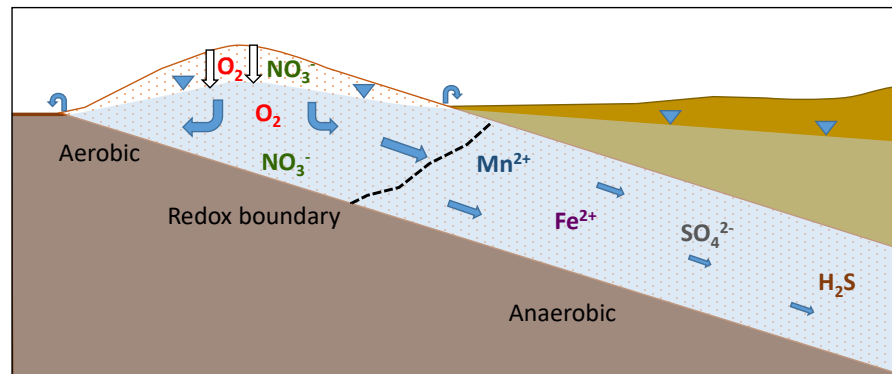




Review of denitrification potential in groundwater of England

Groundwater Programme

Open Report OR/18/011



BRITISH GEOLOGICAL SURVEY

GROUNDWATER PROGRAMME

OPEN REPORT OR/18/011

Review of denitrification potential in groundwater of England

M E Stuart

The National Grid and other
Ordnance Survey data © Crown
Copyright and database rights
2018. Ordnance Survey Licence
No. 100021290 EUL.

Keywords

Aquifer; nitrate; redox; chalk;
Sherwood Sandstone;
Lincolnshire Limestone.

Cover

Conceptual model of
denitrification in confined zones

Bibliographical reference

STUART, M E. 2018. Review of
denitrification potential in
groundwater of England. *British
Geological Survey Open Report*,
OR/18/011. 61pp.

Copyright in materials derived
from the British Geological
Survey's work is owned by
UK Research and Innovation
(UKRI) and/or the authority that
commissioned the work. You
may not copy or adapt this
publication without first
obtaining permission. Contact the
BGS Intellectual Property Rights
Section, British Geological
Survey, Keyworth,
e-mail ipr@bgs.ac.uk. You may
quote extracts of a reasonable
length without prior permission,
provided a full acknowledgement
is given of the source of the
extract.

Maps and diagrams in this book
use topography based on
Ordnance Survey mapping.

BRITISH GEOLOGICAL SURVEY

The full range of our publications is available from BGS shops at Nottingham, Edinburgh, London and Cardiff (Welsh publications only) see contact details below or shop online at www.geologyshop.com

The London Information Office also maintains a reference collection of BGS publications, including maps, for consultation.

We publish an annual catalogue of our maps and other publications; this catalogue is available online or from any of the BGS shops.

The British Geological Survey carries out the geological survey of Great Britain and Northern Ireland (the latter as an agency service for the government of Northern Ireland), and of the surrounding continental shelf, as well as basic research projects. It also undertakes programmes of technical aid in geology in developing countries.

The British Geological Survey is a component body of UK Research and Innovation.

British Geological Survey offices

**Environmental Science Centre, Keyworth, Nottingham
NG12 5GG**

Tel 0115 936 3100

BGS Central Enquiries Desk

Tel 0115 936 3143

email enquiries@bgs.ac.uk

BGS Sales

Tel 0115 936 3241

email sales@bgs.ac.uk

**The Lyell Centre, Research Avenue South, Edinburgh
EH14 4AP**

Tel 0131 667 1000

email scotsales@bgs.ac.uk

Natural History Museum, Cromwell Road, London SW7 5BD

Tel 020 7589 4090

Tel 020 7942 5344/45 email bgs_london@bgs.ac.uk

**Cardiff University, Main Building, Park Place, Cardiff
CF10 3AT**

Tel 029 2167 4280

**Maclean Building, Crowmarsh Gifford, Wallingford
OX10 8BB**

Tel 01491 838800

**Geological Survey of Northern Ireland, Department of
Enterprise, Trade & Investment, Dundonald House, Upper
Newtownards Road, Ballymiscaw, Belfast, BT4 3SB**

Tel 01232 666595

www.bgs.ac.uk/gsni/

**Natural Environment Research Council, Polaris House,
North Star Avenue, Swindon SN2 1EU**

Tel 01793 411500

Fax 01793 411501

www.nerc.ac.uk

**UK Research and Innovation, Polaris House, Swindon
SN2 1FL**

Tel 01793 444000

www.ukri.org

Website www.bgs.ac.uk

Shop online at www.geologyshop.com

Foreword

This report is the first published product of a study by the British Geological Survey (BGS) on denitrification potential in groundwater of England. It was co-funded by the Environment Agency and BGS.

Acknowledgements

The author is grateful to Alwyn Hart, Natalie Philips, Polly Wallis and Tim Besien from the Environment Agency who provided useful review comments.

Contents

Foreword	i
Acknowledgements	i
Contents	ii
Summary	v
1 Introduction	1
1.1 Background.....	1
1.2 Aims and approach	1
1.3 Structure.....	1
2 Processes, measurements and indicators	2
2.1 Denitrification process.....	2
2.2 Other N cycle processes.....	4
2.3 Measurements of denitrification	5
2.4 Other potential indicators	7
2.5 Regional/national approaches	12
3 Typical settings	14
3.1 Aquifers	14
3.2 Riparian zones, hyporheic zones and floodplains.....	15
4 UK aquifers	21
4.1 Literature.....	21
4.2 Baseline data	26
4.3 Environment Agency Groundwater Monitoring Review reports	33
5 Construction of a UK denitrification map	36
5.1 Approach.....	36
5.2 Construction of map	37
Appendix 1 Summary of Environment Agency Groundwater Quality monitoring reports	
38	
References	42

FIGURES

Figure 2.1	The sequence of reaction zones developing as groundwater moves along flow pathways from recharge to confined conditions (after Shand et al., 2007) (from Appelo and Postma, 2005)	3
Figure 2.2	Schematic redox boundary in the Lincolnshire Limestone aquifer (after Griffiths et al., 2006).....	7
Figure 2.3	Areas of England and Wales where the NVZ designation process showed that the nitrate source term was significant (pressure score >3) but nitrate concentrations measured in groundwater were not high leading to an intermediate risk (score is between 3 and 8) (Stuart et al., 2017)	10
Figure 2.4	Annual average measured concentrations of (a) aerosol NO ₃ ⁻ and (b) volume-weighted concentrations of NO ₃ ⁻ in precipitation in 2008 (from RoTAP, 2012).....	11
Figure 3.1	Flow paths in the riparian zone (from Stuart and Lapworth (2011)).....	16
Figure 3.2	Simplified longitudinal cross-sectional view of a stream HZ with commonly observed microbially mediated pathways for nitrate transformations (modified from Zarnetske et al., 2011b Labile dissolved organic carbon supply limits hyporheic denitrification. Journal of Geophysical Research: Biogeosciences, Vol. 116, G04036. https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2011JG001730)....	18
Figure 3.3	Schematic cross-section illustrating processes controlling the distribution of N species in the Chalk of north-east Norfolk (simplified from Feast et al. (1998)).....	20
Figure 4.1	Variation in redox sensitive parameters and species across the Lincolnshire Limestone aquifer. Samples plotted across down-dip sections in the north (red) centre (green) and south (blue) of the study area to illustrate geochemical evolution as groundwater moves downgradient from the outcrop area (from Griffiths et al. (2006)). The corresponding edge of the outcrop area for each section across the aquifer is represented as a dashed line	27
Figure 5.1	Map component layers	37
Figure 5.2	Overlay of data layers	37

TABLES

Table 2.1	Electron acceptor sequence for oxidation of organic carbon (after Edmunds et al., 1984; Lovley and Chapelle, 1995; Rivett et al., 2008).....	3
Table 2.2	Methods for assessing denitrification in soils, sediments and water (after Groffman et al., 2006).....	6
Table 2.3	Redox processes in order of decreasing energy yield and criteria for assigning redox status (in Stuart and Lapworth (2011) after Lyngkilde and Christensen (1992) and Bjerg et al. (1995)).....	8
Table 2.4	Threshold concentrations for identifying redox processes in regional aquifer systems (after McMahon and Chapelle, 2008).....	8
Table 4.1	Ranges of literature values of chemical characteristics of redox zones identified in UK aquifers (all in mg/L except Fe and Mn (µg/L) and Eh (mV))	25

Table 4.2	Comparison of median data from unconfined and confined zones from baseline data (N species as N).....	28
Table 4.3	Summary data from Environment Agency Groundwater Quality Monitoring Reports where confined conditions are identified within the area	34

Summary

An understanding of the fate of nitrate in groundwater is vital for managing risks associated with nitrate pollution, and to safeguard groundwater supplies and groundwater-dependent surface waters. One of the main measures to control nitrate is the designation of nitrate vulnerable zones (NVZs). Recent review of the designation process in England has highlighted that in some locations measured groundwater nitrate concentrations were not as high as expected. A possible reason for this is that the nitrate is being transformed through denitrification. This review forms the first stage in the development of a tiered approach to assessing denitrification potential across groundwater in England (and Wales) using three main lines of evidence: groundwater quality indicators, geological mapping of confined aquifers and superficial deposits which can influence redox status and a mass balance approach

Denitrification can take place either heterotrophically, where microorganisms use a sequence of ions as electron acceptors to enable the consumption of organic carbon, generating intermediates or by-products that can be used as process indicators, or autotrophically where pyrite is used as an electron donor and is oxidised to sulphate. Other nitrogen cycle processes which can produce some similar intermediates can include dissimilatory nitrate reduction directly to ammonia (DRNA), assimilatory nitrate reduction to organic nitrogen, anaerobic ammonium oxidation (anammox) and nitrification.

Demonstrating and quantifying denitrification is difficult, requiring specialist measurements and with different problems in environment and scale. Stable isotopic methods have been the most widely applied. Only a mass balance approach appears to be feasible in groundwater without new specialist measurements

Groundwater quality indicators

A sequence of threshold concentrations for identifying redox processes have already been developed by other workers and these combined with existing monitoring data should form the basis for identifying areas where denitrification is either likely or unlikely. Groundwater quality from the Environment Agency strategic monitoring network includes nitrogen species, TON or NO_3^- , NO_2^- and NH_4^+ and other parameters that could be indicative of reducing conditions, dissolved O_2 , dissolved organic C, Mn^{2+} , Fe^{2+} , SO_4^{2-} and Eh.

Mapping of confined zones and key superficial deposits

Many studies have confirmed the presence of redox boundaries in confined aquifers. Literature data on low redox zones indicating denitrification has focussed predominantly on the confined zones of major aquifers. In England and Wales, these have included the Chalk, Permo-Triassic sandstone and the Lincolnshire Limestone. The boundary occurs some distance down dip from the start of confinement depending on the aquifer flow regime. Both BGS/Environment Agency Baseline reports and the Environment Agency's groundwater quality reports contain qualitative statements about denitrification in areas of confined aquifers. These include the limestones of the Corallian, the Great and Inferior Oolites, the Zechstein Group (Magnesian Limestone) and the Carboniferous, and the sandstones of the Palaeogene, Crag, Lower Greensand, Millstone Grit and the Old Red Sandstone. The confined zones of aquifers or groups of aquifers can be represented by defining aquifer subcrop from the BGS 3D model and applying a lower depth limit (conventionally 400 m).

Superficial deposits also have a role, both in confinement of underlying aquifers and as a source of organic rich infiltration. The hyporheic zone can also have a role and this needs to be taken into account in assessing the extent of denitrification potential. These can be represented from superficial cover mapping. Predisposing settings include were sediment thickness and

permeability, groundwater baseflow index as a measure of groundwater–stream connectivity, and sediment geochemistry.

Mass balance approach

In some areas, inputs of nitrogen do not appear to be reflected in current groundwater concentrations. Inputs could include applications to arable land, urban areas and aerial deposition. One example of this is the area defined during NVZ designation.

Each of these lines of evidence is likely to provide a partial picture of denitrification potential. A tiered approach will be developed to combine these into a useful format together with applicability and limitations for each type of evidence.

1 Introduction

1.1 BACKGROUND

An understanding of the fate of nitrate in groundwater is vital for managing risks associated with nitrate pollution, and to safeguard groundwater supplies and groundwater-dependent surface waters Rivett et al. (2008). In recognition of the risks and observed impacts, the European Commission introduced a directive to control the inputs of agricultural sources of nitrate to groundwater and surface water through the Nitrates Directive and the more recent Water Framework Directive. One of the main measures to control nitrate is the designation of nitrate vulnerable zones (NVZs). Recent review of the designation of NVZs in England has highlighted that in some locations measured groundwater nitrate concentrations were not as high as expected based on the model used. A possible reason for this is that the nitrate is being transformed through denitrification.

1.2 AIMS AND APPROACH

To develop a tiered approach to assessing denitrification potential across groundwater in England (and Wales) using literature and existing groundwater and other relevant data. It is proposed to use three main lines of evidence:

1. Literature data on documented low redox zones indicating denitrification. These are predominantly in the confined zones of major aquifers. Sources will include papers and other published material, such as the BGS/Environment Agency Baseline reports and the Environment Agency's groundwater quality reports.
2. Groundwater monitoring data. In the first instance, values from the Environment Agency strategic monitoring network will be used. This will include nitrogen species, TON or NO_3^- , NO_2^- and NH_4^+ . It will also include parameters that could be indicative of suitable reducing conditions, dissolved O_2 , dissolved organic C, Mn^{2+} , Fe^{2+} , SO_4^{2-} and Eh. These will also be used to attempt to delineate areas where widespread denitrification is unlikely.
3. Mass balance approaches. These will identify areas where inputs of N do not appear to be reflected in current groundwater concentrations. Inputs could include N applications to arable land and urban areas, and aerial deposition.

Each of these lines of evidence is likely to provide a partial picture of denitrification potential. A tiered approach will be developed to combine these into a useful format together with applicability and limitations for each type of evidence. The results will be related to the geological setting for both bedrock and superficial deposits.

1.3 STRUCTURE

This report addresses the first line of evidence. Section 2 provides a high-level review of denitrification processes, their measurement and parameters that could be used as potential indicators to be taken forwards to the evaluation of monitoring data. Section 3 reviews typical settings from the international literature and Section 4 reviews relevant data and estimates from the UK related to denitrification; this will include both published literature and Environment Agency and BGS reports. This will provide conceptual type settings in England where denitrification is likely to occur. Section 5 provides an approach to data requirements and construction of the map.

2 Processes, measurements and indicators

2.1 DENITRIFICATION PROCESS

Nitrogen is an essential nutrient for plant and animal growth, and is cycled in the natural environment in a complex series of biological and chemical processes (Hiscock et al., 1991). In groundwater, denitrification is the dominant nitrate (NO_3) attenuation process and becomes active where oxygen is depleted. In aerobic heterotrophic respiration, organic carbon is oxidized preferentially with the electron acceptor that supplies most energy to the microorganisms, namely free oxygen (O_2) (Rivett et al., 2008). With an excess of organic carbon, aerobic bacteria consume dissolved oxygen (DO) until it is depleted whereupon reduction of other electron acceptors becomes energetically favourable. Once DO is consumed, facultative anaerobes (bacteria capable of growing with or without O_2) use NO_3^- as an electron acceptor for anaerobic respiration, the denitrification process. The sequence of predominant terminal electron-accepting processes (TEAPs) was set out by Lovley and Chapelle (1995).

Denitrification is the reduction of NO_3^- normally carried out by anaerobic bacteria to form N species ultimately lost to the atmosphere. This process produces a series of intermediates, including the nitrite ion (NO_2^-), nitric oxide (NO) and nitrous oxide (N_2O), with the final step being the production of gaseous nitrogen (N_2). Denitrification is thus a dissimilatory NO_3 reduction process with N being lost from the groundwater system. These intermediaries have been used to demonstrate denitrification (Anderson et al., 2014; Bragan et al., 1997; Duff and Triska, 1990; Groffman et al., 1998; Li et al., 2013; Mühlherr and Hiscock, 1997, 1998). Isotopic fractionation has also been used (Granger et al., 2008).

HETEROTROPHIC DENITRIFICATION

There have been a number of reviews of groundwater denitrification in the UK context. Hiscock et al. (1991) reviewed the necessary environmental conditions for denitrification in groundwater and extended these to artificial denitrification. They stated that most denitrifying bacteria are heterotrophic and are able to utilize a wide range of carbon compounds (sugars, organic acids, amino acids) as electron sources. Nutrient requirements are further discussed by Champ et al. (1979) and Bitton and Gerba (1984). Historical evidence appeared to show that NO_3 reduction was not observed at concentrations above 0.2 mg/L (Skerman and MacRae, 1957). This did not take account of more modern concepts of small, protected niches (hotspots) which enable organisms to live in conditions different from the bulk conditions. A biofilm even just a few cells thick can provide enough cover to have an anaerobic layer in an ostensibly aerobic environment. Dependence on pH range and temperature are covered by Gauntlett and Craft (1979). However Rivett et al. (2008) concluded that the critical limiting factors are oxygen tension and electron donor concentration and availability. Variability in other environmental conditions such as NO_3 concentration, nutrient availability, pH, temperature, presence of toxins and microbial acclimation appears to be less important, exerting only secondary influences on denitrification rates. Korom (1992) included both denitrification and dissimilatory reduction to ammonia (DNRA) in their review of saturated zone processes. They concluded that natural denitrification can decrease NO_3 contamination in modern waters but that it was difficult to predict the rate.

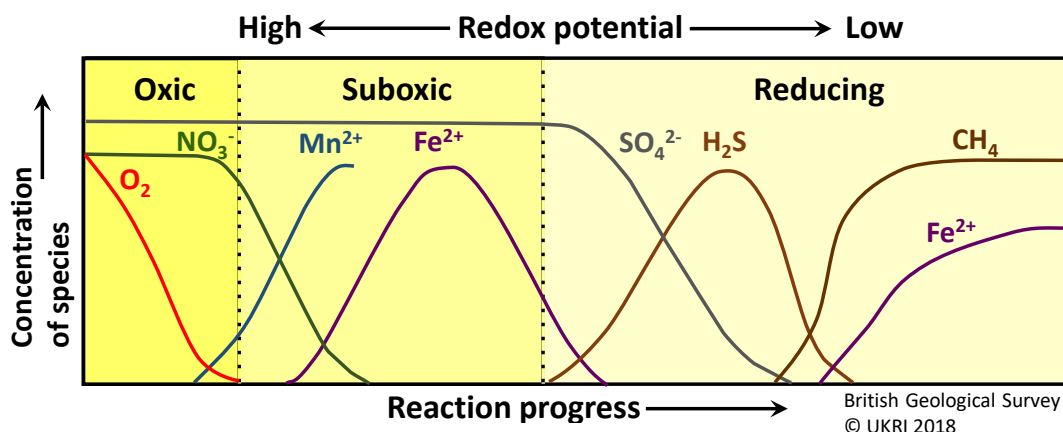


Figure 2.1 The sequence of reaction zones developing as groundwater moves along flow pathways from recharge to confined conditions (after Shand et al., 2007) (from Appelo and Postma, 2005)

Table 2.1 Electron acceptor sequence for oxidation of organic carbon (after Edmunds et al., 1984; Lovley and Chapelle, 1995; Rivett et al., 2008)

Electron acceptor	Initial species	Product	Process	ΔG kJ/eq	Relative energy yield	Solution Eh (mV)
Oxygen	O ₂	H ₂ O	Aerobic oxidation	-125 – -120	100	+334
Nitrate	NO ₃ ⁻	N ₂	Denitrification	-119 – -114	93	+231
		NH ₄	DNRA	-82		
Manganese	Mn ⁴⁺ sp.	Mn ²⁺ sp.	Manganese reduction	-81.3	87	+62
Iron	Fe ³⁺ sp.	Fe ²⁺ sp.	Iron reduction	-27.7	84	-468
Sulphate	SO ₄	HS ⁻	Sulphate reduction	-25	6	-699
Carbon dioxide	CO ₂	CH ₄	Methanogenesis	-23--22	3	-

After consumption of NO₃⁻ a further sequence of ions can be used as electron acceptors with decreasing energetic yields in a step-wise process. These include reduction of Mn⁴⁺ then Fe³⁺ to soluble oxidation states (Mn²⁺ and Fe²⁺ species) with increase in observed concentrations, reduction of sulphate (SO₄²⁻) to S species, and finally the reduction of carbon dioxide to methane (Figure 2.1 and Table 2.1). The presence or absence of these parameters can be used as indicators of low redox and therefore of denitrification potential (McMahon and Chapelle, 2008). This reaction sequence is commonly seen along groundwater flow lines (Edmunds et al., 1982; Edmunds et al., 1984) typically as aquifers become confined.

Most likely denitrifying organisms possess truncated pathways which require synergistic relationships among different denitrifying species to complete reduction to N₂ (Jones et al., 2013) and this can be the source of the accumulation of N₂O as a greenhouse gas (Müller et al., 2014). Seitzinger et al. (2006) argue that groundwater is an important location for denitrification due to long groundwater residence times, but the uncertainty is large.

AUTOTROPHIC DENITRIFICATION

Korom (1992) also discuss the denitrification process in the context of addition of NO_3^- to groundwater where Mn, Fe or SO_4^{2-} have already been reduced, where autotrophic denitrification may occur using the reduced inorganic compounds as electron donors. They found that groundwater containing Fe^{2+} did not contain any observable NO_3^- . Autotrophic denitrification coupled to sulphide or Fe oxidation has been proven for microbiological isolates ((Straub et al., 1996; Weber et al., 2006) but demonstrating this at the field-scale is more difficult. Nitrate reduction by oxidation of pyrite should lead to increased concentrations of SO_4^{2-} .

Schwientek et al. (2008) looked for evidence that denitrification could be regulated by pyrite oxidation. A combination of sulphur isotopes coupled with assessment of long (c 100 years) travel times indicated that this was likely to be at a very slow rate. Zhang et al. (2009) showed that NO_3^- removal from the groundwater below cultivated fields at Oostrum, Netherlands, correlated with SO_4^{2-} production, and the release of dissolved Fe^{2+} and pyrite-associated trace metals (e.g. As, Ni, Co and Zn). These results, and the presence of pyrite in the sediment matrix within the NO_3^- removal zone, indicated that denitrification coupled to pyrite oxidation (autotrophic denitrification) was a major process in the aquifer. A number of modelling studies also indicated that pyrite oxidation was a potential pathway (e.g. Wriedt and Rode, 2006). These processes via Fe or sulphur oxidation are termed chemoautotrophic denitrification (Burgin and Hamilton, 2007).

Jahangir et al. (2013) found a positive correlation between groundwater SO_4^{2-} concentration and denitrification rate and suggest that, due to low DOC in most groundwater environments, denitrification may well be autotrophic. A similar correlation with NH_4^+ was attributed to possible DRNA.

2.2 OTHER N CYCLE PROCESSES

Denitrification is only part of the nitrogen cycle and a number of other processes leading to the immobilisation of N or to the production of similar intermediate species may be operating. These include:

- *Dissimilatory nitrate reduction directly to NH_4^+ (DRNA)*. DRNA occurs under much the same conditions as denitrification, but is less commonly observed in practice. Compared to NO_3^- the resultant NH_4^+ is a more biologically available and less mobile form of inorganic N (Burgin and Hamilton, 2007). The partitioning of NO_3^- between denitrification and DNRA is believed to be controlled by the availability of organic matter: DNRA is the favoured process when NO_3^- (electron acceptor) supplies are limiting and denitrification is favoured when carbon (electron donor) supplies are limiting (Korom, 1992). There are two recognised DRNA pathways, fermentation of organic matter and autotrophic sulphur oxidation, where N_2 may be produced (Burgin and Hamilton, 2007).
- *Assimilatory nitrate reduction ($\text{NO}_3^- \Rightarrow$ organic N)*. In the presence of NH_4^+ , this is generally taken up preferentially from water by biomass. It can also be taken up by phreatophytes such as poplars or willows (Rivett et al., 2008).
- *Anaerobic ammonium oxidation (anammox) ($\text{NO}_2^- + \text{NH}_4^+ \Rightarrow \text{N}_2$)*. This mainly occurs in soils and in the marine environment and estuaries (Dalsgaard et al., 2005).
- *Nitrification ($\text{NH}_4^+ \Rightarrow \text{N}_2\text{O} \Rightarrow \text{NO}_2^-$ and NO_3^-)*. Buss et al. (2004) reviewed the attenuation of ammonium, although in the context of landfill leachate contamination, and showed this to be predominantly due to nitrification and to cation exchange predominantly on clay minerals. The presence of N_2O as an indicator of denitrification is not necessarily conclusive as it may form from partial nitrification of ammonium (De Groot et al., 1994; Kinniburgh et al., 1999).

