

## Quantification of nitrate storage in the vadose (unsaturated) zone: a missing component of terrestrial N budgets

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## Abstract

National terrestrial nitrogen budgets for many developed countries have been calculated as part of the management of impacts of N on the environment, but these rarely represent the subsurface explicitly. Using estimates of vadose zone travel time and agricultural nitrate loading, we quantify, for the first time, the total mass of nitrate contained in the vadose zone of aquifers in England and Wales. This mass peaked in 2008 at 1400 kt N (800 to >1700 kt N from sensitivity analyses) which is approximately 2.5 to 6 times greater than saturated zone estimates for this period and indicates that the subsurface is an important store of reactive nitrogen. About 70% of the nitrate mass is estimated to be in the Chalk, with the remainder split between the Permo-Triassic sandstones, the Jurassic Oolitic limestones and minor aquifers. Current controls on fertiliser application mean that the vadose zone is now a nitrate source and in 2015 we estimate the net flux from the unsaturated zone to groundwater to be 72 kt N/annum. The mass of nitrate in the vadose zone should be included in future terrestrial nitrogen budgets at national and global scales to improve ecosystem management.

**Keywords:** Nitrate; Nitrate budget; Groundwater; Unsaturated zone; Vadose zone

# 1 Introduction

Modern intensive agriculture has significantly affected the earth's nitrogen (N) cycle (Vitousek et al. 1997). It is estimated that the input rates of reactive nitrogen to the terrestrial biosphere are now over double pre-industrial levels (Galloway et al. 2004) through changes in agricultural land use practices, including the development and application of N fertilizers. This reactive nitrogen cascades through the environment with a number of deleterious and costly effects (Galloway et al. 2003). Groundwater and surface water quality for public supply has deteriorated, resulting in expensive “end-of-pipe” solutions such as nitrate removal or blending of waters (Kapoor and Viraraghavan (1997), Pretty et al. (2000), UKWIR (2004)) and this has been recognised in the UK and elsewhere for several decades (ENDS 2004). As a result, measures such as the Nitrates Directive (European Union 1991) and Water Framework Directive (WFD) (European Union 2000) have been introduced to control farming practices in order to reduce pollution of ground and surface water. In addition to drinking water impacts, groundwater discharges to rivers, wetlands and marine systems have also contributed to long term ecological degradation (Vitousek et al. 1997). However, whilst a drinking water standard for nitrate has been developed in Europe (50 mg/L, European Union (1991)), no standard currently exists for surface water.

In order to manage public water supplies and protect aquatic ecosystems, estimates of N budgets and fluxes at both national and continental scales have been developed. These N budget approaches often assume the N cycle is in a steady state with no net change in terrestrial N storage (Galloway et al. 2004). Bouwman et al. (2013), for example, developed steady-state soil N budgets to explore changes in global nitrogen cycles. Budget inputs are from biological N fixation ( $N_{\text{fix}}$ ), atmospheric deposition ( $N_{\text{dep}}$ ), fertilizer applications ( $N_{\text{fert}}$ )

and animal manure ( $N_{man}$ ) and outputs are from withdrawals ( $N_{withdr}$ ) from harvesting, cutting and animal grass consumption. The soil budget ( $N_{budget}$ ) was derived from:

$$N_{budget} = N_{fix} + N_{dep} + N_{fert} + N_{man} - N_{withdr}$$

In such a steady state approach, positive  $N_{budget}$  values represent a loss of N to the environment and negative values indicate depletion of soil N. Whilst this may be appropriate at the global scale, these assumptions do not consider changes at national and regional scales. Worrall et al. (2009) showed that Great Britain is a net sink of reactive nitrogen. They postulated that the sink is associated with reactive nitrogen storage in groundwater and made the first attempt at quantifying the amount of transient N storage. By considering that approximately 10 – 50% of the land surface of Great Britain is underlain by aquifers with an effective depth of water of between 1 to 10 m, they equate a 1 mg/L N increase in average groundwater concentration to be equivalent to a store of 300 kt of N. Subsequently, Worrall et al. (2015) estimated the storage of total N in the unsaturated and saturated zones of the Thames Basin, a lowland agricultural catchment in England. Whilst the individual storage of N in each zone was not presented, they presented a range of maximum accumulation rates for the unsaturated zone of 1.4 to 5.5 kt N/yr and state the time series for the flux into unsaturated zone storage will reflect that of the saturated zone. Given this range of maximum accumulation rates and the range and time series of accumulation rates to the saturated zone presented by Worrall et al. (2015), we estimate the peak in total accumulation in the unsaturated zone derived by the approach of Worrall et al. (2015) in 2000 to 2004 to be between 16.4 to 195 kt N.

At the catchment scale, Chen et al. (2014) developed a dynamic watershed model which demonstrated the importance of transient N storage when evaluating catchment management

measures. Recently, Hale et al. (2015) developed a model to evaluate the roles of nutrient inputs, infrastructure and runoff on N and P fluxes. They acknowledge that a significant data limitation in their study was the lack of information on subsurface nutrient transport via groundwater. Further national scale work has shown that there are substantial delays in the leaching of N from the base of the soil zone reaching groundwater in some areas (Howden et al. (2011); Wang et al. (2012)). This delay can be of the order of decades. This is the result of the thick vadose zones and slow travel times present above aquifers of the United Kingdom (Foster et al. 1982).

