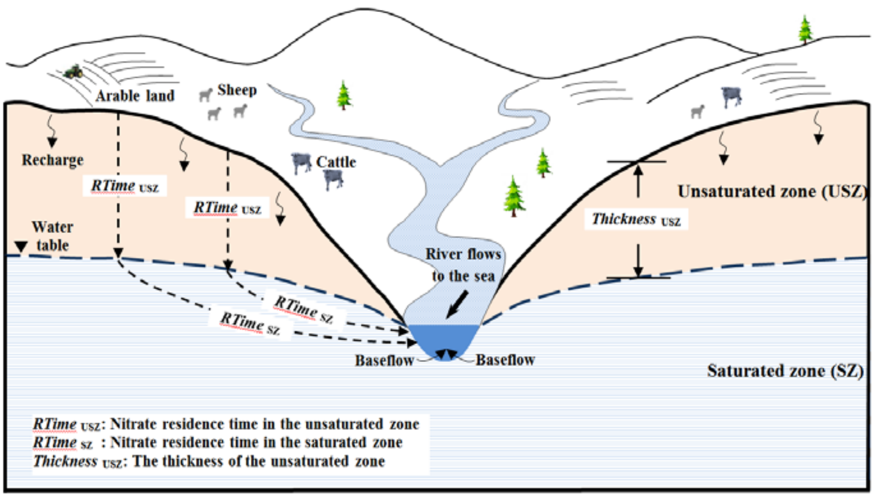
Modelling the groundwater nitrate legacy

Groundwater Science Directorate

Open Report OR/16/036



BRITISH GEOLOGICAL SURVEY

GROUNDWATER SCIENCE DIRECTORATE

OPEN REPORT OR/16/036

Modelling the groundwater nitrate legacy

M E Stuart, L Wang, M Ascott, R S Ward, M A Lewis, A J Hart

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Foreword

This report is a deliverable of a project jointly funded by the British Geological Survey (BGS) and Defra through the Environment Agency to consider the potential for incorporating the unsaturated zone travel time in the nitrate risk model that is used as part of the nitrate vulnerable zones (NVZs) groundwater designation process. NVZs are delineated by the Environment Agency in support of Defra's implementation of the Nitrate Regulations which in turn stem from the European Nitrates Directive (91/676/EEC). A further consideration has been how the model may provide additional evidence to support the implementation of the European Water Framework Directive (2000/60/EC) (WFD) and in particular the starting point for trend reversal and justification for alternative (environmental) objectives.

This report presents the results of the further development of a national scale model of unsaturated zone movement of pollutants, in this case nitrate (the 'Nitrate Time Bomb' model). This includes improved process representation in the model, better input data and also an evaluation of its performance at different scales through comparison with results of independent discrete modelling studies. The model improvements are shown to significantly improve its performance and the case studies demonstrate the value of its application to support future designation (and performance) of NVZs and achieving/managing environmental objectives under the WFD.

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The following students from the University of Nottingham also contributed to the development of the national groundwater recharge model which underpins some of the work described in this report: Xueliang Mu, Yuepeng Hu, Weibin Lin, and Rongmeihui Zheng**.**

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Executive summary

This report details the findings of a project jointly funded by the British Geological Survey (BGS) and Defra through the Environment Agency. The overall aim of the work was to investigate the use of new models to inform decision-making on nitrate pollution in groundwater and the potential for incorporating unsaturated zone processes into the model currently used by the Environment Agency to delineate Nitrate Vulnerable Zones (NVZs). The potential application as supporting evidence for the Water Framework Directive has also been considered as nitrate pollution of groundwater remains the most significant reason for failure of WFD environmental objectives across England. The background to the nitrate legacy in groundwater and to the approaches to NVZ designation is described in Stuart et al. (2016).

A series of developments to the BGS Nitrate Time Bomb (NTB) model have been made to improve a number of areas and approaches used in the first version of the model. The improvements included a spatially and temporally distributed nitrate input function, improved unsaturated zone thickness estimation, travel time attribution using a 1:250,000 geological map, estimating nitrate velocity in the unsaturated zone using groundwater recharge and aquifer properties, and introducing nitrate transport processes in low permeability superficial deposits and the saturated zones. These now allow the model to be applied at sub national scale. Using the improved model we have also made the first estimate of the mass of nitrate stored within the unsaturated zone and how this will change over time to improve UK nitrate budget estimates.

The new version of the BGS NTB approach was applied in three case studies at different scales which compared its outcomes to the results from other modelling to demonstrate that the model can be benchmarked against the other nitrate modelling approaches:

- For a basin-scale model of the Thames Chalk (Howden et al., 2010 & 2011). The NTB model gave comparable results to the original study back to 1925 provided that the same nitrate input function was used. Both models failed to predict nitrate concentrations in the Thames after the mid-1980s.
- At the multi-borehole scale in the Permo-Triassic. A similar approach was used to the BGS model in the Eden Valley. This replicated the existing model for the area used by the Environment Agency both in terms of trend assessment and in the lack of dilution available within the aquifer block for blending purposes.
- At the single borehole scale in the Chalk of the South Downs. The existing Environment and National Park model constructed by AMEC treated the unsaturated zone very similarly to the NTB model. This model provided a good fit to observed concentrations and confirmed the importance of estimating unsaturated zone delays. The assessment of modelled travel time from different areas of the catchment clearly illustrated the arable areas that would give a relatively rapid respond to changes in nitrate management.

To illustrate the potential application of the BGS NTB model to support the Environment Agency's NVZ designation methodology, areas of England were identified where unsaturated zone lags may be significant and where there is uncertainty in the NVZ designation. A major advantage of the BGS NTB model is that it covers the whole of England (and Wales) in a consistent way. A national overview of areas of designation uncertainty identified large areas of England, in particular the chalk outcrop of southern and eastern England. These were compared to areas with significant unsaturated zone travel time indicating where travel time may be contributing to designation uncertainty. The results suggest that the model may be useful both for identifying currently impacted groundwater which reflects legacy fertilizer application and also where additional designation could be needed as impacts have not yet emerged.

Application of the model to support implementation of the WFD has also been considered and whilst no quantitative analysis has yet been carried out there are a number of ways that the model could be of significant benefit. For example, the model could be used to estimate when trend

reversal would be expected to occur as a result of measures (at a specific location or across a groundwater body) and the time required to achieve good chemical status (alternative objective setting). A further application could be for scenario testing such as evaluating the effects of different land use/management measures as part of cost benefit analysis or considering the long term impacts of climate change through changing fertiliser use and/or recharge.

1 Introduction

1.1 BACKGROUND

As described by Stuart et al. (2016) in the project Phase 1 briefing report, the increase of nitrate in groundwater was first identified as an issue for the Chalk of the Eastbourne area in the 1970s. Awareness of the extent of high and rising nitrate in groundwater nationally and across the European Union gradually increased, and it became clear that concentrations in public supply sources often exceeded the World Health Organisation (WHO) drinking water values used at this time. By the late 1970s the importance of storage of nitrate in unsaturated zone porewater had also become recognised. Pioneering work showed that at sites with good cropping records a relationship between historical land use and porewater nitrate concentration could be determined and that retention in the unsaturated zone can retard the migration of nitrate for years or decades.

In response to the growing European-wide problem the European Commission implemented the Nitrates Directive (91/676/EEC). This sets out a series of requirements on Member States to assess and control the potential for pollution of waters with nitrogenous compounds generated from agricultural sources. One of these requirements is that Member States carry out an assessment of all waters every four years. In England the Environment Agency advises Defra on this matter and proposes areas subject to potential pollution from nitrate for designation as nitrate vulnerable zones (NVZs) in compliance with the Directive.

More widely groundwater is protected by the European Water Framework Directive (2000/60/EC). As part of this groundwater bodies have to achieve a series of environmental objectives which include preventing or limiting (in the case of nitrate) inputs of pollutants, achieving good status and reversing upward trends in pollutant concentrations. Good status has to be achieved by the end of 2015 although an extension (up to 2027) is allowed, provided that an acceptable justification can be provided. This includes delays in achieving the objective due to natural conditions. Whereas the Nitrates Directive focuses on delivering measures to address agricultural sources of nitrate, the WFD requires measures for <u>all</u> sources of nitrate pollution. The WFD also has different dates for achieving objectives, standards/thresholds and reporting cycles (6 years compared to 4 years for the nitrates directive). However the measures implemented under the Nitrates Directive contribute significantly to achieving WFD objectives.

For delineation of groundwater NVZs the Environment Agency developed a numerical risk assessment procedure that uses a range of risk factors including both nitrate concentration data and nitrate-loading data to assess the risk of nitrate pollution. The loading data is based on farm census returns made to Defra and combined using the NEAP-N methodology developed by ADAS (Lord and Anthony, 2000). The overall risk assessment assesses both current observed and predicted future concentrations as well as current N loadings. However, this approach has a number of disadvantages, including the lack of consideration of the time of travel to the water table and the potential emergence of pollutant both into groundwater and to groundwater discharge points that support surface water features.

A key question for Defra and the Environment Agency is how long it will take for nitrate concentrations to peak and then stabilise at an acceptable, lower level, in response to existing and future land management control measures. This is most important for soils, aquifers, lakes and groundwater-fed wetland, systems that respond less quickly to changes in loading. Groundwater and lake catchment models can provide first-order estimates of likely response times, but can be difficult and costly to set-up for many different situations and are difficult to apply consistently at the national scale.

A previous review of nitrate vulnerable zones suggests a range of further needs to:

- Understand the recent developments in nitrate pollution simulation and particularly the potential to understand/characterise past nitrate loading from changing land management practices and correlate these with observed nitrate concentrations over time.
- Evaluate the retention of nitrate in catchments, particularly in unsaturated zone of soils and aquifers.
- Examine the recent and future anticipated decreases in nitrate loading by sectors within the UK.
- Understand the likely time taken for nitrate concentrations to peak and then stabilise at an acceptable, lower level, in response to existing and future control measures. Without evidence of how long it may take systems to recover it is difficult to evaluate the effectiveness of existing measures or decide whether additional measures are necessary.

1.2 PROJECT OBJECTIVES

The aim of the project is to investigate the potential use of new numerical models to inform decision-making on nitrate pollution in groundwater and the potential for giving consideration to incorporating such models of unsaturated zone processes in the NVZ process. The background to the nitrate legacy in groundwater and to the approaches to NVZ designation was described in Stuart et al. (2016).

The work described here formed the main part of the project and aimed to evaluate the potential role for the application of modelling the unsaturated zone in the NVZ process, in particular using the BGS Nitrate Time Bomb (NTB) model (Wang et al. 2012). This report describes three areas addressed by the project. These were:

- The development of the BGS NTB model using improved water level and geological classification datasets and new approaches to nitrate transport in low permeability deposits and to estimating nitrate velocity in groundwater systems using groundwater recharge and aquifer properties. This work is described in Chapter 2.
- A series of case studies comparing the application of the BGS approach to other nitrate modelling. These were selected to provide comparison at different scales. The Thames case study is at the river basin scale in the Chalk and is referenced to the study of Howden (2010 & 2011). The South Downs study considers the approach to modelling of a catchment in the Chalk. The reported study contains an approach to the unsaturated zone which is very similar to the BGS model. It also highlights the value of linking work carried out under the WFD with NVZ designation. The third study is at multi-borehole scale in the Permo-Triassic sandstone and uses an approach to the saturated zone similar to that reported by Wang et al. (2013) for the Eden Valley. These studies are described in Chapters 3-5.
- A contextual section which forms Chapter 6 evaluates the areas where the NTB model could be of value in a future NVZ designation process and implementation of the WFD. This includes an evaluation of the benefits and limitations of the BGS model in terms of its structure, effective use of data and, in particular, evidence of improved explanatory or predictive skill. This section also aims to detail some potential approaches to integration of the NTB model with the Environment Agency's NVZ designation methodology and its potential application to support certain aspects of WFD implementation.

2 Development of the BGS unsaturated zone model

Nitrate units of measurement

Nitrate concentrations can either be quoted as nitrate or NO_3 (mg NO_3 l^{-1}) or as the equivalent amount of N (mg NO_3-N l^{-1}). These units are converted using the factor (molecular weight NO_3/molecular weight N = 62/14 =4.43. For example the drinking water limit for nitrate is 50 mg NO_3 l^{-1} or 11.3 mg NO_3-N l^{-1}. In this report mg NO_3-N l^{-1} is used except where existing graphical material uses other units. Nitrogen in fertilisers is quoted as kg N ha^{-1}.

2.1 INTRODUCTION

This chapter describes a series of new developments to the BGS NTB model (Wang et al, 2012). In the original model the distribution of nitrate arriving at the water table depended on only three functions: the nitrate input at the land surface, the rate of travel of nitrate through the unsaturated zone and the thickness of the unsaturated zone (Figure 2.1).

The unsaturated zone thickness and nitrate velocity are combined to estimate the spatial distribution of nitrate travel time in the unsaturated zone and from this the input year for nitrate reaching the water table at any defined time. A nitrate input function over time can then be used to estimate the concentration reaching the water table at any point and defined time, assuming that nitrate is conservative.

These changes described in the following section address a number of simplifications used in this first version of the model including:

- A distributed nitrate input function to replace the original single function.
- A revised unsaturated zone thickness using Ordnance Survey (OS) river data instead of assumed river locations from the Nextmap DTM.
- Travel time attribution using the 1:250,000 geological mapping rather than the 1:625,000.
- Estimating nitrate velocity in the unsaturated zone for key aquifers using a process-based model replacing single values for lithological types.

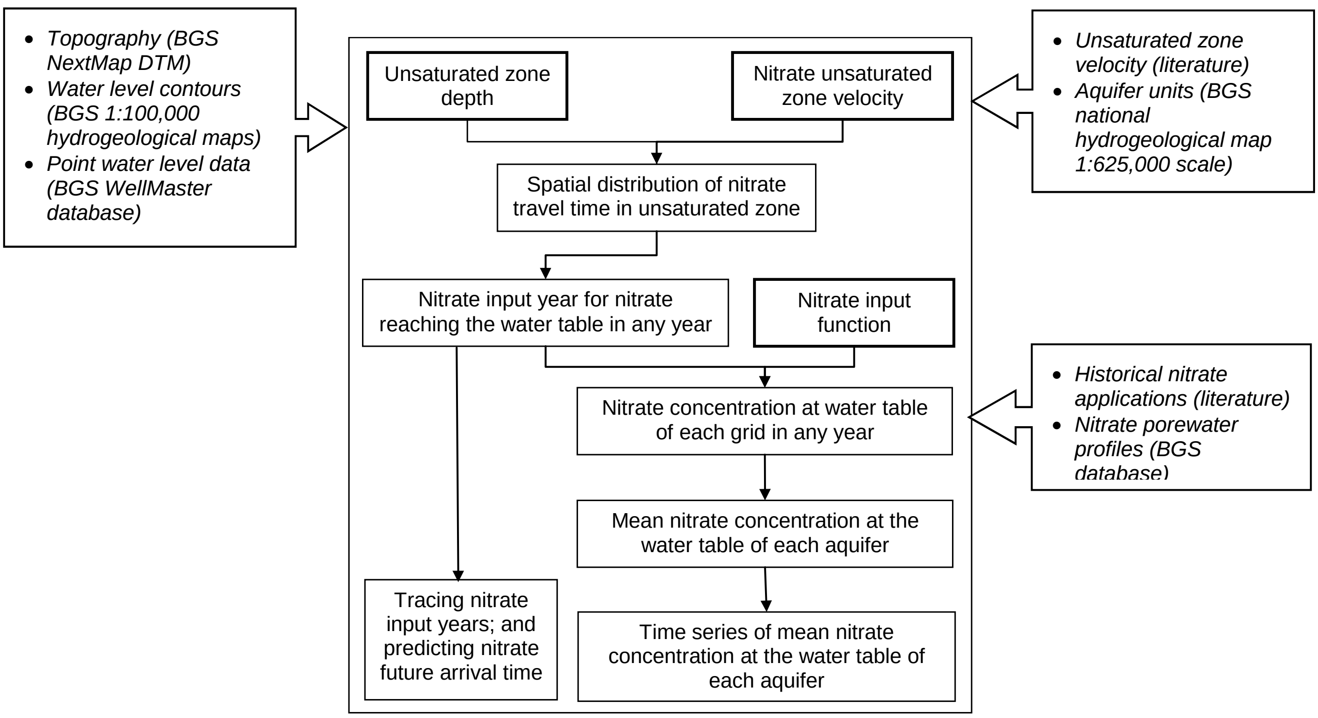


Figure 2.1 Flow chart of the spatial-temporal NTB GIS model and main data sources

- Introducing nitrate transport processes in low permeability superficial deposits. Nitrate transport to the underlying aquifer was originally assumed to be zero.

The improvements introduced as part of this project should allow the national model to be applied more effectively at the sub-national scale. This section also includes the first estimate of the mass of nitrate stored within the unsaturated zone across the UK, made possible as a result of the improved model.

2.2 NITRATE INPUT FUNCTION

2.2.1 Model development

The BGS NTB model previously used a single nitrate input function (NIF) (Wang et al., 2012) providing a national average rather than a spatially distributed input based on agricultural activity. This reflected historical and future agricultural activity from 1925 to 2050 and was validated using mean pore-water nitrate concentrations from 300 cored boreholes across the UK in the BGS database (Figure 2.2).

A low nitrogen loading rate between 1925 and 1940 reflects a pre-World War II low level with very limited use of non-manure-based fertilizers. The gradual intensification of agriculture during and just after the war resulted in a 1 kg N ha^{-1} $year^{-1}$ rise in nitrogen input to 40 kg N ha^{-1} by 1955. A more rapid rise of 1.5 kg N ha^{-1} $year^{-1}$ between 1955 and 1975 was due to increases in the use of chemical based fertilizers to meet the food needs of an expanding population. The nitrogen input declines from 70 kg N ha^{-1} in 1991 to 40 kg N ha^{-1} in 2020 with a rate of 1 kg N ha^{-1} $year^{-1}$ as a result of restrictions on fertilizer application under the Nitrate Directive. Finally, the model assumes a return to nitrogen input levels similar to those associated with early intensive farming in the mid-1950s, i.e., a constant 40 kg N ha^{-1} nitrogen loading rate from 2020 to 2050 (Wang et al., 2012). The model could readily be adapted to incorporate any agreed forward look (scenarios).

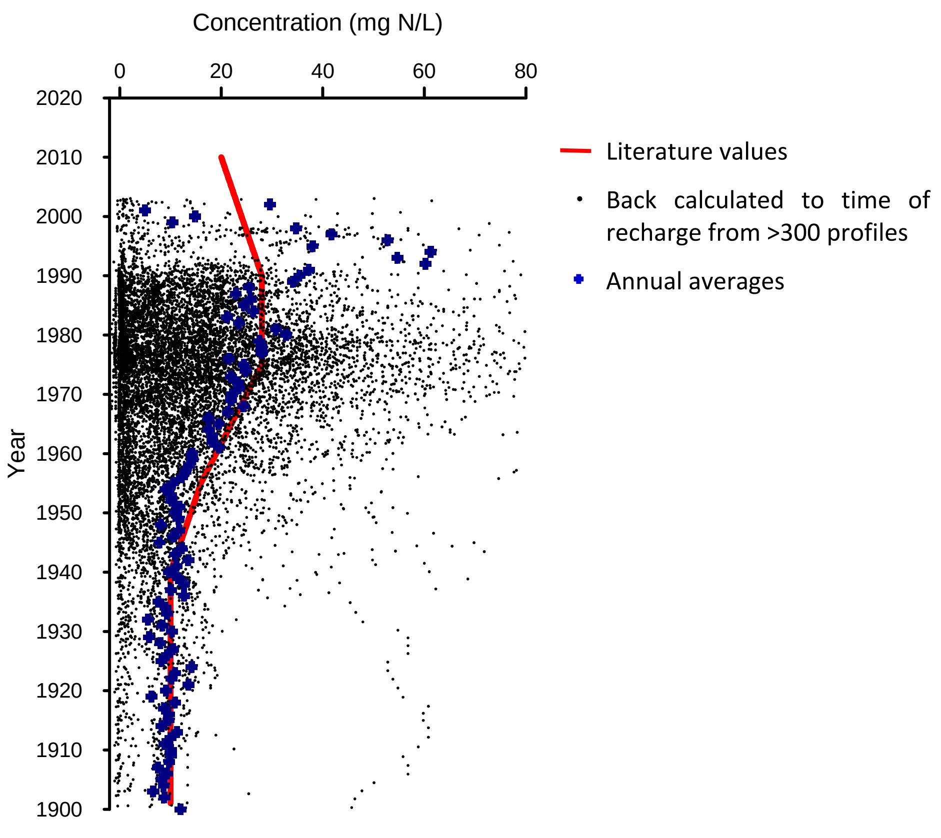


Figure 2.2 BGS NTB nitrogen input function

The historical (and future) nitrate loading information was developed into a temporally- and spatially- distributed NIF using modelled nitrate leaching data from NEAP-N (Anthony et al., 1996; Environment Agency, 2007; Lord and Anthony, 2000; Silgram et al., 2001). NEAP-N is a meta-model of the NITCAT (Lord, 1992) and NCYCLE (Scholefield et al., 1991) models, with adjustments for climate and soil type (Anthony et al., 1996). It includes a water balance model and a leaching algorithm. Nitrate loss potential coefficients are assigned to each crop type, grassland type and livestock categories within the agricultural census data to represent the short and long-term increase in nitrate leaching risk associated with the cropping, keeping of stock and the spreading of manures. The model predicts the total annual nitrate loss from agricultural land for England and Wales and the associated water flux (hydrologically effective rainfall).

For this study, the NEAP-N loss potential coefficients used were revised for each of the prediction years available - 1980, 1995, 2000, 2004 and 2010 (corresponding to years with full agricultural census data for farms across England and Wales) - to account for changes in nutrient applications (fertiliser and manure), crop yields and livestock yields (meat or milk) over time. The predicted NEAP-N nitrogen loadings (1km by 1km) for these years were used in this study to derive the distributed nitrate-input-functions (NIFs). This enabled a nitrogen loading map to be calculated for each year from 1920 to 2040. Figure 2.3 shows examples of the derived nitrate-input functions for locations in the principal aquifers of the Chalk of South England and the Permo-Triassic sandstone of Yorkshire and the Coal Measures of Wales and the Forest of Dean.

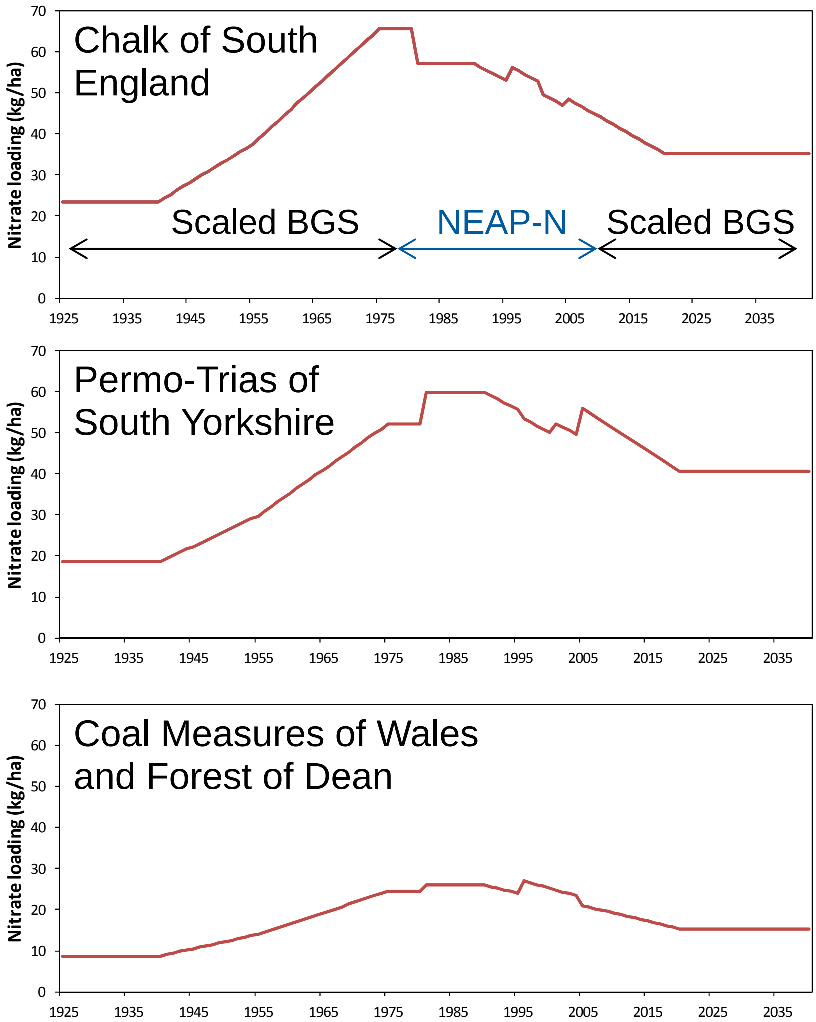


Figure 2.3 Extrapolating NEAP-N input data using the BGS NIF function for a typical point in: a) The Chalk of South England; b) The Permo-Triassic Sandstone of South Yorkshire; c) Coal Measures of Wales and Forest of Dean

2.2.2 Results and implications

Figure 2.4 shows the impact of using a temporally and spatially-distributed NIF. The most significant spatial differences are for non-agricultural and low productivity areas, such as moorland, in Northern England and Wales. Areas, such as the Coal Measures, which have a considerable unsaturated zone thickness due to their deeply incised nature, may be of low agricultural productivity and therefore not significant with respect to unsaturated zone nitrate.

The temporal distribution of nitrate applications is also clearly shown in Figure 2.4. The impact of high nitrate applications peaking in 1980-1990 is most obvious in East Anglia, North Yorkshire, Wessex and the Welsh borders.

The new composite NIF function provides a credible estimate of nitrogen applications that could be made back to the early 20th century to provide a source term for very long groundwater flowpaths and can also be projected forwards using agreed scenarios to assess future impacts of nitrogen management measures.

2.3 WATER LEVEL MAPPING

2.3.1 Updated water level mapping

The first (original) version of the NTB model included the use of water levels derived from assumed river locations from the Nextmap DTM as well as autumn minimum groundwater level values available from hydrogeological maps. A new version of groundwater level mapping which uses OS river data has been applied in this study.

2.3.2 Results and implications

Figure 2.5 shows the impact of these changes on estimated unsaturated zone travel time. The unsaturated zone is considerably thinner in some areas e.g. in parts of the Chalk and this results in reduced travel times.

The use of this new version of groundwater levels is considered to be much more realistic as these levels control the extent of flushing of nitrate from the unsaturated zone in each year.

2.4 RECLASSIFICATION OF GEOLOGY

2.4.1 Scale

The original model used geology attributed at the 625k scale corresponding to the most recently issued hydrogeological mapping. A project objective was to improve hydrogeological representation by using more detailed geological map data and ideally the 50k scale maps. An evaluation of the very large number of formations, which would need to be considered if the 50k maps were to be used, suggested that this would be extremely onerous and disproportionate to the anticipated benefits. Instead it was decided to use 250k scale maps. These are of a large-enough scale to allow the layering of rock strata to be addressed for example in the Coal Measures and the Jurassic limestones. There are a few instances where the 250k maps do not appear to correspond well lithologically with the 625k scale maps and in these cases a comparison with the 50k scale mapping was made to resolve the differences and incorporate the necessary refinements.

2.4.2 Attribution of aquifer properties

In addition to the estimated travel times used in the original model, a range of additional aquifer properties were attributed from Allen et al. (1997) and Jones et al. (2000) for selected aquifer zones to provide parameters which would be required by the processed-based model (Table 2.1).