- *Abiotic processes* Burgin and Hamilton (2007) review the relative importance of these processes for the removal of N and conclude that although relatively little is known, they may still be significant in the removal of up to 50% of NO₃ loading.

2.3 MEASUREMENTS OF DENITRIFICATION

Groffman et al. (2006) set out the available approaches to demonstrating and quantifying denitrification (Table 2.2). They conclude that this process is very difficult to measure with different problems in various environments and at different scales. They predicted that mass balance and stoichiometric approaches combined with point measurements would be likely to provide the greatest improvements to current understanding. The references provided in Table 2.2 were added from the groundwater literature during compilation of this report. These demonstrate that stable isotopic methods have been the most widely applied. Rivett et al. (2007) also describe some of these methods to confirm NO₃ attenuation occurrence. Of the methods shown in Table 2.2, only the mass balance approach appears to be feasible in groundwater without new specialist measurements.

2.3.1 Rates

There appear to be very few estimates of denitrification rates in groundwater. Korom (1992) tabulated a range of laboratory denitrification rates for aquifer samples in the range of 0.004 to 1.16 mgN/kg dry sediment/day and for aquifers of <LOD to 3.1 mgN/L/day. They also include half-lives of 1.2 to 2.1 years in sand and gravelly sand from Kölle et al. (1985) and Böttcher et al. (1989).

Tesoriero et al. (2000) investigated the rate and mechanisms of NO₃ removal in an unconfined sand and gravel aquifer using a series of well nests in the Abbotsford-Sumas aquifer on the west USA-Canadian border. Little or no denitrification was observed in the upland portions of the aquifer but a gradual redox gradient as water moved deeper into the aquifer was observed. A complete loss of NO₃ was observed and pyrite oxidation was considered to be the electron source. Denitrification rate estimates were based on mass balance calculations using NO₃ and excess N₂ coupled with groundwater travel times. Denitrification rates in the deep, upland portions of the aquifer were found to range from <0.01 to 0.14 mM of N per year; rates at the redox gradient along the shallow flow path range from 1.0 to 2.7 mM of N/year.

Zhang et al. (2009) estimated the rate of denitrification in the Oostrum study to be 0.6 mM NO₃/year for a 5-m section of depleted aquifer at the top of a well with NO₃ concentration of 3 mM in the lower sections.

Jahangir et al. (2013) measured in-situ groundwater denitrification rates in subsoil, at the bedrock interface and in bedrock at two sites in Ireland, grassland and arable, using an in-situ ‘push–pull’ method with ¹⁵N-labelled NO₃⁻. Measured groundwater denitrification rates ranged from 1.3 to 469.5 µg N/ kg/day. Exceptionally high denitrification rates observed at the bedrock interface at the grassland site (470±152 µg N /kg/day) suggest that deep groundwater can serve as substantial hotspots for NO₃⁻-N removal. However, denitrification rates at the other locations were low. Denitrification rates were negatively correlated with ambient DO, redox potential, permeability and NO₃⁻ (all p values, p<0.01) and positively correlated with SO₄²⁻ (p<0.05). A higher mean N₂O/(N₂O+N₂) ratios at an arable site (0.28) compared to a grassland site (0.10) revealed that the arable site had higher potential to indirect N₂O emissions.

Table 2.2 Methods for assessing denitrification in soils, sediments and water (after Groffman et al., 2006)

Method	Approach	Measurements	References
Acetylene-based methods	Inhibit the reduction of N ₂ O to N ₂	N ₂ O	Bragan et al. (1997); Groffman et al. (1999); Mühlherr and Hiscock (1997, 1998); Weymann et al. (2008)
¹⁵ N tracers	Addition of radio-labelled NO ₃	Isotope fractionation, or dilution, ¹⁵ N mass balance, direct measurement of ¹⁵ N-labelled gases	Christensen et al. (1990). Few recent references for groundwater
Direct N ₂ quantification	Direct estimation from soil	N ₂	Vogel et al. (1981); Wilson et al. (1990)
N ₂ :Ar quantification	Estimate excess N ₂	Needs precise MS measurements	Blicher-Mathiesen et al. (1998)
Mass balance approaches	Estimate by difference	Measure all other fluxes- generally whole catchment	Böhlke et al. (2002); Lindsey et al. (2003); Tesoriero et al. (2000)
Stoichiometric approaches	Uses constant C:N:P in organic matter to estimate N losses	Problems with surface water due to changes in C & P	Works for marine environment
Stable isotopes to measure isotopic fractionation	Use δ ¹⁵ N and δ ¹⁸ O (plus S and C isotopes)	Mass spectrometry	Aravena and Robertson (1998); Böhlke and Denver (1995); Böhlke et al. (2002); Böttcher et al. (1990); Chen and MacQuarrie (2005); Fukada et al. (2003); Kellman and Hillaire-Marcel (1998, 2003); Komor and Anderson (1993); Mariotti et al. (1988); Wilson et al. (1994)
In-situ gradients	Use environmental tracers as age indicators	CFCs, SF ₆ , ³ H, ¹⁴ C	Böhlke et al. (2002); Cook and Böhlke (2000)
Molecular approaches	Study microbial community	Functional genes in denitrification pathway- DNA probes, PCR	Barrett et al. (2013); Wakelin et al. (2011)

Keuskamp et al. (2012) attempted to model the extent of denitrification and N₂O production at the European scale using an improved version of the IMAGE model. They assumed a first order decay process with a range of half-lives for NO₃, based on lithology, texture and effective porosity. These ranged from 1 year for silici-clastic medium fine consolidated rocks (pyrite-bearing), 2 years for alluvial materials to 5 years for unconsolidated coarse sediments, based on the data from Korom, (2002) and Zessner et al. (2005). In all river basins modelled deep groundwater NO₃ outflow was much less than the outflow from shallow groundwater. Modelled N₂O production was very heterogeneous, with large regions having no groundwater and therefore short travel times or no deep groundwater, and therefore no denitrification or N₂O production expected.

2.4 OTHER POTENTIAL INDICATORS

2.4.1 Redox sequence ions

It is anticipated that there will be a sequence of redox changes as water migrates from upland recharge areas to lowland discharge areas under confined conditions. Champ et al. (1979) identified 3 zones O₂-NO₃, Fe-Mn, sulphide. Hiscock et al. (1991) showed change in redox potential is often accompanied by a sequential reduction in dissolved groundwater species which is cited as proof of denitrification.

This reaction sequence is commonly seen along groundwater flow lines (Edmunds et al., 1982; Edmunds et al., 1984) typically as aquifers become confined. Water at recharge is generally saturated with DO at the partial pressure of the atmosphere (10-12 mg/L depending upon barometric conditions). Passing through the soil and the unsaturated zone some of this O₂ will react as a result of microbiological processes and oxidation-reduction reactions. However, almost all water reaching the water table still contains several mg/L O₂. Geochemical and microbial reactions progressively remove the O₂ along flow lines. Once all the O₂ has reacted an abrupt change of water chemistry takes place (redox boundary). Down-gradient of the redox boundary, denitrification occurs and it is likely that Fe²⁺ concentrations will increase. Sulphate reduction and the production of sulphide (H₂S as S₂⁻ in solution) may also occur at greater depths (Figure 2.2).

Denitrification can also be important in shallow groundwater where recharge contains an elevated loading of organic carbon. (Smith et al., 1991; Spalding and Parrott, 1994; Zarnetske et al., 2011b). In their review of floodplain processes, Stuart and Lapworth (2011) tabulated a set of criteria characterising the redox zones (Table 2.3) based on earlier work. These used a series of indicators including the electron acceptors O₂, NO₃ and SO₄, intermediates NO₂ and N₂O and the solid phase acceptors Mn⁴ and Fe³, indicated by the presence of dissolved Mn and Fe, and eventually methane. The values shown in Table 2.3 were applied to landfill leachate plumes and some concentrations, particularly for Fe, are high.

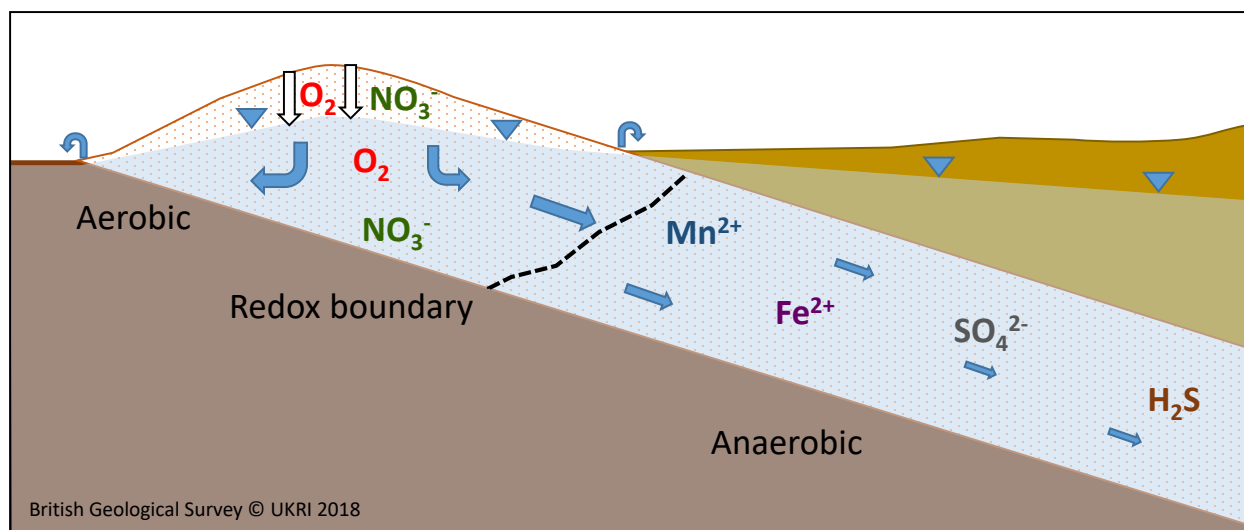


Figure 2.2 Schematic redox boundary in the Lincolnshire Limestone aquifer (after Griffiths et al., 2006)

Table 2.3 Redox processes in order of decreasing energy yield and criteria for assigning redox status (in Stuart and Lapworth (2011) after Lyngkilde and Christensen (1992) and Bjerg et al. (1995))

Respiration	Energy yielding process	Concentration									
		O ₂ mg/L	NO ₃ mgN/L	NO ₂ mgN/L	N ₂ O µg/L	NH ₄ mgN/L	Mn mg/L	Fe mg/L	S mg/L	SO ₄ mgS/L	CH ₄ mg/L
Aerobic	O ₂ reduction	>1	-	<0.1	-	<1.0	<0.2	<1.5	<0.1		<1
Anaerobic	NO ₃ ⁻ reduction	<1	-	>0.1	>1	-	<0.2	<10	<0.1		-
	Mn ⁴⁺ reduction	<1	<0.2	<0.1	<1	-	<5	<10	-	-	-
	Fe ³⁺ reduction	<1	<0.2	<0.1	<1	-	<5	>150	-	-	-
	SO ₄ ²⁻ reduction	<0.2	<0.2	<0.1	<1	-	<5	<150	>0.1		-
	Methano-genesis	<1	<0.2	<0.1	<1	-	<5	<150		<40	>25

Table 2.4 Threshold concentrations for identifying redox processes in regional aquifer systems (after McMahon and Chapelle, 2008)

Status	Redox process	Water quality criteria (mg/L)					Reference for criteria
		DO	NO ₃ ⁻	Mn ²⁺	Fe ²⁺	SO ₄ ²⁻	
Oxic	O ₂ reduction	≥0.5	-	<0.05	<0.1		Seitzinger et al. (2006); Tiedje (1988)
Suboxic		<0.5	>0.5	<0.05	<0.1		Further definition not possible
Anoxic	NO ₃ ⁻ reduction	<0.5	≤0.5	<0.05	<0.1		
	Mn ⁴⁺ reduction	<0.5	<0.5	≥0.05	<0.1		Chapelle and McMahon (1991); Chapelle et al. (1995); Christensen et al. (2000); Elliot et al. (1999); Murphy and Schramke. (1998); Plummer et al. (1990)
	Fe ³⁺ /SO ₄ ²⁻ reduction	<0.5	<0.5	-	≥0.1	≤0.5	Chapelle et al. (2002)
	Methano-genesis	<0.5	<0.5	-	≥0.1	<0.5	
Mixed		-	-	-			Criteria for more than one process are met

McMahon and Chapelle (2008) evaluated redox conditions in 15 principal aquifers across the USA. They used a series of indicators including the electron acceptors DO, NO₃ and SO₄, and the solid phase acceptors Mn⁴ and Fe³, indicated by the presence of dissolved Mn²⁺ and Fe²⁺ (Table 2.4). Parameters included were chosen because they were relatively inexpensive and easy to measure, and most of them were commonly measured in regional water quality assessments.

They recommended that other redox indicators, such as NH_4 , H_2S , CH_4 , and H_2 , should be measured whenever possible. An internally consistent set of threshold criteria was developed and applied to the aquifers using data from the NWQA Program. These were then related to both natural (As) and anthropogenic (NO_3 and VOCs) contaminant distribution. The redox conditions explained many of the observed water quality trends at the regional scale. Identification of zones of redox heterogeneity were also important for assessing the fate and transport of contaminants. This approach is similar to that of Lyngkilde and Christensen (1992) and Bjerg et al. (1995) above but uses lower concentrations.

Zhang et al. (2009) studied NO_3 removal from a sandy aquifer below cultivated fields and forested areas at Oostrum in the Netherlands. Nitrate loss correlated with SO_4 production, and increase in dissolved Fe^{2+} and pyrite-associated trace metals (e.g. As, Ni, Co and Zn) in a zone between 10 and 20 m deep. These results indicated that denitrification coupled to pyrite oxidation is a major process in the aquifer. Significant NO_3 loss coupled to SO_4 production was further confirmed by comparing historical estimates of regional SO_4 and NO_3 loadings to age-dated groundwater SO_4 and NO_3 concentrations, for the period 1950–2000. This highlights a warning against always anticipating SO_4 removal as redox decreases.

Lee et al. (2008) characterised the redox conditions in an arsenic-affected aquifer in the Lanyang Plain, Taiwan. Discriminant analysis was adopted to delineate three redox zones (oxidative, transitional and reductive zones) in different aquifers and yielded over 90% agreement with groundwater quality data. According to the DA results, the groundwater of the Lanyang plain was classified as Zone 1 (oxidizing zone) if $\text{DO} \geq 1$ mg/L or $\text{NO}_3 \geq 0.35$ mg/L, Zone 2 (transitional zone), if DO was between 0.3 and 1 mg/L or $\text{NO}_3 < 0.35$ mg/L and Zone 3 (reducing zone) if $\text{DO} < 0.3$ mg/L or $\text{HS} \geq 0.07$ mg/L.

2.4.2 Predisposing settings approach

Smith et al. (2009) proposed a classification scheme for pollutant attenuation at the groundwater-surface water interface/mixing zone. They assumed that a variety of factors influence the rate and magnitude of natural attenuation processes in the subsurface. These included contaminant-specific properties, such as structure, composition, sorption properties and recalcitrance, and environmental properties including sediment geochemistry, hydrochemistry, transport velocity and residence time in reactive zones. The primary properties included were sediment thickness and permeability (as a measure of relative residence time within the GW–SW interface), groundwater baseflow index as a measure of groundwater–stream connectivity, and sediment geochemistry using cation exchange capacity, the fraction of organic carbon (f_{oc}) and total inorganic carbon (TIC) to represent the retardation potential.

They postulated that in the case of denitrification the f_{oc} of the sediments may be used as a proxy measure of denitrification potential, on the assumption that denitrifying bacteria are ubiquitous in the environment and that f_{oc} is a reasonable indicator of redox conditions (Rivett et al., 2008). Where the f_{oc} value is high, anaerobic conditions conducive to denitrification are more likely to dominate. Thresholds were proposed as 3% organic carbon content along a riparian flow line based on work by Dahl et al. (2007) and Hoffman et al. (2000). The work was focussed on data collected under river baseflow conditions and analysis using national scale data and was related to surface water aquifer conditions.

2.4.3 Absence of predicted N

Denitrification can be inferred from the absence of groundwater concentrations which would be predicted from the nitrogen source term. Inputs could include N applications to arable land and urban areas, and aerial deposition.

NVZs

An example of this approach was produced by Stuart et al. (2017). Figure 2.3 uses data compiled for the NVZ designation process to highlight areas where N applications are high but groundwater concentrations do not reflect this and the overall risk is not high enough for NVZ designation. Areas where this may be due to a long travel time from the surface have been excluded by defining a travel time of <10 years.

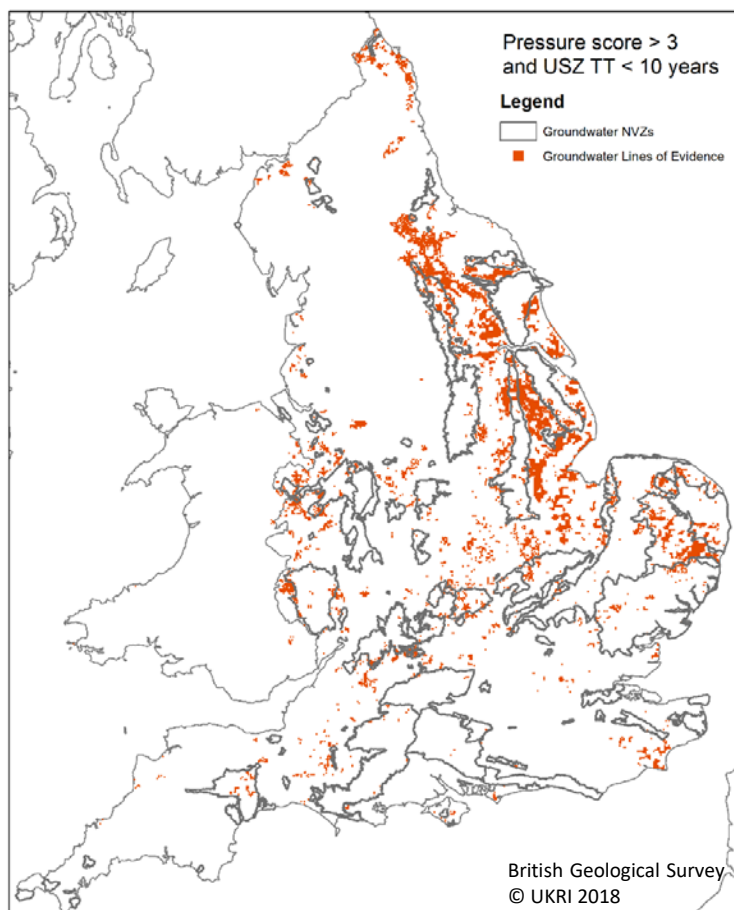


Figure 2.3 Areas of England and Wales where the NVZ designation process showed that the nitrate source term was significant (pressure score >3) but nitrate concentrations measured in groundwater were not high leading to an intermediate risk (score is between 3 and 8) (Stuart et al., 2017)

N IN RAINFALL

Nitrogen species in rainfall recharge has been estimated for the individual areas covered by the BGS Baseline Survey. These reports indicate that evaporated rainfall, concentrations multiplied by 3, is likely to contain between 0.75 and 5.5 mg/L of N as NO_3 and NH_4 . Assuming this is all oxidised to NO_3 , this would represent between 3.2 and 23.5 mg/L in recharge. Lowest concentrations were measured in North Yorkshire and Wessex, and in other sites in the west and southwest and, and the highest in Derbyshire and the North Downs. Areas in central England tended to have about 2-3 mg/L N in evaporated rainfall. Highest concentrations of NO_3 were estimated for the North Downs, Derbyshire Carboniferous Limestone and sites up the east coast. Highest concentrations of NH_4 were also estimated in East Anglia.

Clearly, this simple pattern does not allow for a number of processes that could intercept N including runoff and plant up-take.

RoTAP (2012) have also modelled nitrogen concentrations in rainfall. Figure 2.4 shows both aerosol and volume weighted concentrations of NO_3^- in precipitation in 2008. Note precipitation units in $\mu\text{eq/L}$. The lower limit (11 $\mu\text{eq/L}$) corresponds to 0.7 mg/L NO_3^- (0.22 mg/L as N) and the upper (32 $\mu\text{eq/L}$) to 1.98 mg/L (0.49 mg/L NO_3^- as N). Multiplying these by 3 as above indicates areas of Wales and Western Scotland to be receiving <0.66 mg/L NO_3^- -N and East Anglia to be receiving rainfall with >1.5 NO_3^- -N.

A similar RoTAP map for reduced N species indicates a similar distribution for particulate NH_3 with masses about 1.5 times higher, but with higher masses extending to London and to the extreme southwest. The conversion into concentrations in precipitation was not estimated but it can be assumed that the amount deposited could be 1.5 times that of NO_3^- . Gaseous concentrations however have a different distribution.

This could suggest N deposition in rainfall to be between <1.7 mg/L and >3.8 mg/L or assuming this all to be oxidised to NO_3^- as <7.6 to >17 mg/L. This broadly agrees with estimates made in the baseline reports.

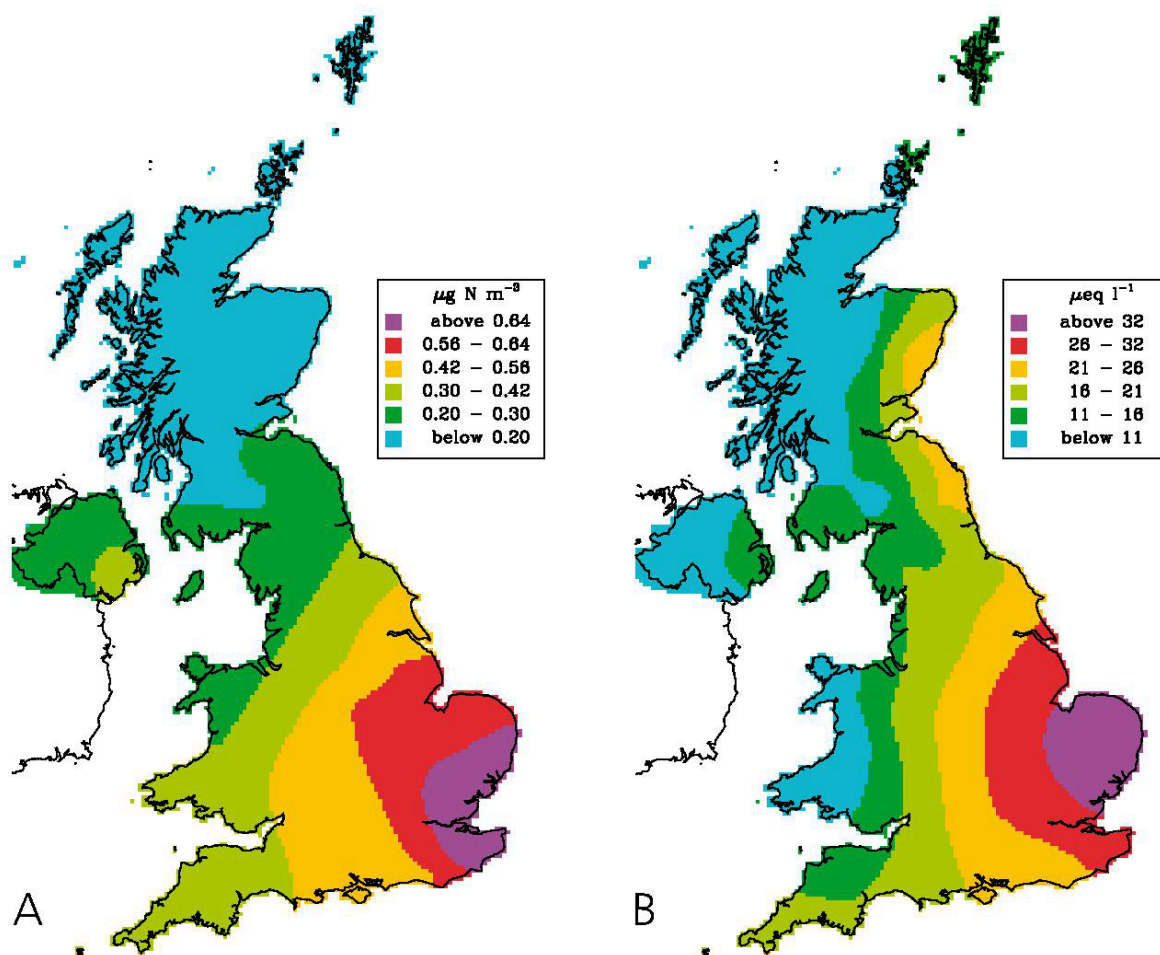


Figure 2.4 Annual average measured concentrations of (a) aerosol NO_3^- and (b) volume-weighted concentrations of NO_3^- in precipitation in 2008 (from RoTAP, 2012)

2.5 REGIONAL/NATIONAL APPROACHES

2.5.1 Modelling approach

Keuskamp et al. (2012) describe a spatial model for simulating the fate of N in both soil and groundwater with the aim of predicting both N leaching and N₂O emissions. This used an improved version of the global IMAGE model (Bouwman et al., 2006) which takes spatial heterogeneity at the European scale into account.