Representation of this delay and the associated vadose zone storage in national and continental scale N budgets has not been attempted to date. Figure 1 shows the global distribution of thick vadose zones (> 20 m) and cropland areas as estimated by Fan et al. (2013) and Ramankutty et al. (2010) respectively. Thick vadose zones in England and Wales as derived using the river base level model discussed in this study are also shown. There are large areas of Europe, Asia and the Americas where vadose zones are likely to be thick and agricultural N losses to the environment may be important. In these areas transient N storage in the vadose zone may seriously constrain the usage of conventional nitrate budget approaches. Consequently it is crucial that a generic, simple-to-apply approach to estimating this storage is available.

Sutton et al. (2011) detail methods for national nitrate budgeting using a range of approaches across Europe. Most of these adopt a simple leaching and runoff factor approach to agricultural nitrate losses. They conclude that the largest uncertainties in budgets are associated with N leaching to groundwater and that future research should focus on this area.

If global water resources and ecological security are to be managed and protected effectively in the future, improved approaches to quantifying the role of groundwater and the vadose zone in nitrate budgets are urgently required. This study presents a first quantification of the vadose zone nitrate budget at the national scale. We hypothesise that the lag between nitrate loss at the base of the soil zone and its impact on groundwater results in the vadose zone being an important store of nitrate in the terrestrial environment which needs to be properly considered for effective ecosystem management. We use a conceptually straightforward and generic approach which can be readily adopted in other locations to improve national and continental scale N budgets. By linking estimates of nitrate leaching at the base of the soil zone with depth-to-groundwater maps and vadose zone velocities, we use a simple summation approach to derive the total unsaturated zone nitrate mass at the national scale.

## **2 Materials and Methods**

### **2.1 Study Area**

The countries of England and Wales were used as the study area; this together with the overall methodology is outlined in Figure 2. England and Wales have extensive areas of agricultural land (70% of the total area of the United Kingdom (DEFRA 2012)) and are underlain by numerous important groundwater bodies (British Geological Survey 2010). The three primary aquifers in England and Wales are the Chalk in Southern and Eastern England, the Permo-Triassic Sandstone in the Midlands and Northern England and the Jurassic Oolitic Limestones in Western England and the East Midlands. These aquifers provide the majority of the 35% of public water supply derived from groundwater in England and Wales (DETR 1997) and support numerous groundwater-dependent ecosystems and the baseflow to many major rivers. Stuart et al. (2007) assessed long term trends in groundwater nitrate data across the aquifers of the UK and found an average annual rise in concentration of  $0.34 \text{ mg NO}_3\text{I}^{-1}$

a<sup>-1</sup>, with 34% of sites analysed exceeding the 50 mg l<sup>-1</sup> EU drinking water standard. Consequently, understanding the storage of nitrate in the vadose zone above these aquifers is of critical importance if future nutrient loadings to public water supply abstractions, groundwater dependent ecosystems and marine environments are to be suitably managed.

Wang et al. (2012) derived predictions of peak nitrate concentrations for the study area which were validated against historic nitrate trend data (Stuart et al. 2007). In this study we further develop the verified approach of Wang et al. (2012) with additional datasets to derive the mass of nitrate in the vadose zone across England and Wales.

### **2.1.1 Identification of Aquifers**

High and moderate productivity aquifers (as defined by borehole yields > 1 L/s) were selected for this study using 1:625,000 scale digital hydrogeological mapping by the British Geological Survey (2010). Where bedrock aquifers are overlain by low permeability superficial deposits, recharge rates will be restricted and denitrification may occur (Jørgensen et al. (2004); Fragalà and Parkin (2010)). Consequently, these areas were excluded from the analysis using a national scale model of the recharge potential of superficial deposits (SNIFFER (2006); Griffiths et al. (2011); Wang et al. (2012)). Recharge potential mapping undertaken by Griffiths et al. (2011) used a domain-based methodology considering both primary and secondary lithological characteristics for each formation. Areas north of the limit of glaciation, where primary and secondary recharge potentials are low, were assumed to have no nitrate transport to underlying aquifers. Figure 2 shows the aquifer areas used in this study derived from the hydrogeological bedrock and superficial mapping. The total outcrop area of these aquifers excluding areas overlain by low permeability superficial deposits is 43805 km<sup>2</sup> or approximately 29% of the land surface of England and Wales.

## 2.2 Nitrate Input to the Vadose Zone

It was assumed that the dominant form of reactive nitrogen in the subsurface is nitrate. This is supported by national surveys of groundwater quality across England and Wales (Shand 2007) showing that median nitrate-N concentrations are at least an order of magnitude higher than median ammonium-N and nitrite-N concentrations. Dissolved organic nitrogen (DON) concentrations in the subsurface are generally considered to be low in comparison to nitrate as evidenced by low levels of dissolved organic carbon (Durand et al. 2011). Data for Chalk baseflow dominated streams in lowland agricultural catchments show significantly lower DON than inorganic N concentrations even where affected by sewage treatment work effluents (10 – 20%, Yates and Johnes (2013)). DON may be locally significant in more pristine or peat-rich environments (e.g upland moors; Lapworth et al. (2008)) and should be taken into consideration when reviewing results at small scales.

