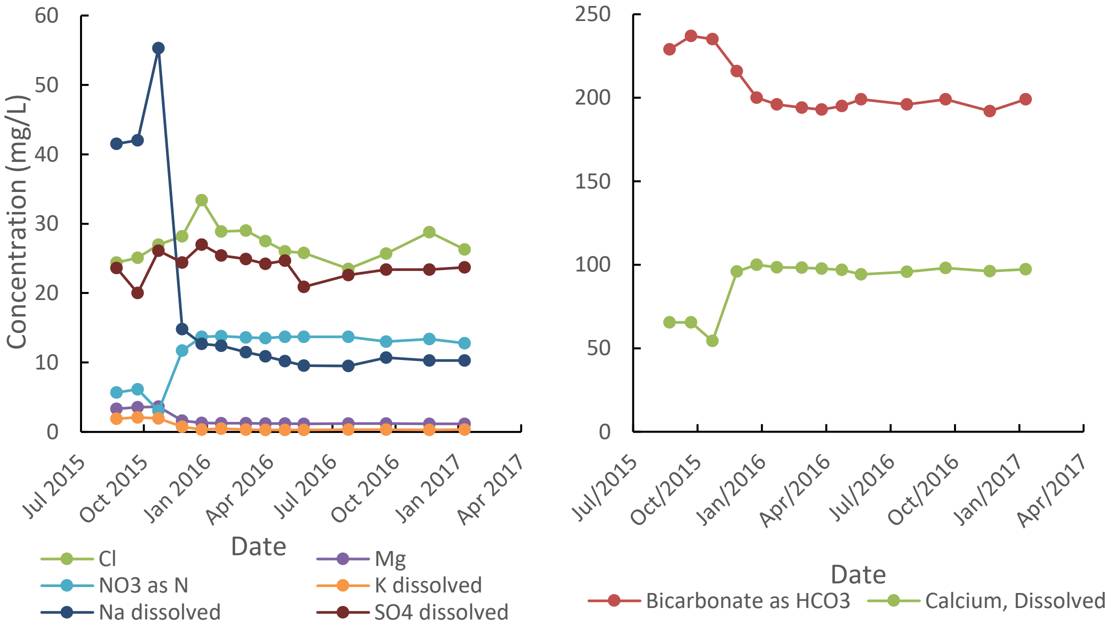

Figure 5.18: Hydrochemistry at FWF in the Kilham catchment from 2015 to 2017. Ca and HCO_3 concentrations presented on separate plot (right) to aid clarity. FWF was newly drilled at the beginning of the current study. Data from the Environment Agency (2020).

5.2.3 Nitrate to chloride ratios in the Northern Province Chalk catchments

Cl is not affected by chemical or biological processes and therefore its concentration can be indicative of pollution source or key processes (Li et al., 2010). Changes in its concentration can imply a physical process: dilution or evaporation. Hence, paired with NO_3 concentrations, NO_3-N:Cl can be used to further constrain possible NO_3 sources and give validation to conclusions. The NO_3-N:Cl ratio of freshwater can be indicative of mixing or biological processes, as demonstrated by Yue et al. (2017). It can also help differentiate dilution from denitrification e.g. Mengis et al. (1999), Widory et al. (2005). Inorganic fertiliser sources tend to have a high ratio of NO_3-N:Cl whereas sewage or manure sources have higher Cl and therefore a lower ratio (Liu et al., 2006, Widory et al., 2005). When both Cl and NO_3 concentrations are low, the source is likely natural processes. While there are N and Cl sources that will defy these principles, interpretation of NO_3-N:Cl may help in identifying dominant N sources in the study catchments. Generally, comparison of climate in the Yorkshire Wolds catchments with that studied by Yue et al. (2017), see Appendix 1, shows that in the Yorkshire Wolds NO_3 concentrations are higher than Yue et al. (2017) while evapotranspiration effects are much less significant. Due to the relatively small influence of evapotranspiration in the Yorkshire catchments, it is not thought to be the main driver of changes in NO_3-N:Cl.

Most samples for the Kilham and Haisthorpe catchments were clustered just below 0.001 moles Cl (approx. 35 mg/L), giving NO_3-N:Cl ratios of 0.6-1.5 (Figure 5.19); they also fit the theoretical "increasing Cl with constant NO_3" curve. Figure 5.19 shows that Cl concentrations were relatively constant between most sites, however the range including outliers in the Kilham and Haisthorpe catchments was still substantial, from 0.0004 to 0.003 moles Cl (approx. 14 to 106 mg/L), excluding site SHW, which had higher Cl and is discussed in Section 5.2.2 and presented in Figure 5.17. The data for SHW are similar to the theoretical trendline for increasing Cl with constant NO_3 (see dashed curve on Figure 5.19), indicating that the change in ratio was primarily due to an increase in Cl and not a change in NO_3 concentration.

Several sites, aside from SHW, did not fit on the increasing Cl, constant NO_3 trendline: DOF, MOF and PTH had high NO_3 and intermediate Cl concentrations and form a near-vertical trend distinct from the theoretical trendline. The ratios from FWF, BAR, BA2 and WIN fall on similar gradients to those from sites DOF, MOF and PTH on Figure 5.19, i.e. nearly vertical gradient. However, FWF, BAR, BA2 and WIN had low Cl and low NO_3-N:Cl ratios, so more natural sources could have dominated. Given FWF was newly drilled, and only local groundwater conditions were observed to begin with, a more natural NO_3 source in comparison to other sites would be feasible. The near vertical gradient implies mixing between sources with constant Cl concentrations but variable NO_3.

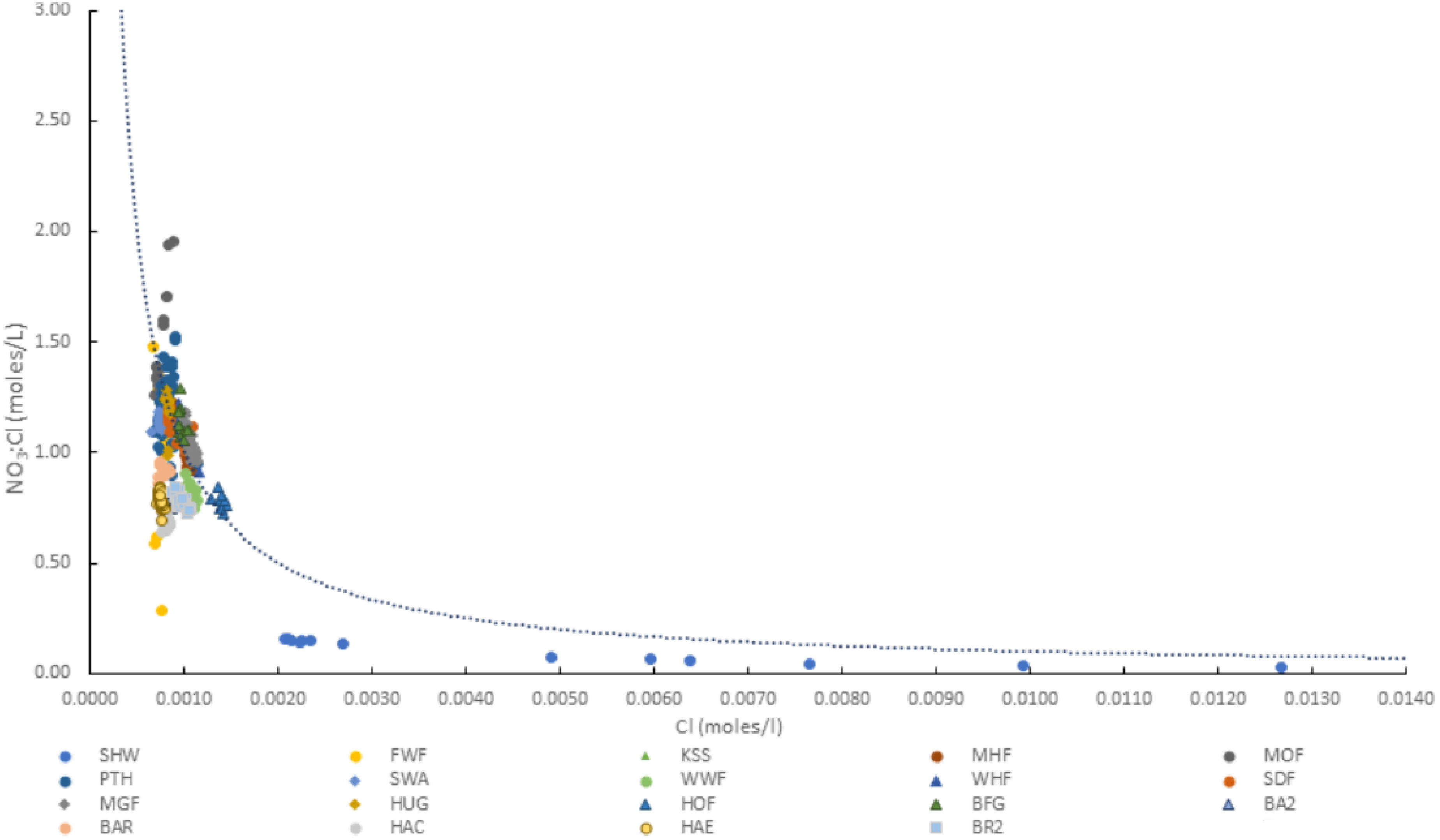

Figure 5.19: NO_3-N:Cl ratios for the Kilham and Haisthorpe catchments, with a theoretical trendline for increasing Cl and constant NO_3-N concentrations.

5.2.3.1 Seasonality of nitrate to chloride ratios in the Northern Chalk catchments

There does not appear to be a uniform seasonal signal for NO_3-N:Cl ratios across the Kilham and Haisthorpe catchments; some of the sites show more pronounced seasonal variations than others (Figure 5.20, Figure 5.21). However, some sites appear to have an individual seasonal response, with a peak in the ratio often falling between February and March, towards the end of the recharge season (Figure 5.21).

The NO_3-N:Cl ratio increased during the recharge period (typically November to April) at four sites (MOF, DOF, ROO and MHF). At sites DOF and MOF (Figure 5.21c, f) there were both higher NO_3 and Cl concentrations during recharge, however the increase in NO_3 was proportionally larger than the Cl increase. At sites MHF and ROO NO_3 concentrations increased during recharge while Cl concentrations decreased (Figure 5.21e, i), while at WHF NO_3 concentrations were constant and Cl decreased during the recharge period (Figure 5.21m). At sites SDF and SHW (Figure 5.21j, k), higher Cl in the recharge season resulted in lower NO_3-N:Cl ratios. Site FWF appeared to show lower NO_3 during the recharge period and therefore a lower ratio of NO_3-N:Cl (Figure 5.22), however this is likely because FWF was newly drilled when sampled at the beginning of the hydrogeological year and thus local conditions rather than catchment-wide conditions were captured initially (discussed in more detail in Section 5.5.4).

Increased NO_3 and Cl concentrations were observed periodically at DOF, MOF and possibly PTH (Figure 5.21c, f and h), whereas decreased Cl concentration during recharge season was observed for ROO and MHF (Figure 5.21e and i). At SHW (Figure 5.21k) NO_3 concentrations stayed stable over the recharge season but Cl increased; SDF had similarly stable NO_3.

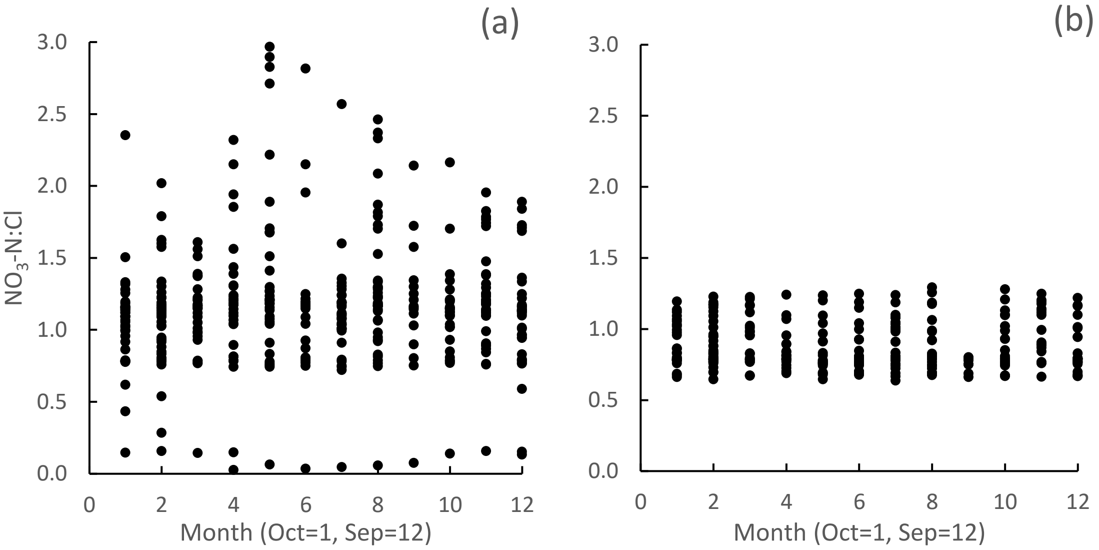

Figure 5.20: Seasonal NO_3-N:Cl for (a) Kilham and (b) Haisthorpe catchments. Months begin from the start of the hydrogeological year thus Oct=1 and Sep=12.

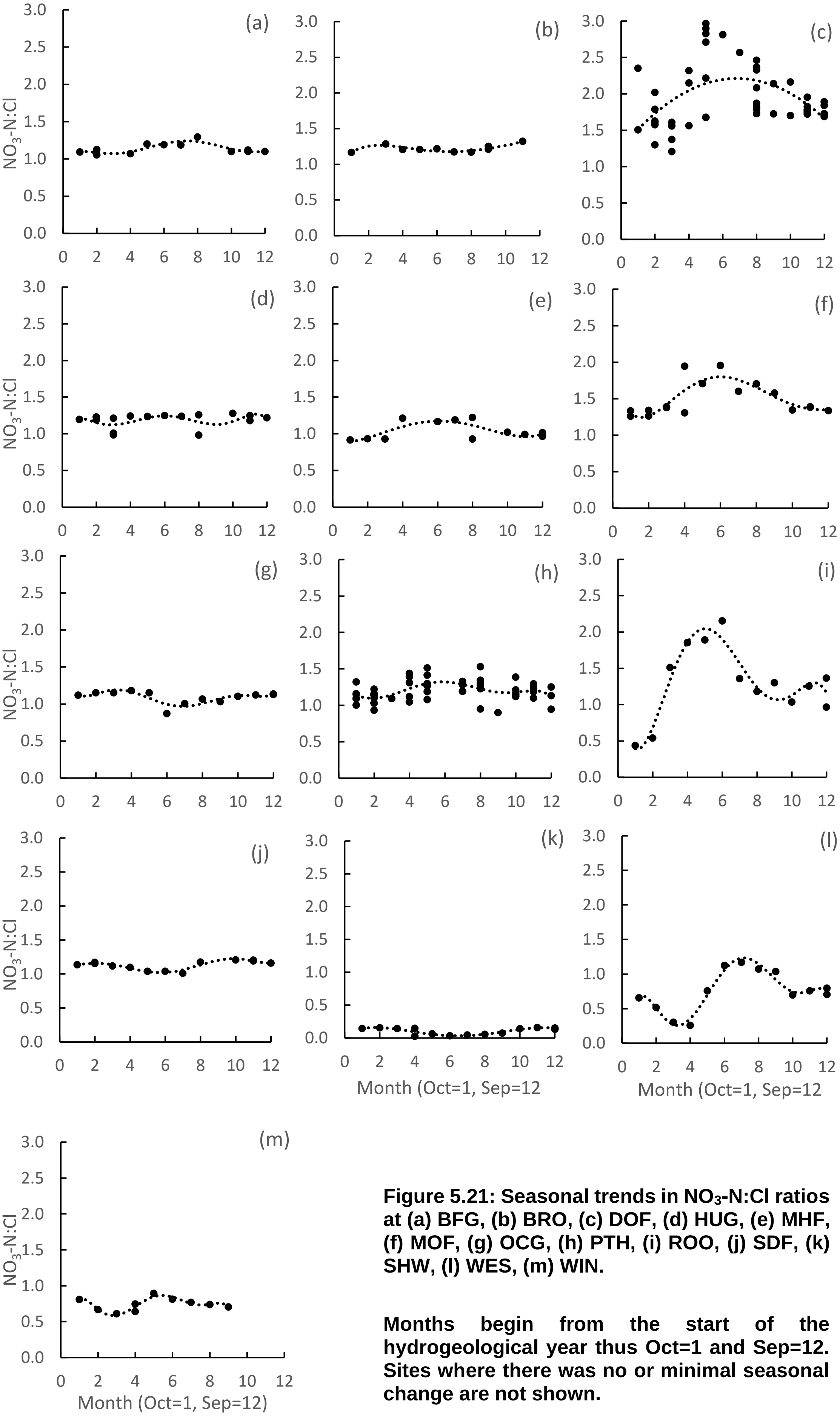

Figure 5.21: Seasonal trends in NO_3-N:Cl ratios at (a) BFG, (b) BRO, (c) DOF, (d) HUG, (e) MHF, (f) MOF, (g) OCG, (h) PTH, (i) ROO, (j) SDF, (k) SHW, (l) WES, (m) WIN.

Months begin from the start of the hydrogeological year thus Oct=1 and Sep=12. Sites where there was no or minimal seasonal change are not shown.

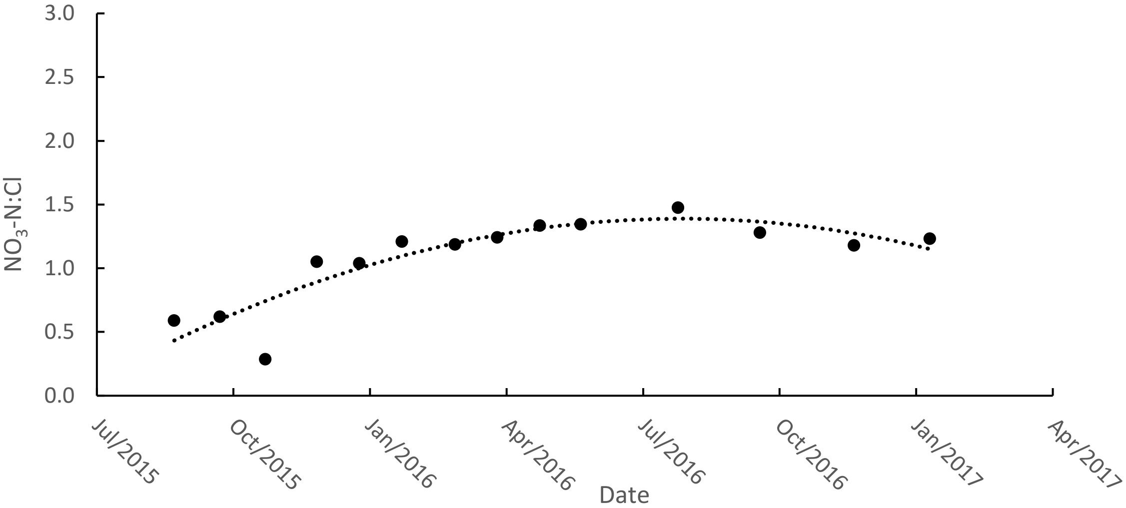

Figure 5.22: NO_3-N:Cl ratios at FWF from the first sampling date after the borehole was drilled. (Note different x-axis to Figure 5.21.)

5.3 Results of dual stable isotope analysis of the Northern Province Chalk groundwater catchments

Of the analyses for stable isotopes of N and O in NO_3, all of the Haisthorpe catchments and the majority of Kilham catchment samples, fall within the "Soil N box" on the fingerprinting diagram (Figure 5.23). Some also fall within the "ammonium in fertiliser" and "manure and sewage" boxes. However, it is key to note that isotope analyses only produce the mean signature of a sample and so the fingerprinting plot cannot identify where transformations have occurred (discussed in further detail in Section 5.4 and Chapter 7). Analyses of groundwater samples from both catchments cluster around a similar point (δ^{15}N of +4 to +6‰ and δ^{18}O of 0 to +4‰). Samples from the Haisthorpe catchments show less variation in signatures than samples from Kilham catchment (Figure 5.23). Four of the sites in Kilham catchment were springs (BEL, BRA, KSS, KPS; marked on Figure 5.23 in red) and account for some of the points that plot outside of the cluster described above (δ^{15}N of +4 to +6‰ and δ^{18}O of 0 to +4‰) in the Kilham data. BEL and BRA had amongst the lowest δ^{15}N of all samples (+1.86 and +1.88‰, respectively; only OCG in November 2015 was lighter with δ^{15}N of -1.6‰[1]) while KSS and KSP fell within the cluster for δ^{15}N. δ^{18}O was heavier than the cluster (δ^{18}O greater than +4‰) for all four spring sites, except KSS in April

---

[1] Excluded from analyses as it was an outlier.

2016 (+3.0‰). Haber-Bosch (HB) NO_3 fertiliser signatures, with heavy-$\delta^{18}O$, were not identified though dual stable isotope analysis (Figure 5.23). However, some signatures have heavier $\delta^{18}O$ than the identified cluster, which could be contributed by a small proportion of fertiliser with heavy-$\delta^{18}O$.

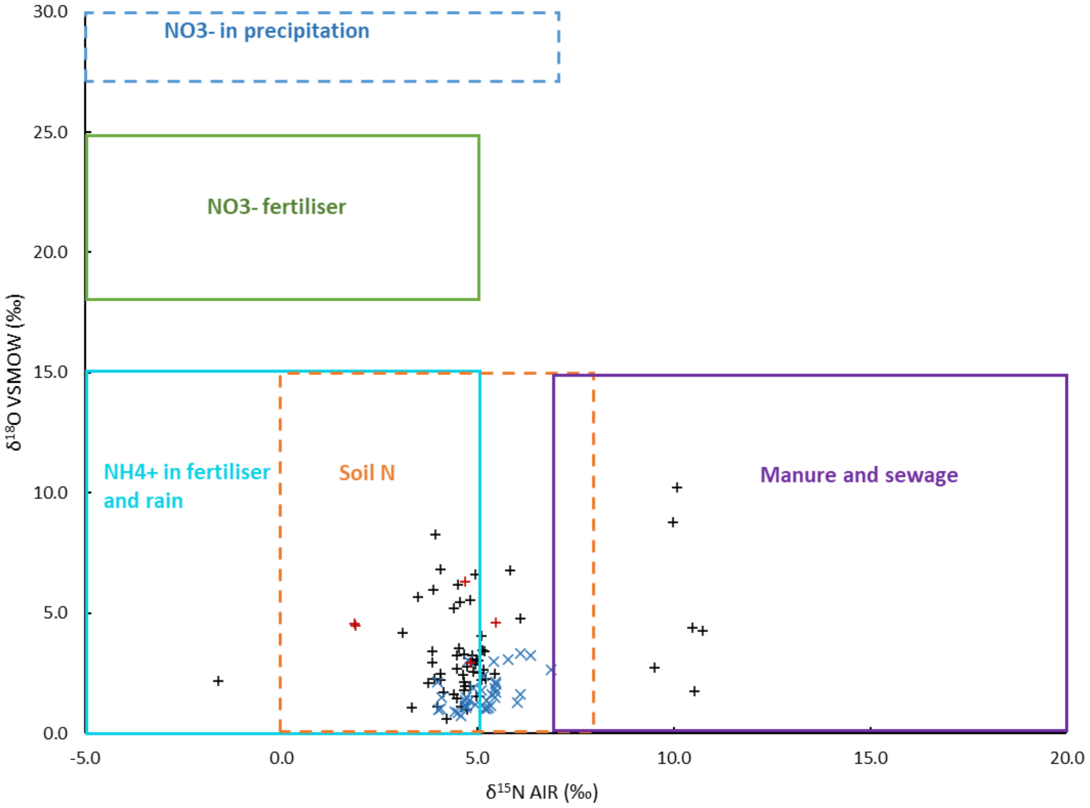

Figure 5.23: Dual stable isotope analysis of N and O in NO_3, for the Kilham (groundwater in black, springs in red) and Haisthorpe (blue) catchments.

All six of the samples plotting within the manure and sewage box in Figure 5.23 are from the Kilham catchment, five of which are from DOF, an intensive pig farm. The final point was from KOB and given its difference from other KOB samples taken on other dates it may be an erroneous result or the consequence of a point source event. No manure signatures are observed for the groundwater samples from Haisthorpe catchments (Figure 5.23) despite a chicken farm reportedly being near to the HAC abstraction.

$\delta^{15}N$ and $\delta^{18}O$ signatures were plotted against NO_3 concentration (Figure 5.25) to interpret sources, mixing and transformation processes e.g. Vitòria et al. (2008). The $\delta^{15}N$ signature became heavier with increasing NO_3 concentration (Figure 5.25), however the trend is only weak and caused by points from a single sample site (DOF), where the highest concentrations are associated with manure or slurry leaching ($\delta^{15}N > 9‰$) (Figure 5.24). The $\delta^{18}O$ shows no trend with NO_3 concentration.

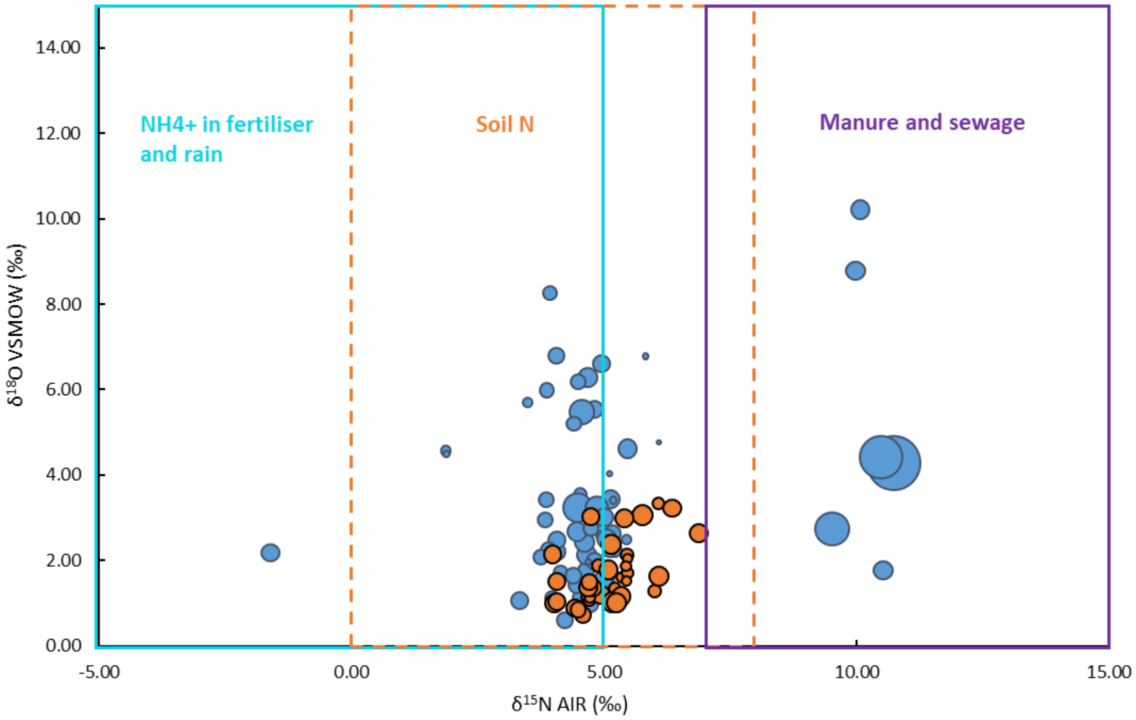

Figure 5.24: Dual stable isotope analysis of N and O in NO_3 for the Kilham (blue) and Haisthorpe (red) catchments. The size of the points demarcate NO_3 concentrations.

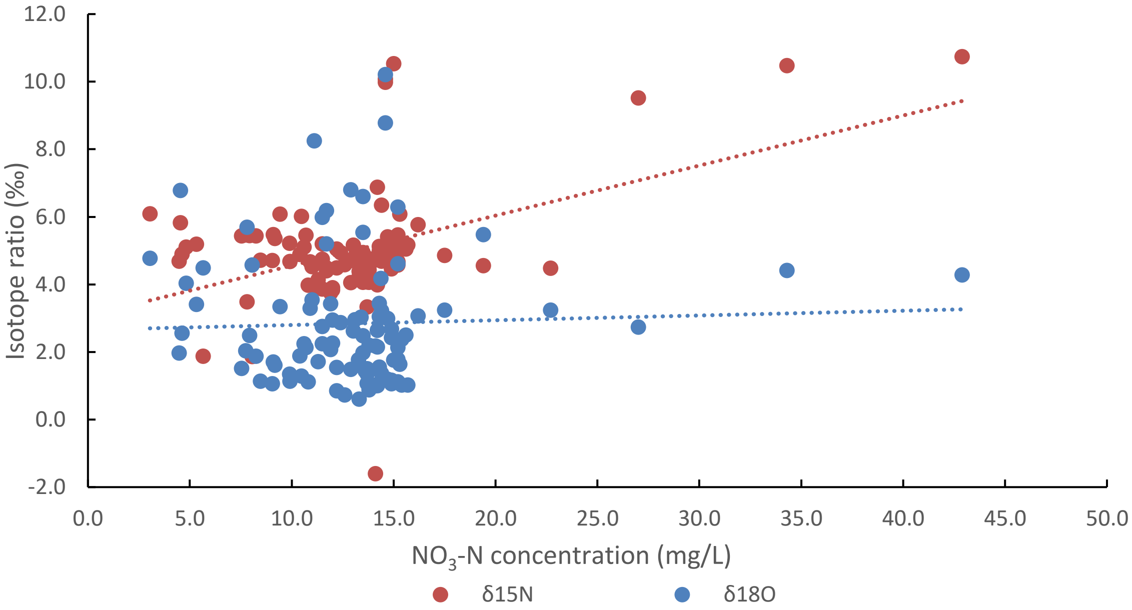

Figure 5.25: NO_3 as N concentration versus O and N stable isotope ratios for the Kilham and Haisthorpe catchments.

5.3.1 Seasonality in isotope signatures on the Northern Chalk catchments

All sample sites where more than two isotope analyses were successfully carried out were plotted individually to identify any changes that occurred over a hydrogeological year. No single trend was identified across the Kilham and Haisthorpe catchments, however seasonal changes in isotopic ratio were generally larger in the Kilham catchment than the Haisthorpe catchments (Figure 5.26 and Figure 5.27).

Samples from several sites followed a trend whereby $\delta^{18}O$ increased near the beginning of the recharge season, while $\delta^{15}N$ shows minimal change (Figure 5.26). This trend is particularly visible at SHW (Figure 5.26h), with a 1‰ increase in $\delta^{15}N$ and a 5‰ increase in $\delta^{18}O$ between December 2015 and January 2016. Other sites showed a similar trend but with $\delta^{18}O$ variation of only 1-2‰ (Figure 5.27a-c, i-k; BA2, BAR, BFG, SDF, WHF, WWF). Several further sites showed the increase in $\delta^{18}O$ during recharge, but also showed more variable $\delta^{15}N$ (Figure 5.27d-h; BR2, HAC, HOF, HUG, MGF), whereas the previously described sites had minimal change in $\delta^{15}N$. The majority of samples showed this trend and this process is likely to be dominant in the wider aquifer.

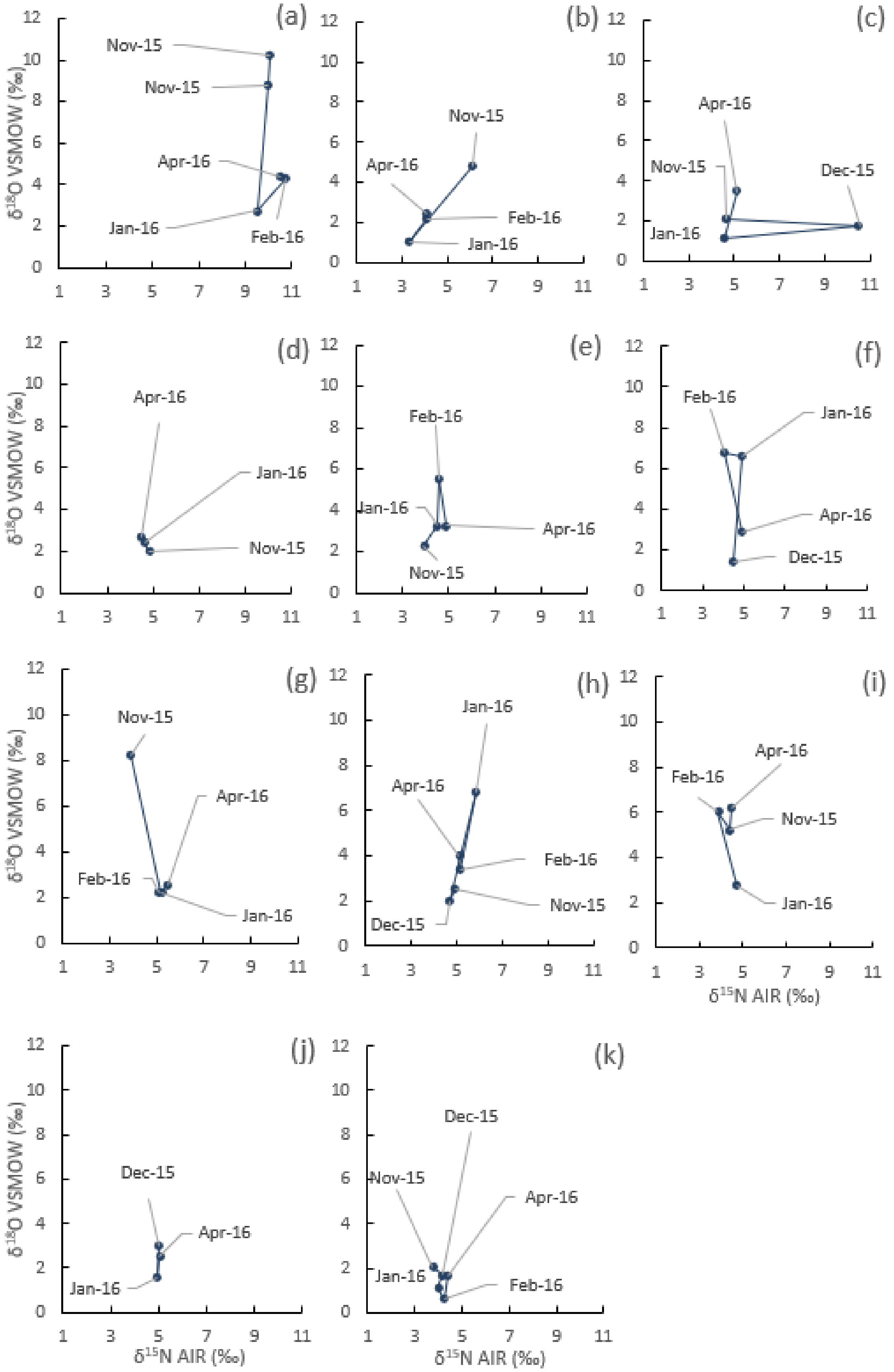

Figure 5.26: Dual stable isotope ratios for the Kilham catchment, by sample site (a) DOF, (b) FWF, (c) KOB, (d) MHF, (e) MOF, (f) OCG, (g) ROO, (h) SHW, (i) SWA, (j) WEA, (k) WES.

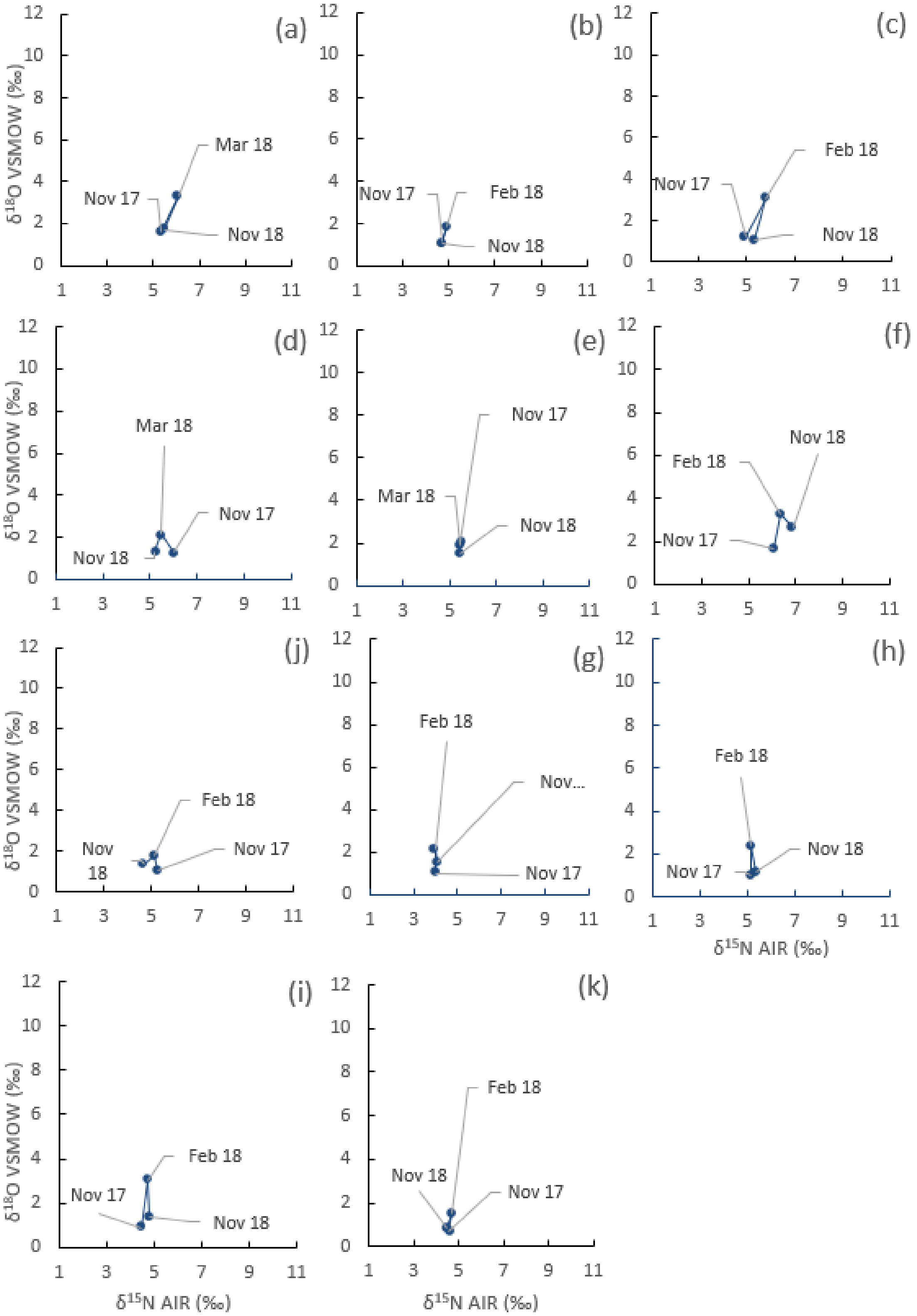

Figure 5.27: Dual stable isotope ratios for the Haisthorpe catchments, by sample site (a) BA2, (b) BAR, (c) BFG, (d) BR2, (e) HAC, (f) HOF, (g) HUG, (h) MGF, (i) SDF, (j) WHF, (k) WWF.

5.4 Discussion of characteristics of typical groundwater in the Northern Chalk aquifer in Yorkshire

Groundwater in the Kilham and Haisthorpe catchments were broadly similar and were generally typical of unconfined Chalk groundwater (Figure 5.9, Figure 5.10): Ca and HCO_3 dominated, mean pH was approximately 7.3 and SEC was 620-630 µS/cm. Ca concentrations in the south-east of the Haisthorpe catchments were as low as 86.6 mg/L, suggesting Quaternary deposits are sufficient to confine or partially confine the aquifer. NO_3 concentrations generally did not show an increasing trend over time but many sites, especially in Kilham, were approaching or breaking the PCV of 11.3 mg/L NO_3-N. Dual stable isotope analysis of NO_3 produced a cluster of signatures for both the Kilham and Haisthorpe catchments (δ^{15}N of +4 to +6‰ and δ^{18}O of 0 to +4‰). Although groundwater major ion chemistry and isotopic analysis from the Kilham and Haisthorpe catchments are broadly similar, results of tracer tests in previous studies did not suggest that there is mixing between catchments (Ward and Williams, 1995, Ward et al., 1998). Uniformity between catchments is therefore more likely due to similarity in geology, sources and processes, as well as within-catchment mixing.

Given the majority of samples fell within the “soil N” box on the fingerprinting diagram (Figure 5.23) these samples likely have major NO_3 sources and processes in common. NO_3 concentrations were higher than natural (1 mg/L NO_3-N estimated in Limbrick, 2003), so the dominant source of NO_3 in these samples is unlikely natural soil N. The soil N signature is instead likely the result of N cycling under standard agricultural practices, given the prevalence of agriculture in the region. However, as isotope analysis will only identify the average signature, NO_3 sources could a mixture and not necessarily the result of soil N-type processes. Although a highly simplified instrument, NO_3-N:Cl analysis (Figure 5.19) suggested mixing often occurred, with samples appearing to be on a continuum between fertiliser-like and manure-like sources.

Artificial NO_3 fertiliser is currently applied in the region (Section 4.2.1) and it is most likely that it has been applied historically, since development of the Haber-Bosch process for production of NH_3 (as discussed in Chapter 2). The absence of signatures in the “fertiliser NO_3” box in Figure 5.23 implies that, where not removed from the system in crops, much HB NO_3 fertiliser is transformed by soil biomass, as has previously been reported in the literature e.g. Powlson et al. (1986), Macdonald et al. (1989). These transformation processes could result in the cluster of soil N-type signatures described above. This will be discussed further in Section 7.3.4. Complete removal of all fertiliser NO_3 by crops and soil biomass prior to leaching through crop uptake and subsequent harvest is improbable, as NO_3 concentrations in groundwater recorded are too high to likely be entirely naturally sourced (discussed in Section 5.5.5).

5.5 Discussion of variations from the typical Northern Chalk character

From major ion concentrations, isotopic analysis and NO_3-N:Cl, the Kilham catchment showed more variation than the Haisthorpe catchments (Sections 5.2 and 5.3). The greater variation in hydrochemistry in the Kilham catchment could be explained by the different types of sample site in Kilham compared to Haisthorpe. As described in Section 3.1.1.4, only pumped boreholes were sampled in Haisthorpe and therefore analysis is more likely to reflect the wider aquifer due to drawdown, whereas in Kilham some samples were from unpumped, observation boreholes and thus more local conditions may be reflected in hydrochemical analysis. Several sites were also springs, which are downgradient of KIL abstraction (location shown in Figure 5.11), and therefore groundwater may have travelled a longer time and distance through the fracture system than groundwater sampled at other boreholes.