This model uses a 1×1 km grid and computes a steady state annual water balance at the surface.

- Runoff is partitioned into three depth classes, surface runoff in the top 1 metre, shallow groundwater in the next 5 metres draining to local surface water at short distances and deep groundwater below 6 metres and 50 m thick draining to large rivers at greater distances.
- Travel time distribution calculated by using lithological classes and the time distribution described by Meinardi (1994) assuming that the deep system is fed by a vertically, uniformly draining shallow system.
- N leaching factors were based on the MITERRA model (Velthof et al., 2009) and required N inputs per land use type, soil texture, rooting depth, soil temperature and soil organic carbon.
- Denitrification was calculated using a hole-in-the-pipe model and assuming a first order decay process. In this model, the rate of NO flux from soils depends on both the “flow through the pipe”—the rates of nitrification and denitrification—and the size of the “holes in the pipe,” which were determined by environmental conditions such as soil moisture and temperature (Firestone and Davidson, 1989). The more N “flowing through the pipe,” the higher NO fluxes will be for a given set of environmental conditions.

The model predicted that travel times were 0.5 to 10 years in shallow groundwater and mainly between 50 and 200 years for deep systems. At the European scale only what appear to be areas of the Chalk were plotted on the distribution map for the UK. None of the large rivers systems for which a detailed nitrogen budget has been reported are in the UK. Calculated NO₃ delivery to the Thames, Severn and Trent was close to reported values whereas it was greater for the Mersey.

2.5.2 Statistical approaches

DENMARK

In a national assessment, the groundwater nitrate reduction for catchments without monitoring data, was estimated by a statistical model (Blicher-Mathiesen et al., 2014). The N reduction was estimated as the fraction of aerobic/anoxic water flux above and the anaerobic water flux beneath the redox cline in 1 km² grids. The depth to the redox cline was defined from the changes in the sediment colour from 12,000 national boreholes or from geological description. The estimated N reduction was calibrated to the N reduction calculated for 56 large (>50 km²) monitored catchments. The results showed areas over 80% of the loading was removed between the root zone and the marine receptor.

NEW ZEALAND

Linear discriminant analysis (LDA) for predicting groundwater redox status was applied to a major dairy farming region in New Zealand (Wilson et al., 2018). Data cases were developed by assigning a redox status to samples derived from a regional groundwater quality database. This was based on NO₃ <0.5 mg/L, Mn >0.5 mg/L and DO <1.0 mg/L. The majority of groundwater samples were from inland alluvial aquifers.

Pre-existing regional-scale geospatial databases were used as training variables for the discriminant functions. Variables included elevation, slope, drainage, land use and water depth. The models predicted 23% of the region as being reducing at shallow depths (<15 m), and 37% at medium depths (15–75 m). Predictions were made at a sub-regional level to determine whether improvements could be made with discriminant functions trained by local data. The results indicated that any gains in predictive success were offset by loss of confidence in the predictions due to the reduction in the number of samples used.

The regional scale model predictions indicated that subsurface reducing conditions predominated at low elevations on the coastal plains where poorly drained soils are widespread. Additional indicators for subsurface denitrification are a high carbon content of the soil, a shallow water table, and low-permeability clastic sediments. systems.

2.5.3 Review approach

A map for spatially variable nitrate reduction in groundwater covering six countries in the Baltic Sea Basin, Denmark, Sweden, Finland, Lithuania, Poland and Germany was developed (Højberg et al., 2017) designed to provide an independent estimate of the nitrogen reduction in groundwater. The total area discharging to the Baltic Sea is about 1,720,270 km² spanning large climatic and land use variations. Mapping was based on review of national data and studies including process-based models, source apportionment models and hydrological and drainage maps. Depending on availability, different approaches were used for the countries ranging from national modelling for Denmark and Sweden to expert judgement for Poland..

The review revealed large variations in the hydrogeochemical conditions important for transport and degradation of nitrogen in groundwater. This included the hydrogeology, the reducing conditions of the subsurface, and the fraction of water transported by drainage systems bypassing the reducing subsurface environments. Significant variations in groundwater reduction between the countries and within most of the countries were found, indicating that strategies for nitrogen regulation and mitigation measures may be optimised, if variation in the natural reduction of nitrate is considered.

3 Typical settings

3.1 AQUIFERS

3.1.1 Confined zones

Many studies have confirmed the presence of redox boundaries in confined aquifers similar to Figure 2.2. The boundary occurs some distance down dip from the start of confinement depending on the aquifer flow regime. For the UK these studies are described further in Section 4.

In a study of the Triassic sandstone aquifer of Lorraine (LTSA), Celle-Jeanton et al. (2009) found an increase in most of the chemical parameters along the flow path, from unconfined to confined aquifer. This general trend was correlated with the evolution of groundwater residence time and was very close to the conceptual model developed for the East Midlands Aquifer, UK, which showed similar geological and hydrogeological patterns. However, in the LTSA, there was only limited contamination by NO_3 with concentrations varying from 1.2 to 14.3 mg/L.

3.1.2 Unconfined zones

An assessment of NO_3 concentrations in groundwater in the United States by Burow et al. (2010) indicated that concentrations were highest in shallow groundwater beneath agricultural land use in areas with well-drained soils and oxic geochemical conditions. Concentrations were lowest in deep groundwater where groundwater is reduced, or where groundwater is older and concentrations reflect historically low N application rates. Classification and regression tree analysis was used to identify the relative importance of N inputs, biogeochemical processes, and physical aquifer properties in explaining groundwater NO_3 concentrations. The analysis showed that dissolved Fe concentrations explained most of the variation in groundwater NO_3 concentration, followed by Mn, Ca, farm N fertilizer inputs, percent well-drained soils and DO. Overall, NO_3 concentrations in groundwater were most significantly affected by redox conditions, followed by nonpoint-source N inputs, indicating importantly that redox can overcome N inputs.

Geochemical and isotopic tools were applied at aquifer, transect, and subtransect scales by Hinkle et al. (2007) to provide a framework for understanding sources, transport, and fate of dissolved inorganic N in a sandy aquifer near La Pine, Oregon. NO_3 was a common contaminant in shallow ground water in this area, whereas high concentrations of NH_4 (up to 39 mg/L as N) were present in deep ground water. N concentrations, N/Cl ratios, tracer-based groundwater ages, N isotope data, and hydraulic gradients indicated that septic tank effluent was the primary source. Nitrogen isotope data, N/Cl and N/C ratios, ^3H data, and hydraulic considerations pointed to a natural, sedimentary organic matter source for the NH_4 . Low recharge rates and flow velocities largely restricted anthropogenic NO_3 to isolated plumes within several metres of the water table. Geochemical and isotopic data indicated that denitrification also affected NO_3 gradients in the aquifer. Groundwater evolved from oxic to increasingly reduced conditions. Suboxic conditions were achieved after about 15–30 years of transport below the water table. NO_3 was denitrified near the oxic/suboxic boundary. Denitrification was characterized at the aquifer scale with a redox boundary approach that captured spatial variability in the distribution of electron donors.

3.1.3 Superficial deposits

Postma et al. (1991) investigated NO_3 distribution and reduction processes in an unconfined Quaternary sandy aquifer in Denmark. The aquifer was subdivided into an upper 10- to 15-m thick oxic zone that contained O_2 and NO_3^- , and a lower anoxic zone characterized by Fe^{2+} -rich

waters. The redox boundary was very sharp, suggesting that reduction processes were fast compared to the rate of downward water transport. Nitrate-contaminated groundwater TDSs were two to four times higher than in groundwater derived from a forested area. The persistence of the high content of TDS in the anoxic zone and the absence of both NO_2 and NH_4 indicated the downward migration of contaminants and that active NO_3 to N_2 reduction was taking place. Possible electron donors in the reduced zone of the aquifer were organic matter and small amounts of pyrite. Electron balances based on concentrations of O_2 , NO_3^- , SO_4^- and total inorganic carbon indicated that pyrite was by far the dominant electron donor even though organic matter was much more abundant.

Puckett and Cowdery (2002) used a combination of ground-water modelling, chemical and dissolved gas analyses, and age dating of water to determine the relation between changes in agricultural practices, and NO_3 concentrations in ground water of a glacial outwash aquifer in Minnesota. The results revealed a redox zonation throughout the saturated zone with O_2 reduction near the water table, NO_3 reduction immediately below it, and then a large zone of Fe^{3+} reduction, with a small area of SO_4 reduction and methanogenesis near the end of the transect. Modelling supported the hypothesis that OC was the electron donor. Denitrification rates were small and were limited by the small amounts of OC, 0.01 to 1.45%. In spite of the OC limitation, denitrification was virtually complete because residence time (50-70 years) was sufficient to allow even slow processes to reach completion.

3.1.4 Organic rich recharge

We find mention of increased rates of denitrification under areas where recharge is high in DOM. It is believed that the organotrophic denitrification in groundwater relies mainly on sedimentary, “autochthonous” organic carbon (Ghiorse and Wilson, 1988; Obermann, 1990). The rate of denitrification is most often related to the amount of dissolved organic carbon (DOC) in porewater or groundwater, or the amount of soluble organic carbon rather than the total amount of solid fraction (Rivett, 2008).

Work by Siemens et al. (2003) under a range of soils, organic-rich plaggic anthrosols and reducing gleyic podzols and eutric gleysols where the water table was high, to determine whether DOC from soils could be a carbon source for organotrophic denitrification. They found that leached DOC contributed negligibly to the denitrification process because the DOC in the soils themselves appeared not to be bioavailable and concentration patterns did not appear to correspond to distribution of denitrification. They concluded that denitrification in the groundwater below was being controlled by the limited translocation of organic carbon to the soils by crop roots. Denitrification is also likely in aquifers affected by infiltration of DOC-rich surface water. See following section

3.2 RIPARIAN ZONES, HYPORHEIC ZONES AND FLOODPLAINS

Floodplains act as the collection point for groundwater, overland flow and river water (Burt et al., 2002) (Figure 3.1). As a result, the water table is usually close to the surface and the soil and any unsaturated zone will be close to saturation. A number of studies have shown that flow paths are affected by inundation pattern, hydraulic connectivity in the system and the degree of floodplain saturation. On the landscape scale the floodplain is the reactive interface between the upland and the river (Lewandowski and Nützmann, 2010). On the floodplain scale the hyporheic zone is the reactive interface between the aquifer and surface water. In both interfaces the flow paths and flow velocities are of importance for biogeochemical processes. The same processes that occur in the floodplain also occur in the hyporheic zone although higher concentrations in the riverbed sediments indicate more intense processes.

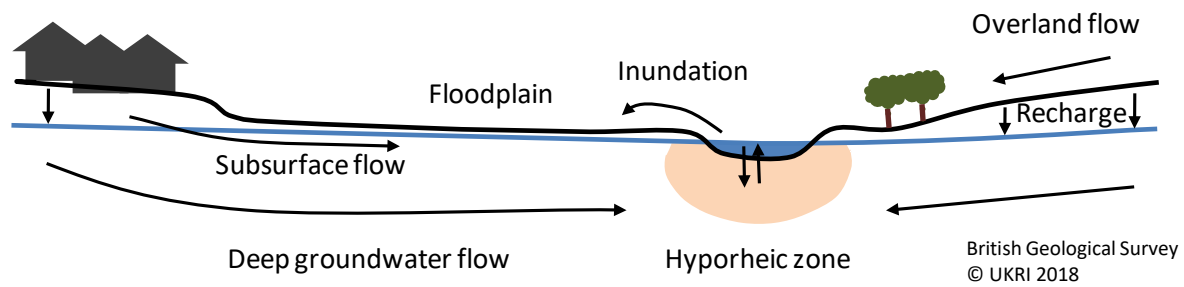


Figure 3.1 Flow paths in the riparian zone (from Stuart and Lapworth (2011))

3.2.1 Heterogeneity

McClain et al. (2003) showed that rates and reactions of biogeochemical processes vary in space and time and these variations are often enhanced at terrestrial-aquatic interfaces. They defined biogeochemical “hot spots” as patches that show disproportionately high reaction rates relative to the surrounding matrix, whereas “hot moments” were short periods of time that exhibit disproportionately high reaction rates relative to longer intervening time periods. Hot spots occur where hydrological flow paths converge with substrates or other flow paths containing complementary or missing reactants. Hot moments occur when episodic hydrological flow paths reactivate and/or mobilize accumulated reactants.

Many previous studies have confined measurements of denitrification and NO_3 retention to shallow sediments (<5 cm deep). Stelzer et al. (2011) determined the extent of NO_3 processing in deeper sediments of a sand plains stream by measuring denitrification in core sections to a depth of 25 cm and by assessing vertical NO_3 profiles, to a depth of 70 cm. Denitrification rates of sediment slurries based on acetylene blocking were higher in shallower core sections. However, core sections deeper than 5 cm accounted for 68% of the mean depth-integrated denitrification rate. Vertical profiles showed that NO_3 concentration in shallow ground water was about 10–60% of the NO_3 concentration of deep ground water.

3.2.2 Floodplains and riparian zones

Denitrification also occurs in other areas of groundwater where confined conditions exist, such as in riparian zones and floodplains (Hanson et al., 1994; Hill et al., 2000; Lowrance, 1992; Pinay et al., 1998; Watson et al., 2010).

Triska et al. (1993) investigated the terrestrial-aquatic interface beneath the riparian corridor at Little Lost Man Creek, California to assess hydrological and biological control of nutrient fluxes. Subsurface flow paths were defined from the channel toward the riparian zone and also from the riparian zone toward the channel using tracer-injection studies. Solute transport had a rapid channel component and a slow hyporheic flow component. DO concentration in the hyporheic zone ranged from <1.0 to 9.5 mg/L due to permeability variations in bankside sediments and the proportion of stream water in the lateral hyporheic zone. Both nitrification potential and channel exchange decreased with distance from the channel and were absent at sites lacking effective exchange, due to low DO. Denitrification potential was inversely related to channel exchange and was insignificant in channel sediments.

Vidon and Hill (2005) examined the linkages between hydrologic flow paths, patterns of electron donors and acceptors and the importance of denitrification as a NO_3 removal mechanism in riparian zones on glacial till and outwash landscapes in Ontario, Canada. NO_3 -N concentrations in shallow groundwater from adjacent cropland declined from 10–30 mg/L near the field-riparian edge to 1 mg/L in the riparian zones. Chloride data suggested that dilution could not account for this NO_3 decline. The riparian zones displayed a well-organized pattern of electron donors and

acceptors that resulted from the transport of oxic NO_3^- -rich groundwater to portions of the riparian zones where low DO concentrations and an increase in DOC concentrations were encountered. Work with $\delta^{15}\text{N}$ and in-situ acetylene injection to piezometers indicated that denitrification was the primary mechanism of NO_3^- removal in all zones. A shallow water table was not always necessary for efficient NO_3^- removal by denitrification.

In the Lake Waco Wetland, Texas, NO_3^- concentrations were reduced by more than 90% in the first 500 m downstream of the inflow, creating a distinct gradient in NO_3^- concentration along the flow path of water (Scott et al., 2008). The relative importance of sediment denitrification, DNRA and N fixation was assessed along the NO_3^- concentration gradient in the wetland. Potential denitrification was observed in all months, potential DNRA was observed only in summer months and N fixation was variable. Both sediments and the wetland were NO_3^- sinks and accounted for 50% of wetland NO_3^- removal. Sediments were an ammonium source, but the wetland was often a net sink. The importance of DNRA in freshwater sediments appeared to be minor relative to denitrification.

For the Spree River, Germany, Lewandowski and Nützmann (2010) found that the biogeochemical composition of subsurface water showed little temporal variability while spatial heterogeneity was high on the hectometre scale of the study site as well as on the centimetre scale of the bed sediments. Nitrate was eliminated very efficiently by denitrification in the anoxic aquifer of the floodplain while NH_4^+ concentrations increased under anoxic conditions. Ammonium was thought to originate from the mineralization of OM. The redox patchiness of floodplain aquifers favoured NO_3^- removal, i.e. a temporal and spatial sequence of anoxic and oxic conditions eliminates N.

3.2.3 Hyporheic zones

The hyporheic zone (HZ) is the active zone between the surface stream and groundwater. Figure 3.2 shows a sketch cross-section of the HZ illustrating the common microbially-mediated N transformation processes. Surface waters supply NO_3^- , dissolved organic nitrogen (DON) and DOC to the hyporheic zone. In aerobic regions of the hyporheic zone, DON can be mineralized to NH_4^+ , which can be transformed via nitrification to create additional NO_3^- . The DOC and NO_3^- also can be retained in the hyporheic zone via microbial assimilation processes. DOC and NO_3^- entering anaerobic portions of the hyporheic zone can be utilized for denitrification, which produces N_2O and N_2 , which can degas out of the stream system and return to the atmosphere.

Boulton et al. (1998) showed that exchanges of water, nutrients, and organic matter (OM) occur in response to variations in discharge and bed topography and porosity. Upwelling subsurface water supplies stream organisms with nutrients while downwelling stream water provides DO and OM to microbes and invertebrates in the hyporheic zone.

Dynamic gradients exist at all scales in the hyporheic zone and vary temporally (Boulton et al., 1998):

- Microscale - gradients in redox potential control chemical and microbially mediated nutrient transformations occurring on particle surfaces
- Stream-reach scale - hydrological exchange and water residence time are reflected in gradients in hyporheic faunal composition, uptake of dissolved organic carbon, and nitrification
- Catchment scale - the hyporheic corridor concept describes gradients, extending to alluvial aquifers kilometres from the main channel.

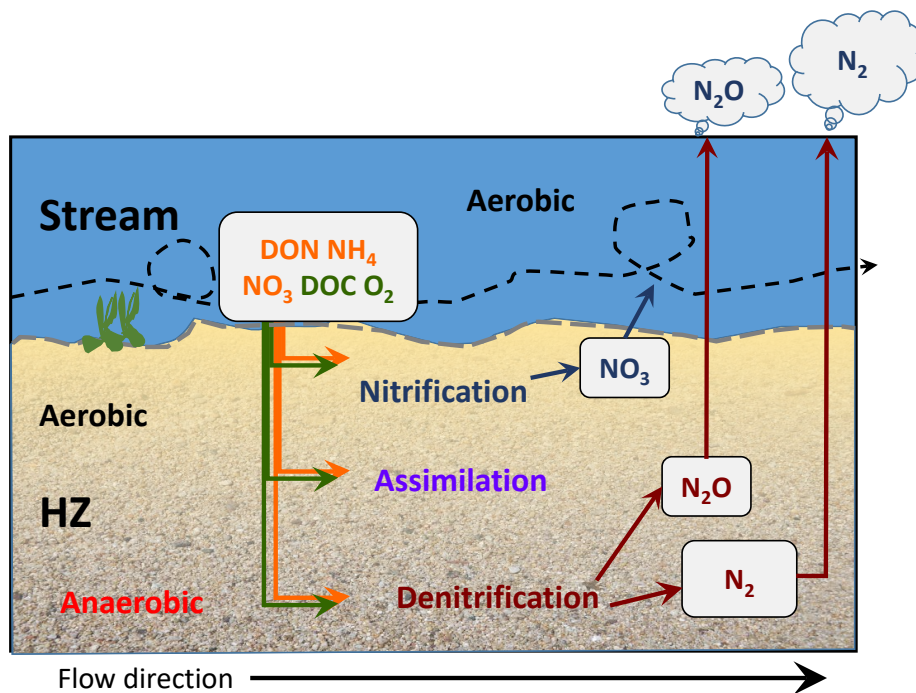


Figure 3.2 Simplified longitudinal cross-sectional view of a stream HZ with commonly observed microbially mediated pathways for nitrate transformations (modified from Zarnetske et al., 2011b Labile dissolved organic carbon supply limits hyporheic denitrification. *Journal of Geophysical Research: Biogeosciences*, Vol. 116, G04036. <https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2011JG001730>).

Across all scales, the functional significance of the HZ relates to its activity and connection with the surface stream. HZs have been identified as potential active areas for denitrification in many studies. Biogeochemical reactions associated with stream nitrogen cycling, such as nitrification and denitrification, can be strongly controlled by water and solute residence times in the HZ.

Denitrification in hyporheic sediments in a small forested stream in Canada was assessed by Duff and Triska (1990). Samples were obtained along transects perpendicular to the stream at two sites. In-situ denitrification was evident at all locations tested. Denitrifying potentials increased with distance from the stream channel. Both NO_3 and DOC decreased over summer in wells at the base of the forested slope. Acetylene-block experiments coupled with the chemistry data suggested that denitrification could modify the chemistry of water during passage through the HZ.

Roley et al. (2012) studied denitrification in the HZ and floodplains of an agriculturally-influenced headwater stream in Indiana, USA. They measured seasonal denitrification rate and NO_3 concentrations profiles in stream sediments to examine the potential for N removal in the HZ. Nitrate concentration and denitrification rates declined with depth into the HZ, but denitrification was still measureable to a depth of 20 cm. Floodplain denitrification rates increased over the course of an inundation event particularly where vegetation was present. Deep groundwater tended to be oxic ($6.9 \text{ mg O}_2/\text{L}$) but approached anoxia ($0.8 \text{ mg O}_2/\text{L}$) after passing through shallow, organic carbon-rich sediments, which suggested that the decline in the NO_3 concentrations of upwelling ground water was due to denitrification. Collectively the results suggest that there was substantial NO_3 removal occurring in deep sediments, below the HZ.

Storey et al. (2004) determined the distribution of nitrogen-transforming processes, and rate-controlling factors within the HZ of an agricultural lowland stream in Ontario, Canada. Physicochemical parameters were measured along a 10 m-long hyporheic flow line between down and upwelling zones. Sediment cores from the streambed surface and from various depths

in each zone and water from the corresponding depth was percolated through each core in the laboratory. Denitrification was measured using a $^{15}\text{N}\text{-NO}_3$ tracer.

Physicochemical conditions, microbial processes and nitrogen processing distinguished shallow and downwelling zone samples from deeper and upwelling zone samples. Denitrification was highest in surface and downwelling zone cores, despite high O_2 levels, probably due to high pore-water NO_3 concentrations in these cores and isolation of denitrifying bacteria from O_2 in the bulk water by hyporheic biofilms. Denitrification was limited by DO inhibition in the downwelling group, and by NO_3 availability in the upwelling group. Strong evidence indicated that DNRA occurred in almost all cores, and outcompeted denitrification. Field patterns and lab experiments indicated that the HZ at this moderately N-rich site was a strong sink for NO_3 , fitting current theories that predict where HZs are NO_3 sinks or sources.