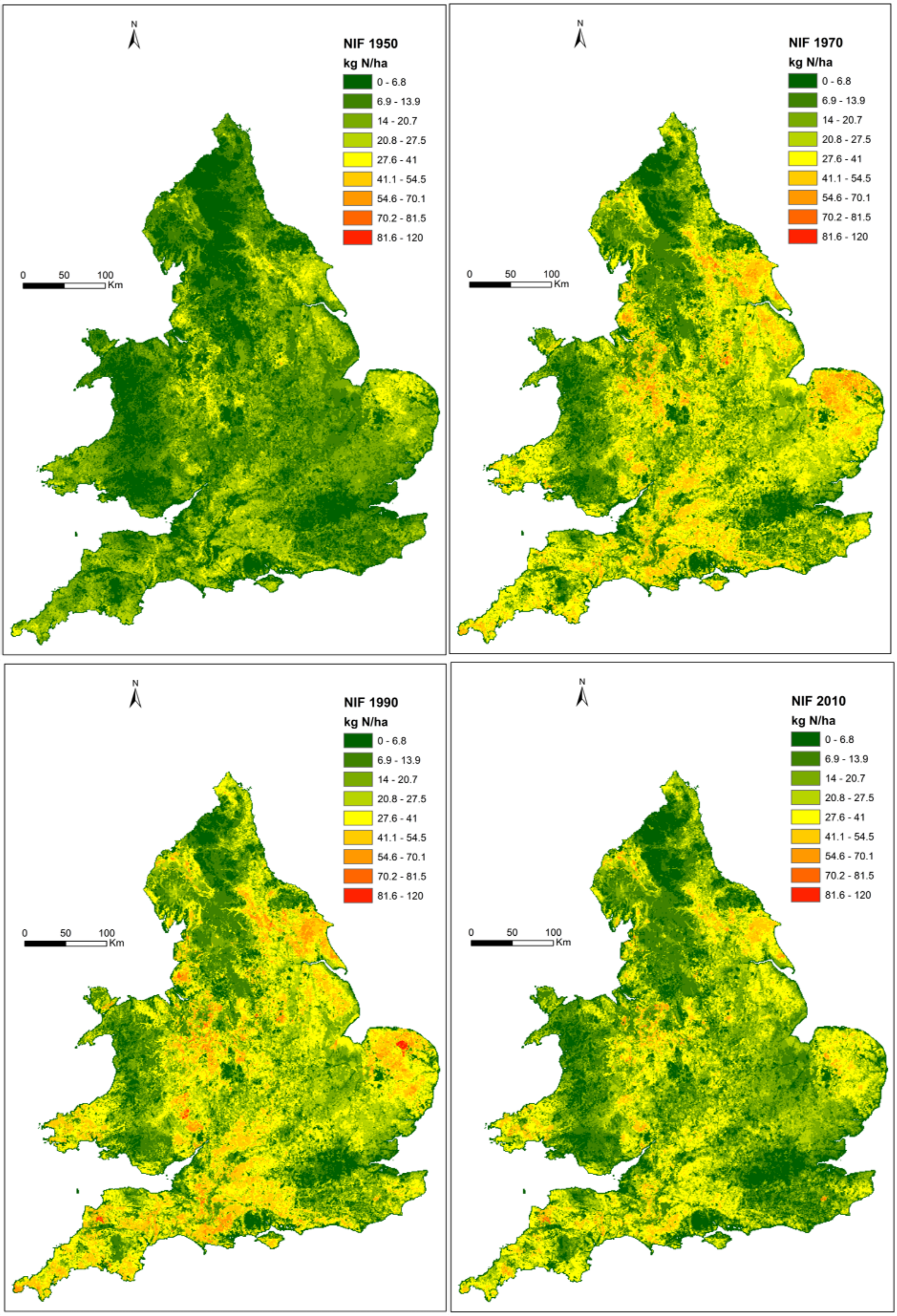


Figure 2.4 Spatial distribution of modelled NIF values for 1950, 1970, 1990 and 2010

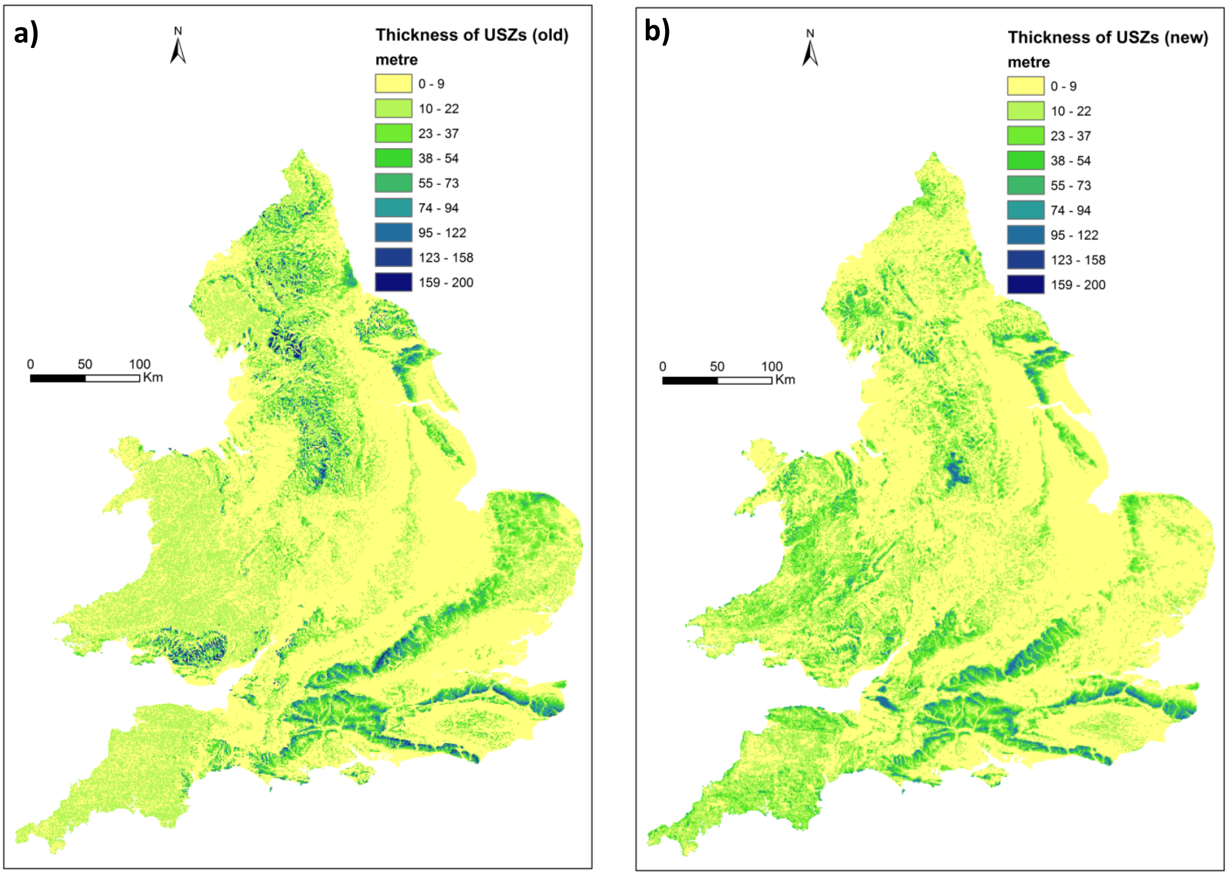


Figure 2.5 Unsaturated zone thickness maps showing the impact of using: a) old water levels and b) new water levels

The water table response shown in Table 2.1 was calculated by cross-correlating groundwater levels and rainfall for each aquifer zone. The value was set to the period of time over which there was a correlation with a greater than 95% confidence level. Further details are given in Wang et al. (2016).

2.4.3 Overall improvements

The original NTB model principally focussed on the major and minor aquifers as these were considered most likely to have a significant unsaturated travel time. These zones were addressed using \ process-based model described in the next section.

Table 2.2 summarises the statistic information on the old and new datasets of the USZ thickness and nitrate velocity in the USZs. Although the maximum USZ thickness is half of the old one, the mean value is slightly smaller than the old average USZ thickness. The calculated nitrate travel time in the USZs is 1.6 times higher than the old one on average. This implies that the newly derived nitrate velocity is lower than the previous one.

The new nitrate travel time in the USZ across the England and Wales was calculated using the more detailed geological information and the new unsaturated zone thickness map (Figure 2.5) and nitrate velocity derived from the 250k hydrogeological map. Figure 2.6 shows its comparison to the old map derived in the previous study.

Table 2.1 Summary table for zones where aquifer properties were attributed

Aquifer zone name	Principal / secondary aquifer	Zone area (km^2)	Water table response time to recharge (months)
Chalk, S England	P	4,965	8
Chalk, Thames	P	5,062	12
Chalk, East Anglia	P	5,603	20
Chalk, NE England	P	3,304	13
Lower Greensand, Bedford-Cambridge	P	440	11
Lower Greensand. Weald	P	1,183	13
Upper Greensand	P	964	11
Corallian, S England	S	773	11
Corallian, Yorkshire	P	449	11
Millstone Grit, Cumbria, Durham and Northumberland	S	2,730	11
Permo-Triassic Sandstone, Lancashire-West Midlands	P	4,701	26
Permo-Triassic Sandstone, SW England	P	957	8
Hastings Beds, Weald	S	2,235	11
Carboniferous Limestone, N England	S	5112	11
Carboniferous Limestone, N Wales	P	442	11
Carboniferous Limestone, S Wales and SW England	P	893	1
Carboniferous Limestone, Derbyshire	P	448	4
Permo-Triassic Sandstone, Nottingham-N Yorkshire	P	2,953	11
Middle Jurassic limestone, Cotswolds-Dorset	P	2,196	7
Lincolnshire Limestone	P	820	4
Middle Jurassic limestone (excluding Lincolnshire Limestone), Lincolnshire-Oxfordshire	P	2,451	9
Middle Jurassic, Yorkshire	S	961	11
Coal Measures, Pennines	S	3,235	11
Coal Measures, S Wales and Forest of Dean	S	2,258	11
Coal Measures, Durham-Northumberland	S	1,584	11
Millstone Grit, S Pennines	S	4,318	11
Magnesian Limestone, Durham	P	635	11
Magnesian Limestone, Nottingham-N Yorkshire	P	888	11

Table 2.2 Statistical information on old and new USZ thickness and nitrate velocity in the USZs

Datasets	Minimum	Maximum	Mean	Standard deviation
Old USZ thickness (m)	0	200	13.7	21.4
New USZ thickness (m)	2	100	13.2	16.4
Old nitrate travel time in the USZs (m/year)	0	434.8	15.7	23.9
New nitrate travel time in the USZs (m/year)	0.2	973	25.8	40.3

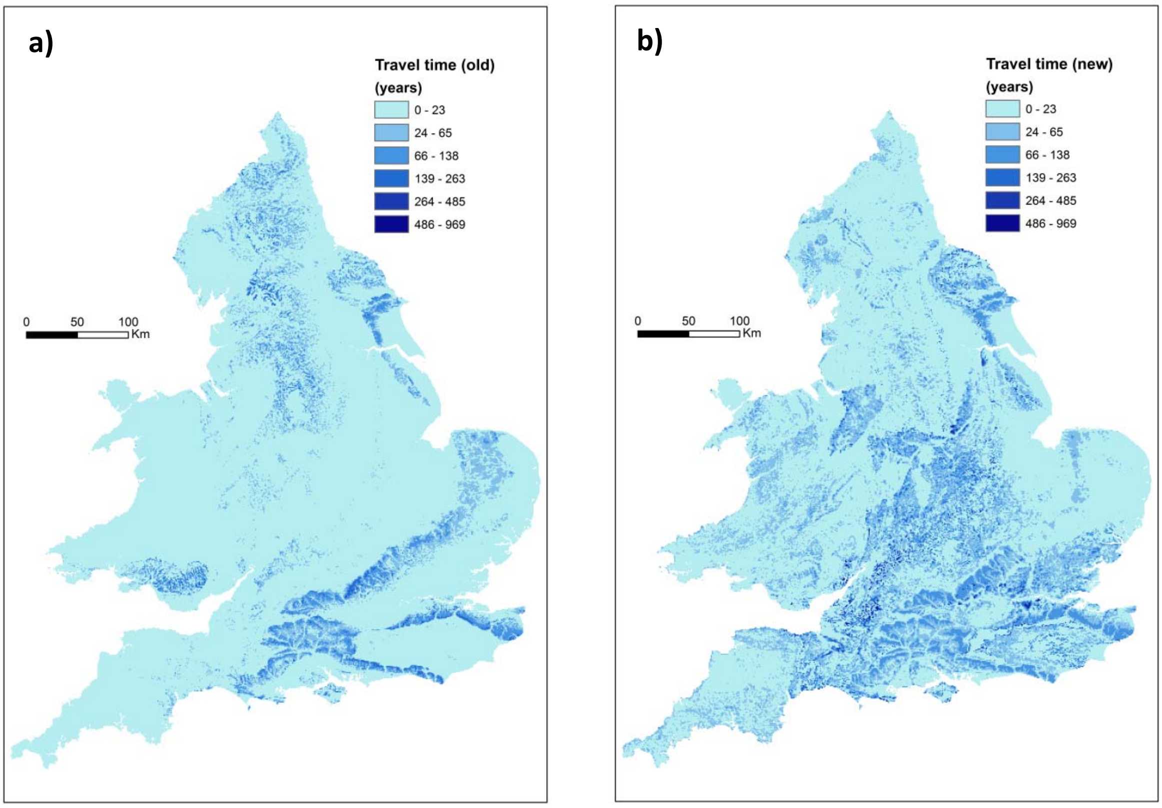


Figure 2.6 Travel time maps using; a) original model; b) model with revised USZ thickness and 250k scale geological mapping

2.5 PROCESS MODELLING

2.5.1 Building a national-scale conceptual model

The first stage of building a national-scale process model is to develop a simple conceptual model:

- Nitrogen from arable land and from livestock is applied to the surface of the soil; this is oxidised to nitrate and a proportion is leached from the base of the soil.
- Nitrate is transported in infiltration through the unsaturated zone at a rate controlled by recharge and individual aquifer properties.
- Nitrate reaches the saturated zone and is transported by water movement towards surface water at a rate controlled by the groundwater gradient and by aquifer properties.

Nitrate reaches surface water as baseflow or other surface receptors In order to simulate nitrate transport and dilution processes in aquifers at national scale for England and Wales, a simplified hydrogeological conceptual model was developed (Figure 2.7). The groundwater system in England and Wales can be conceptualised as an island system on the basis of the following assumptions:

- Groundwater recharge supplies water to aquifers as an input.
- Groundwater flows out of the system through rivers in the form of baseflow as an output.
- Groundwater recharge and baseflow reach dynamic equilibrium whereby the amount of recharge equals that of baseflow in a simulation year. This implies that the volume of groundwater in an aquifer remains the same at the beginning and end of each simulation year, and is called the background volume ($Vol_{background}$). The total volume of groundwater (Vol_{total}) for an aquifer in a simulation year is the sum of the background volume and the annual groundwater recharge reaching the water table ($Vol_{recharge}$).

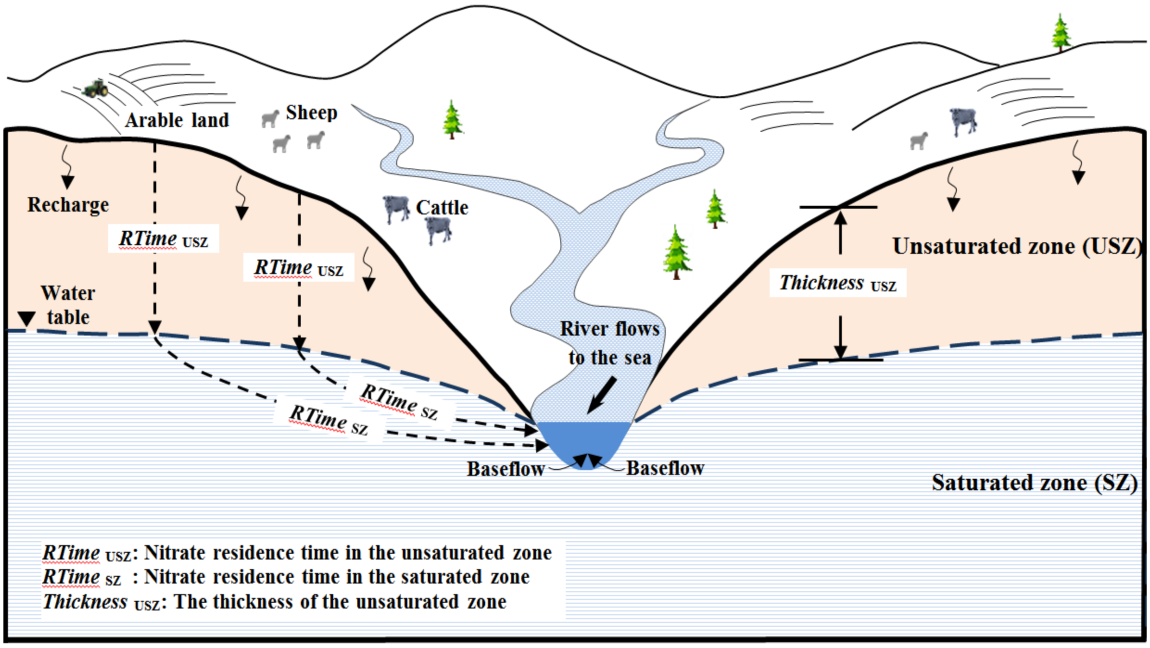


Figure 2.7 Conceptualisation of nitrate transport in the unsaturated and saturated zones

- Nitrate entering an aquifer is diluted throughout the total volume of groundwater in a simulation year.
- The velocity of nitrate transport in aquifers is a function of aquifer permeability, hydraulic gradient and porosity, and.
- The transport length for groundwater and nitrate can be simplified as the total distance between the location of recharge and nitrate entering the aquifer at the water table and their discharge point on the river network.

2.5.2 Developing a national recharge model for the UK

HYDROLOGICAL PROCESSES IN THE RECHARGE MODEL

A national-scale groundwater recharge model was built using the soil water balance model SLiM (Wang et al., 2012a), which objectively estimates recharge and runoff using information on rainfall intensity, potential evapotranspiration, topography, soil type, crop type, and Base Flow Index *(BFI)*. Figure 2.8 illustrates the principal soil zone hydrological processes associated with the SLiM method.

There are many potential pathways that water can take through the system. Rainfall could, in part, be intercepted by plants, while the remaining rainfall reaches the ground surface and infiltrates the soil to reduce soil moisture deficit (*SMD)*. Soil water is extracted by plant roots for transpiration or drawn to the bare soil surface for evaporation. When soil moisture reaches field capacity (*SMD* becomes zero), water drains freely from the saturated soil, and the additional water added to the soil system, called the excess water of *SMD*, can flow laterally overland as runoff (including surface runoff and interflow) if a slope gradient exists towards adjacent locations, or percolate downwards through saturated soil as recharge. Runoff flows to nearby areas, called run-on, can join in the soil hydrological processes at the new location. SLiM explicitly derives both runoff and recharge based on the calculated *SMD* and other datasets, such as *BFI* and slope, instead of expert judgment. Figures 2.8 and 2.9 show how these are represented in the SLiM model.

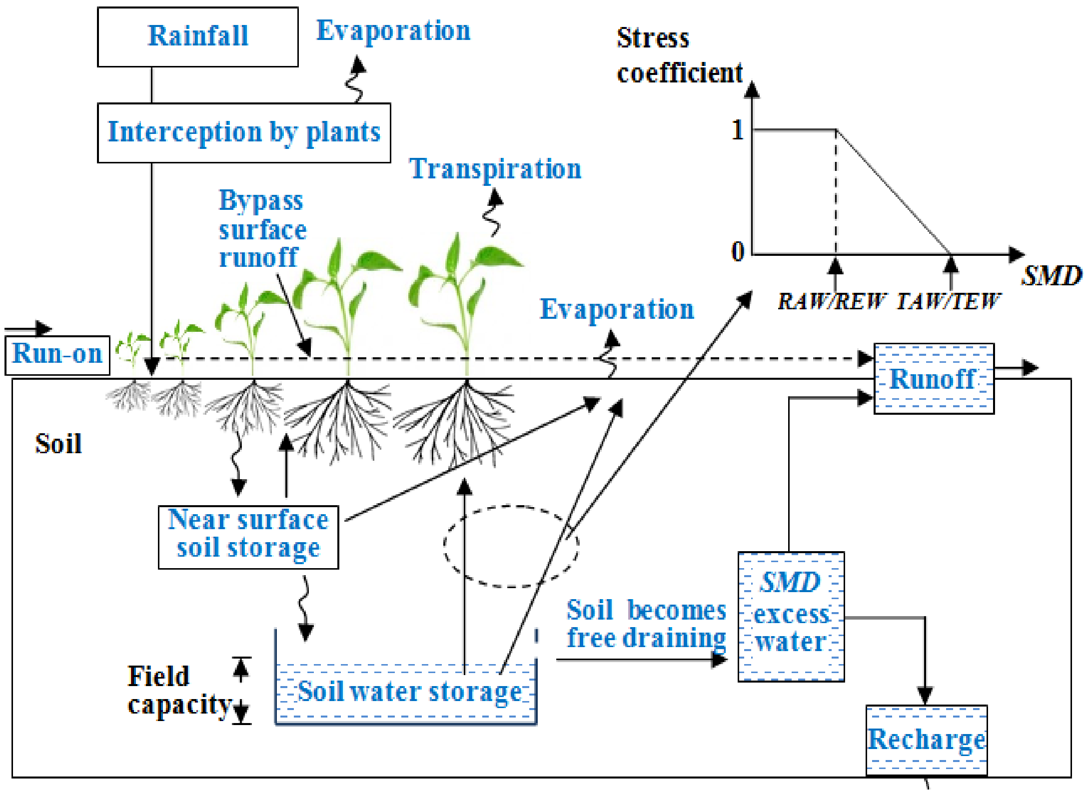


Figure 2.8 Hydrological processes in the SLiM model

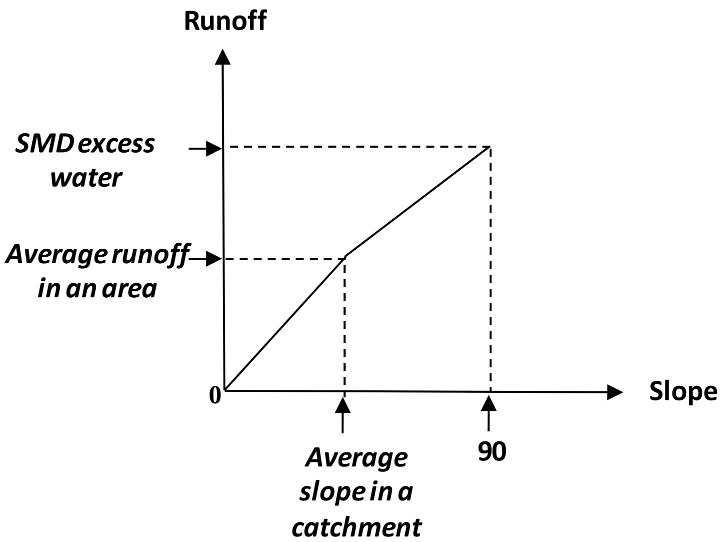


Figure 2.9 Relationship between slope and runoff

BFI, representing an average ratio of annual baseflow to annual river flow in a watershed or catchment, is strongly related to topographical, soil, hydrogeological and precipitation characteristics and less influenced by the land-cover properties of a catchment. *BFI* is one of the key characteristics in explaining the hydrological processes and allows separation of the total river flow into baseflow (slow flow through the groundwater system) and surface flow (fast flow through the overland process) portions (Haberlandt et al., 2001). The equations for calculating runoff and recharge in a cell are as follows:

$$RECH = E_{SMD} \cdot BFI \quad [1]$$

$$Ro = E_{SMD} \cdot (1 - BFI) \quad [2]$$

where E_{SMD} (mm) is the depth of *SMD* excess water when soil becomes free draining; $RECH$ (mm) is the depth of water that move downwards to recharge groundwater system; and Ro (mm) is the runoff calculated from E_{SMD}.

Many studies (see for example Haan et al., 2006; Lange et al., 2003; Tani, 1997) show that the topographic gradient is an important factor that controls runoff generation. In general, greater runoff is observed in areas with steeper slopes. As mentioned above, *BFI* is a long-term average ratio reflecting different catchment characteristics including average catchment slope. Therefore, the runoff and recharge calculated using equations 1 and 2 can be understood as the averages generated at the locations with an average slope in a study area. If a location has a higher than average slope, greater runoff and reduced recharge will be generated. In a flat area, where a zero slope gradient exists towards neighbouring locations, all *SMD* excess water becomes recharge and no runoff will be generated. The relationship between runoff and slope is shown in Figure 2.8. Equation 2 can be further formulated as:

$$Ro = \frac{E_{SMD} \cdot (1 - BFI) \cdot Slp}{Slp_{mean}} \text{ when } Slp \le Slp_{mean} \qquad \textbf{[3]}$$

$$Ro = \frac{(Slp - Slp_{mean}) \cdot E_{SMD} \cdot BFI}{(90 - Slp_{mean})} + E_{SMD} \cdot (1 - BFI) \text{ when } Slp_{mean} < Slp < 90 \qquad \textbf{[4]}$$

$$RECH = E_{SMD} - Ro \qquad \textbf{[5]}$$

where Slp_{mean} (degree) is the average slope value in a catchment; and Slp (degree) is the slope value at a cell with the area.

Compared to longer less intense rainfall, high intensity short duration rainfall is more likely to exceed the capacity of the soil to infiltrate water and generate more overland flow. Tani and Abe (1987) show that rainfall intensity and antecedent soil water storage in a forested catchment affect the amount of runoff and, if the rainfall intensity is larger than a threshold (e.g. 100 mm day^{-1}), the increase in storm runoff is almost the same as the increase in rainfall, even with dry antecedent soil water conditions. Therefore, a rainfall intensity threshold is introduced in SLiM, to represent bypass runoff, where the amount of rainfall above this threshold becomes runoff. If the rainfall intensity is less than this threshold, the *SMD* excess water method is used for calculating runoff. The rainfall intensity threshold needs to be calibrated.

Recharge model construction and calibration

The recharge model has the same spatial resolution as the other components of the BGS NTB model -1km×1km - giving a total area of 229,619 km^2. In contrast to the NTB model, it uses a daily time step over the period 1962-2011. It included the catchments for all 102 gauging stations providing observed river flows (http://www.ceh.ac.uk/data/nrfa/).

Monte Carlo (MC) simulations were carried out in calibrating the model against the river flow data. The Nash-Sutcliffe efficiency NSE (Nash and Sutcliffe, 1970) was adopted to calculate the goodness of fit between observed and modelled surface flow time series:

$$NSE = 1 - \frac{\sum_{i=1}^{N} (Vobs_i - Vsim_i)^2}{\sum_{i=1}^{N} (Vobs_i - \overline{Vobs})^2} \qquad \textbf{[6]}$$

where $Vobs_i$ is the observed surface flow at the i^{th} time step; $Vsim_i$ the simulated flow at the i^{th} time step; N is the total number of simulation time steps; and $\overline{Vobs}$ is the average value of observed flow in N simulation times.

In general, a negative *NSE* indicates that the observed mean is a better predictor than the modelled results. Where *NSE* is zero modelled data are considered as accurate as the mean of the observed data, and *NSE* between zero and one can be treated as acceptable levels of model performance. The closer to 1, the more accurate the model is and an *NSE* of one corresponds to a perfect match of modelled to observed data (Nash and Sutcliffe, 1970).

Field experiments (e.g. Butcher et al., 2009) showed that the thickness of low permeability superficial deposit affects the amount of water and soluble pollutants (such as nitrate) entering the groundwater system. Traditionally the thickness of superficial deposits has seldom been considered in simulating groundwater recharge. Other factors such as changes in composition within the deposits and fracturing are also important but were not addressed here as it is difficult to model these at a national scale. Enhanced recharge at the margins of low permeability deposits was also not included.

A method was developed in this study to objectively estimate recharge considering the spatial distribution and thickness of low permeability superficial deposits. These were divided into five thickness classes, i.e., 0 – 2m, 2m – 5m, 5m – 10m, 10m – 30m, and >30m. The reduction of recharge for each class was identified based on MC simulations (Figure 2.10):

- 0-2m: 0.095 %;
- 2-5m: 4.23 %
- 5-10m:9.10 %;
- 10-30m:15.3 %
- 30-50m: 99.99 %.