Where carbonate dissolution is the dominant reaction pH is typically 7.5-8.5. pH in the Northern Chalk catchments was between 6.07-8.18, suggesting carbonate did not completely remove acidity for all samples. Acidity is introduced to groundwater from bacterial activity in the soil zone (c. pH 4.3) and from rainfall (c. pH 5.7); it can be neutralised rapidly via carbonate dissolution or more slowly via silicate dissolution. More acidity could have been introduced than could be buffered, leading to peaks in Ca and HCO_3 concentrations, possibly from anthropogenic sources like NH_4 fertilisers or by selective uptake of bases by crops e.g. Knutsson (1994). Alternatively, the water could have been relatively new recharge and thus did not have sufficient contact with the carbonate rock for the buffering effect to occur.

Plotting $\delta^{15}N$ and $\delta^{18}O$ signatures against NO_3 concentration was a useful tool in elucidating variation in sources, mixing and transformation processes. While $\delta^{18}O$ showed no trend with NO_3 concentration in this study, a weak positive correlation of $\delta^{15}N$ NO_3 concentration (Figure 5.25) highlighted that a single sample site (DOF) differed from the majority. The highest concentrations of NO_3 were thus most likely associated with manure or slurry leaching ($\delta^{15}N > 9‰$) (Figure 5.24). This conclusion is supported by the NO_3:Cl plots and fingerprinting diagram (Figure 5.19, Figure 5.20, Figure 5.21 and Figure 5.23). If extensive natural attenuation processes, such as denitrification, were occurring in these catchments then a trend would be expected across more samples. Thus, as theorised by Medici et al. (2020) with regards to unconfined dolostone aquifer in the same geographical area, it is unlikely that NO_3 extensive attenuation is occurring in Chalk groundwater.

5.5.1 The extent of manure-nitrate isotope signatures in the Kilham and Haisthorpe catchments

NO_3-N:Cl ratios suggested that a few samples were dominated by inorganic fertilisers (0.0004 moles Cl, c. 15 mg/L) or manure (0.003 moles Cl, c. 100 mg/L), as opposed to being a mixture. High NO_3 concentrations were recorded at site DOF (Figure 5.16) and given a heavy $\delta^{15}N$ signature, could be a result of local infiltration from the surrounding pig farm as the borehole is reported to be in close proximity to intensive pig housing. A drop in pH and a spike in Cl, SO_4, NO_3, Na and K occurred just following to the highest concentration of HCO_3 being recorded, indicative of a pollution event. Pollution may have induced increased acidity and led to increased carbonate dissolution. Effects appeared to be localised, or rapidly diluted by surrounding waters as surrounding sample sites did not record manure-type isotopic signatures.

It is notable that not all sites that appeared to have a manure N input (i.e. boreholes located on a livestock farm) produced a manure-NO_3 isotope signature. For instance, sites DOF, MOF and PTH in Kilham are an intensive pig farm, an intensive chicken farm and a mixed farm including pigs, respectively, so manure or slurry may be an influential N source. In addition, chickens were reported to be farmed near the HAC abstraction in the Haisthorpe catchment. However, only groundwater samples from DOF had a manure-like isotope signature (Figure 5.23), possibly due to a particularly high concentration of manure-NO_3 in the DOF samples or high bioavailability (introduced in Section 2.3.5). Any manure-NO_3 at MOF, PTH or HAC could have mixed with other sources or been utilised by the soil biomass and thus were not apparent in the fingerprinting diagram (Figure 5.23).

Sites DOF, MOF and PTH had high NO_3 and intermediate Cl concentrations, and in terms of NO_3-N:Cl formed a near-vertical trend distinct from the theoretical trendline presented in Figure 5.19. On Figure 5.19, ratios for HAC were indistinguishable from the theoretical trendline, implying any manure-NO_3 sources were sufficiently diluted. Manure and sewage tends to have high Cl and low NO_3 (Yue et al., 2017), due to N being immobilised in organic compounds, however DOF, MOF and PTH do not follow this trend. Instead, they bear similarity to some samples in a study of the Ile du Chambon catchment, France (Widory et al., 2005), where high NO_3 and Cl were recorded. Low NO_3 samples with high Cl were hypothesised by Widory et al. to have been caused by denitrification. This seems unlikely to be the case in the largely unconfined Kilham and Haisthorpe catchment as oxic conditions prevail. However, if high volumes of manure were applied near DOF, and NO_3 produced by nitrifying microbes leached into the unsaturated zone before soil biomass could recapture it, higher Cl and higher NO_3 groundwater could result. The trends observed at MOF and PTH are less conspicuous than at DOF, therefore could indicate NO_3 source mixing, or a less pronounced example of the aforementioned hypothesis.

In conclusion, despite the presence of some manure signatures on the fingerprinting diagram, manure signatures were not observed for all sites with proximity to manure sources. This could imply that a small, or well controlled, application of manure does not produce a manure-type isotope signature. Therefore, only where there is a substantial manure application, with a considerable amount of nitrification occurring, will more NO_3 be produced than can be metabolised by plants and the soil biomass, thus making the area vulnerable to leaching of manure-NO_3. Alternatively or in addition, there is variation in bioavailability between manure from different species, so the manure-type signatures could result from more highly bioavailable manure or slurry, such as poultry (Section 2.3.5; Wortman et al., 2006). A less bioavailable manure contains mostly organic N and NH_4, and little NO_3, therefore any available NO_3 may be utilised by plants and not leach to the groundwater.

5.5.2 Potential causes of high chloride concentrations observed on the Northern Province Chalk catchments

Site SHW frequently had higher Cl concentrations than other sites (Figure 5.17, Figure 5.19); variations in Cl were also observed at ROO and SDF (Figure 5.21). Fresh Chalk groundwaters tend to have Cl of less than 40 mg/L, and higher concentrations can be due to contributions from seawater or connate water (Elliot et al., 2001). These variations are unlikely explained by influence from seawater, connate water, or by evapotranspiration as the high Cl concentration is not similarly observed at surrounding sites. NO_3-N:Cl data for SHW show a much lower ratio than observed at any other site, strongly correlated with Cl concentration (Figure 5.19). This suggests a non-NO_3 Cl source. High Na, SO_4 and an increase in K were recorded concurrent to the Cl peak at SHW (Figure 5.17). High Na concentrations suggest NaCl as the source, which could be from road salt, but in such a rural location leaching following a NaCl application to a sugar beet crop may be more likely e.g. Draycott and Bugg (1982). K and SO_4 that increased concurrently could have been from a leached application of K_2SO_4, another fertiliser applied to sugar beet.

5.5.3 Potential causes of lower nitrate concentrations in the Northern Province Chalk aquifer

Lower NO_3 concentrations than typical for the Northern Chalk catchments samples were recorded at BA2, HAE, HAC, BR2 and BAR in the Haisthorpe catchments (Figure 5.11). These sites showed limited variation in hydrochemistry as well as isotopic signatures, and were within or adjacent to the cluster described in Section 5.3 ($\delta^{18}O$ +1.1 to +2.1‰ and $\delta^{15}N$ +4.7 to +6.1‰). These sites could have lower, more stable NO_3 concentrations if they access a different groundwater regime, with a lower NO_3 concentration, to the more northerly sites. This horizon may consist of older water, which has resided in the aquifer for longer, since before inorganic fertiliser use was ubiquitous. Alternatively, these sites are superficially covered by Devensian till, which may confine the aquifer, providing suitable conditions for denitrification, thus lowering NO_3 concentrations and other ions that could be indicative of pollution. Four of these five sites are abstractions for public supply and so while these locations may have been selected for their low contaminant concentrations, drawdown may reduce contact between groundwater and NO_3 trapped in the vadose zone.

Sites SHW in the Kilham catchment also produced groundwater with lower NO_3 concentrations than typical (Figure 5.14). Other major ion concentrations as well as isotopic signatures ($\delta^{18}O$ +1.96 to +6.78‰ and $\delta^{15}N$ +4.69 to +5.82‰) were variable as compared to other sites (Figure 5.17 and Figure 5.26h). This site is at the top of the escarpment so although located in a vulnerable unconfined part of the Yorkshire Wolds it could have been exposed to more rainfall, thus diluting terrestrial ion inputs. NO_3 concentrations remained fairly constant, however, so there is little evidence of seasonal dilution that might be expected at the initiation of effective rainfall.

5.5.4 The extent of more "natural" N sources in the Northern Province Chalk aquifer

As stated in Section 5.4, most NO_3 concentrations recorded in the Haisthorpe and Kilham catchments were too high to result solely from natural N sources. However, NO_3-N concentrations at FWF in the Kilham catchment were initially very low (3.0-6.1 mg/L). Over the study period (2015-2017) they increased to 12.8-13.8 mg/L (Figure 5.18). The borehole was first drilled in 2015, so these changes could suggest that the localised area had low NO_3, but that higher NO_3 groundwater was drawn in as the borehole was. This implies that local NO_3 concentrations can be low if there is no local contaminant, however as borehole development occurs, conditions that reflect the wider aquifer become visible.

Over the same period, marked changes to Ca and HCO_3 were also observed (see Section 5.2.2). Shortly after drilling the following reaction may initially have occurred:

$$CaCO_3 + CO_2 + H_2O \rightarrow 2HCO_3{}^- + Ca^{2+} \tag{5.1}$$

producing a lot of HCO_3, then once the borehole developed a second reaction dominated:

$$CaCO_{3(s)} + H^{+} \rightarrow Ca^{2+} + HCO_{3^{-}} \tag{5.2}$$

The former reaction is more closely associated with natural conditions, however the increased acidity required for the second reaction is likely anthropogenic in origin. This again implies that when the borehole was drilled, local less polluted conditions prevailed. Whereas when the borehole developed, increased connectivity with the wider aquifer led to an influx of more polluted groundwater. Protons are released when NH_4 is oxidised to NO_3, so NH_4 fertilisers could be a cause of increased acidity (Böhlke, 2002).

Consistently low NO_3 concentrations were recorded at SHW (Figure 5.17) and similar to those recorded at FWF when newly drilled. As discussed in Section 5.5.3, SHW is at the top of the Yorkshire Wolds escarpment. Consistently low, as opposed to seasonal, NO_3 concentrations do not imply there was dilution of groundwater from effective rainfall. Low NO_3 could instead relate to less intensive land management e.g. if a biennial crop is planted, such as sugar beet, then N fertilisers may not be necessary every year (Yara, n.d.).

5.5.5 Untransformed HB N fertiliser in the Northern Province Chalk aquifer

While no oxygen isotopic signatures expected from HB N fertiliser were recorded in the groundwater samples ($\delta^{18}O$ +17 to +25‰), the input from HB NO_3 is unlikely nil. Artificial NO_3 fertiliser is currently applied in the region (Section 4.3.1) and it is most likely that it has been applied historically, since development of the Haber-Bosch process for production of NH_3 (as introduced in Chapter 2). Some dual stable isotope signatures had heavier $\delta^{18}O$ than the identified cluster ($\delta^{18}O$ 0 to +4‰) but with $\delta^{15}N$ approximately consistent with the cluster ($\delta^{15}N$ +4 to +6‰). No sample site continually produced isotopic ratios of this description, however sites where spikes in $\delta^{18}O$ but not $\delta^{15}N$ included KSS, MHF, MOF, OCG, SHW and SWA (Figure 5.26). Assuming that the cluster of signatures is primarily due to NO_3 that has been subject to soil N processes, signatures with heavier $\delta^{18}O$ could be indicative of a small proportion of untransformed NO_3 fertiliser entering groundwater (discussed in greater detail in Section 7.2.3). $\delta^{18}O$ peaks varied temporally between sites, which could result from different fertiliser regimes, or variations in local geology.

5.6 Seasonality of nitrate in the Chalk catchments

Seasonality in major ion concentrations, NO_3-N:Cl ratios and isotope signatures was observed for some sample sites in the Kilham and Haisthorpe catchments. Seasonal variation tended to be less clear for pumped than observation boreholes, as discussed in Section 5.5. There was no single seasonal response in major ion concentrations, NO_3-N:Cl and isotope signatures, indicating that other factors such as land management practices were key. However, the initiation of recharge often corresponded with changes in hydrochemistry or isotopic ratios. Several sites showed an increase in NO_3 concentrations during recharge, especially at the beginning (e.g. DOF, PTH, MOF), while the dominant trend in dual stable isotope ratios was for heavier $\delta^{18}O$ during recharge. This implies that NO_3 stored in the vadose zone was transported to the saturated zone with the first effective rainfall. A peak in NO_3-N:Cl was recorded in Kilham slightly towards the end of recharge season (February and March). There was, however, no evidence that NO_3 concentration correlated with $\delta^{18}O$ (Figure 5.25).

Samples from several sites followed a trend whereby $\delta^{18}O$ increased near the beginning of the recharge season, while $\delta^{15}N$ showed minimal change (Figure 5.26). This most likely means that a pulse of water containing NO_3 with heavier $\delta^{18}O$ entered the groundwater at the beginning of recharge. Over the course of the year this NO_3 pool became lighter in terms of $\delta^{18}O$ and more similar to the cluster identified in Section 5.5, possibly via equilibrium processes occurring in the groundwater. Given the limited number of data points, conclusions must be drawn cautiously, but $\delta^{18}O$ in fresh recharge water-NO_3 entering via fractures could be heavier than older matrix groundwater $\delta^{18}O$-NO_3 because it has been subject to fewer bacterially mediated transformations or equilibrium processes (discussed in more detail in Section 7.2.3 and Section 7.3.4). It is possible that the decrease in $\delta^{18}O$ over the rest of the hydrogeological year could be explained by mixing with the enormous pool of NO_3 in the aquifer mixing with the “new” recharge water, however over time the recharge-type signature would be expected to become more prevalent in the aquifer. Instead, an isotope exchange process occurring within the aquifer is more probable: with O atoms from water (O-H_2O) switching with the nitrate oxygen (O-NO_3). The trend was particularly visible at SHW as the borehole was unpumped and had consistently low NO_3 concentrations during the period of study, and therefore this seasonal pattern may be similar to "natural" conditions. Other sites that also had a change in $\delta^{18}O$, but more variable $\delta^{15}N$, may also have been subject to source mixing, perhaps between transformed NO_3 fertiliser and a manure NO_3 source.

Variations from the typical cluster of isotopic signatures often appeared to be due to pollution events and may have been observed seasonally due to land management practices e.g. the times of year when manure spreading is permitted (see Section 2.3.5). Increased NO_3 and Cl concentrations were observed periodically at DOF, MOF and possibly PTH (Figure 5.21c, f and h) and are indicative of contamination from high volumes of manure. Bacteria may nitrify organic compounds in manure applied towards the end of the growing season, few plants utilise it as the weather cools, thus manure NO_3 is drawn into groundwater when recharge begins. Higher NO_3-N:Cl ratios, caused by decreases in Cl concentration, as observed at ROO and MHF (Figure 5.21e and i), was most likely due to a change in N source to inorganic fertiliser. The fertiliser may have been applied in spring, but then travelled to below the root zone until recharge season when it was transported to groundwater.

At SHW NO_3 concentrations stayed stable over the recharge season but Cl increased (Figure 5.21k). No additional input of NO_3 suggests that Cl was likely from an alternative source, such as NaCl. NaCl is commonly applied to roads in winter as road grit, however in a rural area such as SHW, NaCl is more likely to be applied to fields as a fertiliser of sugar beet (Draycott and Bugg, 1982). Peaks in other major ions at SHW could also have feasibly been applied as fertiliser. SDF may be similarly influenced by an additional Cl source that contributes negligible NO_3 (Figure 5.21j). Cl often enters groundwater from NaCl, however Na is often retained in the soil due to ion exchange with Ca and so may not be captured in groundwater, whereas Cl more easily leaches below the soil zone into groundwater.

Sites with little seasonality in major ion concentrations, NO_3-N:Cl and isotope ratios included public water supply abstractions (KIL, HAC, HAE, BA2, BR2). All five of these sites are overlain by superficial cover (Figure 3.1), which may impede some fast flow from the ground surface and thus reduce seasonal changes. However, the extent to which each site is confined is unclear e.g. KIL is on the feather edge of Quaternary cover and still has higher NO_3 concentrations as compared to the majority of the catchments. These sites are more frequently pumped than most other sites sampled, which may serve to reduce pulses of NO_3 and other pollutants due to drawdown.

5.7 Summary of groundwater nitrate in the Northern Province Chalk

Hydrochemistry was broadly similar between the catchments implying that the groundwaters were subject to similar inputs and processes. At DOF several pollution events could be identified using major ion concentrations, including SO_4 and Cl, as well as NO_3 (Figure 5.16). The majority of these events occurred during the recharge season, most at the beginning of recharge, implying that effective rainfall provides a means of transportation for NO_3 to the saturated zone. Isotope analysis revealed the most likely source of NO_3 pollution at DOF was manure (Figure 5.23).

A wide range of NO_3 concentrations were observed across the Kilham and Haisthorpe catchments. Most sites had NO_3 concentrations above the legal drinking water limit, of 11.3 mg/L NO_3-N, during at least part of the study period (25 of 32 sites). NO_3 concentrations were rarely low enough to be considered as possibly natural in origin. This highlights the urgency of the NO_3 problem: there are few low-NO_3 abstractions with which high NO_3 water can be blended. Current public abstraction boreholes at BA2, BR2, HAC and HAE have lower NO_3 concentrations of c. 8-10 mg/L NO_3-N, as compared to the rest of the studied catchment, possibly due to a protective effect from Quaternary cover.

Seasonality in major ion concentrations and isotope data was observed at many sample sites in the Kilham and Haisthorpe catchments, which is evidence for “new” recharge water mixing with a less mobile groundwater with a longer residence time. This highlights the vulnerability of the Northern Chalk aquifer, as pollutants can pass quickly through the unsaturated zone. Several sites, particularly within the Kilham catchment, showed peaks in NO_3 concentration and changes to isotopic ratios during the recharge season (e.g. SHW; Figure 5.12, Figure 5.26h). Analysing seasonality of isotope ratios identified a common trend of heavier $\delta^{18}O$ at the beginning of recharge, except where there were heavy manure/slurry inputs, in which case $\delta^{18}O$ and $\delta^{15}N$ were often both lighter during recharge.

NO_3-N:Cl ratio, as applied in Yue et al. (2017) proved a valuable tool for constraining NO_3 sources. It demonstrated that the majority of sites sat on a spectrum between fertiliser NO_3 as a source (high NO_3, low Cl) and manure as a source (low NO_3, high Cl). However, several sites showed high NO_3 and moderately high Cl (e.g. DOF). At these sites a heavy application of manure may have occurred, which led to nitrification taking place at a much faster rate than plants or soil biomass could exploit, ultimately leading to substantial NO_3 leaching.

Dual stable isotope analysis revealed that the majority of sites in the Kilham and Haisthorpe catchments shared a signature: $\delta^{15}N$ between +4 and +6‰, and $\delta^{18}O$ between +0 and +4‰. NO_3 sources and processes in aquifer are similar and can be explained by common framework. The expected NO_3 fertiliser signature, with heavy $\delta^{18}O$, is not identified in the isotope analysis, implying bacterially mediated NO_3 transformations have occurred. [These transformations likely occur in the soil as opposed to the groundwater based on the literature, however this question was addressed directly by subjecting a Southern Chalk catchment and a River Terrace Gravel catchment to the same analyses (discussed in Chapter 6).] Samples in the “Soil N” box on the fingerprinting diagram may thus represent transformed NO_3 from inorganic fertiliser. NO_3 fertiliser is utilised by the crop or microbial biomass leading to transformation prior to entering groundwater, thus changing the isotopic signature primarily of O within NO_3 to resemble soil NO_3 (Macdonald et al., 1989). Five Kilham samples from within the manure and sewage box are from DOF, an intensive pig farm, so manure and slurry is expected.

Whether the borehole is pumped or not may have a substantial effect on the hydrochemistry, including isotopic composition. Unpumped wells may have very localised characters, while pumped wells draw water from a greater area and therefore may have a more general hydrochemistry, characteristic of the wider aquifer. FWF may be evidence of this: when the well was first drilled it had high HCO_3, low Ca and low NO_3. As the borehole developed and increased connectivity with the catchment HCO_3 concentrations dropped while Ca and NO_3 increased.

Although identifying some NO_3 signatures using the fingerprinting diagram is challenging, manure/slurry/sewage sources can be identified with confidence.

Results of dual stable isotope analysis in the Kilham and Haisthorpe catchments present no evidence for denitrification within the aquifer. The weak positive relationship between NO_3 concentration and $\delta^{15}N$ can be explained by manure leaching at DOF.

Chapter 6 Southern Province Chalk and River Terrace Gravels

In this chapter the geology and hydrogeology of regions other than the Northern Province Cretaceous Chalk aquifer, namely the Southern Province Cretaceous Chalk in Hampshire and River Terrace Gravels (RTG) on the Medway in Kent, are considered. Both catchments are drinking water sources for South East Water and thus the continuing ability of the catchments to produce high quality potable water is key.

The national significance of the Chalk aquifers as a drinking water source in England (Hartmann et al., 2007) was discussed in Section 2.7.3, however it is largely due to the Southern Province Cretaceous Chalk that this is the case. In Southern England population density is comparatively high and there are fewer surface water reservoirs, in addition to lower rainfall totals, than in Northern England (Allen et al., 1997). As a result, groundwater supplies around 70% of drinking water in Southern and Eastern areas (Stuart and Smedley, 2009) and consequently the longevity of groundwater sources is a priority for South East Water, who operate in the region.

As the Southern Chalk catchment studied in this chapter is largely unconfined, and due to the fractured nature of the Chalk, the aquifer is vulnerable to pollutants. The Chalk in this part of Hampshire is extensively researched however, to the author’s knowledge, dual stable isotope analysis of nitrate has not been carried out. The RTG, however, is less thoroughly researched in comparison and thus much of the analysis in this chapter is novel. Nitrate concentrations in both the Southern Chalk catchment and the RTG were lower than for the Northern Chalk catchments studied, but were reported to be increasing apart from two sample sites on the RTG that were frequently very low.

The rationale behind this chapter was to identify nitrate sources in these catchments, as well as ascertaining why the two RTG sites had such low nitrate concentrations. Furthermore, extending the study area beyond the Northern Chalk aquifer enabled investigation of the extent to which processes affecting nitrate are the same for the Northern and Southern Province Chalks, and whether these processes differ for aquifers with a markedly shorter groundwater residence period (decades versus days for the Chalk and RTG, respectively).

For each geology, pre-existing data relating to the catchments are considered and analysed (summarised in Table 3.5), as well as assessment of data collected in the current study. Then, catchment-specific conclusions are drawn. A comparison of all the catchments investigated is presented in Chapter 7, in addition to discussion of overarching themes and findings.

6.1 Groundwater sampling regime

A total of 32 groundwater samples were collected by South East Water on a quarterly basis, from four sites within the Woodgarston catchment on the Southern Province Chalk and four sites in the Hartlake catchment, on the Medway RTG (introduced in Sections 3.1.2 and 3.1.3, respectively). These were analysed for selected ions by South East Water and for dual stable isotope analysis of NO_3 at University of Leeds (data ownership outlined in Table 3.5), according to the methods summarised in Section 0. Additional hydrochemical data were obtained for site HARSPF from the Environment Agency Water Quality Archive.

6.2 Hydrochemistry in the Woodgarston catchment on the Southern Province Chalk

In the Woodgarston catchment sample site WPit had the most complete, long-term hydrochemistry dataset. WPit had stable pH, varying between 7.03 and 7.43, while specific electrical conductivity (SEC) was generally stable at 635 to 812 µS/cm. These data fit with the expected Chalk groundwater pH and SEC of around pH 7.5 and 700 µS/cm, respectively (Gooddy et al., 2002). In August 2017 there was a drop in SEC to 370 µS/cm. Measurements returned to normal by the next sample, making human or instrument error a likely cause. The groundwater was dominated by HCO_3 and Ca (Figure 6.2); Ca concentrations at WPit varied between 124 and 150 mg/L, while HCO_3 varied between 295 and 317 mg/L (Figure 6.3). These figures were broadly similar to previous research in the Woodgarston catchment (Elliot et al., 1999). The concentrations of other major ions at WPit, except for NO_3, were low compared to figures characteristic of Chalk groundwater (i.e. 50 mg/L Cl, 50 mg/L Na and 6 mg/L K; Gooddy et al., 2002), as shown in Figure 6.3. When there was a Cl peak at WPit in June 2018, NO_3 and SO_4 also peaked (Figure 6.3). WPit had largely similar NO_3 and Cl to the other sampling sites (Figure 6.4, Figure 6.6), but with higher peak concentrations. There were comparable ranges in SO_4 concentration at WPit and WMals, however WPBH1 and WPBH2 showed much less variation and lower concentrations.

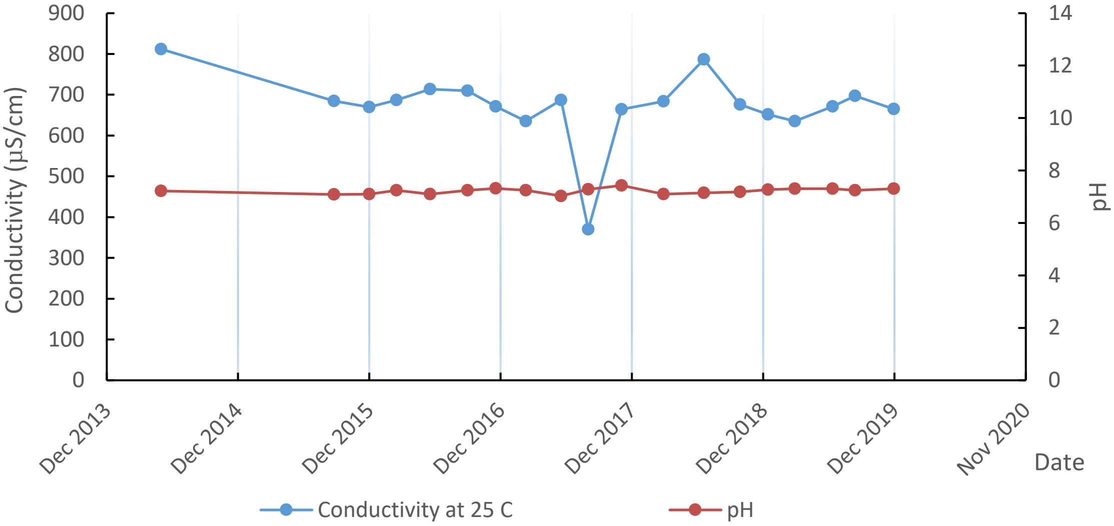

Figure 6.1: SEC and pH at WPit from May 2014 to November 2019. Gridlines mark 31st December. Data from the Environment Agency (2020).

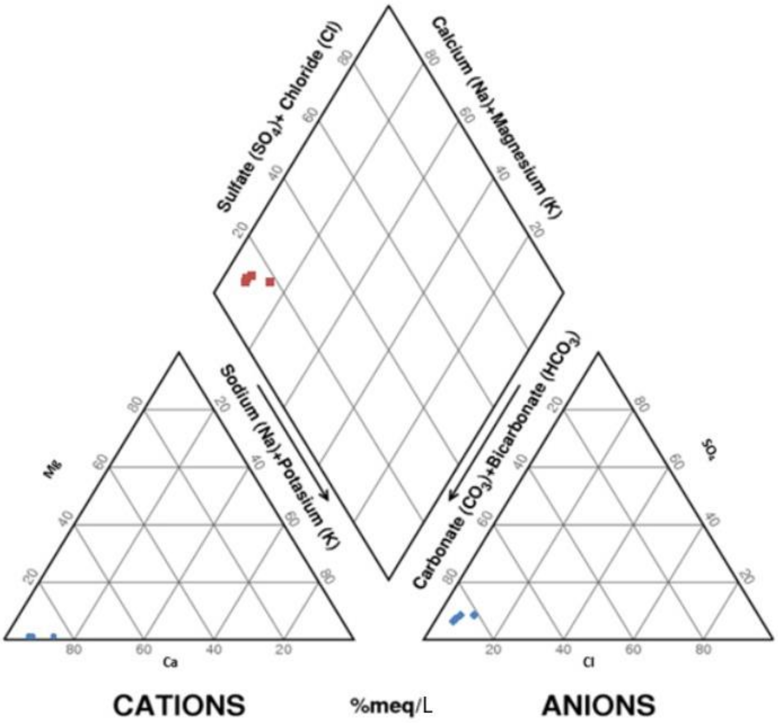

Figure 6.2: Piper plot for WPit for 2014 to 2019 demonstrating that WPit has Ca-HCO_3 type, as expected for Chalk groundwater. Data from the Environment Agency (2020).

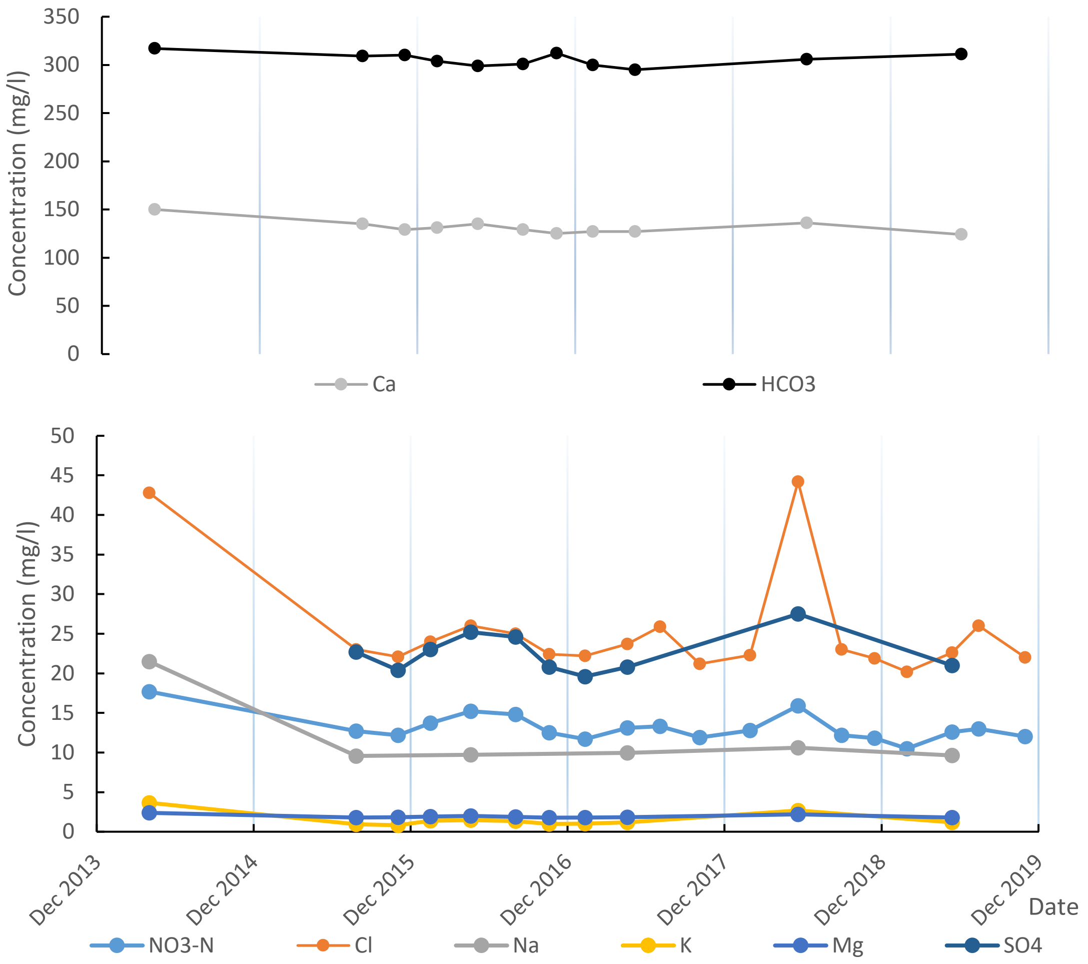

Figure 6.3: Major ion concentrations for WPit from May 2014 to November 2019. Data from the Environment Agency (2020).

In terms of Cl for the four sample sites, WPit had the most variable and highest concentrations (Figure 6.4). WPBH2 and WMals had stable Cl concentrations of around 20 mg/L, very similar to the concentration reported by Elliot et al. (1999). One spike in Cl concentration of 48.0 mg/L was observed at WPBH2 in October 2019, but had returned to normal levels on the next sample, suggesting user error or a single point source input. WPBH1 shows greater variation then WPBH2 and WMals; concentrations were generally 20 to 30 mg/L, however in June 2018 and February 2020 concentrations peaked at 45.9 and 37.9 mg/L, respectively (Figure 6.4).

SO_4 concentrations were relatively stable at WPBH1 (approximately 10-15 mg/L) and WPBH2 (approximately 12-18 mg/L), while WMals and WPit showed similar ranges (approximately 13-30 mg/L; Figure 6.5). The SO_4 concentration from Elliot et al. (1999) is very low in comparison (7.7 mg/L). Periods of greater Cl and SO_4 variation generally seem to be at similar times for each of the four sites.

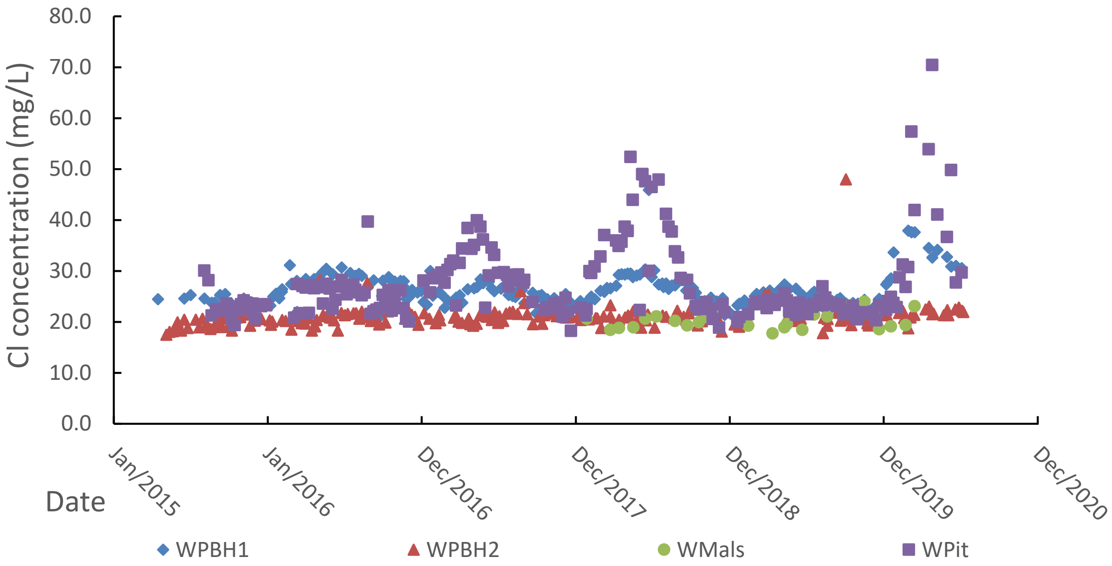

Figure 6.4: Cl concentration at the four Woodgarston sample sites from 2015 to 2020. Data courtesy of South East Water (2019b).

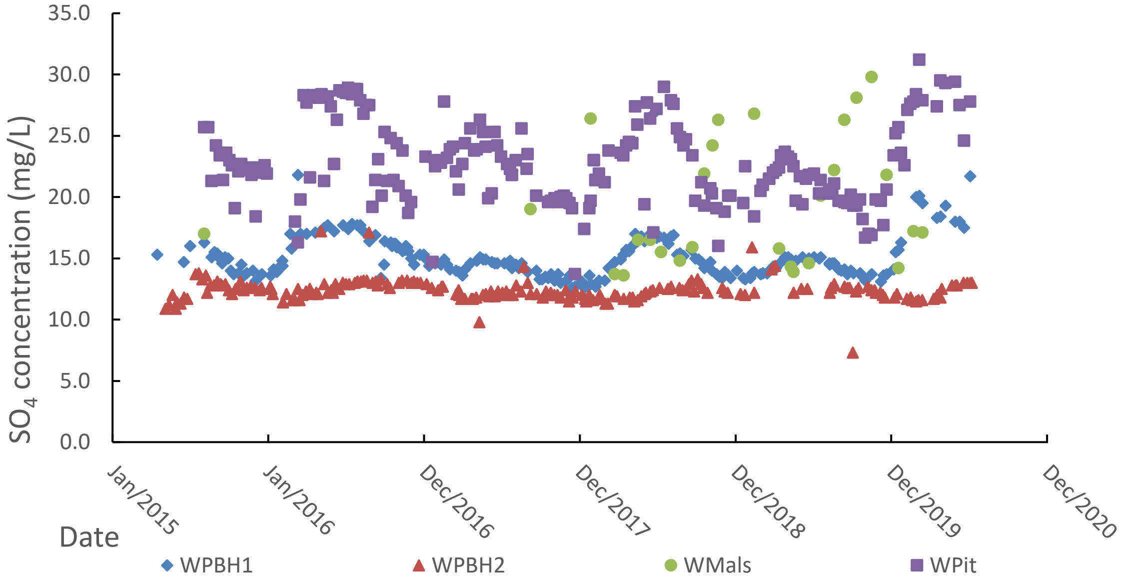

Figure 6.5: SO_4 concentrations at the four Woodgarston samples from 2015 to 2020. Data courtesy of South East Water (2019b).

6.2.1 Nitrate concentrations in the Woodgarston catchment

NO_3 concentrations at WMals and WPBH2 did not go over the legal drinking water limit (PCV) of 11.3 mg/L NO_3-N (50 mg/L NO_3) during the study year from November 2018 to August 2019. During the same period WPBH1 was consistently over 11.3 mg/L NO_3-N; WPit was over the PCV for three of the four samples and had the greatest amplitude of variation (Table 6.1; Figure 6.6).

WMals and WPBH2 have rarely ever broken the PCV, according to the long-term data (Table 6.1; Figure 6.6). Whereas at WPBH1, NO_3 concentrations increased over time, from 7.2 mg/L NO3-N in July 1997 to 14.6 mg/L NO_3-N in July 2020 and at WPit samples have been over the PCV since 2014 (Table 6.1; Figure 6.6). Of the four sites, WPit had the highest NO_3 concentrations. WPBH1 showed the most variation (Table 6.1) but this is most likely a result of WPBH1 having the longest records.

Table 6.1: NO_3 concentrations are the four sites sampled in the Woodgarston catchment. Bold red marks values over the legal drinking water limit of 11.3 mg/L NO_3-N. Data supplied by Environment Agency (2020) and South East Water (2019b).

Site name (dates monitored)		**NO_3-N concentration (mg/L)**		**Site name** (dates monitored)		**NO_3-N concentration (mg/L)**
WMals (Aug 2015-Nov 2019) *n=29*	Min	7.4		**WPBH1** (Jul 1997-Jul 2020) *n=402*	Min	6.9
	Mean	8.2			Mean	**11.7**
	Max	10.6			Max	**16.5**
WPit (May 2014-Nov 2019) *n=209*	Min	8.3		**WPBH2** (Jan 1997-Nov 2019) *n=366*	Min	5.9
	Mean	**13.0**			Mean	10.6
	Max	**17.8**			Max	10.8

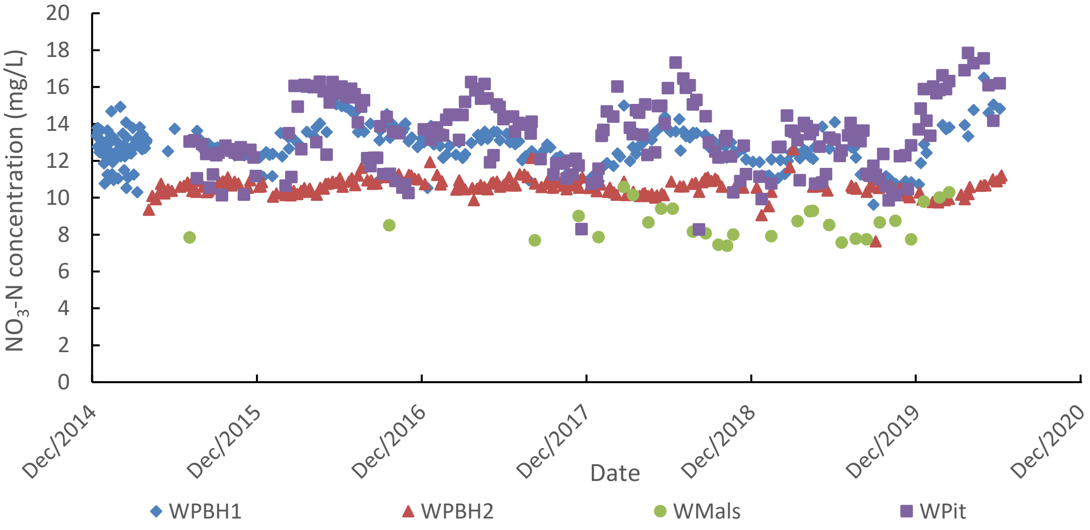

Figure 6.6: NO_3-N concentrations for sites sampled in the Woodgarston catchment, from January 2015 to July 2020. Data courtesy of South East Water (2019b).

6.2.2 Nitrate to chloride ratios in the Woodgarston catchment

As described in Section 5.2.3, Cl is not affected by chemical or biological processes and so its concentration can be a useful tool. Any changes in Cl concentration can indicate a pollution source, or imply a physical process like dilution or evaporation has occurred (Liu et al., 2006). The NO_3-N:Cl ratio can be used to further constrain possible NO_3 sources and validate conclusions as the ratio will not change with evaporation. While some sources will defy the trend, inorganic fertiliser tends to have a high NO_3-N:Cl ratio whereas sewage or manure has higher Cl and therefore a lower ratio (Liu et al., 2006, Widory et al., 2005).

The data are closely grouped for all four sample sites (Figure 6.7). Generally, the data are indicative of limited change in Cl concentrations, with the majority of variation from NO_3 concentrations. Given that this dataset shows mostly NO_3 variation this suggests that inorganic fertiliser is the primary source. However, as there are neither remarkably high NO_3 or Cl concentrations, the NO_3 is likely of mixed source to some extent. NO_3 concentrations are not low enough for their source to be considered the result of natural soil N cycling, or pre-agricultural.