It was assumed that diffuse nitrate inputs to the vadose zone are primarily from agriculture. It has been shown that over 70% of nitrate in groundwater and surface water in England is derived from agricultural land (Foster (2000); Hunt et al. (2004); DEFRA (2006)). Point source discharges have been considered as insignificant at the national scale given the high potential for dilution in groundwater (Goody et al. 2001) and have been estimated as contributing < 1% of the total nitrate flux to groundwater in the United Kingdom (Sutton et al. 2011). Consequently these discharges have not been considered further in this study. At the local scale, non-agricultural diffuse nitrate sources may be significant (Wakida and Lerner 2005) but have not be considered given the national scale of the work presented in this study. The modelling approach of Lord and Anthony (2000) was adopted which derives



nitrate losses from agriculture at the base of the soil zone. Within the model (NEAP-N), cropping and livestock data from agricultural censuses are integrated with land cover, soils, climate data and interpolated to a 1 km grid for England and Wales for 5 specific years (1980, 1995, 2000, 2004 and 2010). Annual, spatially distributed, diffuse nitrate inputs for intermediate years were derived by interpolation. Inputs back to 1925 and forward to 2050 were derived by scaling those of Lord and Anthony (2000) using a time variant nitrate input function (NIF) (Wang et al. 2012). This produced spatially distributed annual estimates of nitrate inputs for 1925 to 2050. A time series of the total annual nitrate input for England and Wales and the NEAP-N years is shown in Figure 3 (a). The NIF was based on estimates of historic nitrate loading trends based on land use data detailed by numerous workers (Foster et al. (1982); Lord et al. (1999); ADAS (2003); Addiscott (2005) and summarised by Wang et al. (2012)).

### **2.3 Vadose Zone Nitrate Transport and Total Mass**

Figure 2 outlines the methodology for the derivation of nitrate flux, travel time and total mass in the vadose zone. Transport of nitrate through the unsaturated zone on a 1 km scale was derived using the approach of Wang et al. (2012). We assume that nitrate is conservative in the vadose zone above aquifers. This assumption is supported by studies which suggest that denitrification in the unsaturated zone is likely to be very limited (Kinniburgh et al. (1994), Rivett et al. (2007)). Field data indicate that vadose zone denitrification results in decreases in concentrations which represent just 1 – 2 % of nitrate input (Rivett et al. 2007). We also assume that nitrate moves through the vadose zone with a constant vertical velocity, no hydrodynamic dispersion and undergoes vertical transport through the matrix when in dual porosity media.

Depth to water table was derived from observation borehole data, where available, and from a model deriving groundwater levels from river base levels and a digital terrain model (NEXTMap; Intermap Technologies (2007)). The river base level model derives an interpolated groundwater level surface on the assumption that groundwater is in direct hydraulic connection with rivers. This is shown conceptually in Figure 2. The spatial distribution of depth to water across moderate and highly productive aquifers is shown in Figure 3.

Vadose zone velocities for each groundwater body were derived from historic work assessing water flows through the unsaturated zone (Chilton and Foster 1991). Historic literature data for vadose zone travel times were available for the Chalk, Permo-Triassic Sandstones, Oolitic Limestones and Oxford Clay. For all other formations, a heuristic approach was adopted and vadose zone velocities were attributed based on expert judgement considering aquifer layering, permeability and grain size (Wang et al. 2012). The velocities used for moderate and highly productive aquifers are shown in Table 1.

The total mass of nitrate in the vadose zone was derived for each year (1925 to 2050) for each 1 km grid cell using a conceptually simple summation approach and aggregated to the national scale by aquifers. For any year,  $t$  (*years*), the total nitrate in vadose zone,  $N_{VZ}$  (kt N) for a given grid cell with an vadose travel time,  $TT_{VZ}$  (year) and a time-variant nitrate input function,  $NIF$  (*kg N*), can be calculated as:

$$N_{VZ} = \sum_{i=t-TT_{VZ}}^t NIF_i / 10^6$$

We derive changes in nitrate storage in the vadose zone through time using a simple mass balance approach;

$$NIF_t - Nout_t = \Delta N_{VZ}$$

Where  $Nout_t$  is the nitrate flux from the vadose zone to the saturated zone and  $\Delta N_{VZ}$  is the change in vadose zone nitrate storage for any year  $t$ .

## 2.4 Sensitivity Analysis

A number of assumptions have been made regarding nitrate inputs and transport in the vadose zone. In order to address the uncertainty in nitrate losses from agriculture at the base of the soil zone and transport in the vadose zone, a sensitivity analysis has been undertaken. Sensitivity of the nitrate storage to vadose zone travel time was assessed by considering ranges of travel times. A conservative sensitivity analysis was undertaken using a heuristic approach by deriving the total mass using travel times 15% greater and less than the baseline travel time distribution. Additionally, a wide range travel time sensitivity analysis was undertaken using the maximum and minimum vadose zone velocities reported in the published literature. For the Chalk, unsaturated zone velocities of 40% and 180% of the mean velocity have been reported (Chilton and Foster (1991); Wang et al. (2012)) and this range of values has been used to estimate the sensitivity of the nitrate storage to vadose zone. It should be noted that it is highly unlikely that these maximum and minimum velocities are extensive nationally and consequently represent worst/best case scenarios for nitrate storage in the vadose zone. Uncertainty in the nitrate input from the base of the soil zone is likely to be temporally variable. Between 1980 and 2010 the nitrate input is reasonably well constrained by the NEAP-N data. Uncertainty in the nitrate input is likely to increase going forward from 2010 and back from 1980. Consequently a time variant error distribution was used. This is shown in Figure 3 (b). A stationary error of +/- 15% is used between 1980 and 2010. This is increased to +/-30% to 2050 and back to 1940.