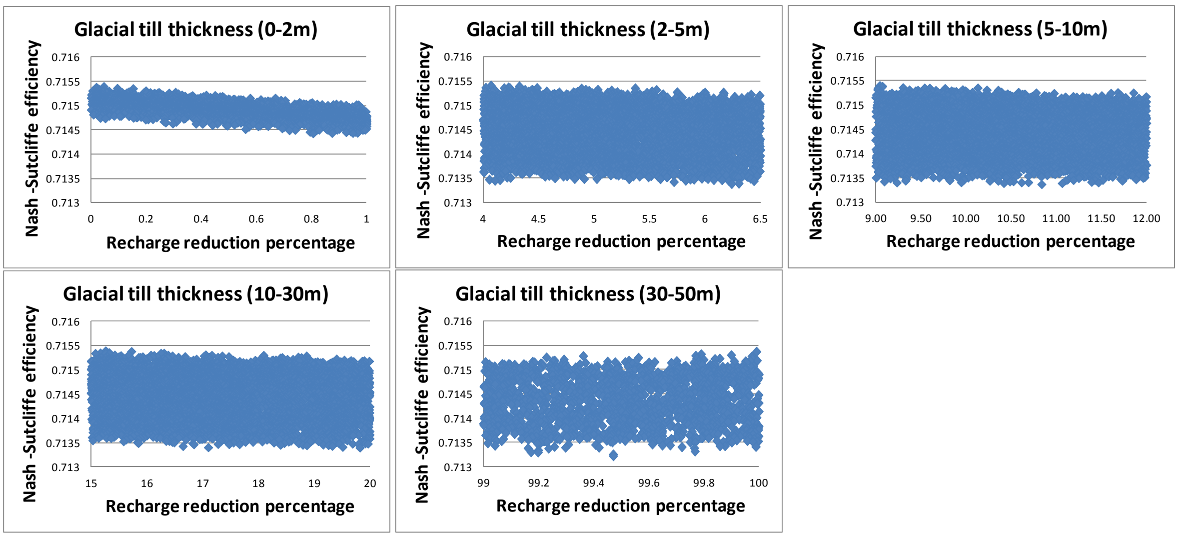


Figure 2.10 Scatter plots showing recharge reduction for each low permeability superficial thickness group.

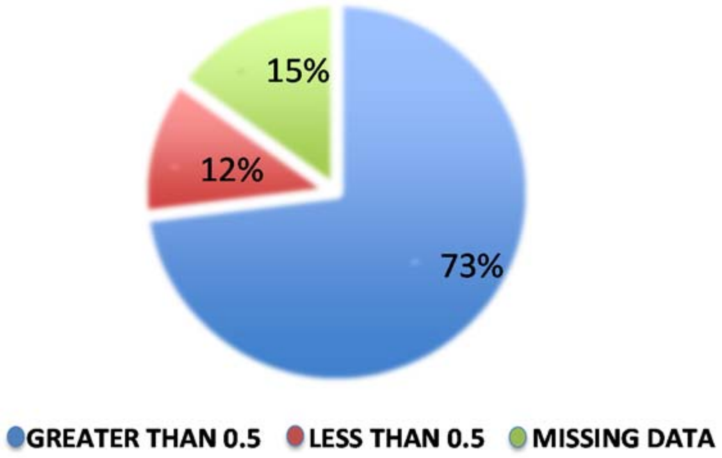


Figure 2.11 NSE values of national recharge model performance

RECHARGE MODEL CALIBRATION RESULTS

The model showed an acceptable performance for 73 % of the surface water gauging stations used for model testing/calibration with a *NSE* > 0.5 (Figure 2.11). Twelve percent of results had *NSE* < 0.5 which is considered reasonable performance for a simple model running at the national scale. Since 15 % of the gauging stations have the problem of missing values for observed flow data, they were excluded when calibrating the national recharge model.

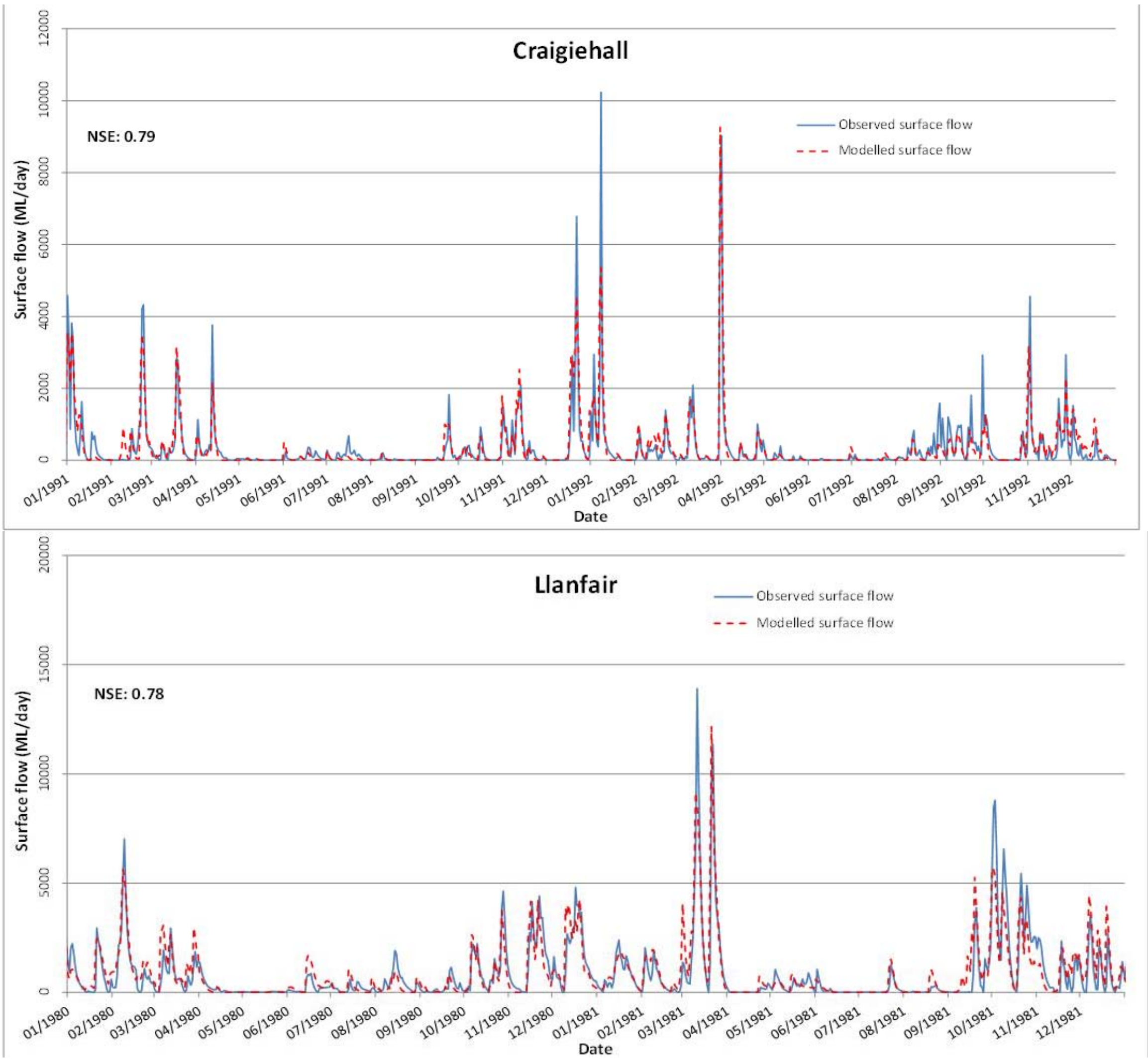


Figure 2.12 Examples of modelled surface flow compared with monitoring data

Two examples, i.e. Craigiehall and Llanfair, were randomly chosen from many results to demonstrate how the modelled hydrographs match with observed ones (Figure 2.12). It shows that modelled results are in line with observed hydrographs with NSE values larger than 0.5 and the model defines the episodes of higher flows very well but does not always estimate the transient high peaks.

Figure 2.13 sets out a series of recharge parameters over the annual cycle for a point randomly selected within the model. This shows rainfall to be distributed over the year but there is little or no recharge over the summer and autumn due to evapotranspiration and development of an increased soil moisture deficit (SMD). There are a few runoff events throughout the year. This is the typical pattern as recharge occurs generally during the winter when plant growth is minimal in a temperate climate (Rushton et al., 2006).

The outputs from this model, the long-term-average (Figure 2.14), daily (e.g., Figure 2.14a) and yearly (e.g., Figure 2.14b) recharge estimates, were then used to simulate nitrate-transport velocity in the USZ and the groundwater volume $Vol_{total}(t)$, respectively.

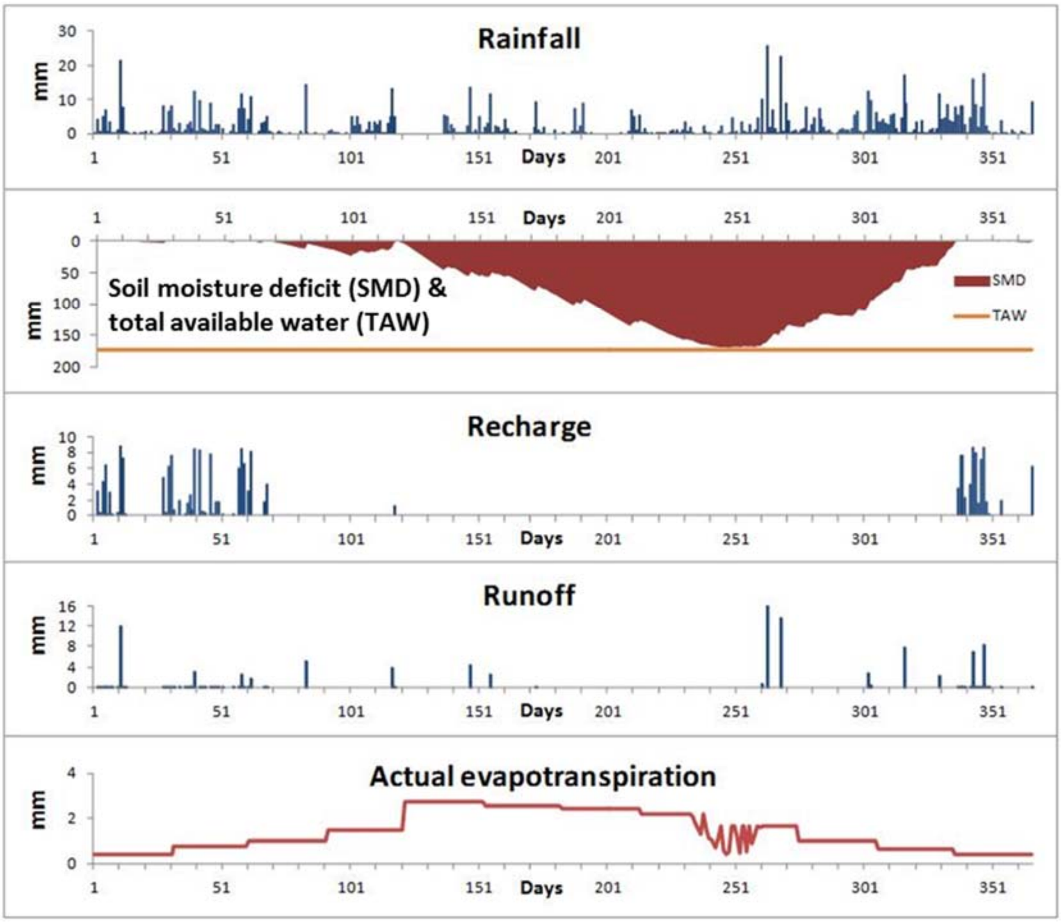


Figure 2.13 Modelled major soil water processes for a location

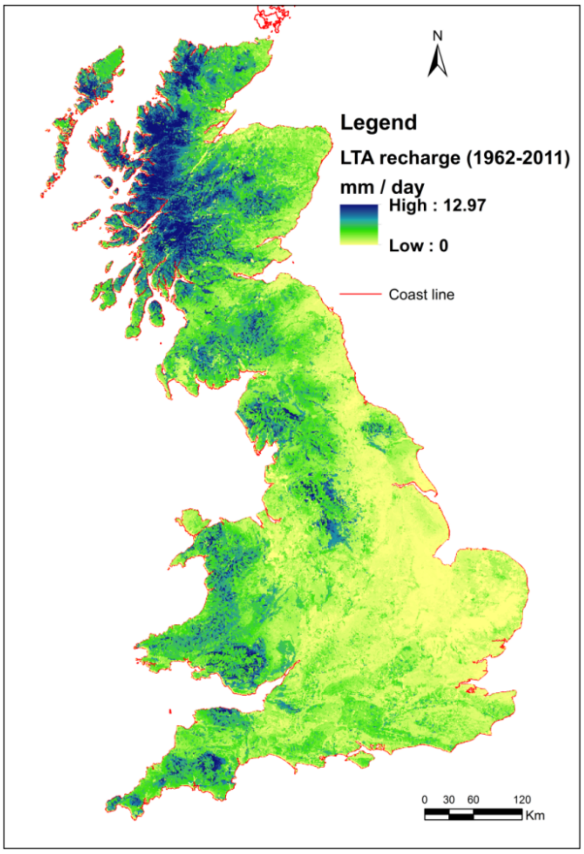


Figure 2.14 Modelled estimate of long-term-average recharge across Great Britain

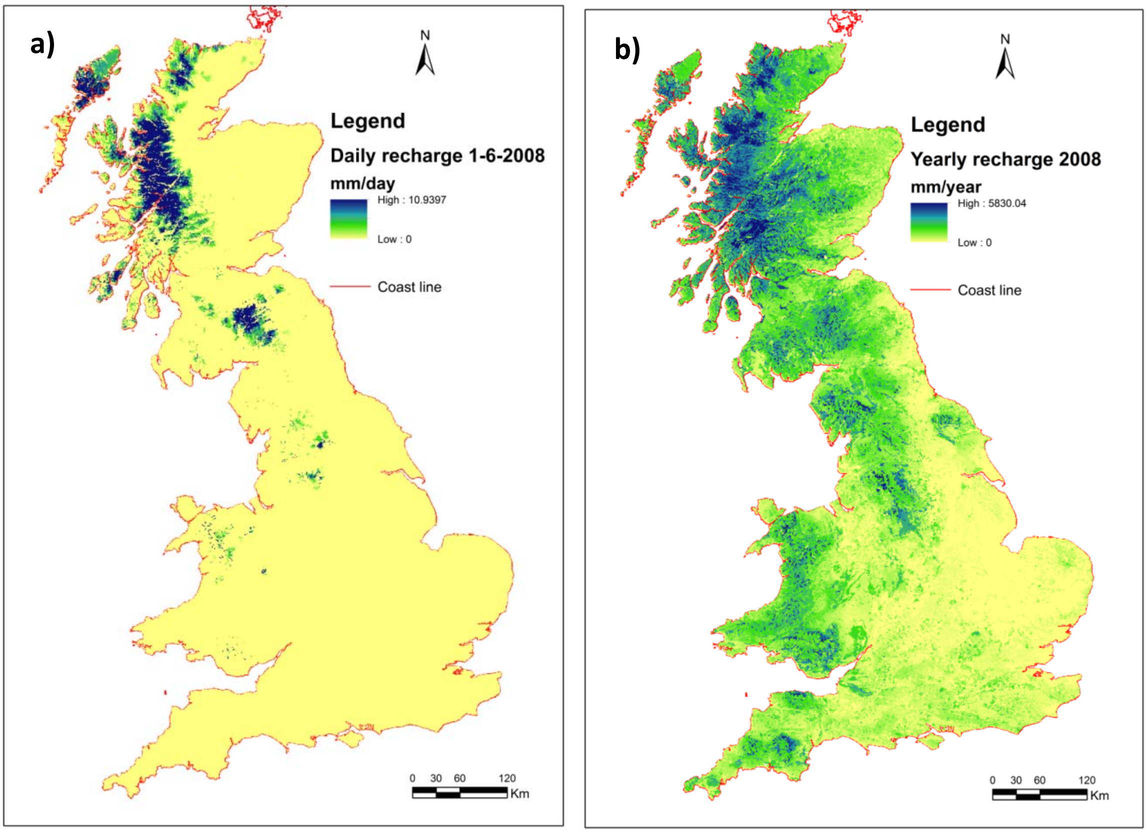


Figure 2.15 Modelled estimate across Great Britain of a) daily recharge on the first June 2008; b) yearly recharge in 2008

2.5.3 Estimating nitrate transport velocity in the unsaturated zone

In the original version of the model nitrate velocities were estimated from measured values for three of the most important aquifers in the UK; the Chalk, Permo-Triassic sandstone and the Lincolnshire Limestone together with literature values and professional judgement for the others.

In order to estimate velocities a number of aquifer properties are required. Recharge, aquifer porosity and storage coefficient/specific yield are major factors affecting pollutant transport in the USZ (Leonard and Knisel, 1988). The nitrate velocity in the USZ and hence the residence time can be expressed as (Rao et al., 1985; Rao and Jessup, 1983):

$$V_{USZ,i} = \frac{q_i}{Sr_{aquifer} \cdot Rf_{aquifer}} \qquad [\mathbf{7}]$$

$$RTime_{USZ,i} = Thickness_{USZ,i} / V_{USZ,i} \qquad [\mathbf{8}]$$

where $Thickness_{USZ,i}$ is the thickness of USZ at cell i (Figure 1); $V_{USZ,i}$ (m year^{-1}) is the nitrate-transport velocity in the unsaturated zone; q_i (m year^{-1}) is groundwater recharge at cell i; $Rf_{aquifer}$ (-) is the retardation factor determined in the calibration procedure, and; $Sr_{aquifer}$ (-) is the specific retention for the rock. The specific retention represents how much water remains in the rock after it is drained by gravity, and is the difference between porosity and specific yield. Model calibration is described in section 2.5.5.

Recharge can be modelled and aquifer property data, such as porosity and specific yield are available for major and minor aquifers from Allen et al. (1997) and Jones et al. (2000). However these specific yields have been estimated for the saturated zone and assume that the aquifer remains fully saturated. These may not adequately represent conditions in the unsaturated zone.

2.5.4 Estimating nitrate transport velocity and dilution in the saturated zone

Model calibration and estimation of errors are described in section 2.5.5.

VELOCITY

Nitrate transport velocity can be estimated using the following equations:

$$VS_i = \frac{365 T_{aquifer} G_i}{D_{aquifer} \Phi_{aquifer}} \qquad [\mathbf{9}]$$

$$G_i = \frac{GWL_i - RL_i}{Dist_i} \qquad [\mathbf{10}]$$

$$VS_{mean} = \frac{\sum_{i=1}^{n} VS_i}{n} \qquad [\mathbf{11}]$$

where VS_i (m year^{-1}) is the nitrate velocity for cell i, $T_{aquifer}$ (m^2 day^{-1}) is the transmissivity of the aquifer, G_i (-) is the hydraulic gradient between a cell and its nearest river discharge point, $Dist$ (m) is the distance between a cell and its nearest river discharge point

DILUTION

Groundwater available for dilution of nitrate in the saturated zone can be estimated using the following equations:

$$Vol_{total}(t) = Vol_{background} + Vol_{recharge}(t)$$

[12]

$$Vol_{background} = \sum_{i=1}^{n} A_i D_{aquifer} Sy_{aquifer} \quad [13]$$

$$Vol_{recharge}(t) = \sum_{i=1}^{n} A_i q_i (t - Rp_q) \quad [14]$$

where A_i (m^2) is the area of cell i; $D_{aquifer}$ (m) is the depth of active groundwater (for nitrate dilution) in an aquifer; $Sy_{aquifer}$ (-) is the specific yield representing the aquifer drainable porosity, and; n is the total number of cells in the aquifer model; Rp_q (year) is the water table response time to recharge events;

It can be argued that recharge events at the bottom of the soil effectively occur at the same time as rainfall events within a monthly time step (Lee et al., 2006; Mackay et al., 2014). Therefore, Rp_q was determined using the cross-correlation between the time series of monthly rainfall (1961-2011), from the Meteorological Office Rainfall and Evaporation Calculation System (MORECS) (Hough and Jones, 1997) and groundwater level for 57 boreholes across the study area. Rp_q, the time taken for an instantaneous flux of recharge to reach the water table, was set to the period over which there is a significant correlation at the 95% confidence level. Figure 2.16 gives an example of cross-correlation results for the borehole at Tank Hall in the Chalk, East Anglia, which is randomly chosen from many results, and shows that groundwater level and rainfall event are correlated (larger than 95 % confidence level) for 24 months. This indicates that 24 months are needed for the groundwater level to fully respond to the monthly rainfall event. The average values of Rp_q were calculated for aquifer zones where there was more than one borehole and these are given in Table 2.1.

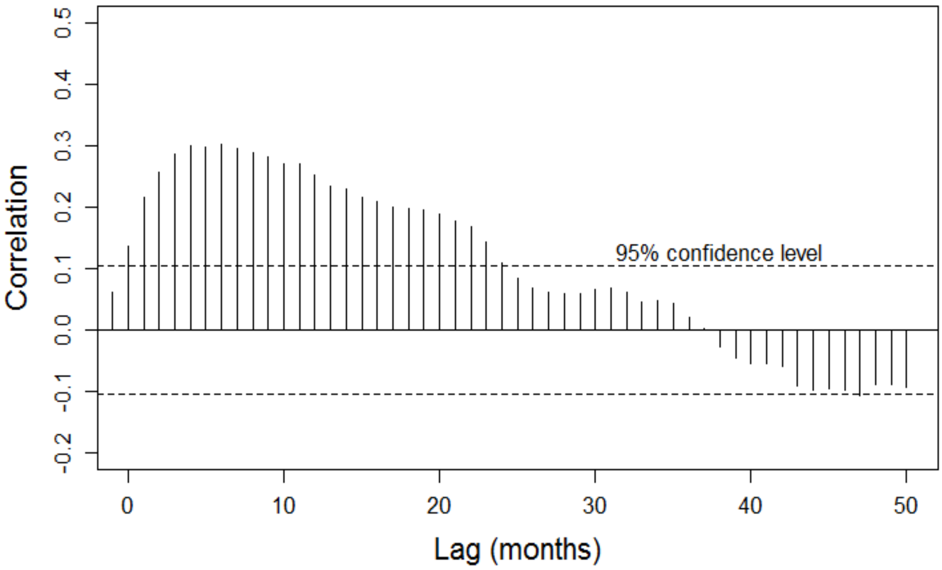


Figure 2.16 Example of cross-correlation results for the Tank Hall borehole in the Chalk

ANNUAL NITRATE CONCENTRATION IN GROUNDWATER

Annual nitrate concentration $Con_{aquifer}(t)$ (NO_3 mg L^{-1}) in the SZ in year t can be calculated aquifer by aquifer, assuming there is no groundwater flow between aquifers:

$$Con_{aquifer}(t) = \frac{\sum_{i=1}^{n} M_i(t - RTime_{total,i}) \cdot (1 - ATT)}{Vol_{total} \cdot 1000} \qquad [15]$$

$$RTime_{total,i} = RTime_{USZ,i} + RTime_{SZ,aquifer} \qquad [16]$$

$$RTime_{SZ,aquifer} = \frac{\sum_{i=1}^{n} Dist_i / VS_{mean}}{n} \qquad [17]$$

where $RTime_{total,i}$ (year) is the total residence time for nitrate to travel through both the USZ and an aquifer at cell i (Figure 2.7); $RTime_{USZ,i}$ (year) is the nitrate residence time at cell i in USZ; $RTime_{SZ,aquifer}$ (year) is the average residence time for nitrate dilution and transport in the aquifer; $M_i(t - RTime_{total,i})$ (mg NO_3) is the amount of nitrate loading from the base of soil into USZ at cell i in the year of $t - RTime_{total,i}$, and; ATT is the attenuation factor representing the percentage of nitrate mass that is attenuated in the USZs.

NITRATE TRANSPORT IN LOW PERMEABILITY SUPERFICIAL DEPOSITS

As mentioned in section 2.5.2, some water and nitrate can pass through low permeability superficial deposits (drift). This process was ignored in the original NTB model to reduce the number of parameters in the national-scale model as it was previously assumed that no nitrate can be transported downwards through the low permeability superficial deposits. However, nitrate transport through (and below) these deposits has now been introduced to address the previous over simplification. This has been possible as a result of newly available datasets, such as the split between runoff and recharge derived from a national-scale groundwater recharge model.

This model was built using the soil water balance model SLiM (Wang et al., 2012a) which objectively estimates recharge and runoff using information on rainfall intensity, potential evapotranspiration, topography, soil type, crop type, and *BFI* (Wang, 2015; Wang et al., 2014). The model was calibrated using the observed river-flow data for 102 gauging stations (http://www.ceh.ac.uk/data/nrfa/). The long-term-average and time-variant recharge estimates were then used to simulate nitrate-transport velocity in the USZ and the groundwater volume, respectively.

The revised low permeability superficial deposits model addresses three aspects:

- The nitrate loading from superficial deposits now depends on their thickness and is consistent with groundwater recharge estimates
- The nitrate travel time in superficial deposits is calculated using velocity from literature and the deposit thickness
- The nitrate is transferred to the underlying bedrock aquifer and is then subject to unsaturated and saturated travel time and dilution process in the saturated zone.

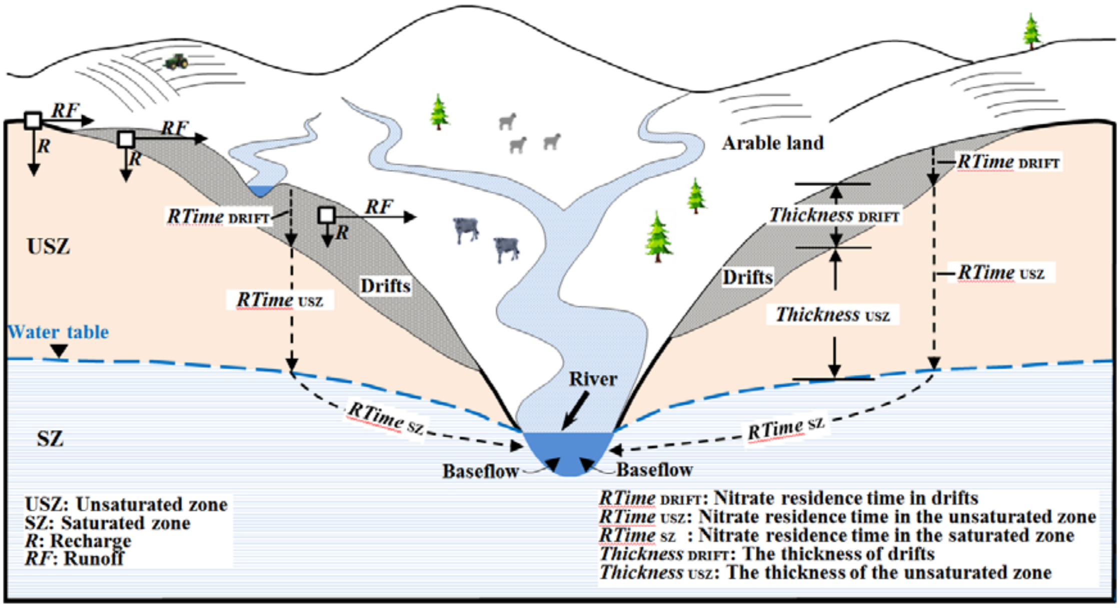


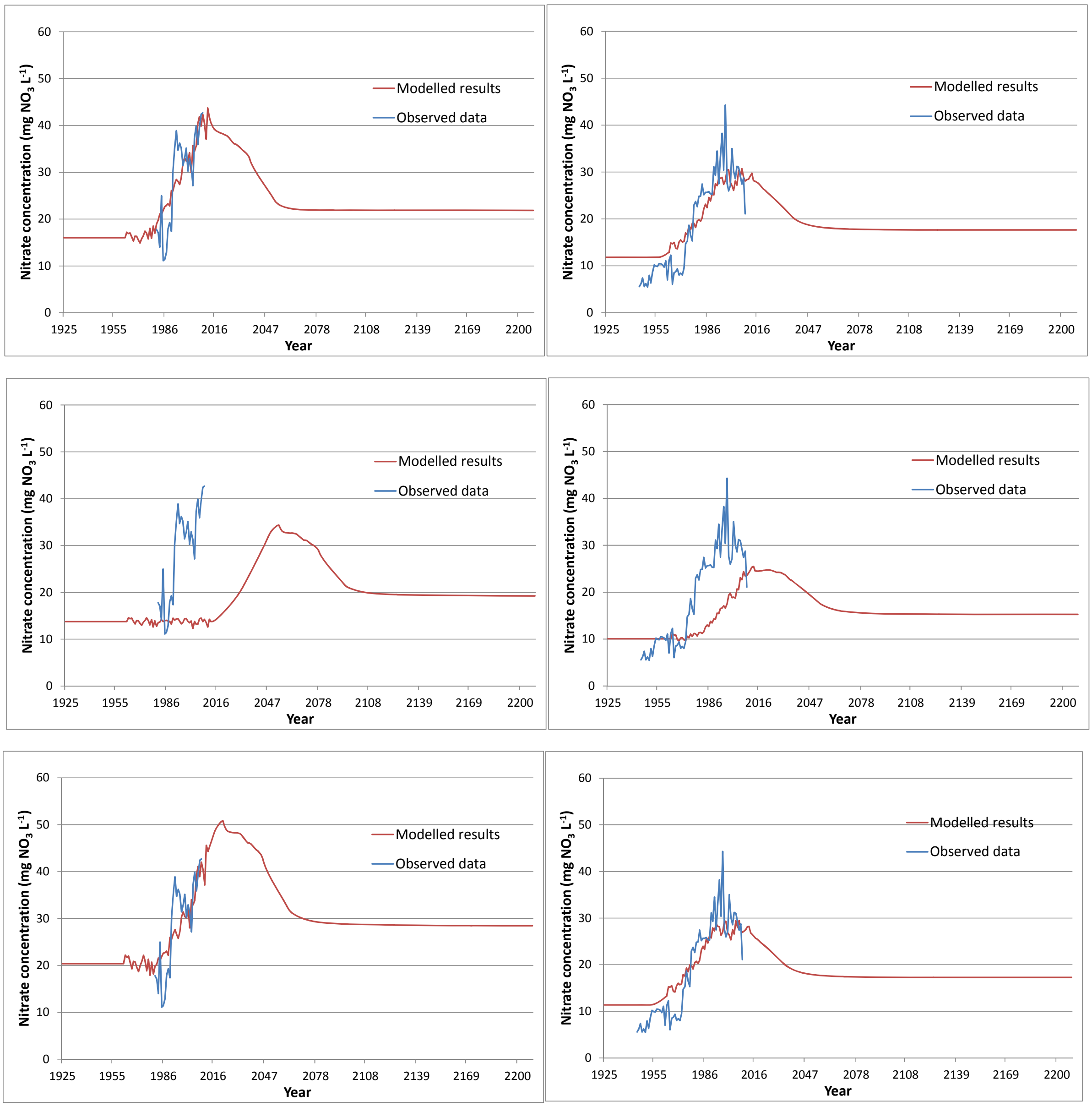
Figure 2.17 Conceptual model of low permeability drift impact on nitrate transport in the subsurface

The thicker the low permeability superficial deposits are, the less water and nitrate can pass through them and enter the groundwater system. This is consistent with the concept of the splitting of runoff and recharge from excess water of SMD in section 2.5.2. The reduced recharge is then diverted into surface water to increase runoff, and the same portion of nitrate in it is also flushed into surface water (Figure 2.17). Therefore, the amount of nitrate entering the groundwater system is a function of *BFI*, topography and the thickness of superficial deposits. All modelling cells in the selected aquifer zones were included to simulate nitrate dilution in groundwater regardless of the presence of overlying low permeability deposits. The model does not address enhanced recharge at the margins of these deposits.