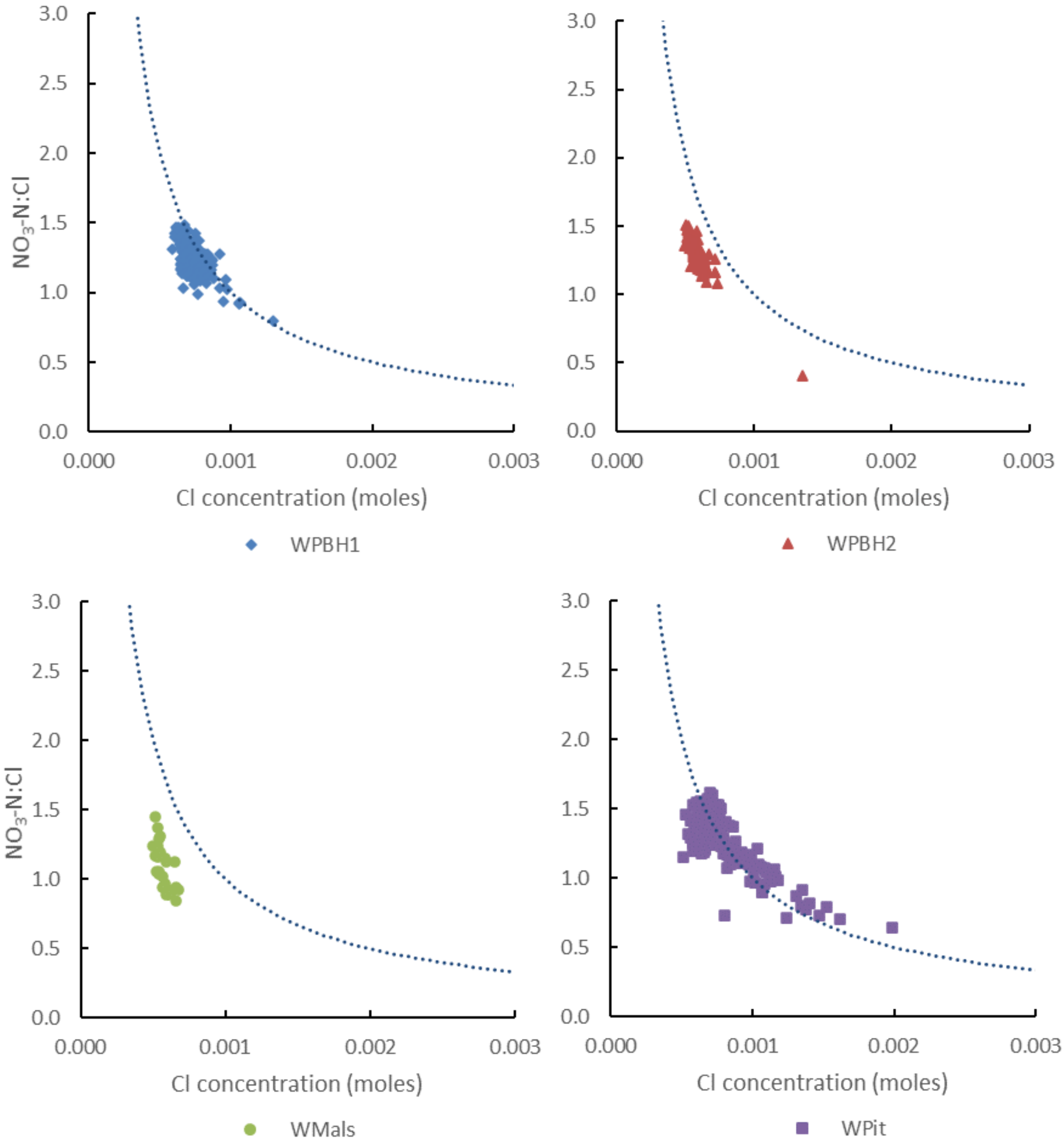

Figure 6.7: NO_3-N:Cl ratios for the four Woodgarston sample sites, with a theoretical trendline for increasing Cl and constant NO_3-N concentrations ($y = 0.001x^{-1}$). Data from April 2015 to July 2020, courtesy of South East Water (2019b).

6.2.3 Results of dual stable isotope analysis in the Woodgarston catchment

Samples for all four sites produced very tightly grouped dual stable isotope data in the “Soil N” region of the fingerprinting diagram ($\delta^{15}N$ between +4 and +7‰ and $\delta^{18}O$ between +2 and +6‰; Figure 6.8). Several of the samples also fit within the NH_4 fertiliser box. There is no evidence in Figure 6.8 to suggest a dominant manure source in any of the Woodgarston sites sampled, despite the presence of a known dairy farm with an active slurry lagoon 400 m from the Woodgarston

WTW. There is also an absence of heavy oxygen signatures, suggestive of a dominant inorganic NO_3 fertiliser source, in Figure 6.10. However, as previously discussed in Section 5.4, isotope analysis can only identify the average signature, so NO_3 sources could a mixture and not necessarily the result of a single process or source. This could lead to some distinctive sources being disguised and appearing more like the cluster define above.

Of the four sites sampled, none showed any evidence of denitrification, in terms of changes in NO_3 concentration or isotopic signatures (Figure 6.6, Figure 6.9). Plotting NO_3-N:Cl ratio versus $\delta^{18}O$ (Figure 6.9) provided a further check on whether denitrification occurred (Vitòria et al., 2008). If denitrification occurred a negative correlation would be expected, as $\delta^{18}O$ became heavier and NO_3 concentrations decreased. There is no correlation when the data are aggregated. When considered individually, WPit does show a negative correlation and suggest denitrification, however given this conflicts with the tight cluster of dual stable isotope data for WPit further analysis would be required.

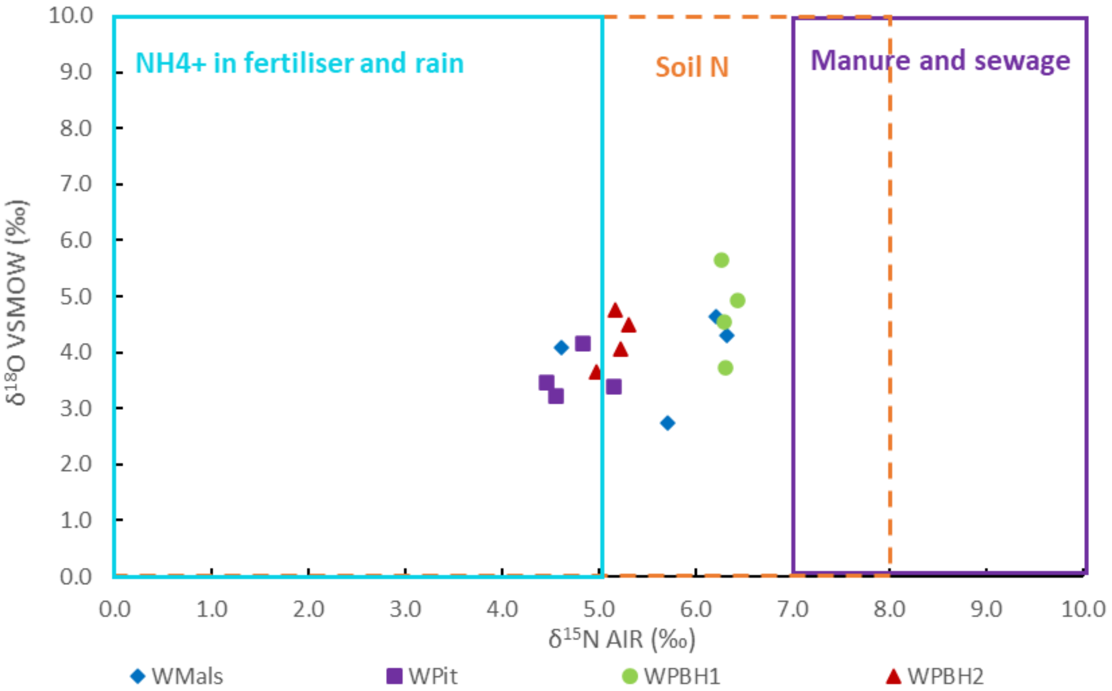

Figure 6.8: Fingerprinting diagram for dual stable isotope analysis of N and O in NO_3 for the four sample sites in the Woodgarston catchment. Adapted from Kendall (1998) and Nestler et al. (2011).

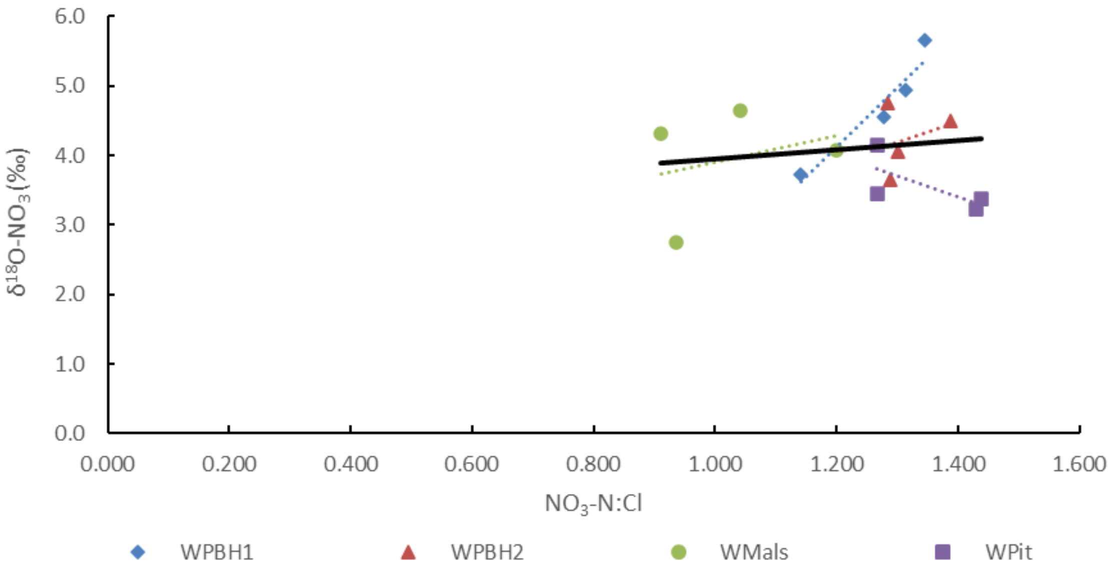

Figure 6.9: NO_3-N:Cl versus $\delta^{18}O$ for all four sites sampled in the Woodgarston catchment. If denitrification was occurring a negative correlation would be expected, as $\delta^{18}O$ would become enriched as NO_3 concentrations decreased.

6.2.4 Seasonality of nitrate in the Woodgarston catchment

Seasonality in NO_3 concentrations were observed at WPBH1, WMals and WPit (Figure 6.6). From 2015 to 2020 peaks were observed March to July at WPBH1, April to July at WPit and March to May at WMals. Similar trends for other major ions were also observed (Figure 6.1 to 6.5).

In terms of isotopic ratios, $\delta^{18}O$ increased during the recharge season (November and February) at all four sample sites (Figure 6.10). $\delta^{15}N$ remained approximately constant at WPBH1 and WPBH2 (Figure 6.10a and b) while samples at WMals and WPit showed variation in $\delta^{15}N$ (Figure 6.10c and d). This trend for heavier $\delta^{18}O$ in recharge season is similar to that identified for some of the Chalk samples in Yorkshire (Chapter 5), however the heaviest isotopic signatures were often observed later in the recharge season in the Woodgarston catchment as compared to the Yorkshire catchments.

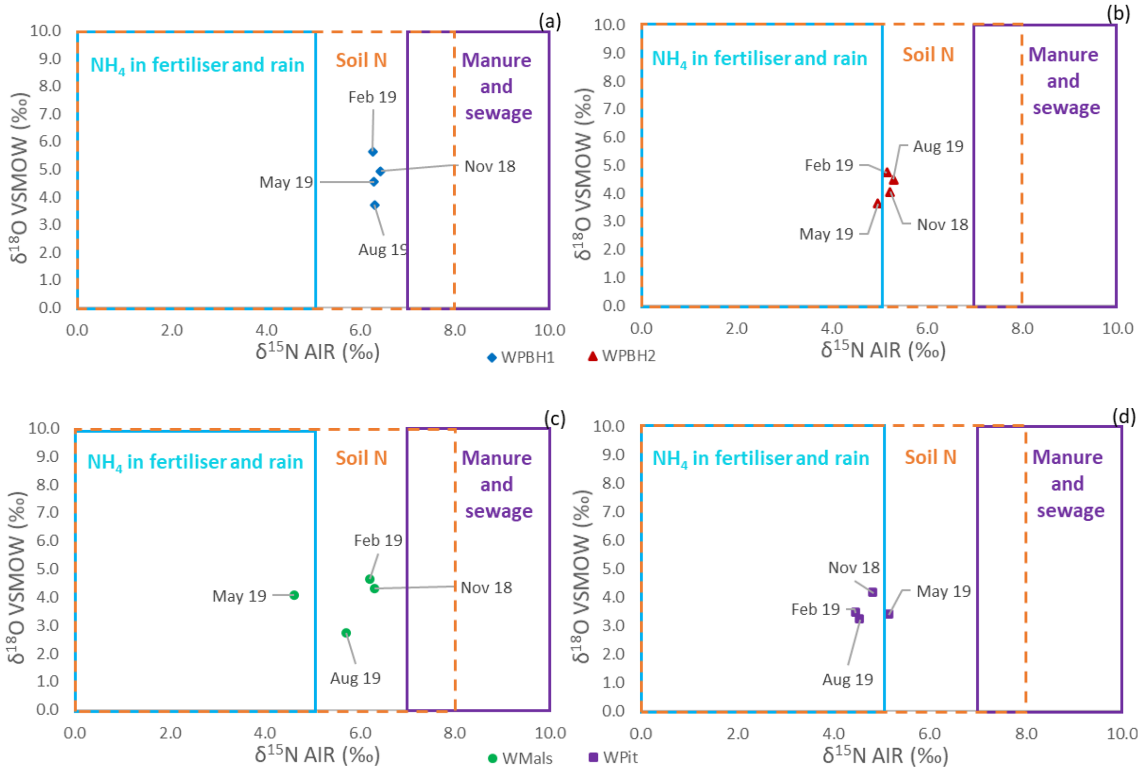

Figure 6.10: Dual stable isotope analysis of N and O in NO_3 for individual sites to assess seasonal trends (a) WPBH1, (b) WPBH2, (c) WMals and (d) WPit.

Plotting NO_3-N:Cl by month enabled assessment of seasonal variation from recharge to dry season; Cl concentrations were also plotted independently to identify what proportion of variation was due to Cl (Figure 6.11). NO_3-N:Cl had no clear pattern, but ratios from March to July occasionally had proportionally higher Cl concentrations in comparison to NO_3.

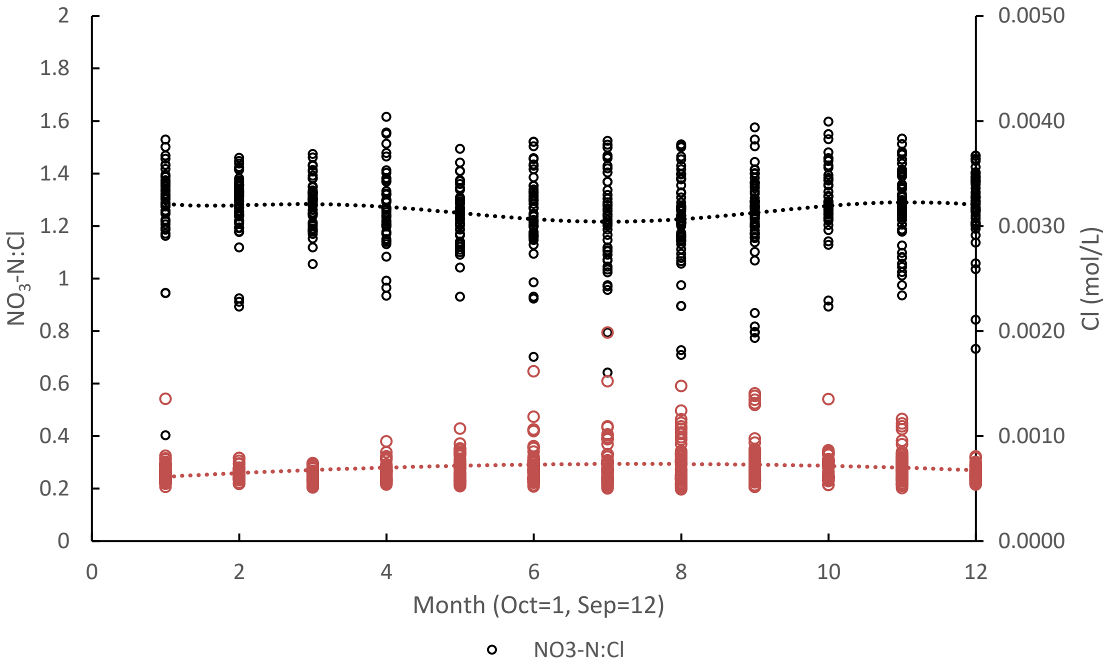

Figure 6.11: NO_3-N:Cl and Cl concentrations for samples from the Woodgarston catchment by month. Months begin from the start of the hydrogeological year, thus Oct=1 and Sep=12.

6.2.5 Discussion of groundwater characteristics in the Woodgarston catchment on the Southern Chalk

The most complete long-term data were available for WPit. Although there were some differences between parameters available for the four sites, these were mostly minor, thus their close proximity may mean conclusions drawn from major ions at WPit can be extrapolated across the sampling locations. WPit had a stable pH, varying between 7.03 and 7.43, similar to the findings of Elliot et al. (1999). Where carbonate mineral dissolution dominates, such as in Chalk groundwaters, the pH tends towards 7.5 to 8.5 (Gooddy et al., 2002). This suggests that most acidity introduced from soil and rainfall into groundwater that feeds WPit was removed by carbonate dissolution. The pH was sometimes slightly lower than 7.5, so other reactions may be involved, however the range stated by Gooddy et al. (2002) is based on porewaters, which may have resided in the aquifer and been subjected to carbonate dissolution for longer than the Woodgarston groundwater samples. Ca concentrations at WPit (124 to 150 mg/L) implied that the groundwater is more characteristic of unconfined Chalk groundwater than confined, as 80 mg/L Ca is considered typical for confined Chalk groundwater while 170 mg/L is common in unconfined Chalk groundwaters, (Gooddy et al., 2002). HCO_3 was similarly typical of unconfined systems, varying between 295 and 317 mg/L (300 mg/L is considered standard for Chalk groundwater).

Of the four sites sampled in the Woodgarston catchment, groundwater samples from WMals and WPBH2 never broke the PCV of 11.3 mg/L NO_3-N, while WPit and WPBH1 were frequently over this limit with observed maximum concentrations of 17.8 and 16.5 mg/L NO_3-N, respectively. A previous study sampled the Woodgarston WTW, where WPBH1 and WPBH2 are located, and reported a concentration of 2.48 mg/L NO_3 (0.56 mg/l N NO_3-N)[2] (Elliot et al., 1999); even considering the troughs observed in the South East Water dataset this concentration seems very low in comparison to the ranges reported in this study.

Variation in NO_3 concentrations were largely seasonal, however a gradual increase over time may have occurred at WPBH1, WPBH2 and WMals (Figure 6.6). The increase in NO_3 concentration at WPBH1 has led to it no longer being operated as a primary drinking water source. Periods of greater NO_3, Cl and SO_4 variation often occurred in parallel for the four sites, at the end of recharge c. March to July (Figure 6.4, Figure 6.5 and Figure 6.6). This could suggest that in the Woodgarston catchment effective rainfall during recharge diluted ion concentrations. It is notable that NO_3, Cl and SO_4 concentrations were stable at WPBH2 compared to WPBH1, given their close proximity (200 m apart). WPBH2 is 10 m deeper than WPBH1 so may be able to access a deeper horizon, less vulnerable to surface pollution, than WPBH1.

The ratio of NO_3 to Cl showed changes in NO_3 concentration caused most variation in Figure 6.7 and so, using the principles identified in Li et al. (2010) and described in Section 5.2.3, inorganic fertiliser could be the primary source of NO_3 in the Woodgarston catchment. However, as there are neither remarkably high NO_3 or Cl concentrations, the NO_3 is likely of mixed source to some extent. NO_3 concentrations are not low enough for their source to be considered the result of natural soil N cycling, or pre-agricultural.

---

[2] In Elliot et al. (1999) data were quoted as being in µmol/L, however it is assumed that this was a mistake and the data are actually in mmol/L, otherwise the data are around 1000 times too small and would be lower than rainfall concentrations. Samples were likely taken in mid-1990s so the data are unlikely to be from historical, less polluted waters.

6.2.6 Potential sources of nitrate contamination in the Woodgarston catchment

The dual stable isotope ratios for groundwater NO_3 in the Woodgarston catchment were within a tight cluster ($\delta^{15}N$ between +4 and +7‰ and $\delta^{18}O$ between +2 and +6‰). This is similar to the cluster identified for the Northern Chalk groundwater samples ($\delta^{15}N$ between +4 and +6‰ and $\delta^{18}O$ between +0 and +4‰). These signatures are indicative of NO_3 from soil N and NH_4 sources. However, the fingerprinting diagram in isolation cannot reveal the extent to which source mixing has occurred, and mixing of inorganic NO_3 fertiliser with a NO_3 source with lighter $\delta^{18}O$ could result in the isotopic signatures observed in the present study.

There is no evidence in the dual stable isotope ratios (Figure 6.8) to suggest a dominant manure source in any of the Woodgarston sites sampled. This is despite the presence of a known dairy farm with an active slurry lagoon 400 m from the Woodgarston WTW. It is possible that the lagoon is downgradient of the WTW as its exact location is unknown, but it is thought to be within SPZ1. The absence of a dominant manure signature could mean that the clay lining of the lagoon is sufficient and therefore little NO_3 leaches. Alternatively, NO_3 could leach at a slow enough rate to become diluted, to mix with other NO_3 sources, or for the soil biome to utilise and attenuate the manure NO_3.

There is a notable absence of isotopic signatures with a heavier $\delta^{18}O$ of +17 to +25‰ in the fingerprinting diagram (Figure 6.8), indicative of a dominant inorganic fertiliser signature. Given inorganic NO_3 fertilisers are known to be applied currently (Section 4.2.2) a signal would be expected if NO_3 were passing through the soil and aquifer unprocessed. It is likely that a transformation or re-equilibration process changed the isotopic signature of NO_3, in particular the O signature, as has previously been reported in the literature e.g. Powlson et al. (1986), Macdonald et al. (1989). A small proportion of inorganic fertiliser likely passes into groundwater untransformed and the extent to which this could occur is discussed in Section 7.4.

6.2.7 The extent of seasonality in the Woodgarston catchment

Peaks in groundwater NO_3, SO_4 and Cl concentrations occurred at the end of, or following, recharge season for WPBH1, WMals and WPit. These peaks differ to those observed on the Northern Chalk catchments, which tended to occur during recharge. This difference between the Northern and Southern catchments could reflect differences in processes or agricultural activities. NO_3-N:Cl plots implied that Cl concentrations increased in proportion to NO_3 during March to July (Figure 6.11). Higher salinity has been reported in the Southern Chalk, with connate water cited as likely source (see Section 3.1.2.4), so connate water from low permeability horizons could have greater influence during summer months due to the change in position of the water table. Alternatively, higher Cl could also be due to greater evapotranspiration during summer months. However, given the increase in NO_3 and SO_4 concentrations, an anthropogenic source introduced in early spring may be more feasible.

In terms of isotopic ratios, all four sites demonstrated a similar trend of heavier $\delta^{18}O$ in recharge season to that identified for some of the Northern Chalk groundwater samples in Yorkshire (Chapter 5). This increase indicates that NO_3 with a heavier O signature reached pumped groundwater during the recharge period, from approx. November to April. As hypothesised for the Northern Chalk catchments (in Section 5.5.1), a pulse of recharge water containing NO_3 with heavier $\delta^{18}O$ (e.g. untransformed inorganic NO_3 fertiliser) may enter groundwater on initiation of recharge. The NO_3 source may have become progressively more greatly transformed as the hydrogeological year continued. This concept is developed further in Sections 7.2.3, 7.3.5 and 7.4. The observed seasonality may also imply there is a proportion of fracture flow in the unsaturated zone enabling recharge water to bypass the Chalk matrix. $\delta^{15}N$ remained fairly constant at WPBH1 and WPBH2, while samples at WMals and WPit showed variation in $\delta^{15}N$ (Figure 6.10). Sources at WMals and WPit may have shown more seasonality in N signatures as they are working farms, whereas WPBH1 and 2 are a public abstraction and therefore likely subject to fewer, more homogenous, N inputs.

6.3 Summary of groundwater nitrate in the Woodgarston catchment

The Chalk aquifers of England are important sources of drinking water, with the Southern Province Cretaceous Chalk aquifer having particular significance due to the volume of people who rely on it for wholesome water. The Southern Chalk aquifer differs from its Northern counterpart in that it tends to be less indurated and brittle, with higher matrix porosity than in the North, therefore it is prone to becoming highly weathered: putty Chalk is more common in the Southern than the Northern Province. Fractures and in some regions extensive karstic features, are recorded in the published literature for the Southern Province Chalk, which can lead to localised high hydraulic conductivity. Chalk beds containing many marls create horizons of lower permeability. Permeability also tends to vary with depth: it is high where solutional weathering has enhanced fracture apertures to produce fissures and conduits, and where moderate weathering produces very highly fractured Chalk and “Chalk bearings” i.e. gravel. Much lower permeability regions exist where extreme weathering produces putty Chalk.

In the study catchment, the Upper Chalk (Newhaven, Seaford and Lewes Nodular Chalk) crops out and at the Woodgarston WTW a thin bed of Clay-with-Flints has been identified, however it unlikely extends as far south as WMals. During the study period NO_3 concentrations appeared to increase at WPBH1 and WPBH2, but appeared stable at WMals and WPit. This may be due to the lower volumes of water pumped at the latter two sites. The hydrochemistry of the four sites are typical of Chalk groundwater: dominated by HCO_3 and Ca. Frequent peaks and troughs are visible in ionic concentrations at all four sample sites, which, in addition to variation in isotope signatures seasonally, may imply fracture flow. This does not, however, rule out potential influence from exchange with matrix water.

The most significant NO_3 source in the Woodgarston catchment is likely from agriculture. However, dual stable isotope analysis revealed no clear evidence of a manure-type or NO_3 fertiliser-type isotope signature. The data were tightly clustered indicating a fairly uniform source, likely a ubiquitous agricultural signature, similar to that observed in Chapter 5. The ratio of NO_3 to Cl is indicative of mixed NO3 sources such as manure and inorganic fertilisers.

All of the Woodgarston samples had heavier $\delta^{18}O$ during the recharge period, similar to the trend observed for several sites in the Yorkshire catchments. This trend would suggest that NO_3 with a heavier O signature was transported to sample sites during the recharge period. This change in signatures during recharge season could be the result of different NO_3 sources dominating in different seasons or it may be due to NO_3 transformations. WMals and WPit showed more variation in $\delta^{15}N$ than WPBH1 and WPBH2. $\delta^{15}N$ may be more variable at WMals and WPit than the two sample sites at the WTW as they are working farms, which may produce more variable NO_3 sources than a WTW. There was no single seasonal pattern to NO_3-N:Cl ratios but Cl concentrations were occasionally higher in the summer. Higher salinity has been reported in the Southern Chalk, with connate water cited as likely source. Higher evapotranspiration in summer months or application of anthropogenic Cl in spring could also be influential.

6.4 Hydrochemistry in the Hartlake catchment on the Medway RTG

Little hydrochemical data are available for Hartlake as water quality monitoring by South East Water focussed on NO_3, carbendazim (fungicide) and metaldehyde (pesticide). A full suite of hydrochemistry data were available for a farm abstraction borehole, HARSPF, around 3 km from the Hartlake catchment (Figure 3.7). Both locations tap the RTG aquifer, however at Hartlake the RTG are largely overlain by Alluvial deposits, which may influence hydrochemistry. The HARSPF borehole is on unconfined RTG and also much deeper than the study sites, therefore likely accesses deeper horizons as well as the RTG. Although NO_3 concentrations presented below suggest HARSPF was subject to greater pollution than HARA or HARC, the similarity in other ions imply that useful inferences may be drawn from studying hydrochemical data at HARSPF.

At HARSPF between 2007 and 2019, SEC ranged from 645 to 698 µS/cm and pH from 6.62 to 7.02 (Figure 6.12). The groundwater appeared to be Ca-HCO_3-SO_4 type, on the assumption that SO_4 was naturally occurring e.g. via pyrite dissolution in the soil. Alternatively the groundwater may be Ca-HO_3 type, with a source of SO_4 pollution (Figure 6.13). Most major ion concentrations were stable during this period, apart from SO_4 concentrations, which showed a decreasing trend (Figure 6.14).

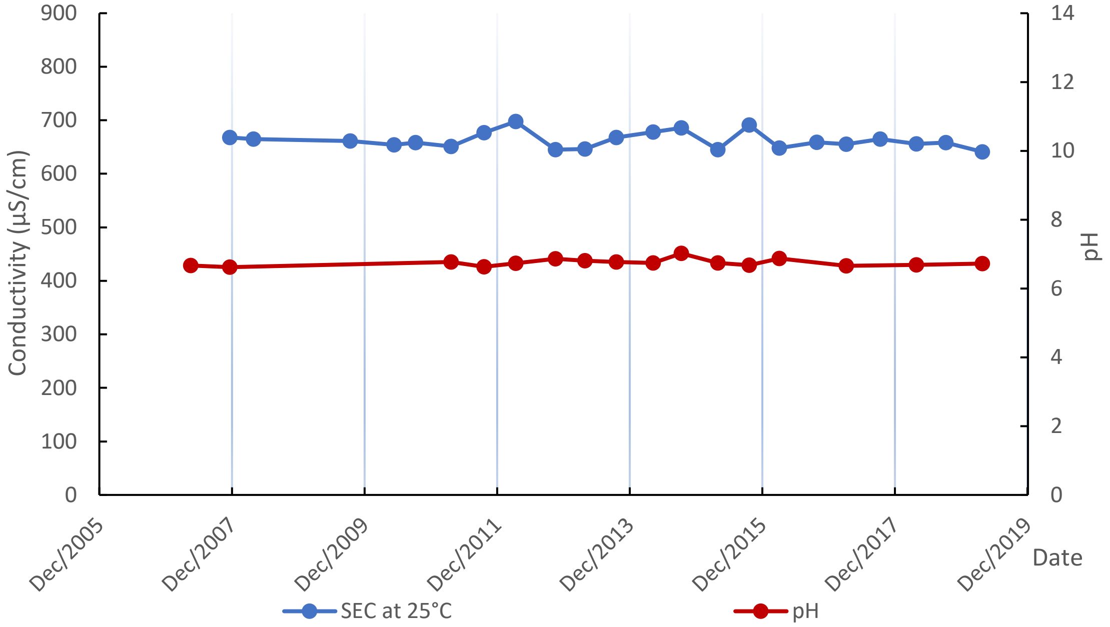

Figure 6.12: SEC and pH at HARSPF from May 2007 to April 2019. Gridlines mark 31st December. Data from Environment Agency (2020).

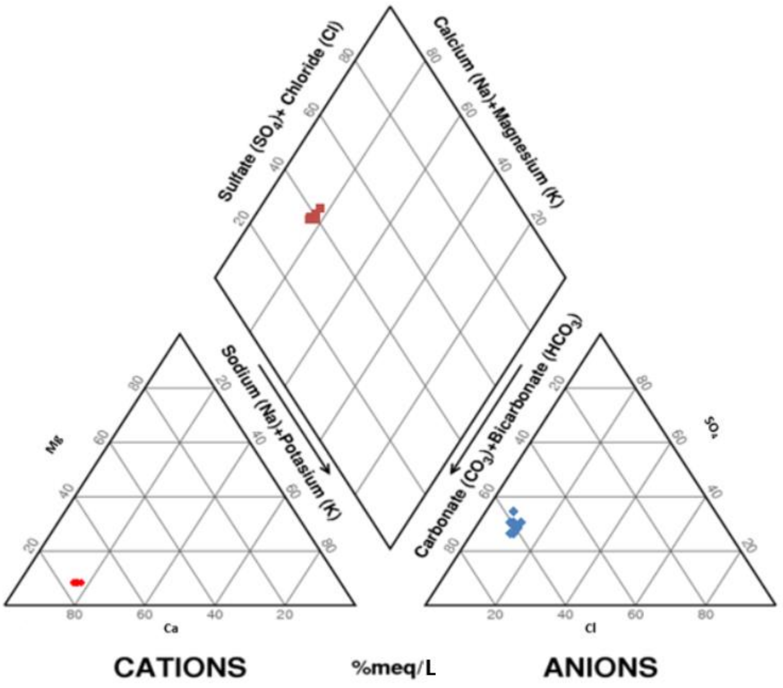

Figure 6.13: Piper plot of major ions at HARSPF from 2009 to 2014, utilising data from Environment Agency Water Quality Archive.

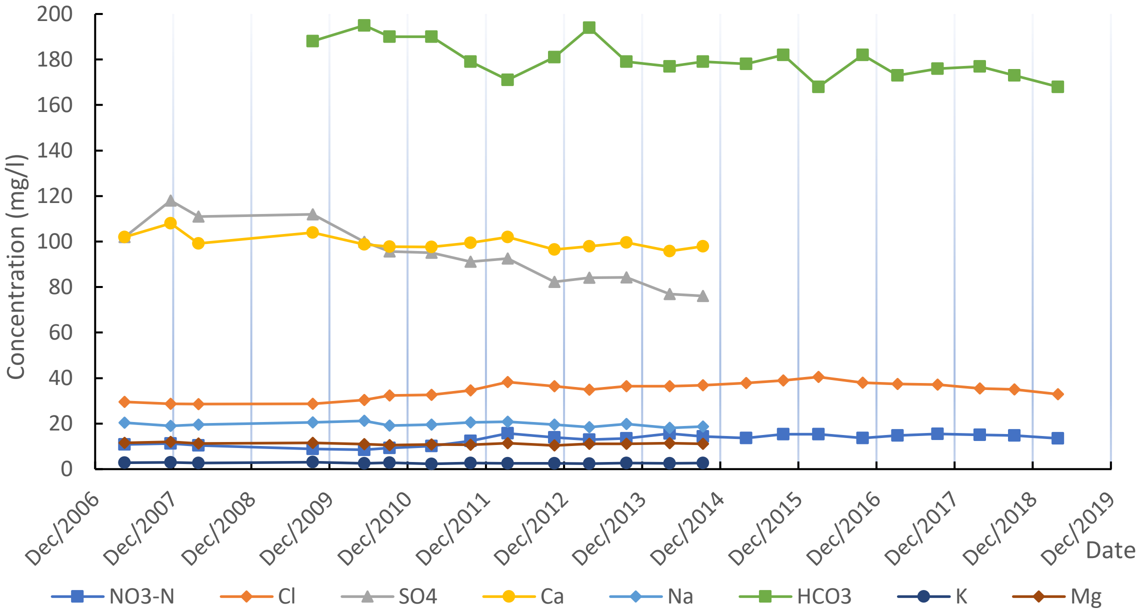

Figure 6.14: Major ion concentrations at HARSPF from 2007 to 2019. Gridlines mark 31st December. Data from Environment Agency (2020).

In comparison to HARA and HARC, SO_4 concentrations at HARSPF were high initially, but decreased below 100 mg/L in the 2010s so HARSPF and HARA became more comparable (Figure 6.15). SO_4 concentrations at HARA ranged from approximately 50 to 80 mg/L and HARC was significantly lower at 24 to 44 mg/L (Figure 6.15). Cl concentrations are fairly similar at all three sites, ranging from 29 to 44 mg/L (Figure 6.16). Both SO_4 and Cl concentrations at HARC fluctuate regularly as more frequent sampling was introduced, although variation is within a slightly narrower range than at HARA.

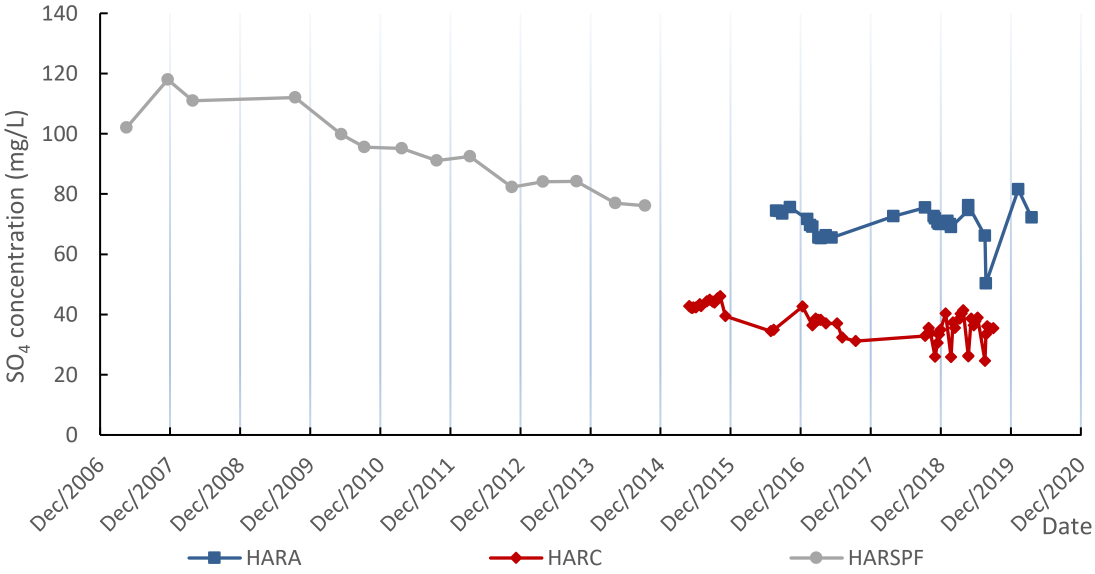

Figure 6.15: SO_4 concentrations at HARA and HARC production boreholes in the Hartlake catchment and HARSPF.

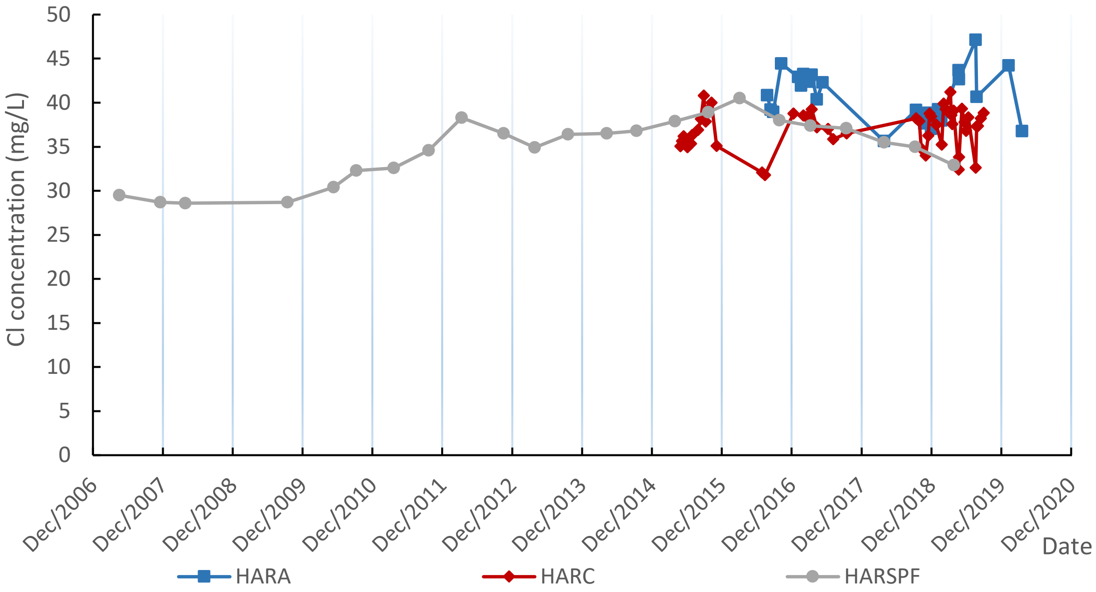

Figure 6.16: Cl concentrations at HARA and HARC production boreholes in the Hartlake catchment and HARSPF.

6.4.1 Nitrate concentrations in the Hartlake catchment

Very low NO_3 concentrations were recorded at two sites within the Hartlake catchment (HARC and HAROB1), while two had higher concentrations, but still beneath the PCV (HARA and HAROB3) (Table 6.2, Figure 6.17). NO_3 concentrations were below the detection limit from HARC in May 2019, and all samples from HAROB1; consequently it was not possible to carry out dual stable isotope analysis on these samples. NO_3 concentrations at HARSPF were much greater than for the sample sites, which when considered alongside high SO_4 concentrations is indicative of anthropogenic pollution.

NO_3 concentrations from samples at HARA, HARC and HAROB3 fluctuated seasonally with peaks in concentration observed between October and March (Figure 6.17). Groundwater from the observation borehole HAROB3 showed particularly variable NO_3 concentrations within seasons. While NO_3 concentrations differed between sample sites, peaks in concentration occurred at similar times at each site.

Table 6.2: NO_3-N concentrations at the four Hartlake sites sampled for dual stable isotope analysis, in addition to HARSPF included for geological and hydrochemical context. The periods where data were available varied thus is included in brackets, and NO_3 values greater than the legal drinking water limit of 11.3 mg/L NO_3-N in bold red. *NO_3 concentrations frequently beneath the limit of detection (1 or 2 mg/L NO_3), therefore these data have less accuracy than other sites analysed.