Zarnetske et al. (2011a) used a steady state ^{15}N -labelled NO_3 and Cl tracer to investigate the spatial and temporal conditions controlling denitrification dynamics in the HZ of an upland agricultural stream, Drift Creek, Oregon, USA. They measured solute concentrations ($^{15}\text{NO}_3^-$, $^{15}\text{N}_2$, as well as NO_3^- , NH_3 , DOC, DO, Cl), and hydraulic transport parameters of the reach and along HZ flow paths of an instrumented gravel bar. HZ exchange was observed across the entire bar with flow path lengths up to 4.2 m and median residence times greater than 28.5 h. The HZ transitioned from a net nitrification environment at its head (short residence times) to a net denitrification environment at its tail (long residence times). NO_3^- increased at short residence times from 0.32 to 0.54 mgN/L until a threshold of 6.9 h and then consistently decreased from 0.54 to 0.03 mgN/L.

Along these same flow paths, declines were seen in DO and DOC. The rates of the DO and DOC removal and net nitrification were greatest during short residence times, while the rate of denitrification was greatest at long residence times. An injection of labile DOC increased the rate of N removal suggesting that denitrification in anaerobic portions of the HZ is limited by labile DOC supply (Zarnetske et al., 2011b). $^{15}\text{NO}_3^-$ tracing confirmed that a fraction of the NO_3^- removal was via denitrification across the entire bar HZ. Production of $^{15}\text{N}_2$ across all observed flow paths and residence times indicated that denitrification microsites were present even where nitrification was the net outcome. These findings showed that the HZ was an active nitrogen sink in this system and that the distinction between net nitrification and denitrification in the HZ was a function of residence time and threshold behaviour.

3.2.4 Complex settings

Feast et al. (1998) applied a detailed hydrochemical sampling programme to the River Bure catchment on the Chalk aquifer system of northeast Norfolk to understand the source and fate of NO_3 . The Chalk aquifer is covered by a variety of superficial deposits including Pleistocene sand and the Lowestoft Till which are up to 30 m thick (Figure 3.3). Modern contaminants of a mainly agricultural origin produced high concentrations of NO_3 (>60 mg/L) in the unconfined valley areas, whereas in confined regions the levels of NO_3 were low and commonly below detection limits (<0.02 mg/L).

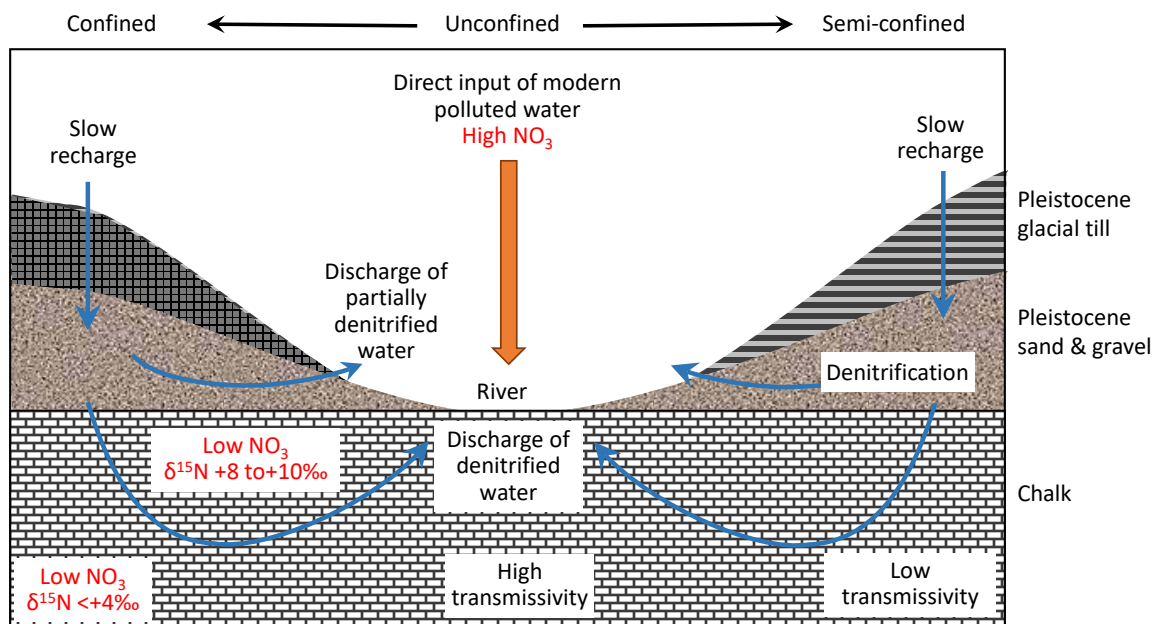


Figure 3.3 Schematic cross-section illustrating processes controlling the distribution of N species in the Chalk of north-east Norfolk (simplified from Feast et al. (1998))

Samples from within the glacial deposits had $\delta^{15}\text{N}$ values of 13.7‰ and 9.3‰ while samples from the chalk alone had a narrower range of -2.1‰ to 11.5‰ and from the confined and semi-confined zones +4‰ and +10‰, characteristic of nitrified soil organic nitrogen. There was no apparent relationship between $\delta^{15}\text{N}$ and NO_3 concentration as would be anticipated if in-situ denitrification were controlling NO_3 concentrations. However, many Chalk groundwaters had high N_2/Ar ratios (39–72) indicating a significant contribution to dissolved N_2 from denitrification. Denitrification was believed to be occurring within the overlying glacial deposits, providing a mechanism for naturally improving groundwater quality. $\delta^{15}\text{N}$ values of low- NO_3 groundwaters from the confined zone were isotopically light (-3‰ to +4‰), inconsistent with an origin from denitrification: it is suggested that these waters had a pre-anthropogenic NO_3 signature.

Landon et al. (2011) used data from multiple sources to determine interrelations among hydrogeological factors, redox conditions, and temporal and spatial distributions of NO_3 in a 2,700- km^2 area of the eastern San Joaquin Valley, California, USA. The primary aquifers were a complex sequence of alluvial fan sediments deposited by major tributaries to the San Joaquin River. The main water-bearing units included unconsolidated alluvial-fan deposits and deeper Pleistocene and Pliocene-aged strata, and semi-consolidated rocks derived from fluvial deposits of predominantly andesitic volcanic detritus. Groundwater was predominantly modern, with detectable NO_3 and oxic conditions, but some zones were anoxic or mixed. Anoxic conditions were associated with long residence times that occurred near the valley trough and in areas of historical groundwater discharge with shallow depth to water and with interactions of shallow, modern groundwater with soils. NO_3 concentrations were significantly lower in anoxic than oxic or mixed redox groundwater, because residence times of anoxic waters exceed the duration of increased pumping and fertilizer use associated with modern agriculture. Effects of redox reactions on NO_3 concentrations were relatively minor. Dissolved N_2 gas data indicated that denitrification had eliminated $>5\text{mg/L}$ $\text{NO}_3\text{-N}$ in about 10% of 39 wells. Increasing NO_3 concentrations over time were slightly less prevalent in anoxic than oxic or mixed redox groundwater. Spatial and temporal trends of NO_3 were primarily controlled by water and NO_3 fluxes of modern land use.

4 UK aquifers

4.1 LITERATURE

Foster et al. (1985) set out some of the first collated evidence for biological denitrification in British aquifers. This was related to the Lincolnshire Limestone near Lincoln and the Chalk of Norfolk and was based on penetration of modern tritium-containing groundwater to depths where NO_3 is negligible and the presence of bacterial consortia with denitrifying capability to depth. Denitrification has been demonstrated in other major aquifers in England, such as the Sherwood Sandstone where these become confined or very deep and there is a clear redox boundary (Edmunds et al., 1982; Smedley and Edmunds, 2002). There are also other more complex settings, where denitrification has been invoked to explain observations, such as zones of aquifers constrained by important marl bands. Other settings include floodplains and the hyporheic zone.

Approaches to the estimation of denitrification in the aquifers of the UK have been reviewed by Rivett et al. (2007). The text below has been predominantly summarised from this review. These studies indicate that the potential for denitrification in the unsaturated and unconfined saturated zones of major British aquifers is low.

4.1.1 Unsaturated zone

CHALK

Mass balance investigations to track the progress of a packet of water through the unsaturated zone was used by Kinniburgh et al. (1999) on an extensive set of repeated drillings undertaken at five sites in East Anglia (Parker et al., 1991a). Although the approach was of limited value in quantifying small amounts of denitrification, it could be concluded that, at the scale of metres to tens of metres, denitrification was probably insignificant in the unsaturated zone of the Chalk.

Gale et al. (1994) examined evidence for denitrification in core profiles at Ogbourne St. George on the Wiltshire Chalk. The site exhibited a NO_3 front moving downward at about 0.8 m/year with input NO_3 peaks smoothed by the large seasonal water table fluctuations of about 20 m. Nitrate, DO and OC were all thought to be replenished annually by rapid fissure flow to the water table. Nitrate, N_2O and excess N_2 were estimated to represent, at most, a few per cent decrease in the NO_3 load. Supporting microbiological studies showed that denitrifiers were present at all depths. Laboratory microcosms using core indicated a 2% NO_3 to NO_2 conversion over 21 days.

More recent studies of gases in the Chalk at Bridget's Farm, Hampshire, used carbon isotope evidence to indicate that most of the unsaturated zone CO_2 was from bacterial breakdown of organic matter in overlying soils (Kinniburgh et al., 1999). Although some N_2O was detected the source could have been the soil zone or nitrification of NH_4 (Buss et al., 2004). Marginally elevated N_2/Ar ratios indicating an excess N_2 of about 0.5% were indicative of denitrification, but accounted for a decrease in NO_3 of 0.4 mg N/L, compared with the mean unsaturated zone concentration of 26 mg N/L. Slightly negative values of $\delta^{15}\text{N}-\text{N}_2$ supported the above, implying minor denitrification at rates that were not quantifiable. Examination of the $\delta^{15}\text{N}$ composition of infiltrating NO_3 relative to the underlying groundwater NO_3 similarly confirmed that denitrification was not a significant process in the unsaturated zone.

SHERWOOD SANDSTONE

The most significant NO_3 attenuation study on the Sherwood Sandstone unsaturated zone was undertaken at Gleadthorpe, Nottinghamshire (Kinniburgh et al., 1999). The unsaturated zone thickness was 8–12 m and influenced by nearby public water supply abstractions. Similar

research methods were employed as at the Bridget's Farm site. Denitrification was not found to be a significant process overall, although there was some evidence of its occurrence, including the following:

- Nitrate depletion just beneath the water table in one borehole, where NO_3 concentrations declined with depth whereas nitrite increased;
- In one near-surface sample, $\delta^{15}\text{N-N}_2$ and N_2/Ar data were consistent with minor denitrification;
- Denitrifying bacteria were found at all depths, indicating the potential for denitrification;
- N_2O was above atmospheric concentrations, though it was unclear whether this was due to soil-zone denitrification or oxidation of ammonium: sufficient (small) quantities of ammonium were present throughout.

The N_2/Ar data suggested that denitrification accounted for a maximum decrease of 0.8 mg N/L compared with an average unsaturated zone concentration of 37 mg N/L. Kinniburgh et al. (1999) concluded that denitrification is limited in the sandstone unsaturated zone as a result of low supplies of labile organic carbon, leading to low rates of microbial activity and little chance of the development of anaerobic hotspots.

4.1.2 Saturated zone

CHALK

Circumstantial evidence for denitrification within the drift and Chalk aquifer system of Norfolk, U.K. was reported by Parker and James (1985). Results from core analyses showed that tritium had penetrated to the base of the overlying 30 m of glacial sand (19-58 TU) and into the upper levels of the Chalk (9-39 TU). This confirmed that there was at least a component of modern water in the Chalk, which in the absence of NO_3 (< 0.2 mg N/L) in the Chalk groundwater, was evidence for denitrification. A bacteriological survey in the area revealed potential denitrifiers in cores from the top of the Chalk. Regular analysis of pumped water from the Chalk showed that the mobile fissure water contained less than 2 mg/L DOC. Preliminary investigations suggested that the pore water contained 10-20 mg/L DOC) and that the rock matrix perhaps greater than 1000 mg of organic carbon per kg dry weight. If correct, to obtain a porewater DOC of 30 mg/L for Chalk with a porosity of 40% would have required the dissolution of about 1% of the matrix. However, Bishop and Lloyd (1990) used isotope and hydrochemical modelling to suggest that substantial amounts of NO_3 reduction had not occurred and that the low NO_3 concentrations in the confined part of the aquifer were predominantly the result of lower NO_3 inputs in the past.

Mühlherr and Hiscock (1997) measured N_2O and other nitrate species in samples collected from boreholes and springs in the unconfined chalk aquifer of Cambridgeshire in an area of intensive arable farming. A very good positive correlation between N_2O and NO_3 concentrations was obtained but no relationship was established between N_2O and NO_2 or NH_4 concentrations. Concentrations of N_2O and NO_3 increased continuously in the direction of groundwater flow, within the range reported in previous studies of nitrification. Corresponding DO concentrations in groundwater samples were moderately undersaturated, further indicating that the main source of N_2O in this area is probably nitrification. No consumption of N_2O seemed to take place within the unconfined aquifer with degassing to the atmosphere apparently being the sole mechanism for N_2O removal from groundwater.

SHERWOOD SANDSTONE

Although NO_3 concentrations are commonly low where the sandstones are confined, there is little direct evidence of denitrification. The south Yorkshire Sherwood Sandstone aquifer is variably

covered by drift deposits. Many of the large water abstractions are located on sandstone 'islands' that protrude through the drift). A key study showed that deep (50–100 m) penetration of NO_3 in these unconfined portions contrasted with immediately adjacent areas confined beneath low-permeability superficial deposits that contained near undetectable concentrations of NO_3 throughout the water column (Parker et al., 1985). It is significant that an abrupt change in NO_3 concentration has been maintained at the confined–unconfined boundary, despite the presence of major abstractions in the confined zone. Denitrification, although not definitively proven at the site, was considered to be probable (Parker et al., 1991b).

The potential for denitrification was also explored in the Nottinghamshire sandstone, mainly differentiated by less drift cover than the south Yorkshire counterpart and more oxygenated groundwater (Wilson et al., 1990). Widespread denitrification was not observed in the aquifer except in two isolated locations, where it was ascribed to relatively low DO concentrations being present.

LINCOLNSHIRE LIMESTONE

Foster et al. (1985) provided NO_3 , tritium and bacterial activity data for cores taken from the Lincolnshire Limestone that supported denitrification, e.g., penetration of thermonuclear tritium further down-dip from outcrop than both NO_3 and DO. Wilson et al. (1990) also presented evidence for denitrification that included concentrations of excess nitrogen and isotopic ratios.

Bottrell et al. (2000) more recently explored the control exerted on bacterial reduction reactions by the dual-porosity characteristics of the Lincolnshire Limestone. By analogy with SO_4 -reducing reactions in the aquifer, they concluded that the potential for denitrification in the shallow confined zone is poor. Reaction rates were limited by lack of an electron donor in the fissures; were NO_3 to diffuse into the pores where organic carbon and sulphides were present, NO_3 -reducing bacteria would be excluded by the narrow pore throats of the matrix (similar to the Chalk).

Roberts and McArthur (1998) highlighted the importance of greater DOC inputs to the Lincolnshire Limestone aquifer in unconfined areas. Where the River Glen crossed the aquifer it recharged the aquifer year-round because of drawdown due to the proximity of large public water supplies. In winter, NO_3 -rich surface waters generated by rainfall-runoff recharge the aquifer, led to the development of NO_3 plumes emanating from rivers and swallow holes. In summer, runoff was negligible and groundwater baseflow was low, so the rivers comprised mostly DOC-rich effluent from small sewage treatment works: this then recharged into the aquifer. Denitrification was significant in the anaerobic groundwaters thus created but the contribution to denitrification from reduction of in-situ sulphide, appeared greater than that from DOC.

Mühlherr and Hiscock (1998) measured N_2O and other N species in groundwater from important limestone aquifers in the UK. Nitrous oxide levels were generally very high, with concentrations exceeding the concentration of air-equilibrated water by up to 320 times. The correlations between N_2O , NO_3 and DO, as well as the spatial distribution of these chemical parameters, were used to identify nitrification as the main N_2O production mechanism in the investigated aquifers. Most of the N_2O in groundwater appeared to be produced via nitrification in the unsaturated zone, which was probably strongly supplemented by nitrogenous compounds from anthropogenic land applications. Nitrous oxide production in the saturated zone was less substantial and could have also been denitrification mediated; denitrification under very reducing aquifer conditions can result in nitrous oxide consumption. The observed high N_2O concentrations in groundwater, which were most likely caused by agricultural aquifer pollution.

4.1.3 Redox boundaries

Evidence of denitrification comes from the confined (anoxic) parts of some British aquifers from the work of Edmunds and others. This has also been confirmed by the occurrence of modern tritium-enriched groundwater with negligible NO_3 (Lawrence and Foster, 1986) and from the demonstration of appropriate bacteria in core samples.

Sequential redox processes have been described in three contrasting principal UK aquifers that have confined zones (Edmunds and Walton, 1983; Edmunds et al., 1982; Edmunds et al., 1984):

- The Berkshire Chalk on the western rim of the London Basin has an average thickness of 250 m. It dips to the east, is confined below Palaeogene sands and clays in the centre of the syncline and is underlain by the Upper Greensand and then the Gault Formation that serves as the basal aquiclude. It is a dual-porosity aquifer with moderate transmissivity in this area (270–450 m^2/day) decreasing with depth.
- The Jurassic Lincolnshire limestone is some 30 m thick at outcrop thinning down dip to the east. It is confined above and below by predominantly clay rich sequence of the Rutland and Grantham Formations and is artesian at depth. It showed a clear sequence of hydrochemical changes from a sharp redox boundary some 12 km from outcrop. The unaltered limestone at depth was grey due to fine-grained Fe sulphides but diagenesis by migrating groundwater has progressively oxidised the rock to a light brown. Groundwater movement is maintained by fissure flow and transmissivities are in excess of 1000 m^2/day .
- Hydrochemical processes have been studied along a downgradient profile of some 30 km in the Sherwood Sandstone. It is confined by the Mercia Mudstone and underlain by generally impermeable Permian sequences. It dips to the east at about 1 in 50 and varies in thickness between 120 m in the south to 300 m in the north. It has a typical redbed lithology devoid of reducing horizons. Groundwater movement is predominantly intergranular, but is enhanced by fissures. Transmissivities in the confined zone vary between 350 and 850 m^2/day (Edmunds et al., 1982).

At the time of reporting all three aquifers had high input levels of anthropogenic NO_3 . The occurrence of NO_3 -free groundwater was coincident with the redox boundary and with the complete reaction of DO in all three. Edmunds and Walton (1983) followed several indicators of agricultural pollution (Ca, K, SO_4 and NO_3) across the redox boundary in the Lincolnshire Limestone. The migration eastwards of Ca, K and SO_4 but not NO_3 provided circumstantial evidence of denitrification. Ammonia was found only in the NO_3 -free zones in all three aquifers, produced by DNRA or to the accumulation of NH_4^+ by incongruent reaction of clays.

Water quality in the Lincolnshire Limestone has been interpreted in a number of ways. Peach (1984) found that in the northern Lincolnshire Limestone, modern recharge appeared not to flow down dip to a large extent, as there was little evidence for high NO_3 , SO_4 , Cl or Ca groundwater downgradient. In the north, Peach described three ages of water with different origins:

- 1) Relatively modern recharge water with leakage of high-Na water from the overlying Rutland Formation (Thorncroft Sand);
- 2) Old recharge water, probably post-last glaciation to present;
- 3) Very old saline water, probably emplaced during Rutland Formation times.

Edmunds (1973, 1976) studied hydrochemical variations along a 28-km flow line in the southern Lincolnshire Limestone in 1969 and found solution, redox and ion-exchange reactions, SO_4 reduction and mixing with saline formation water to all be important processes within the aquifer. Edmunds and Walton (1983) re-sampled the same aquifer profile after 10 years to look at hydrogeochemical evolution with time and found that the overall sequence was remarkably similar in both distance from outcrop and absolute concentration but that, close to the redox

boundary, down-gradient increases in Ca, SO₄ Cl and NO₃ had occurred, together with a less abrupt redox boundary. Edmunds and Walton (1983) postulated that these changes were initiated by the migration of agricultural pollutants and that the results indicate that the aquifer has a considerable capacity for in-situ NO₃ reduction.

Howard (1985) defines water type in his study of the Lincolnshire Chalk by origin and his confined water represents old low-salinity water that replenished the aquifer when groundwater levels began to recover after the Devensian glacial episode. This has low N but does not necessarily represent denitrification as initial N would have depended on vegetation at the time of recharge. Some of this reducing water contained NH₄.

Table 4.2 summarises the range of values measures for key parameters in redox zones of the three main UK aquifers. These demonstrate a consistent pattern with the anaerobic zone characterised by DO <0.4 mg/L, NO₃ generally <1, Fe >100 µg/L Mn >4 µg/L. Edmunds and Elliot also suggest the use the decline of DO to indicate reducing conditions. Smedley and Edmunds (2002) however use temperature (in this case 13°C) as an indicator of confinement.

Table 4.1 Ranges of literature values of chemical characteristics of redox zones identified in UK aquifers (all in mg/L except Fe and Mn (µg/L) and Eh (mV))

Lithology	Area	Zone 1 (Aerobic)	Zone 2 (Intermediate)	Zone 3 (Anaerobic)	Reference
Chalk	Berkshire	DO = 4–10 NO ₃ = 20–30 Eh = +350–00 NH ₄ = <0.01 Fe = <0.3 Mn = <0.03		DO = <LOD NO ₃ = <LOD Eh = 0–+50 NH ₄ = 0.05–0.85 Fe = 7–170 Mn = 4–57	Edmunds et al. (1984)
	Lincolnshire	NO ₃ = 26–77 Eh = >+300		NO ₃ = <4 Eh = --50–+100	Howard (1985)
	London Basin	NO ₃ = 2.5–51	NO ₃ = 2.5	NO ₃ = 0.04	Elliot et al. (1999)
Sherwood Sandstone	East Midlands	DO = 2.5–10 NO ₃ = 6.8–54 Eh = +127–336 Fe = <4–236 Mn = <0.5–21	DO = <0.5–8.7 NO ₃ = 0.02–6.7 Eh = -7–+406 Fe = 6–372 Mn = 1.5–6	DO = <0.1 NO ₃ = 0.04–1.15 Eh = -5–0–+78 Fe = 115–1970 Mn = 5.5–37	Edmunds et al. (1982)
		DO = 2–10 NO ₃ = 3–54 Eh = +250–400 Fe = <15 µg/L		DO = <LOD NO ₃ = <LOD Eh = 0–+100 Fe = 130–2000	Edmunds et al. (1984)
		DO = 0.5–10.1 NO ₃ = <0.04–67 Eh = +116–485		DO = <0.4 NO ₃ = <0.4–2.1 Eh = -99–+183	Smedley and Edmunds (2002)
Lincs. limestone	Lincolnshire 1969	DO = 1.5–7 NO ₃ = 6–40 Eh = +400 Fe = <LOD		DO = <LOD NO ₃ = <LOD Eh = 0–+100 Fe = 100–1800	Edmunds et al. (1984)
	Lincolnshire 1983	DO = 0.5–7 NO ₃ = 10–62 Eh = +400 Fe = <LOD		DO = <LOD NO ₃ = <LOD Eh = 0–+100 Fe = 30–2800	Edmunds et al. (1984); Edmunds and Walton (1983)
	Lincolnshire	NO ₃ = 25		NO ₃ = <5	Lawrence and Foster (1986)

4.1.4 Deeper systems

In deeper aquifer systems, input of organic carbon from the soil reservoir is not important, and so the likely source of degradable organic carbon is the geologic material comprising the aquifer matrix (Hiscock et al., 1991).