The low permeability superficial deposit zones were identified using the classifications of Griffiths et al. (2011) and comprised the Low-Medium and the Low-Low zones. The average nitrate velocities derived from the work of Ross et al. (1989), Klinck et al. (1996) and Marks et al. (2004) were used for this modelling.

Based on the previously calibrated NTB model, the initial results of introducing nitrate processing in low permeability superficial deposits (before the new calibration) suggest that areas where impact is significant are the:

- Chalk of East Anglia
- Chalk, Northern
- Lower Greensand of Bedfordshire & Cambridge
- Permo-Triassic Sandstone of Lancashire – West Midlands
- Carboniferous Limestone of Northern England
- Permo-Triassic Sandstone of Nottingham – N Yorkshire
- Middle Jurassic limestone of Lincolnshire – Oxfordshire (excluding Lincolnshire Limestone)
- Coal Measures of Durham – Northumberland
- Magnesian Limestone of Nottingham – N Yorkshire.



a)

b)

c)

Chalk of East Anglia | Permo-Triassic sandstone Lancs to W Midlands

Figure 2.18 Results of impact on predicted concentrations taking account of nitrate transport in low permeability drift: a) results before considering nitrate transport in low permeability drift; b) initial results after the model improvement before the calibration and; c) the calibrated results from the final calibrated model

Figure 2.18 shows examples of the impact of taking account of nitrate transport through low permeability superficial deposits above two aquifer zones. It is shown that modelled nitrate concentration peak values decreased and the time to the peak has been delayed after introducing the nitrate transport in low permeability superficial deposits before undertaking calibration (Figure 2.18b). This might be explained by longer nitrate travel time through low permeability deposits and more groundwater for dilution after considering modelling cells in aquifers overlain by low permeability deposits. After model recalibration (Figure 2.18c) a good fit with the observed data is obtained, but for the Chalk of East Anglia the modelled peak is enhanced and broadened.

Table 2.3 Summary of parameters used in Monte-Carlo simulations

Method	Parameter (units)	Description
Fixed	A_i (m^2)	The area for cell i
	q_i (m $year^{-1}$)	The recharge value for cell i
	NIF (kg ha^{-1})	The nitrate-input-function
	Rp_q (year)	The water table response time to recharge events
	GWL_i (m)	The groundwater level for cell i
	RL_i (m)	The river level for cell i
	ATT (-)	The nitrate attenuation factor in the USZ
	$Thickness_{USZ,i}$	The thickness of USZ at cell i
Monte Carlo Calibration	$\Phi_{aquifer}$ (-)	The porosity for an aquifer zone
	$Sy_{aquifer}$ (-)	The specific yield for an aquifer zone
	$Rf_{aquifer}$ (-)	The retardation factor for calculating the nitrate velocity in USZs
	$T_{aquifer}$ (m^2 day^{-1})	The transmissivity for an aquifer zone
	$D_{aquifer}$ (m)	Depth of active groundwater for an aquifer zone

2.5.5 Estimating annual nitrate concentrations in groundwater

MODEL CALIBRATION

Model calibration (MC) simulations were also undertaken to calibrate the improved NTB model. Parameters were randomly sampled within a finite parameter range to produce one million parameter sets. The upper and lower bounds of the range for each parameter were defined based on observed results or expert judgment. Performing MC simulations is a computer-intensive task especially when many parameters are involved. Therefore, it is good practice to reduce the number of parameters for MC simulations, by fixing some parameters using available information on the aquifer zones. All parameters used in this study are summarised in Table 2.3. The fixed parameters were identified based on observations and knowledge from hydrogeologists.

Two sets of MC simulations were conducted to calibrate the model against: 1) the nitrate velocity values in USZs derived from measurements of porewaters from drill cores (Wang et al., 2012), and; 2) the observed average nitrate concentrations for each aquifer zone calculated from monitoring data provided by the Environment Agency. In the former, the bias (absolute difference) between simulated and observed nitrate velocity in USZs was used to evaluate the model fit. In the latter, the NSE score was adopted to calculate the goodness-of-fit between observed and modelled nitrate concentrations.

SENSITIVITY ANALYSIS

A sensitivity analysis of the model parameters was undertaken to determine which parameters contribute most to the model efficiency, and which of these parameters are identifiable within a specific range linked to known physical characteristics of an aquifer zone. Scatter plots for parameter values against the biases or NSE scores from MC simulations were produced, to show how the model efficiency changes as each parameter is randomly perturbed. Figure 2.19 shows some examples of the scatter plots in estimating nitrate velocity values in USZs using specific yield, porosity and the retardation factor. Although the sensitivity of the model to these parameters differs for each aquifer zone, in general, the model is most sensitive to the retardation factor and least sensitive to specific yield. The models for Chalk, Southern England, Upper Greensand and Corallian Limestone Yorkshire show clear V-shaped response surfaces for the retardation factor, indicating that this parameter is identifiable although there is more than one value with a bias close to zero. The optimum parameter values result in the minimum bias in the MC simulations. In contrast, the response surfaces for specific yield are nearly flat in these three aquifer zones and do not show a unique optimum. The response surfaces for porosity show that the model is sensitive to this parameter to some extent.

Figure 2.20 shows some examples of the scatter plots of the *NSE* scores against depth of active groundwater and transmissivity in the second set of MC simulations. The model is sensitive to both the depth of active groundwater and the transmissivity and these parameters are, to different extents, identifiable for the different aquifer zones. The results show that 16 aquifer zones have an increasing trend in nitrate concentration, while average nitrate concentrations in the remaining 12 are declining. Examples are shown in Figure 2.21.

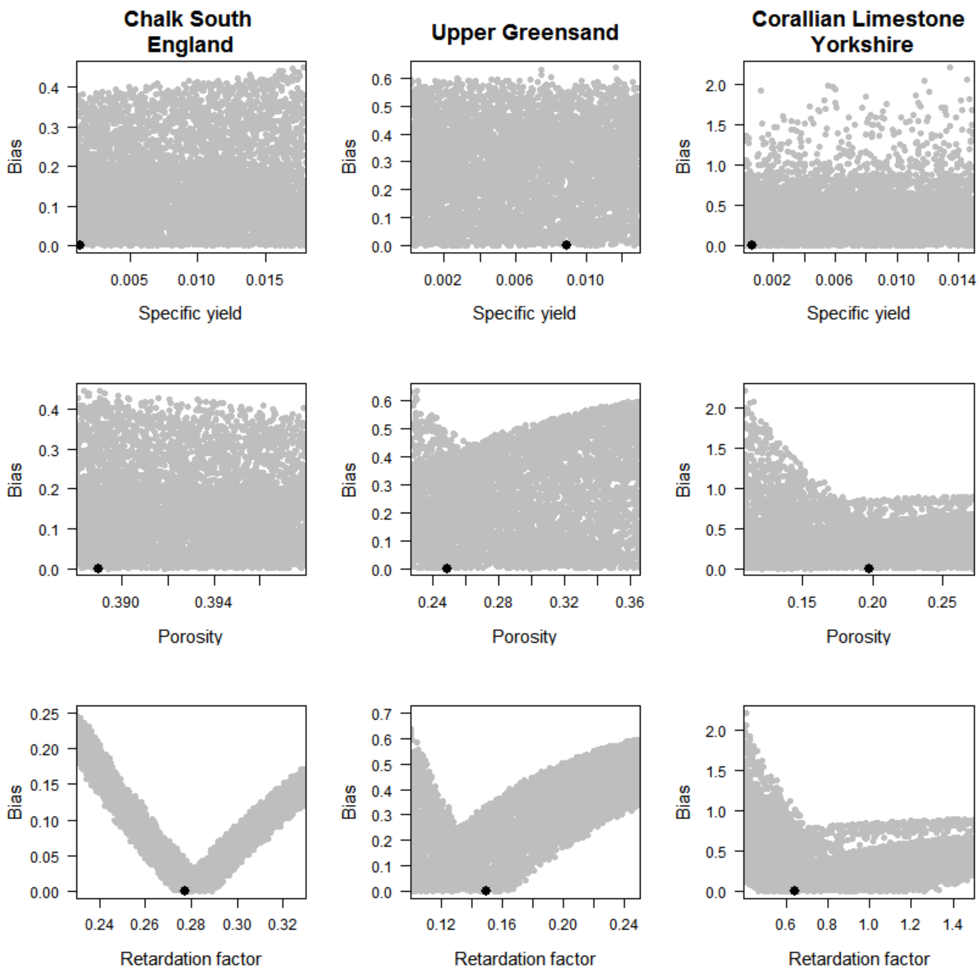


Figure 2.19 Sensitivity scatter plots for parameter values for specific yield, porosity and the retardation factor in estimating the nitrate velocity in USZs of selected aquifer zones. Grey dots are individual parameters from Monte Carlo simulations and the black dots denote the optimum parameter value

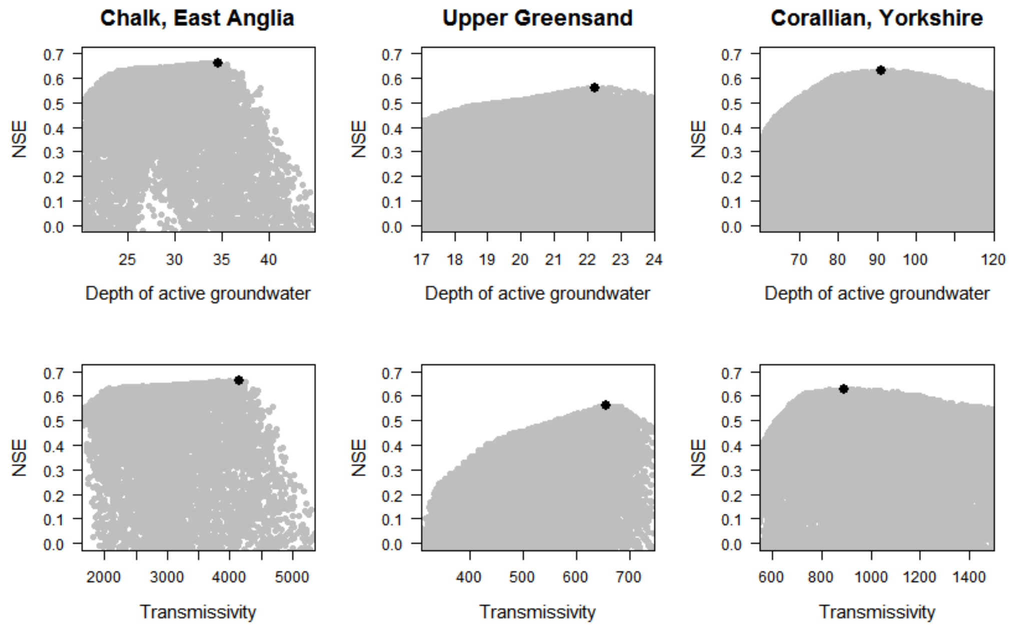


Figure 2.20 Sensitivity scatter plots for parameter values for depth of active groundwater and transmissivity in estimating the nitrate velocity in USZs of selected aquifer zones. Symbols as for Figure 2.18

MODEL ASSUMPTIONS/LIMITATIONS

The revised model still depends on a number of assumptions and these could limit its use for some applications. These are:

- Nitrate transport is only by intergranular movement through the matrix in the USZ,
    - It does not fully take account of bypass flow in transporting nitrate rapidly to the water table. Bypass flow is likely to be important in all fractured and karst aquifers, e.g. the Corallian and Carboniferous limestones as well as the Chalk, particularly where there is very low matrix permeability.
    - The impact of diffusion will be accounted for I in measured values but is not otherwise included.
- Nitrate attenuation in the USZ was ignored. This was because:
    - Nitrate is negatively charged and will not be affected by cation exchange (Close, 2010; Environment Agency, 2005).
    - Rivett et al. (2007) suggested that denitrification only accounts for a loss of 1-2% in the unsaturated zone. In the saturated zone reaction rates are generally limited by a lack of electron donors (most often dissolved organic carbon and/or sulphide) so most denitrification occurs only in the confined aquifer, where depleted in dissolved oxygen; exceptions are where there is elevated DOC due to the presence of pollutants or surface water infiltration. However, although nitrate may diffuse into the small pore throats of the Chalk and Jurassic limestones, even if organic carbon and sulphides are present and oxygen is absent, denitrification may not occur, as nitrate reducing bacteria are excluded by the small pore throats.
    - Denitrification was found to be relatively limited in the unconfined aquifers selected in this study (e.g. Butcher et al., 2005; Kinniburgh et al., 1999).
- Climate and long-term average values for recharge in the future (2011-2150) will be the same as the recent past (1961 to 2011).
- The future NIF is extrapolated from the composite NIF based on the BGS NIF and ADAS NEAP-N for 1980, 1995, 2000, 2004 and 2010. For realistic projections a future NIF, or a series of scenarios, which reflect anticipated nitrate management needs to be agreed.

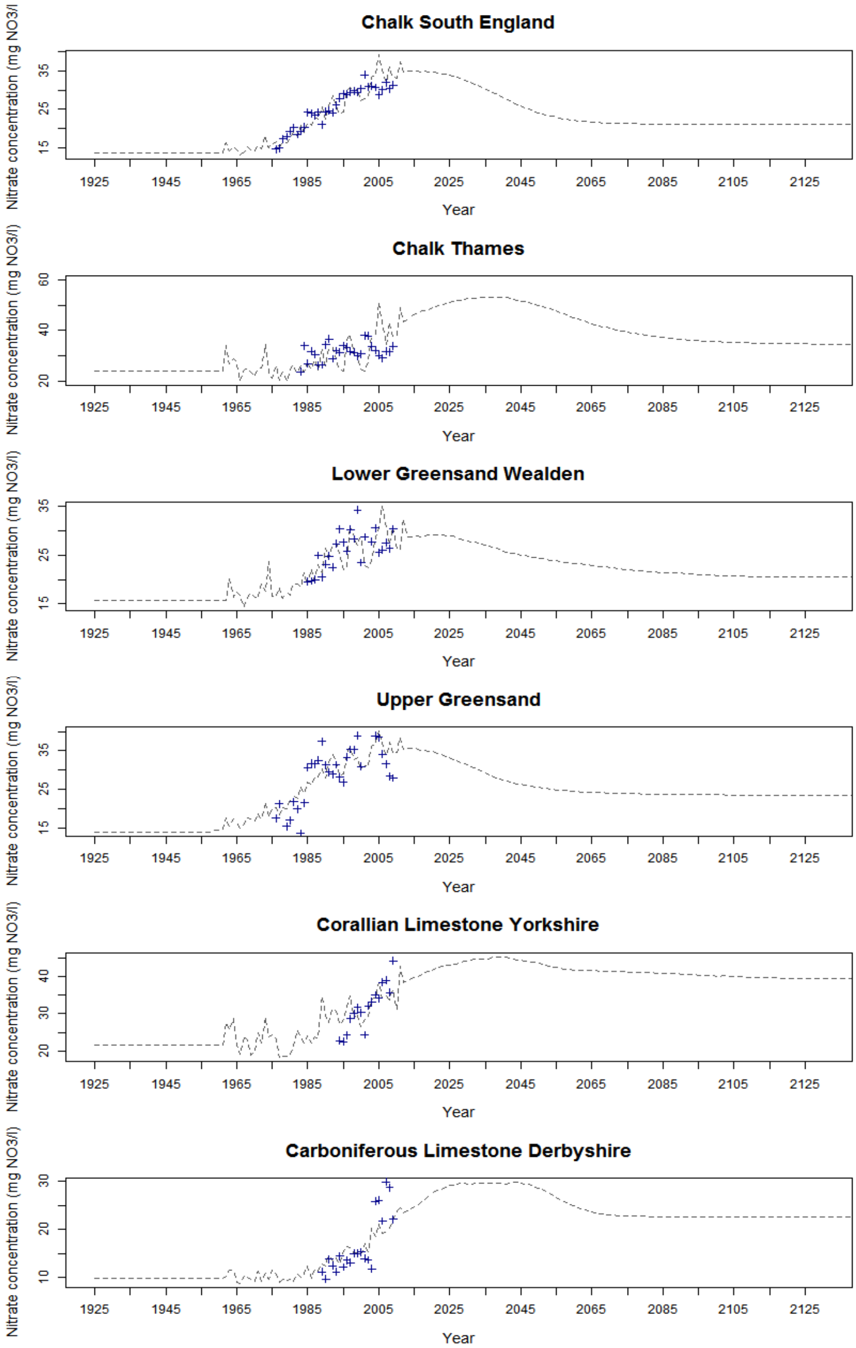


Figure 2.21 Modelled and actual concentrations in selected areas

2.6 TOTAL UNSATURATED ZONE NITRATE STORAGE

2.6.1 Introduction

Management of legacy nitrate in groundwater in England and Wales both at national and local levels requires an understanding of the storage of nitrate in the unsaturated zone. Work by Wang et al. (2012b) has identified the peak year for nitrate to arrive at the water table. Parris (1998) and Worrall et al. (2009) show that Great Britain is a net sink of reactive nitrogen, with potentially 300 kt N stored in groundwater. However, estimations of the total mass of nitrate in the unsaturated zone have not been undertaken to date. This section details an approach that has estimated the total mass of nitrate in the unsaturated zone of England and Wales.

2.6.2 Methodology

In this high level national scale quantification of nitrate storage in the unsaturated zone it was deemed suitable to select high and moderate productivity aquifers based on BGS 1:625,000 scale hydrogeological mapping. Areas overlain by low permeability superficial deposits (Griffiths et al., 2011) were excluded from the analysis. The time and spatially variable NIF derived from NEAP-N and the BGS NIF as discussed in section 0 was used as a nitrate input. Point source discharges of nitrate, such as slurry heaps or septic tanks, have previously been estimated as contributing < 1% of the total nitrate flux to groundwater (Sutton et al., 2011) and have not been considered in this study. It is possible that these could be important for some areas or aquifers. Transport of nitrate through the unsaturated zone on a 1 km scale was derived using the approach of Wang et al. (2012). The total mass of nitrate in the unsaturated zone was derived for each year (1925 to 2050) for each 1 km grid cell and summed across the study area by aquifer. For any year, *t*, the total nitrate in unsaturated zone, N_{USZ} for a given grid cell with an unsaturated travel time, TT_{USZ} and a time-variant nitrate input function, *NIF*, can be calculated as:

$$N_{USZ} = \sum_{i=t-TT_{USZ}}^{t} NIF_i$$

2.6.3 Results and discussion

Figure 2.22 shows the temporal change in total nitrate stored in the unsaturated zone divided by aquifer. The total mass of nitrate in the unsaturated zone has increased substantially through time, peaking at approximately 1400 kiloton (kt) N in 2008. From 2008 onwards, the unsaturated zone becomes a net source of nitrate to groundwater and subsequently to surface water. The temporal change in nitrate storage in the unsaturated zone in 2015 is estimated to be approximately -5 kt N year$^{-1.}$ In 2015, the flux from the unsaturated zone to groundwater was approximately 72 kt 5 kt N year^{-1}.

The increase in unsaturated zone nitrate storage is dominated by the Chalk, with 70% of the total mass in 2015. Increases are also observed in other aquifers such as the Permo-Triassic Sandstones (4% total mass in 2015), Oolitic Limestones (3% total mass) and numerous other locally important formations (23%). The Chalk, Permo-Trias and Oolites have peak mass years of 2015, 1991 and 1992 respectively. The year in which the total peak mass of unsaturated zone nitrate for England and Wales occurs is significantly affected by the majority of mass being in the Chalk.

The Chalk dominates the increase in unsaturated zone storage because of its large outcrop area, extensive agricultural land use (87%) and thick unsaturated zones (Wang et al., 2012b). Thick unsaturated zones results in long travel times and consequently a large increase in nitrate storage. Figure 2.22 shows the spatial distribution of nitrate stored in the unsaturated zone in 1960 and 2015. Increases in nitrate storage in the chalk of southern and north east England can be observed. Increases are particularly large in interfluve areas where travel times are long due to thick unsaturated zones.

The estimated peak nitrate mass of 1400 kt N is substantially greater than previous first approximations of 300 kt N (Worrall et al., 2009). However, in general this study corroborates with previous work suggesting that the subsurface is a significant store of reactive nitrogen. Whilst the total nitrate storage in the unsaturated zone is now decreasing, travel times in the saturated zone can be considerable (Wang et al., 2016) and consequently the peak saturated zone mass may not have occurred yet. Further research is required to assess how this storage compares with other postulated terrestrial stores such as in-stream N retention and terrestrial N uptake in land not in production.

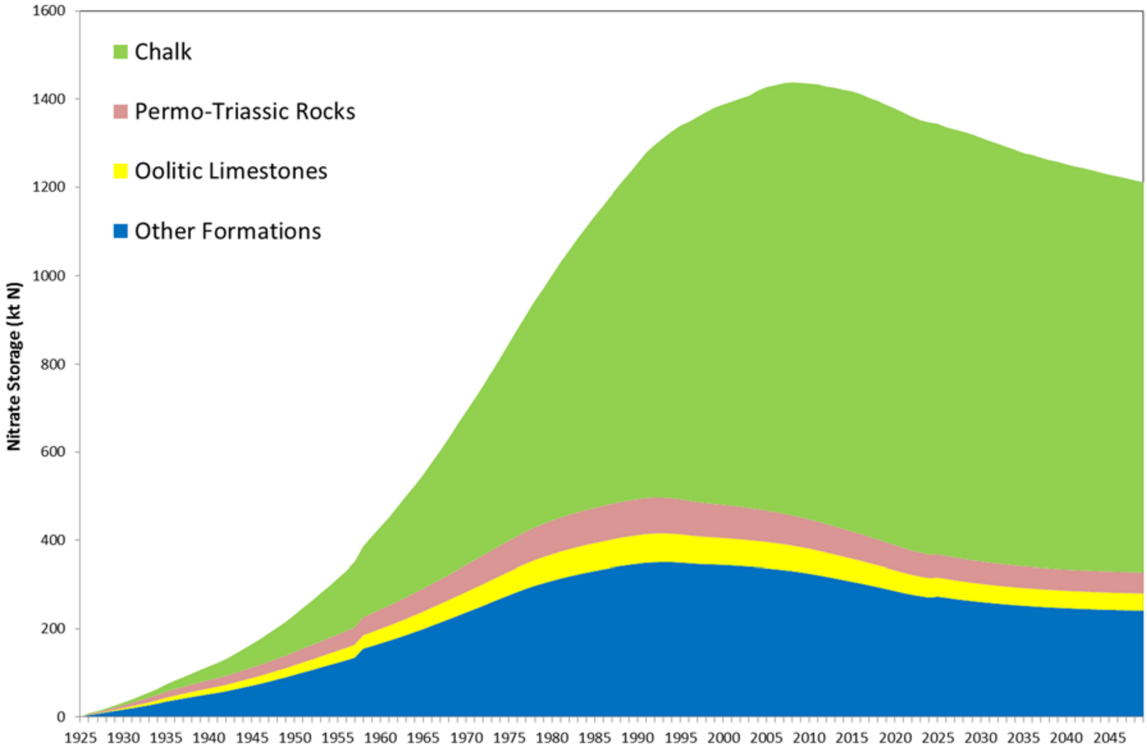


Figure 2.22 Change in unsaturated zone nitrate storage for 1925 – 2050 for moderate and highly productive aquifers

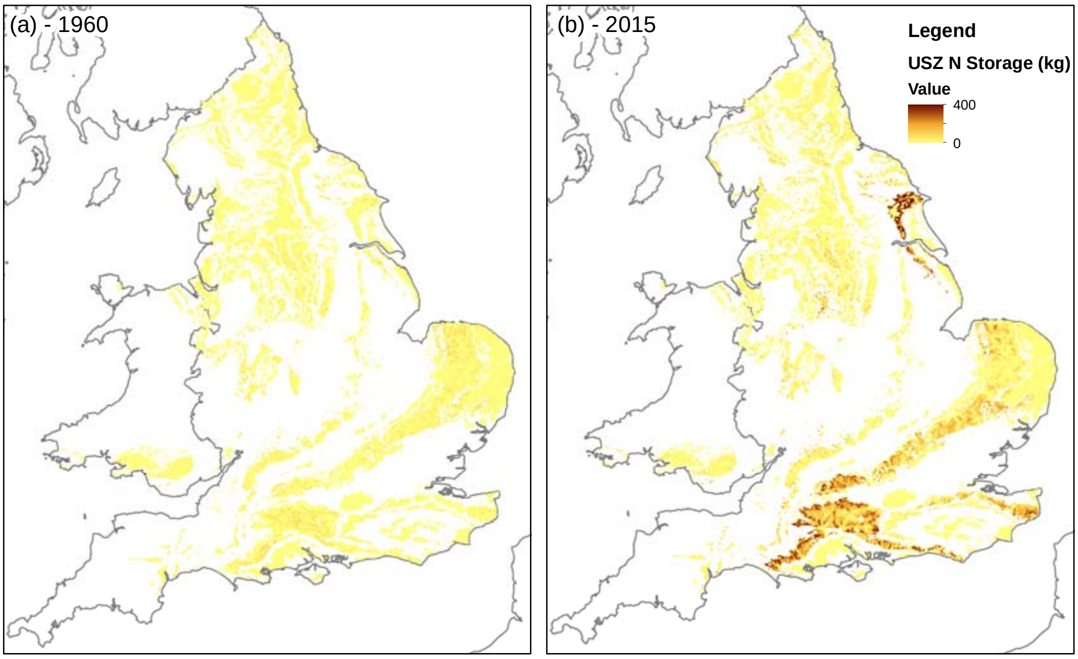


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Figure 2.23 Spatial distribution of total unsaturated zone nitrate mass (as kg N) in England and Wales in: a) 1960 and b) 2015

The approach adopted in this analysis and that of Wang et al. (2012b) is likely to be beneficial for the targeting of catchment management activities at national and regional scales. For example, Figure 2.22 illustrates that legacy nitrate in the unsaturated zone at a national scale is dominated by the Chalk. Figure 2.23 shows that within the Chalk, there a substantial historical mass of nitrate in the unsaturated zone of southern England, particularly in interfluve areas where travel times are long. Consequently, environmental managers should take into account this mass when considering the implementation of catchment mitigation measures in attempts to improve groundwater and surface water quality. This could also be important when setting environmental objectives (such as for the WFD status assessment) which involve a simple assessment of water quality metrics, e.g. measured concentrations and associated statistics, and to demonstrate their achievement.