Site name (dates monitored)		**NO_3-N concentration (mg/L)**	**Site name** (dates monitored)		**NO_3-N concentration (mg/L)**
HARA (Aug 2016-Apr 2020) *n=28*	Min	2.8	**HAROB1*** (Apr 2016-Mar 2020) *n=98*	Min	0.2
	Mean	5.8		Mean	0.5
	Max	8.4		Max	1.6
HARC (May 2015-Nov 2019) *n=52*	Min	0.1	**HAROB3** (May 2016-Mar 2020) *n=95*	Min	1.0
	Mean	1.4		Mean	3.2
	Max	2.3		Max	6.8
HARSPF (Apr 2015-Apr 2019) *n=23*	Min	**13.5**			
	Mean	**14.6**			
	Max	**15.5**			

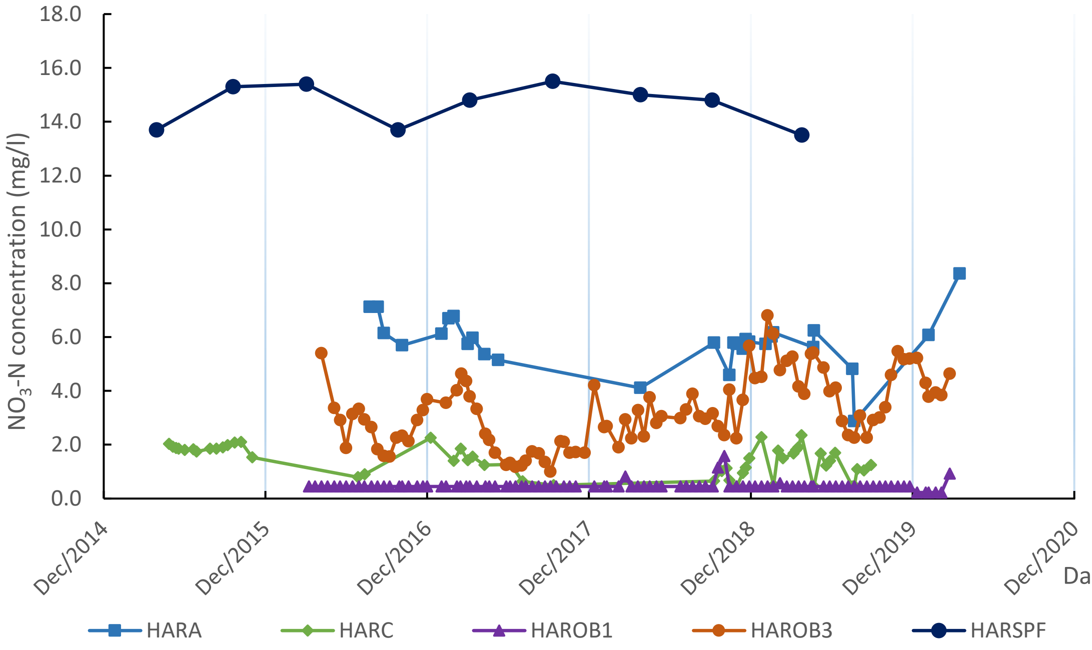

Figure 6.17: NO_3-N concentrations at the four Hartlake sampling sites and HARSPF. Samples with <2 mg/L until December 2019, and <1 mg/L NO_3 from January 2020 onwards (0.45 and 0.23 mg/L NO_3-N, respectively) were below the detection limit. Gridline mark 31st December. Data courtesy of South East Water (2019a) and Environment Agency (2020)

6.4.2 Nitrate to chloride ratios in the Hartlake catchment

As discussed in Section 5.2.3, Cl is unaffected by chemical or biological processes and so its concentration can be a useful tool. While there are N and Cl sources that will defy these principles, changes in the ratio of NO_3 to Cl concentration could indicate a pollution source, or that a physical process (dilution or evaporation) has occurred (Liu et al., 2006). Sufficient NO_3 and Cl data were available for the two production boreholes, HARA and HARC. Figure 6.18 shows much lower NO_3-N:Cl ratios for HARA and HARC than identified for the Chalk catchments. Cl concentrations were similar between HARA and HARC, and while not markedly high, Hartlake Cl concentrations were above the median Cl concentrations for the Chalk sites sampled (median Chalk Cl concentration is 27.0 mg/L). HARA has higher NO_3 than HARC (Figure 6.17), which are reflected in the NO_3-N:Cl ratios presented in Figure 6.18. Variations in NO_3-N:Cl are therefore largely due to changes in NO_3 concentration. Timeseries in Figure 6.17 suggest that N input is seasonal, with the highest NO_3 concentrations for both sites occurring in winter months.

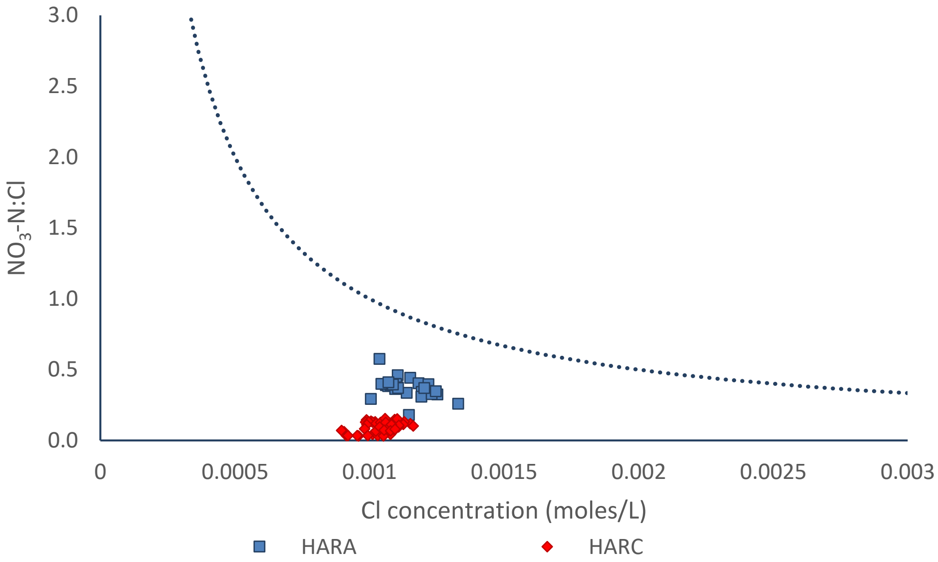

Figure 6.18: NO_3-N:Cl for HARA and HARC, in the Hartlake catchment, with the theoretical trendline used in Chapter 5 for increasing Cl and constant NO_3-N concentrations ($y = 0.001x^{-1}$).

6.4.3 Results of dual stable isotope analysis of groundwater nitrate in the Hartlake catchment

Figure 6.19 shows the results of dual stable isotope analysis for three sites (HARA, HARC, HAROB3) in the Hartlake catchment. Signatures plot within the manure/sewage box, with HAROB3 signatures overlapping with the soil N box. There are no data points in the inorganic NO_3 fertiliser box (with associated Haber-Bosch, HB, heavy $\delta^{18}O$) in Hartlake groundwaters, even though NO_3

fertiliser definitely currently being applied (Chapter 4, Section 4.2.3). Although the lack of signatures with heavy $\delta^{18}O$ implies that untransformed NO_3 fertiliser did not dominate, all ratios are an average of the N and O nitrate signatures a sample contains, thus a proportion of NO_3 fertiliser could have mixed with other NO_3 sources to produce a lighter $\delta^{18}O$ signature. No NH_4 fertiliser signature was observed either, despite these being amongst current land management techniques (Chapter 4, Section 4.2.3).

$\delta^{15}N$ for one sample from HARC was far heavier than recorded for either of the Chalk catchments analysed, and paired with very low NO_3 concentrations (Figure 6.19).The fingerprinting diagram (Figure 6.19) was thus further interrogated to assess the likelihood of the isotopic signatures representing manure NO_3 sources. The gradient of the signatures loosely fits that expected for denitrification (2:1 N to O, shown by the dashed line in Figure 6.19), assuming the original end member was NH_4 fertiliser or a soil N-type signature. Plotting $\delta^{18}O$ and $\delta^{15}N$ against NO_3 concentrations, as well as $\delta^{18}O$ against NO_3-N:Cl ratio, produced gradients that imply both isotope ratios became heavier when NO_3 concentrations were lower (Figure 6.20 and Figure 6.21). Such trends are also consistent with denitrification as during denitrification NO_3 concentration reduces while the isotopic ratio in the substrate becomes heavier, as a result of preferential metabolism of NO_3 containing lighter isotopes.

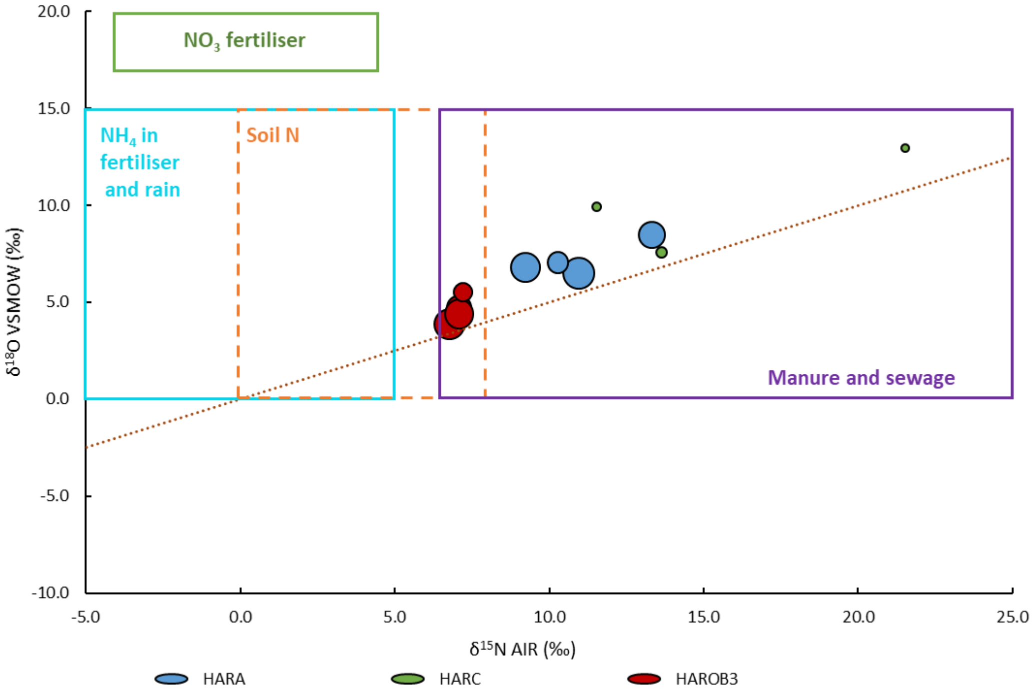

Figure 6.19: Dual stable isotope analysis of HARA, HARC and HAROB3 in the Hartlake catchment. Dual stable isotope analysis was not possible for HAROB1 as NO_3 concentrations were too low. Larger bubbles demarcate higher NO_3 concentrations. A hypothetical denitrification trend, with a 2:1 ratio of change of $\delta^{15}N$ to $\delta^{18}O$, is marked in red.

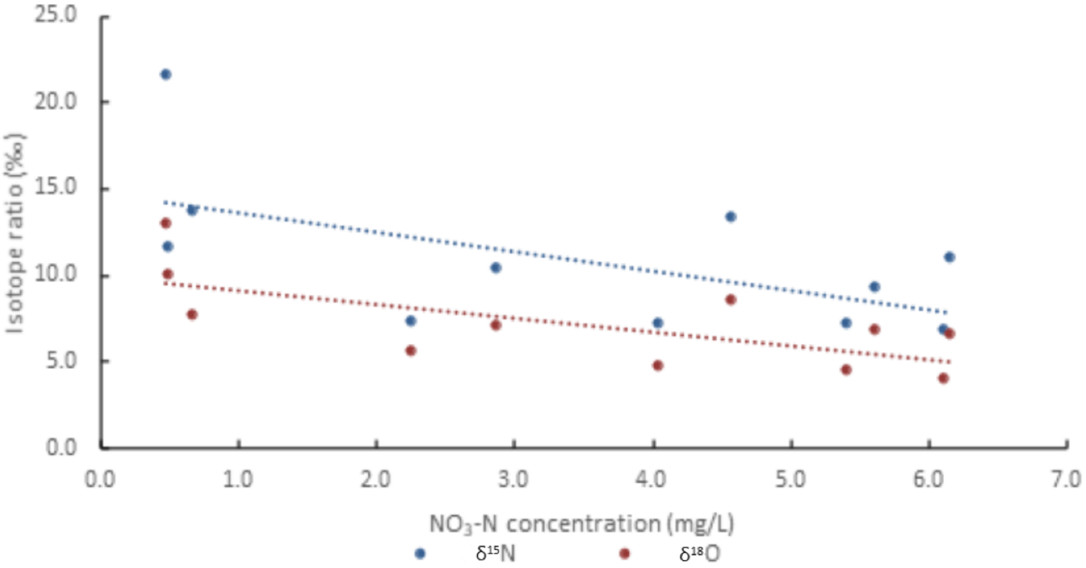

Figure 6.20: NO_3 concentrations versus $\delta^{18}O$ and $\delta^{15}N$ for the three Hartlake sites where NO_3 concentration was sufficient to allow dual stable isotope analysis. Plotting NO_3 against $\delta^{18}O$ and $\delta^{15}N$ identifies any correlations between isotopic ratios and concentration, thus whether a fractionation process could have occurred.

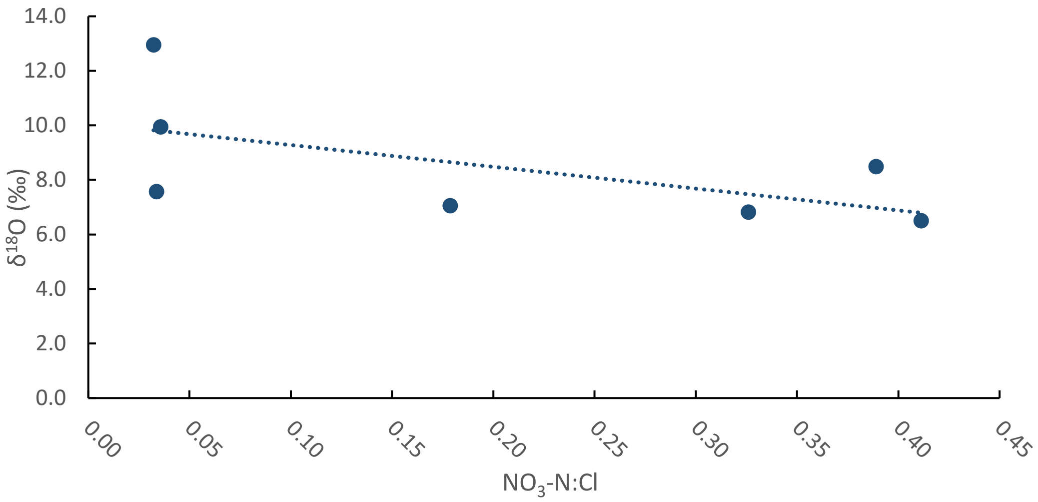

Figure 6.21: NO_3-N:Cl versus $\delta^{18}O$ for HARA and HARC production boreholes. Plotting NO_3-N:Cl against $\delta^{18}O$ identifies any correlation between the parameters and thus whether a fractionation process could have occurred.

6.4.4 Seasonality of nitrate in groundwater nitrate in the Hartlake catchment

In Figure 6.22 dual stable isotope signatures are presented labelled with the sample date to better consider seasonality of NO_3 isotopic ratios. Dual stable isotope results from HAROB3 were very closely grouped, in comparison to the other two Hartlake sites samples. There is a 2‰ increase in $\delta^{18}O$ between February and August 2019, and negligible change in $\delta^{15}N$. Dual stable isotope results for HARA and HARC show broad data distribution, with a greater change in $\delta^{15}N$ than $\delta^{18}O$, which could indicate denitrification at these two locations (approximate gradient plotted in Figure 6.19).

NO_3 concentrations fluctuated seasonally, with highest concentrations recorded during recharge (Section 6.4.1). Higher winter NO_3 is reflected in NO_3-N:Cl ratios with a slight trend for higher NO_3-N:Cl during recharge season (Figure 6.23). Higher NO_3 concentrations correlated with lighter $\delta^{15}N$ and $\delta^{18}O$, which could be additional evidence for denitrification (Figure 6.20).

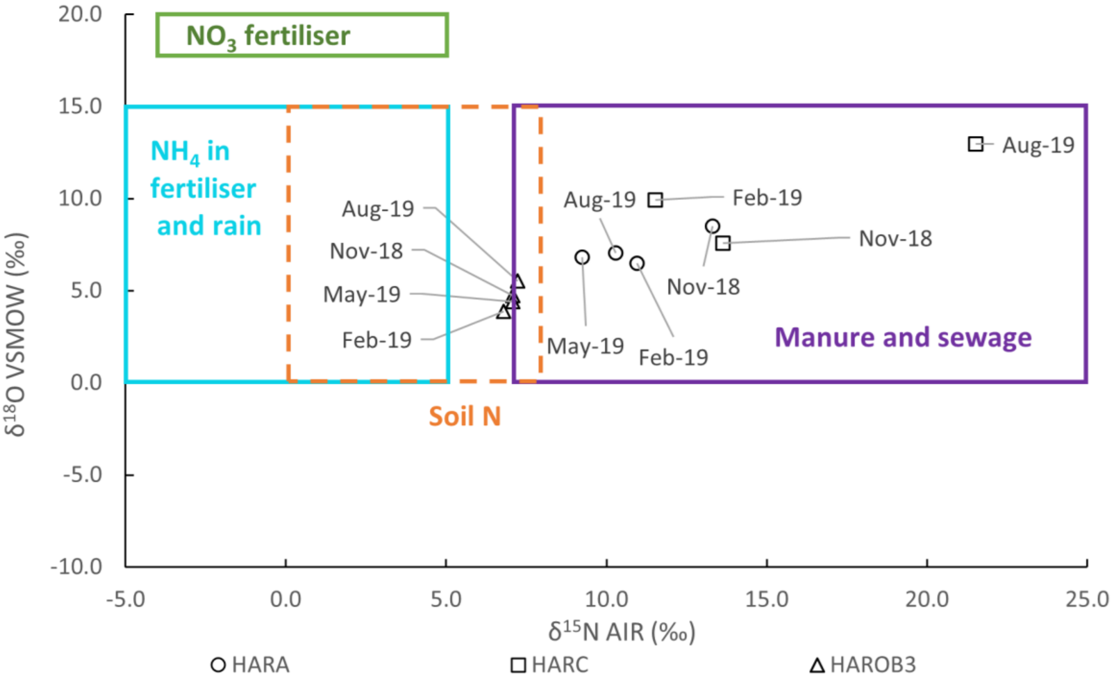

Figure 6.22: Dual stable isotope analysis of N and O in NO_3, grouped by sample site and showing dates the samples were taken.

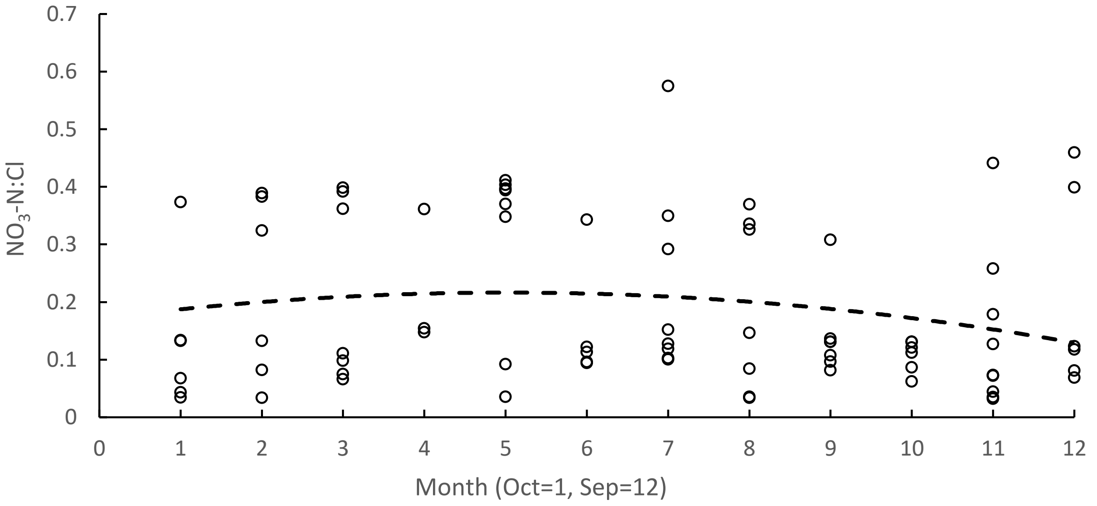

Figure 6.23: NO_3-N:Cl for samples from the Hartlake catchment by month. Months begin from the start of the hydrogeological year, thus Oct=1 and Sep=12.

6.4.5 Discussion of groundwater characteristics in the Hartlake catchment

Using the long-term dataset from HARSPF to gauge the general characteristics of local groundwater, the Hartlake catchment is likely Ca-HO_3 type with pH and SEC of approximately 6.5 to 7.0 and 650 to 700 µS/cm, respectively (Figure 6.12).

The groundwater at HARSPF could be Ca-HCO_3-SO_4 type, assuming SO_4 is naturally occurring (e.g. via pyrite dissolution in the soil). However, given SO_4 decreased over time to concentrations similar to those at HARA the initial high concentrations may have been indicative of recovery after a pollution event (Figure 6.13, Figure 6.15).

Unlike the Chalk catchments, NO_3 concentrations in the four sites sampled in the Hartlake catchment were all below the PCV. One site (HAROB3) had such consistently low concentrations that dual stable isotope analysis was not possible. NO_3 concentrations at HARSPF were much greater than for the sample sites, and more comparable to some sites on the Chalk catchments studied, which potentially demonstrates the protective effects that low permeability superficial cover can have on groundwater vulnerability to surface pollution. (Superficial cover was absent at HARSPF and the majority of the studied Chalk catchments; geology is discussed in detail in Section 2.7).

The difference in NO_3 and SO_4 concentrations between adjacent HARA and HARC sample sites suggests that the boreholes access waters with different characters. High SO_4 and NO_3 at HARA may be indicative of increased influence of anthropogenic pollution compared to the water from HARC. HARC is only 1.2 m deeper than HARA (Table 3.3) but the boreholes could access different horizons, with HARA receiving water from an area less protected by superficial cover. Both SO_4 and Cl concentrations at HARC fluctuated regularly; many fluctuations within a year could be the result of dilution of the shallow groundwater with rainfall recharge, interaction between the aquifer and the River Medway, or multiple chemical applications to the soil.

Cl concentrations for HARA and HARC were above the median Cl concentrations for the Chalk sites sampled; this may be due to differing geology, or influence from the River Medway. Given similarities in Cl concentrations between HARA and HARC, variations in NO_3-N:Cl were therefore due to changes in NO_3 concentration. HARA had higher NO_3 concentrations than HARC, which implies anthropogenic input at HARA and more natural N inputs at HARC, however given the similar Cl concentration it could also be evidence of denitrification at HARC. Trends in Figure 6.17 suggest that N input was seasonal, with the highest NO_3 concentrations for both sites corresponding to the latter half of the recharge period.

6.4.6 Discussion of potential nitrate sources and dominant processes in the Hartlake catchment

The results of dual stable isotope analysis for the Hartlake catchment showed a manure-like signature, with isotopic ratios from HAROB3 also corresponding with soil N signatures (Figure 6.19). Unlike observations from the Chalk catchments, high NO_3 concentrations were not associated with heavy isotopic signatures in Hartlake and isotopic data loosely fell on a linear positive trend of heavier $\delta^{15}N$ heavier $\delta^{18}O$. These trends could be explained by denitrification of NO_3 from soil N or NH_4 fertiliser.

The gradient of the trend in Figure 6.19 loosely fit that expected for denitrification (2:1 $\delta^{15}N$ to $\delta^{18}O$), assuming the original end member was NH_4 fertiliser or a soil N-type signature. From isotope analysis groundwater NO_3 at HAROB3 appeared like soil-N, so could represent a feasible end-member. Denitrification acting on such end-member compositions (i.e. falling in lower left of the plot) is one possible explanation of the observed trend. Alternatively, the trend could result from manure or sewage end-members (falling in the upper right of the plot), mixing with transformed NO_3 or soil N. It is possible that manure signatures were dominant given the downland is used for grazing, however grazing is unlikely to be as great a producer of manure as an intensive dairy or pig farm. In addition, dominant manure signatures on the Chalk catchments studied are only hypothesised to occur where an especially bioavailable, or large volume of, manure or slurry was applied (i.e. the soil biomass cannot absorb NO_3 quickly enough to avoid leaching). So unless the Hartlake catchment is subject to different soil processes to those in the Chalk catchments studied, it makes a manure dominated NO_3 source improbable.

Figure 6.20 and Figure 6.21 produced trends indicating that both isotope ratios became heavier when NO_3 concentrations were lower; this may be further evidence for denitrification, or alternatively indicate that animal feed with different N isotopic ratios from the other catchments may be used in Hartlake, leading to an especially heavy-N manure signature. Clayey Alluvium deposits overlying the RTG at Hartlake are understood to provide some protection from surface contamination (Howe et al., 2017) and these same deposits confine the aquifer beneath, and could create low oxygen conditions required for denitrification as would seem to be the case given the presence of Fe and Mn in these waters.

Groundwater-NO_3 $\delta^{15}N$ is also heavier than the signatures identified for the Chalk in this study (Section 5.5, and Section 6.5), providing further evidence indicating denitrification as an influential process in the RTG. Denitrification may have occurred due to saturated soil conditions, or because the aquifer is confined in the area sampled, as evidenced by its low storage co-efficient values.

These RTG catchment data were included in the investigation to identify whether aquifers with short residence times, in comparison with the Chalk, produced a stronger untransformed, HB-type, NO_3 fertiliser signature. Data presented in Figure 6.19 show this was not the case during the study period, thus transformation of O isotopes in NO_3 is likely ubiquitous and not unique to long-residence Chalk aquifers. As it is not a product of the aquifer, transformation processes are likely occurring in the soil, prior to water passing into the unsaturated zone. The gradient of isotopic data in Figure 6.19 is positive, which is not indicative of mixing between inorganic NO_3 fertiliser with heavy $\delta^{18}O$ and manure NO_3, instead it again implies that transformation processes are occurring. This hypothesis is explored further in Chapter 7.

6.4.7 Seasonality in the Hartlake catchment

In the Hartlake catchment, isotopic ratios were closely grouped at HAROB3, while the data distribution at HARA and HARC was very broad (Figure 6.19). For HAROB3 there was a 2‰ increase in $\delta^{18}O$ between February and August 2019, and negligible change in $\delta^{15}N$. This is a similar magnitude change to that observed on the Chalk and so could represent the transformation process as described in Sections 5.3.1 and 6.2.7. Alternatively, it could be caused by mixing with a NO_3 source such as soil N or manure, with a heavier oxygen signature. For sites HARA and HARC the broad data distribution was associated with a greater change in $\delta^{15}N$ than $\delta^{18}O$, which could indicate denitrification at these two locations (Figure 6.19). Mixing with a NO_3 source of much heavier $\delta^{15}N$ such as manure or sewage is also possible given that the NO_3 concentration of an individual site did not appear to reduce with higher $\delta^{15}N$. Figure 6.20 did, however, present a correlation between NO_3 concentration and isotopic ratios for the Hartlake catchment that would support the hypothesis that denitrification was an influential process in Hartlake groundwater.

The gradient of change for $\delta^{15}N$ at HARA and HARC in Figure 6.19 is dissimilar to that observed on the Chalk and therefore implies dominance of a process other than the transformations discussed in Section 5.3.1, feasibly denitrification. If seasonality like that observed in the Chalk aquifers (Sections 5.3.1 and 6.2.7), was occurring at HARA and HARC then its signatures were masked by the magnitude of the denitrification-type signatures at these two sites. The lighter of the isotope signatures recorded at HARA and HARC (Figure 6.19) suggest an influx of water containing NO_3 with lighter $\delta^{15}N$ and $\delta^{18}O$, such as the soil-type NO_3 as observed at HAROB3; the source of this could be the River Medway when it responds to heavy or sustained rainfall. Variation in major ion concentrations suggested that HARA and HARC access different horizons, possibly due to differences in borehole depth, providing a potential explanation for the difference in isotopic ratios.

6.5 Summary of groundwater nitrate in the Hartlake catchment

Groundwater in the locally-important River Terrace Gravels (RTG) aquifer has a shorter residence time, as the aquifer is thin and relatively uniform, in comparison to the Chalk aquifers, which have residence times into the decades. As introduced in Section 3.1.3, the study catchment, Hartlake, is underlain by superficial deposits including Alluvium and RTG, which are in turn underlain by Weald Clay. The Alluvium confines the RTG in some locations. Hydrochemical data from reference site, HARSPF, show groundwater to be Ca-HCO_3-SO_4 type, or Ca-HO_3 type with a source of SO_4 pollution (Figure 6.13).

Groundwater NO_3 concentrations for all samples from HARA, HARC, HAROB1 and HAROB3 boreholes in the Hartlake catchment within the RTG were within the PCV during the period studied, and at HAROB1 were often below the limit of detection of 2 mg/L NO_3. NO_3 concentrations at HARSPF were always above the PCV during this period. Analysis of NO_3-N:Cl revealed constant Cl concentrations, with increasing NO_3 concentrations indicative of inorganic fertiliser applications. This trend is opposite to that expected where manure NO_3 sources dominate, as these natural fertilisers also contain high concentrations of Cl. Dual stable isotope analysis, however, revealed no heavy-O inorganic NO_3 or NH_4 fertiliser signatures. The lack of inorganic NO_3 fertiliser signatures (despite current fertiliser applications of this type) is similar to that observed on the Chalk catchments sampled. Given this similarity it is unlikely that the processes that drive the loss of the heavy-O signature associated with HB NO_3 is a product of residence time. This process likely occurs in the soil zone prior to water entering the aquifer (discussed further in Section 7.3.4).

Dual stable isotope signatures from groundwaters from the Hartlake catchment show strong evidence for denitrification: there is consilience between hydrochemistry and isotope data that the water has undergone conditions that would reduce NO_3. Notably that there were high concentrations of Fe and Mn reported by South East Water, $\delta^{18}O$ becomes heavier as NO_3-N:Cl decreases, and that isotope ratios from NO_3 follow the denitrification trend of 2:1 N to O, (i.e. both $\delta^{18}O$ and $\delta^{15}N$ become heavier as NO_3 concentration decreases). Denitrification may occur due to saturated soil conditions, or because the aquifer is confined in the area sampled, as evidenced by its low storage co-efficient values.

Chapter 7 Synthesis of findings from the Chalk and River Terrace Gravels catchments

The aim of this chapter is to synthesise data from Chapters 4 and 6 to assess the extent to which processes affecting nitrate are the same for the Chalk aquifers and the Medway River Terrace Gravels (RTG) aquifer, and therefore whether these processes differ for aquifers with a markedly shorter groundwater residence period (decades versus days for the Chalk and RTG, respectively). This improved understanding of the mechanisms that lead increasing nitrate concentrations in some aquifers will help inform effective mitigation measures and thus is a significant step forward in approving nitrogen use efficiency (see Section 2.3.7).

In this chapter the influence of sampling site is first explored, followed by a comparison of hydrochemical data from the Northern and Southern Province Chalk aquifers. Hydrochemistry of the Chalk and RTG aquifers are then compared to enable conclusions to be drawn regarding likely nitrate sources and dominant processes. The suitability and limitations of the fingerprinting approach using the diagram developed by Kendall (1998) are also discussed.

7.1 Influence of sampling site

The volume pumped from a borehole will affect its hydrochemistry: the more water abstracted, the greater the drawdown and therefore the greater the volume of aquifer that groundwater is abstracted from, yielding more uniform hydrochemistry. An abstraction borehole would likely have an average signature of a large volume of aquifer, whereas an observation borehole would only be reflective of a small, local portion of the aquifer. There is, however, the risk that an observation borehole that is not purged prior to sampling may represent stale water, unless the water is sampled from an active flow horizon.

Greater variation was noted in hydrochemistry and isotope data for the Kilham catchment than for the Haisthorpe catchments (Chapter 5). Given their similar geology and location, this variation is largely explained by the types of site from which the samples were collected (of 20 pumped boreholes, eight observation boreholes and four springs). In the Hampshire Chalk catchment, Woodgarston, there were far fewer sites for comparison, but WPBH2, showed generally constant ion concentrations in contrast to the other three sites (Sections 6.2-6.6). All four boreholes sampled in Woodgarston were purged prior to sampling, however only WPBH2 is currently used for public abstraction (WMals and WPit are private abstractions, and WPBH1 is out of use due to high NO_3), and therefore has the highest volume of water abstracted. WPBH2 did, however, did still show variation in hydrochemistry, suggesting the groundwater still had some seasonality, even in this “highly-averaged” sample.

Grouping dual stable isotope data from the Kilham catchment by site type shows pumped sites form tighter cluster of isotopic ratios than sites that were unpumped (Figure 7.1). Spring sites had slightly higher $\delta^{18}O$ than the majority of pumped borehole sites; possibly indicating springs have a greater influence from artificial fertilisers at the ground surface with the heavy-O signature. The springs at BEL and BRA have low $\delta^{15}N$ of 1.86 to 1.88‰, however the similar signals may be due to their close proximity (<1 km overland) rather than being a signal attributable to springs in general. Boxplots of NO_3-N:Cl values for pumped and unpumped wells overlapped (Figure 7.2) while spring sites had mostly lower ratios, implying that spring sites have a different character to either borehole type, represented by higher $\delta^{18}O$ than average and lower NO_3 than many boreholes. The overlap in ratios between pumped and unpumped, observation boreholes may be due to variation in pumping frequency and volume among the pumped sites, leading some infrequently used boreholes to bear more similarity to an observation borehole than an abstraction for public supply. $\delta^{15}N$ and $\delta^{18}O$ might be more appropriately plotted against the volume of water pumped from each borehole than by sample type as in Figure 7.1 and Figure 7.2, however this information was not readily available.

Any difference between pumped and unpumped, observation wells may be due to how the source of water changes in response to pumping. Samples from observation boreholes are more likely to represent shallow flow horizons associated with the fluctuating water table than deep groundwaters, e.g. Agbotui et al. (2020). A shallow flow horizon is likely to have better connectivity with the surface and therefore more strongly reflect recharge hydrochemistry than deeper horizons, whereas, pumped boreholes are more likely to be a mixture of shallow and deep flow horizons. Deep flow horizons are more likely to contain older water. Pumped boreholes, are therefore more likely to have an average signature, i.e.

cluster identified at all locations during dual stable isotope analysis (Figure 7.1). Deviation from this signature e.g. in some observation wells, may represent increased influence from shorter residence time recharge water. The O isotope signature in some observation wells became lighter, as the hydrogeological year continued (Section 5.3.1), which could be explained by increased mixing from longer residence time recharge waters.

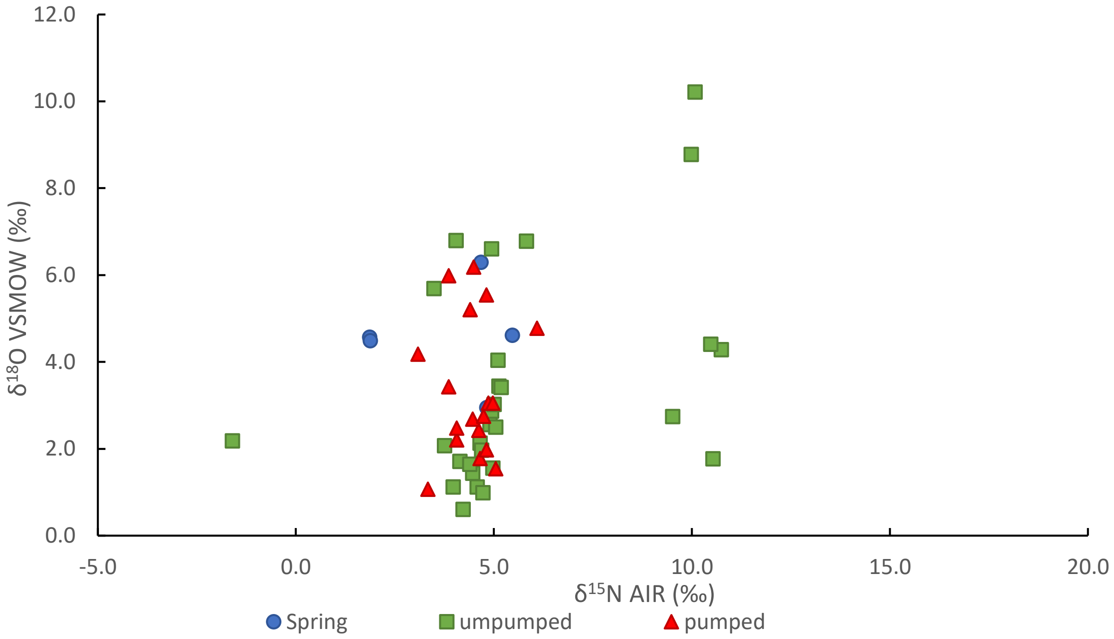

Figure 7.1: Dual stable isotope data for sites where the pumping status at time of sampling was confirmed, from Kilham catchment (the only catchment where there was more than one sample type).

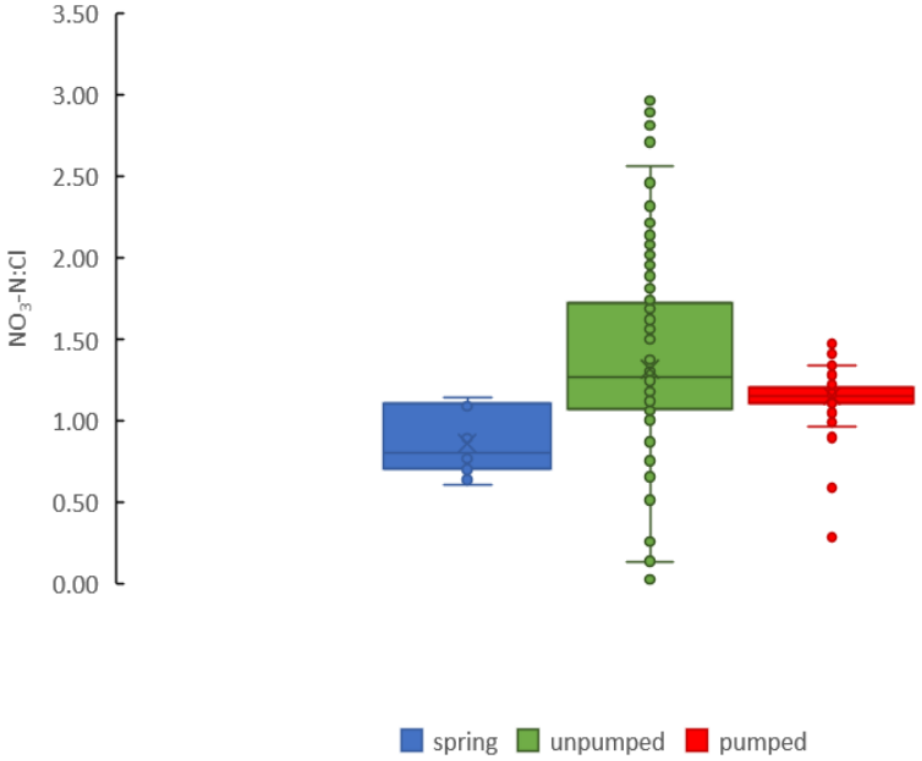

Figure 7.2: Box and whisker plot of NO_3-N:Cl for sites where the pumping status at time of sampling was confirmed, from the Kilham catchment where there was more than one sample type. The top and base of the box represent the upper and lower quartiles, respectively, while the inner line shows the median and the "x" the mean. Whiskers represent the range. Points are considered outliers if they are 1.5 times above or below quartiles.

7.1.1 Implications of different sample site types

Understanding that sampling from a pumped or unpumped borehole affects the data collected enables better experimental design. If identifying local conditions is useful, for example if determination of pollution sources is sought, then unpumped borehole samples may be most valuable. However, if the objective is to assess overall water quality of an aquifer, then a frequently pumped well may provide samples with the overall groundwater character, including deeper waters. Under some circumstances both local and general conditions will be beneficial, for example if a new abstraction borehole is to be drilled. The Haisthorpe public abstraction consistently has a lower NO_3 concentration than most other sample sites (both pumped and observation wells) to the north-west of the Wolds (Figure 5.11). At sample site, FWF, however, the groundwater changed dramatically over the first year after drilling: initially there were low NO_3 concentrations, then after six months NO_3 concentrations were similar to the rest of the catchment. At first the well may have pumped older waters with little NO_3 pollution, followed by modern waters with higher NO_3 concentrations as the borehole developed. Alternatively, the low NO_3 water may be a consequence of local land management, that was negated as the borehole developed.

7.2 Northern Province vs Southern Province Chalk

Both the Yorkshire Wolds catchments sampled and the Woodgarston catchment in Hampshire are situated on England's Chalk aquifers. Despite both being traditionally characterised as having three primary beds, the Upper, Middle and Lower Chalk, both have now been redescribed (Section 5.2.1, Section 6.1.1). Both study sites have dual porosity (Allen et al., 1997) but the Northern Chalk is considered to be more indurated and brittle than the Southern Chalk and therefore clean fractures are more likely to form, while the matrix is less permeable. This could mean that the Northern Chalk has more bypass fracture flow enabling faster transport of surface pollutants into the aquifer, thus making it more vulnerable. Hydrogeological parameters are, however, roughly comparable (Table 7.1). Both study sites contain marl and flint beds that could affect dissolution rates and flow paths and both show dissolution close to the water table resulting in high permeability horizons.

Superficial deposits may provide some protection against contamination in both the North and South, however only sample sites in the south-east of the Haisthorpe catchments are thought to benefit from this; the rest of the Northern Chalk aquifer is understood to be unconfined. Paleogene cover in Hampshire may also be associated with increased dissolution of the Chalk beneath it (MacDonald et al., 1998). Within the studied regions there are several NVZs in the Kilham and Haisthorpe catchments to protect water quality, and the Woodgarston pumping station (WPBH1 and 2) is within a SPZ; WPit and WMals are just outside SPZ3 (zone within which all groundwater is thought to discharge at the abstraction site).

Table 7.1: Hydrogeological parameters described in published research for the Yorkshire Wolds and Hampshire Chalk aquifers. Transmissivity of both Provinces covers confined and unconfined regions of the aquifers; the confined values are the lower end of the range.