## 2.5 Model Validation

Validation of national scale models should be ideally undertaken at the same scale. However, there is very limited empirical data for vadose zone nitrate storage at the national scale. Howarth (2008) and Chen et al. (2014) highlight that it is nearly impossible to measure transient N storage at the watershed scale due to landscape heterogeneity. It should be noted that the primary input datasets to the modelling approach (depth to water estimates, unsaturated zone velocities and nitrate input (NEAP-N) data) have been validated against empirical observations in previous studies (Lord and Anthony (2000); Wang et al. (2012)).

In this study, two approaches were taken to model validation. Model estimates of vadose zone storage were compared with estimates of storage in this zone in the Thames basin as undertaken by Worrall et al. (2015) and discussed in section 0. Additional validation of model outputs was undertaken at the site scale where a body of vadose zone observation data exists. Model results for nitrate storage in the vadose zone at a 1 km grid scale were compared with estimates of nitrate storage derived from observed porewater concentration profiles from cored boreholes in England and Wales (Stuart 2005). Over 400 boreholes are present in the database and an extensive screening process was undertaken to ensure the boreholes used in validation would be representative. The following criteria were used to select boreholes for validation; (1) Boreholes within the model area (where moderate and highly productive aquifers outcrop), (2) Boreholes where the full thickness of the vadose zone was sampled (98 boreholes in the model area), (3) Exclusion of boreholes where point source pollution issues were known. This resulted in 43 borehole nitrate profiles remaining for validation. It should be noted that validation at this scale is itself challenging as site-scale heterogeneity will not be captured on a 1 km grid scale. Consequently, this approach to validation can be considered as a “sense-check” for model results using empirical data.

By assuming a fully saturated matrix and that the borehole porewater data reflect the concentration within the corresponding 1 km grid cell which is underlain by agricultural land, the vadose zone nitrate storage was calculated by numerical integration. For a given vadose zone borehole porewater profile with  $n$  sampling intervals each of thickness  $b$  (m) with observed concentration  $[NO_3]$  (mg/L N) and porosity data  $\phi$  (-), the total observed nitrate stored in the vadose zone  $N_{VZ OBS}$  (tonnes/km<sup>2</sup>) for the corresponding 1 km cell can be calculated as:

$$N_{VZ OBS} = \sum_{i=1}^n \phi_i \cdot b_i \cdot [NO_3]_i \cdot f_a$$

Where  $f_a$  is the proportion of agricultural land in each 1 km grid cell as derived from the NEAP-N model (Lord and Anthony 2000). This approach assumes that the fraction of each grid cell not underlain by agriculture does not contribute nitrate to the vadose zone. In a large number of cases, multiple borehole profiles were present at the same site and within the same 1 km grid cell. In these cases an average of these boreholes was taken. This resulted in 15 sites being used for model validation, as shown in Figure 2. The sites cover the Chalk which is the principal aquifer of England.

### 3 Results and Discussion

#### 3.1 Vadose zone nitrate storage in England and Wales

Figure 3 (c and d) shows the total nitrate mass in the vadose zone above aquifers in England and Wales. The total mass of nitrate in the vadose zone has increased substantially through time, peaking at approximately 1400 kt N in 2008. From 2008 onwards, the mass of nitrate in the vadose zone has been decreasing (i.e. the unsaturated zone is now a net source of nitrate to groundwater). The temporal change in nitrate storage in the vadose zone in 2015 is estimated to be approximately -5 kt N/a. In 2015, the flux from the vadose zone to groundwater ( $N_{out}$ , equation 2) was approximately 72 kt N/a.

Figure 3 (c) shows the variability in total nitrate mass associated with using greater or smaller nitrate inputs as shown in Figure 3 (b). Nitrate mass peaks of 1700 and 1200 kt N are estimated for the greater and smaller nitrate inputs respectively. Using conservative estimates of longer and short vadose zone travel times (Figure 3 (d), +/- 15%) results in nitrate mass peaks of 1500 and 1300 kt N respectively. This also results in the peak nitrate mass occurring earlier (2007) for the shorter travel time distribution and later (2011) for longer travel times. Using a wider range of vadose zone travel times based on reported maximum and minimum unsaturated zone velocities (Figure 3 (d), + 80%/-60%) results in a wider range of unsaturated zone nitrate masses. Using the -60% travel time, the peak mass is reduced to 800 kt N and occurs in 1991. The +80% travel time results in a nitrate mass of 1750 kt N in 2050 however this is still increasing.