2.7 ASSESSMENT OF NTB MODEL IMPROVEMENTS

Table 2.4 sets out the improvements to the model and their influence on modelled results. Of these, the use of a spatially variable NIF function is probably the most important. Figure 2.24 shows the impact on nitrate concentrations in groundwater from the use of the spatially variable (composite) NIF in the 28 zones of the process-based model. This highlights the overestimate for non-agricultural areas, particularly uplands in the original NIF.

The NIF function and the revised water levels were used in the process-based modelling but the nitrate velocities from 250k scale mapping were not incorporated at this stage.

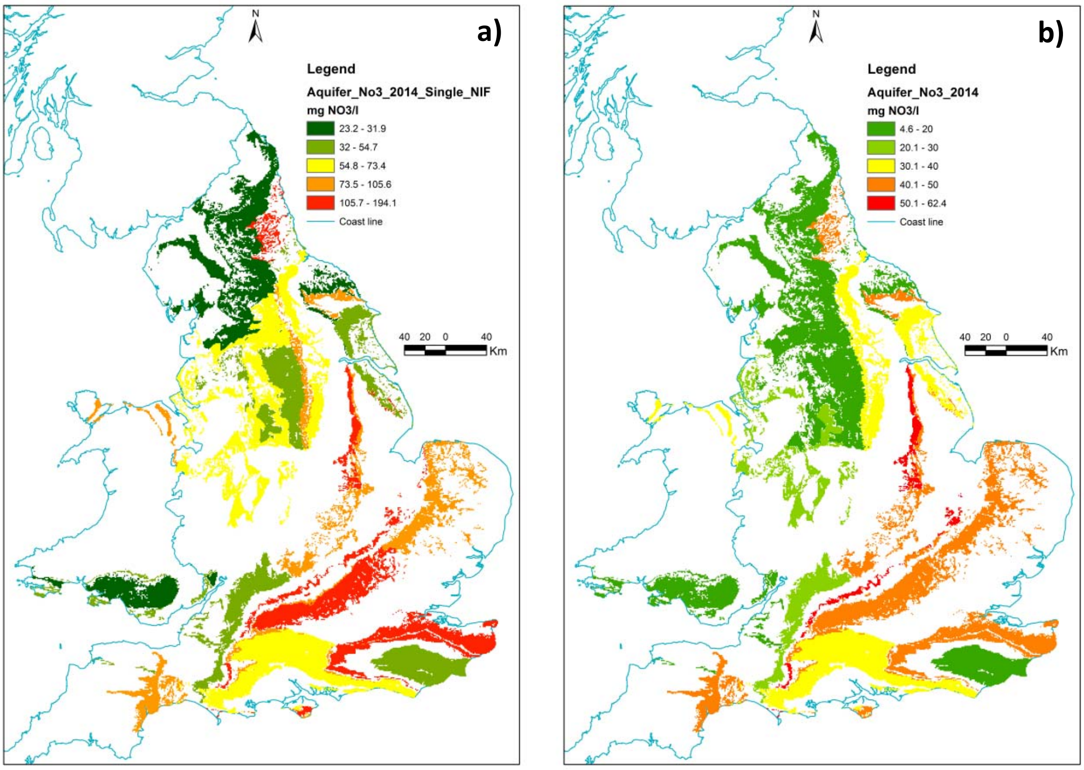


Figure 2.24 Simulated nitrate concentrations from the process-based model using: a) the original NIF; b) spatially variable NIF

Table 2.4 Summary of BGS model developments

Component	Development	Improvement	Importance	Comment
NIF function	Spatially and temporarily variable	1. Better represent spatially distributed land-uses 2. Realistic concentrations at the water table	National scale	Previously, when using the single NIF, it was assumed that a single arable land-use covers aquifers across the England and Wales, thus leading to over-estimated nitrate concentrations in aquifers overlain by non-agricultural land
Water levels	Now uses OS river data	More realistic unsaturated zone thickness can be used to derive nitrate travel time in the USZs	National scale	Allowed estimation of more reasonable parameters such as transmissivity and aquifer thickness
Geological mapping scale	250 k	Represents layered aquifers better	Regional and catchment scale	Important in Jurassic limestones and Carboniferous strata, such as the Coal Measures. Provides potential for process-based treatment depending on data availability
Processed based model	Quantifiable unsaturated zone travel time for 28 aquifer areas	1. The simplified nitrate dilution conceptual model provides a way to evaluate/calibrate the NTB model 2. Make the model applicable at regions where have limited information on the nitrate velocity in the USZs 3. Allows impact of future scenarios - e.g. climate change	Regional and catchment scale	It provides ways to evaluate the modelled results and make it possible to use alternative available datasets to simulate the nitrate transport in the groundwater system. For example, it can use nitrate velocities in the USZs or derive these values using recharge and aquifer properties.
	Represents low permeability superficial deposits	1. Nitrate routed between surface runoff and recharge to ground 2. This makes it possible to consider the nitrate transport time in low permeability drift 3. The nitrate dilution simulation in aquifers became more realistic when involving the modelling cells of aquifers overlain by low permeability drift	Regional and catchment scale	The final improved model has been successfully calibrated. However, Fig. 2.18 shows how the introduction of low permeability drifts impact the modelled results. Table 2.5 shows how parameters changed after considering the nitrate transport in low permeability drifts taking the Chalk of East Anglia as an example.
Unsaturated zone storage	National scale summary	Delineates bulk unsaturated storage of nitrate and temporal changes	All scales	Targeting of catchment management issues

Table 2.5 Parameters comparison in the Chalk of East Anglia when introducing nitrate transport in low permeability drift into the model

Parameter (units)	Before considering the nitrate transport in low permeability drift	After considering the low permeability drift
$\Phi_{aquifer}$ (-)	0.371	0.371
$Sy_{aquifer}$ (-)	0.01	0.01
$Rf_{aquifer}$ (-)	0.022	0.022
$T_{aquifer}$ (m^2 day^{-1})	1280	1470
$D_{aquifer}$ (m)	32	21

3 Thames Case Study

3.1 HYDROGEOLOGICAL SETTING

The Thames catchment provides drinking water to 11 million people from both groundwater and surface water, rivers and reservoirs (Howden et al., 2011). The catchment is underlain by two principal aquifers; the Jurassic limestone of the Upper Thames and the Chalk of the Middle Thames (

Figure 3.1 3.1). Groundwater discharge from these aquifers forms the majority of river flows in the Thames (BFI = 0.66) (NRFA, 2014).

In this case study we address nitrate transport in the Chalk aquifer of the Thames basin. In the Chalk, nitrate transport in the unsaturated zone occurs predominantly through the matrix by a piston flow mechanism. Unsaturated zone velocities in the chalk and limestone are considered to be approximately 1 m yr^{-1} respectively (Wang et al., 2012b and others). These slow velocities, in conjunction with the thick unsaturated zones present in the Chalk, result in long travel times for nitrate in the unsaturated zone. Consequently, nitrate in the saturated chalk and in groundwater discharge to the river reflects nitrate inputs to the soil zone from decades previously.

3.2 SOURCES AND RECEPTORS

Rural areas in the basin have been used intensively for agriculture and this forms the dominant source of nitrate in the catchment. The ultimate receptor in the catchment is the River Thames, with groundwater and public water supplies also being receptors. Nitrate in soils that has not been assimilated by crops reaches the river by one of two pathways. Rapid transport of nitrate in soils to rivers can occur through runoff and shallow interflow. Nitrate can also leach through the soils and unsaturated zone into the underlying aquifers, which subsequently contribute to river flows. The latter pathway exhibits a substantial lag in some cases.

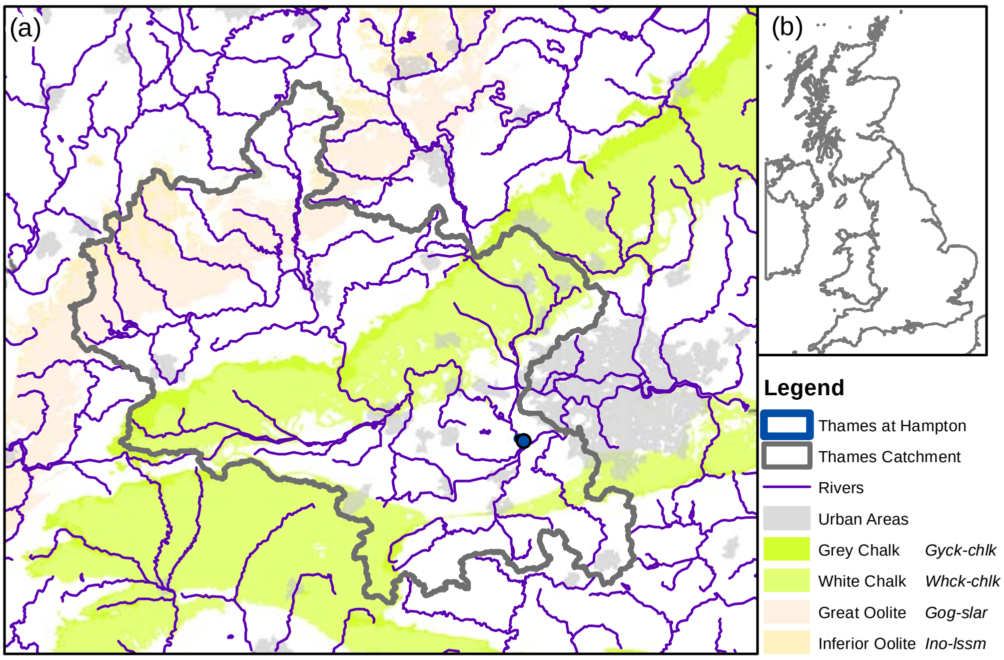


Figure 3.1 Location and geology of the Thames catchment

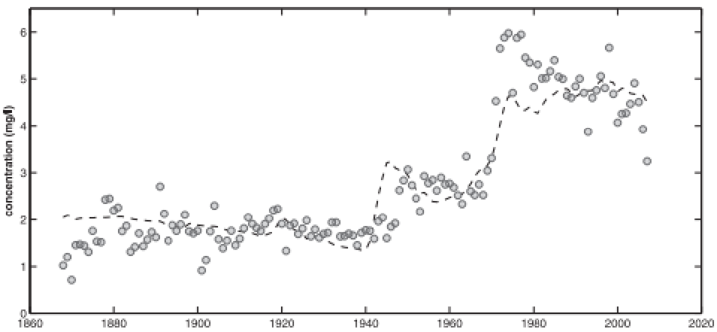


Figure 3.2 Observed and modelled nitrate concentrations in the Thames at Hampton (Howden et al., 2011)

3.3 MONITORING

The Thames catchment has unique datasets for both nitrate inputs and water quality. Nitrate data for the Thames at Hampton is the longest continuous water chemistry dataset in the world, starting in 1868 (Figure 3.2). Land use, management and population data for 1861 to date are also available for the catchment. These long datasets are of considerable benefit to long-term nitrate modelling studies of the catchment.

3.4 MODELLING APPROACH OF HOWDEN ET AL (2010 & 2011)

Howden (2010) considered that land use change is the only basin-wide driver that can account for the observed nitrate concentrations in the Thames over time. Howden et al. (2011) collected data for calendar years from 1868 onward from the following sources:

- Landuse from parish records (1875-1988) and interpolated from national data from 1988 onwards.
- N loading data from the UK literature.
- N loading from sewage from population data from census returns.
- Riverflow mean daily flows at Kingston.

Land use data was combined with literature leaching values and other N loading information to provide an integrated loading. Howden et al. (2010) then used a simple two reservoir transfer function to route the loading through a rapid runoff and a slow groundwater pathway. All processes were lumped together over the whole catchment due to the lack of spatial information to define inputs at a sub-basin scale over such a long period. The split between runoff and groundwater was assumed to be similar to the baseflow index of the Thames as Kingston (BFI = 0.65) but this was adjusted during model calibration to approximately 0.55. A 1-D advection dispersion equation was used to attenuate nitrate loading for both the fast and slow pathways.

Figure 3.2 shows observed and modelled nitrate concentrations. The model appears to replicate the observed increases in concentrations reasonably well. A 30-year lag in the groundwater component of the model was required in the calibration of the model. Consequently it was argued that the step increases in nitrate concentrations in the Thames in the 1950s and 1970s are the result of intensification of agriculture during the 1920s and 1940s (the “Dig for Victory” period). Using a number of input function scenarios, it was shown that changes in basin-wide land use would take decades to be effective. Howden et al. (2011) also argued that an accurate input function is more important than a complex flow model, as demonstrated in the case of the Thames.

3.5 MODELLING APPROACH OF BGS TO THE THAMES BASIN CHALK

3.5.1 Methodology

INITIAL APPROACH

Section 2 of this report details the unsaturated zone nitrate transport methodology used in the BGS model. In order to subsequently route nitrate arriving at the water table to rivers, a simple saturated transport model was used. The saturated model is detailed in section 2.5.4. Using long term average groundwater levels for the UK and river elevations, a direction and hydraulic gradient for each model cell to the river is derived. Permeability, porosity, saturated thickness, national groundwater levels and river networks are used to simulate the nitrate transport to the nearest river node.

The model was used in the Thames Basin by modelling the Chalk at outcrop. The initial model was run for the Thames catchment using the original parameters set out in Wang et al. (2016). Subsequently, a range of different parameters were used to attempt to improve the match between observed and modelled nitrate concentrations as detailed in Table 3.1 chalk aquifer permeability was increased to increase saturated transport rates. Using higher water level data from April 1975 (Lewis et al., 1993) reduces unsaturated zone travel times and increases saturated transport rates.

MODIFICATION OF INPUT FUNCTIONS

Following modification of the model parameterisation, the nitrate input function to the model was modified. The input function used by Howden et al. (2011) was used and linearly scaled to fit the BGS NTB NIF. A further nitrate input function was derived to represent potential loss of nitrate from the catchment. This synthetic NIF was developed during model calibration as an approach to match the observed nitrate concentrations in the River Thames. Figure 3.3 shows the original NIF and the modified NIFs based on Howden et al. (2011). Table 3.1 shows the base model parameterisation and the changes made using different parameterisations and input functions.

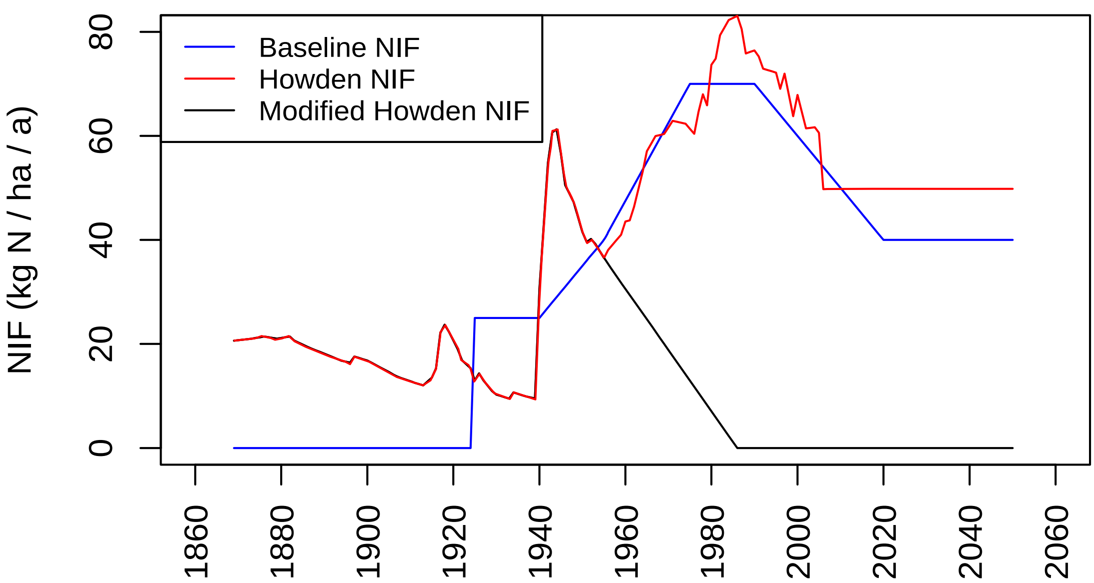


Figure 3.3 Nitrate input functions used in the application of the BGS model to the Thames basin

Table 3.1 BGS nitrate model run log for the Thames Basin

Run Number	Run details
1	Baseline model run (K = 125 m d^{-1})
2	Higher permeability (K = 200 m d^{-1})
3	April 1975 Water Levels
4	Baseline (K = 125) using scaled Howden NIF
5	Baseline (K = 125) using modified Howden NIF

3.5.2 Results and discussion

CALIBRATION

Figure 3.4 shows the model results for the original calibration and modifications to the parameterisation. It can be observed that the original calibration using the baseline NIF does not show any significant rises in concentration between 1940 and 1980, where the observed concentrations show two distinct increases around 1950 and 1970. Increasing the permeability of the aquifer to 200 m d^{-1} and increasing the groundwater levels in the model to those of April 1975 gives a relatively small improvement in the model calibration, shifting the increase in nitrate forward in time by up to 10 years. However, in overall terms the model even with changes in parameterisation struggles to replicate the magnitude and timing of observed increases in nitrate concentrations.

Figure 3.5 shows the original model calibration and results from model runs using the nitrate input function derived byHowden et al. (2011) and the declining NIF. It can be observed that using the Howden NIF, the observed trends in riverine nitrate concentrations are well replicated to approximately 1984. The timing and magnitude of the increases in nitrate in the 1950s and 1970s are well matched by the model (R_2 = 0.79, Nash and Sutcliffe Efficiency (NSE) = 0.53). Following 1984, monitored nitrate concentrations in the Thames stabilise and begin to decline.

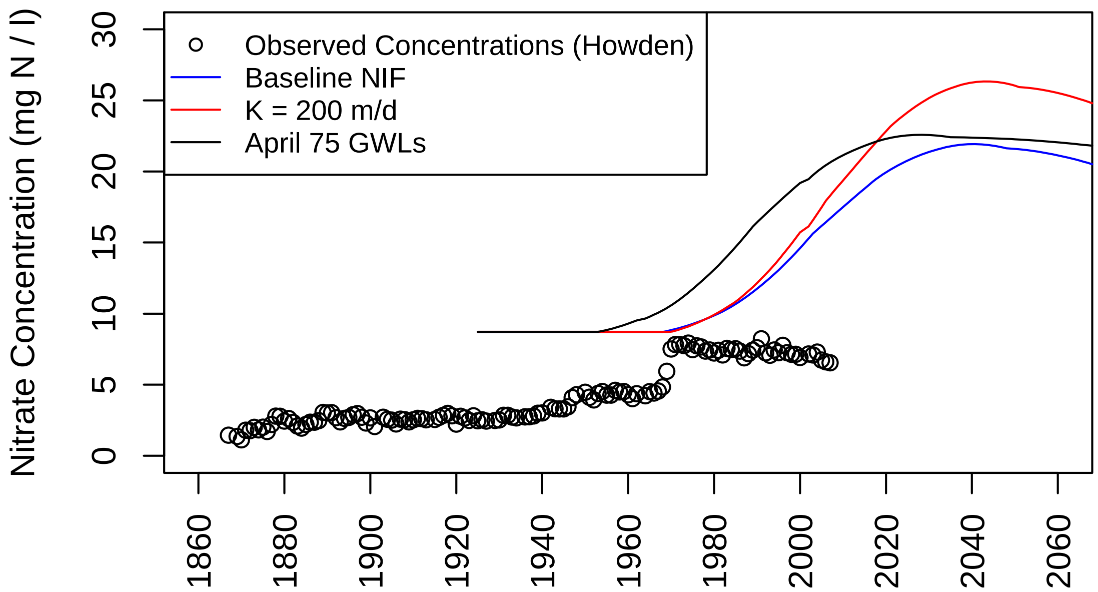


Figure 3.4 Observed and modelled nitrate concentration in the Thames at Hampton using the BGS nitrate model with changes to the model parameterisation

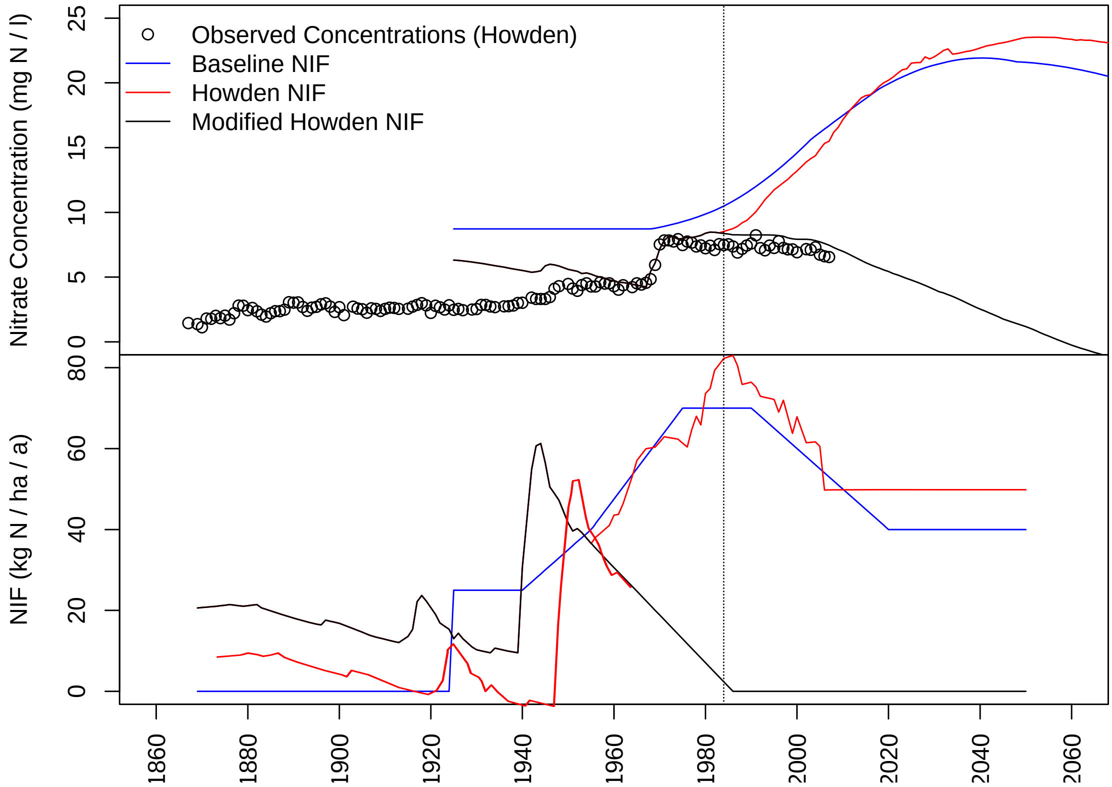


Figure 3.5 Observed and modelled nitrate concentration in the Thames at Hampton using the BGS nitrate model: a) with changes to the NIF; b) the different input functions

However, both the original and Howden NIF show large increases in nitrate loadings between 1970 and 1990. These increases in nitrate loading are reflected in the model output by the large increases in modelled nitrate concentrations from 2000 to 2040. Such increases are at odds with the measured declining trend on nitrate in the river. A declining NIF (black, Figure 3.5) was derived to estimate the extent of nitrate loss and attenuation likely to be required within the catchment to meet the actual nitrate concentration trends. The resultant model nitrate concentrations match the observed concentrations for 1980 to 2000 reasonably well although this is not reflected statistically as there is a very limited trend in the data ($R_2 = 0.42$, NSE = -6.2). It should be noted that the declining NIF is likely to be highly unrealistic and it is likely that other catchment processes are occurring to attenuate nitrate loading in groundwater which are discussed in section 3.7.

Model Discrepancies

As discussed above, both the original BGS and the Howden NIF result in large increases in model riverine nitrate concentration which are at odds with observed concentration trends. Figure 3.6 shows modelled outputs and observed concentration data for sites on the Lower Thames up and downstream of Hampton at Walton and Teddington respectively. It can be observed that the nitrate concentration data at these sites match the data for Hampton reasonably well and do not show increases in nitrate concentration as predicted by the nitrate modelling. Significant reductions in model nitrate loadings are required to match the observed trends. This suggests that a number of loss and attenuation processes are likely to be occurring within the catchment.

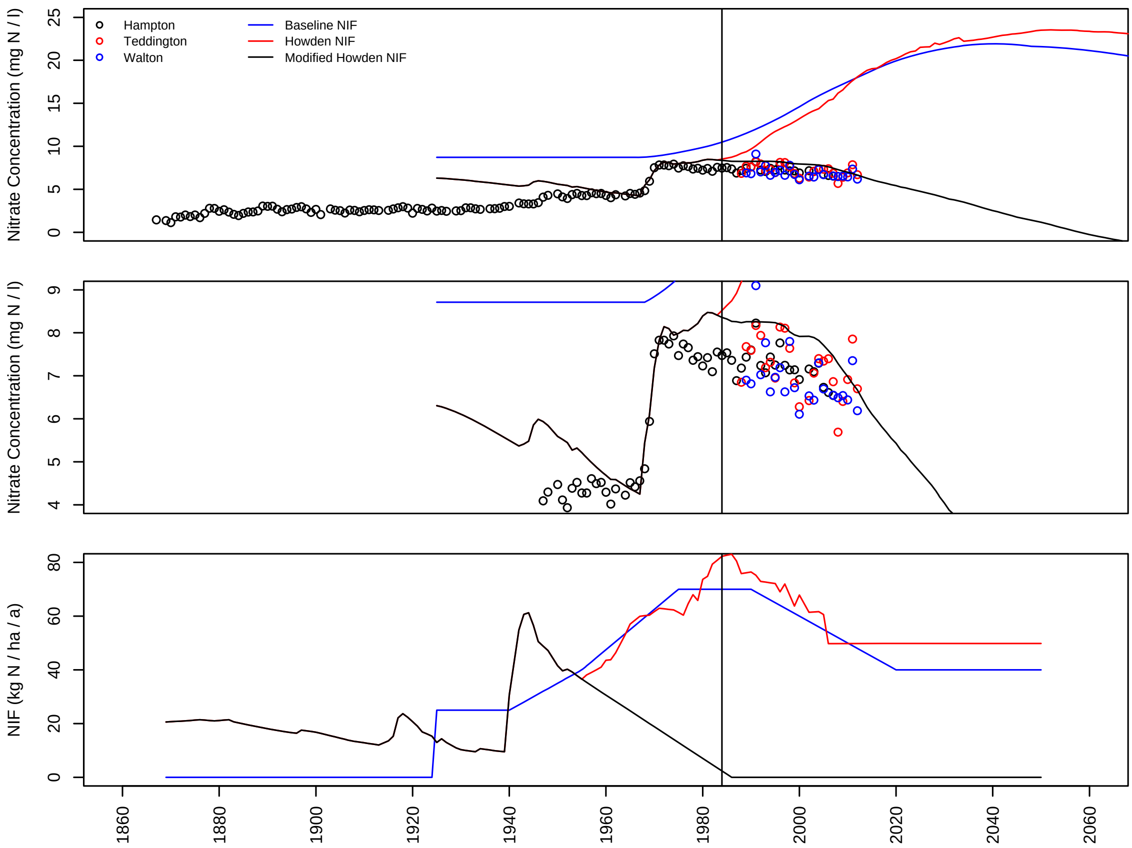


Figure 3.6 Observed and modelled nitrate concentration in the Thames at Hampton, Teddington and Walton: a) and b) using the BGS nitrate model; c) the different input functions

3.6 SUMMARY AND CONCEPTUAL MODEL

The work described here demonstrates clearly that the BGS model is able to replicate the results obtained by Howden if the same NIF is used. The overall travel time in the catchment is similar and shows the peaks of war activity carried through into riverine concentrations. Both models suggest that the up to the mid-1980s the observed concentrations in the Thames can be explained by assuming that it depends wholly on the input function and a delay, either empirical or taking account of modelled unsaturated travel time. This delay is in the order of 30 years. For periods after this neither model is able to replicate the observed concentrations and other factors must need to be taken into account. A number of possible processes which could affect nitrate concentrations are reviewed in the next section.