	Woodgarston (Hampshire)	**Yorkshire Wolds**
Matrix hydraulic conductivity	10^{-4} to 10^{-3} m/day (Elliot et al., 1999)	10^{-4} m/day (Price, 1987)
Fracture hydraulic conductivity	0.1 to 1 m/day (Price, 1987)	0.01 to 10 m/day (Gale and Rutter, 2006)
Bulk hydraulic conductivity	<200 m/day (Younger, 1989)	<200 m/day (Foster, 1974)
Transmissivity	0.55 to 29,000 m^2/day (Allen et al., 1997)	1250 m^2 d^{-1}; range 1-10000 m^2 d^{-1} (Gale and Rutter, 2006)
Porosity	Averages for “Upper”, “Middle” and “Lower” Chalks were 39, 28 and 23% respectively (Bloomfield et al., 1995)	20.6 to 35.4% (Gale and Rutter, 2006)

Both the Southern and the Northern Chalk Province catchments are primarily agricultural. Following the Second World War, the agricultural revolution brought about an increase in ploughing, which will have caused a release of N. The regions will also have been affected simultaneously by the introduction of artificially derived N fertilisers following development of the Haber-Bosch process. In addition to inorganic fertilisers, manure and slurry application or leaching are likely occurring. There are several intensive pig and poultry farms in the Yorkshire Wolds, while a dairy farm is within 500 m of the Woodgarston abstraction.

7.2.1 Comparison of hydrochemistry in the Northern and Southern Province Chalk catchments studied

Similar pH was recorded in both Woodgarston and the Yorkshire Wolds, with both being dominated by HCO_3 and Ca, as would be expected of Chalk groundwater. The Environment Agency recorded pH between 7.03 and 7.43 for WPit (May 2014-Nov 2019) and Elliot et al. (1999) reported pH 7.0 at Woodgarston. In the Yorkshire Wolds catchments pH was generally around 7.5, however it ranged from 6.07 to 8.18. Gooddy et al. (2002) stated that where carbonate dissolution is a dominant reaction in groundwater pH should be between 7.5 and 8.5 for porewaters, as carbonate dissolution neutralises acidity introduced from the soil and rainfall. A lot of samples from both the North and South were lower than this, however this may due to the much shorter residence time of sample water compared to porewater. Alternatively, additional sources of acidity could be continual degradation of dissolved organic matter, or anthropogenic e.g. protons are produced when NH_4 fertilisers are nitrified to NO_3 (Böhlke, 2002).

Specific electrical conductivity (SEC) was generally typical of Chalk groundwater in both regions, with SEC between 500 and 700 µS/cm for Kilham, 550 to 750 µS/cm in Haisthorpe. Data for the Woodgarston catchment were only available for WPit, where SEC was usually between 650 and 800 µS/cm. The highest recorded peak in SEC was at SHW in the Kilham catchment at 2144 µS/cm (concurrent with raised Cl, Na and SO_4), and ion concentrations were more variable in Kilham than Haisthorpe or WPit.

Fewer ion concentration data were available for Woodgarston, however from Cl and SO_4 the abstraction sites (WPBH1 and WPBH2) look stable, with more variation at WPit and WMals. Elliot et al. (1999) recorded a Cl concentration of 19.1 mg/L at Woodgarston and data for the SEW sample site largely concur with this for WPBH2 and WMals. At WPit Cl concentrations were variable and much greater: 20.2 to 44.2 mg/L. WPBH1 was also more variable than WPBH2 with concentrations generally between 20 and 30 mg/L Cl, except for June 2018 and February 2020 when concentrations peaked at 45.9 and 37.9 mg/L respectively (Section 6.4.2). Elliot et al. (1999) reported the ratio of Br:Cl was around $1.5\text{x}10^{-3}$, reportedly close to the value expected for seawater, therefore increased Cl with depth is expected to be marine in origin (i.e. connate water). In the Yorkshire Wolds, the highest Cl concentration was at SHW (449 mg/L). SHW was always high in comparison to other sites, with 73 mg/L Cl minimum. There was however an increase in Na, SO_4 and K concurrently, suggesting the source was agricultural pollution (e.g. sodium sulphate and potassium chloride fertiliser application, as discussed in Section 5.4.3). Cl was also highly variable at DOF, and given the strong response of most other ions recorded at DOF, it is likely high ion concentrations are here associated with anthropogenic pollution (Figure 5.16). Generally, Cl and sometimes Na was higher in Haisthorpe than Kilham catchment, and as Haisthorpe catchment is nearer to the coast, implying that sea spray could be a source of Cl.

SO_4 was variable at WPit, with concentrations reported of 19.6 to 27.5 mg/L and trends largely mimicked those of NO_3, suggesting pulses of pollution may be the cause. The data suggest these pulses occurred in summer months (May to August), so could result from effluent discharge or soak-aways that are able to bypass the soil zone. This could suggest a fast flow mechanism influences this site and that pollutants have an easy path to the aquifer. Variation in SO_4 was also recorded at WMals too (13.9 to 29.8 mg/L). Both WPit and WMals still had low SO_4 concentrations compared to the Yorkshire Wolds, where figures centred around 25-35 mg/L. Higher SO_4 concentrations in the Yorkshire catchments possibly stemmed from nearby coal power stations (now closed) or local agricultural practices.

7.2.2 Nitrate concentrations in the Chalk catchments studied

The majority of samples in the Yorkshire Wolds catchments exceeded the Prescribed Concentration or Volume (PCV) of 11.3 mg/L NO_3-N, whereas only a quarter of all samples were greater than 11.3 mg/L NO_3-N in Woodgarston. The Paleogene cover may provide protection there, alternatively agriculture may be less intensive or more appropriately managed for N leaching. WPBH1 has not been pumped for abstraction since 2010 due to its high NO_3 concentrations. This suggests that WPBH1 and WPBH2 may be supplied from different horizons (WPBH2 is 10 m deeper than WPBH1), as NO_3 concentrations at WPBH2 are still within the PCV.

The range in NO_3 concentrations is greater in the Yorkshire Wolds catchments than in Woodgarston. The maximum recorded in the Wolds was 46.0 mg/L NO_3-N at DOF, while in Woodgarston the maximum, 16.5 mg/L NO_3-N, was at WPBH1. This implies that the Wolds catchments are more prone to point source pollution events. However, a greater number of sample sites were monitored in the Wolds than Woodgarston, which may have resulted in pollution events being more frequently captured. DOF borehole is near an intensive pig farm and appeared to suffer several pollution events (high NO_3, in addition to other major ions) over the period of study (e.g. Feb 2008, Feb 2013, Feb 2016 and Feb 2018) so potentially more manure and slurry was being fed into the environment than the soil biomass and crops can utilise without major N leaching events, particularly given that in winter soil biomass is far less active. In both regions some sites had concentrations that stayed fairly constant all year round, however some showed seasonal variation. Those with the least variation tended to those used for public abstraction, as discussed in Section 7.1. In the Wolds catchments NO_3 concentrations tended to be highest at the beginning of recharge season, however in the Woodgarston catchment NO_3 concentrations peaked towards the end of recharge (Section 5.2.1 and 6.2.1). This variation could be due to differences in geology, as the Northern Province Chalk tends to be more highly fractured than its Southern counterpart fast bypass flow may be more likely to occur. In the Wolds, NO_3 may be transported from the vadose zone into the saturated zone at the initiation of effective rainfall thus peak concentrations are observed at the beginning of recharge (as described in Section 7.2.2.1). In the Woodgarston catchment the above process may be slower, or recharge may dilute groundwater NO_3 and thus peak concentrations are observed when effective rainfall ceases. Alternatively, seasonal variations could be due to differences in land management.

7.2.2.1 The relationship between groundwater levels and nitrate concentration

NO_3 stored within the unsaturated zone enters groundwater may enter groundwater via two possible methods. Either via rainwater accumulating NO_3 as it percolates towards the saturated zone, or by groundwater levels becoming high enough to reach the unsaturated zone where NO_3 is stored. In the Yorkshire Wolds the former is most likely as NO_3 tends to be stored in the uppermost 10 m below ground level, above water table fluctuations and the unsaturated zone is frequently deep (Allshorn, 2008).

NO_3 concentrations were plotted against Environment Agency rainfall data and groundwater levels (Figures 7.3 to 7.9). Rainfall monitoring and monitored boreholes were not necessarily in identical locations, however it was assumed that most rainfall, crucially effective rainfall, would be similar locally. Heavy rainfall did not appear to correlate closely with NO_3 concentrations, as might be anticipated if the rainfall accumulates NO_3 as it percolates through the unsaturated zone (Figure 7.3 and Figure 7.4). Groundwater levels did appear to correlate with nitrate concentrations (Figure 7.5 to 7.9). This is likely due to stored NO_3 only being released once rainfall is effective and recharge begins (Zaidman et al., 1999), as increased groundwater levels is another result of recharge.

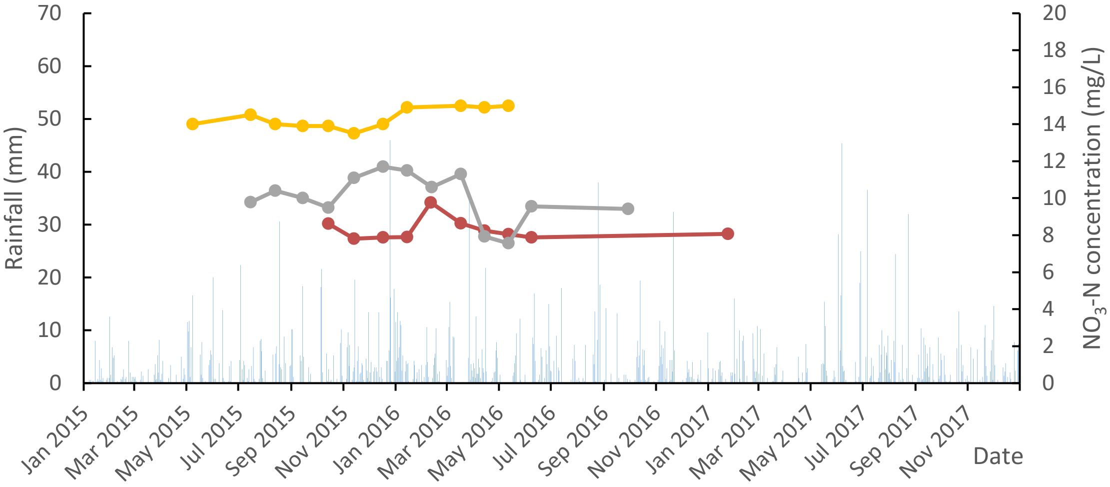

Figure 7.3: Rainfall for High Mowthorpe (blue) and NO_3-N concentrations for three neighbouring sites, MHF (yellow), ROO (grey) and WIN (red). Graph reproduced from McSherry (2019).

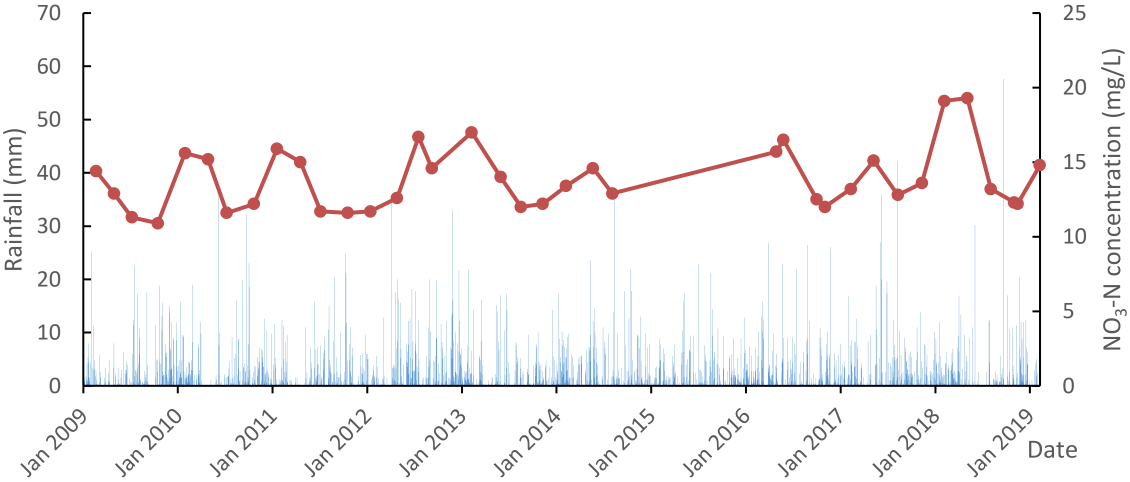

Figure 7.4: Rainfall at Driffield (blue) and NO_3-N concentrations at nearby borehole PTH (orange). Graph reproduced from McSherry (2019).

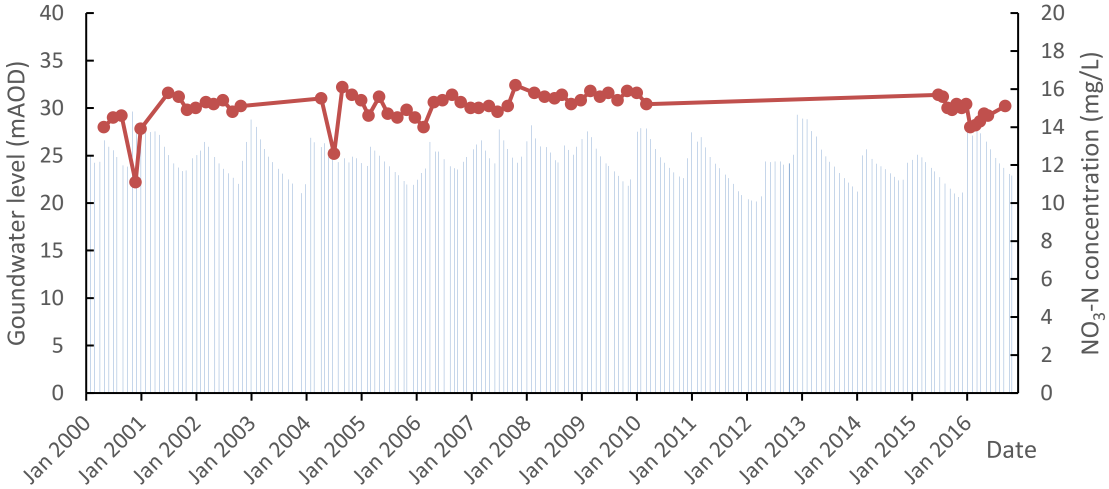

Figure 7.5: Borehole levels for Kilham pumping station and nitrate concentrations for KOB. Blue = groundwater level, orange = nitrate-N concentrations. Graph reproduced from McSherry (2019).

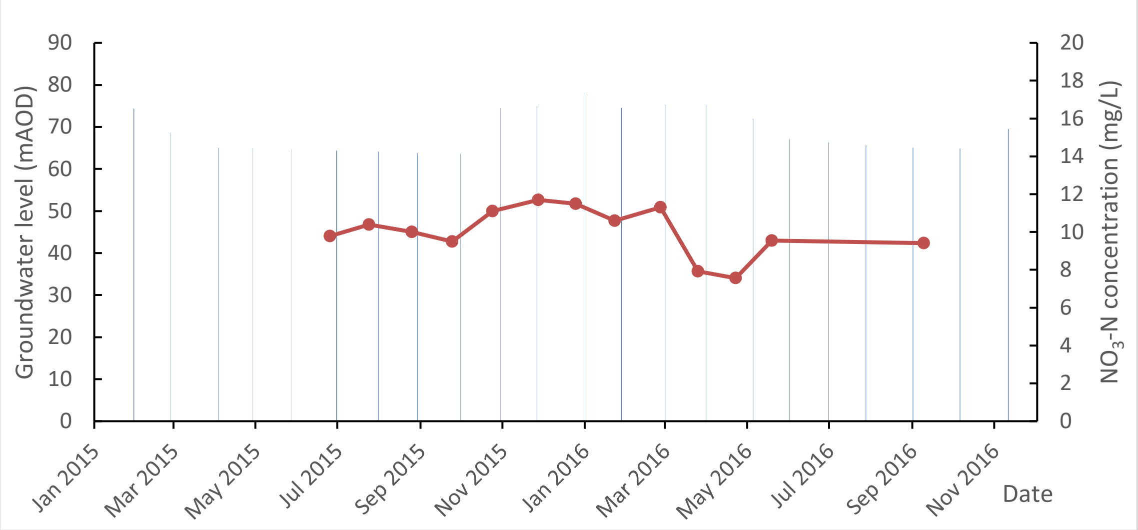

Figure 7.6: Groundwater levels and nitrate-N concentrations at ROO. Blue = groundwater level, red = nitrate-N concentrations. Graph reproduced from McSherry (2019).

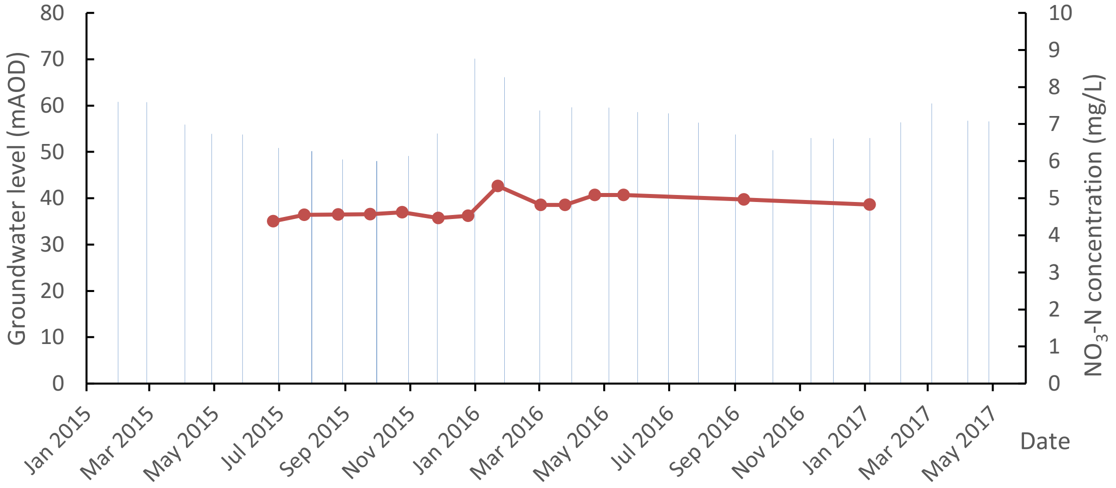

Figure 7.7: Groundwater levels and nitrate-N concentrations at SHW borehole. Blue = groundwater level, red = nitrate-N concentrations. Graph reproduced from McSherry (2019).

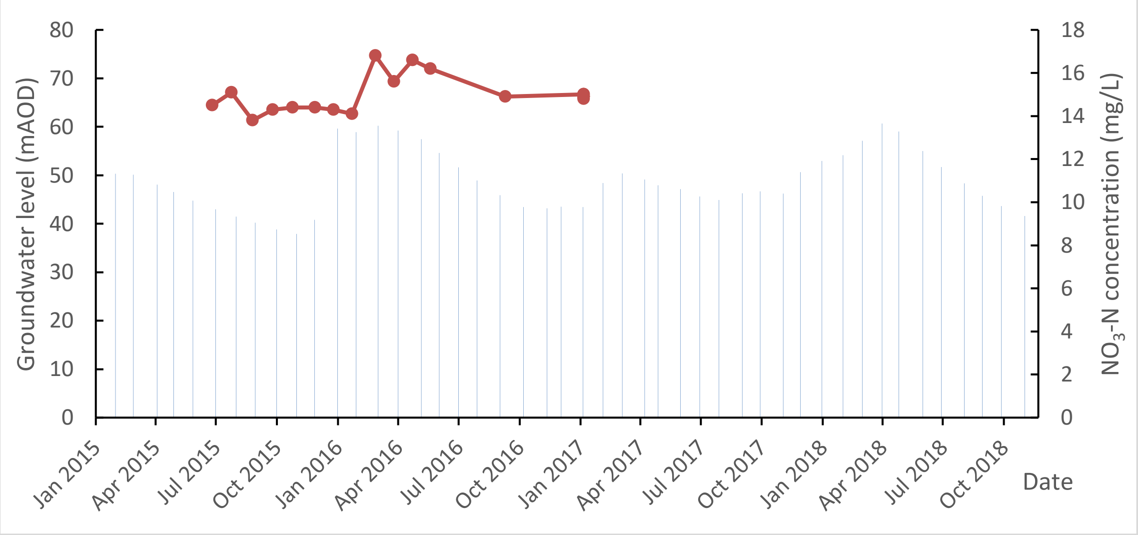

Figure 7.8: Groundwater levels and nitrate-N concentrations at WEA borehole. Blue = groundwater level, red = nitrate-N concentrations. Graph reproduced from McSherry (2019).

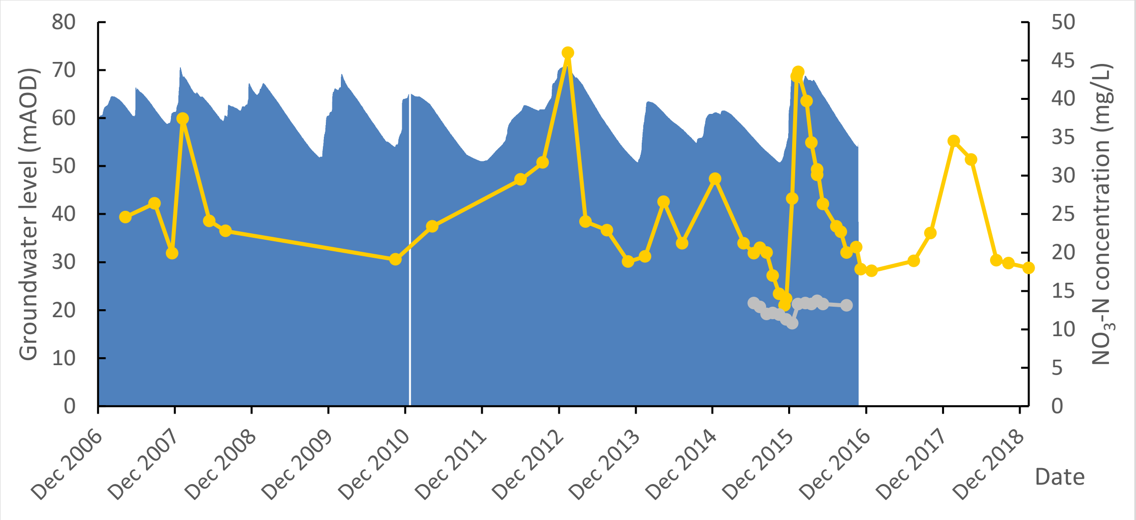

Figure 7.9: Groundwater levels at WES, and nitrate-N concentrations at WES borehole (grey) and neighbouring borehole sample site, DOF (yellow). Blue = groundwater level. Graph reproduced from McSherry (2019).

7.2.3 Dual stable isotope analysis of groundwater in the Chalk catchments

The majority of samples from all sites produced dual isotope signatures that fell within the soil N box on the fingerprinting diagram (Figure 5.23, Figure 6.10). This cluster had $\delta^{15}N$ of +4 to +6‰ and $\delta^{18}O$ of 0 to +4‰) and suggests the majority of Chalk sites were subject to similar processes. However, it must be noted at the soil N signature may also result from a mixture between several sources including manure and NH_4 fertiliser. Clear manure signatures were only recorded in the Kilham catchment, one at KOB and the remaining five from DOF, despite manure being likely at several locations throughout the Yorkshire Wolds and a manure source only several hundred metres from the Woodgarston abstraction. This would suggest that a manure signature only dominates under certain conditions, for instance where excessive volumes of manure or slurry are applied or the manure is especially bioavailable, resulting in more nitrification than crops or soil biomass can utilise before it leaches into the unsaturated zone.

Under normal conditions denitrification was not considered a dominant reaction in these Chalk catchments, given they are typically oxic and low oxygen conditions are required for denitrification (Section 2.3.4). DOF and the Woodgarston pumping stations were the most likely candidates for denitrification as the process has been reported beneath slurry lagoons on Chalk (Gooddy et al., 2002) and manure pollution events occur at the former, and a dairy farm near the latter has an open slurry pit. The fingerprinting diagrams, however, present no evidence of significant denitrification at any Chalk groundwater site. Although some denitrification likely occurs in the soil, the process typically results in a 2.1‰ change in nitrogen per 1‰ change in oxygen and no sites sampled on the Chalk followed this trend (Figure 5.23, Figure 5.26, Figure 5.27, Figure 6.8 and Figure 6.10).

Given all catchments were dominated by agriculture, and agricultural activities are the most likely NO_3 sources and the absence of the heavy-O signature associated with NO_3 fertilisers is conspicuous. A process is therefore occurring that is making the oxygen signature lighter. Possibilities considered are as follows:

- Mixing with water that has NO_3 with a light oxygen signature. This is unlikely to be a dominant process for the commonly identified seasonal trend (with the highest $\delta^{18}O$ seen during recharge, slight increase in $\delta^{15}N$ e.g. SHW; Figure 5.26) as it doesn't have a feasible end member (high $\delta^{15}N$ and high $\delta^{18}O$). Some other trends observed in Chapter 5 could, however, be described by mixing.
- Transformation processes via metabolism by crops and soil biomass and their subsequent decomposition after the growing season. As demonstrated in Figure 7.10 a crop or microbe may absorb NO_3 fertiliser, with its associated heavy O signature, and metabolise it to form amino acids. At the end of the growing season crops will be harvested and the discard left in the field to decompose. While N may remain in the soil for many years, during this process a proportion of N may become renitrified, likely using two O atoms from water ($O\text{-}H_2O$) and one from the atmosphere (O_{atm}). This causes the resulting NO_3 to have lighter $\delta^{18}O$ than the pool it originated from, with 66% $O\text{-}H_2O$ and 33% O_{atm}. Broadly this is what is seen in the Kilham, Haisthorpe and Woodgarston catchments (Figure 5.23 and Figure 6.10), assuming $\delta^{18}O\text{-}H_2O$ is -7.5‰ (Darling et al., 2003).

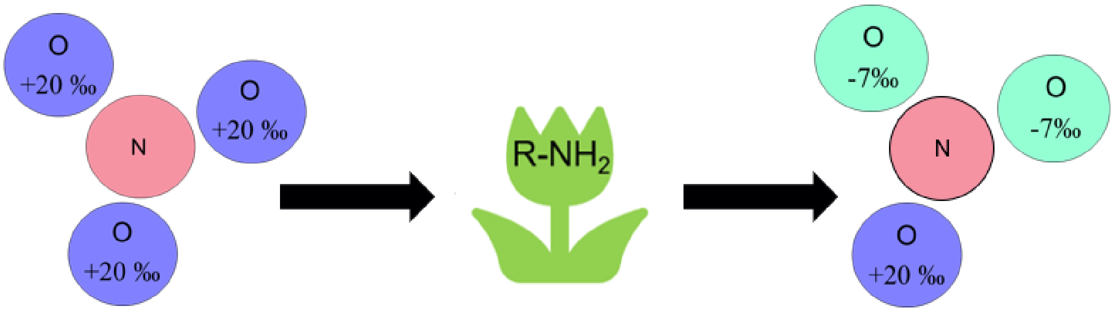

Figure 7.10: Possible transformation process, whereby Haber-Bosch (HB) NO_3 is metabolised by plants and soil biomass, then re-nitrified resulting in a loss of the HB $\delta^{18}O$ signature. This process tends to occur in autumn, but not all NO_3 is subjected to this annually. Fertiliser N may reside in the soil zone for many years e.g. Sebilo et al. (2013) found 12-15% of labelled fertiliser N in the soil 30 years after application.

- Microbe-mediated equilibrium processes in the aquifer: one oxygen atom is swapped out of the NO_3 molecule at a time, and an oxygen from water replaces it (Figure 7.11), in order to obtain equilibrium in the solution. This process would be most likely occurring in the aquifer rather than the soil because it is a slow reaction and would rely on the long residence time of water in the aquifer. [The River Terrace Gravels were sampled in order to test the hypothesis that the majority of the changes in dual stable isotope signatures occurs in the soil zone as opposed to the saturated zone: if Haber Bosch (HB) NO_3, with associated heavy-O isotope signature, was seen in the short residence time aquifer then the process was likely reliant on the long residence time in the Chalk aquifer itself.]

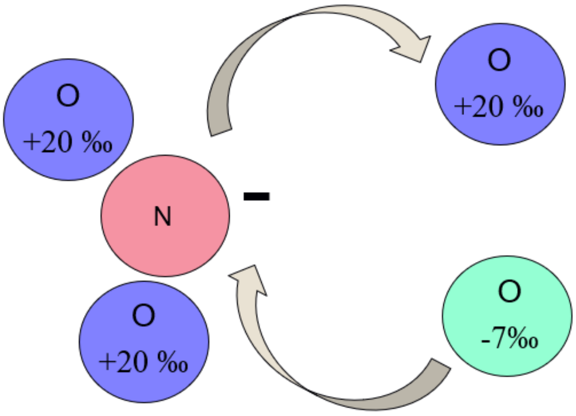

Figure 7.11: Equilibrium exchange process resulting in lighter $\delta^{18}O$.

7.2.4 Nitrate to chloride ratios in the Chalk catchments

The ratios of NO_3 to Cl for all sites and dates sampled is presented in Figure 7.12 and show that the Kilham catchment was subject to the most variation in terms of NO_3-N:Cl. Ratios for Woodgarston fall within the variation of the Kilham and Haisthorpe data. Woodgarston and Haisthorpe data are particularly similar, possibly as all samples were from pumped boreholes, whereas the unpumped boreholes in Kilham are a cause of variation (Section 5.5). Within the data there appear to be two trends: constant NO_3 and increasing Cl (demonstrated by the dotted trendline in Figure 7.12), and increasing NO_3 with constant Cl that would have a vertical trend. Woodgarston, Haisthorpe and a portion of the Kilham data most closely fit with constant NO_3 and increasing Cl. This trend could represent a mixing between fertiliser NO_3 (low Cl, high NO_3) and manure (high Cl, low NO_3). Several sites in the Kilham catchment have a near-vertical trend of increasing NO_3 with slightly increasing Cl. These sites included DOF, which previous evidence has suggested is a manure source but with very high NO_3 concentrations. Therefore, this near-vertical trend in ratios may be an indication of large, or highly bioavailable, manure applications, contributing Cl, where rapid nitrification is occurring leading to a substantial NO_3 input. Poultry and liquid organic manures tend to have highly readily available N and therefore may produce NO_3 particularly rapidly (see Section 2.3.5). Site type may also influence NO_3-N:Cl, resulting in deviation from the mixing trend by unpumped or infrequently pumped boreholes.

Ratios at Woodgarston were very tightly grouped (Figure 7.12). Variation was mostly observed in NO_3 concentrations, suggesting that NO_3 was primarily inorganic in origin. However, data did not approach either end member (and therefore sources themselves could be relatively mixed at Woodgarston). Given the proximity of an established dairy farm to Woodgarston Pumping Station, a mixed signature source is possible. However, low NO_3 and low Cl concentrations observed on some occasions could also suggest influence from natural soil N.

NO_3-N:Cl evidence suggests that largely similar processes are at play between the Yorkshire Wolds and the Woodgarston Chalks. The relatively large variation seen within the Kilham catchment could be primarily a result of unpumped wells presenting a more localised sampling. The variation could also be a relic of high sample site numbers: a pollution event is more likely to be captured with more sampling locations and occasions. Alternatively, with the increased brittleness of the Northern Chalk, the Kilham catchment may be more heavily fractured than the Woodgarston catchment, thus NO_3 is less likely to attenuate before it enters the aquifer, leading to the high-NO_3 trend noted in Figure 7.12.

Over the course of a hydrogeological year, no clear trend in NO_3-N:Cl ratios was observed between the three Chalk catchments, however some samples from March to July had higher Cl concentrations compared to the rest of the year. These higher concentrations could be due to higher evapotranspiration, or the introduction of a Cl source in early Spring**.** Alternatively they could be indicative of a switch in the mixing proportions of NO_3 sources from dominated by fertilisers to dominated by manure.

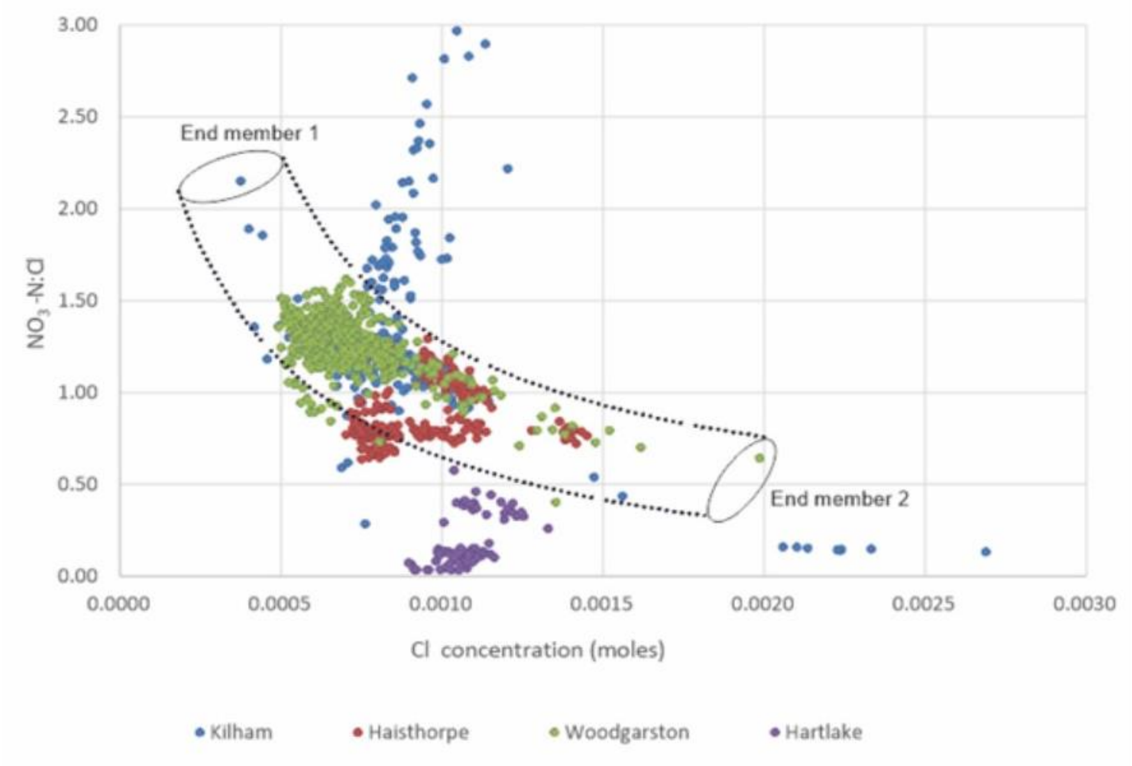

Figure 7.12: NO_3-N:Cl for the Kilham, Haisthorpe, Woodgarston and Hartlake catchments. The two ellipses approximate two hypothesised end members: inorganic fertiliser (1) and manure (2) between which black dotted trendlines ($y = Ax^{-1} + B$) demarcate a theoretical trend of constant NO_3 with increasing Cl concentration that implies source mixing. The x-axis is truncated compared to Figure 5.11, to ease interpretation: many of the SHW data points are likely from a NO_3-free Cl source, and therefore pertain to Cl concentrations greater than the NO_3-containing end member.

As observed for dual stable isotope analysis, the seasonal trends for NO_3-N:Cl were highly variable for Kilham, with smaller variation observed for Haisthorpe or Woodgarston. These seasonal changes could be evidence for bypass flow, seasonally active flow horizons or chemical changes to soil conditions due to anthropogenic additions. Where NO_3 concentrations remained constant while Cl increased, there could be a seasonal exchange in NO_3 sources, dependent on land management regimes. At some sites there were decreases in Cl concentrations during recharge season, which may suggest dilution. Where Cl concentrations were generally low, inorganic fertiliser could be the primary source of NO_3 (e.g. at the ROO site). At other sample sites high NO_3 correlated with increasing Cl (highest ratios March to June) may be indicative of a high volume application of manure or slurry in early Spring (e.g. at the DOF site), with recharge aiding it to quickly enter groundwater.

7.2.4.1 Seasonality in Chalk

Seasonality hydrochemistry and nitrate isotopic signatures in the Chalk groundwaters may result from physical or chemical processes, or both. Dual porosity is a known characteristic of Chalk and so the variation in hydrochemistry within and between catchments could be the result of fast flow bypassing matrix via fractures, enabling “new” water to move quickly between the field and the sampled borehole, bringing NO_3 different to the groundwater pool with it. Alternatively, NO_3 with a different character to that of the groundwater may be collected by rising groundwater during recharge season, having been stored in the unsaturated zone during summer months. Comparison with behaviour of groundwater in a catchment on the River Terrace Gravels was undertaken in order to identify where the majority of NO_3 transformation occurs.

7.3 Comparison of RTG and Chalk catchments

A RTG catchment in the Hartlake catchment on the River Medway in Kent was analysed for dual stable isotopes of N and O in NO_3. It provided a useful comparison with the Northern and Southern Province Chalk catchments due to the very short residence time of groundwater in the aquifer. The RTG is highly heterogeneous; as it contains, and is overlain by, clays and silts, making conditions within it more variable than the Chalk and possibly less oxic, providing greater potential for denitrification.

Compared to the Chalk, the RTG is more porous and permeable, with hydraulic conductivity in the RTG of 1×10^{-4} to 1×10^{-1} m/sec, and in the Chalk of approx. 10^{-4} m/day. There is a greater range in transmissivity across the Chalk (see Table

7.1) than the RTG, highlighting the remarkable difference in hydraulic conductivity between fractures and matrix in Chalk. The RTG, however, is more predictably transmissive: 482 to 994 m^2/day (Howe et al., 2017). Confined aquifer storativity reported on the RTG appears lower than that reported for the Chalk (for instance, 2.0×10^{-6} to 4.55×10^{-6} versus 0.3 to 3.5×10^{-4}, in Wilfholme, Yorkshire respectively; Howe et al. 2017, Hartmann et al. 2007). The RTG is different to the Chalk in that it is relatively thin and shallow, and non-marine deposited, likely having effects on the hydrochemistry in that it is unlikely to retain any marine signature. At Hartlake, the RTG is between 2.5 and 4.8 m thick, and span around 7 km of flood plain (Howe et al., 2017). As a result of its comparatively small volume it is considered an aquifer of local importance, rather than national, strategic importance, like the Chalk.

7.3.1 Comparison of hydrochemistry in the RTG and Chalk catchments

Minimal hydrochemical data are available for the Hartlake catchment, however they were available for a site 3 km from the Hartlake catchment, HARSPF, monitored by the Environment Agency. Groundwater at this farm had higher SO_4 (mean 94.3 mg/L), generally lower HCO_3 (mean 180 mg/L), and lower, more stable Ca (range 96-108 mg/L, between 2007 to 2019) than the Chalk catchments studied. SO_4 concentrations were broadly similar at HARA1, however HARC was much lower, and more comparable to the Chalk (24.6 to 46.0 mg/L, South East Water data). The pH was lower than for the Chalk (6.62-7.02) suggesting $CaHCO_3$ dissolution is a less dominant reaction than for the Chalk. Nonetheless, groundwater at Hartlake appears to be $CaHCO_3$ type (Figure 6.13), so likely has a similar buffering capability to the Chalk.

7.3.2 Comparison of nitrate to chloride ratios in the RTG and Chalk catchments

While there are N and Cl sources that defy the principles the NO_3-N:Cl tool is based upon, interpretation of NO_3-N:Cl assisted in identifying dominant N sources in the study catchments. The NO_3-N:Cl ratios at Hartlake do not appear to follow the same trend as the majority of the pumped Chalk sample sites. The Hartlake trend shows moderately high and constant Cl with relatively low but variable NO_3 (Figure 7.12), most similar to FWF site in Kilham or HAC site in Haisthorpe.

Hartlake, however, has lower NO_3 concentrations than recorded at most other sites, which could enable natural soil N to be the dominant N source. Alternatively, low Cl additions could be indicative of artificial fertiliser being the primary NO_3 source in the catchment, as may be the case at the FWF site in the Kilham catchment. However, at FWF the ratio became greater with time after drilling, suggesting the trend is due to the borehole being newly dug at the beginning of the study and containing groundwater dominated by low concentrations of NO_3 possibly from natural soil N sources, to becoming more highly developed and dominated by higher NO_3 concentrations, possibly fertiliser N. This similarity between FWF and the Hartlake sites could suggest that like FWF, Hartlake is either old groundwater uncontaminated by agricultural inputs or that the locality is subject to less intensive land management. In the RTG aquifer at Hartlake, groundwater is unlikely old (discussed in Section 6.7.2), so less intensive land management seems more likely.

Across the four sampling locations at Hartlake the majority of sites had NO_3-N:Cl indicative of fertiliser NO_3, mixing with manure NO_3. Several sites from the Kilham and Hartlake catchments had consistently high Cl and also high NO_3 (inferred from Figure 7.12). NO_3 at these sites could result from a more highly bioavailable manure than the low NO_3, high Cl sources. Alternatively, the high NO_3, high Cl trend could be the result of fertiliser NO_3 applications concurrent with high Cl concentrations from other sources.

In this study, NO_3-N:Cl has proved useful to begin identifying differences between study sites and catchments. Although in isolation the ratios are not sufficient for assigning N sources, they support findings of the dual stable isotope analysis.

7.3.3 Nitrate concentrations in the RTG versus the Chalk catchments

For the three Chalk catchments NO_3 concentrations were usually between 7 and 15 mg/L NO_3-N, whereas the RTG catchment concentrations were mostly less than 5 mg/L NO_3-N (Figure 7.13). All catchments are largely agricultural, so N inputs and land management strategies are expected to be broadly similar, although Hartlake may be subject to lower N applications due to the Safeguard Zone surrounding, and upgradient of, the public abstraction site. Hartlake may, however, receive proportionally more urban N inputs than the Chalk catchments.

The RTG may not possess the “nitrate timebomb” arising from long-term unsaturated zone storage of nitrate that is reported to occur on the Chalk (Wang et al., 2013) and thus the low NO_3 concentrations could be a reflection of the effects of modern land management. Differences in geology may also explain the lower NO_3 concentrations in the RTG groundwater compared to the Chalk: the clay and silt atop the RTG aquifer may provide some protection against surface pollutants. Clay and silt may also provide a (sub-)soil zone with low oxygen conditions suitable for natural NO_3 attenuation processes such as denitrification.

Alternatively, the RTG may be subject to less N inputs from manure due to fewer livestock: pasture is reported in the Hartlake NEP (Howe et al., 2017). However there is no indication of livestock numbers comparable to intensive farms, such as those seen on the Yorkshire Wolds. With fewer livestock, manure application out of necessity (to dispose of waste) may also be less frequent on the RTG catchment than on the Yorkshire Wolds, creating a smaller NO_3 pool in the soil. Occasional or small manure applications may mean that any N that is nitrified can be utilised by plants thus is not leached, whereas plants cannot metabolise the volume of NO_3 produced following a major, or succession of, manure applications. Manure from silos on intensive farm, such as those on the Yorkshire Wolds may be applied where it is least expensive to do so i.e. closest to farm buildings, whereas on pastures animal movement may result in manure being more widely distributed.