An example of denitrification at depth in a confined aquifer is described by Lawrence and Foster (1986) for the Lincolnshire Limestone in the U.K. In this fissured limestone aquifer, an eastward decline in NO_3 concentration accompanies progressive removal of DO and lowering of the redox potential. Over a distance of 10 km the groundwater NO_3 concentration declines from a maximum of 25 mg N/l at outcrop to less than 5 mg N/l when confined, representing a NO_3 removal rate of 0.01-0.05 mg N/l/d (expressed as NO_3 loss per rate of flow of groundwater through the aquifer). Four cored boreholes were drilled along a groundwater flow line and the material recovered examined for organic carbon content and the presence of denitrifying bacteria. The results showed that the DOC content of the pore water ranges between 13 and 28 mg/l and that of the mobile groundwater between 1.6 and 3.4 mg/l. Denitrifying bacteria were cultured from samples scraped from fissure walls, but not from samples incubated with pore water. Thus, it appears that the source of organic carbon supporting denitrification is contained in the limestone matrix, and that the very small pore size of the matrix restricts denitrification to short distances from fissure walls.

4.1.5 Floodplains

Goody et al. (2014) investigated a peri-urban floodplain of the River Thames adjoining the city of Oxford, UK, over a period of three years through repeated sampling of groundwaters from existing and specially constructed piezometers. An intensive study of nitrogen dynamics through the use of N-species chemistry, nitrogen isotopes and dissolved nitrous oxide reveals that there is little or no denitrification in the majority of a landfill plume, and neither is the ammonium significantly retarded by sorption to the aquifer sediments.

4.2 BASELINE DATA

Baseline data for NO_3 concentrations in water for England and Wales have been assumed to demonstrate denitrification where NO_3 concentrations were below the limit of detection (Shand et al., 2007). These authors also assess the presence of NO_2 as a good indicator of on-going denitrification.

Figure 4.1 shows that the redox potential (Eh) and DO concentration provide the primary indicators of the redox status of natural groundwaters in the Lincolnshire Limestone (Griffiths et al., 2006). As the aquifer becomes increasingly confined, DO becomes depleted due to redox reactions. Once contact with O_2 ceases, Eh falls by ca. 300 mV. This marked redox boundary has considerable implications for the subsequent down-gradient hydrogeochemistry. On the basis of the samples collected as part of the Baseline project the initial Eh values appear to have been lower (+100 to +300 mV) and the reduction in Eh with distance down gradient less marked. The change in redox conditions is more obviously seen in the DO concentrations that were reduced to less than detection (< 0.1 mg/L) within a couple of kilometres of the aquifer becoming confined.

The decrease in NO_3 concentrations down the hydraulic gradient (Figure 4.1) was consistent with denitrification: NO_3 is only stable in the presence of DO. Although old (pre-intensive agriculture) groundwaters were expected to have lower concentrations, it is likely that recharge waters contained detectable NO_3 . Edmunds and Walton (1983) observed that NO_3 levels decreased gradually due to dispersion and in situ microbial reduction and became consistently low (<1 mg/L as $\text{NO}_3\text{-N}$) once DO was below 0.2 mg/L as $\text{NO}_3\text{-N}$ (or even less).

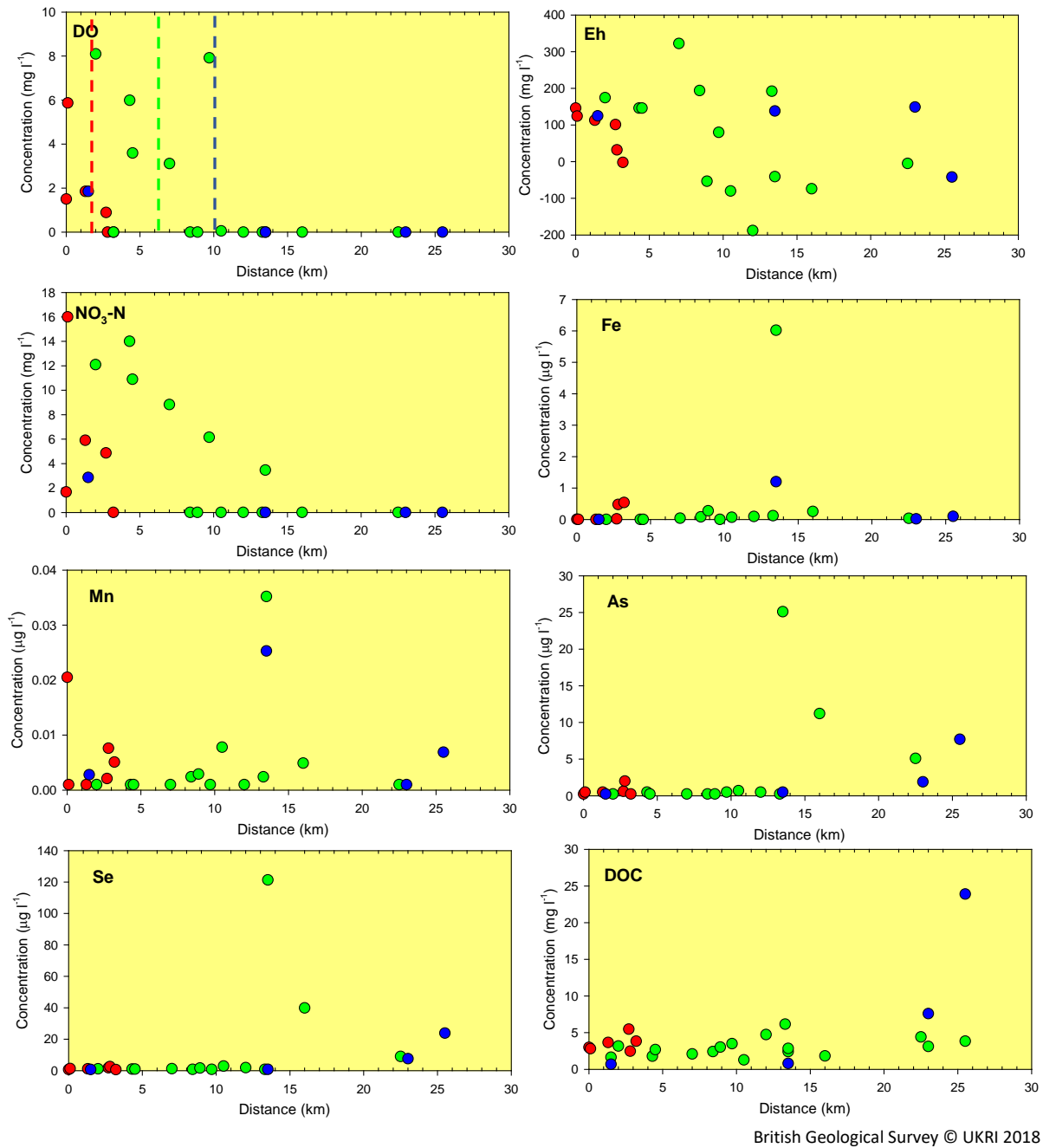


Figure 4.1 Variation in redox sensitive parameters and species across the Lincolnshire Limestone aquifer. Samples plotted across down-dip sections in the north (red) centre (green) and south (blue) of the study area to illustrate geochemical evolution as groundwater moves downgradient from the outcrop area (from Griffiths et al. (2006)). The corresponding edge of the outcrop area for each section across the aquifer is represented as a dashed line.

Table 4.2 sets out data from the confined and unconfined zones where these have been separately tabulated within the Baseline project. For the Chalk and the limestone, the differences in NO₃, Fe and Mn are clear and are in line with suggested indicator values for low redox zones. The Lower Greensand is low in Mn and elevated concentrations are not seen. Denitrification is identified in many of the other Baselines reports and these are discussed below.

Table 4.2 Comparison of median data from unconfined and confined zones from baseline data (N species as N)

Area	Unconfined				Confined				Reference
	NO ₃ -N (mg/L)	NO ₂ -N (mg/L)	Fe (µg/L)	Mn (µg/L)	NO ₃ -N (mg/L)	NO ₂ -N (mg/L)	Fe (µg/L)	Mn (µg/L)	
Yorkshire Humber Chalk	8.81	<0.01	<30	<10	<0.5	<0.01	2270	100	Smedley et al. (2004)
Colne-Lee Chalk	5.9	0.002	15	5	0.1	0.002	140	6	Shand et al. (2003b)
North Downs Chalk	6.4	<0.005	<30	<10	<0.3	<0.005	191	19.6	Smedley et al. (2003)
Lincolnshire Limestone	11.5	0.002	<30	<50	<0.003	0.0008	340	<50	Griffiths et al. (2006)
Lower Greensand – Folkestone Formation	4.23	0.004	65	33	0.02	0.5	185	11	Shand et al. (2003a)

CHALK

In the Chalk aquifer of the North Downs NO₃-N concentrations in groundwaters from the unconfined aquifer often reach close to or in excess of the EC maximum permissible value for drinking water of 11.3 mg/L (up to 28 mg/L observed) (Smedley et al., 2003). In the confined aquifer, the reducing conditions observed produce groundwaters with low NO₃ concentrations, either due to denitrification or to the presence of pre-modern (unpolluted) recharge. The relatively high concentrations of NH₄-N observed in the confined aquifer (up to 4.4 mg/L) are a relatively common feature of groundwaters from reducing aquifers and were considered to be naturally-derived, rather than as a result of local pollution. In the Colne-Lee Chalk, the most dramatic changes in water quality occur where the Chalk becomes confined beneath Palaeogene sediments coinciding approximately with the redox boundary in the aquifer (Shand et al., 2003b). This is partly due to the development of a redox boundary, situated close the boundary with overlying Palaeogene rocks. Oxygen decreases to less than detection limit in the confined aquifer and consequently NO₃ is removed from the system by denitrification or NO₃ reduction and Fe and Mn increase. In the Chalk of Dorset NO₃ concentrations were uniformly high across the unconfined aquifer, even at deeper sites Edmunds et al. (2002). Deeper groundwater is probably slow moving Holocene recharge separated from the main groundwater circulation of the present day. To the east of the unconfined/confined contact groundwaters were reducing.

Other areas of the Chalk have similar water quality. In the Chalk of Yorkshire the presence of NO₃ at concentrations greater than the EC maximum permissible value (11.3 mg/L) in some groundwater sources is one of the most significant problems (Smedley et al., 2004). Further east where the Chalk is covered by thick Superficial deposits, the aquifer becomes confined. Here, redox processes exert an important influence, with the redox boundary marking a zone of significant change in the concentrations of a number of elements. In the semi-confined dip-slope groundwaters of the Beverley–Driffield area, where superficial cover is largely arenaceous, NO₃-N concentrations were generally in the range 2–10 mg/L. Concentrations in the confined aquifer were low (usually <1 mg/L and often much lower), either as a result of denitrification or recharge

of the groundwaters at a time before the use of modern agricultural chemicals. Since the $\text{NO}_3\text{-N}$ concentrations in pre-pollution recharge are likely to have been of the order of 3–4 mg/L this implies that some degree of denitrification has taken place in the confined aquifer.

In the Chalk of north Norfolk $\text{NO}_3\text{-N}$ concentrations vary across the aquifer, with lowest concentrations in boreholes beneath the Palaeogene cover and highest in the unconfined coastal aquifer, and shows an inverse relationship with Fe (Smedley et al., 2004). Both Fe and Mn would be expected to be ubiquitous in the aquifer, with the Mn being released from the calcite phase during re-precipitation. Ammonium (NH_4^+) concentrations were elevated in several of the samples associated with reducing conditions, and were probably derived from clays. The low redox potential, and thus $\text{NO}_3\text{-N}$ concentrations found in the Waveney catchment may reflect the protective function of the more argillaceous nature of the till that is dominant in this area, compared to North Norfolk. The groundwaters of the Crag have varying redox status across the outcrop. Many samples in the Waveney catchment did not contain DO, whilst in the North they were generally oxidising. Concentrations of Fe generally exceeding 2 mg/L in the Waveney catchment while concentrations of both Mn and Fe were generally low in the North Norfolk region.

In contrast, Ander et al. (2004) only found one low NO_3 sample associated with low DO, and high Mn and Fe in the Chalk of central East Anglia and Stuart and Smedley (2009) found the Chalk aquifer of Hampshire to have elevated NO_3 concentrations and low concentrations of Fe, Mn, NO_2 and NH_4 .

In summary, a pattern of reducing conditions in the Chalk is found where the aquifer is confined by overlying Palaeogene strata or by low permeability argillaceous superficial deposits.

PERMO-TRIASSIC SANDSTONE

For the Sherwood Sandstone Shand et al. (2002) describe the presence of “windows” in the superficial deposits in the Vale of York, where NO_3 -rich recharge occurs. Beneath the impermeable superficial deposits, redox boundaries have developed allowing NO_3 reduction to occur. The redox control is also manifested by increases of Fe, Mn and NO_2 along flow lines beneath the clays. Griffiths et al. (2003a) reported that little denitrification was occurring in the sandstones of Cheshire at Mickledale but that low NO_3 found in some samples in the survey may indicate that some denitrification or NO_3 reduction has occurred. In Staffordshire Tyler-Whittle et al. (2002) found that oxidising conditions extended up to depths of 380 m and concentrations of NO_3 were high throughout most of the region. Reducing conditions were present where the sandstone is confined beneath the Mercia Mudstone, to the southeast and at isolated sites within the outcrop due to the presence of less permeable horizons within the aquifer. The reduced nitrogen species NO_2 and NH_4 were only present in the confined reduced groundwater, taken to indicate that denitrification and/or NO_3 reduction has occurred. The decrease in NO_3 concentrations at depth in the unconfined aquifer was thought to represent baseline conditions not reduced water. In the Manchester area, the presence of thick impermeable drift over much of the aquifer has allowed reducing conditions to exist even at shallow depths. This has given rise to high dissolved Fe, and NO_3 concentrations were very low due to denitrification (Griffiths et al., 2003b).

For the Liverpool area, Griffiths et al. (2005) found that high NO_3 concentrations were often associated with permeable drift, especially in some of the shallower boreholes, or unconfined conditions. High concentrations were also found in areas covered by impermeable drift deposits but these tend to be located along river valleys where drift thicknesses may be less due to erosion and local drift windows. NO_3 concentrations were higher, as expected, in oxidising waters with denitrification probably creating low concentrations where the groundwaters were reducing. For

Shropshire (Smedley et al., 2005) considered that the limited occurrence of observed reducing groundwaters suggested that either such conditions are of localised extent or that they have not been developed significantly for groundwater use. The reducing groundwaters were apparently distributed sporadically across the aquifer, related to the distribution of superficial deposits. Bearcock and Smedley (2012) do not report evidence of denitrification in the Otter Sandstone of Devon and Somerset.

In summary, a pattern of reducing conditions in the Permo-Triassic Sandstone is found where the aquifer is confined by overlying Mercia Mudstone Group strata or by low permeability argillaceous superficial deposits.

OTHER LIMESTONES

The Jurassic contains a number of limestone-bearing strata that provide significant aquifers. In the Corallian of Oxfordshire and Wiltshire there is a large range of NO_3 concentrations (Cobbing et al., 2004). The highest were from unconfined sources with shallow groundwater the most seriously affected. However the median was low at 0.25 mg/L ($\text{NO}_3\text{-N}$), reflecting the reducing conditions in many of the groundwaters. The highest Fe concentrations were found in the circumneutral low-Eh reducing groundwaters. Manganese is more soluble over a wider range of pH-Eh conditions than Fe. In the Corallian of the Vale of Pickering, most of the groundwaters sampled had NO_3 concentrations consistent with oxidising conditions, although the lowest suggest that conditions were reducing in some (Bearcock et al., 2015). Iron has a wide range of concentrations similar to the Cotswolds Oolites, but less than the Corallian of Oxfordshire and Wiltshire.

In the Great and Inferior Oolite of the Cotswolds the majority of unconfined groundwaters, and in particular, spring waters in the region were affected by high NO_3 concentrations (Neumann et al., 2003). In confined groundwaters, where DO is reduced or absent, NO_3 concentrations were lower indicating that in-situ denitrification is likely to have occurred. However, some of these waters may even be of sufficient age to represent pre-modern water. In the Great Oolite limestone, the onset of reducing conditions at depths occurs before the aquifer becomes confined. Within the Inferior Oolite aquifer, all unconfined groundwaters appear to be oxidising. The redox boundary lies within the confined part of the Inferior Oolite aquifer. All groundwater samples obtained from the confined Inferior Oolite show reducing conditions the redox-boundary occurs some 7-8 km down gradient of nominal confinement. Iron concentrations increase in groundwaters beyond the redox boundary, reaching up to 1260 $\mu\text{g/L}$ towards the end of the sampled flow line. Manganese concentrations are also high in some confined groundwater samples. Sulphate reduction is believed to have occurred in two boreholes drawing water from the confined limestone aquifers.

In the Lincolnshire Limestone $\text{NO}_3\text{-N}$ concentrations display a particularly wide range from below detection limit to 20.7 mg/L which reflects the high NO_3 concentrations of the unconfined aquifer and low concentrations within the confined aquifer to the east (Griffiths et al., 2006). However, low NO_3 concentrations in the confined part of the aquifer were considered to be predominantly the result of lower NO_3 inputs in the past.

In the Permian Magnesian Limestone of County Durham and north Yorkshire (Bearcock and Smedley, 2009), the complex lithology and variable chemistry of the strata mean that sites with groundwaters of a very different chemistry occur in close proximity. The most oxidised waters were found in the east of the aquifer, and there is a general north-south trend, with groundwaters becoming more reducing towards the south. The $\text{NO}_3\text{-N}$ has the largest concentration range, which can be related to the large variation in redox conditions, the population of low $\text{NO}_3\text{-N}$ concentrations could represent NO_3 lost in reducing conditions through denitrification.

Concentrations of Fe, Mn and SO₄ were particularly variable. Of those investigated, the element most frequently exceeding the drinking-water limit was Mn (28% of samples in the dataset had concentrations exceeding 50 µg/L and concentrations ranged up to 1300 µg/L).

In the Carboniferous Limestone of northern England concentrations of NO₃ were generally low (Abesser et al., 2005b). Some groundwaters clearly show enhanced levels particularly shallow groundwaters (< 40 m) and springs, but even in the deeper parts of the aquifer. Because many of the waters were relatively reducing, denitrification or DNRA may have lowered the concentrations. Nitrite and in particular NH₄-N concentrations above the EU MAC of 0.03 mg/L and 0.38 mg/L occur more commonly, although median values for the aquifer were low. Oxygen depletion and low redox conditions were typically associated with deeper groundwaters that frequently show increased Fe and Mn concentrations. However, concentrations in excess of the drinking water limits of 250 µg/L for Fe and 50 µg/L for Mn only occur where DO levels <2 mg/L and Eh <350 mV provide favourable conditions for reductive oxide dissolution. Similarly, NH₄-N concentrations in excess of 0.5 mg/L were found in deeper, mostly reducing (Eh <350 mV) groundwaters. The NO₃-N levels of these high NH₄-N groundwaters were generally low, signifying that DNRA may take place. The distribution of redox status in the groundwaters of the study area is complex, due to the variations in the occurrence of impermeable superficial deposits as well as due to the layered nature of the aquifer where limestones provide the water-bearing strata whereas the interbedded mudstones act as aquicludes or aquitards.

In the Derbyshire Dome, NO₃ is present in most groundwaters (<0.05–12.6 mg/L as N) (Abesser and Smedley, 2008). Concentrations were mostly low (median 3.06 mg/L) but were generally higher in the groundwaters on the Carboniferous Limestone outcrop than on the Millstone Grit (except for one very young groundwater) as fractures in the limestone provide pathways of rapid transport to the water tables. Concentrations were generally highest in oxic groundwaters Nitrate is also detectable in most thermal waters (except for St Anne's Well), indicating the presence of a component of recent recharge. Denitrification may have lowered NO₃-N concentrations in some groundwaters, as indicated.

In summary, limestones commonly exhibit a complex distribution of zones of low redox. These do occur in confined zones although the distance of the redox boundary from the confined/unconfined boundary is variable. Distribution may also be related to the distribution of superficial deposits and to layering in the aquifer. It has also been demonstrated that low redox does not necessarily imply that denitrification does occur.

OTHER SANDSTONES

In the confined sand aquifers of the Palaeogene in southeast England there is a large range of redox conditions with some samples exhibiting low NO₃ (Bearcock and Smedley, 2010). There appear to be “pockets” of reduced groundwaters throughout the London Palaeogene beds. There is a weak negative correlation between the Eh and the NH₄-N concentration, suggesting that NO₃ reduction occurs under the most reducing conditions. However, several fully oxidised sites have a relatively high NH₄-N concentration. A site near Ascot shows strongly reducing conditions sufficient to support SO₄ reduction. This is evidenced by a low SO₄ concentration (0.215 mg/L), a low NO₃-N concentration (0.23 mg/L), and a corresponding high NH₄-N concentration (6.7 mg/L). In Wessex the majority of unconfined groundwaters in the Palaeogene sediments have elevated NO₃ concentrations (Neumann et al., 2004). However, 70% of sampled groundwaters were strongly reducing, with some waters having a strong H₂S smell. In these waters, Fe and Mn concentrations were elevated while NO₃ concentrations were low indicating that denitrification is likely to have occurred.

In the Cretaceous Lower Greensand aquifer of southern England, NO_3 varies in concentration from below detection limit in the more reducing groundwaters to 16.3 mg/L $\text{NO}_3\text{-N}$ in the more oxidising groundwaters (Shand et al., 2003a). The unconfined Folkestone Formation has predominantly high NO_3 . The Hythe Formation show a wide range in $\text{NO}_3\text{-N}$ concentrations (<0.03–15.8 mg/L) the lower concentrations being from parts of the aquifer confined beneath the Folkestone, Bargate and Sandgate strata. Many reducing groundwaters also have concentrations of NO_3 below the detection limit. In the Slough boreholes, the presence of H_2S gas was noted whilst sampling. The confined parts of the aquifer therefore, contain elevated concentrations of Fe. In contrast, Mn is often low most likely due to the low Mn concentrations in the aquifer.

Nitrate concentrations were variable in the Jurassic Bridport Sand Formation aquifer of southwest England (Shand et al., 2004). The highest concentrations occur in the more oxidising groundwaters. Fe and Mn provide a good indicator of the redox conditions in these circum-neutral pH groundwaters where DO and Eh are poorly constrained. Water quality is consistent with the removal of NO_3 by denitrification under reducing conditions. Water quality is influenced by both limitations on vertical hydraulic conductivity and by compartmentalisation of the aquifer by fracturing.

Nitrate concentrations were generally low throughout the Carboniferous Millstone Grit aquifer of northern England (mean <1 mg/L) partly due to denitrification or DNRA in these relatively reducing waters and partly due to the protection of the aquifer provided by its multi-layered nature as well as by the overlying superficial deposits (Abesser et al., 2005a). Groundwaters with Eh values below 350 mV and low concentrations of DO also contain high concentrations of dissolved Fe.

In the Devonian Old Red Sandstone aquifers in Wales and Herefordshire, groundwater is moderately pristine but with local inputs of NO_3 (Moreau et al., 2004). Most of the groundwaters studied contained DO and had moderately high Eh. The samples where NO_3 was below the limit of detection were moderately reducing and have most likely undergone denitrification. Ammonium concentrations were generally highest in the reducing groundwaters (up to 0.07 mg/L), but the sample with the highest NO_3 (15.6 mg/L $\text{NO}_3\text{-N}$) also contained NH_4 with a concentration of 0.11 mg/L, probably as a result of pollution. The abundance of oxidising groundwaters is reflected in low median concentrations of Fe and Mn (0.02 and 0.003 mg/L respectively), even though Fe oxides are abundant as cements in the aquifer. However, under reducing conditions, Fe and Mn are mobile and the more reducing groundwaters contain relatively high concentrations, up to 3.2 and 0.95 mg/L respectively.