3.7 IMPLICATIONS AND NEXT STEPS

3.7.1 Potential additional processes

The nature of the discrepancy between modelled and observed concentrations (occurring at late time in the time series, and at the highest observed nitrate concentrations) means that the processes occurring in the catchment controlling this discrepancy must be dependent on time and/or nitrate concentration.

DENITRIFICATION

Denitrification in unconfined oxic chalk groundwaters is unlikely to be a significant process (Rivett et al., 2007). However, there is evidence for denitrification in soils and riparian and hyporheic zones, but this is likely to be spatially variable (Boyer et al., 2006). There is also evidence that denitrification exhibits first-order kinetics, i.e. denitrification increases as nitrate concentration increases. However, it is denitrification is generally modelled as a Michaelis-Menten reaction (Boyer et al., 2006):

$$DNF = \frac{DNF_{max}[NO_3^-]}{K + [NO_3^-]}$$

Where DNF is the denitrification rate, DNF_{max} is the maximum denitrification rate, $[NO_3^-]$ is the nitrate concentration and K is the Michaelis constant that is the nitrate concentration (with the same units as $[NO_3^-]$) when DNF = DNF_{max} / 2. The relationship between denitrification rate and concentration is illustrated in Figure 3.7. The reaction kinetics results in smaller increases in denitrification rate at higher concentrations. Consequently this would be of limited benefit in reducing the discrepancy between modelled and observed riverine nitrate concentrations. Any further modelling including interflow and surface flow to the Thames would encounter similar problems representing denitrification.

CHANGES IN RIVER MANAGEMENT

It is plausible that changes in river management such as sewage treatment works discharges may be affecting river concentrations. This requires further consideration.

CHANGES IN RIVER FLOWS

Changes in river flows could potentially affect riverine nitrate concentrations. Under droughts nitrate concentrations in the Thames may be higher due to more baseflow contribution and less dilution by surface water. In floods more surface water flow and more anoxic conditions may dilute nitrate loadings. Figure 3.8 shows nitrate concentrations, input functions and annual average river flows for the Thames at Kingston. It can be observed that in general river flows in the Thames do not appear to be significantly higher or lower than average after 1984. Consequently, it seems unlikely that changes in river flows are exerting a significant control on riverine nitrate concentrations.

3.7.2 Next steps

Since NTB itself does not produce nitrate concentration in rivers, it would be useful to couple it with river models to produce more reliable results for analysis. NEAP-N or other spatially and temporally distributed nitrate leaching data could also be used to simulate the nitrate concentration trend.

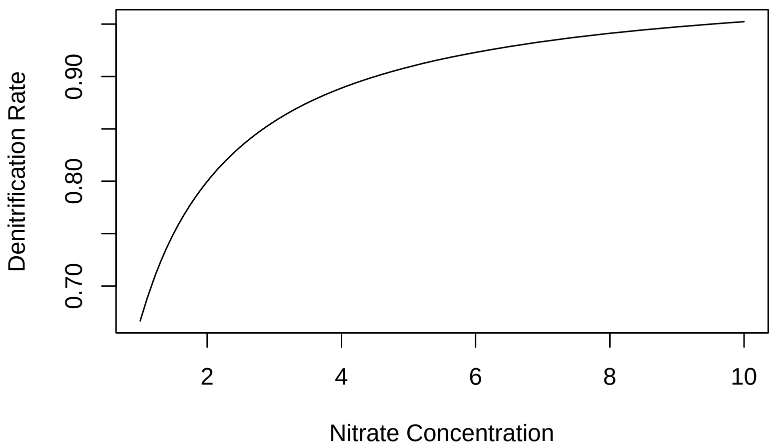


Figure 3.7 Michaelis-Menten reaction kinetics of denitrification

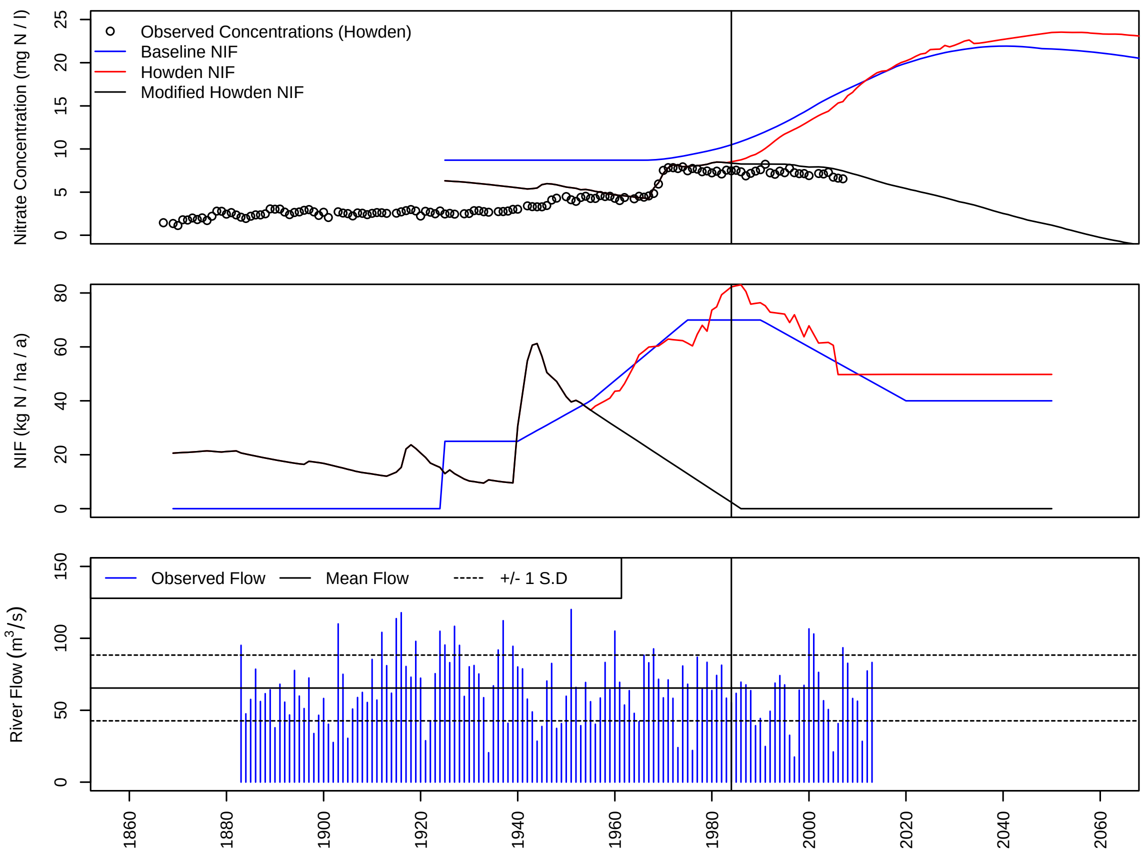


Figure 3.8 The Thames at Kingston: a) observed and modelled nitrate concentrations; b) nitrate input functions; c) river flows

Few case studies are able to test capacity of the nitrate modelling approaches to predict very long term trends as typically water quality records are not long enough. In this regard the application of the BGS model to the Thames Basin and the work by Howden is critical. The BGS model linked to a simple saturated zone model can replicate observed nitrate trends if an appropriate input function is used. This highlights the importance of the nitrate input function to the modelling approach. Both the BGS model and work by Howden use very simple transport models but can replicate observed downstream nitrate trends. This gives some confidence in the NTB model if driven by appropriate data. The discrepancy between modelled and observed nitrate concentrations at late times is not fully resolved and large increases in concentrations are predicted. Reviewing model predictions with the latest nitrate data for the Thames (2007 to 2014) may be of benefit, as would evaluating improvements in the efficiency of sewage treatment.

Given the predicted increases in nitrate concentrations there is a clear need to consider lags in the unsaturated zone in the NVZ process.

4 South Downs Case Study

4.1 HYDROGEOLOGICAL SETTING

The South Downs Collaborative Nitrate Modelling Project was commissioned by the South Downs National Park Authority. Its purpose was to build a compelling evidence base in support of existing or new initiatives to deliver groundwater quality improvements through sustainable land management in the South Downs Way Ahead Nature Improvement Area (NIA). The work also helps the Environment Agency to meet WFD requirements to improve groundwater quality and tackle rising trends in nitrate. The work was carried out by AMEC (now Amec Foster Wheeler) and funded through the South Downs Way Ahead Nature Improvement Area (NIA), the Environment Agency and the Downs and Harbours Clean Water Partnership. Additional technical support and advice has been provided by Southern Water Services Ltd and Portsmouth Water Ltd.

The Eastergate and Westergate public water supply sources operated by Portsmouth Water lie to the north of the village of Eastergate, about 750 m apart (Figure 4.1). The abstractions lie inside the Arun and Western Streams CAMS area and are located in the Chichester Chalk. As part of the South Downs Nitrate Modelling Collaborative Project their catchments have been delineated using the Flowsource tool (© Groundwater Science) and the East Hants and Chichester Chalk (EHCC) regional groundwater model (AMEC, 2014a, b) using actual abstraction rates. The catchments both extend to the north and slightly west from the sources, onto the South Downs. The catchment to Eastergate covers an area of 45.3 km^2 with substantial overlap to Westergate and their combined footprint is similar in extent to that of the combined existing SPZ 3. These boundaries are now being updated for Portsmouth Water, based on more realistic longer-term abstraction data. As AMEC used average rate for 2012/2013 only, the final maps produced for Portsmouth Water will be slightly different.

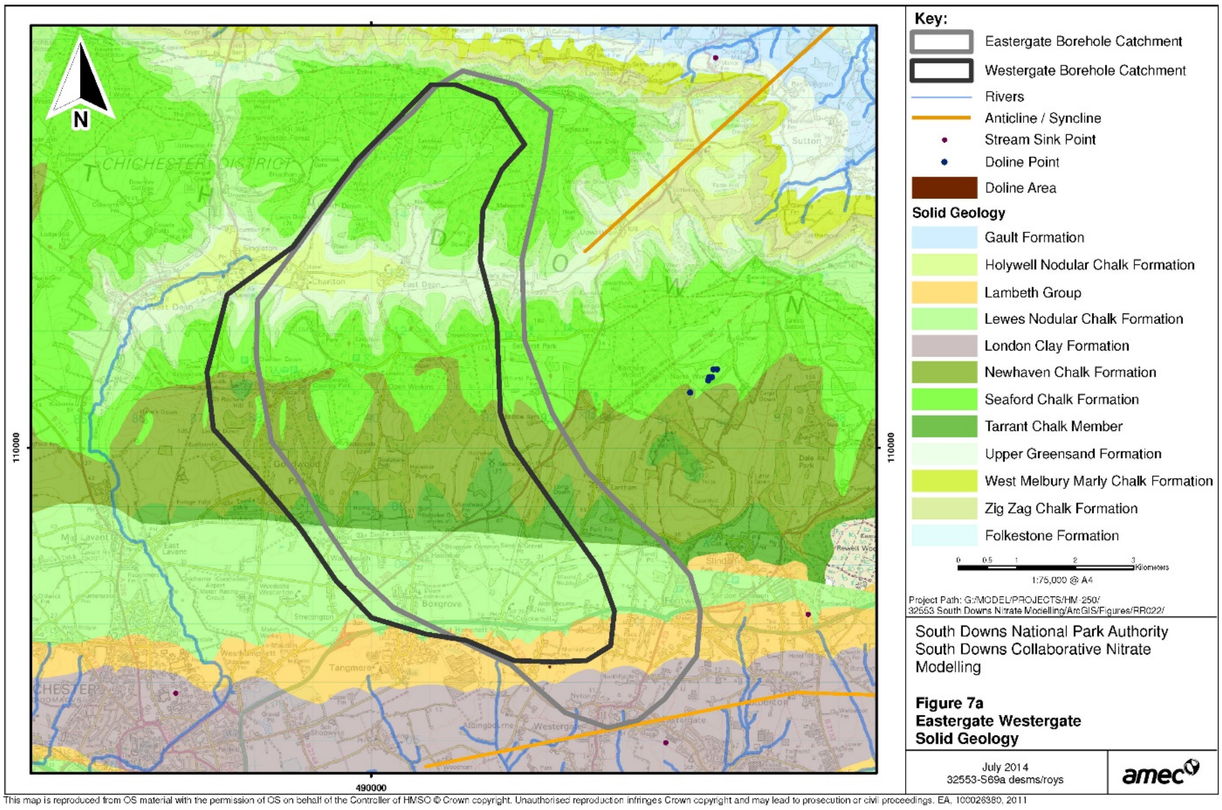


Figure 4.1 Borehole catchments of Westergate and Eastergate PWS on solid geology (from AMEC, 2014a). Reproduced by permission of the South Downs National Park Authority.

The underlying aquifer comprises the Newhaven and Seaford Chalk, with a small area of Lewes Nodular Chalk close to the sources (Figure 4.1). The sources themselves penetrate the Lambeth Group whilst to the south of the boreholes the catchments extend onto the London Clay. The confinement of the Chalk by the Lambeth Group may provide protection to the underlying aquifer, however this formation is notoriously highly variable over short distances and should not be considered a true aquitard. The Lambeth group and Chalk interface is prone to solution feature formation. The majority of the catchment is on unconfined Chalk. The depth to the water table is estimated to lie in the range 20 – 30 m in the southern part of the catchment, increasing to over 100 m in the northern part.

4.2 SOURCES AND RECEPTORS

The Eastergate catchment contains significant areas of woodland (44% of the area), particularly in the central and northern parts of the catchment (Figure 4.2). A further 24% of the catchment is under arable land, and 22% under improved grassland or rough grazing. 3% of the catchment is urban. There are small areas of field vegetables in the catchment (0.4 – 0.5%).

As well as agriculture there are non-agricultural diffuse sources and point sources of nitrate in the catchment, which include:

- Sewer leakage from mains sewers serving the villages of Eastergate and Westergate and the adjacent area, close to the sources.
- Consented discharges to ground in the catchments. The majority are located towards the south of the catchments, near the sources, and are private sewage discharges.
- Landfill sites. There are four authorised and three historical landfill sites in the Eastergate catchmen.t
- Manure heaps and slurry stores associated with livestock enterprises.

The receptor in this case study is the Eastergate public water supply.

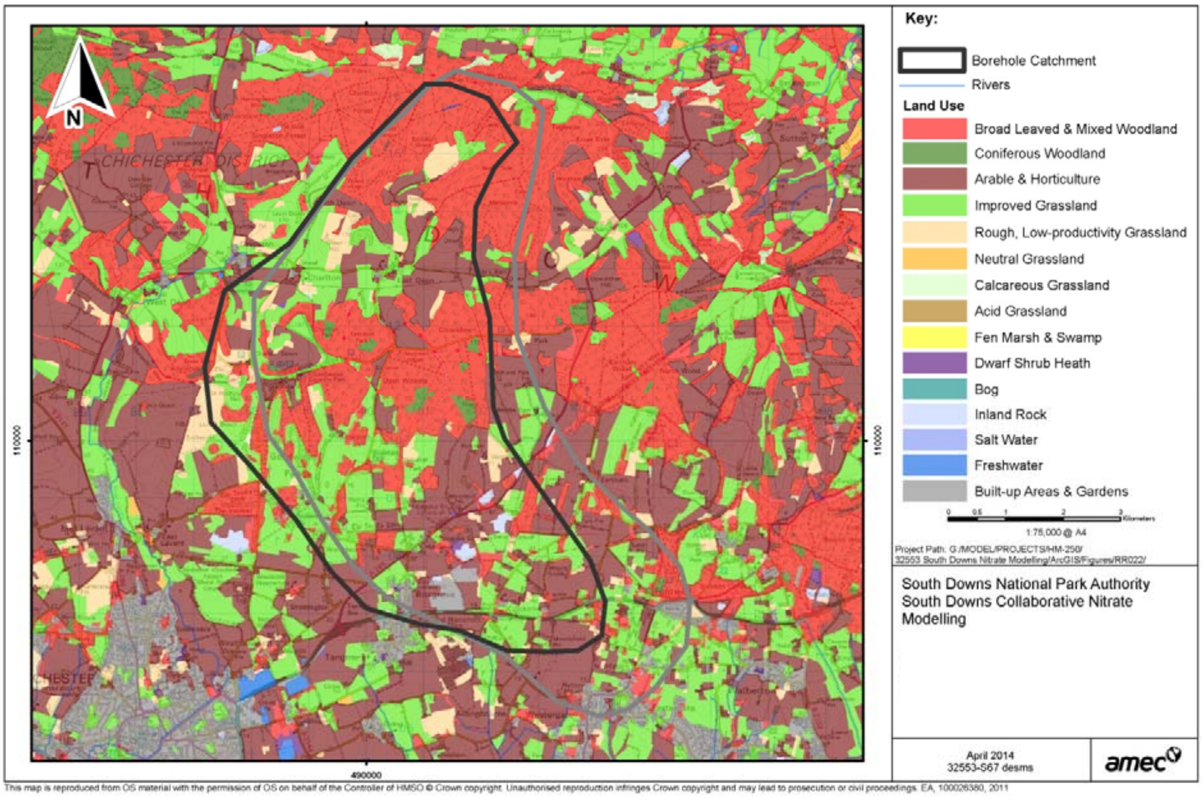


Figure 4.2 Landcover map for the Westergate and Eastergate catchments based on CEH (2011). c

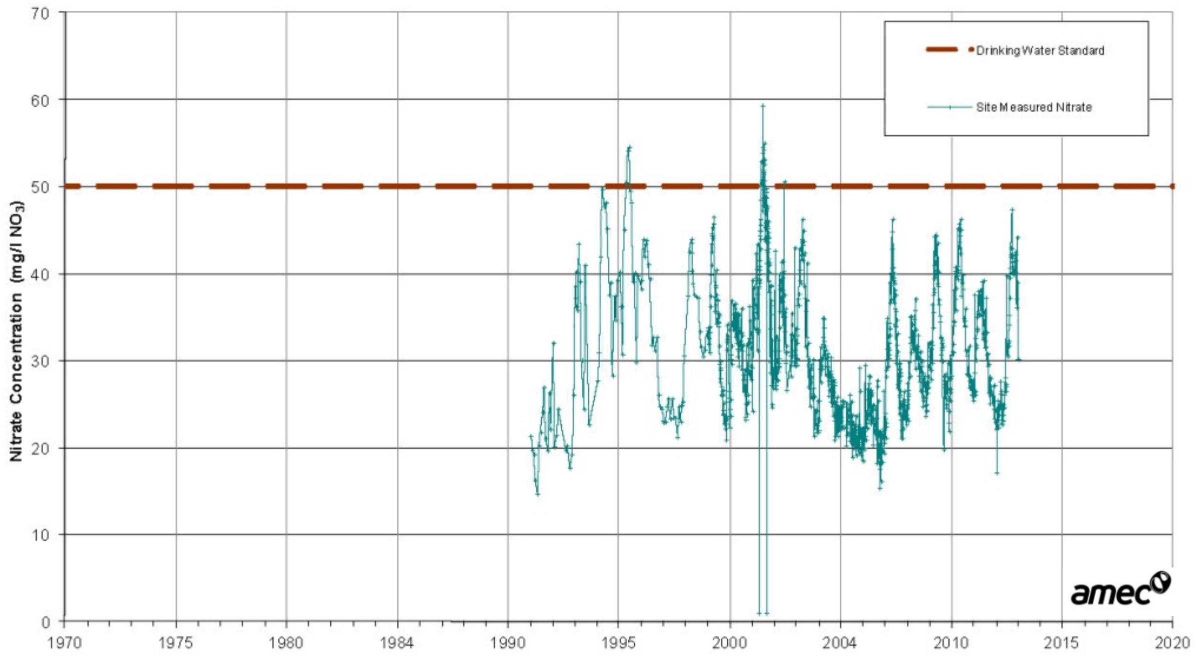


Figure 4.3 Pumped water quality at Eastergate PWS. Reproduced by permission of Portsmouth Water

4.3 MONITORING

Nitrate concentrations at Eastergate are high, and have exceeded the Drinking Water Standard (DWS) of 50 mg NO_3 l^{-1} in 1994, 1995, 2001 and 2002. Concentrations also show marked seasonal variation, with peaks occurring in the winter and spring. Eastergate also had DWS failures in 2013, 2014 and 2015, all between May and September, due to nitrate. Concentrations also show an overall slightly rising trend over the period of measurement but with periods of stronger upward trend, e.g. 1992 – 1996 and 2005 – 2013) and also periods showing a downward trend, e.g. between 2000 and 2005 (Figure 4.3). The more recent data indicate an upward trend.

4.4 INITIAL CONCEPTUAL THINKING

The AMEC nitrate trend model was constructed based on the following assumptions:

- Nitrate is leached from the soil zone based on landuse and soil type. Crop rotations are implicitly represented by historical arable and improved grassland nitrate leaching trends which were constructed from empirical information – historical fertiliser usage, livestock density and porewater profiles and adjusted using observed nitrate concentrations in a number of other catchments.
- Water (and nitrate) moves by piston flow through the unsaturated zone at a rate controlled by recharge and effective chalk porosity. By pass flow was not considered, although it may well be important in this karst chalk setting close to the edge of the Palaeogene.
- Water moves through the saturated zone to the abstraction point as defined by the catchment flow modelling.
- Abstraction rates and regime at the source have stayed the same over the modelled period
- Any attenuation of nitrate is not significant enough to be modelled. The presence of Superficial and Palaeogene cover will provide some attenuation but the volume is assumed to be negligible compared to the water from the unconfined aquifer.

4.5 MODELLING RESULTS

Topography for use in depth to water calculations was taken from the OS panoramic topography layer (1:50:000). Dominant soil type was based on the National Soil Map of England and Wales - NATMAP. Historic groundwater levels for a number of observation boreholes were supplied by the Environment Agency.

Arable and improved grassland leaching were estimated over the period 1900 to 2012 using CEH Land Cover Map 2007 and arable changes, with other landuses – semi-natural vegetation, woodland and urban areas assumed to remain constant.

Infiltration to the Chalk was based on the long term average values from the 4R recharge model (AMEC, 2014b). In the nitrate trend model unsaturated zone and saturated zone travel time to the abstraction are calculated based on unsaturated zone thickness and porosity and this was used to back calculate the starting nitrate concentration for the year the water left the soil zone for each grid square based on the soil zone and landuse. Unsaturated zone moisture content for the Chalk as a proxy for effective porosity was initially assumed to be 30%.

Long term trends were calculated for the period 1945 to 2012 based on soil leaching trends and the unsaturated zone delay. Observed nitrate data at the abstraction point were used to calibrate the model. Seasonal fluctuations in nitrate concentrations have been simulated using water level data from a nearby observation borehole. Short term “spikes” in nitrate concentration are not simulated by the trend models.

The trend model generally provides a good fit to observed nitrate concentrations at Eastergate (Figure 4.4), including the rising trend in the 1990s and, to some extent, simulation of the temporary drop in nitrate concentrations between 2003 and 2006. The model does not simulate the spikes that exceeded the Drinking Water Standard (DWS) in 1996 to 2003.

Under the baseline scenario (assuming current leaching rates continue), the model predicts that the underlying trend will result in nitrate concentrations continuing to slowly rise before levelling off by about 2030. Seasonal variations in concentrations linked to fluctuations in water level may continue to cause occasional failures of the DWS at the sources, however, and spikes caused by rapid recharge events (not simulated by the model) are likely to cause additional failures.

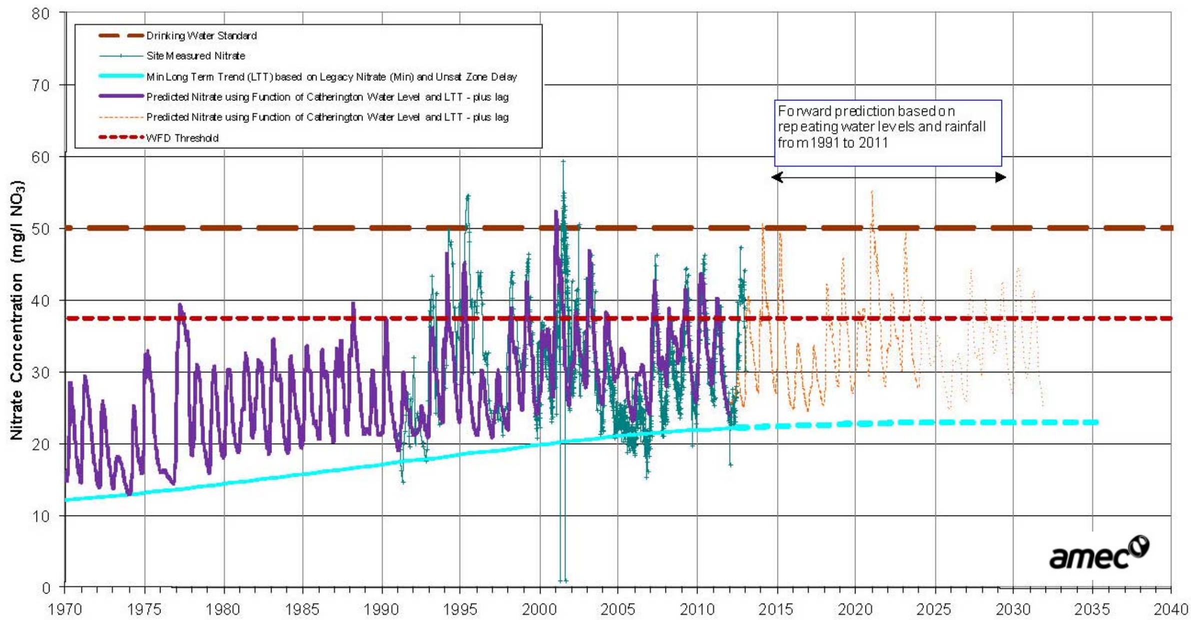


Figure 4.4 Forward prediction of nitrate at Eastergate PWS assuming baseline leaching scenario and including point source contributions. Reproduced by permission of Portsmouth Water.

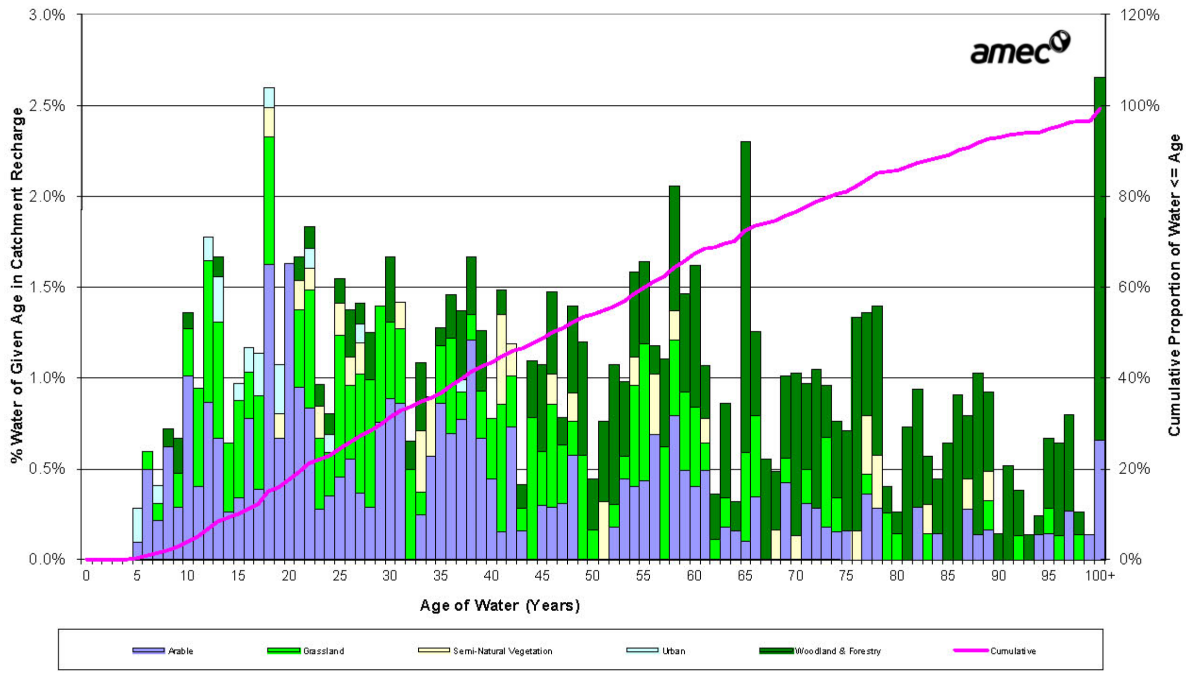


Figure 4.5 Age of water at Eastergate based on unsaturated zone time of travel at low water level (from AMEC, 2014a). Reproduced by permission of the South Downs National Park Authority.