If inorganic fertilisers are more commonly used on the RTG than the Chalk then lower NO_3 concentrations on the RTG than the Chalk catchments could be due to inorganic fertiliser breaking down in a more predictable manner than manure. This could allow applications to be precisely timed for maximum crop benefit and as a result less NO_3 could leach into the groundwater. Other differences in land management techniques could also effect change in underlying groundwater NO_3 concentrations.

Woodgarston, Haisthorpe and Hartlake show similar magnitudes of variation in NO_3 concentrations, whereas Kilham shows around three times more variation (Figure 7.13). Some variation at Kilham can be assigned to the sample type: some boreholes were observational, whereas all in other catchments were pumped boreholes. Kilham also had the highest NO_3 concentrations, suggestive of higher incidence of N pollution; such events could cause greater deviation from baseline concentrations. The Kilham catchment is not reported to be especially karstic, as compared to parts of the Chalk in the South East of England or even areas of Hampshire, therefore it is unlikely that the greater variation could result from notably fast flowing fracture pathways.

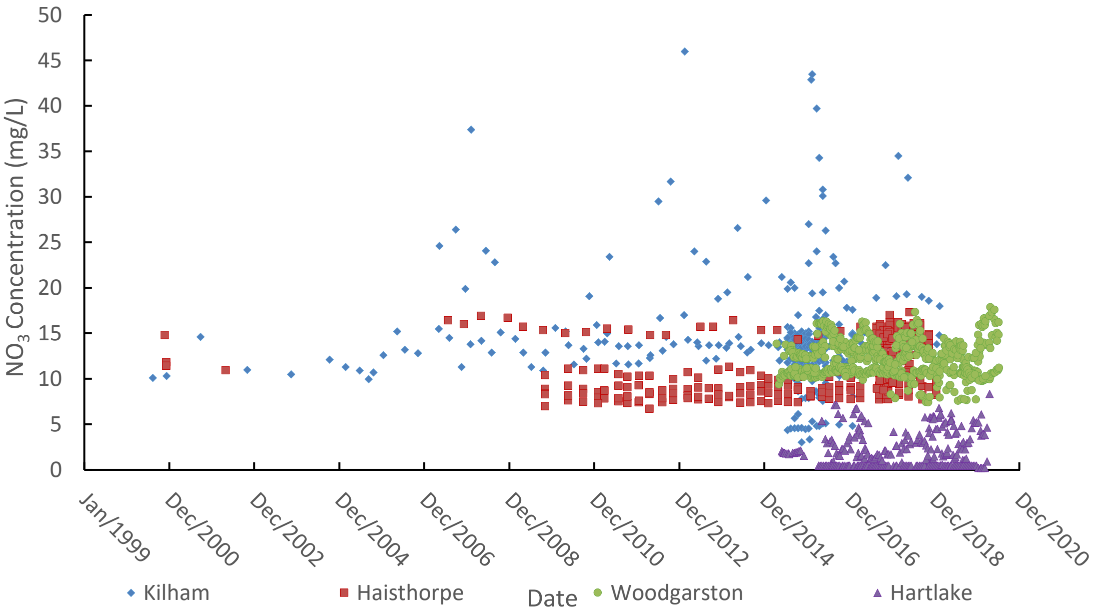

Figure 7.13: NO_3 concentrations for all four sampled catchments: Kilham, Haisthorpe, Woodgarston and Hartlake.

7.3.4 Dual stable isotopes in the Hartlake catchment on the Medway RTG as compared to the Chalk catchments

Hartlake catchment groundwater, from the RTG, had different isotopic signatures to most of the Chalk groundwater samples (Figure 7.14). No Hartlake sample fell within the cluster (ranges of $\delta^{15}N$ +4 to +6‰ and $\delta^{18}O$ 0 to +4‰) containing the bulk of the Chalk samples, discussed in Section 6.10. There were only a few samples taken on the RTG compared to the Chalk, so definitive conclusions cannot be drawn, however differences between isotope ratios suggest that different NO_3 sources or processes dominate the N cycle in Hartlake compared to the majority of Chalk sites.

Unlike the Chalk catchments sampled, there is no evidence to suggest HB NO_3 fertiliser dominates signatures in the RTG groundwater samples. Because the RTG aquifer has a shorter residence time than the Chalk, and therefore less time for NO_3 transformation to occur in the aquifer, this therefore implies that transformation of NO_3 fertiliser primarily occurs in the soil prior to entering the unsaturated or saturated zones, as reported across the literature e.g. Macdonald et al. (1989).

Macdonald et al. (1989) used ^{15}N labelled fertiliser to show that only 17% fertiliser was left unused in the top 0-23 cm of soil at the end of the growing season. Powlson et al. (1986), on the same long-term experiment at Broadbalk, Rothamsted, stated that only an additional 5% of labelled fertiliser was recovered in the 23-70 cm soil layer, while 51 to 66% was captured in the crop. This implies an estimated N fertiliser loss of 10%; this could be volatilised to NH_3 or leached below the root zone, suggesting minimal HB N fertiliser would leach into the unsaturated zone. Given minimal ^{15}N fertiliser was found in inorganic forms at harvest, this suggests that the labelled fertiliser N was mostly locked up as organic matter. Organic N is unlikely to mineralise until the following Spring, when soil biomass is active, and therefore the pool of N that leaches into the unsaturated zone may have cycled through the soil N cycle several times over multiple years before it leaches into the unsaturated zone. This conclusion would explain the ubiquity of the absence of HB NO_3 in the groundwater samples.

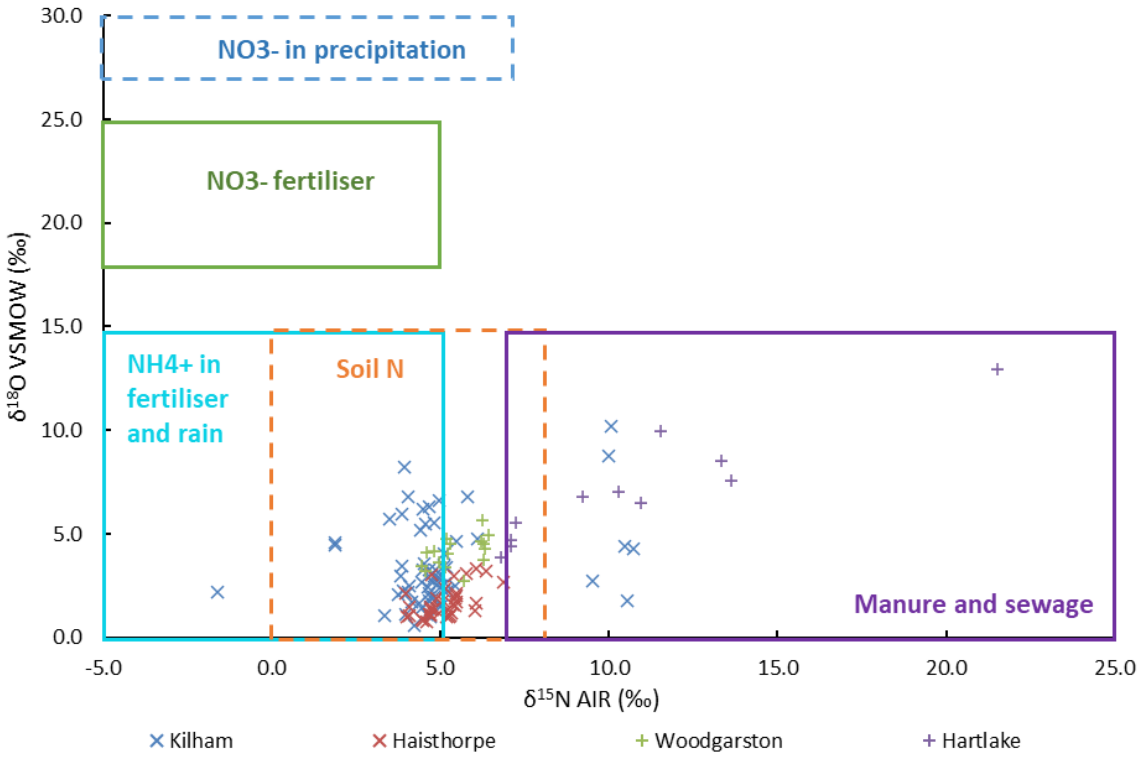

Figure 7.14: Fingerprinting diagram for all four sample catchments. Based on Kendall (1998), Xue et al. (2009) and Nestler et al. (2011) with a theoretical trend for denitrification, assuming a trend of 2.1:1 N:O and a possible source from the soil N-type cluster (Mariotti et al., 1981).

7.3.4.1 Manure signatures

The Chalk samples produced isotope signatures largely falling within the soil N box (Figure 7.14), however only four of the eleven RTG samples also did. The majority of the RTG samples fall in the “manure and sewage” box and appear most similar to DOF in Kilham, however NO_3 concentrations and NO_3-N:Cl ratios are disparate, suggesting quite different origins. Although both primarily agricultural, the two sites likely have different uses, with DOF being an intensive pig farm, while the RTG at Hartlake is mostly pasture and arable, implying the latter has a markedly smaller livestock community. Sewage and manure signatures would appear alike on the fingerprinting diagram, and so a human source of NO_3 cannot be ruled out for either DOF or Hartlake, however human population densities at both locations are low. This is particularly true of DOF: an intensive pig farm could house over 750 animals, while only a handful of humans likely access the site. NO_3 of manure origin is therefore less likely for Hartlake than for DOF, unless the isotopic ratios signified a sewage source, perhaps point-source from a leaky septic tank or pipe, or biosolid application. Other waste products such as anaerobic digestate may also be applied in the Hartlake catchment, which would also likely bear a similar signature to manure and may be applied to land as a fertiliser. It is worth noting that while DOF and Hartlake appear similar isotopically, other hydrochemical data suggest they may be dominated by different processes; this demonstrates that multiple lines of hydrochemical evidence are required to draw conclusions.

The maximum $\delta^{15}N$ for artificial inorganic N fertilisers is approximately +5 to +6‰. Kendall and Caldwell (1998) and Nestler et al. (2011) recorded +5‰ as the maximum , whereas this study recorded $\delta^{15}N$ of up to +6‰ for Double Top (50:50 $(NH_4)_2SO_4$:NH_4NO_3) fertiliser, in addition to laboratory grade NH_4NO_3 (Chapter 4). Xue et al., 2009 and Vitòria et al., 2004 also report similar figures of up to +6‰. Many groundwater samples in this study have $\delta^{15}N$ of >+5‰ and some >+6‰. For these samples there is likely some influence from manure NO_3 sources as $\delta^{15}N$ is higher than could be contributed by fertiliser alone. Natural soil N could also be a possible source, however given natural soil NO_3 concentrations are low, their influence is likely to be small for most sites.

Manure-type isotope signatures would be expected to have low NO_3-N:Cl due to high Cl (Liu et al., 2006, Yue et al., 2017), however in this study heavier $\delta^{15}N$ has not simply equated to lower NO_3-N:Cl. Variation in NO_3-N:Cl between samples with similar isotope ratios could be indicative of different degrees of mixing. For some samples, the highly bioavailable N in liquid slurry, (such as that found on an intensive pig farm) and poultry manure may lead to proportionally higher NO_3 than Cl, than is typical (i.e. proportionally higher than identified by Liu et al., 2006 or Yue et al., 2017.) For instance, the intensive pig farm in the Kilham catchment, DOF, had high $\delta^{15}N$ but did not have low NO_3-N:Cl, possibly due to moderate Cl, rather than high, but also very high NO_3 concentrations. An intensive poultry farm, MOF, also in the Kilham catchment, may have a similar trend of NO_3-N:Cl to DOF for this reason. $\delta^{15}N$ at MOF, however, did not suggest a dominant manure isotope signature, implying that groundwater NO_3 at MOF was also influenced by the arable agriculture undertaken for poultry feed.

Several sample sites in the study catchments had slurry pits or other intensive farms nearby, so it is notable that more manure and sewage isotope signatures were not found. Gooddy et al. (2002) analysed groundwater in the unsaturated zone beneath unlined slurry pits on the Chalk in Wiltshire and identified that one of the study lagoons formed a seal at its base, which limited the impact of slurry on the groundwater, as compared to the other pit investigated. If a similar seal has formed beneath pits used adjacent to sampling locations, this may explain why higher ion concentrations and manure-dominant signatures were not seen. Previous studies have identified contamination 75-80 m away from unlined slurry pits (Gooddy et al., 1998, Kanazawa et al., 1999), but perhaps the plume begins to dissipate sufficiently after this distance for a dominant manure isotope signature to be not ubiquitous at current study sites. Interestingly Cl concentrations were up to an order of magnitude lower at DOF than the sites studied by Gooddy et al. (2002), which could suggest that DOF was not totally dominated by manure or the pollution was less severe, however baseline conditions could also be higher at the sites monitored by Gooddy et al. Alternatively, as described in Section 7.3.4, N may remain in the soil for several seasons before leaching, thus in the case of minor or diffuse manure pollution the manure signature may become mixed and less pronounced.

Other processes resulting in heavier $\delta^{15}N$ than anticipated could be abiotic, for instance volatilisation of NH_3, resulting in heavier $\delta^{15}N$-NH_4 in the soil (Section 2.4.2.). When nitrified, this could result in a heavier pool of NO_3. However, whether volatilisation could vary sufficiently to result in the spatial and temporal variation noted in this dataset is questionable.

7.3.4.2 Denitrification

There was little clear evidence for substantial denitrification in the stable isotope ratios for the Chalk catchments sampled (Figure 7.14). Seasonal variations in isotope ratios were not on the expected gradient for denitrification of 2.1:1, $\delta^{15}N$ to $\delta^{18}O$ (Mariotti et al., 1981), implying that a different chemical process dominated. It is possible for denitrification to occur in limestone aquifers (Panno et al., 2001) but is likely limited in low temperature groundwaters (McMillan et al., 2014) such as those in the Chalk catchments investigated (typically 10°C). Denitrification is also likely to be limited in aquifers with considerable fracture flow. The majority of denitrification likely occurs in the soil in these locations (Medici et al., 2020), and depends upon temperature, pH, and NO_3 and dissolved organic carbon (DOC) concentrations, and therefore will vary between geologies and locations (Panno et al., 2001, Rivett et al., 2008, Mellander et al., 2012, Yang et al., 2020). Low oxygen conditions are generally required and thus thin and fine Chalk soils are not likely to offer optimum conditions for denitrification.

Hartlake was the most likely candidate of the catchments investigated to support considerable levels of localised denitrification in the soil zone. Unlike the clustered Chalk samples, the RTG isotope ratios are highly variable ($\delta^{15}N$ approx. +7 to +21‰ and $\delta^{18}O$ from +4 to +13‰) (Figure 7.14). Some of the NO_3 concentrations at Hartlake are very low while the $\delta^{15}N$ is heavy, in addition the change in $\delta^{18}O$ is approximately half the change in $\delta^{15}N$, suggesting a denitrification trend (as discussed in Section 3.4.5). The clayey, silty nature of the confining layers overlying the RTG, potentially provide anoxic conditions required for denitrification. The isotope signatures fall within the manure and sewage box on the fingerprinting diagram (Figure 7.14) as discussed above, however if denitrification is the dominant trend then the data points could either originate from a manure-type signature with a lighter $\delta^{15}N$ and $\delta^{18}O$, or even the soil N cluster (as theorised in Figure 7.14).

7.3.5 Seasonality in RTG and Chalk groundwaters

Sites on the Northern Province Chalk demonstrated a seasonal trend whereby NO_3 concentration and $\delta^{18}O$ increased near the beginning of the recharge season, with minimal change for $\delta^{15}N$.[3] In the Southern Province Chalk catchment heaviest isotopic signatures and highest NO_3 concentrations were observed towards the end of recharge. This suggests that a pulse of water containing NO_3 with comparatively heavy $\delta^{18}O$ entered the groundwater at the beginning of recharge for the Kilham and Haisthorpe catchments, and near the end of recharge in the Woodgarston catchment. This would fit with less-transformed, more HB-like NO_3 entering the aquifer. This NO_3 may leach to just beneath the soil root zone without being transformed in the N cycle, prior to recharge season, able to travel no further before the soil becomes saturated, then be released during recharge. The Southern Chalk is often described as softer than the Northern Chalk e.g. Price et al. (1993), thus the former could have fewer fractures that enable fast bypass flow. Alternatively there may be differences in land management between the catchments.

The release of NO_3 with heavier $\delta^{18}O$ into groundwater during recharge might fit with the “nitrate timebomb” type concept, e.g. Wang et al. (2013). Alternatively, NO_3 with $\delta^{18}O$ closer to HB-type signatures may be cycled only a few times through the soil N-cycle before being released from biomass in autumn and leached to the aquifer. Seasonal changes could otherwise be caused by mixing of discrete sources, but the typical change in isotope ratios on the Chalk (heavier-N and heavier-O during recharge) are less likely to be produced by mixing because there are no identified end members with both heavier $\delta^{15}N$ and $\delta^{18}O$.

Following the recharge season the typical trend showed $\delta^{18}O\text{-}NO_3$ became lighter. In addition to biologically-mediated transformations in the soil, equilibrium reactions in the groundwater could reduce $\delta^{18}O\text{-}NO_3$ *in situ* (discussed in Section 2.3.1.1), thus O in groundwater NO_3 would progressively become lighter than the soil equivalent. The lightest $\delta^{18}O\text{-}NO_3$ could alternatively be a product of mixing with older chalk matrix water: this was transported more slowly and therefore has NO_3 that has cycled through the N cycle many times. Then, on entering the

---

[3] The one observation well sampled in the Hartlake catchment (HAROB3) showed little variation, with signatures closest, of all the Hartlake sites, to the soil N cluster noted on the Chalk ($\delta^{15}N$ approx. +7‰ and $\delta^{18}O$ +4 to +6‰). NO_3 concentrations at HAROB3 were, however, noticeably lower than on the Chalk catchments (2.3 to 6.1 mg/L NO_3-N). The 2‰ increase in $\delta^{18}O$ between Feb and Aug 2019 with negligible change in $\delta^{15}N$ is similar to change identified on the Chalk, thus could also be the result of the processes discussed above.

unsaturated zone, it could have been exposed to equilibrium processes while stored in the Chalk matrix (Figure 7.15). Given how slowly equilibrium processes occur, substantial effects from them are unlikely to be observed from fracture flow, but with assistance from terrestrial enzymes for example, equilibrium effects could be observed within the timescale of matrix storage. Alternatively, the decrease in $\delta^{18}O$-NO_3 observed outside of recharge season could be explained by mixing of the NO_3 in the "new" recharge water with the enormous pool of NO_3 already in the aquifer (either pre-agricultural or transformed over time), however over time the recharge-type signature would be expected to become more concentrated in the aquifer.

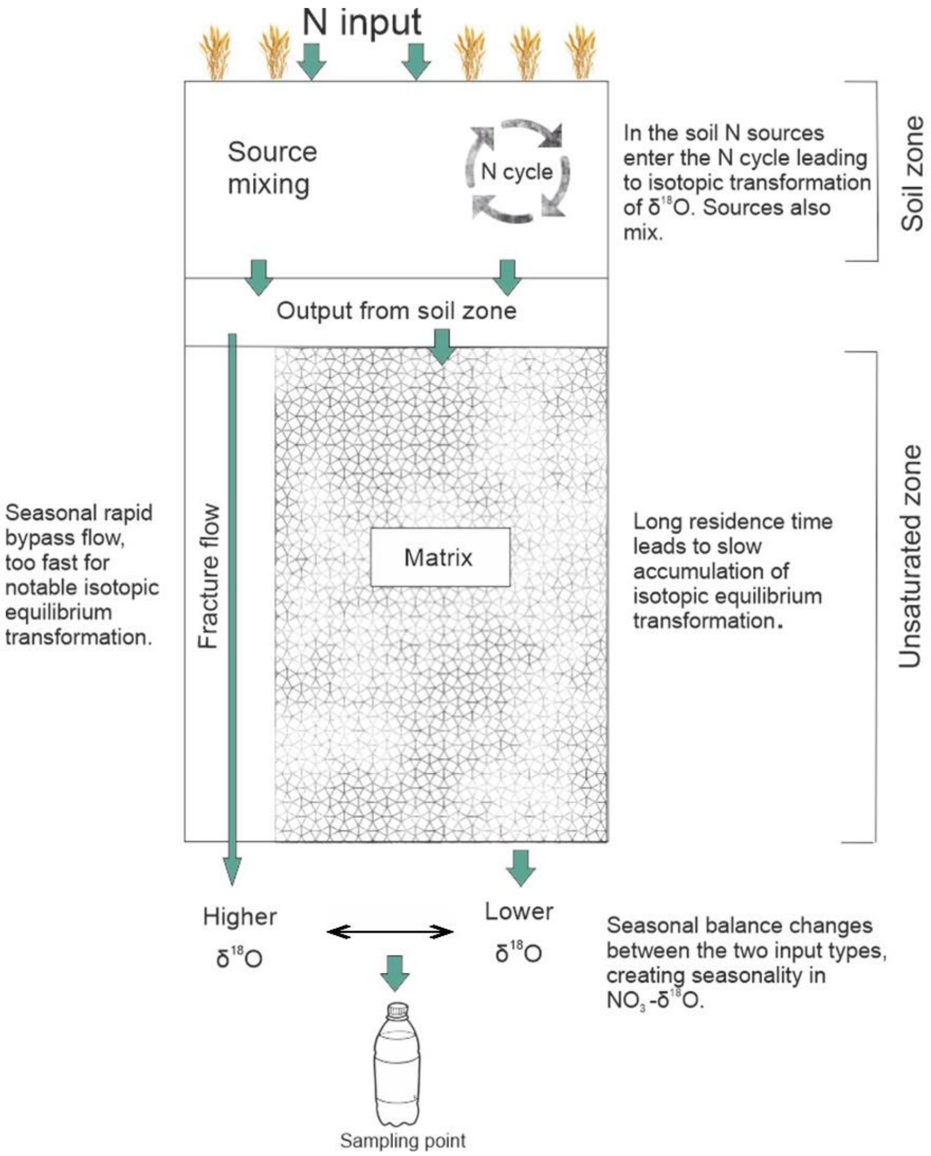

Figure 7.15: Conceptual model to describe seasonal variation in NO_3-$\delta^{18}O$ in Chalk groundwater. NO_3 is stored in the matrix for a much longer period than in fractures, allowing for accumulation of light O signatures that result from equilibrium processes as described in Figure 7.11. Although potentially mediated by bacteria, via incomplete denitrification/ NO_3 assimilation etc. in the soil, equilibrium processes occurring in the unsaturated zone would not necessitate presence of bacteria in the unsaturated zone itself. If equilibrium processes are causing the lighter NO_3-$\delta^{18}O$ then the required timescale must be between fracture flow timescale of days and matrix residence time of several decades.

Across the seasons some sites in the Chalk catchments showed variable $\delta^{15}N$ as well as $\delta^{18}O$. This suggests that mixing occurred as well as HB-fertiliser transformation and equilibrium processes. There are several feasible end-members that could mix to result in the $\delta^{15}N$ observed: NH_4 fertiliser, transformed NO_3 fertiliser, soil N and manure/sewage. In Woodgarston, isotope ratios at WMals and WPit form a cluster, rather than linear trends as at WPBH1 and WPBH2. NO_3 sources could be more complex at small scale abstractions at working farms, as opposed to pumping stations. Water companies are likely cautious about inputs within their Safeguard Zones, and thus N inputs are likely to be more diffuse and homogenous. $\delta^{18}O$ was highest during recharge (i.e. Nov 2018) for both WMals and WPit farms.

Six Yorkshire sites showed an opposing trend whereby $\delta^{18}O$ decreased during recharge, with $\delta^{15}N$ decreasing concurrently at two of these sites. This trend was most evident at DOF, which appears manure-dominated. If all these six sites have an input from manure or slurry then the lighter $\delta^{18}O$ could be explained by an influx of soil N-type NO_3 (with lighter $\delta^{15}N$ and $\delta^{18}O$ than manure-type) during recharge. At DOF, the highest NO_3 concentrations, associated with pollution events with manure isotope signatures, occurred more frequently at the beginning of recharge. This was likely due to rain washing NO_3 derived from manure and slurry out of the soil and into groundwater. Chambers et al 2000 and Medici et al. (2020) also identified that the highest concentrations of NO_3 leached following autumnal applications of slurry.

At HARA and HARC, abstraction boreholes in the RTG catchment, the gradient of seasonal change is different to the Chalk samples. There is a greater range in $\delta^{15}N$ than $\delta^{18}O$ (Figure 6.22), with a gradient similar to that expected for denitrification. $\delta^{15}N$ became heavier over the summer months which could indicate denitrification dominates during this season, a feasible scenario as this is when bacteria are most active. Similar to the six Chalk sites that exhibited lighter isotope ratios in winter, indicative of the heavy signatures mixing with an influx of soil N-type NO_3 during recharge. It is, however, difficult to ascertain whether the same soil N transformation processes are occurring at HARA and HARC as its signature would be masked by the magnitude of the denitrification-type signatures. Although the site with the most prominent denitrification-type gradient did have very low NO_3 concentration, concentration did not appear to reduce with heavier $\delta^{15}N$, which would be expected if denitrification occurred. The gradient could also suggest a very heavy manure-type NO_3 source mixing with HB NO_3 or another manure source but with lighter $\delta^{15}N$ and heavier $\delta^{18}O$.

Due to the short residence time on the RTG it is probable that changes in soil conditions are quickly reflected in the groundwater, therefore seasonal variation in NO_3 concentrations or isotopic ratios could be easily visible. Whereas on the Chalk, little variation in NO_3 concentration or isotopes was generally identified at most pumped wells, whereas more variation was often observed at observation wells. On the Chalk, bypass flow may also accelerate passage of heavier, less transformed $\delta^{18}O$ signatures to the aquifer. Where flow is primarily intergranular rather than via fractures less seasonal variation in hydrochemistry would be expected.

NO_3-N:Cl had no uniform pattern between sites and seasons, but ratios in Spring and Summer in Woodgarston and a couple of the Yorkshire sites occasionally had higher Cl concentrations, while NO_3 concentrations remained consistent. This could be a result of greater evapotranspiration during summer months and entering the groundwater rapidly via fractures, or a Cl source such as manure being introduced in early Spring. The majority of sites in the Yorkshire catchments had higher NO_3 in recharge season, so higher NO_3-N:Cl during recharge was common unless Cl increased concurrently.

7.4 Isotopic mass balance for source apportionment

Under some circumstances isotopic mass balance calculations can be used to estimate proportional contribution of each NO_3 source to groundwater NO_3 contamination (Section 2.3.2). The equations rely upon the principle of mass conservation and assume that the system is closed and is in isotopic equilibrium. Where two isotopes have been analysed mass balance can be calculated using simultaneous equations if there are up to three distinct sources, as described in Section 2.3.2. This approach assumes that isotopic signatures of sources are constant.

In this study the isotopic signatures of sources had a range of values, rather than constant, meaning quantitative mass balance with simultaneous equations is not feasible, as end members cannot accurately be defined. Firstly, although inorganic N fertilisers are usually manufactured using the Haber-Bosch process and therefore manufactured NO_3 generally contains heavy-O due to the incorporation of atmospheric-O, this signature is not identical between brands and formulations ($\delta^{18}O$ of +18.87 to +21.40‰ reported in Section 4.6.2. of the current study). In addition, two distinct groups of signatures were also identified for $\delta^{15}N$-NO_3, with $\delta^{15}N$ of +0.90‰ for Nitram (NH_4NO_3) and +5.78 to +5.98‰ for Laboratory NH_4NO_3 and Double Top ($(NH_4)_2SO_4$ and NH_4NO_3), respectively (Section 4.6.2.). NH_4 and urea fertilisers are also applied, which are subject to nitrification in the soil to produce the NO_3^- signatures observed in this study. $\delta^{15}N$ of N-NH_4 was between −0.98‰ and +1.22‰, but that in the resultant NO_3 likely varies depending on the number of times the N has passed through the N cycle. For all inorganic fertiliser NO_3 sampled, the more passes the NO_3 pool takes through the N-cycle the lower the $\delta^{18}O$-NO_3, tending towards the signature of natural soil N.

Natural soil N will also have an influence over isotopic signatures however it is likely minor in comparison to the anthropogenic input, which, as stated above, will tend towards being indistinguishable from natural soil N. The proportion of a sample that is transformed fertiliser NO_3 and the proportion that is natural soil N will vary between geologies, seasons and groundwaters. The $\delta^{18}O$ of groundwater in Yorkshire is reportedly −7.5‰ (Darling et al., 2003), so for groundwater O-NO_3 signatures within the typical cluster of +1 to +4‰ it appears that approximately two thirds of O-NO_3 has been exchanged with O-H_2O, assuming initial $\delta^{18}O$ is that of locally applied NO_3 fertilisers (Section 4.6.2).

The varying diet of livestock will lead to varying manure signatures, which means a single signature cannot be calculated for manure, slurry and sewage. Feedstuff may be marine or terrestrial in origin, which results in different manure $\delta^{15}N$ (Sweeney et al., 1978) and suppliers likely change sporadically, depending on price (Section 4.2.4). There may also be multiple microbial processes in response to manure, depending on bioavailability of N or volume, that could affect $\delta^{15}N$. Abiotic processes also affect isotopic fractionation e.g. volatilisation of NH_3 ($\delta^{15}N$-NH_4 becomes heavier).

Minimal untransformed fertiliser is expected as where it has been applied appropriately as the majority will have passed through the soil biomass e.g. Macdonald et al. (1989). The majority of fertiliser will therefore have a soil N-type isotope signature and thus soil-type signatures are likely to dominate in most circumstances. Signatures will likely only have $\delta^{18}O$ approaching +18‰ when far too much fertiliser has been applied, or if there has been substantial rainfall shortly after application. However, a small proportion of fertiliser NO_3 may pass through the soil zone without transformation and this can be estimated. When NO_3 forms in the soil, two of the oxygen molecules will come from water (−7.5‰ in Yorkshire, according to Darling et al. 2003) and the third from atmospheric O_2 (23.5‰, from Kroopnick and Craig, 1972), thus:

$$Soil\ NO_3\ \delta^{18}O(‰) = \frac{(2 \times -7.5) + (1 \times 23.5 + e)}{3}$$

(7.1)

Where *e* is a small negative constant, representing the fractionation of molecular O_2 on incorporation in NO_3. Soil N is therefore estimated to have a $\delta^{18}O$ of $2.8 + \frac{e}{3}$‰. There is a paucity of experimental evidence, but *e* is likely small and is often excluded from estimates e.g. Kendall and Aravena (2000). Where O isotope signatures deviate from the cluster, as presented in Figure 7.14 (the cluster range was approximately $\delta^{15}N$ +4 to +6‰ and $\delta^{18}O$ 0 to +4‰), with a heavier $\delta^{18}O$, this implies presence of untransformed HB fertiliser. For instance, under theoretical conditions where Nitram is the sole NO_3 source and $\delta^{18}O$ is between +5 and +8‰, it can be concluded that 12.6 to 30.0% of fertiliser is entering the groundwater untransformed, as illustrated in Figure 7.16. This range of fertiliser leaching fits with the existing published literature e.g. Powlson et al. (1992).

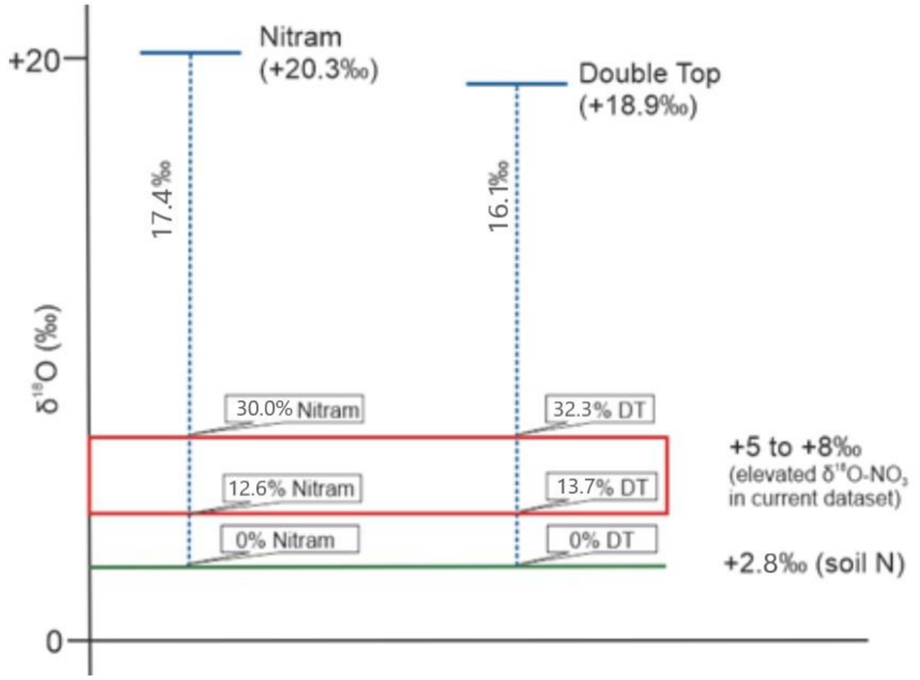

Figure 7.16: Diagrammatic aid to demonstrate what estimated proportion of a $\delta^{18}O$-NO_3 signature may be untransformed HB-NO_3 fertiliser, using a theoretical scenario where Nitram or Double Top (DT) are the only NO_3 source. +20.3‰ and 18.9‰ are the $\delta^{18}O$ for Nitram and DT, respectively. Soil N $\delta^{18}O$-NO_3 is calculated using equation 7.1, assuming e is negligible and thus can be omitted, as by Kendall and Aravena (2000).

In a few samples manure appears to dominate the NO_3 isotope signature. Given the frequency with which manure, slurry, biosolids or anaerobic digestate (all bearing similar isotopic signatures) are likely applied as fertiliser or waste disposal the lack of heavy $\delta^{15}N$ manure-type signatures is notable. This suggests that there is significant amount of mixing occurring, disguising the heavy $\delta^{15}N$. The traditional fingerprinting diagram does not enable mixed signatures to be differentiated from pure signatures. However, using major ion concentrations, such as NO_3-N:Cl assists in elucidating NO_3 sources. N and Cl may have alternative sources than those described in this method (e.g. Liu et al., 2006 an Li et al., 2010) however Figure 7.12 shows sample data are largely on a continuum between hypothesised end members. A handful of sites deviate, where different sources or processes may dominate.

7.5 Applicability of the fingerprinting diagram for source identification in short and long residence time groundwater

The fingerprinting diagram, as developed by Kendall (1998), Xue et al. (2009) and Nestler et al. (2011), Xue et al. (2009) intended to enable differentiation between common NO_3 sources, cannot always be interpreted at face value. This is particularly true for groundwater NO_3 and where there is influence from microbial processes, such as when water percolates through the soil zone. Biotic and abiotic transformation processes are not accounted for in the diagram and are key to deciphering the isotopic signatures observed in groundwater. Additional hydrochemical data are required to glean greater understanding of isotopic signatures and NO_3 concentrations and NO_3-N:Cl ratio were crucial in this respect for the current study. For instance, DOF (Chalk catchment) and HARC (RTG catchment) sites produced similar isotopic ratios, with the implication that both were dominated by manure/slurry NO_3, however NO_3 concentrations and NO_3-N:Cl ratios show that the processes producing each are different.

Inorganic NO_3 fertiliser signatures with heavy $\delta^{18}O$ were not identified in any samples in this study, demonstrating that microbial and crop activity render HB NO_3 fertiliser signatures indistinguishable from natural soil N on the traditional fingerprinting diagram, even in aquifers where residence time is only days to weeks. Knowledge of local $\delta^{18}O$-H_2O from groundwater (e.g. Darling et al., 2003, for the present study) and $\delta^{18}O$-O_2 from the atmosphere are necessary to interpret the resulting NO_3 isotopic signature that is plotted on the fingerprinting diagram in terms of the extent to which biotic and abiotic processes have acted on the $\delta^{18}O$-NO_3, as discussed in Section 7.4.

Locally important NO_3 sources are also key for interpreting $\delta^{15}N$ on the fingerprinting diagram. Given the substantial overlap between NH_4 and soil N signatures, discrimination between sources using the diagram was unfeasible in many circumstances encountered in this study. Analysing N, and where possible O, stable isotopes for locally-applied NO_3 and NH_4 fertilisers assisted in differentiating sources within the context of this investigation. Other studies have adjusted the fingerprinting diagram, to make it more applicable for local use e.g. Mengis et al. (2001) and Vitòria et al. (2008). This may prove helpful for small field-scale studies where all NO_3 inputs can be analysed, however for catchment or larger scale experiments it may result in misinterpretation, as livestock feed is not necessarily locally purchased and may have a wide range of isotope values. Inorganic fertilisers may also have varying isotope ratios depending on manufacturing method and location.

Although very little data from this study fell outside the constraining boxes on the fingerprinting diagram, there are suggestions in the literature that outliers are often mistakenly identified as products of denitrification e.g. Venkiteswaran et al. (2019). Denitrification can be identified using the fingerprinting diagram, where multiple data points fall on a 2.1:1 gradient of $\delta^{15}N:\delta^{18}O$ (Mariotti et al., 1981), however the increase in $\delta^{15}N$ in residual NO_3 can be difficult to detect unless most of the original NO_3 pool has denitrified (Gooddy et al., 2002). In addition, the picture is further complicated by other processes that also result in heavy $\delta^{15}N$ in the substrate e.g. volatilisation. Venkiteswaran et al. (2019) also observed that viewing all dual isotope data on a single fingerprinting plot, irrespective of season and location, can be misleading. However, in this study it has proved a valuable starting point for interpreting landscape-scale processes, that can be built upon and validated by additional individual isotope plots.

7.6 Summary of nitrate sources and processes observed in RTG and Chalk catchments

The behaviour of NO_3 in the Northern versus the Southern Chalk provinces was largely similar, with the major sources of variation being difference in land use and the types of site sampled (pumped or observation boreholes). In contrast, NO_3 concentrations were lower in the RTG catchment than in the majority of samples from the Chalk. Whether this is a result of differing land uses or processes is difficult to identify from only a few sampling events and locations, however the clayey, silty soil associated with the RTG provide suitable conditions for denitrification in some locations, enabling highly localised NO_3 attenuation. It is possible that low NO_3 concentrations in the Hartlake catchment result from “old” pre-agricultural groundwater, however given the low aquifer volume (see Section 6.7.3.), this is unlikely.

While complete denitrification is not desirable in soil, it is useful beneath the root zone to reduce concentrations of NO_3 entering groundwater. Chalk soil and groundwater in the unconfined zones create an oxidising environment therefore denitrification will rarely be a dominant process. DOF is a possible outlier, with the amount of manure/slurry pollution potentially creating conditions suitable for denitrifying bacteria. However, the manure signature can be explained without additional processes, by proximity of the borehole to pig housing, and in addition, NO_3 concentrations were high with no evidence of attenuation.

This study demonstrated that manure can be identified in cases where there has been a substantial point source pollution event, therefore addressing inappropriate use or disposal of manure and slurry could be beneficial in reducing groundwater NO_3 contamination. Timely application of manure is more difficult than for manmade fertilisers. It is more difficult to identify its exact composition, and both liquid and solid manures vary dramatically within a store or heap so testing is problematic (AHDB, 2020). Composition will also vary with feed, and potentially bedding practices as well (AHDB, 2020). Manure and slurry are also waste products, and therefore disposal is the primary consideration, not timeliness of application for crop use. Due to the increased cost of fuelling transport to the furthest fields, a disproportional amount may be applied to fields close to farm buildings, providing more NO_3 than the crops can utilise, therefore leaching is more likely to occur. However, fewer manure-type isotope signatures were observed in this study than might be expected, given manure, slurry, biosolid or anaerobic digestate (with similar isotope signatures) are likely widely applied to agricultural land. There may be varying responses to manure/slurry application depending on its bioavailability or the volume that is applied: if lots of NO_3 rapidly enters the soil, crops and biomass may not be able to absorb all of it before it leaches below the root zone.

Chapter 8 Conclusions and recommendations

8.1 Conclusions

Previous work has shown that as a limiting nutrient nitrate is an important additive to arable fields e.g. Addiscott et al. (1991). However, as it is highly water soluble, nitrate is vulnerable to leaching from the soil into surface and groundwater, particularly when not applied correctly or at the appropriate time (Goss et al., 1988). When in drinking water, nitrate has been considered a health risk, hence the introduction of a maximum of 50 mg/L nitrate. In surface water, nitrate in combination with phosphate is responsible for eutrophication, a process which reduces biodiversity and in extreme cases results in ecosystem collapse, as well as reducing aesthetics. Groundwater is particularly vulnerable to nitrate ingress where there is fast transport of water between the surface and the saturated zone, for instance via fractures, as observed on the Cretaceous Chalk e.g. Allshorn et al. (2007). With fast transport there is limited opportunity for attenuation. However, in Chalk, nitrate is stored in the matrix as well as in fractures, and Chalk matrix has very small pore throats; this may mean solutes are trapped within it for extended periods; in this location there may be greater opportunity for attenuation.

Groundwater and spring water samples were initially taken from adjacent catchments on the Northern Province Cretaceous Chalk (Kilham and Haisthorpe in the East Riding of Yorkshire). Two further catchments were later added to the study: a catchment on the Southern Province Cretaceous Chalk (Woodgarston in Hampshire) and a River Terrace Gravels (RTG) catchment in Hartlake, Kent. The samples were analysed for dual stable isotope composition of nitrogen and oxygen in nitrate. Major ion concentrations were analysed, and historical major ion concentrations were obtained from the Environment Agency or relevant water company, where possible. Dual stable isotope analysis of nitrate had not before been performed on any of the catchments to the author's knowledge. The Medway RTG is little researched compared to the Chalk, and the Haisthorpe catchments less researched than the Kilham catchment, so this work provides a substantial contribution to this field of knowledge.

The results of dual stable isotope analysis and relevant hydrochemical data from the four catchments were compared to identify to what extent nitrate sources and processes were similar between geologies, aquifer lithology and flow mechanism. Chalk aquifers are reported to have average residence times of several decades, whereas in RTG aquifers residence time is shorter (30-40 days; D. Wilkinson, 2018, personal communication, 11 July 2018).