In summary, the Lower Greensand demonstrates low redox zones related to confinement by the overlying Gault, but the pattern in the Palaeogene is more complex. Distribution may also be related to the distribution of superficial deposits and to layering in the aquifer. In older indurated sandstones, NO_3 concentrations were generally lower.

OTHER

In the Silurian and Ordovician strata of the Plynlimon catchment in Wales (Shand et al., 2005) NO_3 concentrations were low in both the upper catchments of the Severn and Wye. Nitrate concentrations varied from <LOD up to 1-2 mg l⁻¹ and NH_4 is present at up to 0.7 mg/L in the more reducing groundwaters. Manganese and Fe were high in many of the shallow groundwaters, particularly in the Wye catchment. This may be due to reducing conditions caused by more extensive superficial deposits in this part of the Wye catchment. In the Teifi catchment NO_3 concentrations were higher ranging up to 9.3 mg/L in the bedrock and 4.3 mg/L in the superficial deposits and NH_4 is present up to 1.7 mg/L in the bedrock. TOC concentrations may also reach moderately high concentrations, up to 7 mg/L. A strong smell of H_2S was noted in several

boreholes, indicating that SO₄-reducing conditions occur at depth, and in shallow ground waters beneath organic-rich soils and clay.

In the granites of southwest England, a large range of NO₃-N concentrations is observed at the shallowest depths (Smedley and Allen, 2004). Only three samples in the database used in this study were from boreholes with recorded depths greater than 80 m. These had comparatively low, though still detectable, NO₃-N concentrations around 5 mg/L.

In summary, whilst there is evidence of low redox conditions, related to confinement by organic-rich superficial deposits, there is no direct evidence for denitrification.

4.3 ENVIRONMENT AGENCY GROUNDWATER MONITORING REVIEW REPORTS

Table 4.3 shows summary quality data for Environment Agency Groundwater Quality Monitoring Review reports where the text identifies that parts of the aquifer are confined. The full list of report summaries are in Appendix 1. These are taken from summaries showing the percentage of concentrations over the DWL. Where these were not provided data from the mean, 95 percentile and maximum have been used.

All areas which have been assessed as partly confined, except the Magnesian Limestone of the East Midlands show elevated concentrations of Fe and Mn and many of NO₂ as well. Measurements for DO do not appear to be reliable and many indicate minimum concentrations of >1 mg/L. Comments suggest that elevated concentrations of NH₄ were likely to be derived from local pollution.

These areas include the Carboniferous limestones and sandstones of northern England, parts of the Magnesian Limestone, Permo-Triassic sandstones of the northwest, Jurassic limestones of the Cotswolds and the Corallian, the Lower Greensand, areas of the Chalk confined by the Palaeogene or by low permeability superficial deposits and the Crag.

This dataset will be evaluated in greater detail as part of the construction of the map

Table 4.3 Summary data from Environment Agency Groundwater Quality Monitoring Reports where confined conditions are identified within the area

Report Area	Monitoring unit	DO (mg/L)	NO ₃ -N (%>QL-11.3 mg/L)	NO ₂ -N (%>QL-0.03 mg/L)	NH ₄ -N (%>QL-0.39 mg/L)	Fe (%>QL-200 µg/L)	Mn (%>QL-50 µg/L)	SO ₄ (%>QL-250 mg/L)	Evidence for confined conditions	Reference
Ang 2*	Norfolk and Suffolk Crag	0-sat	Mean>QL	95%ile>QL	Yes	Mean>QL	Mean>QL	Max>QL	Yes –by drift	Environment Agency (2009c)
S 1*	East Hampshire Chalk	>1.7	Max>QL	0	0	Max>QL	0	0	Yes along tertiary edge semi-confined	Environment Agency (2004d)
S 13*	Chichester Chalk	>1.9	Max>QL	Max>QL	Max>QL	95%ile>QL	95%ile >QL	0	Yes in Littlehampton inlier	ENTEC (2008b)
Tham 3	Confined Chalk of the London Basin	0-sat	1.7	1.1	14	25.4	2.4	4.6	Yes	ESI (2006a)
Tham 5	Kennet Valley Chalk	0.16-12	8.9	2.7	13	8.7	0.8	0	Yes	ESI (2005a)
Ang 1*	Norfolk and Suffolk Chalk	0-sat	Mean>QL	95%ile>QL	95%ile>QL	95%ile>QL	95%ile>QL	95%ile>QL	Yes	Environment Agency (2009b)
Ang 3*	North Essex Chalk	1.1-9.8	0	-	95%ile>QL	Mean>QL	95%ile>QL	0	Yes	Environment Agency (2009d)
Ang 4*	South Essex Chalk	0-7.8	0	Max>QL	Mean>QL	Mean>QL	95%ile>QL	Max>QL	Yes mainly confined	Environment Agency (2009e)
S 8*	Kent Lower Greensand	>2.5	95%ile >QL	95%ile >QL	0	Max>QL	95%ile >QL	0	Yes. In northern boundary	ENTEC (2008e)
S 16*	Isle of Wight Lower Greensand	>1.32	Max>QL	Max>QL	Max>QL	95%ile>QL	95%ile >QL	0	Yes	ENTEC (2008d)
S 17*	Western Lower Greensand	>1.1	Max>QL	Max>QL	Max>QL	80	95%ile >QL in Folkestone	0	Yes	ENTEC (2008j)
Tham 6	Lower Greensand	0-8.7	6.3	2.9	5.9	27	9.5	0	Yes	ESI (2006e)
MID1	Jurassic Limestone of Cotswolds Edge		18.3	0		3	1.4	0	Yes	Besien et al. (2006)
Tham 1	Corallian	0.1-10.4	10	1	0	63	21	5	Yes	Duncan et al. (2004)
NW3	Permo-Triassic sandstones of the Wirral and West Cheshire		8.3	6.5	3.1	12	15	Low 2.2	Yes	ESI (2006i)

Report Area	Monitoring unit	DO (mg/L)	NO ₃ -N (%>QL-11.3 mg/L)	NO ₂ -N (%>QL-0.03 mg/L)	NH ₄ -N (%>QL-0.39 mg/L)	Fe (%>QL-200 µg/L)	Mn (%>QL-50 µg/L)	SO ₄ (%>QL-250 mg/L)	Evidence for confined conditions	Reference
NW4	Permo-Triassic sandstones of Eden Valley and Carlisle Basin		5	2.3	0.95	13	21	8.1 from evaporites	Yes	ESI (2006b)
NW8	Sherwood Sandstone of Furness and West Cumbria	> 0.02	All		3.67	24.7	23.7	1	Yes	ESI (2006c)
MID3	Magnesian Limestone of the East Midlands	1.02-9.61	22	11	0	0	0	33	Yes	Besien and Pearson (2007b)
NE4	Skerne Magnesian limestone		0	3.1	2.1	22	30	14	Yes	ESI (2004a)
NE1	Till and Northumberland rivers Fell sandstone		Low except arable area	10	2.2	High in N centre. Up to 7.7 mg/L	33	9	Yes	ESI (2004b)
NE2	Tyne Fell Sandstone		0	NQ	0	74	All	0	Yes	ESI (2004c)
NW2	Carboniferous Limestone, Millstone Grit and Coal Measures of the Lune and Kent		Low, 1.2% Low 0.79	13% 0	3.2 both	28 67	16 54	Low	Yes	ESI (2006f)
NW6	Carboniferous Limestone, Millstone Grit and Coal Measures of the Ribble		0 0 2.1	2.1 0.03 0	8.4 0.39 6	30 37 60	33 34 52	0	Yes	ESI (2006h)
NW9	Millstone Grit and Coal Measures of Northern Manchester	0.2	5	-	14	72	73	71	Yes	ESI (2006g)

5 Construction of a UK denitrification map

5.1 APPROACH

It is proposed to use a “lines of evidence” based approach. This will develop a series of GIS layers that will be overlain to provide the three main lines.

5.1.1 Hydrological settings favouring development of low redox zones

This line of evidence will draw on the material set out in Section 4. Literature data are predominantly related to the confined zones of the three principal aquifers. The distance of the redox boundary from outcrop has been established for these aquifers. This approach will be extended to the confined zones of other principal and secondary aquifers where this can potentially be corroborated by monitoring data.

Other areas that need to be considered are areas where there are significant low permeability or high organic carbon superficial deposits and areas of floodplain deposits that may confine underlying shallow groundwater

Data which need to be collected are:

- Aquifer subcrop – This will be derived from the BGS 3D model. This can provide depths for the top of the main formations, e.g. Chalk Group, Lower Greensand Group, Corallian Group, Great and Inferior Oolite Groups, Lias, Sherwood Sandstone Group, Zechstein Group, Coal Measures, Dinantian Limestone, Devonian. The total aquifer depth will be defined as 400 m below the surface to retain consistency with other approaches.
- Superficial deposits:
 - Low permeability deposits classified using the approach of Griffiths et al. (2011). This approach will need to take account of both lithology and thickness
 - Organic deposits will include peat
 - Alluvium will be used as a simple surrogate for the presence of a hyporheic zone

5.1.2 Groundwater monitoring data indicating potential denitrification

In the first instance, values from the Environment Agency strategic monitoring network will be used. This will include oxidised nitrogen species, TON or NO_3^- , NO_2^- and NH_4^+ . It will also include parameters which could be indicative of suitable reducing conditions, DO, DOC, Mn^{2+} , Fe^{2+} , SO_4^{2-} . These will also be used to attempt to delineate areas where widespread denitrification is unlikely. Indicator values for the presence of denitrification will be drawn from Sections 2 and 4, mainly from Table 2.4.

Data which need to be collected are:

- Environment Agency strategic monitoring data for TON or NO_3^- , NO_2^- , NH_4^+ . DO, DOC, Mn^{2+} , Fe^{2+} , SO_4^{2-} , including designated aquifer, borehole depth and confined/unconfined.

5.1.3 Mass balance approaches.

These will identify areas where inputs of N do not appear to be reflected in current groundwater concentrations. Particularly where N is absent Inputs could include N applications to arable

land and urban areas which will be drawn from data used in the NVZ delineation process, and also aerial deposition. Aerial deposition is represented within the NEAP-N model.

- nitrate loading concentrations related to the NVZ designation process
- Estimate of nitrate in recharge – The Baseline series reports make an estimation for each area

5.2 CONSTRUCTION OF MAP

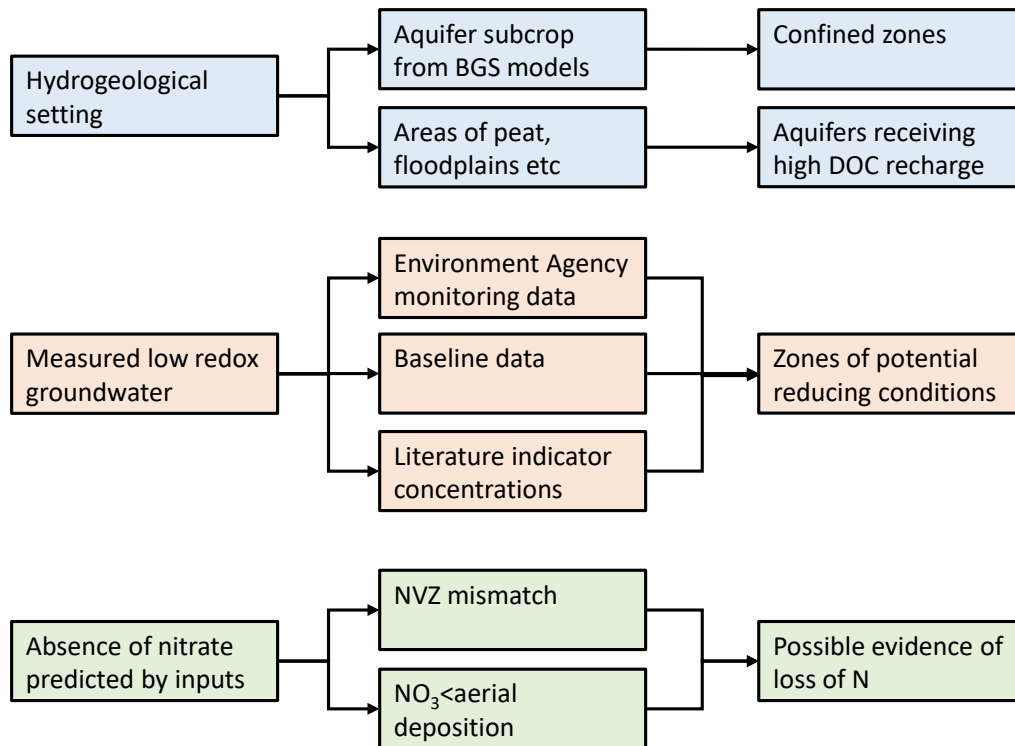


Figure 5.1 Map component layers

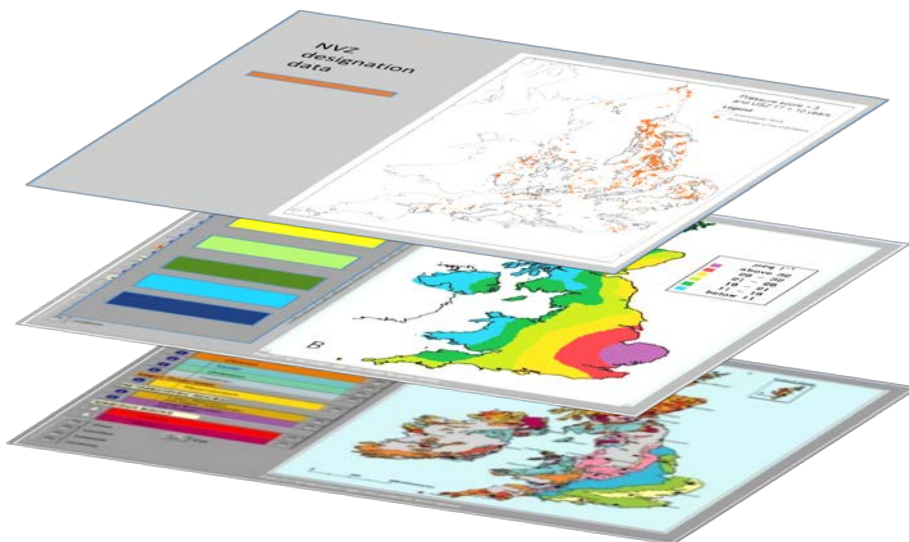


Figure 5.2 Overlay of data layers

Appendix 1 Summary of Environment Agency Groundwater Quality monitoring reports

No	Monitoring unit	Strata	DO (mg/L)	NO ₃ -N (%>QL- 11.3 mg/L)	NO ₂ -N (%>QL- 0.03 mg/L)	NH ₄ -N (%>QL- 0.39 mg/L)	Fe (%>QL- 200 µg/L)	Mn (%>QL- 50µg/L)	SO ₄ (%>QL-250 mg/L)	Evidence for confined conditions	Reference
NE1	Till and Northumberland rivers Fell sandstone			Low except arable area	High around Berwick. 10% >QL	2.2	High in N centre. Up to 7.7 mg/L	High in centre. 33% >QL	Elevated. 9	Yes	(ESI, 2004b)
NE2	Tyne Fell Sandstone			0	NQ	0	74	All	0	Yes	(ESI, 2004c)
NE4	Skerne Magnesian limestone			High in west. V low where confined	3.1% >QL	2.1	High. 22% >QL	Max around Newton Aycliffe. 30% >QL	14	Yes	(ESI, 2004a)
NW1	Lake District	-		Low. 1.4	2.4	High near Kendall. 2	Low but 5.1	6.1	Low. High related to pyrite	No	(ESI, 2006d)
NW2	Carboniferous Limestone, Millstone Grit and Coal Measures of the Lune and Kent	Limestone Grit&Coal		Low, 1.2% Low 0.79	13% 0	3.2 both	28 67	16 54	Low	Yes	(ESI, 2006f)
NW3	Permo-Triassic sandstones of the Wirral and West Cheshire			High on western margin 8.3	6.5	3.1 at polluted site	12	15	Low 2.2	Yes	(ESI, 2006i)
NW4	Permo-Triassic sandstones of Eden Valley and Carlisle Basin	St Bees Penrith		5 13	2.3 3.3	0.95 0.63	13 8	21 4.2	8.1 from evaporites 0	Yes No	(ESI, 2006b)
NW6	Carboniferous Limestone, Millstone Grit and Coal Measures of the Ribble	Limestone Grit Coal		0 0 2.1	2.1 0.03 0	8.4 0.39 6 possibly anthropogenic	30 37 60	33 34 52	0	Yes	(ESI, 2006h)
NW8	Sherwood Sandstone of Furness and West Cumbria	Furness W Cumbria	> 0.02 >5.5	All		3.67 2	24.7 17	23.7 13	1 4	Yes no	(ESI, 2006c)

No	Monitoring unit	Strata	DO (mg/L)	NO ₃ -N (%>QL- 11.3 mg/L)	NO ₂ -N (%>QL- 0.03 mg/L)	NH ₄ -N (%>QL- 0.39 mg/L)	Fe (%>QL- 200 µg/L)	Mn (%>QL- 50µg/L)	SO ₄ (%>QL-250 mg/L)	Evidence for confined conditions	Reference
NW9	Millstone Grit and Coal Measures of Northern Manchester	Grit Coal	0.2 0.2	0 5	-	0 14	42 72	70 73	0 71	No Yes	(ESI, 2006g)
MID1	Jurassic Limestone of Cotswolds Edge			18.3	0		3	1.4	0	Yes	(Besien et al., 2006)
MID2	Carboniferous sandstones of Coventry			30	ND	ND	ND	ND	0	No	(Besien and Pearson, 2007a)
MID3	Magnesian Limestone of the East Midlands		1.02- 9.61	22 Low in confined zone	11	0	0	0	33	Yes	(Besien and Pearson, 2007b)
MID4	Coal Measures of Wyre Forest		>6	30	0	0	16	21	23	No	(Pearson, 2007)
Anglian 1*	Norfolk and Suffolk Chalk		0-sat	Mean>QL	95%ile>QL	95%ile>QL	95%ile>QL	95%ile>QL	95%ile>QL	Yes	(Environment Agency, 2009b)
Anglian 2*	Norfolk and Suffolk Crag		0-sat	Mean>QL	95%ile>QL	Yes	Mean>QL	Mean>QL	Max>QL	Yes –by drift	(Environment Agency, 2009c)
Anglian 3*	North Essex Chalk		1.1-9.8	0	-	95%ile>QL	Mean>QL	95%ile>QL	0	Yes	(Environment Agency, 2009d)
Anglian 4*	South Essex Chalk		0-7.8	0	Max>QL	Mean>QL	Mean>QL	95%ile>QL	Max>QL	Yes mainly confined	(Environment Agency, 2009e)
Anglian 5*	Essex gravels		2.4-sat	0	0	0	Max>QL	Max>QL	0	No	(Environment Agency, 2009a)
Thames 1	Corallian		0.1-10.4	10	1	0	63	21	5	Yes	(Duncan et al., 2004)
Thames 2	Upper River Lee Chalk		>3.8	7.6	1.4	0.2	1	0	0	Rarely but by till	(ESI, 2005e)
Thames 3	Confined Chalk of London Basin		0-sat	1.7	1.1	14	25.4	2.4	4.6	Yes	(ESI, 2006a)
Thames 4	Thames Valley gravels		>2.2	22.4	6.4	0.6	6.3	8.5	0.3	No	(ESI, 2005f)
Thames 5	Kennet Valley Chalk		0.16-12	8.9	2.7	13	8.7	0.8	0	Yes	(ESI, 2005a)
Thames 6	Lower Greensand		0-8.7	6.3	2.9	5.9	27	9.5	0	Yes	(ESI, 2006e)
Thames 7	Mid-Chilterns and Colne Chalk		0.92-12	1.0	4.9	5.3	1.1	0.2	0	No	(ESI, 2005b)

No	Monitoring unit	Strata	DO (mg/L)	NO ₃ -N (%>QL- 11.3 mg/L)	NO ₂ -N (%>QL- 0.03 mg/L)	NH ₄ -N (%>QL- 0.39 mg/L)	Fe (%>QL- 200 µg/L)	Mn (%>QL- 50µg/L)	SO ₄ (%>QL-250 mg/L)	Evidence for confined conditions	Reference
Thames 8	North Downs Chalk		-	0.3	33.5	0.4	0.7	0	0	NO ₂ ascribed to mixing. Confined at 1 site	(ESI, 2005c)
Thames 9	SW and Twyford Chalk		>5.1	19	1.0	0.11	1.6	0	0	No	(ESI, 2005d)
SW1	Dorset Stour Chalk		>4.5	12	0	0	0	0	0	No	(Environment Agency, 2004c)
SW2	Frome Piddle Chalk		>5.5	9	0	0	0	0	0	No	(Environment Agency, 2004e)
SW3	Hampshire Avon Chalk		>3	9	0	0	5	2.3	0	No	(Environment Agency, 2004f)
SW4	Jurassic Limestone	Great & Inferior Oolite	0.1-11.3	0	0	0	9	0	0	No	(Environment Agency, 2004g)
SW5	Mendips Limestone		>5.4	0	0	0	0	0	0	No	(Environment Agency, 2004h)
SW6	Otter Sandstone		>6.1	14	0	0	14	14	0	None, but few points in confined	(Environment Agency, 2004i)
Southern 11*	Seaford & Eastbourne Chalk		>2.9	0	Yes	0	Yes	Yes	0	No, Fe attributed to pipework	(ENTEC, 2008h)
Southern 12*	East Kent Stour Chalk		>1.2	Yes	0	Max>QL	0	Yes	0	No	(ENTEC, 2008c)
Southern 13*	Chichester Chalk		>1.9	Max>QL	Max>QL	Max>QL	95%ile>Q L	95%ile >QL	0	Yes in Littlehampto n inlier	(ENTEC, 2008b)
Southern 14*	North Kent Medway Chalk		0.56-4.2	95%ile>QL	Max>QL	Yes	0	Max>QL	0	No	(ENTEC, 2008f)
Southern 15*	West Kent Darent and Cray Chalk		6.6-11.7	Max>QL	Max>QL	0	95%ile>Q L	Max>QL	0	No	(ENTEC, 2008i)
Southern 16*	Isle of Wight Lower Greensand		>1.32	Max>QL	Max>QL	Max>QL	95%ile>Q L	95%ile >QL	0	Yes	(ENTEC, 2008d)

No	Monitoring unit	Strata	DO (mg/L)	NO ₃ -N (%>QL-11.3 mg/L)	NO ₂ -N (%>QL-0.03 mg/L)	NH ₄ -N (%>QL-0.39 mg/L)	Fe (%>QL-200 µg/L)	Mn (%>QL-50µg/L)	SO ₄ (%>QL-250 mg/L)	Evidence for confined conditions	Reference
Southern 17*	Western Lower Greensand	Folkestone and Hythe Fms	>1.1	Max>QL	Max>QL	Max>QL	80	95%ile >QL in Folkestone Fm	0	Yes	(ENTEC, 2008j)
Southern 1*	East Hants Chalk		>1.7	Max>QL	0	0	Max>QL	0	0	Yes along tertiary edge semi-confined	(Environment Agency, 2004d)
Southern 2*	Isle of Wight Central Downs Chalk			0	0	0	0	0	0	No	(Environment Agency, 2004a)
Southern 3*	Isle of Wight Southern Downs Chalk			0	0	0	Max>QL	Max>QL	0	No	(Environment Agency, 2004b)
Southern 4*	River Itchen Chalk		?	Max>QL	95%ile >QL	Max>QL	95%ile >QL	95%ile >QL	0	?	(Environment Agency, 2004j)
Southern 5*	River Test Chalk		?	0	0	Max>QL	95%ile >QL	Max>QL	0	?	(Environment Agency, 2004k)
Southern 6*	Thanet Chalk		?	Mean>QL	0	0	0	0	0	No	(Environment Agency, 2004l)
Southern 7*	North Kent Swale Chalk		?	Max>QL	0	Max>QL	0	Max>QL	0	No, CWF?	(ENTEC, 2008g)
Southern 8*	Kent Lower Greensand	Folkestone and Hythe	>2.5	95%ile >QL	95%ile >QL	0	Max>QL	95%ile >QL	0	Yes. In northern boundary	(ENTEC, 2008e)
Southern 9*	Worthing Chalk		>2.2	Max>QL	Max>QL	Max>QL	0	Max>QL	0	No	(ENTEC, 2008k)
Southern 10*	Brighton Chalk		>2.3	Max>QL	Max>QL	Max>QL	95%ile >QL	Max>QL	0	No	(ENTEC, 2008a)