Figure 4 shows the temporal change in total nitrate stored in the vadose zone expressed by aquifers. The increase in vadose zone nitrate storage is dominated by the Chalk, containing an estimated 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 vadose 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 vadose zone storage because of its large outcrop area (Figure 2), extensive agricultural land use (87%) and extensive thick unsaturated zone (Wang et al. 2012). Thick vadose zones result in long travel times and consequently a large increase in nitrate storage. Figure 5 shows the spatial distribution of nitrate estimated to be stored in the vadose 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 interfluvial areas where travel times are very long due to thick vadose zones.

### **3.2 Validation**

The total nitrate storage in the Thames catchment as derived in this study is estimated to be 198 kt N. Considering the range of peak nitrate storage values for England and Wales estimated using the maximum and minimum unsaturated zone velocities (800 to >1750 kt N) compared to the best estimate mass (1400 kt N), we estimate the equivalent range for the Thames catchment to be 113 to 240 kt N. This generally corroborates work undertaken by Worrall et al. (2015) from which a range of N storage values of 16 to 195 kt N has been estimated. Figure 6 shows nitrate storage for the 15 boreholes as derived from the model and from porewater data as discussed in section 2.5. It can be observed that in general there is a poor correlation between nitrate storage derived from the model and from pore-water data. This is not surprising as the model has been developed at the national scale and does not

capture the site-specific heterogeneity which is present at the borehole scale. Local scale hydrogeological complexities such as stratigraphic variability in aquifer properties which may enhance or inhibit nitrate transport and storage have not been considered in the national scale model. Moreover, boreholes have been drilled for porewater profiles for specific investigations related to nitrate, and consequently are likely to show bias towards both particularly high and low concentrations. Boreholes have been drilled in areas where overlying land use is known to have had either extensive fertilizer applications or areas which are permanently unfertilised. Consequently, estimates of nitrate storage derived from point porewater profiles may be expected to both over and underpredict the amount of nitrate stored relative to model outputs at the 1 km scale.

Given the uncertainties in relating borehole-scale estimates of nitrate storage with national scale model outputs discussed above, it is encouraging that model results for a number of sites in the Chalk appear to be reasonably close to porewater results (10 sites with difference of less than 30 tonnes  $\text{NO}_3\text{-N}$ ). This sense-check suggests that the model results may be reasonable at the national scale. However, model results at the local scale should be treated with caution and require further site-specific assessment and validation prior to use to inform decision making.

### **3.3 Implications**

#### **3.3.1 Methodologies for derivation of national scale nitrogen budgets**

This study corroborates previous work (Worrall et al. (2009); Chen et al. (2014)) suggesting that the subsurface is an important store of reactive nitrogen and that the steady state assumption at a national scale over one year is unlikely to be valid. The estimated peak nitrate mass in the vadose zone of 1400 kt N (range of 800 to >1700 kt N from sensitivity



analysis) is 2.5 to 6 times greater than the first approximations for the saturated zone of 300 kt N (Worrall et al. 2009). Whilst the total nitrate storage in the vadose zone is now likely to be decreasing, travel times in the saturated zone can also be considerable. Consequently, peak nitrate concentrations at aquifer discharge points such as public water supply wells, rivers and groundwater dependent terrestrial ecosystems may not have occurred yet in some areas.

As discussed in section 2.1, the approach adopted in this study builds on a verified methodology used to derive peak nitrate concentrations at the water table (Wang et al. 2012). We have adopted a deterministic approach to the derivation of vadose zone nitrate storage and undertaken sensitivity analyses to assess the uncertainty in these estimates. However, we consider that further work to refine model inputs such as nitrate loadings and travel times will reduce the uncertainty in derived vadose zone budgets. Nevertheless, the methodology presented here for estimation of nitrate storage in the vadose zone is an important first step in improving nutrient budget estimations. Further research is required to assess how this storage compares with other postulated terrestrial stores such as in-stream N retention, terrestrial N uptake in land not in agricultural production and N accumulation in subsoils (Worrall et al. (2009); Worrall et al. (2015)). Future terrestrial N budgets at the national scale and at timescales of < 10 years should consider incorporation of these nutrient stores for effective management of N in the environment.

### 3.3.2 Targeting catchment management: From national to catchment scale

The approach adopted in this study is also likely to be beneficial for high-level targeting of catchment management activities at a wide range of scales. For example, Figure 4 illustrates that legacy nitrate in the vadose zone at a national scale in England and Wales is dominated by the Chalk. Figure 5 shows at a regional scale there a substantial historical mass of nitrate in the unsaturated zone of the Chalk of southern England. At the catchment scale, nitrate mass is concentrated in interfluvial areas where travel times are long due to thick vadose zones.

Environmental managers should take into account this mass when considering the implementation of catchment mitigation measures in attempts to improve groundwater, surface water and ecological quality. These measures typically consist of changes to agricultural practices through on-farm approaches (Zhang et al. 2012) and larger scale interventions such as nitrate vulnerable zones (Johnson et al. 2007). At the national scale, assessing where there is significant vadose zone N storage would be useful in setting timescales and objectives for improvements in waterbody environmental status. The approach used in this study can help managers understand whether such improvements due to catchment measures are likely to be delayed by the flux of legacy N stored in the vadose zone to groundwater and surface water.