There is a large spread in ages of water at Eastergate, from 5 years to over 100 years' time of travel (Figure 4.5). Much of the younger water (less than 30 years) derives from arable land. Under the baseline leaching scenario the model predicts that nitrate concentrations will occasionally exceed the DWS until about 2024.

4.6 SUMMARY AND CONCEPTUAL MODEL

The main conclusions of the modelling work were as follows:

- The majority of nitrate reaching the water table originates from arable land and agricultural (improved) grassland.
- It is predicted that the impacts of catchment management could take some years to significantly reduce nitrate concentrations in pumped water.
- However, management of nitrate inputs in the area close to the boreholes could help to reduce the frequency and severity of spikes in the shorter term, and this could reduce the need for treatment or blending. There may still be spikes from further away reaching the borehole by karst flow.

It is predicted that spikes in nitrate concentration in excess of the Drinking Water Standard will continue to occur until about 2024. This is currently being addressed by the water company through blending with lower nitrate sources to ensure that drinking water meets the required standard at customers' taps. The annual average nitrate concentration is currently at or below the WFD threshold of 37.5 mg NO_3 l^{-1} and is not predicted to increase. However, the thick unsaturated zone in much of the catchment suggests that the impact of the peak in fertiliser use in the 1980s will not arrive at the source until approximately the 2030s, and the large distribution of ages of water will result in a slow decline in nitrate concentrations after this time.

4.7 IMPLICATIONS

4.7.1 Use of BGS approach

The AMEC approach to the modelling of the unsaturated zone is very similar to that in the BGS NTB model. The inclusion of this component allows the nitrate trend to be effectively modelled and for the model to be used to make realistic predictions of the impact of future improvements in nitrate management.

The inclusion of the unsaturated zone travel time allows the association of woodland in the upper part of the catchment with long travel time water as shown in Figure 4.5. This provides a ready view of the location of the arable/improved grassland areas of the catchment where travel times are shorter and which will respond more rapidly to changes in nitrate management.

The estimation of nitrate leaching used here provides an alternative to the ADAS NEAP-N model.

4.7.2 NVZ designation

The modelling work could potentially be used to inform a future NVZ designation process. The upper part of the modelled catchment is not currently an NVZ (Figure 4.6). Although the majority of the upper catchment is woodland there is also some arable land and due to the unsaturated zone thickness and the consequent age of the water, the peak from this part of the catchment may not yet have arrived. The legacy from the northern part of the catchment and the effect of current activities in the future should be considered in the designation process, although due to the woodland component and the size and geology of the catchment it may be small in this particular example.

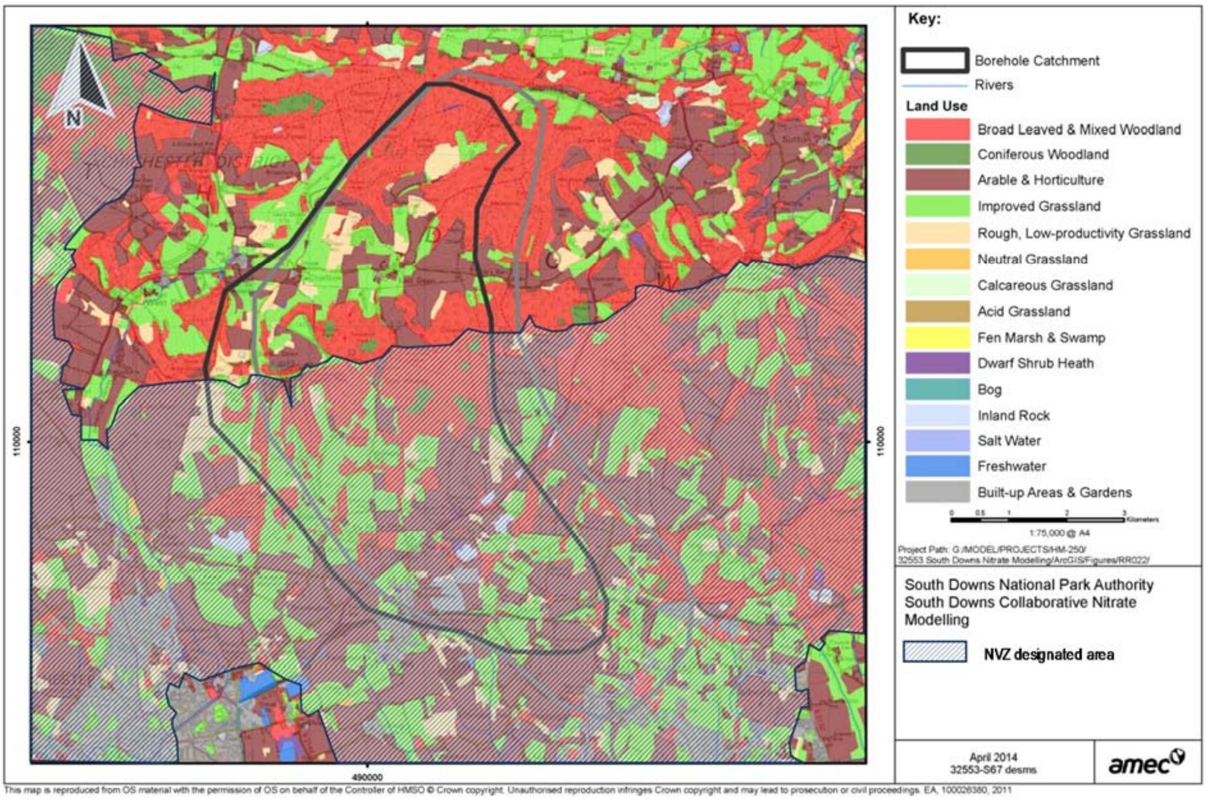


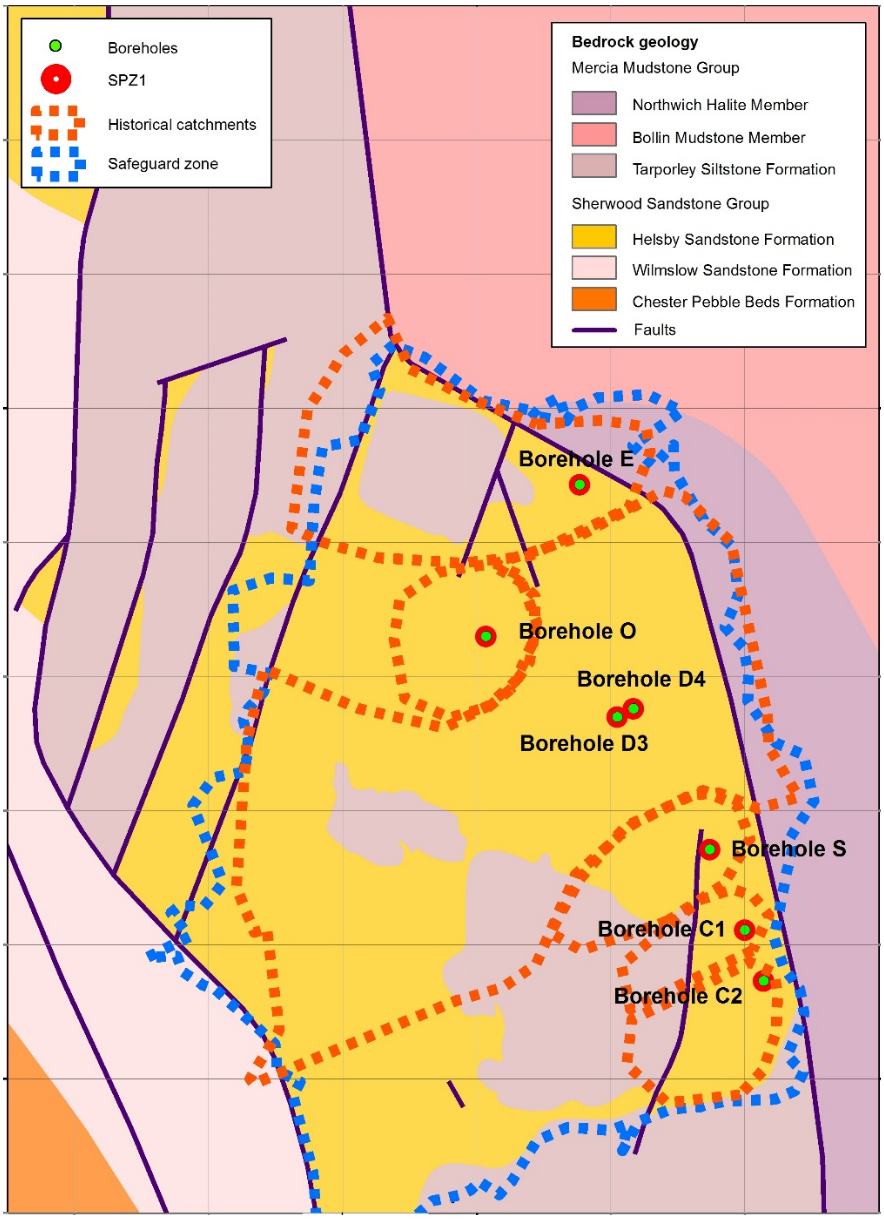
Figure 4.6 Relationship of catchments and most recent NVZ designated areas. Reproduced by permission of the Environment Agency.

5 Permo-Triassic Sandstone Case Study

5.1 HYDROGEOLOGICAL SETTING

This catchment is located in the northern part of the Cheshire Basin (Figure 5.1). This basin was formed in late Permian times with the main period of extension during the Triassic. Subsequent removal of Jurassic and Cretaceous strata have allowed the establishment of freshwater aquifers within the Triassic strata, in the Helsby and Wilmslow Sandstone Formations of the Sherwood Sandstone Group. Parts of the area are confined by the low permeability Tarporley Siltstone Formation of the Mercia Mudstone Group, but the Sherwood Sandstone outcrops at the surface in the remainder of the catchment. Superficial deposits, predominantly fluvio-glacial sands and gravels, can form a localised secondary aquifer.

Groundwater flow in the Sherwood Sandstone is towards the north and northwest. Annual groundwater fluctuations are commonly < 4 m. The water table is estimated to be approximately 40 mAOD. Perched water tables may be present in fine-grained strata. A fault system exhibits a significant control on the boundary conditions of the catchment.



Geological linework
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Figure 5.1 Locations of the study boreholes and bedrock geology of the catchment

5.2 SOURCES AND RECEPTORS

In this case study we focus on Boreholes D3 and D4. These boreholes have long and relatively complete datasets of nitrate concentration which show significant increases over the past 25 years. There are a number of other sources in the group which have been excluded from this case study. Borehole E and Borehole O show similar increasing trends to the D sources and are not reported here to avoid repetition. The Borehole C and Borehole s sources currently show decreasing trends in nitrate concentrations which are challenging to model.

The primary source of nitrate in the Borehole D 3/4 catchment is agriculture. For the historical D catchment, the 2000 CORINE dataset indicates that 60% of the catchment is made up of arable and pasture land. The historical catchment is within a Nitrate Vulnerable Zone.

5.3 MONITORING

Nitrate concentrations at Boreholes D3 and D4 have been recorded since the 1950s. Observed nitrate concentrations are presented in Figure 5.2. The Environment Agency have provided BGS with data from 1990 onwards. Whilst this captures the most rapid rises in concentrations, historic rises in concentrations in the 1950s to 1990s are not present.

5.4 INITIAL CONCEPTUAL THINKING

The Sherwood Sandstone is at outcrop in the historic catchment and forms the principal aquifer in the area. Faults to the east and the north of the area are considered as boundaries to groundwater flow. Boreholes D3 and D4 are screened to different depths and consequently receive different proportions of shallow and deep groundwater. There is also evidence that varying abstraction in the shallow borehole affects concentrations in the deep borehole. The thickness of the unsaturated zone is estimated to be 40 to 50 metres close to these boreholes.

5.5 EXISTING MODELLING

Trend modelling of nitrate concentrations at Boreholes D3 and D4 has been carried out for the Environment Agency assuming:

- A soil model derives annual nitrate concentration at the base of the soil zone. National annual fertiliser use data from DEFRA are scaled to NEAP-N data for the historic borehole catchments and diluted by a specified infiltration rate.
- The outputs from the soil model are then lagged based on a travel time delay and diluted by unpolluted groundwater to derive concentrations at the borehole.

Figure 5.2 shows the outputs of this modelling work and illustrates that the overall general trend of increases in nitrate concentrations are reasonably well replicated.

5.6 MODELLING USING THE BGS APPROACH

5.6.1 Methodology

Nitrate concentrations at the case study boreholes have been modelling using outputs from the BGS nitrate time bomb model linked to a simple saturated zone borehole dilution model. This approach has been demonstrated by Wang et al. (2013) for the Permo-Triassic sandstones of the Eden Valley, Cumbria and has been detailed previously in the briefing report (Stuart et al., 2016).

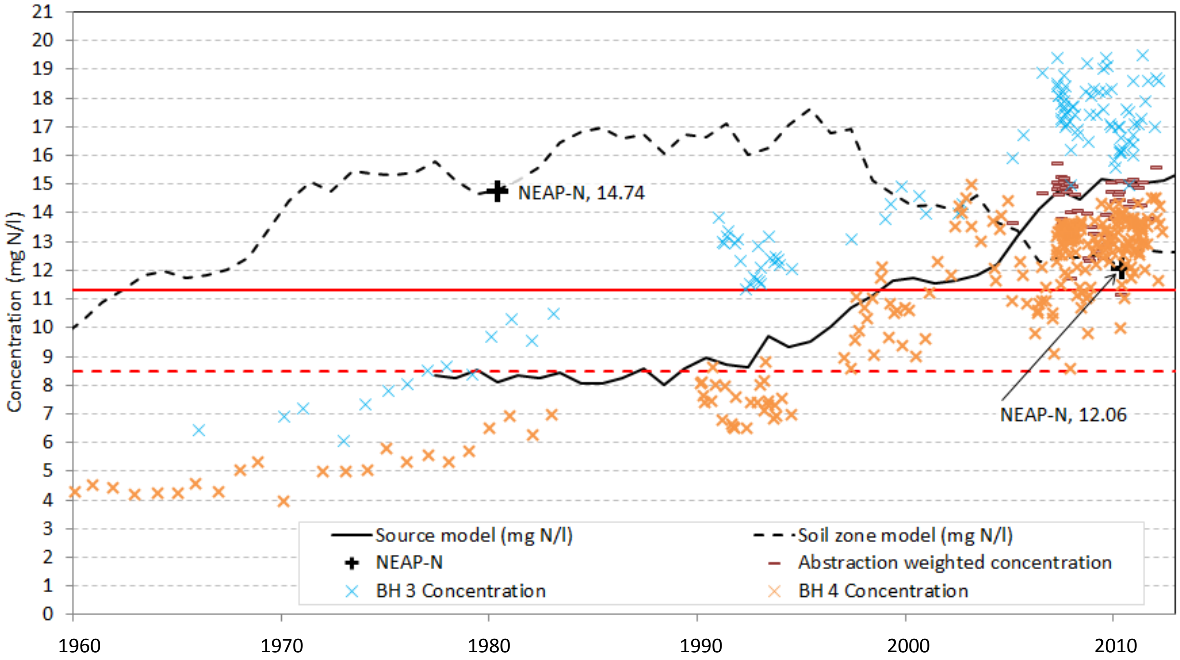

Figure 5.2 Observed and existing modelled nitrate concentrations at Boreholes D3 and D4. Reproduced by permission of the Environment Agency

Nitrate loadings at the base of the soil zone are derived from an interpolated nitrate input function based on the original BGS nitrate input function and NEAP-N data for the historic borehole catchment. Nitrate concentrations at the water table are derived from estimates of historic long term average recharge and unsaturated zone travel time from the original nitrate timebomb model. Water table concentrations are then lagged to account for saturated zone travel time and reduced by a factor to account for dilution by deep nitrate-low groundwater.

5.6.2 Results

Figure 5.3 shows the result of the BGS modelling for the case study sources. In general, the model replicates the observed nitrate concentrations well in terms of trends and absolute levels for both boreholes (Borehole 3 – R_2 = 0.62, Nash and Sutcliffe Efficiency = 0.35, Borehole 4 – R2 = 0.84, Nash and Sutcliffe Efficiency = 0.76). Increases in nitrate concentrations are well replicated by the model. The decline after 2020 is driven by the shape of the NIF used.

The nitrate timebomb model predicts an unsaturated zone travel time of approximately 30 years. Allowing for some additional lag in the saturated zone, this generally agrees with total travel time estimates derived by the existing modelling of 36 years. Using the scaled NEAP-N nitrate input function with long term average recharge results in no dilution required for borehole 3 and limited dilution (30%) required for borehole 4. This generally agrees with work undertaken by the utility which suggests that dilution by unpolluted groundwater is limited for these sources.

5.6.3 Implications

This modelling work benchmarks the BGS approach with other similar approaches. The key difference in the approaches used to estimate the unsaturated zone travel time. Whereas the existing modelling estimates the travel time during calibration, we use previously existing estimates of travel time based on the national scale nitrate timebomb model. The fact that the travel times predicted from the national scale model agree with those estimated in model calibration suggests that using the BGS nitrate timebomb model with local scale NEAP-N data would be a useful first step in assessing the significance of unsaturated zone N storage in NVZ designations.

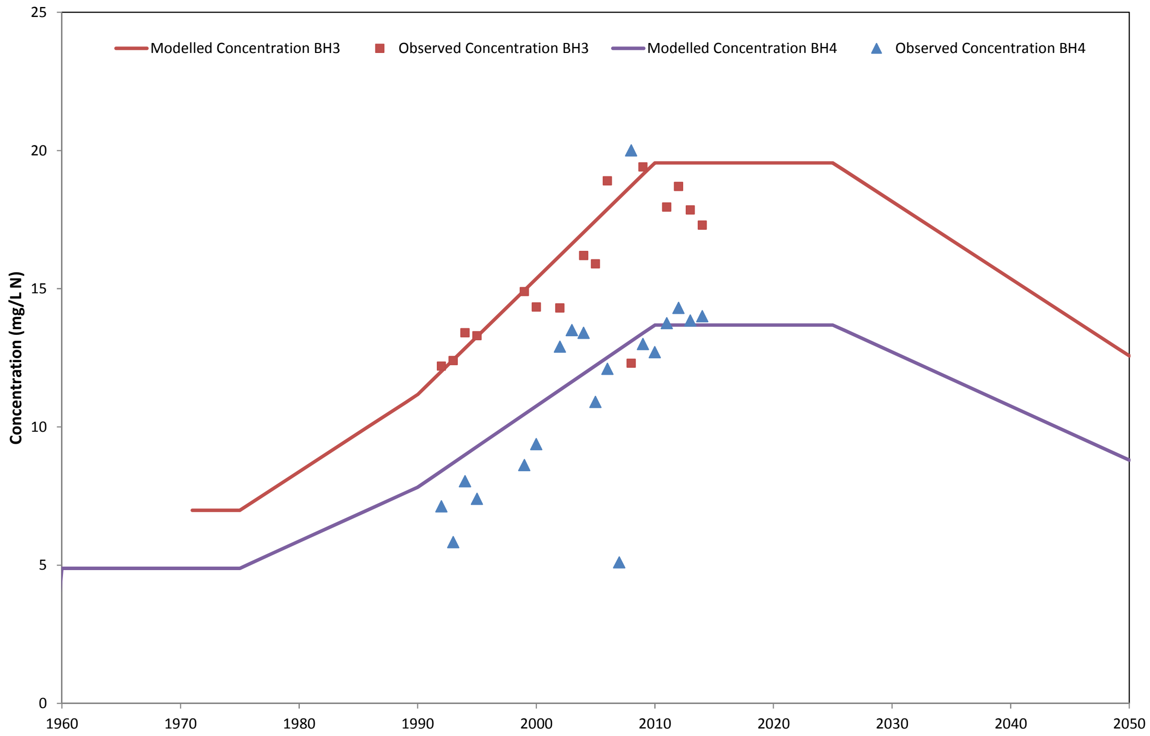

Figure 5.3 Observed and modelled (BGS) nitrate concentrations at Boreholes D3 and D4

5.7 SUMMARY & CONCEPTUAL MODEL

These group of sources abstract water from unconfined Permo-Triassic Sandstones of Northwest England. The Boreholes D3 and D4 show rising nitrate trends which are attributed to agriculture. The observed nitrate trends have been simulated for the Environment Agency using a trend model which links nitrate at the base of the soil zone derived from NEAP-N and national DEFRA fertilizer use statistics with a simple lag and dilution model. BGS linked outputs from the national scale nitrate timebomb which estimates the unsaturated zone travel time a priori with a simple saturated zone model. Both approaches show reasonable agreement with the observed nitrate concentration data at the D boreholes.

5.8 IMPLICATIONS AND NEXT STEPS

The primary implication of this case study is the benchmarking of the BGS modelling approach with other approaches used to model groundwater nitrate concentrations. The BGS modelling approach has been demonstrated to produce similar outputs to simple lag and dilution models. However, the key difference between the BGS model and other approaches is a priori knowledge of the unsaturated zone travel time.

Given the ability of the BGS NTB approach to model the observed trends at this case study, it is suggested that outputs from the NTB model could be used in other locations where public water supply boreholes show long term rises in nitrate concentrations.

6 Contextual review

6.1 BENEFITS AND LIMITATIONS OF THE REVISED BGS MODEL

6.1.1 Benefits

The present study has allowed the development of improvements to a number of aspects of the first version of the BGS Nitrate Time Bomb (NTB) model.

NITRATE INPUT FUNCTION

The model combines the BGS Nitrate Input Function (NIF) and the ADAS NEAP-N model data into an effective NIF. This composite NIF is spatially as well as temporally distributed and allows the model to be run over a wide timescale. It has the unique potential to be projected forwards using agreed nitrate inputs from future programmes of measures to control nitrate. This could provide a powerful predictive tool for policy development.

TREATMENT OF THE UNSATURATED ZONE

The use of water levels derived from OS river data gives a better unsaturated zone (USZ) thickness, representing the thickness which remains unflushed during annual cycles in the water table.

The use of the larger-scale geological mapping (250k) rather than the original 625k allows layered aquifers such as the Coal Measures and Jurassic Limestones to be more adequately represented in the model.

The application of a national recharge model has also several advantages. A process-based model of the unsaturated zone recharge has been developed and applied to two areas of the NTB model to demonstrate the improvements it delivers.

For principal and secondary aquifers which have good data available in the aquifer properties manuals (Allen et al., 1997; Jones et al., 2000), spatially varying USZ velocity can be better estimated rather than using a fixed value. This is of particular significance for formations where there are no measured USZ velocities. This would also allow the impact of changes in recharge under a range of climate change scenarios to be assessed.

The improvement also allows a more realistic treatment of low permeability superficial deposits, portioning the nitrate at the surface between runoff and recharge and providing a vertical velocity in the superficial deposits. In the previous version of the model all nitrate movement in these deposits was set to zero.

DATA REQUIREMENTS

The model remains relatively parsimonious with different levels of data required to simulate USZ nitrate velocity depending on the application:

- For less important secondary aquifers and low productivity strata it requires only USZ thickness, USZ velocity and NIF.
- For principal and important secondary aquifers a process-based approach to USZ velocity also requires modelled recharge and aquifer properties.
- Where low permeability superficial deposits are present the process-based approach allows the routing of a proportion of the nitrate to runoff and the estimation of a realistic travel time through the deposits. This requires the lithological class and the thickness of the superficial deposits to be included.
- For borehole and catchment scale applications the NTB model can be linked to a saturated zone model which routes groundwater to river baseflow.

APPLICABILITY

The case studies demonstrate that the model can be benchmarked against other nitrate modelling approaches, both for borehole catchment studies which use a similar approach and for basin-scale models which use a different approach.

The case studies show that accounting for the unsaturated zone lag using modelled USZ travel time has value for work under the WFD and for water utilities as well as for NVZ designation. The NTB model could:

- Form a numerical component of an updated NVZ delineation methodology/model and/or provide supporting evidence at the review stage. Model output can readily be combined with other Environment Agency models to demonstrate where a thick USZ may be contributing to inconsistencies between nitrate loading and monitored nitrate in groundwater during NVZ designation.
- Provide evidence to support the determination and characterisation of pollutant (nitrate) trends in groundwater, starting points for trend reversal and/or justification for establishment of alternative (or less stringent) objectives as part of WFD implementation.
- Contribute to public water supply and catchment management and protection measures as is already the case.

6.1.2 Limitations

The new version of the NTB model although much improved still has a number of limitations which will continue to be addressed as the model develops. For example the model:

- Uses heuristic values for USZ velocity for less well characterised strata where aquifer properties are not available.
- Does not include variable infiltration in these areas (e.g. for investigating climate change scenarios.)
- Does not account for bypass flow. The model includes a general attenuation factor but in the current version this is set uniformly across the whole modelled area. The model does not yet include either a means of routing this directly to the water table or providing values of proportion of bypass flow to individual formations.
- Does not currently represent denitrification since we lack reliable data to adequately describe the extent, both spatial and in amount.

6.2 LINKING THE NITRATE TIMEBOMB MODEL WITH NVZ DESIGNATIONS

6.2.1 Overview, sources of data and approach

This section aims to detail some potential options for integration of the BGS NTB model with the Environment Agency’s NVZ designation methodology. A number of datasets from both the Environment Agency and BGS have been used in the analysis:

- BGS national mapping of unsaturated zone travel time at 1 km grid scale.
- Environment Agency groundwater NVZ mapping.
- Environment Agency “Groundwater Lines of Evidence” NVZ designation risk model at a 1km grid scale including pressure information, observation data and final risk scores.

A GIS approach has been used to identify areas of England where unsaturated zone lags may be significant and where there is uncertainty in the NVZ designation. A national overview of areas of designation uncertainty is initially provided, followed by national and regional scale assessments of where the risk model indicates there are mismatches between monitoring and loading data. This analysis results in suggestions of where the BGS NTB model might be usefully applied/integrated to support a future NVZ designation process.

6.2.2 Summary of Environment Agency risk assessment process

The risk model is fully described in Environment Agency (2012) and summarised in Stuart et al. (2016). It consists of eight components (Table 6.1). Three components describe pressures and are mainly derived from modelled inputs of nitrate data where the higher the pressure, the greater the risk that groundwater nitrate concentrations will exceed 50 mg NO_3 l^{-1}. The other five components describe the observed nitrate and draw upon a combination of water quality monitoring data and local Environment Agency evidence. Four of the components were derived using national datasets; nitrate monitoring data were interpolated to produce national maps of current (2010) and future (2027) groundwater nitrate concentration and agricultural and urban nitrate leaching were estimated from land use. The other four components were derived from professional judgement by local area Agency staff.

Weightings were designed to give the greatest importance to groundwater monitoring data and secondary importance to agricultural nitrate loss data derived from the NEAP-N model. The model could incorporate the understanding of local Environment Agency hydrogeologists but scores were set using national lines of evidence. Each component was given a score (positive scores increase the overall risk and negative scores decrease the overall risk) and weightings were applied to these scores. The weighted scores were then combined to yield an overall risk score indicating the strength of evidence that the groundwater was polluted by nitrate from agricultural sources.

If the risk that groundwater nitrate concentration is exceeding 50 mg NO_3 l^{-1} and agriculture is the source, the score will be higher than 8. This will lead to potential groundwater NVZ designations. A medium score ranges from 8 to 3 and shows that either the monitoring or modelling assessments exceeded or were likely to exceed 50 mg NO_3 l^{-1}. These areas are likely to be included in potential designation areas around high risk areas dependent on the hydrogeological setting. A low score is lower than 3 where both the monitoring and modelling assessments show that nitrate concentrations were not likely to exceed 50 mg NO_3 l^{-1}. These are generally not considered for designation and any low risk areas that are repeatedly shown to be so may be considered for removal from designation.