References

- ABESSER, C, SHAND, P, AND INGRAM, J. 2005a. Baseline Series Report 18: The Millstone Grit of Northern England. *British Geological Survey Commissioned Report CR/05/015N & Environment Agency Report NC/99/74/18*.
- ABESSER, C, SHAND, P, AND INGRAM, J. 2005b. Baseline Series Report 22: The Carboniferous Limestone of Northern England. *British Geological Survey Commissioned Report CR/05/076N & Environment Agency Report NC/99/74/22*.
- ABESSER, C, AND SMEDLEY, P L. 2008. Baseline groundwater chemistry: the Carboniferous Limestone aquifer of the Derbyshire Dome. *British Geological Survey Open Report OR/08/028*.
- ANDER, L, SHAND, P, LAWRENCE, A R, GRIFFITHS, K J, HART, P, AND PAWLEY, J. 2004. Baseline Series Report 13: The Great Ouse Chalk aquifer, East Anglia. *British Geological Survey Commissioned Report CR/04/236N & Environment Agency Report NC/99/74/13*.
- ANDERSON, T R, GROFFMAN, P M, KAUSHAL, S S, AND WALTER, M T. 2014. Shallow groundwater denitrification in riparian zones of a headwater agricultural landscape. *Journal of Environmental Quality*, Vol. 43, 732-744.
- APPELO, C A J, AND POSTMA, D. 2005. *Geochemistry, Groundwater and Pollution* (2nd edition). (Boca Raton: CRC Press.)
- ARAVENA, R, AND 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. *Ground Water*, Vol. 36, 975-982.
- BARRETT, M, JAHANGIR, M M, LEE, C, SMITH, C J, BHREATHNACH, N, COLLINS, G, RICHARDS, K G, AND O'FLAHERTY, V. 2013. Abundance of denitrification genes under different piezometer depths in four Irish agricultural groundwater sites. *Environmental Science and Pollution Research*, Vol. 20, 6646-6657.
- BEARCOCK, J M, AND SMEDLEY, P L. 2009. Baseline groundwater chemistry: the Magnesian Limestone of County Durham and north Yorkshire. *British Geological Survey Open Report OR/09/030*.
- BEARCOCK, J M, AND SMEDLEY, P L. 2010. Baseline groundwater chemistry: the Palaeogene of the Thames Basin. *British Geological Survey Open Report OR/10/057*.
- BEARCOCK, J M, AND SMEDLEY, P L. 2012. Baseline groundwater chemistry: the Sherwood Sandstone of Devon and Somerset. *British Geological Survey Open Report OR/11/060*.
- BEARCOCK, J M, SMEDLEY, P L, AND MILNE, C J. 2015. Baseline groundwater chemistry: the Corallian of the Vale of Pickering, Yorkshire. *British Geological Survey Open Report OR/15/048*.
- BESIEN, A, AND PEARSON, A. 2007a. Groundwater Quality Review: Coventry Carboniferous Sandstones GWQR-MID-D9. *Environment Agency Report* (Bristol).
- BESIEN, A, AND PEARSON, A. 2007b. Groundwater Quality Review: Magnesian Limestone of the East Midlands GWQR-MID-E1. *Environment Agency Report* (Bristol).
- BESIEN, A, PEARSON, A, BOLAND, M, AND CONE, S. 2006. Groundwater Quality Review: Cotswold Edge Jurassic Limestones GWQR-MID-G9. *Environment Agency Report* (Bristol).
- BITTON, G, AND GERBA, C P. 1984. *Groundwater pollution microbiology* (John Wiley and Sons, Inc., New York.)
- BJERG, P J, RUEGGE, K, PEDERSEN, J K, AND CHRISTENSEN, T H. 1995. Distribution of redox-sensitive groundwater quality parameters downgradient of a landfill (Grindsted, Denmark). *Environmental Science & Technology*, Vol. 29, 1387-1394.
- BLICHER-MATHIESEN, G, ANDERSEN, H E, CARSTENSEN, J, BØRGESEN, C D, HASLER, B, AND WINDOLF, J. 2014. Mapping of nitrogen risk areas. *Agriculture, Ecosystems & Environment*, Vol. 195, 149-160.
- BLICHER-MATHIESEN, G, MCCARTY, G W, AND NIELSEN, L P. 1998. Denitrification and degassing in groundwater estimated from dissolved dinitrogen and argon. *Journal of Hydrology*, Vol. 208, 16-24.
- BÖHLKE, J, AND DENVER, J. 1995. Combined use of groundwater dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic coastal plain, Maryland. *Water Resources Research*, Vol. 31, 2319-2339.

- BÖHLKE, J, WANTY, R, TUTTLE, M, DELIN, G, AND LANDON, M. 2002. Denitrification in the recharge area and discharge area of a transient agricultural nitrate plume in a glacial outwash sand aquifer, Minnesota. *Water Resources Research*, Vol. 38, 1105.
- BÖTTCHER, J, STREBEL, O, AND DUYNISVELD, W H. 1989. Kinetik und Modellierung gekoppelter Stoffumsetzungen im-Grundwasser eines Lockergesteins-Aquifers. *Geologisches Jahrbuch Reihe C*, Vol. 51, 3-40.
- BÖTTCHER, J, STREBEL, O, VOERKELIUS, S, AND 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*, Vol. 114, 413-424.
- BOULTON, A J, FINDLAY, S, MARMONIER, P, STANLEY, E H, AND VALETT, H M. 1998. The functional significance of the hyporheic zone in streams and rivers. *Annual Review of Ecology and Systematics*, Vol. 29, 59-81.
- BOUWMAN, A F, KRAM, T, AND KLEIN GOLDEWIJK, K. 2006. Integrated modelling of global environmental change. An overview of IMAGE 2.4. *Netherlands Environmental Assessment Agency Publication 500110002/2006* (Bilthoven).
- BRAGAN, R J, STARR, J L, AND PARKIN, T B. 1997. Shallow groundwater denitrification rate measurement by acetylene block. *Journal of Environmental Quality*, Vol. 26, 1531-1538.
- BURGIN, A J, AND HAMILTON, S K. 2007. Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways. *Frontiers in Ecology and the Environment*, Vol. 5, 89-96.
- BUROW, K R, NOLAN, B T, RUPERT, M G, AND DUBROVSKY, N M. 2010. Nitrate in groundwater of the United States, 1991– 2003. *Environmental Science & Technology*, Vol. 44, 4988-4997.
- BURT, T P, BATES, P D, STEWART, M D, CLAXTON, A J, ANDERSON, M G, AND PRICE, D A. 2002. Water table fluctuations within the floodplain of the River Severn, England. *Journal of Hydrology*, Vol. 262, 1-20.
- BUSS, S R, HERBERT, A W, MORGAN, P, THORNTON, S F, AND SMITH, J W N. 2004. A review of ammonium attenuation in soil and groundwater. *Quarterly Journal of Engineering Geology and Hydrogeology*, Vol. 37, 347-359.
- CELLE-JEANTON, H, HUNEAU, F, TRAVI, Y, AND EDMUNDS, W M. 2009. Twenty years of groundwater evolution in the Triassic sandstone aquifer of Lorraine: impacts on baseline water quality. *Applied Geochemistry*, Vol. 24, 1198-1213.
- CHAMP, D R, GULENS, J, AND JACKSON, R E. 1979. Oxidation–reduction sequences in ground water flow systems. *Canadian Journal of Earth Sciences*, Vol. 16, 12-23.
- CHAPELLE, F H, BRADLEY, P M, LOVLEY, D R, O'NEILL, K, AND LANDMEYER, J E. 2002. Rapid evolution of redox processes in a petroleum hydrocarbon-contaminated aquifer. *Ground Water*, Vol. 40, 353-360.
- CHAPELLE, F H, AND MCMAHON, P B. 1991. Geochemistry of dissolved inorganic carbon in a coastal plain aquifer. 1. Sulfate from confining beds as an oxidant in microbial CO₂ production. *Journal of Hydrology*, Vol. 127, 85-108.
- CHAPELLE, F H, MCMAHON, P B, DUBROVSKY, N M, FUJII, R F, OAKSFORD, E T, AND VROBLESKY, D A. 1995. Deducing the distribution of terminal electron-accepting processes in hydrologically diverse groundwater systems. *Water Resources Research*, Vol. 31, 359-371.
- CHEN, D J Z, AND MACQUARRIE, K T B. 2005. Correlation of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in NO₃⁻ during denitrification in groundwater. *Journal of Environmental Engineering and Science*, Vol. 4, 221-226.
- CHRISTENSEN, P B, NIELSEN, L P, SØRENSEN, J, AND REVSBECH, N P. 1990. Denitrification in nitrate-rich streams: Diurnal and seasonal variation related to benthic oxygen metabolism. *Limnology and Oceanography*, Vol. 35, 640-651.
- CHRISTENSEN, T H, BJERG, P L, BANWART, S A, JAKOBSEN, R, G.HERON, AND ALBRECHTSEN, H-H. 2000. Characterization of redox conditions in groundwater contaminant plumes. *Journal of Contaminant Hydrology*, Vol. 45, 165-241.
- COBBING, J, MOREAU, M, SHAND, P, AND LANCASTER, A. 2004. Baseline Series Report 14: The Corallian of Oxfordshire and Wiltshire. *British Geological Survey Commissioned Report CR/04/262N & Environment Agency Report NC/99/74/14*.
- COOK, P G, AND BÖHLKE, J-K. 2000. Determining timescales for groundwater flow and solute transport. 1-30 in *Environmental tracers in subsurface hydrology*. (Springer.)

- DAHL, M, NILSSON, B, LANGHOFF, J, AND REFSGAARD, J. 2007. Review of classification systems and new multi-scale typology of groundwater–surface water interaction. *Journal of Hydrology*, Vol. 344, 1-16.
- DALSGAARD, T, THAMDRUP, B, AND CANFIELD, D E. 2005. Anaerobic ammonium oxidation (anammox) in the marine environment. *Research in Microbiology*, Vol. 156, 457-464.
- DE GROOT, C, VERMOESEN, A, AND VAN CLEEMPUT, O. 1994. Laboratory study of the emission of N₂O and CH₄ from a calcareous soil. *Soil science*, Vol. 158, 355-364.
- DUFF, J H, AND TRISKA, F J. 1990. Denitrifications in sediments from the hyporheic zone adjacent to a small forested stream. *Canadian Journal of Fisheries and Aquatic Sciences*, Vol. 47, 1140-1147.
- DUNCAN, S M, LANCASTER, A, AND THOMAS, J. 2004. Groundwater Quality Review: The Corallian. *Environment Agency Report GWQR020* (Bristol).
- EDMUNDS, W, AND WALTON, N. 1983. The Lincolnshire Limestone—hydrogeochemical evolution over a ten-year period. *Journal of Hydrology*, Vol. 61, 201-211.
- EDMUNDS, W M, BATH, A H, AND MILES, D L. 1982. Hydrochemical evolution of the East Midlands Triassic sandstone aquifer, England. *Geochimica et Cosmochimica Acta*, Vol. 46, 2069-2081.
- EDMUNDS, W M, DOHERTY, P, GRIFFITHS, K J, SHAND, P, AND PEACH, D W. 2002. Baseline Series Report 4: The Chalk of Dorset. *British Geological Survey Commissioned Report CR/02/268N & Environment Agency Report NC/99/74/4*.
- EDMUNDS, W M, MILES, D L, AND COOK, J M. 1984. A comparative study of sequential redox processes in three British aquifers. 55-70 in *Hydrochemical Balances in Freshwater* ERIKSSON, E (editor). Vol. 150. (Wallingford: IAHS-AISH.)
- ELLIOT, T, ANDREWS, J N, AND EDMUNDS, W M. 1999. Hydrochemical trends, palaeorecharge, and groundwater ages in the fissured Chalk aquifer of the London and Berkshire Basins, UK. *Applied Geochemistry*, Vol. 14, 333-363.
- ENTEC. 2008a. Groundwater Body Water Quality Report: Brighton Chalk. *Environment Agency Report* (Bristol).
- ENTEC. 2008b. Groundwater Body Water Quality Report: Chichester Chalk. *Environment Agency Report* (Bristol).
- ENTEC. 2008c. Groundwater Body Water Quality Report: East Kent Stour Chalk. *Environment Agency Report* (Bristol).
- ENTEC. 2008d. Groundwater Body Water Quality Report: Isle of Wight Lower Greensand *Environment Agency Report* (Bristol).
- ENTEC. 2008e. Groundwater Body Water Quality Report: Kent Lower Greensand *Environment Agency Report* (Bristol).
- ENTEC. 2008f. Groundwater Body Water Quality Report: North Kent Medway Chalk. *Environment Agency Report* (Bristol).
- ENTEC. 2008g. Groundwater Body Water Quality Report: North Kent Swale Chalk. *Environment Agency Report* (Bristol).
- ENTEC. 2008h. Groundwater Body Water Quality Report: Seaford & Eastbourne Chalk. *Environment Agency Report* (Bristol).
- ENTEC. 2008i. Groundwater Body Water Quality Report: West Kent Darent and Cray Chalk *Environment Agency Report* (Bristol).
- ENTEC. 2008j. Groundwater Body Water Quality Report: Western Lower Greensand *Environment Agency Report* (Bristol).
- ENTEC. 2008k. Groundwater Body Water Quality Report: Worthing Chalk. *Environment Agency Report* (Bristol).
- ENVIRONMENT AGENCY. 2004a. Groundwater Quality Review: Chalk of the Central Downs, Isle of Wight GWQR009. *Environment Agency Report* (Bristol).
- ENVIRONMENT AGENCY. 2004b. Groundwater Quality Review: Chalk of the Southern Downs, Isle of Wight GWQR010. *Environment Agency Report* (Bristol).
- ENVIRONMENT AGENCY. 2004c. Groundwater Quality Review: Dorest Stour Chalk GWQR014. *Environment Agency Report* (Bristol).
- ENVIRONMENT AGENCY. 2004d. Groundwater Quality Review: East Hampshire Chalk GWQR008. *Environment Agency Report* (Bristol).

ENVIRONMENT AGENCY. 2004e. Groundwater Quality Review: Frome Piddle Chalk GWQR015. *Environment Agency Report* (Bristol).

ENVIRONMENT AGENCY. 2004f. Groundwater Quality Review: Hampshire Avon Chalk GWQR016. *Environment Agency Report* (Bristol).

ENVIRONMENT AGENCY. 2004g. Groundwater Quality Review: Jurassic Limestone GWQR017. *Environment Agency Report* (Bristol).

ENVIRONMENT AGENCY. 2004h. Groundwater Quality Review: Mendips Limestone GWQR018. *Environment Agency Report* (Bristol).

ENVIRONMENT AGENCY. 2004i. Groundwater Quality Review: Otter Sandstone GWQR019. *Environment Agency Report* (Bristol).

ENVIRONMENT AGENCY. 2004j. Groundwater Quality Review: River Itchen Chalk GWQR011. *Environment Agency Report* (Bristol).

ENVIRONMENT AGENCY. 2004k. Groundwater Quality Review: River Test Chalk GWQR012. *Environment Agency Report* (Bristol).

ENVIRONMENT AGENCY. 2004l. Groundwater Quality Review: Thanet Chalk GWQR013. *Environment Agency Report* (Bristol).

ENVIRONMENT AGENCY. 2009a. Groundwater Quality Review: Summary Report Essex Gravels. *Environment Agency Report* (Bristol).

ENVIRONMENT AGENCY. 2009b. Groundwater Quality Review: Summary Report Norfolk and Suffolk Chalk. *Environment Agency Report* (Bristol).

ENVIRONMENT AGENCY. 2009c. Groundwater Quality Review: Summary Report Norfolk and Suffolk Crag. *Environment Agency Report* (Bristol).

ENVIRONMENT AGENCY. 2009d. Groundwater Quality Review: Summary Report North Essex Chalk. *Environment Agency Report* (Bristol).

ENVIRONMENT AGENCY. 2009e. Groundwater Quality Review: Summary Report South Essex Chalk. *Environment Agency Report* (Bristol).

ESI. 2004a. Groundwater Quality Review: Skerne Magnesian limestone. GWQRNE4. *Environment Agency Report 6234DR2D3* (Bristol).

ESI. 2004b. Groundwater Quality Review: Till and Northumberland Rivers Fell Sandstone. GWQRNE1. *Environment Agency Report 6234DR11D1* (Bristol).

ESI. 2004c. Groundwater Quality Review: Tyne Fell Sandstone. GWQRNE2. *Environment Agency Report 6234DR8D2* (Bristol).

ESI. 2005a. Groundwater Quality Review: Chalk of the Kennet Valley GWQR024. *Environment Agency Report* (Bristol).

ESI. 2005b. Groundwater Quality Review: Chalk of the Mid-Chilterns and Colne Valley GWQR026. *Environment Agency Report* (Bristol).

ESI. 2005c. Groundwater Quality Review: Chalk of the North Downs GWQR027. *Environment Agency Report* (Bristol).

ESI. 2005d. Groundwater Quality Review: Chalk of the South-West Chilterns and Twyford Brook GWQR028. *Environment Agency Report* (Bristol).

ESI. 2005e. Groundwater Quality Review: Chalk of the Upper River Lee GWQR021. *Environment Agency Report* (Bristol).

ESI. 2005f. Groundwater Quality Review: Thames Valley Gravels GWQR023. *Environment Agency Report* (Bristol).

ESI. 2006a. Groundwater Quality Review: Confined Chalk of the London Basin GWQR022. *Environment Agency Report* (Bristol).

ESI. 2006b. Groundwater Quality Review: Eden Valley and Carlisle Basin. GWQRNW4. *Environment Agency Report 6438AR1* (Bristol).

ESI. 2006c. Groundwater Quality Review: Furness and West Cumbria. GWQRNW8. *Environment Agency Report* (Bristol).

ESI. 2006d. Groundwater Quality Review: Lake District. GWQRNW1. *Environment Agency Report 6438AR2* (Bristol).

ESI. 2006e. Groundwater Quality Review: Lower Greensand, Southern Limb, London Basin GWQR025. *Environment Agency Report* (Bristol).

- ESI. 2006f. Groundwater Quality Review: Lune and Kent. GWQRNW2. *Environment Agency Report 6438AR4* (Bristol).
- ESI. 2006g. Groundwater Quality Review: North Manchester Carboniferous. GWQRNW9. *Environment Agency Report* (Bristol).
- ESI. 2006h. Groundwater Quality Review: Ribble. GWQRNW3. *Environment Agency Report 6438AR6* (Bristol).
- ESI. 2006i. Groundwater Quality Review: Wirral and West Cheshire. GWQRNW3. *Environment Agency Report 6438AR5* (Bristol).
- FEAST, N A, HISCOCK, K M, DENNIS, P F, AND ANDREWS, J N. 1998. Nitrogen isotope hydrochemistry and denitrification within the Chalk aquifer system of north Norfolk, UK. *Journal of Hydrology*, Vol. 211, 233-252.
- FIRESTONE, M K, AND DAVIDSON, E A. 1989. Microbial basis of NO and N₂O production and consumption in soils. 7-22 in *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere*. ANDREAE, M O, AND SCHIMMEL, D S (editors). (New York: John Wiley & Sons.)
- FOSTER, S S D, KELLY, D P, AND JAMES, R. 1985. The evidence for zones of biodegradation in British aquifers. 356-369 in *Planetary Ecology*, . CALDWELL, D E, BRIERLEY, J A, AND BRIERLEY, C L (editors). (New York: Van Nostrand Reinhold Company Incorporated.)
- FUKADA, T, HISCOCK, K M, DENNIS, P F, AND GRISCHEK, T. 2003. A dual isotope approach to identify denitrification in groundwater at a river-bank infiltration site. *Water Research*, Vol. 37, 3070-3078.
- GALE, I N, MARKS, R J, DARLING, W G, AND WEST, J M. 1994. Bacterial denitrification in aquifers: Evidence from the unsaturated zone and the unconfined Chalk and Sherwood Sandstone aquifers. *National Rivers Authority R&D Note 215* (Bristol).
- GAUNTLETT, R B, AND CRAFT, D G. 1979. Biological removal of nitrate from river water. *Water Research Centre Technical Report TR98* (Medmenham).
- GHIORSE, W C, AND WILSON, J T. 1988. Microbial ecology of the terrestrial subsurface. *Advances in applied microbiology*, Vol. 33, 107-172.
- GOODY, D C, MACDONALD, D M J, LAPWORTH, D J, BENNETT, S A, AND GRIFFITHS, K J. 2014. Nitrogen sources, transport and processing in peri-urban floodplains. *Science of the Total Environment*, Vol. 494, 28-38.
- GRANGER, J, SIGMAN, D M, LEHMANN, M F, AND TORTELL, P D. 2008. Nitrogen and oxygen isotope fractionation during dissimilatory nitrate reduction by denitrifying bacteria. *Limnology and Oceanography*, Vol. 53, 2533-2545.
- GRIFFITHS, K, MACDONALD, A, ROBINS, N, MERRITT, J, BOOTH, S, JOHNSON, D, AND MCCONVEY, P. 2011. Improving the characterization of Quaternary deposits for groundwater vulnerability assessments using maps of recharge and attenuation potential. *Quarterly Journal of Engineering Geology and Hydrogeology*, Vol. 44, 49-61.
- GRIFFITHS, K J, SHAND, P, AND INGRAM, J. 2003a. Baseline Series Report 2: The Permo-Triassic Sandstones of West Cheshire and the Wirral. *British Geological Survey Commissioned Report CR/02/109N & Environment Agency Report NC/99/74/2*.
- GRIFFITHS, K J, SHAND, P, AND INGRAM, J. 2003b. Baseline Series Report 8: The Permo-Triassic Sandstones Manchester and East Cheshire. *British Geological Survey Commissioned Report CR/03/265N & Environment Agency Report NC/99/74/8*.
- GRIFFITHS, K J, SHAND, P, AND INGRAM, J. 2005. Baseline Series Report 19: The Permo-Triassic Sandstones of Liverpool and Rufford. *British Geological Survey Commissioned Report CR/05/161N & Environment Agency Report NC/99/74/19*.
- GRIFFITHS, K J, SHAND, P, MARCHANT, P, AND PEACH, D W. 2006. Baseline Series Report 23: The Lincolnshire Limestone. *British Geological Survey Commissioned Report CR/05/060N & Environment Agency Report NC/99/74/23*.
- GROFFMAN, P M, ALTABET, M A, BÖHLKE, J, BUTTERBACH-BAHL, K, DAVID, M B, FIRESTONE, M K, GIBLIN, A E, KANA, T M, NIELSEN, L P, AND VOYTEK, M A. 2006. Methods for measuring denitrification: diverse approaches to a difficult problem. *Ecological Applications*, Vol. 16, 2091-2122.
- GROFFMAN, P M, GOLD, A J, AND JACINTHE, P-A. 1998. Nitrous oxide production in riparian zones and groundwater. *Nutrient Cycling in Agroecosystems*, Vol. 52, 179-186.