Dual stable isotope data for nitrate were plotted on a fingerprinting diagram (Kendall, 1998, Xue et al., 2009, Nestler et al., 2011) with the objective of estimating the source of the nitrate, while taking care to appreciate the limitations of the plot. Four fertiliser samples were analysed for bulk nitrogen, and where possible nitrogen and oxygen in nitrate, isotope composition to constrain possible agricultural sources. Isotope signatures for nitrate from manure, oxygen in groundwater, and atmospheric oxygen were taken from the published literature to further constrain boundaries.

Nitrate concentrations in Northern Province Chalk catchments often exceeded the Prescribed Concentration or Volume (PCV) of 11.3 mg/L nitrate-N, with the majority of sites breaking this limit during the period studied. Whereas in the Woodgarston catchment (Southern Province Chalk) only a quarter of all samples were greater than the PCV and in the Hartlake catchment (RTG) no samples exceeded the PCV, with one site (HAROB1) below the limit of detection (<2 mg/L nitrate). Analysis of major ion concentrations suggested that anthropogenic pollution events occurred occasionally at several sites on the Northern Province Chalk, with concurrent peaks in concentration for chloride, sulphate and nitrate.

Dual stable isotope analysis of nitrogen and oxygen in nitrate was used first to identify the differences between four fertilisers applied in Yorkshire, in addition to a laboratory grade ammonium nitrate. Bulk $\delta^{15}N$ ranged from −0.21 to +3.09‰; nitrate where applicable ranged from +0.90 to +5.98‰ for $\delta^{15}N$ and +18.87 to +21.40‰ for $\delta^{18}O$. The ammonium-N component was calculated to be between −0.98 and +1.22‰. Lab ammonium nitrate and Double Top had $\delta^{15}N$ signatures greater than those accounted for in the fingerprinting diagram, but only by approx. 1‰. Most inorganic fertilisers are manufactured via the Haber-Bosch process and so although formulations may change, ammonia and nitrate synthesis is likely to have stayed the same since the Second World War, resulting in isotope signatures with a limited range and a characteristically heavy oxygen signature (representing atmospheric oxygen).

Dual stable isotope analysis of nitrogen and oxygen in nitrate was carried out on Chalk and RTG groundwater samples, to differentiate between sources of nitrate and the processes it undergoes. The majority of sample sites on the Chalk, and a site on the RTG, had a soil N-type isotope signature, within a cluster ($\delta^{15}N$ between +4 and +6‰, and $\delta^{18}O$ between +0 and +4‰). The soil N-type signature is considered a near ubiquitous agricultural signature, likely the result of mixing of several sources, in addition to nitrogen cycling in the soil zone. The Haber-Bosch heavy oxygen signature that enters the soil zone via inorganic fertilisers is notably absent in all samples. This suggests that inorganic fertilisers are being used appropriately in all regions sampled: crops and soil biomass were able to assimilate much of the nitrogen. Nitrate is remineralised as crop debris decomposes or the biomass becomes dormant, which results in loss of the heavy oxygen signature. Nitrate therefore likely becomes most vulnerable to leaching into groundwater when it is remineralised at the end of the growing season and just prior to recharge season. An effective solution for farmers, water companies and environmentalists could be realised if nitrate could be retained in the soil overwinter and leaching reduced.

From dual stable isotope analysis, one site on the Northern Province Chalk (DOF) appeared to be subject to several manure, slurry or sewage events ($\delta^{15}N$ +2.74 to +10.21‰, and $\delta^{18}O$ +2.74 to +10.21‰). It is common to apply manure and slurry to fields, but a clear manure signature was rare, which implies that crops and soil biomass are able to utilise it except when a particularly large volume, or a highly bioavailable product is applied. In the RTG catchment, Hartlake, some samples had a manure-type signature, however low nitrate concentrations and the gradient of the data (a trend of 2:1 nitrogen to oxygen, i.e. both $\delta^{18}O$ and $\delta^{15}N$ become heavier as NO_3 concentration decreases) suggest denitrification may be a dominant process for these sites. South East Water reported high concentrations of Fe and Mn, which tends to occur in anoxic conditions once nitrate has been denitrified (DiChristina, 1992, Achtnich et al., 1995). As this RTG aquifer contains clay and silt, is overlain by clayey, silty soils, low oxygen conditions in either the soil or aquifer could facilitate denitrification. Residence times in the RTG aquifer are unlikely to be long enough for the low nitrate concentrations to be due to old groundwater with pre-agricultural hydrochemistry.

Plots of nitrate to chloride ratios revealed many sites were on a spectrum between a fertiliser nitrate source (high nitrate, low chloride) and a manure source (low nitrate, high chloride), supporting the findings from dual stable isotope analysis above that several nitrate sources may mix in the soil zone. Several sites showed a different trend of high nitrate and moderately high chloride (e.g. site DOF on the Northern Province Chalk). At these sites a heavy application of manure is thought to have occurred, which led to nitrification taking place at a much faster rate than plants or soil biomass could exploit, ultimately leading to substantial nitrate leaching. This could explain why the manure isotope signature was observed at DOF and not at other locations. Nitrate to chloride ratios based on Liu et al. (2006) and Li et al. (2010) was a useful tool to support and validate findings from dual stable isotope analysis, and assist in shaping conclusions. As these ion concentrations are often analysed as standard during water quality sampling, this method proved an inexpensive but effective method of rudimentary nitrate source identification.

The majority of sites on Chalk and RTG catchments showed some temporal variation in ion and isotope data; this variation was more distinct at observation boreholes than pumped boreholes. A common observation was heavier $\delta^{18}O$ during the recharge period, which could result from a nitrate source with heavy oxygen (such a inorganic nitrate fertiliser) being introduced during recharge. $\delta^{18}O$ then often became lighter towards the end of recharge. This is possibly due to seasonal variation in the amount of nitrate contributed via fracture flow and from matrix storage. It is hypothesised that biotically-mediated equilibrium transformations occurring between water ($\delta^{18}O$ −7.5‰ in Yorkshire) and nitrate ($\delta^{18}O$ >2‰) resulting in light $\delta^{18}O$, may be more likely to occur in the matrix, as solutes may be stored in the matrix for extended periods.

The nature of the site sampled affects hydrochemistry, including isotopic composition of nitrate. Unpumped wells may have signatures representative of a localised portion of the aquifer, while pumped wells will drawdown water from a greater area and therefore have a more general hydrochemistry, characteristic of the wider aquifer. Of the pumped boreholes, the volume pumped may also influence the signature, with the most uniform isotope signatures often observed at the sites where the highest volumes are abstracted. This could be important to consider when developing a project: if hunting for a point source pollution event then observation wells could be more useful, while pumped wells would give a better overview of wider scale aquifer water quality.

This study has explored transformation processes within the nitrogen cycle bringing together hydrogeochemistry and soil science. It has contributed to understanding methods that may help mitigate the nitrate problem in surface and groundwater. The absence of dominant Haber-Bosch heavy nitrate signatures across all study catchments demonstrates that fertiliser nitrate enters the soil nitrogen cycle prior to leaching, supporting the findings of previous studies e.g. Macdonald et al. (1989). When not absorbed and removed from the soil nitrogen cycle by the crop, it may cycle within the soil zone for several years. Nitrogen fertilisers continue to increase crop yields even where the fertiliser does not enter the crop in the year of application (Powlson et al., 1986). It is not simply fertiliser that causes nitrate contamination of groundwater, but the instability of the soil nitrogen pool resulting from ploughing, possibly in addition to a larger soil nitrogen pool currently inhabiting the soil.

8.2 Recommendations

Once nitrate is in the aquifer there are many techniques for stripping water of nitrate following abstraction for public supply, however these are often expensive e.g. ion exchange, reverse osmosis or electrodialysis (Shrimali and Singh, 2001). As well as financial cost, the carbon cost and sustainability of removing nitrate from water should also be considered, thus impeding nitrate from entering groundwater in the first instance is a more efficient solution for reducing nitrate in groundwater.

The natural first step in this process is to control N applications to the soil, especially in vulnerable regions. Nitrate Vulnerable Zone (NVZ) designations (European Commission, 2000b) address this concept, requiring that inorganic fertilisers and manures are applied to land in NVZs in appropriate volumes, thus avoiding overloading soils with nitrate. They also take into account time of year of applications, in addition to weather and land morphology (e.g. slope, distance to surface water); this avoids applying nitrogen compounds at times when crops cannot efficiently utilise them, or when they may be lost in run-off. As fertiliser improves crop yields and appears to be fulfilling that purpose rather than leaching directly into the aquifer, simply reducing inorganic or manure fertiliser applications far beyond current recommendations may not reduce nitrate concentrations in water supplies. Ensuring applications are appropriate for the crop, however, will avoid overloading the soil zone and minimise nitrate leaching.

Technology is also being used to improve breakdown of fertilisers once in the soil. For instance, urea fertilisers can be coated with sulphur or polymers for a more controlled release of nitrate to the soil, reducing both application frequency and the risk of nitrate leaching. In addition, slurry improvers can enhance predictability of manure and slurry decomposition, with the aim of increasing application precision. Slurry improvers may, therefore, reduce manure point source pollution events such as those observed on occasion in this study.

Planting cover crops following cash crops has reduced nitrate leaching e.g. Macdonald et al. (2005) and Cooper et al. (2017), as this increases the amount of nitrogen that is stored in organic forms over winter, rather than as water-soluble nitrate that is vulnerable to leaching. However, which species to plant and when for greatest benefit is an ongoing discussion (Thapa et al., 2018). Brassicas (e.g. radish) and oats are popular as they are fast growing and non-leguminous, but different species will have varying efficacy in reducing nitrate leaching on different soil types. Depending on soil type, in some locations (e.g. poor draining, heavy soils) supporting growth of weeds and cereal volunteers may be just as efficacious as sowing a specific cover crop (Macdonald et al., 2005). Cover crops have additional benefits, including reduced soil erosion, but some farmers have reported an increase in pest populations following cover crop use (Storr et al., 2019) so further research is required to ensure cover cropping does not result in pollution swapping of nitrate for pesticides.

Reducing ploughing (“min-till” or “no-till”) could also help preserve natural soil structure and thus its ability to retain N as stable organic matter. Although tilling soil allows weeds and the remains of the previous season’s crop to be folded into the earth encouraging decomposition, in addition to aerating and warming the soil, it also harms soil microbes and weakens the soil structure, leading to increased risk of erosion and nutrient leaching (Huggins and Reganold, 2008). The more stable soil structure achieved with no-till, or min-till, methods supports microbial communities that more closely mimic natural systems, thus enabling more natural N cycling and storage.

Many techniques for reducing nitrate leaching on agricultural land also come with negative effects e.g. increased pesticide or herbicide use on min-till or no-till land, and the initial cost of converting between farming practices. Therefore, where reduction in nitrate leaching is key, for example surrounding a Drinking Water Safeguard Zone, rewilding would be the ideal case. Ploughing caused a large increase in nitrate leaching following World War Two, but recent case studies have seen this trend reversed as improved grassland is returned to a more natural state.

8.3 Further work

To develop on the findings of this thesis the effect of the volume of water abstracted through a borehole on nitrate isotope values could be further assessed. Although collecting sufficient pumping data to a suitable accuracy was too onerous to be attempted as part of this thesis, the development of a standard protocol for sampling that includes recording the pumped volume, and ensures wells are purged prior to sampling could be beneficial.

Analysing both nitrogen and oxygen in nitrate was key for this study, supported by nitrate to chloride concentration ratio data; $\delta^{15}N$ alone is not sufficient for understanding nitrate sources and processes. However, further stable isotope analysis could also have been employed and could be beneficial for future studies seeking to understand nitrate behaviour in a given catchment, for instance, boron ($^{11}B/^{10}B$). There are a broad range of $^{11}B/^{10}B$ ratios naturally occurring in rocks and waters, however it can also be used to identify anthropogenic inputs. Typical boron concentrations in pristine waters are low, while concentrations in fertilisers and manures are higher, e.g. Tirez et al. (2010), thus $\delta^{11}B$ can prove a sensitive tool for analysing input from nitrate sources. It may also allow some differentiation between animal manures and fertiliser types (Widory et al., 2005), as well as human wastewater via the presence of sodium perborate in detergents (Vengosh et al., 1994), which could allow sources to be identified with greater precision. As it is not affected by denitrification (Vengosh et al., 1994) $\delta^{11}B$ could be useful to validate samples where denitrification is suspected to have taken place. $\delta^{13}C$, or $\delta^{34}S$ and $\delta^{18}O$ from sulphate, could be analysed to further investigate the role of denitrification e.g. Aravena and Robertson (1998). Chloride stable isotope ratios could also be applied to further trace nitrate sources; analysis of $\delta^{37}Cl$ would enable the nitrate to chloride concentration ratio to be plotted against δ^{37}Cl, allowed greater precision in identifying nitrate sources as demonstrated in Zhang and Wang (2020). Stable isotope ratios of hydrogen and oxygen in water could ease identification of key nitrogen transformation processes (Zhang and Wang, 2020).

The traditional fingerprinting diagram does not enable mixed signatures to be differentiated from pure signatures. A mixing model could assist with quantification of source input, such as the Bayesian isotopic mixing model (Parnell et al., 2010) as employed by Stable Isotope Analysis in R (SIAR) or MixSIAR, and applied by e.g. Zhang and Wang (2020) and Ming et al. (2020), respectively. If additional isotope data were collected as discussed in the above paragraph, these could be used to more tightly constrain a mixing model, ensuring high confidence in the outputs. Better definition of end-member components would also provide valuable constraint. This could include analysing the nitrate in rainfall columns collected during this study for their isotopic composition, in addition to evaluation of dry deposition, rock and organic manure nitrate.

Greater understanding of nitrate transformation processes both in soil and the unsaturated zone could be achieved using lysimeter studies so agricultural inputs with known isotopic signatures could be applied. Temporal variation in the groundwater nitrate isotope ratios in this study suggest that transformations occur slowly enough for a small proportion of the heavy oxygen Haber-Bosch nitrate fertiliser to appear in the groundwater. Lysimeter studies could clarify how fast transformations occur. Additionally, the hypothesis described in Figure 7.16 could be tested, (that oxygen signatures in nitrate become lighter due to biotically-mediated equilibrium processes while in the Chalk matrix), would be of value. Drilling to obtain core samples of the Chalk matrix could enable analysis of porewater for nitrate isotope composition.

References

2006. Natural Environment and Rural Communities Act 2006. *2006/2541.* England.

ACHTNICH, C., BAK, F. & CONRAD, R. 1995. Competition for electron donors among nitrate reducers, ferric iron reducers, sulfate reducers, and methanogens in anoxic paddy soil. *Biology and fertility of soils,* 19**,** 65-72.

ADDISCOTT, T. M., WHITMORE, A. P. & POWLSON, D. S. 1991. *Farming, fertilizers and the nitrate problem,* Wallingford, CAB International (CABI).

AGBOTUI, P. Y. 2019. *Characterisation of flow regimes of the East Yorkshire Chalk Aquifer.* University of Leeds.

AGBOTUI, P. Y., WEST, L. J. & BOTTRELL, S. H. 2020. Characterisation of fractured carbonate aquifers using ambient borehole dilution tests. *Journal of Hydrology***,** 125191.

AHDB 2017. The nutrient management guide (RB209).

AHDB 2020. Nutrient Management Guide (RB209) Section 2: Organic Materials. Kenilworth: AHDB.

AL-ZAHRANI, S. 1999. Controlled-release of fertilizers: modelling and simulation. *International Journal of Engineering Science,* 37**,** 1299-1307.

ALLEN, D., BREWERTON, L., COLEBY, L., GIBBS, B., LEWIS, M., MACDONALD, A., WAGSTAFF, S. & WILLIAMS, A. 1997. The physical properties of major aquifers in England and Wales.

ALLEN, D. & CRANE, E. 2019. The Chalk aquifer of the Wessex Basin. Nottingham, UK: British Geological Survey.

ALLSHORN, S. J. L. 2008. *Flow and solute transport in the unsaturated zone of the Chalk in East Yorkshire.* University of Leeds.

ALLSHORN, S. J. L., BOTTRELL, S. H., WEST, L. J. & ODLING, N. E. 2007. Rapid karstic bypass flow in the unsaturated zone of the Yorkshire chalk aquifer and implications for contaminant transport. *Geological Society, London, Special Publications,* 279**,** 111-122.

ANDERSSON, K. K. & HOOPER, A. B. 1983. O2 and H2O are each the source of one O in NO− 2 produced from NH3 by Nitrosomonas: 15N-NMR evidence. *Febs Letters,* 164**,** 236-240.

APPL, M. 2006. Ammonia. In Ullmann's Encyclopedia of Industrial Chemistry, (Ed.). *Ullmann's Encyclopedia of Industrial Chemistry.* Wiley-VCH.

ARAVENA, R. & ROBERTSON, W. D. 1998. Use of multiple isotope tracers to evaluate denitrification in ground water: Study of nitrate from a large-flux septic system plume. *Groundwater,* 36**,** 975-982.

BANKS, D., DAVIES, C. & DAVIES, W. 1995. The Chalk as a karstic aquifer: evidence from a tracer test at Stanford Dingley, Berkshire, UK. *Quarterly Journal of Engineering Geology and Hydrogeology,* 28**,** S31-S38.

BARKER, J. & FOSTER, S. 1981. A diffusion exchange model for solute movement in fissured porous rock. *Quarterly Journal of Engineering Geology and Hydrogeology,* 14**,** 17-24.

BARRACLOUGH, D., GARDNER, C. M. K., WELLINGS, S. R. & COOPER, J. D. 1994. A tracer investigation into the importance of fissure flow in the unsaturated zone of the British Upper Chalk. *Journal of Hydrology,* 156**,** 459-469.

BATEMAN, A. S. & KELLY, S. D. 2007. Fertilizer nitrogen isotope signatures. *Isotopes in Environmental and Health Studies,* 43**,** 237-247.

BEDARD-HAUGHN, A., VAN GROENIGEN, J. & VAN KESSEL, C. 2003. Tracing 15N through landscapes: potential uses and precautions. *Journal of Hydrology,* 272**,** 175-190.

BERGSTRÖM, L. F. & KIRCHMANN, H. 1999. Leaching of Total Nitrogen from Nitrogen-15-Labeled Poultry Manure and Inorganic Nitrogen Fertilizer. *Journal of Environmental Quality,* 28**,** 1283-1290.

BIGELEISEN, J. 1949. The relative reaction velocities of isotopic molecules. *The journal of chemical physics,* 17**,** 675-678.

BIRKS, D., WHITTALL, S., SAVILL, I., YOUNGER, P. L. & PARKIN, G. 2013. Groundwater cooling of a large building using a shallow alluvial aquifer in Central London. *Quarterly Journal of Engineering Geology and Hydrogeology,* 46**,** 189-202.

BLOM-ZANDSTRA, M. 1990. *Some physiological aspects of nitrate accumulation in lettuce (Lactuca sativa L.)*, Ponsen & Looijen.

BLOOMFIELD, J. 1996. Characterisation of hydrogeologically significant fracture distributions in the Chalk: an example from the Upper Chalk of southern England. *Journal of Hydrology,* 184**,** 355-379.

BLOOMFIELD, J. 1997. The role of diagenisis in the hydrogeological stratification of carbonate aquifers: an example from the chalk at Fair Cross, Berkshire, UK. *Hydrology and Earth System Sciences Discussions,* 1**,** 19-33.

BLOOMFIELD, J., BREWERTON, L. & ALLEN, D. 1995. Regional trends in matrix porosity and dry density of the Chalk of England. *Quarterly Journal of Engineering Geology and Hydrogeology,* 28**,** S131-S142.

BÖHLKE, J.-K. 2002. Groundwater recharge and agricultural contamination. *Hydrogeology Journal,* 10**,** 153-179.

BÖHLKE, J., MROCZKOWSKI, S. & COPLEN, T. 2003. Oxygen isotopes in nitrate: New reference materials for 18O: 17O: 16O measurements and observations on nitrate-water equilibration. *Rapid Communications in Mass Spectrometry,* 17**,** 1835-1846.

BÖHLKE, J. K. & COPLEN, T. B. 1995. Interlaboratory comparison of reference materials for nitrogen-isotope-ratio measurements. Vienna (Austria): International Atomic Energy Agency.

BÖTTCHER, J., STREBEL, O., VOERKELIUS, S. & SCHMIDT, H.-L. 1990. Using isotope fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial denitrification in a sandy aquifer. *Journal of Hydrology,* 114**,** 413-424.

BOURAOUI, F., GALBIATI, L. & BIDOGLIO, G. 2002. Climate change impacts on nutrient loads in the Yorkshire Ouse catchment (UK).

BOUSTEAD, I. 2005. Eco-profiles of the European plastics industry. *A report prepared for PlasticsEurope, Bruxelle, Belgium*.

BRABAN, C., NEMITZ, E., SUTTON, M. 1985-2019. UK Acidifying and Eutrophying Atmospheric Pollutants: Precipitation network (UKEAP: Precip-Net). *In:* ENVIRONMENT, R. E. (ed.).

BRAND, W. A., COPLEN, T. B., AERTS-BIJMA, A. T., BÖHLKE, J., GEHRE, M., GEILMANN, H., GRÖNING, M., JANSEN, H. G., MEIJER, H. A. & MROCZKOWSKI, S. J. 2009. Comprehensive inter-laboratory calibration of reference materials for δ18O versus VSMOW using various on-line high-temperature conversion techniques. *Rapid Communications in Mass Spectrometry: An International Journal Devoted to the Rapid Dissemination of Up-to-the-Minute Research in Mass Spectrometry,* 23**,** 999-1019.

BRIDGLAND, D. R. 2003. The evolution of the River Medway, SE England, in the context of Quaternary palaeoclimate and the Palaeolithic occupation of NW Europe. *Proceedings of the Geologists' Association,* 114**,** 23-48.

BRISTOW, R., MORTIMORE, R. & WOOD, C. 1997. Lithostratigraphy for mapping the Chalk of southern England. *Proceedings of the Geologists' Association,* 108**,** 293-315.

BRITISH GEOLOGICAL SURVEY. 2020. The BGS Lexicon of Named Rock Units [online]. Available: https://www.bgs.ac.uk/technologies/the-bgs-lexicon-of-named-rock-units/.

BRYAN, N. S., ALEXANDER, D. D., COUGHLIN, J. R., MILKOWSKI, A. L. & BOFFETTA, P. 2012. Ingested nitrate and nitrite and stomach cancer risk: An updated review. *Food and Chemical Toxicology,* 50**,** 3646-3665.

CAMERON, K. C., DI, H. J. & MOIR, J. L. 2013. Nitrogen losses from the soil/plant system: a review. *Annals of Applied Biology,* 162**,** 145-173.

CASCIOTTI, K. L., SIGMAN, D. M., HASTINGS, M. G., BÖHLKE, J. & HILKERT, A. 2002. Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. *Analytical Chemistry,* 74**,** 4905-4912.

CEY, E. E., RUDOLPH, D.L., ARAVENA, R., PARKIN, G. 1999. Role of the riparian zone in controlling the distribution and fate of agricultural nitrogen near a small stream in southern Ontario. *Journal of Contaminant Hydrology,* 37**,** 45-67.

CHAMBERS, B. & DAMPNEY, P. 2009. Nitrogen efficiency and ammonia emissions from urea-based and ammonium nitrate fertilisers. *Proceedings - International Fertiliser Society***,** 20 pp.

CHAMBERS, B. J., SMITH, K. A. & PAIN, B. F. 2000. Strategies to encourage better use of nitrogen in animal manures. *Soil Use and Management,* 16**,** 157-166.

CHANG, C. C. Y., LANGSTON, J., RIGGS, M., CAMPBELL, D. H., SILVA, S. R. & KENDALL, C. 1999. A method for nitrate collection for δ15N and δ18O analysis from waters with low nitrate concentrations. *Canadian Journal of Fisheries and Aquatic Sciences,* 56**,** 1856-1864.

CHEN, J.-S., WANG, F.-Y. & HE, D.-W. 2006. Geochemistry of water quality of the Yellow River basin. *Dixue Qianyuan/ Earth Science Frontiers,* 13**,** 58-73.

CHILTON, P., WILLIAMS, A., MARKS, R., BUCKLEY, D., COLEBY, L. & GIBBS BRAND BIRD, M. 1997. Trends in nitrate concentrations in the Yorkshire Chalk aquifer. *British Geological Survey Report WD/97 C,* 8.

CHRISTENSEN, S. & TIEDJE, J. M. 1988. Sub-parts-per-billion nitrate method: use of an N2O-producing denitrifier to convert NO3− or 15NO3− to N2O. *Applied and environmental microbiology,* 54**,** 1409-1413.

COOPER, R. J., HAMA-AZIZ, Z., HISCOCK, K. M., LOVETT, A. A., DUGDALE, S. J., SÜNNENBERG, G., NOBLE, L., BEAMISH, J. & HOVESEN, P. 2017. Assessing the farm-scale impacts of cover crops and non-inversion tillage regimes on nutrient losses from an arable catchment. *Agriculture, Ecosystems & Environment,* 237**,** 181-193.

CRISS, R. E. 1999. *Principles of stable isotope distribution*, Oxford University Press on Demand.

DAKYNS, J. R. & FOX-STRANGWAYS, C. 1885. *The Geology of Bridlington Bay: (Explanation of Quartersheet 94 N. E.) (New Series Sheet 65)*, H.M. Stationery Office.

DARLING, W., BATH, A. & TALBOT, J. 2003. The O and H stable isotope composition of freshwaters in the British Isles. 2, surface waters and groundwater. *Hydrology and Earth System Sciences,* 7**,** 183-195.

DARLING, W. G. & BATH, A. H. 1988. A stable isotope study of recharge processes in the English Chalk. *Journal of Hydrology,* 101**,** 31-46.

DAVIES, D. & 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**,** 399-406.

DEFRA 2017. Farming rules for water - getting full value from fertilisers and soil. London: DEFRA.

DEFRA 2018. Using nitrate fertiliser in nitrate vulnerable zones. *In:* DEPARTMENT FOR ENVIRONMENT, F. R. A. (ed.).

DEFRA 2020a. British survey of fertiliser practice dataset *In:* DEFRA (ed.) *British survey of fertiliser practice.* London.

DEFRA 2020b. Consultation on reducing ammonia emissions from solid urea fertilisers. York: DEFRA.

DEFRA. 2020c. *Reducing ammonia emissions from urea fertlisers* [Online]. London: DEFRA. Available: https://consult.defra.gov.uk/air-quality-and-industrial-emissions/reducing-ammonia-emissions-from-urea-fertilisers/ [Accessed 21/08/2021 2021].

DEFRA. 2020d. *UKEAP PrecipNET: High Muffles* [Online]. Available: https://uk-air.defra.gov.uk/networks/network-info?view=ukeap [Accessed 22/1/22 2022].

DEFRA 2021. *Fertiliser Use On Farm Crops For Crop Year 2020,* London, DEFRA.

DELWICHE, C. C. & STEYN, P. L. 1970. Nitrogen isotope fractionation in soils and microbial reactions. *Environmental Science & Technology,* 4**,** 929-935.

DEPARTMENT OF ENVIRONMENT, T. A. T. R. 2000. The Water Supply (Water Quality) Regulations. *SI no. 3184.* United Kingdom: The Stationary Office Limited.

DEUTSCH, B. 2006. *Identification and quantification of diffuse nitrogen inputs by means of stable nitrogen and oxygen isotopes in nitrate: Investigations in the Warnow River system,* Rostock, Germany, Universität Rostock.

DI, H. J. & CAMERON, K. C. 2002. Nitrate leaching in temperate agroecosystems: sources, factors and mitigating strategies. *Nutrient Cycling in Agroecosystems,* 64**,** 237-256.

DICHRISTINA, T. J. 1992. Effects of nitrate and nitrite on dissimilatory iron reduction by Shewanella putrefaciens 200. *Journal of bacteriology,* 174**,** 1891-1896.

DOLE, M., LANE, G., RUDD, D. & ZAUKELIES, D. 1954. Isotopic composition of atmospheric oxygen and nitrogen. *Geochimica et Cosmochimica Acta,* 6**,** 65-78.

DRAYCOTT, A. P. & BUGG, S. M. 1982. Response by sugar beet to various amounts and times of application of sodium chloride fertilizer in relation to soil type. *The Journal of Agricultural Science,* 98**,** 579-592.

DYNAMCO 1994. Report on the Construction and Test Pumping of the Replacement Well D at Hartlake. West Kent Area: South East Water.

EDMUNDS, W., COOK, J., DARLING, W., KINNIBURGH, D., MILES, D., BATH, A., MORGAN-JONES, M. & ANDREWS, J. 1987. Baseline geochemical conditions in the Chalk aquifer, Berkshire, UK: a basis for groundwater quality management. *Applied Geochemistry,* 2**,** 251-274.

ELLIOT, T., ANDREWS, J. N. & EDMUNDS, W. M. 1999. Hydrochemical trends, palaeorecharge and groundwater ages in the fissured Chalk aquifer of the London and Berkshire Basins, UK. *Applied Geochemistry,* 14**,** 333-363.

ELLIOT, T., CHADHA, D. S. & YOUNGER, P. L. 2001. Water quality impacts and palaeohydrogeology in the Yorkshire Chalk aquifer, UK. *Quarterly journal of engineering geology and hydrogeology,* 34**,** 385-398.

ENVIRONMENT AGENCY 2019a. EASIMAP. Victoria, B.C., Canada: Latitude Geographics.

ENVIRONMENT AGENCY 2019b. Manual for the production of Groundwater Source Protection Zones. Bristol: Environment Agency.

ENVIRONMENT AGENCY 2020. Environment Agency water quality data archive. England: Environment Agency.

ERISMAN, J. W., SUTTON, M. A., GALLOWAY, J., KLIMONT, Z. & WINIWARTER, W. 2008. How a century of ammonia synthesis changed the world. *Nature Geoscience,* 1**,** 636.

EUROPEAN COMMISSION 1998. Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. *In:* ENVIRONMENT, D. C. F. T. (ed.).

EUROPEAN COMMISSION 2000a. *Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy.,* Brussels.

EUROPEAN COMMISSION 2000b. *'Nitrates' directive (91/676/EEC) : status and trends of aquatic environment and agricultural practice : development guide for member states' reports,* Luxembourg, Office for Official Publications of the European Comminuties.

EWING, M. C. & MAYON-WHITE, R. 1951. Cyanosis in infancy from nitrates in drinking-water. *Lancet***,** 931-4.

FENN, M. E., POTH, M. A. & ARBAUGH, M. J. J. T. S. W. J. 2002. A throughfall collection method using mixed bed ion exchange resin columns. 2**,** 122-130.

FERNÁNDEZ-PÉREZ, M., GARRIDO-HERRERA, F., GONZÁLEZ-PRADAS, E., VILLAFRANCA-SÁNCHEZ, M. & FLORES-CÉSPEDES, F. 2008. Lignin and ethylcellulose as polymers in controlled release formulations of urea. *Journal of applied polymer science,* 108**,** 3796-3803.

FOSTER, C. L. N. & TOPLEY, W. 1865. On the Superficial Deposits of the Valley of the Medway, with Remarks on the Denudation of the Weald. *Quarterly Journal of the Geological Society,* 21**,** 443-474.

FOSTER, S. & SMITH-CARINGTON, A. 1980. The interpretation of tritium in the Chalk unsaturated zone. *Journal of Hydrology,* 46**,** 343-364.

FOSTER, S. S. 1975. The Chalk groundwater tritium anomaly—a possible explanation. *Journal of Hydrology,* 25**,** 159-165.

FOSTER, S. S. & MILTON, V. A. 1976. *Hydrological basis for large-scale development of groundwater storage capacity in the East Yorkshire Chalk*, HM Stationery Office.

FOSTER, S. S. D. 1974. Groundwater storage—riverflow relations in a chalk catchment. *Journal of Hydrology,* 23**,** 299-311.

FOWLER, D., O'DONOGHUE, M., MULLER, J. B. A., SMITH, R. I., DRAGOSITS, U., SKIBA, U., SUTTON, M. A. & BRIMBLECOMBE, P.

2004. A Chronology of Nitrogen Deposition in the UK Between 1900 and 2000. *Water, Air, & Soil Pollution: Focus,* 4**,** 9-23.

GALE, I. N. & RUTTER, H. K. 2006. The Chalk aquifer of Yorkshire. *British Geological Survey Research Report.*

GALLOWAY, J. N. & COWLING, E. B. 2002. Reactive Nitrogen and The World: 200 Years of Change. *AMBIO: A Journal of the Human Environment,* 31**,** 64-71, 8.

GALLOWAY, J. N., COWLING, E. B., SEITZINGER, S. P. & SOCOLOW, R. H. 2002. Reactive Nitrogen: Too Much of a Good Thing? *AMBIO: A Journal of the Human Environment,* 31**,** 60-63, 4.

GARAY-BARAYAZARRA, G. & PURI, R. K. 2012. Review of transboundary air pollution (RoTAP): acidification, eutrophication, ground level ozone and heavy metals in the UK.

GARTEN JR, C. T. J. I. J. O. E. A. C. 1992. Nitrogen isotope composition of ammonium and nitrate in bulk precipitation and forest throughfall. 47**,** 33-45.

GEAKE, A. & FOSTER, S. 1989. Sequential isotope and solute profiling in the unsaturated zone of British Chalk. *Hydrological Sciences Journal,* 34**,** 79-95.

GOGU, R. C. & DASSARGUES, A. J. E. G. 2000. Current trends and future challenges in groundwater vulnerability assessment using overlay and index methods. *Environmental Geology,* 39**,** 549-559.

GONFIANTINI, R. 1984. Stable isotope reference samples for geochemical and hydrological investigations. *Report of Advisory Group, Vienna*.

GONZÁLEZ, M., CEA, M., MEDINA, J., GONZÁLEZ, A., DIEZ, M., CARTES, P., MONREAL, C. & NAVIA, R. 2015. Evaluation of biodegradable polymers as encapsulating agents for the development of a urea controlled-release fertilizer using biochar as support material. *Science of the Total Environment,* 505**,** 446-453.

GOODDY, D., CLAY, J. & BOTTRELL, S. 2002. Redox-driven changes in porewater chemistry in the unsaturated zone of the chalk aquifer beneath unlined cattle slurry lagoons. *Applied geochemistry,* 17**,** 903-921.

GOODDY, D. C., WITHERS, P. J., MCDONALD, H. G. & CHILTON, P. J. 1998. Behaviour and impact of cow slurry beneath a storage lagoon: II. Chemical composition of chalk porewater after 18 years. *Water, Air, and Soil Pollution,* 107**,** 51-72.

GOSS, M., COLBOURN, P., HARRIS, G. & HOWSE, K. J. N. E. I. A. S. 1988. Leaching of nitrogen under autumn-sown crops and the effects of tillage. *In:* JENKINSON, D. & SMITH, K. (eds.) *Nitrogen efficiency in agricultural soils.* London, UK: Elsevier Applied Sciences.

GOULDING, K. W. T., BAILEY, N. J., BRADBURY, N. J., HARGREAVES, P., HOWE, M., MURPHY, D. V., POULTON, P. R. & WILLISON, T. W. 1998. Nitrogen deposition and its contribution to nitrogen cycling and associated soil processes. *New Phytologist,* 139**,** 49-58.

GOULDING, K. W. T., POULTON, P. R., WEBSTER, C. P. & HOWE, M. T. 2000. Nitrate leaching from the Broadbalk Wheat Experiment, Rothamsted, UK, as influenced by fertilizer and manure inputs and the weather. *Soil Use and Management,* 16**,** 244-250.

GREENBERG, E. P. & BECKER, G. E. 1977. Nitrous oxide as end product of denitrification by strains of fluorescent pseudomonads. *Canadian Journal of Microbiology,* 23**,** 903-907.

GREENWOOD, D., LEMAIRE, G., GOSSE, G., CRUZ, P., DRAYCOTT, A. & NEETESON, J. J. A. O. B. 1990. Decline in percentage N of C3 and C4 crops with increasing plant mass. 66**,** 425-436.

HAGEN, K. 1990. *Future of ammonium sulphate, co-and by-production,* York, UK, International Fertiliser Society.

HALLBERG, G. R. 1989. Nitrate in ground water in the United States. *Developments in agricultural and managed forest ecology.* Elsevier.

HAMPSHIRE COUNTY COUNCIL 2004. The real story behind local food production. Economic Development Office, Hampshire County Council.

HAMPSHIRE COUNTY COUNCIL, H. E. P. 2007. Hampshire Farming Study Review. Dreweatt Neate for Hampshire County Council and Hampshire Economic Partnership.

HANCOCK, J. 1993. The formation and diagenesis of chalk. *The Hydrogeology of the Chalk of North-West Europe. Clarendon Press, Oxford***,** 14-34.

HANCOCK, J. M. 1975. The petrology of the Chalk. *Proceedings of the Geologists' Association,* 86**,** 499-535.

HARTMANN, S., ODLING, N. E. & WEST, L. J. 2007. A multi-directional tracer test in the fractured Chalk aquifer of E. Yorkshire, UK. *Journal of Contaminant Hydrology,* 94**,** 315-331.

HAWKESFORD, M. J. & RICHE, A. B. 2020. Impacts of G x E x M on Nitrogen Use Efficiency in Wheat and Future Prospects. *Frontiers in Plant Science,* 11.

HAYES, J. M. 2004. An Introduction to Isotopic Calculations. Available: https://www.whoi.edu/cms/files/jhayes/2005/9/IsoCalcs30Sept04_5183.pdf [Accessed 18/12/2019].

HAYFIELD, C. & WAGNER, P. 1995. From dolines to dewponds: a study of water supplies on the Yorkshire Wolds. *Landscape History,* 17**,** 49-64.

HEADWORTH, H. 1978. Hydrogeological characteristics of artesian boreholes in the Chalk of Hampshire. *Quarterly Journal of Engineering Geology and Hydrogeology,* 11**,** 139-144.

HEADWORTH, H., KEATING, T. & PACKMAN, M. 1982. Evidence for a shallow highly-permeable zone in the Chalk of Hampshire, UK. *Journal of Hydrology,* 55**,** 93-112.

HEATON, T. H. 1986. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review. *Chemical Geology: Isotope Geoscience Section,* 59**,** 87-102.

HEM, J. D. 1992. Study and Interpretation of the Chemical Characteristics of Natural Water. *US Geological Survey Water-Supply,* 2254.

HICKEY, P. 2019. Protecting chalk streams. Available from: https://environmentagency.blog.gov.uk/2019/07/19/protecting-chalk-streams/ [Accessed 10/05/2021 2021].

HILTON, J., O'HARE, M., BOWES, M. J. & JONES, J. I. 2006. How green is my river? A new paradigm of eutrophication in rivers. *Science of the Total Environment,* 365**,** 66-83.

HOFMAN, G. & CLEEMPUT, O. 2004. Soil and Plant Nitrogen. *International Fertilizer Industry Association, Paris*.

HÖGBERG, P. 1997. Tansley Review No. 95 15N natural abundance in soil-plant systems. *New Phytologist,* 137**,** 179-203.

HØJBERG, O., JOHANSEN, H. S. & SØRENSEN, J. 1994. Determination of 15N Abundance in Nanogram Pools of NO3- and NO2- by Denitrification Bioassay and Mass Spectrometry. *Applied and Environmental Microbiology,* 60**,** 2467-2472.

HOLMAN, I. P., PALMER, R. C., BELLAMY, P. H. & HOLLIS, J. M. 2005. Validation of an intrinsic groundwater pollution vulnerability methodology using a national nitrate database. *Hydrogeology Journal,* 13**,** 665-674.

HOWARD, K. 1985. Denitrification in a major limestone aquifer. *Journal of Hydrology,* 76**,** 265-280.

HOWE, S. 2019. Woodgarston nutrient data. Berwick, UK: South East Water.

HOWE, S., SWALES, A., WOODWARD, J., EARL, G., STYLES, T. & WILKINSON, D. 2017. National Environment Programme Hartlake Scheme 6SED10001. Berwick, UK: South East Water.

HUBBARD, R. K., NEWTON, G. L. & HILL, G. M. 2004. Water quality and the grazing animal. *Journal of Animal Science,* 82**,** E255-E263.

HUBER, B., BERNASCONI, S. M., LUSTER, J. & PANNATIER, E. G. 2011. A new isolation procedure of nitrate from freshwater for nitrogen and oxygen isotope analysis. *Rapid Communications in Mass Spectrometry,* 25**,** 3056-3062.

HUGGINS, J. & REGANOLD, B. 2008. No-till: the quiet revolution. *Scientific American,* 299**,** 70-77.

HUT, G. 1987. Consultants' group meeting on stable isotope reference samples for geochemical and hydrological investigations. Vienna, Austria: International Atomic Energy Agency.

IGS/SWA 1979. Hydrogeological Map of Hampshire and the Isle of Wight, Scale 1: 100,000. Institute of Geological Sciences/Southern Water Authority London.

IPNI. Nutrient Source Specifics: Diammonium Phosphate. Available: http://ipni.net/publication/nss.nsf/0/66D92CC07C016FA7852579AF00766CBD/$FILE/NSS-17%20Diammonium%20Phosphate.pdf.

IPNI. Nutrient Source Specifics: Monoammonium Phosphate. Available: https://www.ipni.net/publication/nss.nsf/0/2F200FA9C8C946F0852579AF00762904/$FILE/NSS-09%20Monoammonium%20Phosphate.pdf [Accessed 01/05/2020].

IRWIN, J. G., CAMPBELL, G. & VINCENT, K. 2002. Trends in sulphate and nitrate wet deposition over the United Kingdom: 1986–1999. *Atmospheric Environment,* 36**,** 2867-2879.

JAYASINGHA, P., PITAWALA, A. & DHARMAGUNAWARDHANA, H. 2013. Fate of urea fertilizers in sandy aquifers: laboratory and field case study from Kalpitiya, Sri Lanka. *Journal of the National Science Foundation of Sri Lanka,* 41.

JUKES-BROWNE, A. 1880. II.—The Subdivisions of the Chalk. *Geological Magazine,* 7**,** 248-257.

JUNK, G. & SVEC, H. J. 1958. The absolute abundance of the nitrogen isotopes in the atmosphere and compressed gas from various sources. *Geochimica et Cosmochimica Acta,* 14**,** 234-243.

KANAZAWA, K., MIYAJI, N., KUSABA, T., BAN, K., HAYAKAWA, Y. & HATANO, R. 1999. Groundwater pollution by cattle slurry stored in unlined lagoon. *Japan Agricultural Research Quarterly,* 33**,** 7-14.