Table 6.1 Components of the Environment Agency GIS risk model

Risk	**Factors**
Pressure	1. Agricultural nitrate leaching from the NEAP-N model (National) Score: <25= 0, 25-50 = 1, >50 = 2, Weighting = 3
	2. Urban nitrate leaching from the Lerner model (National) Score: <25= 0, 25-50 = 1, >50 = 2, Weighting = -2
	3. Denitrification or mixing lower the nitrate input from agriculture to groundwater (Area) Score: good evidence = 2, some evidence = 1, no evidence = 0, Weighting = -1
Observed	1. Kriged current groundwater nitrate concentration (National) Score: <25= 0, 25-50 = 1, >50 = 2, Weighting = 3
	2. Kriged future (2027) groundwater nitrate concentration (National) Score: <25= 0, 25-50 = 1, >50 = 2, Weighting = 2
	3. Monitored nitrate is representative of point source pollution (Area) Score: good evidence = 2, some evidence = 1, no evidence = 0, Weighting = -5
	4. Monitored nitrate is unrepresentative of real groundwater nitrate concentrations (Area) Score: yes good evidence = 2, yes some evidence = 1, no evidence = 0, no some evidence = -1, no good evidence = -2, Weighting = 3
	5. Surface water – groundwater interactions identify that surface water quality is a reasonable indicator of groundwater quality (Area) Score: good evidence = 2, some evidence = 1, no evidence = 0, Weighting = 1

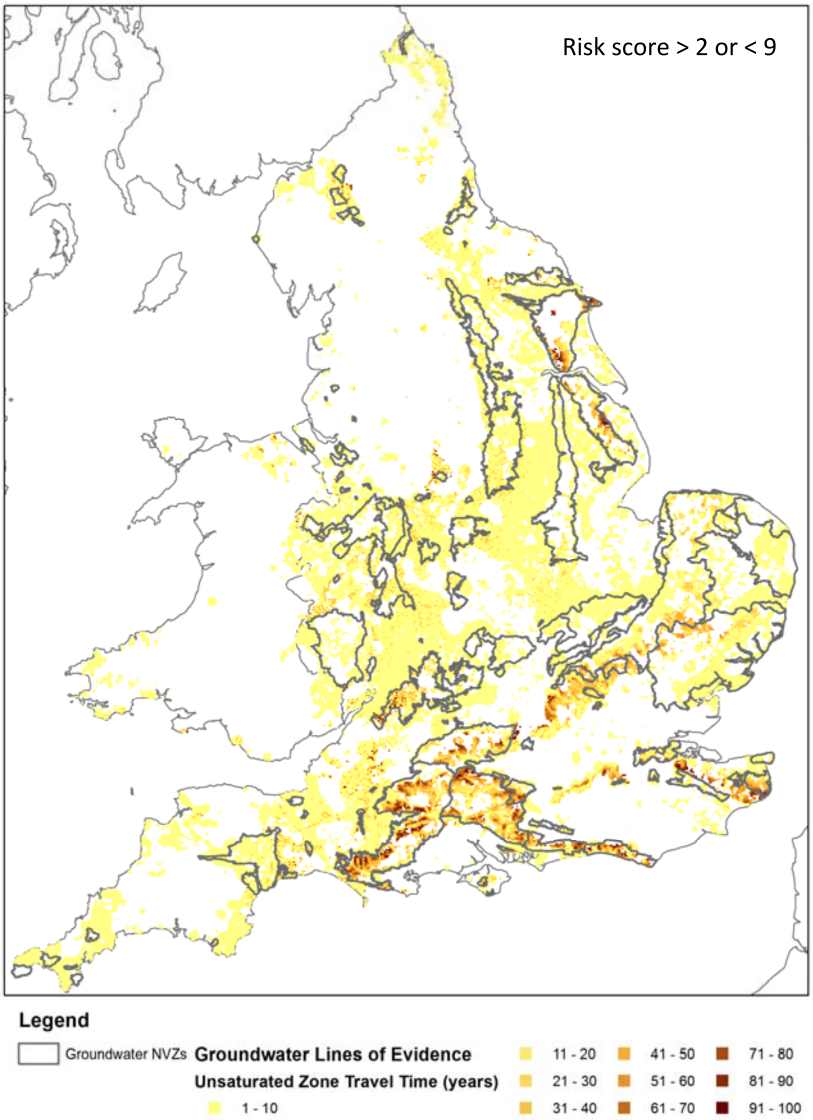

Figure 6.1 Unsaturated zone travel times for areas of England and Wales where final risk score is between 3 and 8 using the 2013 data

6.2.3 Areas of NVZ designation uncertainty

In the Environment Agency risk model, final risk scores between 3 and 8 indicate there is some degree of uncertainty in the monitoring and/or N loading data and consequently may or may not be designated. In these areas there may be a mismatch between the N loading estimations and observed groundwater nitrate concentrations. This may be the result of time lags in the unsaturated zone and potentially nitrate loss processes such as denitrification. Figure 6.1 shows parts of England designated as groundwater NVZs and the unsaturated zone travel time where final scores are between 3 and 8. It can be observed that large areas of England are overlain by this range of final scores, in particular the chalk outcrop of southern and eastern England.

6.2.4 Areas of high N loading and low observed groundwater nitrate

Figure 6.2 (a) shows pressure (N loading) scores in the risk model where the final score is between 3 and 8 and Figure 6.2 (c) shows the unsaturated zone travel time where the final score is between 3 and 8 and the pressure score is greater than 3. This is indicative of areas where nitrate loadings are likely to be significant but observed groundwater concentrations are low. If this case occurs where unsaturated zone travel time is long, it is likely that the nitrate loading is yet to have reached the water table.

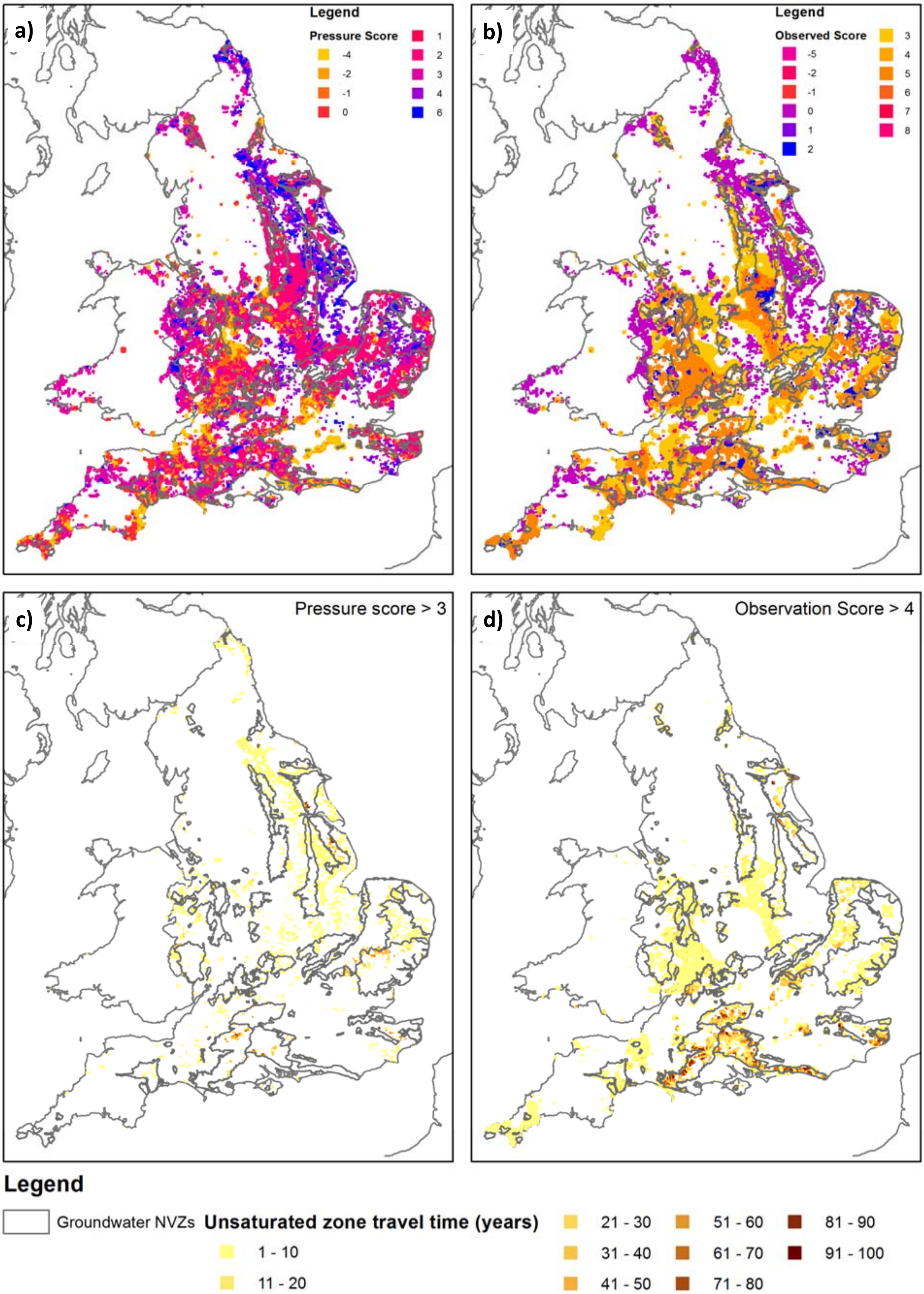

Figure 6.2 (a) Pressure and (b) observation scores for England and Wales where final score is between 3 and 8, (c) unsaturated zone travel times for areas of England and Wales where final risk score is between 3 and 8 and pressure score > 3 and (d) final risk score is between 3 and 8 and observation score > 4 (all using 2013 data)

Pressure scores are highest over East Anglia, Lincolnshire and Yorkshire, with lower scores in the West Midlands and the South West. Travel times where pressure scores are high (Figure 6.2 c)) are generally short but there are some areas with relatively long travel times in the Chalk of Wessex and southern East Anglia.

Figure 6.3 (a & c) shows the same data at a regional scale focussing on the Chalk of Wessex, the South Downs and the Berkshire Downs. Whilst the area of the Chalk where pressure scores are greater than 3 is relatively small, the unsaturated zone thickness is large which results in long travel times (50 -70 years). Areas where N loadings are high but observed concentrations are low are highly likely to be the result of time lag in the unsaturated zone. Review of unsaturated zone travel times in such cases is likely to be beneficial during future designations.

6.2.5 Areas of low N loading and high observed groundwater nitrate

Figure 6.2 (b) shows observation (groundwater nitrate concentration) scores in the risk model where the final score is between 3 and 8 and Figure 6.2 (d) shows the unsaturated zone travel time where the final score is between 3 and 8 and the observation score is greater than 4. These areas are indicative of where groundwater monitoring shows high nitrate concentrations, but N loading data suggests there is a limited current N input to groundwater. It is plausible that this score represents areas where current groundwater nitrate concentrations are a result of historic nitrate loadings. Observed scores are highest over parts of East Anglia, the West Midlands and the Chalk of southern England.

At the regional scale in Southern England (Figure (b & d)), areas with high observation scores are often situated in interfluve areas, with long travel times of up to 80 to 90 years. In these areas a review of the unsaturated zone travel time during the NVZ designation process may be of benefit in order to identify those areas with particularly long travel times where current observed concentrations are a result of legacy inputs.

6.2.6 Areas of potential nitrate loss

Figure 6.4 shows areas of England where pressure scores are > 3, final score > 2 and < 9 and unsaturated zone travel times < 10 years using the 2013 data. This classification indicates areas can be considered to have the following characteristics:

- High nitrate loadings.
- Low nitrate concentrations.
- Short unsaturated zone travel times.
- May be designated as NVZs.

If unsaturated travel times are short and there is a mismatch between nitrate loading and observed concentrations, this suggests some other loss or attenuation process such as denitrification may be occurring. Consequently, Figure 6.4 can be considered to be a simplistic first estimation of a nitrate loss/denitrification map. The spatial distribution of areas where N loss may be occurring generally agree with the conceptual understanding of UK hydrogeology. There are large areas of East Anglia where nitrate loss may be occurring where till layers are present which may result in anoxic conditions and denitrification. There is very little potential for nitrate loss across the chalk outcrop which reflects the oxic conditions of the unsaturated and saturated zones. It must be noted that this distribution is an approximate first estimation of potential nitrate loss and requires further investigation through comparison with other indicators of denitrification (redox conditions, organic content).

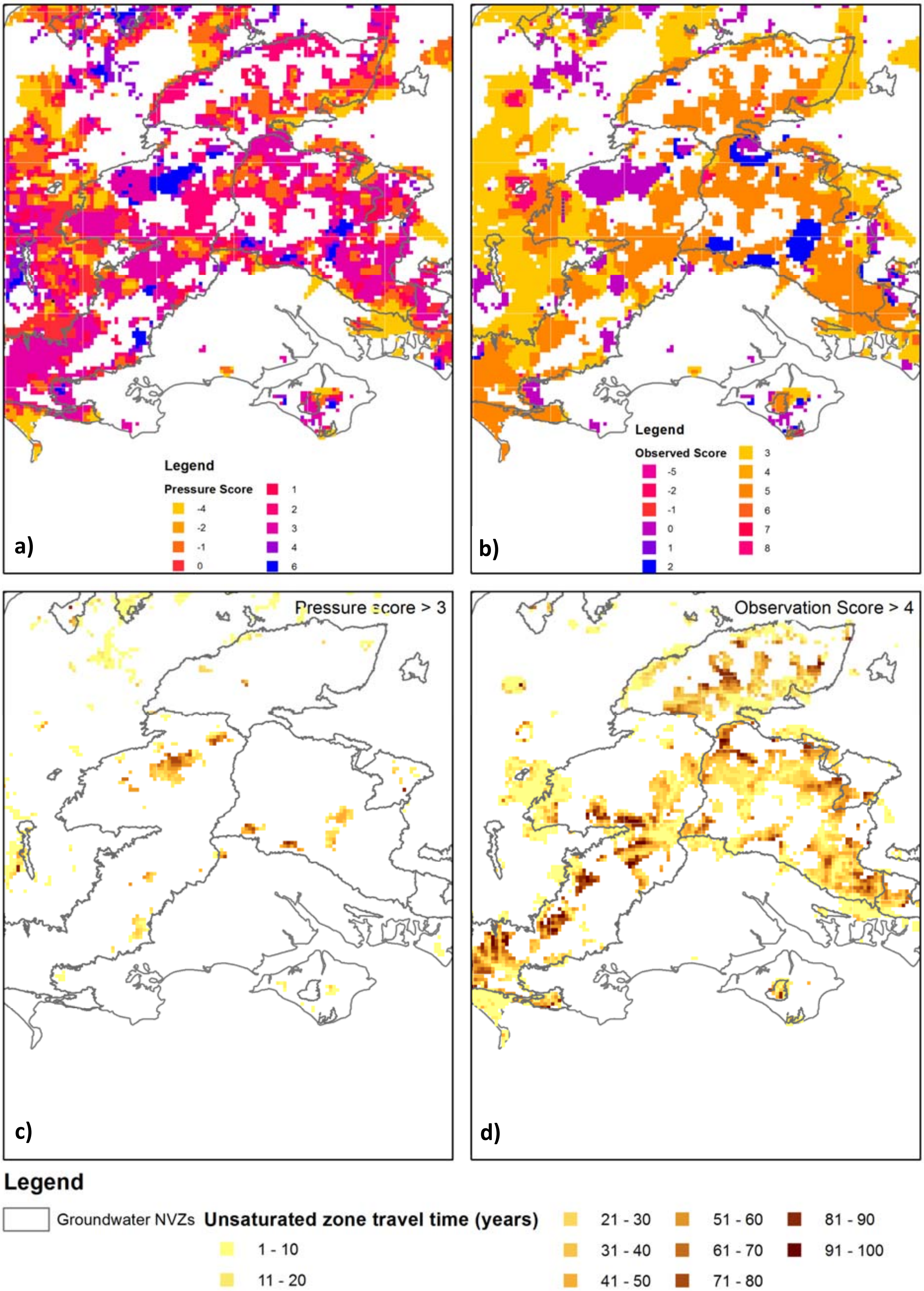

Figure 6.3 (a) Pressure and (b) observation scores for Wessex, South Downs and Berkshire Downs where final score is between 3 and 8, (c) unsaturated zone travel times where final risk score is between 3 and 8 and pressure score > 3 and (d) final risk score is between 3 and 8 and observation score > 4 (all using 2013 data)

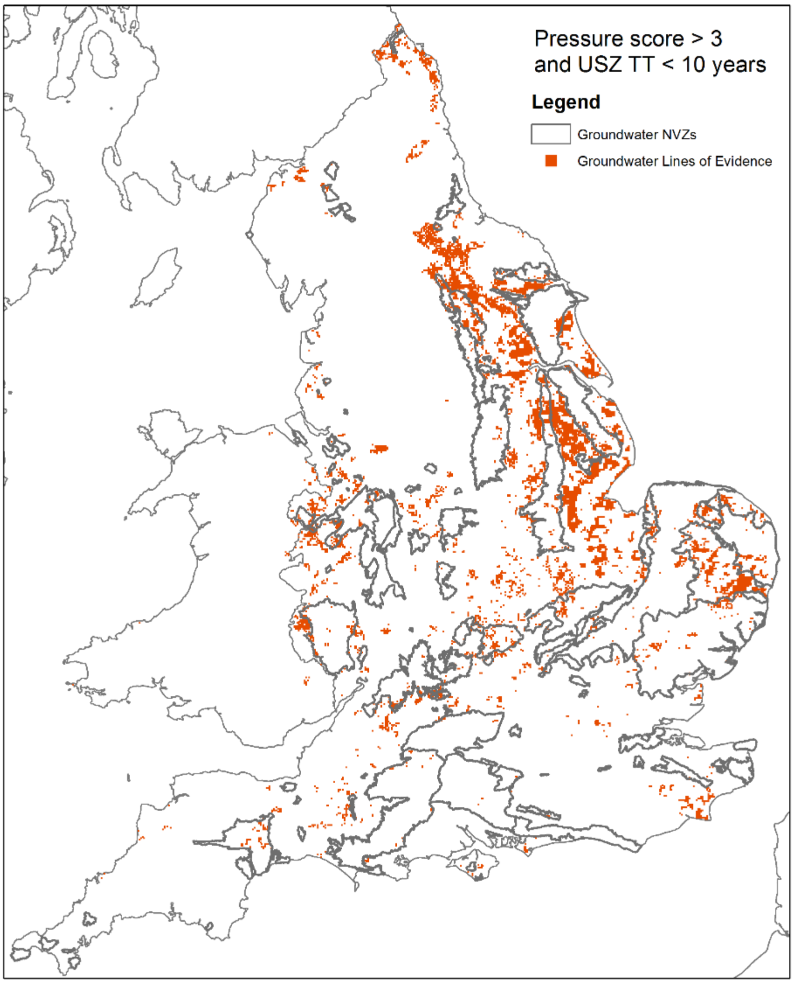

Figure 6.4 Areas of England and Wales where the final risk score is between 3 and 8, pressure score > 3 and unsaturated zone travel times are less than 10 years using 2013 data.

6.2.7 Recommendations for implementation of unsaturated zone travel time in the NVZ designation approach

The examples above illustrate how estimates of the unsaturated zone travel time may be beneficial when designating NVZs and help in understanding and resolving the uncertainties where the final risk score is > 2 and < 9. For example travel time estimates may help resolve mismatches between groundwater monitoring and N input (loading) datasets. It is recommended that unsaturated zone travel times be incorporated in the risk model. The groundwater risk model already takes into consideration a number of additional factors such as potential denitrification, groundwater-surface water interactions and representative monitoring points. However, these in general rely on expert testimony and so lack some transparency and numerical basis. Consequently, unsaturated zone lag could be used as an additional factor depending on the travel time.

6.2.8 Recommendations for using unsaturated zone travel time in WFD implementation

The WFD requires establishment of a series of environmental objectives for groundwater. These include preventing or limiting inputs of pollutants, achieving good status and reversing upward trends in pollutant concentrations. Nitrate is the most widespread groundwater pollutant and as a result makes the greatest contribution to groundwater body status failures and upward trends. The difficulty in achieving good status by 2015 and reversing trends was recognised in the 2009 River Basin Management Plans by the setting of alternative objectives which provided time extensions (up to 2027) for the majority of the groundwater bodies impacted by nitrate. However the supporting evidence that can be deployed in support of this approach has so far been limited.

The improved BGS NTB model has the potential to provide more robust evidence to support the continued establishment of alternative objectives and where less stringent objectives may be necessary. The model and the case studies have shown that future projections of nitrate trends are possible (at points and across geographic areas, e.g. groundwater bodies) to determine if and/or when threshold values are likely to be exceeded or when trends reversed. Further the model can be used to evaluate the impact of measures (under different) scenarios as part of options appraisal and consider the longer term impacts of climate change. The application of a single consistent model to both NVZ and WFD can also ensure consistency and inter-comparability. The model improvements also mean that it can be applied to other pollutants which are of concern under the WFD.

6.3 VIEWS FROM PROJECT WORKSHOP

A project workshop was held on the 27th April 2015 with the aim of identifying the approaches to groundwater nitrate modelling across the Environment Agency and linkages with others working in related activities. This was attended by representatives from the Environment Agency, Defra and the NFU. Water utilities were invited but were not able to attend.

The material presented summarised both the briefing report and the preceding chapters of this report organised into the following subject areas:

- Project aims, timeline, workshop aims.
- The nitrate legacy – Nitrate in the unsaturated zone and the NTB model.
- NVZ briefing material – NVZ storyline, relationship with WFD.
- Case studies – Thames basin, South Downs site, Delamare .
- BGS NTB model development – Nitrate input, water levels, geological scale, process modelling, low permeability superficial deposits, saturated zone.
- Contextual review.

Some main points arising from the discussion were:

VALIDATION OF THE APPROACH

- It is not possible to validate the NTB approach by using current porewater profile data from the unsaturated zone. There are very little current data and the few recently drilled boreholes are likely to have been targeted at problem areas, rather than typical areas similar to those studies in the 1970s and 1980s during the original nitrate work.
- Care is needed when comparing NTB model output with NVZ designation datasets where the point data have been kriged to give areal coverage as these have no hydrogeological basis.

RELATIONSHIP TO WORK UNDER THE WFD

- It was considered that nitrate in groundwater issues identified as part of the WFD process need to be reflected in work carried out for NVZs.
- There is a perceived discrepancy between the results of work carried out by the Environment Agency for WFD status changes and that for NVZ model predictions. In the UK, the recommended WFD threshold (TV) has been set at 37.5 mg NO_3 l^{-1} by UKTAG (UKTAG, 2012) whereas 42 mg NO_3 l^{-1} is used for NVZs. Exceedance of the TV may contribute to failure of one or more environmental objective. The use of the NTB model has the potential to better understand when, under the different regimes, future failures may occur (if there is an upward trend) or when achievement of these objectives may be realised if trends are reversed. It will also be important how to examine the implications of the

differences between the regimes (economic, regulatory failure etc.) in the future and under different scenarios.
- The NTB model could be useful in assessing and setting recovery times under the WFD.
- Trend reversal will be reviewed by UKTAG following publication of the most recent WFD plans. An evidence base for trend reversal is required. Denmark successfully challenged on trend reversal and used residence time indicators as an evidence base to demonstrate long travel times. The NTB approach could provide an alternative to this.

VALUE

- The NTB approach should provide a useful evidence base to the agricultural community. Farmers in West England have been most affected by NVZ designations, but the NTB model shows that long groundwater residence times are more of an issue in the East of England. This may reflect the different balance of surface water to groundwater in these areas and the presence of low permeability superficial deposits.
- The demonstration of groundwater travel time should be valuable in discussions with the EU Commission.

7 Conclusions and further work

7.1 SUMMARY AND CONCLUSIONS

7.1.1 Model development and benchmarking

A series of significant developments to the BGS NTB model have been made as part of this project to address a number of over simplifications used by the first version of the model. The improvements have included incorporation of a spatially and temporally distributed nitrate input function, unsaturated zone thickness derived from OS river data, travel time attribution and application of larger scale geological mapping and process modelling of recharge through the unsaturated zone. They now allow this national model to be applied at sub national scale. The model has the capability to be modified to take account of particular aquifer characteristics.

This has a number of benefits in that it can be applied at the different scales required for effective management and protection of groundwater (and associated receptors) under the EU Nitrates Directive and Water Framework Directive – point, groundwater body and catchment. An important and unique additional benefit is that it is nationally consistent and so its application is not geographically limited unlike other models. It therefore lends itself to providing evidence to support national reporting requirements and to undertake scenario modelling in terms of management option appraisal and environmental (including climate) change. The model improvements have also enabled the first estimate to be made of the mass of nitrate stored within the unsaturated zone. This indicates that previous assumptions have been inaccurate and significantly underestimated the mass of nitrate in the sub-surface.

The BGS approach was evaluated in three case studies using other modelling approaches applied at different scales. These were a basin-scale model of the Chalk (Howden (2010 & 2011), a multi-borehole scale model in the Permo-Triassic sandstone and a catchment in the Chalk of the South Downs (AMEC, 2014a, b) .

- For the Thames the BGS model gave comparable results to the original study back to 1925 provided that the same nitrate input function was used. Both models failed to predict nitrate concentrations in the Thames after the mid-1980s and has raised some very interesting questions about the future behaviour of nitrate in the River Thames and the processes operating.
- For the Permo-Triassic site a similar approach was used to the BGS model in the Eden Valley. This replicated the existing model developed for the EA for both in terms of trend assessment and in the lack of dilution available for blending purposes.
- For the Chalk of the South Downs a model which treated the unsaturated zone in a similar way to the BGS model had already been constructed by AMEC for nitrate catchment management. This model provided a good fit to observed concentrations and confirmed the importance of estimating unsaturated zone delays. The assessment of modelled travel time from different areas of the catchment clearly illustrated the arable areas which would give a relatively rapid respond to changes in nitrate management.

The case studies demonstrate that the BGS NTB model can be benchmarked against other nitrate modelling approaches and gives acceptable results at a range of scales. The NTB has not as yet been parameterised to allow bypass flow or denitrification to be represented.

7.1.2 Potential linkage with Environment Agency NVZ designation and WFD

To illustrate the potential linking of the BGS Nitrate Time Bomb (NTB) model with the Environment Agency's NVZ designation methodology, a GIS approach was used to identify areas of England where unsaturated zone lags may be significant and where there is uncertainty in the NVZ designation. A national overview of areas of designation uncertainty identified large areas of England in particular the chalk outcrop of southern and eastern England. National and regional scale assessments of where the risk model indicates there are mismatches between monitoring and loading data were compared to unsaturated zone travel times.

The results of this analysis suggest a number of areas where the BGS model might be a very useful additional component in any future NVZ delineation method. This could either be through formal integration into the designation modelling methodology or to provide supporting evidence.

There are also a number of ways the model may potentially help with implementation of the WFD. Nitrate is the most significant and widespread cause of failure to achieve environmental objectives for groundwater, especially the good status and trend reversal objectives. The improved BGS NTB model has the potential to provide more robust evidence to support assessment of the monitoring data used to demonstrate compliance with the objectives and the measure being implemented.

The model can be used to assess future nitrate trends at points and across groundwater bodies to determine if and/or when threshold values are likely to be exceeded or when trends reversed. Further the model could be used to:

- Evaluate the impact of programmes of measures (under different) scenarios as part of an options appraisal.
- Consider the longer term impacts of a variety of environmental change factors.
- Be applied to other potential pollutants which are of concern under the WFD.

7.2 FURTHER WORK

There are a number of areas where further development could make the NTB model of greater value:

- Development of different scenario tests, such as nitrate loading changes due to different land use/management measures, and under climate change scenarios.
- Introducing detailed nitrate fate and transport processes in the groundwater system into the NTB model when applying to catchment-scale studies.
- Assessing the potential impact of karst behaviour and bypass flow on nitrate movement.
- Incorporating both nitrate and water processes in the NTB model to contribute to the development of a new model for NVZ designation.

NTB model outputs have the potential to be used for a range of applications

- Providing outputs to the EA for the next round of NVZ designation and integration into the risk scoring methodology.
- Using outputs of USZ modelling to inform AMP6 water company catchment management work.
- Making some outputs of the work publicly available through a web GIS, e.g. through BGS, the Environment Agency or Defra. This could include a high level depth to water/USZ travel time map.

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