The approach can also be used at the basin and catchment scale, although estimates of vadose zone N storage should be reviewed in the context of site and catchment scale groundwater conceptual models (Allen et al. 2014). As detailed in section 3.2, site-scale outputs of the

modelling approach presented here should be treated with caution, particularly in complex hydrogeological settings such as the Permo-Triassic Sandstones. Other forms and sources of reactive nitrogen should also be taken into consideration depending on the overlying land use. In order to maximise the benefits to stakeholders it is suggested that the approach presented here should be integrated with outputs from existing flow and transport models for the saturated zone. This could include public water supply borehole capture zones (e.g. Wellhead Protection Areas (United States Environmental Protection Agency 2014) and Source Protection Zones (Environment Agency 2014)) and flow paths to groundwater dependent terrestrial ecosystems (e.g. Batelaan et al. (2003)). Having identified environmental receptors and potential polluting land uses, the vadose zone N mass can be helpful in assessing whether catchment measures are likely to result in improvements in water quality and the likely timescales for these changes. Without proper consideration of legacy nitrate in the vadose zone and an understanding of saturated zone flow pathways, expectations of these measures to improve water quality may be unrealistic.

Such measures have been implemented to meet recent environmental legislation such as the Water Framework Directive (WFD) (European Union 2000). However, it has been widely acknowledged that WFD targets may not be met due to both socio-economic and hydrogeological delays (Cherry et al. 2008). The approach used in this study can show where vadose zone nitrate storage due to hydrogeological delays is likely to be most important, and consequently where it may be challenging to meet environmental objectives and policy targets. The methodology has the potential to be implemented across other countries in Europe implementing the Water Framework Directive and also internationally in areas where new environmental pollution targets have been set such as China (He et al. (2013); (Yang (2014)).

### 3.3.3 Vadose zone nitrate storage: A global outlook

At the global scale, transient vadose zone storage in nitrogen budgets is likely to be important. To illustrate this and the importance of the approach detailed here internationally, we briefly upscale our methodology to the USA. Based on mapping in Figure 1, we estimate the area of land in the USA where vadose zones are thicker than 20 m and cropland is greater than 40% total land use to be approximately 860,000 km<sup>2</sup>. These areas have an average vadose zone thickness of approximately 35 m (based on Fan et al. (2013)). Using these estimates with a vadose zone velocity of 1 m/year and the nitrate input function shown in Figure 3 (a) converted to kg N/ km<sup>2</sup> and scaled to 40% of the European input (based on (van Grinsven et al. 2015)), we estimate a peak vadose zone nitrate mass for the USA of 29,000 kt N in 2001.

This first approximation of vadose zone nitrate storage for the USA is likely to be highly uncertain but highlights the importance of this storage globally. The method we present here is generic and conceptually simple, with the most complex aspects of the approach associated with the input data. Recent global scale work on depth to groundwater (Fan et al. 2013), groundwater recharge (Döll et al. 2014) and soil N budgets (Bouwman et al. 2013) should allow for the first global estimates of transient vadose zone nitrate storage to be derived. It is suggested that the approach could be particularly useful in areas where thick vadose zones are present above major aquifers. By doing this future N budgets are likely to be more accurate, enabling more informed management decisions to be made regarding groundwater quality and terrestrial and marine aquatic ecosystems.

## 4 Conclusions

This study has presented a generic approach to derive the storage of nitrate in the vadose zone above aquifers at the national scale, validated against observed porewater data and previous basis scale modelling approaches. The peak total mass in England and Wales in 2008 is estimated as 1400 kt N (range 800 to >1700 from sensitivity analysis) which is approximately 2.5 to 6 times greater than previous approximations for the saturated zone (300 kt N). The majority of this mass (>70%) is within the Chalk. This supports the hypothesis that the subsurface is an important terrestrial N store. The methodology is a first step in reducing the uncertainty in national scale N budgets. In conjunction with saturated zone flow model outputs, the methodology can assist environmental managers and policymakers in decision making with regards to national and regional scale catchment mitigation measures to improve water quality. Vadose zone N storage is likely to be an international issue and it is suggested that recently published work on depth to groundwater, recharge and soil budgets could be used to derive a first global estimate of this storage.

## 5 Acknowledgements

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Accepted Article

Table 1: Mean unsaturated zone velocities for moderate and highly productive aquifers used in the model. Observed velocity ranges for the Chalk, Limestone and Sandstone are derived from Chilton and Foster (1991).

| Class                            | Formation  | Unsaturated zone velocity (m/year) |      |
|----------------------------------|--|------------------------------------|------|
|                                  |  | Range                              | Mean |
| Fractured aquifers               | White Chalk  | 0.3 - 1.4                          | 0.76 |
|                                  | Grey Chalk   |                                    | 0.9  |
|                                  | Oolitic Limestone                                    | 0.6 - 2.5                          | 1.1  |
|                                  | Other Karstic formations                             |                                    | 10   |
|                                  | Layered Mesozoic formations                          |                                    | 1    |
|                                  | Palaeozoic formations, igneous and metamorphic rocks |                                    | 1    |
| Aquifers with intergranular flow | Sherwood Sandstone                                   | 0.6 - 1.3                          | 1.06 |
|                                  | Sands  |                                    | 3    |
|                                  | Silts  |                                    | 0.3  |