KANEKO, M. & POULSON, S. R. 2013. The rate of oxygen isotope exchange between nitrate and water. *Geochimica et Cosmochimica Acta,* 118**,** 148-156.

KEIM, D. M., WEST, L. J. & ODLING, N. E. 2012. Convergent flow in unsaturated fractured chalk. *Vadose Zone Journal,* 11.

KENDALL, C. 1998. Chapter 16 - Tracing Nitrogen Sources and Cycling in Catchments. *In:* KENDALL, C. & MCDONNELL, J. J. (eds.) *Isotope Tracers in Catchment Hydrology.* Amsterdam: Elsevier.

KENDALL, C. & ARAVENA, R. 2000. Nitrate Isotopes in Groundwater Systems. *In:* COOK, P. G. & HERCZEG, A. L. (eds.) *Environmental Tracers in Subsurface Hydrology.* Boston, MA: Springer US.

KENDALL, C. & CALDWELL, E. A. 1998. Fundamentals of isotope geochemistry. *Isotope tracers in catchment hydrology.* Elsevier.

KIM, K. S., KIM, J. S., HWANG, I. M., JEONG, I. S., KHAN, N., LEE, S. I., JEON, D. B., SONG, Y. H. & KIM, K. S. 2013. Application of stable isotope ratio analysis for origin authentication of pork. *Food Science of Animal Resources,* 33**,** 39-44.

KIMURA, M. 2013. Testing methods for fertilizers. *Incorporated Administrative Agency*.

KING, B. J., SIDDIQI, M. Y. & GLASS, A. D. J. P. P. 1992. Studies of the Uptake of Nitrate in Barley: V. Estimation of Root Cytoplasmic Nitrate Concentration Using Nitrate Reductase Activity—Implications for Nitrate Influx. 99**,** 1582-1589.

KIRCHMANN, H., JOHNSTON, A. E. J. & BERGSTRÖM, L. F. 2002. Possibilities for Reducing Nitrate Leaching from Agricultural Land. *AMBIO: A Journal of the Human Environment,* 31**,** 404-408, 5.

KNAPP, M. F. 2005. Diffuse pollution threats to groundwater: a UK water company perspective. *Quarterly Journal of Engineering Geology and Hydrogeology,* 38**,** 39-51.

KNUTSSON, G. 1994. Acidification effects on groundwater-prognosis of the risks for the future. *IAHS PUBLICATION***,** 3-3.

KOHL, D. H., SHEARER, G. B. & COMMONER, B. 1971. Fertilizer nitrogen: contribution to nitrate in surface water in a corn belt watershed. *Science,* 174**,** 1331-1334.

KREITLER, C. W. 1975. Determining the source of nitrate in ground water by nitrogen isotope studies. *Virtual Landscapes of Texas*.

KREITLER, C. W. 1979. Nitrogen-isotope ratio studies of soils and groundwater nitrate from alluvial fan aquifers in Texas. *Journal of Hydrology,* 42**,** 147-170.

KROOPNICK, P. & CRAIG, H. 1972. Atmospheric oxygen: isotopic composition and solubility fractionation. *Science,* 175**,** 54-55.

KRUG, E. C. & WINSTANLEY, D. 2002. The need for comprehensive and consistent treatment of the nitrogen cycle in nitrogen cycling and mass balance studies: I. Terrestrial nitrogen cycle. *Science of The Total Environment,* 293**,** 1-29.

LEE, C., HRISTOV, A. N., CASSIDY, T. & HEYLER, K. 2011. Nitrogen isotope fractionation and origin of ammonia nitrogen volatilized from cattle manure in simulated storage. *Atmosphere,* 2**,** 256-270.

LETOLLE, R. 1980. Nitrogen-15 in the natural environment. *Nitrogen-15 in the natural environment.***,** 407-433.

LEVALLOIS, P. & PHANEUF, D. 1994. [Contamination of drinking water by nitrates: analysis of health risks]. *Canadian journal of public health = Revue canadienne de sante publique,* 85**,** 192-196.

LI, S.-L., LIU, C.-Q., LI, J., LIU, X., CHETELAT, B., WANG, B. & WANG, F. 2010. Assessment of the sources of nitrate in the Changjiang River, China using a nitrogen and oxygen isotopic approach. *Environmental Science & Technology,* 44**,** 1573-1578.

LIMBRICK, K. J. 2003. Baseline nitrate concentration in groundwater of the Chalk in south Dorset, UK. *Science of The Total Environment,* 314-316**,** 89-98.

LIU, C.-Q., LI, S.-L., LANG, Y.-C. & XIAO, H.-Y. 2006. Using δ15N- and δ18O-Values To Identify Nitrate Sources in Karst Ground Water, Guiyang, Southwest China. *Environmental Science & Technology,* 40**,** 6928-6933.

MACDONALD, A., BREWERTON, L. & ALLEN, D. 1998. Evidence for rapid groundwater flow and karst-type behaviour in the Chalk of southern England. *Geological Society, London, Special Publications,* 130**,** 95-106.

MACDONALD, A., POULTON, P., HOWE, M., GOULDING, K. & POWLSON, D. 2005. The use of cover crops in cereal-based cropping systems to control nitrate leaching in SE England. *Plant and Soil,* 273**,** 355-373.

MACDONALD, A. J., POWLSON, D. S., POULTON, P. R. & JENKINSON, D. S. 1989. Unused fertiliser nitrogen in arable soils—its contribution to nitrate leaching. *Journal of the Science of Food and Agriculture,* 46**,** 407-419.

MACDONALD, A. M. & ALLEN, D. J. 2001. Aquifer properties of the Chalk of England. *Quarterly Journal of Engineering Geology and Hydrogeology,* 34**,** 371-384.

MAINSTONE, C. P. & PARR, W. 2002. Phosphorus in rivers—ecology and management. *Science of the Total Environment,* 282**,** 25-47.

MARIOTTI, A., GERMON, J. C., HUBERT, P., KAISER, P., LETOLLE, R., TARDIEUX, A. & TARDIEUX, P. 1981. Experimental determination of nitrogen kinetic isotope fractionation: Some principles; illustration for the denitrification and nitrification processes. *Plant and Soil,* 62**,** 413-430.

MARIOTTI, A., LANDREAU, A. & SIMON, B. 1988. 15N isotope biogeochemistry and natural denitrification process in groundwater: Application to the chalk aquifer of northern France. *Geochimica et Cosmochimica Acta,* 52**,** 1869-1878.

MAYER, B., BOLLWERK, S. M., MANSFELDT, T., HÜTTER, B. & VEIZER, J. 2001. The oxygen isotope composition of nitrate generated by nitrification in acid forest floors. *Geochimica et Cosmochimica Acta,* 65**,** 2743-2756.

MCILVIN, M. R. & ALTABET, M. A. 2005. Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater. *Analytical Chemistry,* 77**,** 5589-5595.

MCMILLAN, L. A., RIVETT, M. O., TELLAM, J. H., DUMBLE, P. & SHARP, H. 2014. Influence of vertical flows in wells on groundwater sampling. *Journal of contaminant hydrology,* 169**,** 50-61.

MCSHERRY, J. 2022. Dual stable isotope analysis of nitrogen and oxygen in nitrate in groundwater from Northern Province Chalk in Yorkshire, UK. NERC EDS National Geoscience Data Centre.

MCSHERRY, J. E., THREADGOULD, H., LANCASTER, A. 2019. Haisthorpe and Kilham catchment investigation. Leeds: Environment Agency.

MEDICI, G., BAJÁK, P., WEST, L., CHAPMAN, P. & BANWART, S. 2020. DOC and nitrate fluxes from farmland; impact on a dolostone aquifer KCZ. *Journal of Hydrology***,** 125658.

MELLANDER, P.-E., JORDAN, P., WALL, D. P., MELLAND, A. R., MEEHAN, R., KELLY, C. & SHORTLE, G. 2012. Delivery and impact bypass in a karst aquifer with high phosphorus source and pathway potential. *Water research,* 46**,** 2225-2236.

MENGIS, M., SCHIF, S. L., HARRIS, M., ENGLISH, M. C., ARAVENA, R., ELGOOD, R. J. & MACLEAN, A. 1999. Multiple Geochemical and

Isotopic Approaches for Assessing Ground Water NO3− Elimination in a Riparian Zone. *Ground Water,* 37**,** 448-457.

MENGIS, M., WALTHER, U., BERNASCONI, S. M. & WEHRLI, B. 2001. Limitations of using δ18O for the source identification of nitrate in agricultural soils. *Environmental science & technology,* 35**,** 1840-1844.

MING, X., GROVES, C., WU, X., CHANG, L., ZHENG, Y. & YANG, P. 2020. Nitrate migration and transformations in groundwater quantified by dual nitrate isotopes and hydrochemistry in a karst World Heritage site. *Science of The Total Environment,* 735**,** 138907.

MORTIMORE, R. & WOOD, C. 1986. The distribution of flint in the English Chalk, with particular reference to the 'Brandon Flint Series' and the high Turonian flint maximum. *The scientific study of flint and chert***,** 7-20.

NATELHOFFER, K. J. & FRY, B. 1988. Controls on Natural Nitrogen-15 and Carbon-13 Abundances in Forest Soil Organic Matter. *Soil Science Society of America Journal,* 52**,** 1633-1640.

NESTLER, A., BERGLUND, M., ACCOE, F., DUTA, S., XUE, D., BOECKX, P. & TAYLOR, P. 2011. Isotopes for improved management of nitrate pollution in aqueous resources: review of surface water field studies. *Environmental Science and Pollution Research,* 18**,** 519-533.

NOELLSCH, A., MOTAVALLI, P., NELSON, K. & KITCHEN, N. 2009. Corn response to conventional and slow-release nitrogen fertilizers across a claypan landscape. *Agronomy Journal,* 101**,** 607-614.

O'NEIL, J. R. 1986. Theoretical and experimental aspects of isotopic fractionation. *In:* JOHN W. VALLEY, H. P. T. A. J. R. O. N. (ed.) *Stable Isotopes in High Temperature Geological Processes.* Berlin, Germany: De Gruyter.

OLLEROS, T. 1983. Kinetische isotopeneffekte der arginase-und nitratreduktase-reaktion: Ein beitrag zur aufklärung der entsprechenden reaktionsmechanismen. *Diss. Tech. Univ. Mfinchen Weihenstephan, 158pp*.

PANNO, S. V., HACKLEY, K. C., HWANG, H. H. & KELLY, W. R. 2001. Determination of the sources of nitrate contamination in karst springs using isotopic and chemical indicators. *Chemical geology,* 179**,** 113-128.

PARNELL, A. C., INGER, R., BEARHOP, S. & JACKSON, A. L. 2010. Source partitioning using stable isotopes: coping with too much variation. *PloS one,* 5**,** e9672.

POWLSON, D., HART, P., POULTON, P., JOHNSTON, A. & JENKINSON, D. 1992. Influence of soil type, crop management and weather on the recovery of 15N-labelled fertilizer applied to winter wheat in spring. *The Journal of Agricultural Science,* 118**,** 83-100.

POWLSON, D. S. 1993. Understanding the soil nitrogen cycle. *Soil Use and Management,* 9**,** 86-93.

POWLSON, D. S., ADDISCOTT, T. M., BENJAMIN, N., CASSMAN, K. G., DE KOK, T. M., VAN GRINSVEN, H., L'HIRONDEL, J. L., AVERY, A. A. & VAN KESSEL, C. 2008. When does nitrate become a risk for humans? *J Environ Qual,* 37**,** 291-5.

POWLSON, D. S., PRUDEN, T. L. G., JOHNSTON, A. E. & JENKINSON, D. S. 1986. The nitrogen cycle in the Broadbalk Wheat Experiment: recovery and losses of 15N-labelled fertilizer applied in spring and inputs of nitrogen from the atmosphere. *The Journal of Agricultural Science,* 107**,** 591-609.

PRASAD, R., RAJALE, G. & LAKHDIVE, B. 1971. Nitrification retarders and slow-release nitrogen fertilizers. *Advances in Agronomy.* Elsevier.

PRICE, M. 1987. Fluid flow in the Chalk of England. *Geological Society, London, Special Publications,* 34**,** 141-156.

PRICE, M., DOWNING, R. & EDMUNDS, W. 1993. The Chalk as an aquifer. *The hydrogeology of the Chalk of north-west Europe***,** 35-58.

RAUN, W. R. & JOHNSON, G. V. 1999. Improving Nitrogen Use Efficiency for Cereal Production. *Agronomy Journal,* 91**,** 357-363.

RIVETT, M. O., BUSS, S. R., MORGAN, P., SMITH, J. W. & BEMMENT, C. D. 2008. Nitrate attenuation in groundwater: a review of biogeochemical controlling processes. *Water research,* 42**,** 4215-4232.

ROBINSON, D. 2001. δ15N as an integrator of the nitrogen cycle. *J Trends in ecology and evolution,* 16**,** 153-162.

RYABENKO, E. 2013. Stable isotope methods for the study of the nitrogen cycle. *In:* ZAMBIANCHI, E. (ed.) *Topics in Oceanography.* BoD – Books on Demand.

SEBILO, M., MAYER, B., NICOLARDOT, B., PINAY, G. & MARIOTTI, A. 2013. Long-term fate of nitrate fertilizer in agricultural soils. *Proceedings of the National Academy of Sciences,* 110**,** 18185-18189.

SHRIMALI, M. & SINGH, K. P. 2001. New methods of nitrate removal from water. *Environmental Pollution,* 112**,** 351-359.

SIGMAN, D. M., CASCIOTTI, K. L., ANDREANI, M., BARFORD, C., GALANTER, M. & BÖHLKE, J. 2001. A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. *Analytical chemistry,* 73**,** 4145-4153.

SILVA, S., KENDALL, C., WILKISON, D., ZIEGLER, A., CHANG, C. C. & AVANZINO, R. 2000. A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios. *Journal of hydrology,* 228**,** 22-36.

SIMKIN, S. M., LEWIS, D. N., WEATHERS, K. C., LOVETT, G. M., SCHWARZ, K. J. W., AIR, & POLLUTION, S. 2004. Determination of Sulfate, Nitrate, and Chloride in Throughfall using Ion-Exchange Resins. 153**,** 343-354.

SMEDLEY, P., NEUMANN, I. & FARRELL, R. 2004. Baseline report series. 10, the Chalk aquifer of Yorkshire and North Humberside. Keyworth, UK: British Geological Survey.

SMITH, D. & RICHARDS, H. Selected environmental studies using radioactive tracers. Proceedings of IAEA Symposium ‘Peaceful Uses of Atomic Energy, 1972. 467-480.

SMITH, D. B., WEARN, P. L., RICHARDS, H. J. & ROWE, P. C. 1970. Water movement in the unsaturated zone of high and low permeability strata by measuring natural tritium. *Proc. Syrup. Isotope Hydrology***,** 73-87.

SMITH, K., BECKWITH, C., CHALMERS, A. & JACKSON, D. 2002. Nitrate leaching following autumn and winter application of animal manures to grassland. *Soil Use and Management,* 18**,** 428-434.

SMITH, R. L., CEAZAN, M. L. & BROOKS, M. H. 1994. Autotrophic, Hydrogen-Oxidizing, Denitrifying Bacteria in Groundwater, Potential Agents for Bioremediation of Nitrate Contamination. *Applied and Environmental Microbiology,* 60**,** 1949-1955.

SOUTH EAST WATER 2019a. Hartlake GWQ Data. *In:* WATER, S. E. (ed.).

SOUTH EAST WATER 2019b. Woodgarston GWQ Masterfile. *In:* WATER, S. E. (ed.). Snodland, Kent.

SOUTHERN WATER AUTHORITY 1979. Itchen Groundwater Regulation Scheme; Final Report on the Candover Pilot Scheme. *In:* AUTHORITY, S. W. (ed.). Hampshire: Southern Water Authority.

STORR, T., SIMMONS, R. W. & HANNAM, J. A. 2019. A UK survey of the use and management of cover crops. *Annals of Applied Biology,* 174**,** 179-189.

STUART, M. & SMEDLEY, P. 2009. Baseline groundwater chemistry: the Chalk aquifer of Hampshire. Keyworth, UK: British Geological Survey.

STUART, M. E., CHILTON, P. J., KINNIBURGH, D. G. & COOPER, D. M. 2007. Screening for long-term trends in groundwater nitrate monitoring data. *Quarterly Journal of Engineering Geology and Hydrogeology,* 40**,** 361-376.

SWEENEY, R., LIU, K. & KAPLAN, I. 1978. Oceanic nitrogen isotopes and their uses in determining the source of sedimentary nitrogen. *Stable isotopes in the earth sciences.*

THAPA, R., MIRSKY, S. B. & TULLY, K. L. 2018. Cover Crops Reduce Nitrate Leaching in Agroecosystems:A Global Meta-Analysis. *Journal of Environmental Quality,* 47**,** 1400-1411.

THOMAS, M. 1961. River terraces and drainage development in the Reading area. *Proceedings of the Geologists' Association,* 72**,** 415-IN8.

TIREZ, K., BRUSTEN, W., WIDORY, D., PETELET, E., BREGNOT, A., XUE, D., BOECKX, P. & BRONDERS, J. 2010. Boron isotope ratio (δ11B) measurements in Water Framework Directive monitoring programs: comparison between double focusing sector field ICP and thermal ionization mass spectrometry. *Journal of Analytical Atomic Spectrometry,* 25**,** 964-974.

TODD, D. 1980. *Groundwater Hydrology,* New York, USA, John Wiley & Sons.

TRENKEL, M. E. 1997. *Controlled-release and stabilized fertilizers in agriculture*, International Fertilizer Industry Association Paris.

UKRI. 1964. *Borehole log for HARSPF* [Online]. Available: http://scans.bgs.ac.uk/sobi_scans/boreholes/610016/images/12557267.html [Accessed 25/03/2021].

USDA NRCS 2011. Carbon to Nitrogen Ratios in Cropping Systems. Greensboro, NC: USDA Natural Resources Conservation Service East National Technology Support Center.

VAN DAM, D., HEIL, G., HEIJNE, B. & BOBBINK, R. J. E. P. 1991. Throughfall below grassland canopies: a comparison of conventional and ion exchange methods. 73**,** 85-99.

VAN GRINSVEN, H. J. M., WARD, M. H., BENJAMIN, N. & DE KOK, T. M. 2006. Does the evidence about health risks associated with nitrate ingestion warrant an increase of the nitrate standard for drinking water? *Environmental Health,* 5**,** 26.

VENGOSH, A., HEUMANN, K., JURASKE, S. & KASHER, R. 1994. Boron isotope application for tracing sources of contamination in groundwater. *Environmental Science & Technology,* 28**,** 1968-1974.

VENKITESWARAN, J., BOECKX, P. & GOODDY, D. 2019. Towards a global interpretation of dual nitrate isotopes in surface waters. *Journal of Hydrology X,* 4**,** 100037.

VITÒRIA, L., GRANDIA, F. & SOLER, A. Evolution of the chemical (NH4) and isotopic (d15N–NH4) composition of pig manure stored in an experimental pit. International Atomic Energy Agency (Ed.), Isotope

Hydrology and Integrated Water Resources Management. Conf. Symp. Papers, Vienna, 2004. 260-261.

VITÒRIA, L., SOLER, A., CANALS, À. & OTERO, N. 2008. Environmental isotopes (N, S, C, O, D) to determine natural attenuation processes in nitrate contaminated waters: example of Osona (NE Spain). *Applied Geochemistry,* 23**,** 3597-3611.

VITOUSEK, P. M., ABER, J. D., HOWARTH, R. W., LIKENS, G. E., MATSON, P. A., SCHINDLER, D. W., SCHLESINGER, W. H. & TILMAN, D. G. 1997. Human alteration of the global nitrogen cycle: sources and consequences. *Ecological Applications,* 7**,** 737-750.

VITOUSEK, P. M. & MATSON, P. A. 1993. Agriculture, the global nitrogen cycle, and trace gas flux. *Biogeochemistry of global change.* Springer.

WANG, L., BUTCHER, A. S., STUART, M. E., GOODDY, D. C. & BLOOMFIELD, J. P. 2013. The nitrate time bomb: a numerical way to investigate nitrate storage and lag time in the unsaturated zone. *Environmental Geochemistry and Health,* 35**,** 667-681.

WANG, L., STUART, M. E., BLOOMFIELD, J. P., BUTCHER, A. S., GOODDY, D. C., MCKENZIE, A. A., LEWIS, M. A. & WILLIAMS, A. T. 2012. Prediction of the arrival of peak nitrate concentrations at the water table at the regional scale in Great Britain. *Hydrological Processes,* 26**,** 226-239.

WARD, M. H., DEKOK, T. M., LEVALLOIS, P., BRENDER, J., GULIS, G., NOLAN, B. T. & VANDERSLICE, J. 2005. Workgroup Report: Drinking-Water Nitrate and Health-Recent Findings and Research Needs. *Environmental Health Perspectives,* 113**,** 1607-1614.

WARD, R., CHADHA, D., BREWERTON, L. & ALDRICK, J. 1998. A tracer investigation of groundwater protection zones around Kilham PWS well, East Yorkshire. Keyworth, UK: British Geological Survey.

WARD, R. & WILLIAMS, A. 1995. A tracer test in the Chalk near Kilham, North Yorkshire. . Keyworth, UK: British Geological Survey.

WASSENAAR, L. I. 1995. Evaluation of the origin and fate of nitrate in the Abbotsford Aquifer using the isotopes of 15N and 18O in NO3−. *Applied Geochemistry,* 10**,** 391-405.

WATER RESOURCES BOARD 1972. The hydrogeology of the London Basin with special reference to artificial recharge. WRB, Reading.

WELLINGS, S. & BELL, J. 1982. Physical controls of water movement in the unsaturated zone. *Quarterly Journal of Engineering Geology and Hydrogeology,* 15**,** 235-241.

WELLINGS, S. R. & COOPER, J. D. 1983. The variability of recharge of the English Chalk aquifer. *Agricultural Water Management,* 6**,** 243-253.

WELLS, N. S., BAISDEN, W. T. & CLOUGH, T. J. 2015. Ammonia volatilisation is not the dominant factor in determining the soil nitrate isotopic composition of pasture systems. *Agriculture, Ecosystems & Environment,* 199**,** 290-300.

WHITMORE, A. P., BRADBURY, N. J. & JOHNSON, P. A. 1992. Potential contribution of ploughed grassland to nitrate leaching. *Agriculture, Ecosystems & Environment,* 39**,** 221-233.

WIDORY, D., PETELET-GIRAUD, E., NÉGREL, P. & LADOUCHE, B. 2005. Tracking the Sources of Nitrate in Groundwater Using Coupled Nitrogen and Boron Isotopes: A Synthesis. *Environmental Science & Technology,* 39**,** 539-548.

WILKINSON, D., CEREDA, S., MASON, D. & STYLES, T. 2017. National Environment Programme Woodgarston Scheme SED0005. Snodland, UK: South East Water.

WOOD, C. & SMITH, E. 1978. Lithostratigraphical classification of the chalk in North Yorkshire, Humberside and Lincolnshire. *Proceedings of the Yorkshire Geological Society,* 42**,** 263-287.

WORTMANN, C. S. & SHAPIRO, C. A. 2012. Composting manure and other organic materials. Lincoln, Nebraska: University of Nebraska.

XIAOYU, N., YUEJIN, W., ZHENGYAN, W., LIN, W., GUANNAN, Q. & LIXIANG, Y. 2013. A novel slow-release urea fertiliser: Physical and chemical analysis of its structure and study of its release mechanism. *Biosystems engineering,* 115**,** 274-282.

XUE, D., BOTTE, J., DE BAETS, B., ACCOE, F., NESTLER, A., TAYLOR, P., VAN CLEEMPUT, O., BERGLUND, M. & BOECKX, P. 2009. Present limitations and future prospects of stable isotope methods for nitrate source identification in surface- and groundwater. *Water Research,* 43**,** 1159-1170.

YANG, P., WANG, Y., WU, X., CHANG, L., HAM, B., SONG, L. & GROVES, C. 2020. Nitrate sources and biogeochemical processes in karst underground rivers impacted by different anthropogenic input characteristics. *Environmental Pollution,* 265**,** 114835.

YARA. n.d. *Sugar beet - nutritional summary* [Online]. Grimsby. Available: https://www.yara.co.uk/crop-nutrition/sugar-beet/sugar-beet-nutritional-summary/ [Accessed 22/1/22 2022].

YOUNGER, P. & ELLIOT, T. 1995. Chalk fracture system characteristics: implications for flow and solute transport. *Quarterly Journal of Engineering Geology and Hydrogeology,* 28**,** S39-S50.

YOUNGER, P. L. 1989. Devensian periglacial influences on the development of spatially variable permeability in the Chalk of southeast England. *Quarterly Journal of Engineering Geology and Hydrogeology,* 22**,** 343-354.

YUE, F.-J., LI, S.-L., LIU, C.-Q., ZHAO, Z.-Q. & DING, H. 2017. Tracing nitrate sources with dual isotopes and long term monitoring of nitrogen species in the Yellow River, China. *Scientific Reports,* 7**,** 8537.

YUNG, Y. L. & MCELROY, M. B. 1979. Fixation of Nitrogen in the Prebiotic Atmosphere. *Science,* 203**,** 1002-1004.

ZAIDMAN, M. D., MIDDLETON, R. T., WEST, L. J. & BINLEY, A. M. 1999. Geophysical investigation of unsaturated zone transport in the Chalk in Yorkshire. *Quarterly Journal of Engineering Geology and Hydrogeology,* 32**,** 185-198.

ZHANG, L.-J. & WEN, Z.-C. 2009. Discussion on Silicate Weathering in the Huanghe Drainage Basin [J]. *Periodical of Ocean University of China,* 5.

ZHANG, Q. & WANG, H. 2020. Assessment of sources and transformation of nitrate in the alluvial-pluvial fan region of north China using a multi-isotope approach. *Journal of Environmental Sciences,* 89**,** 9-22.

ZHANG, X., DAVIDSON, E. A., MAUZERALL, D. L., SEARCHINGER, T. D., DUMAS, P. & SHEN, Y. 2015. Managing nitrogen for sustainable development. *Nature,* 528**,** 51-59.

ZHENG, T., LIANG, Y., YE, S. & HE, Z. 2009. Superabsorbent hydrogels as carriers for the controlled-release of urea: Experiments and a mathematical model describing the release rate. *Biosystems Engineering,* 102**,** 44-50.

Appendix 1: Comparison of the Northern Province Chalk catchments with Yue et al. (2017)

Creating a comparison between the nitrate to chloride ratios in this study and those presented in Yue et al. (2017) aids in providing the context to variations and thus aids understanding. Yue et al. studied the Yellow River (or Huang He), which spans 5364 km from the Plateau of Tibet in Western China to the North Pacific Ocean in the East and crosses temperate-arid and semi-arid climates. It earned its name from the great volumes of sediment that spill into the river from the Loess Plateau in the middle reaches. Artificial fertilisers are applied twice a year in agricultural zones (Jul and Oct) but manure is applied intermittently all year round. Other potential nitrogenous inputs come from urban areas supporting approximately three million people, in addition to three large cities of over seven million people each, adjacent to the main stream or major tributaries.

Chloride concentrations in the Yellow River are most commonly 80-90 mg/L, ranging from 4.4 to 586 mg/L (Yue et al., 2017) whereas for the Yorkshire Wolds data in this study the highest frequency is lower at 30-40 mg/L, ranging from 13.3 to 449 mg/L (Figure A1.1). The Wolds, however, has generally higher nitrate concentrations (the most frequent concentration is 12-14 mg/L, range 3-46 mg/L), whereas Yue mostly commonly found a nitrate concentration of 2-4 mg/L (range 0.5-7 mg/L, outlier at 9 mg/L). The nitrate to chloride ratio in this study is higher than presented by Yue et al. (2017). The higher nitrate concentrations in the Wolds are likely the cause of this difference (Figure A1.2), implying that the Wolds has a higher pollutant load than Yue's study area. The higher chloride concentrations in Yue's study is likely the result of higher levels of evapotranspiration, induced by the climate. Evaporation of approximately 1100 mm/year has been recorded in the Yellow River basin (Chen et al., 2006, Zhang and Wen, 2009), as compared to 500 to 560 mm/year recorded for the Ouse in Yorkshire (Bouraoui et al., 2002). The occasional high chloride concentration identified in the Wolds were all from one site (400G0106-SHW); as discussed in Section 5.2.3.

The Yellow River basin, like the Yorkshire Wolds, exhibits seasonal variation in rainfall and temperatures. Yue et al. reported two periods of high flow, the first in March to May caused by snowmelt and the second from May to October due to rainfall. Inorganic fertilisers are applied primarily in the second period of high discharge. This is unlike the scenario in the UK where current practice is to avoid fertiliser applications when rain is expected. In the Yellow River basin nitrate-N and chloride concentrations tend to be higher in low flow season than the high flow season. This could be due to lack of dilution of sewage discharges (δ^{15}N was heavier in low flow, suggestive of sewage influence).

It is important to note that Yue et al. investigated surface water, while the focus of this study is groundwater, thus the end members Yue et al. used for analysis of the nitrate to chloride ratio likely cannot describe all eventualities for groundwater. Fewer biological processes affect groundwater and the hydrological models governing each water body are very different. Nonetheless analysing nitrate to chloride ratios, in addition to dual stable isotope analysis of nitrogen and oxygen in nitrate, can aid conceptualisation of nitrate sources in both catchments.

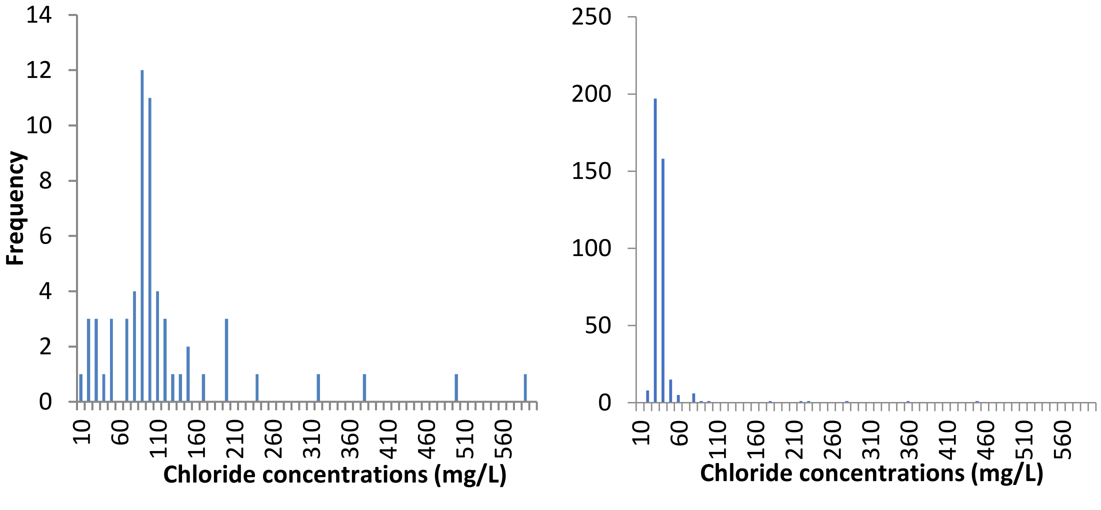

Figure A1.1: Frequency of chloride concentrations from (a) Yue et al. and (b) Yorkshire Wolds data. Note different scale on y-axis as more there are more data points for the current study than Yue's Yellow River study (2017).

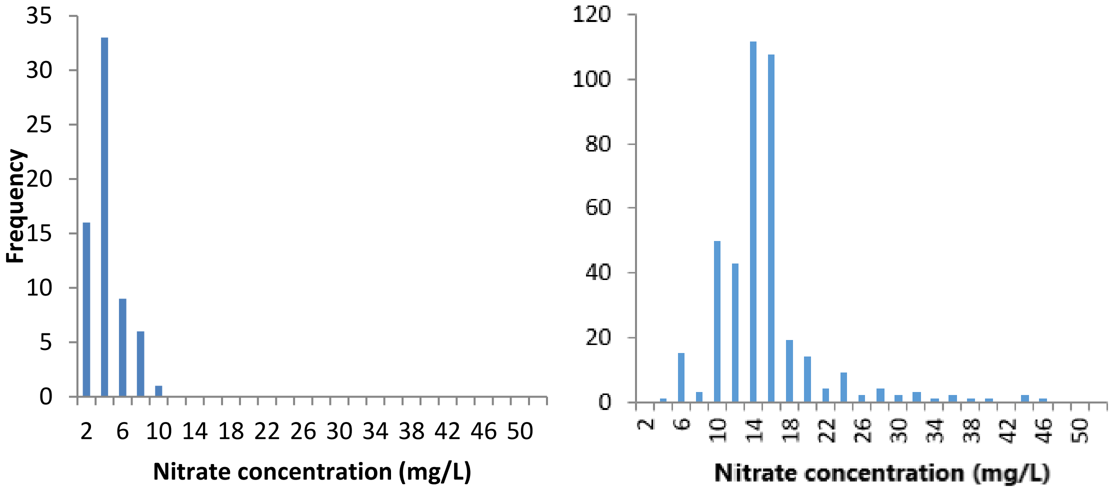

Figure A1.2: Frequency of NO_3 concentrations from (a) Yue et al. and (b) Yorkshire Wolds data. Note different scale on the y-axis as there are far more Wolds data points than Yue.

Appendix 2: Dual stable isotope data

Catchment	Name	Date sampled	Average sample $\delta^{18}O$ (‰ VSMOW)	Average sample $\delta^{15}N$ (‰ AIR)
Kilham	BEL	17/03/2017	4.57	1.86
Kilham	40001257-BRA	17/03/2017	4.49	1.88
Kilham	400F0012-BRO	12/02/2016	3.55	4.53
Kilham	400F0012-BRO	22/03/2016	3.29	4.67
Kilham	400G0082-DOF	13/11/2015	10.21	10.08
Kilham	400G0082-DOF	13/11/2015	8.78	9.98
Kilham	400G0082-DOF	14/01/2016	2.74	9.52
Kilham	400G0082-DOF	04/02/2016	4.28	10.74
Kilham	400G0082-DOF	14/04/2016	4.41	10.48
Kilham	400G0110-FWF	13/11/2015	4.77	6.09
Kilham	400G0110-FWF	14/01/2016	1.07	3.33
Kilham	400G0110-FWF	11/02/2016	2.20	4.06
Kilham	400G0110-FWF	14/04/2016	2.48	4.06
Kilham	400G0093-KIL	27/11/2017	1.77	4.65
Kilham	400F0018-KOB	13/11/2015	2.13	4.65
Kilham	400F0018-KOB	17/12/2015	1.77	10.53
Kilham	400F0018-KOB	14/01/2016	1.12	4.58
Kilham	400F0018-KOB	14/04/2016	3.44	5.13
Kilham	49200297-KSS	01/2016	6.29	4.68
Kilham	49200297-KSS	14/04/2016	2.95	4.82
Kilham	49200298-KSP	01/2016	4.62	5.47
Kilham	400G0093-KIL	02/2018	2.62	5.16
Kilham	400G0027-MHF	13/11/2015	5.54	4.82
Kilham	400G0027-MHF	13/11/2015	1.97	4.81
Kilham	400G0027-MHF	14/01/2016	2.42	4.62
Kilham	400G0027-MHF	14/04/2016	2.68	4.46
Kilham	400G0109-MOF	13/11/2015	2.95	3.84
Kilham	400G0109-MOF	13/11/2015	2.26	3.90
Kilham	400G0109-MOF	14/01/2016	3.24	4.48
Kilham	400G0109-MOF	12/02/2016	5.48	4.56
Kilham	400G0109-MOF	14/04/2016	3.24	4.86
Kilham	400G0107-OCG	13/11/2015	2.18	-1.60
Kilham	400G0107-OCG	17/12/2015	1.44	4.46
Kilham	400G0107-OCG	14/01/2016	6.60	4.94

Catchment	Name	Date sampled	Average sample δ^{18}O (‰ VSMOW)	Average sample δ^{15}N (‰ AIR)
Kilham	400G0107-OCG	11/02/2016	6.80	4.05
Kilham	400G0107-OCG	14/04/2016	2.87	4.95
Kilham	400G0022-PTH	14/11/2018	1.54	5.05
Kilham	400G0108-ROO	13/11/2015	8.25	3.93
Kilham	400G0108-ROO	14/01/2016	2.24	5.20
Kilham	400G0108-ROO	12/02/2016	2.24	5.11
Kilham	400G0108-ROO	14/04/2016	2.49	5.44
Kilham	400G0106-SHW	13/11/2015	2.56	4.90
Kilham	400G0106-SHW	17/12/2015	1.96	4.69
Kilham	400G0106-SHW	14/01/2016	6.78	5.82
Kilham	400G0106-SHW	11/02/2016	3.41	5.19
Kilham	400G0106-SHW	14/04/2016	4.04	5.11
Kilham	400G0023-SWA	14/01/2016	2.75	4.74
Kilham	400G0023-SWA	11/02/2016	5.98	3.86
Kilham	400G0023-SWA	13/11/2015	5.20	4.40
Kilham	400G0023-SWA	04/2016	6.19	4.49
Kilham	400G0023-SWA	14/04/2016	3.42	3.86
Kilham	400G0105-WEA	17/12/2015	3.02	5.01
Kilham	400G0105-WEA	14/01/2016	1.55	4.98
Kilham	400G0105-WEA	14/04/2016	2.50	5.05
Kilham	400G0072-WES	13/11/2015	2.07	3.76
Kilham	400G0072-WES	17/12/2015	1.71	4.14
Kilham	400G0072-WES	14/01/2016	1.12	3.97
Kilham	400G0072-WES	11/02/2016	0.60	4.22
Kilham	400G0072-WES	14/04/2016	1.64	4.39
Kilham	400G0112-WIN	13/11/2015	5.69	3.49
Haisthorpe	400G0008-HUG	20/02/2018	2.1	4.0
Haisthorpe	400G0115-BAR	21/11/2017	1.1	4.7
Haisthorpe	400G0115-BAR	21/02/2018	1.9	4.9
Haisthorpe	400G0115-BAR	13/11/2018	1.1	4.7
Haisthorpe	400G0094-BR2	28/11/2017	1.3	6.0
Haisthorpe	400G0094-BR2	01/03/2018	2.1	5.5
Haisthorpe	400G0094-BR2	22/11/2018	1.3	5.2
Haisthorpe	400G0086-BA2	27/11/2017	1.6	5.4
Haisthorpe	400G0086-BA2	01/03/2018	3.3	6.1
Haisthorpe	400G0086-BA2	22/11/2018	1.7	5.5

Catchment	**Name**	**Date sampled**	**Average sample δ^{18}O (‰ VSMOW)**	**Average sample δ^{15}N (‰ AIR)**
Haisthorpe	400G0117-BFG	22/11/2017	1.1	5.3
Haisthorpe	400G0117-BFG	21/02/2018	3.1	5.8
Haisthorpe	400G0117-BFG	13/11/2018	1.2	4.9
Haisthorpe	400G0090-HAC	27/11/2017	2.0	5.5
Haisthorpe	400G0090-HAC	01/03/2018	1.9	5.4
Haisthorpe	400G0090-HAC	22/11/2018	1.5	5.4
Haisthorpe	400G0091-HAE	27/11/2017	1.1	4.7
Haisthorpe	400G0116-HOF	22/11/2017	1.6	6.1
Haisthorpe	400G0116-HOF	20/02/2018	3.2	6.3
Haisthorpe	400G0116-HOF	13/11/2018	2.6	6.9
Haisthorpe	400G0008-HUG	22/11/2017	1.0	4.0
Haisthorpe	400G0008-HUG	22/11/2017	1.0	4.1
Haisthorpe	400G0008-HUG	13/11/2018	1.5	4.1
Haisthorpe	400G0074-MGF	06/04/2016	2.99	5.41
Haisthorpe	400G0074-MGF	21/11/2017	1.0	5.2
Haisthorpe	400G0074-MGF	21/02/2018	2.4	5.1
Haisthorpe	400G0074-MGF	13/11/2018	1.2	5.3
Haisthorpe	400G0118-SDF	21/11/2017	0.9	4.4
Haisthorpe	400G0118-SDF	20/02/2018	3.0	4.7
Haisthorpe	400G0118-SDF	13/11/2018	1.4	4.8
Haisthorpe	400G0006-WHF	22/11/2017	1.0	5.2
Haisthorpe	400G0006-WHF	20/02/2018	1.8	5.1
Haisthorpe	400G0006-WHF	13/11/2018	1.4	4.7
Haisthorpe	400G0119-WWF	22/11/2017	0.7	4.6
Haisthorpe	400G0119-WWF	20/02/2018	1.5	4.7
Haisthorpe	400G0119-WWF	14/11/2018	0.8	4.5
Hartlake	HARA	12/11/2018	8.49	13.32
Hartlake	HARA	19/02/2019	6.50	10.96
Hartlake	HARA	20/05/2019	6.81	9.23
Hartlake	HARA	21/08/2019	7.05	10.28
Hartlake	HARC	12/11/2018	7.57	13.63
Hartlake	HARC	19/02/2019	9.94	11.53
Hartlake	HARC	21/08/2019	12.95	21.52
Hartlake	HAROB3	12/11/2018	4.72	7.08
Hartlake	HAROB3	19/02/2019	3.89	6.78
Hartlake	HAROB3	20/05/2019	4.40	7.08

Catchment	**Name**	**Date sampled**	**Average sample δ^{18}O (‰ VSMOW)**	**Average sample δ^{15}N (‰ AIR)**
Hartlake	HAROB3	21/08/2019	5.52	7.22
Woodgarston	WPBH1	30/11/2018	4.94	6.43
Woodgarston	WPBH1	13/02/2019	5.65	6.26
Woodgarston	WPBH1	16/05/2019	3.72	6.30
Woodgarston	WPBH1	19/08/2019	4.55	6.29
Woodgarston	WPBH2	30/11/2018	4.06	5.23
Woodgarston	WPBH2	13/02/2019	4.75	5.16
Woodgarston	WPBH2	16/05/2019	3.64	4.98
Woodgarston	WPBH2	19/08/2019	4.50	5.30
Woodgarston	WMals	21/11/2018	4.30	6.31
Woodgarston	WMals	13/02/2019	4.64	6.20
Woodgarston	WMals	16/05/2019	4.08	4.61
Woodgarston	WMals	19/08/2019	2.75	5.71
Woodgarston	WPit	21/11/2018	4.15	4.83
Woodgarston	WPit	13/02/2019	3.45	4.46
Woodgarston	WPit	16/05/2019	3.23	4.55
Woodgarston	WPit	19/08/2019	3.38	5.16