- GROFFMAN, P M, HOLLAND, E, MYROLD, D D, ROBERTSON, G P, AND ZOU., X. 1999. Denitrification. 272-288 in *Standard soil methods for long term ecological research*. ROBERTSON, G P, BLEDSOE, C S, COLEMAN, D C, AND SOLLINS, P (editors). (New York, USA: Oxford University Press.)
- HANSON, G C, GROFFMAN, P M, AND GOLD, A J. 1994. Denitrification in riparian wetlands receiving high and low groundwater nitrate inputs. *Journal of Environmental Quality*, Vol. 23, 917-922.
- HILL, A R, DEVITO, K J, CAMPAGNOLO, S, AND SANMUGADAS, K. 2000. Subsurface denitrification in a forest riparian zone: interactions between hydrology and supplies of nitrate and organic carbon. *Biogeochemistry*, Vol. 51, 193-223.
- HINKLE, S R, BÖHLKE, J, DUFF, J H, MORGAN, D S, AND WEICK, R J. 2007. Aquifer-scale controls on the distribution of nitrate and ammonium in ground water near La Pine, Oregon, USA. *Journal of Hydrology*, Vol. 333, 486-503.
- HISCOCK, K M, LLOYD, J W, AND LERNER, D N. 1991. Review of natural and artificial denitrification of groundwater. *Water Research*, Vol. 25, 1099-1111.
- HOFFMAN, C C, RYSGAARD, S, AND BERG, P. 2000. Denitrification rates predicted by nitrogen-15 labeled nitrate microcosm studies, in situ measurements and modeling. *Journal of Environmental Quality*, Vol. 29, 2020-2028.
- HØJBERG, A L, HANSEN, A L, WACHNIEW, P, ŻUREK, A J, VIRTANEN, S, ARUSTIENE, J, STRÖMQVIST, J, RANKINEN, K, AND REFSGAARD, J C. 2017. Review and assessment of nitrate reduction in groundwater in the Baltic Sea Basin. *Journal of Hydrology*, Vol. Regional Studies 12, 50-68.
- HOWARD, K W F. 1985. Denitrification in a major limestone aquifer. *Journal of Hydrology*, Vol. 76, 265-280.
- JAHANGIR, M M R, JOHNSTON, P, ADDY, K, KHALIL, M I, GROFFMAN, P M, AND RICHARDS, K G. 2013. Quantification of in situ denitrification rates in groundwater below an arable and a grassland system. *Water, Air, & Soil Pollution*, Vol. 224, 1-14.
- JONES, C M, GRAF, D R, BRU, D, PHILIPPOT, L, AND HALLIN, S. 2013. The unaccounted yet abundant nitrous oxide-reducing microbial community: a potential nitrous oxide sink. *The ISME journal*, Vol. 7, 417.
- KELLMAN, L M, AND HILLAIRE-MARCEL, C. 1998. Nitrate cycling in streams: using natural abundances of NO_3^- - $\delta^{15}\text{N}$ to measure *in-situ* denitrification. *Biogeochemistry*, Vol. 43, 273-292.
- KELLMAN, L M, AND HILLAIRE-MARCEL, C. 2003. Evaluation of nitrogen isotopes as indicators of nitrate contamination sources in an agricultural watershed. *Agriculture, Ecosystems & Environment*, Vol. 95, 87-102.
- KEUSKAMP, J A, VAN DRECHT, G, AND BOUWMAN, A F. 2012. European-scale modelling of groundwater denitrification and associated N_2O production. *Environmental Pollution*, Vol. 165, 67-76.
- KINNIBURGH, D G, GALE, I N, GOODDY, D C, DARLING, W D, MARKS, R J, GIBBS, B R, COLEBY, L M, BIRD, M J, AND WEST, J M. 1999. Denitrification in the unsaturated zones of the British Chalk and Sherwood Sandstone aquifers. *British Geological Survey Technical Report WD/99/2*.
- KÖLLE, W, STREBEL, O, AND BÖTTCHER, J. 1985. Formation of sulfate by microbial denitrification in a reducing aquifer. *Water Supply*, Vol. 3, 35-40.
- KOMOR, S C, AND ANDERSON, H W. 1993. Nitrogen isotopes as indicators of nitrate sources in Minnesota sand-plain aquifers. *Ground Water*, Vol. 31, 260-270.
- KOROM, S F. 1992. Natural denitrification in the saturated zone: a review. *Water Resources Research*, Vol. 28, 1657-1668.
- LANDON, M K, GREEN, C T, BELITZ, K, SINGLETON, M J, AND ESSER, B K. 2011. Relations of hydrogeologic factors, groundwater reduction-oxidation conditions, and temporal and spatial distributions of nitrate, Central-Eastside San Joaquin Valley, California, USA. *Hydrogeology Journal*, Vol. 19, 1203-1224.
- LAWRENCE, A R, AND FOSTER, S S D. 1986. Denitrification in a limestone aquifer in relation to the security of low-nitrate groundwater supplies. *Journal of the Institution of Water Engineers and Scientists*, Vol. 40, 159-172.
- LEE, J-J, JANG, C-S, WANG, S-W, LIANG, C-P, AND LIU, C-W. 2008. Delineation of spatial redox zones using discriminant analysis and geochemical modelling in arsenic-affected alluvial aquifers. *Hydrological Processes*, Vol. 22, 3029-3041.
- LEWANDOWSKI, J, AND NÜTZMANN, G. 2010. Nutrient retention and release in a floodplain's aquifer and in the hyporheic zone of a lowland river. *Ecological Engineering*, Vol. 36, 1156-1166.

- LI, X, TANG, C, HAN, Z, CAO, Y, AND ZHANG, C. 2013. Relation between nitrous oxide production in wetland and groundwater: a case study in the headwater wetland. *Paddy and Water Environment*, Vol. 11, 521-529.
- LINDSEY, B D, PHILLIPS, S W, DONNELLY, C A, SPEIRAN, G K, PLUMMER, L N, BÖHLKE, J-K, FOCAZIO, M J, BURTON, W C, AND BUSENBERG, E. 2003. Residence times and nitrate transport in ground water discharging to streams in the Chesapeake Bay Watershed. *US Geological Survey Water-Resources Investigations Report 03-4035* (New Cumberland, Pennsylvania).
- LOVLEY, D R, AND CHAPELLE, F H. 1995. Deep subsurface microbial processes. *Reviews of Geophysics*, Vol. 33, 365-381.
- LOWRANCE, R. 1992. Groundwater nitrate and denitrification in a coastal plain riparian forest. *Journal of Environmental Quality*, Vol. 21, 401-405.
- LYNGKILDE, J, AND CHRISTENSEN, T H. 1992. Redox zones of a landfill leachate pollution plume (Vejen, Denmark). *Journal of Contaminant Hydrology*, Vol. 10, 273-289.
- MARIOTTI, A, LANDREAU, A, AND SIMON, B. 1988. ¹⁵N isotope biogeochemistry and natural denitrification process in groundwater: Application to the chalk aquifer of northern France. *Geochimica et Cosmochimica Acta*, Vol. 52, 1869-1878.
- MCCLAIN, M E, BOYER, E W, DENT, C L, GERGEL, S E, GRIMM, N B, GROFFMAN, P M, HART, S C, HARVEY, J W, JOHNSTON, C A, MAYORGA, E, MCDOWELL, W H, AND PINAY, G. 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. *Ecosystems*, Vol. 6, 301-312.
- MCMAHON, P, AND CHAPELLE, F. 2008. Redox processes and water quality of selected principal aquifer systems. *Ground Water*, Vol. 46, 259-271.
- MEINARDI, C R. 1994. Groundwater recharge and travel times in the sandy regions of the Netherlands. *National Institute for Public Health and the Environment, Report 715501004* (Bilthoven).
- MOREAU, M, SHAND, P, WILTON, N, BROWN, S, AND ALLEN, D J. 2004. Baseline Series Report 12: The Devonian aquifer of South Wales and Herefordshire. *British Geological Survey Commissioned Report CR/04/185N & Environment Agency Report NC/99/74/12*.
- MÜHLHERR, I H, AND HISCOCK, K M. 1997. A preliminary assessment of nitrous oxide in chalk groundwater in Cambridgeshire, UK. *Applied Geochemistry*, Vol. 12, 797-802.
- MÜHLHERR, I H, AND HISCOCK, K M. 1998. Nitrous oxide production and consumption in British limestone aquifers. *Journal of Hydrology*, Vol. 211, 126-139.
- MÜLLER, C, LAUGHLIN, R J, SPOTT, O, AND RÜTTING, T. 2014. Quantification of N₂O emission pathways via a ¹⁵N tracing model. *Soil Biology and Biochemistry*, Vol. 72, 44-54.
- MURPHY, E M, AND SCHRAMKE, J A. 1998. Estimation of microbial respiration rates in groundwater by geochemical modeling constrained with stable isotopes. *Geochimica et Cosmochimica Acta*, Vol. 62, 3395-3406.
- NEUMANN, I, BROWN, S, SMEDLEY, P L, AND BESIEN, T. 2003. Baseline Series Report 7: The Great and Inferior Oolite of the Cotswolds District. *British Geological Survey Commissioned Report CR/03/202N & Environment Agency Report NC/99/74/7*.
- NEUMANN, I, COBBING, J, TOOTH, A F, AND SHAND, P. 2004. Baseline Series Report 15: The Palaeogene of the Wessex Basin. *British Geological Survey Commissioned Report CR/04/254N & Environment Agency Report NC/99/74/15*.
- OBERMANN, P. 1990. Significance of anoxic reaction zones in an aquifer in the lower Rhine region. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft*, Vol. 60, 249-258.
- PARKER, J M, CHILTON, P J, AND BRIDGE, L R. 1991a. Porewater nitrate profiles in the Chalk unsaturated zone: results of 1990 re-drilling. *British Geological Survey, Technical Report WD/91/13C*.
- PARKER, J M, FOSTER, S S D, SHERRATT, R, AND ALDRICK, J. 1985. Diffuse pollution and groundwater quality of the Triassic sandstone aquifer in southern Yorkshire. *British Geological Survey Research Report 17*.
- PARKER, J M, AND JAMES, R C. 1985. Autochthonous bacteria in the Chalk and their influence on groundwater quality in East Anglia. *Journal of Applied Bacteriology*, Vol. 59, s14.
- PARKER, J M, YOUNG, C P, AND CHILTON, P J. 1991b. Rural and agricultural pollution of groundwater. 149-163 in *Applied Groundwater Hydrology*. DOWNING, R A, AND WILSON, W B (editors). (Oxford: Oxford Science Publications.)

- PEARSON, A. 2007. Groundwater Quality Review: Wyre Forest Carboniferous Coal Measures GWQR-MID-D8. *Environment Agency Report* (Bristol).
- PINAY, G, RUFFINONI, C, WONDZELL, S, AND GAZELLE, F. 1998. Change in groundwater nitrate concentration in a large river floodplain: denitrification, uptake, or mixing? *Journal of the North American Benthological Society*, 179-189.
- PLUMMER, L N, BUSBY, J F, LEE, R W, AND HANSHAW., B B. 1990. Geochemical modeling of the Madison aquifer in parts of Montana, Wyoming, and South Dakota. *Water Resources Research*, Vol. 26, 1981-2014.
- POSTMA, D, BOESEN, C, KRISTIANSEN, H, AND LARSEN, F. 1991. Nitrate reduction in an unconfined sandy aquifer: water chemistry, reduction processes, and geochemical modeling. *Water Resources Research*, Vol. 27, 2027-2045.
- PUCKETT, L J, AND COWDERY, T K. 2002. Transport and fate of nitrate in a glacial outwash aquifer in relation to ground water age, land use practices, and redox processes. *Journal of Environmental Quality*, Vol. 31, 782-796.
- RIVETT, M O, BUSS, S R, MORGAN, P, SMITH, J W N, AND BEMMENT, C D. 2008. Nitrate attenuation in groundwater: a review of biogeochemical controlling processes. *Water Research*, Vol. 42, 4215-4232.
- RIVETT, M O, SMITH, J W N, BUSS, S R, AND MORGAN, P. 2007. Nitrate occurrence and attenuation in the major aquifers of England and Wales. *Quarterly Journal of Engineering Geology and Hydrogeology*, Vol. 40, 335-352.
- ROBERTS, S C, AND MCARTHUR, J M. 1998. Surface/groundwater interactions in a UK limestone aquifer. 125-130 in *Gambling with Groundwater - Physical, Chemical and Biological Aspects of Aquifer-Stream Relations, Proceedings of the 28th Congress of the International Association of Hydrogeologists, Las Vegas, September 1998, 125-130*. VAN BRAHANA, J, ECKSTEIN, J, ONGLEY, L K, SCHNEIDER, R, AND MOORE, J E (editors). (St Paul, Minnesota: American Institute of Hydrologists.)
- ROLEY, S S, TANK, J L, AND WILLIAMS, M A. 2012. Hydrologic connectivity increases denitrification in the hyporheic zone and restored floodplains of an agricultural stream. *Journal of Geophysical Research: Biogeosciences*, Vol. 117.
- ROTAP. 2012. Review of transboundary air pollution (RoTAP): acidification, eutrophication, ground level ozone and heavy metals in the UK. *Centre for Ecology and Hydrology: Contract Report to Department for Environment, Food and Rural Affairs* (Wallingford).
- SCHWIENIEK, M, EINSIEDL, F, STICHLER, W, STÖGBAUER, A, STRAUSS, H, AND MALOSZEWSKI, P. 2008. Evidence for denitrification regulated by pyrite oxidation in a heterogeneous porous groundwater system. *Chemical Geology*, Vol. 255, 60-67.
- SCOTT, J, MCCARTHY, M, GARDNER, W, AND DOYLE, R. 2008. Denitrification, dissimilatory nitrate reduction to ammonium, and nitrogen fixation along a nitrate concentration gradient in a created freshwater wetland. *Biogeochemistry*, Vol. 87, 99-111.
- SEITZINGER, S, HARRISON, J A, BÖHLKE, J K, BOUWMAN, A F, LOWRANCE, R, PETERSON, B, TOBIAS, C, AND DRECHT, G V. 2006. Denitrification across landscapes and waterscapes: a synthesis. *Ecological Applications*, Vol. 16, 2064-2090.
- SHAND, P, ABESSER, C, FARR, G, WILTON, N, LAPWORTH, D J, GOODY, D C, AND HARIA, A H. 2005. Baseline Series Report 17: The Ordovician and Silurian metasediment aquifers of Central and South Wales. *British Geological Survey Commissioned Report CR/05/255N & Environment Agency Report NC/99/74/17*.
- SHAND, P, ANDER, L, GRIFFITHS, K J, DOHERTY, P, AND LAWRENCE, A R. 2004. Baseline Series Report 11: The Bridport Sands of Dorset and Somerset. *British Geological Survey Commissioned Report CR/04/166N & Environment Agency Report NC/99/74/11*.
- SHAND, P, COBBING, J, TYLER-WHITTLE, R, TOOTH, A F, AND LANCASTER, A. 2003a. Baseline Series Report 9: The The Lower Greensand of Southern England. *British Geological Survey Commissioned Report CR/03/273N & Environment Agency Report NC/99/74/9*.
- SHAND, P, EDMUNDS, W M, LAWRENCE, A R, SMEDLEY, P L, AND BURKE, S. 2007. The natural (baseline) quality of groundwater in England and Wales. *British Geological Survey Research Report RR/07/06 and Environment Agency Technical Report NC/00/74/24*.
- SHAND, P, TYLER-WHITTLE, R, BESIEN, T, PEACH, D W, LAWRENCE, A R, AND LEWIS, H O. 2003b. Baseline Series Report 6: The Chalk of the Colne and Lee River catchments. *British Geological Survey Commissioned Report CR/03/069N & Environment Agency Report NC/99/74/6*.

- SHAND, P, TYLER-WHITTLE, R, MORTON, M, SIMPSON, E, LAWRENCE, A R, PACEY, J, AND HARGREAVES, R. 2002. Baseline Series Report 1: The Triassic Sandstones of the Vale of York. *British Geological Survey Commissioned Report CR/02/102N & Environment Agency Report NC/99/74/1*.
- SIEMENS, J, HAAS, M, AND KAUPENJOHANN, M. 2003. Dissolved organic matter induced denitrification in subsoils and aquifers? *Geoderma*, Vol. 113, 253-271.
- SKERMAN, V, AND MACRAE, I. 1957. The influence of oxygen availability on the degree of nitrate reduction by pseudomonas denitrificans. *Canadian Journal of Microbiology*, Vol. 3, 505-530.
- SMEDLEY, P L, AND ALLEN, D J. 2004. Baseline Series Report 16: The granites of South-West England. *British Geological Survey Commissioned Report CR/04/255N & Environment Agency Report NC/99/74/16*.
- SMEDLEY, P L, AND EDMUNDS, W M. 2002. Redox patterns and trace-element behavior in the East Midlands Triassic Sandstone aquifer, UK. *Ground Water*, Vol. 40, 44-58.
- SMEDLEY, P L, GRIFFITHS, K J, TYLER-WHITTLE, R, HARGREAVES, R, LAWRENCE, A R, AND T, B. 2003. Baseline Series Report 5: The Chalk of the North Downs, Kent and East Surrey. *British Geological Survey Commissioned Report CR/03/033N & Environment Agency Report NC/99/74/5*.
- SMEDLEY, P L, NEUMANN, I, AND BROWN, S. 2005. Baseline Series Report 20: The Permo-Triassic Sandstone aquifer of Shropshire. *British Geological Survey Commissioned Report CR/05/061N & Environment Agency Report NC/99/74/20*.
- SMEDLEY, P L, NEUMANN, I, AND FARRELL, R. 2004. Baseline Series Report 10: The The Chalk aquifer of Yorkshire and North Humberside. *British Geological Survey Commissioned Report CR/04/128N & Environment Agency Report NC/99/74/10*.
- SMITH, J W N, SURRIDGE, B W J, HAXTON, T H, AND LERNER, D N. 2009. Pollutant attenuation at the groundwater–surface water interface: A classification scheme and statistical analysis using national-scale nitrate data. *Journal of Hydrology*, Vol. 369, 392-402.
- SMITH, R L, HOWES, B L, AND DUFF, J H. 1991. Denitrification in nitrate-contaminated groundwater: Occurrence in steep vertical geochemical gradients. *Geochimica et Cosmochimica Acta*, Vol. 55, 1815-1825.
- SPALDING, R F, AND PARROTT, J D. 1994. Shallow groundwater denitrification. *Science of the Total Environment*, Vol. 141, 17-25.
- STELZER, R S, BARTSCH, L A, RICHARDSON, W B, AND STRAUSS, E A. 2011. The dark side of the hyporheic zone: depth profiles of nitrogen and its processing in stream sediments. *Freshwater Biology*, Vol. 56, 2021-2033.
- STOREY, R G, WILLIAMS, D D, AND FULTHORPE, R R. 2004. Nitrogen processing in the hyporheic zone of a pastoral stream. *Biogeochemistry*, Vol. 69, 285-313.
- STRAUB, K L, BENZ, M, SCHINK, B, AND WIDDEL, F. 1996. Anaerobic, nitrate-dependent microbial oxidation of ferrous iron. *Applied and Environmental Microbiology*, Vol. 62, 1458-1460.
- STUART, M E, AND LAPWORTH, D J. 2011. A review of processes important in the floodplain setting. *British Geological Survey Open Report OR/11/030*.
- STUART, M E, AND SMEDLEY, P L. 2009. Baseline groundwater chemistry: the Chalk aquifer of Hampshire. *British Geological Survey Open Report OR/09/052*.
- STUART, M E, WANG, L, ASCOTT, M, WARD, R S, LEWIS, M A, AND HART, A J. 2017. Modelling the nitrate legacy. *British Geological Survey Open Report OR/16/036*.
- TESORIERO, A J, LIEBSCHER, H, AND COX, S E. 2000. Mechanism and rate of denitrification in an agricultural watershed: Electron and mass balance along groundwater flow paths. *Water Resources Research*, Vol. 36, 1545-1559.
- TIEDJE, J M. 1988. Ecology of denitrification and dissimilatory nitrate reduction to ammonium. 179-244 in *Biology of anaerobic microorganisms*. ZEHNDER, A J B (editor). (New York: John Wiley & Sons.)
- TRISKA, F J, DUFF, J H, AND AVANZINO, R J. 1993. Patterns of hydrological exchange and nutrient transformation in the hyporheic zone of a gravel-bottom stream: examining terrestrial-aquatic linkages. *Freshwater Biology*, Vol. 29, 259-274.
- TYLER-WHITTLE, R, BROWN, S, AND SHAND, P. 2002. Baseline Series Report 3: The Permo-Triassic Sandstones of South Staffordshire and North Worcestershire. *British Geological Survey Commissioned Report CR/02/119N & Environment Agency Report NC/99/74/3*.

- VELTHOF, G L, OUDENDAG, D, WITZKE, H P, ASMAN, W A H, KLIMONT, Z, AND OENEMA, O. 2009. Integrated assessment of nitrogen losses from agriculture in EU-27 using MITERRA-EUROPE. *Journal of Environmental Quality*, Vol. 38, 402-417.
- VIDON, P, AND HILL, A R. 2005. Denitrification and patterns of electron donors and acceptors in eight riparian zones with contrasting hydrogeology. *Biogeochemistry*, Vol. 71, 259-283.
- VOGEL, J C, TALMA, A S, AND HEATON, T H E. 1981. Gaseous nitrogen as evidence for denitrification in groundwater. *Journal of Hydrology*, Vol. 50, 191-200.
- WAKELIN, S A, NELSON, P N, ARMOUR, J D, RASIAH, V, AND COLLOFF, M J. 2011. Bacterial community structure and denitrifier (nir-gene) abundance in soil water and groundwater beneath agricultural land in tropical North Queensland, Australia. *Soil Research*, Vol. 49, 65-76.
- WATSON, T K, KELLOGG, D Q, ADDY, K, GOLD, A J, STOLT, M H, DONOHUE, S W, AND GROFFMAN, P M. 2010. Groundwater denitrification capacity of riparian zones in suburban and agricultural watersheds. *Journal of the American Water Works Association*, Vol. 46, 237-245.
- WEBER, K A, POLLOCK, J, COLE, K A, O'CONNOR, S M, ACHENBACH, L A, AND COATES, J D. 2006. Anaerobic nitrate-dependent iron (II) bio-oxidation by a novel lithoautotrophic betaproteobacterium, strain 2002. *Applied and Environmental Microbiology*, Vol. 72, 686-694.
- WEYMANN, D, WELL, R, FLESSA, H, VON DER HEIDE, C, DEURER, M, MEYER, K, KONRAD, C, AND WALTHER, W. 2008. Groundwater N₂O emission factors of nitrate-contaminated aquifers as derived from denitrification progress and N₂O accumulation. *Biogeosciences*, 1215-1226.
- WILSON, G B, ANDREWS, J N, AND BATH, A H. 1990. Dissolved gas evidence for denitrification in the Lincolnshire Limestone groundwaters, eastern England. *Journal of Hydrology*, Vol. 113, 51-60.
- WILSON, G B, ANDREWS, J N, AND BATH, A H. 1994. The nitrogen isotope composition of groundwater nitrates from the East Midlands Triassic Sandstone aquifer, England. *Journal of Hydrology*, Vol. 157, 35-46.
- WILSON, S R, CLOSE, M E, AND ABRAHAM, P. 2018. Applying linear discriminant analysis to predict groundwater redox conditions conducive to denitrification. *Journal of Hydrology*, Vol. 556, 611-624
- WRIEDT, G, AND RODE, M. 2006. Modelling nitrate transport and turnover in a lowland catchment system. *Journal of Hydrology*, Vol. 328, 157-176.
- ZARNETSKY, J P, HAGGERTY, R, WONDZELL, S M, AND BAKER, M A. 2011a. Dynamics of nitrate production and removal as a function of residence time in the hyporheic zone. *Journal of Geophysical Research: Biogeosciences*, Vol. 116, G01025.
- ZARNETSKY, J P, HAGGERTY, R, WONDZELL, S M, AND BAKER, M A. 2011b. Labile dissolved organic carbon supply limits hyporheic denitrification. *Journal of Geophysical Research: Biogeosciences*, Vol. 116, G04036.
- ZESSNER, M, SCHILLING, C, GABRIEL, O, AND HEINECKE, U. 2005. Nitrogen fluxes on catchment scale: the influence of hydrological aspects. *Water Science and Technology*, Vol. 52, 163-173.
- ZHANG, Y-C, SLOMP, C P, BROERS, H P, PASSIER, H F, AND VAN CAPPELLEN, P. 2009. Denitrification coupled to pyrite oxidation and changes in groundwater quality in a shallow sandy aquifer. *Geochimica et Cosmochimica Acta*, Vol. 73, 6716-6726.