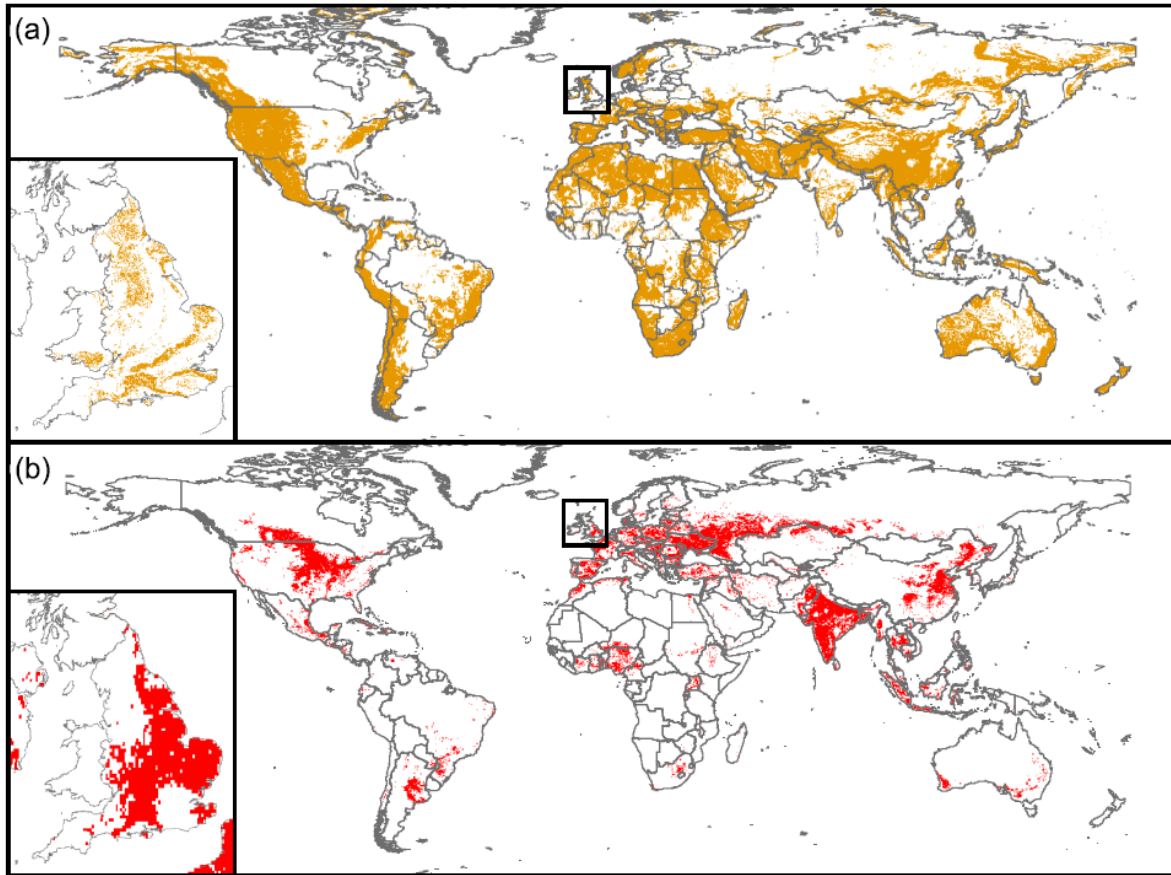


Figure 1: (a) Areas where depth to groundwater is estimated to be  $> 20$  m. From Fan et al. (2013). Reprinted with permission from AAAS. (b) Areas where proportion of cropland is  $> 40\%$  (reproduced after Ramankutty et al. (2010)).

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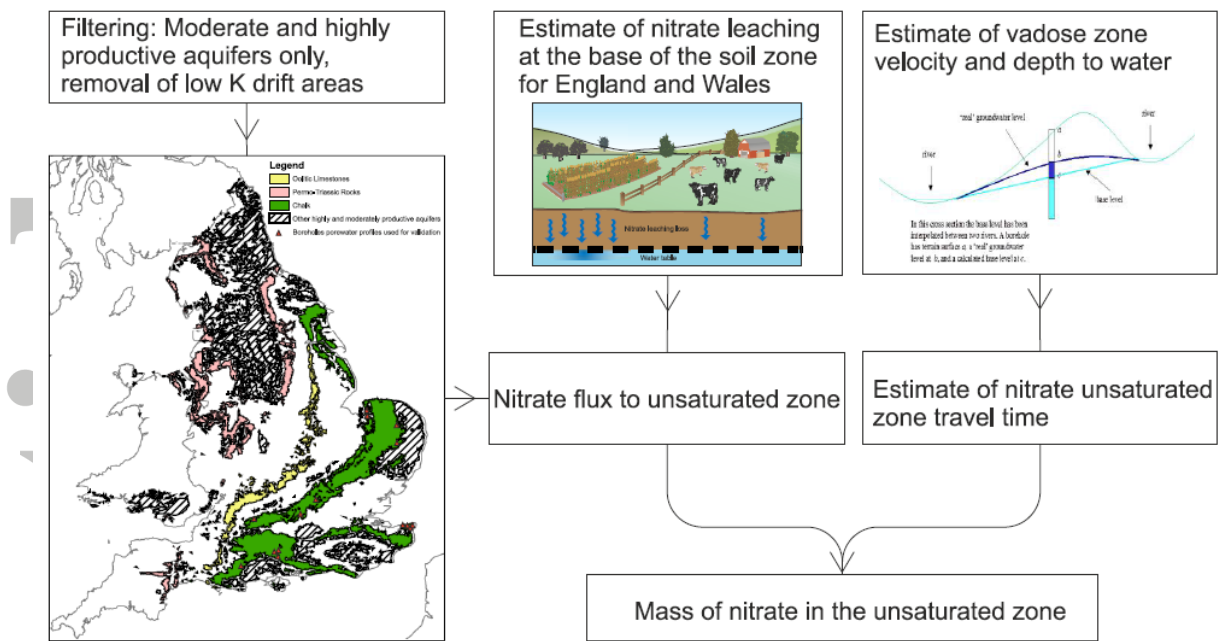


Figure 2: Methodology used to derive the mass of nitrate in the vadose zone in England and Wales. Based upon 1:625,000 scale digital hydrogeological mapping, British Geological Survey © NERC. Depth to water model reproduced after (Wang et al. (2012)).

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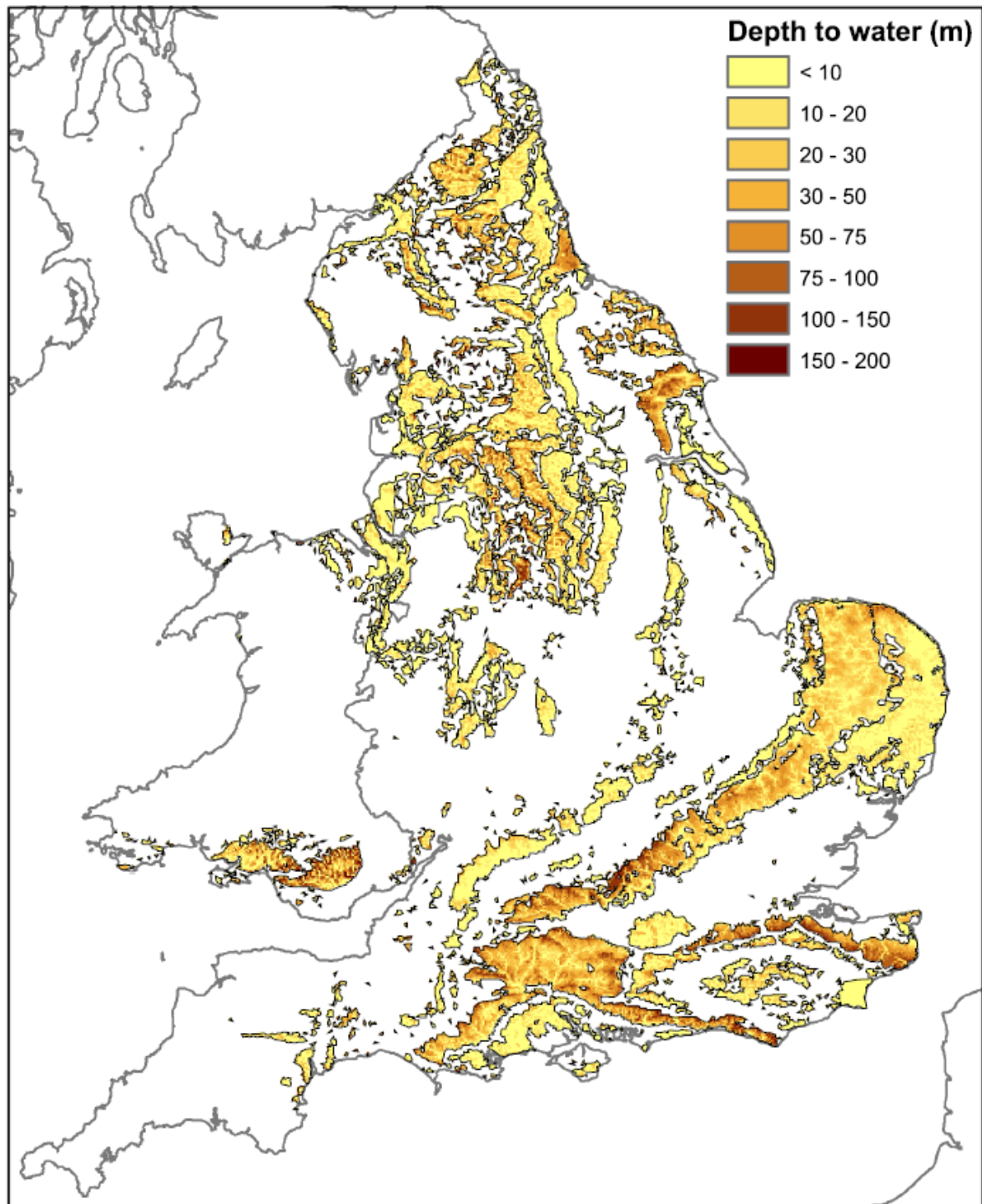


Figure 3: Estimates of depth to water derived from the River Base Level model for moderate and high productive aquifers. Based upon 1:625,000 scale digital hydrogeological mapping, British Geological Survey © NERC.

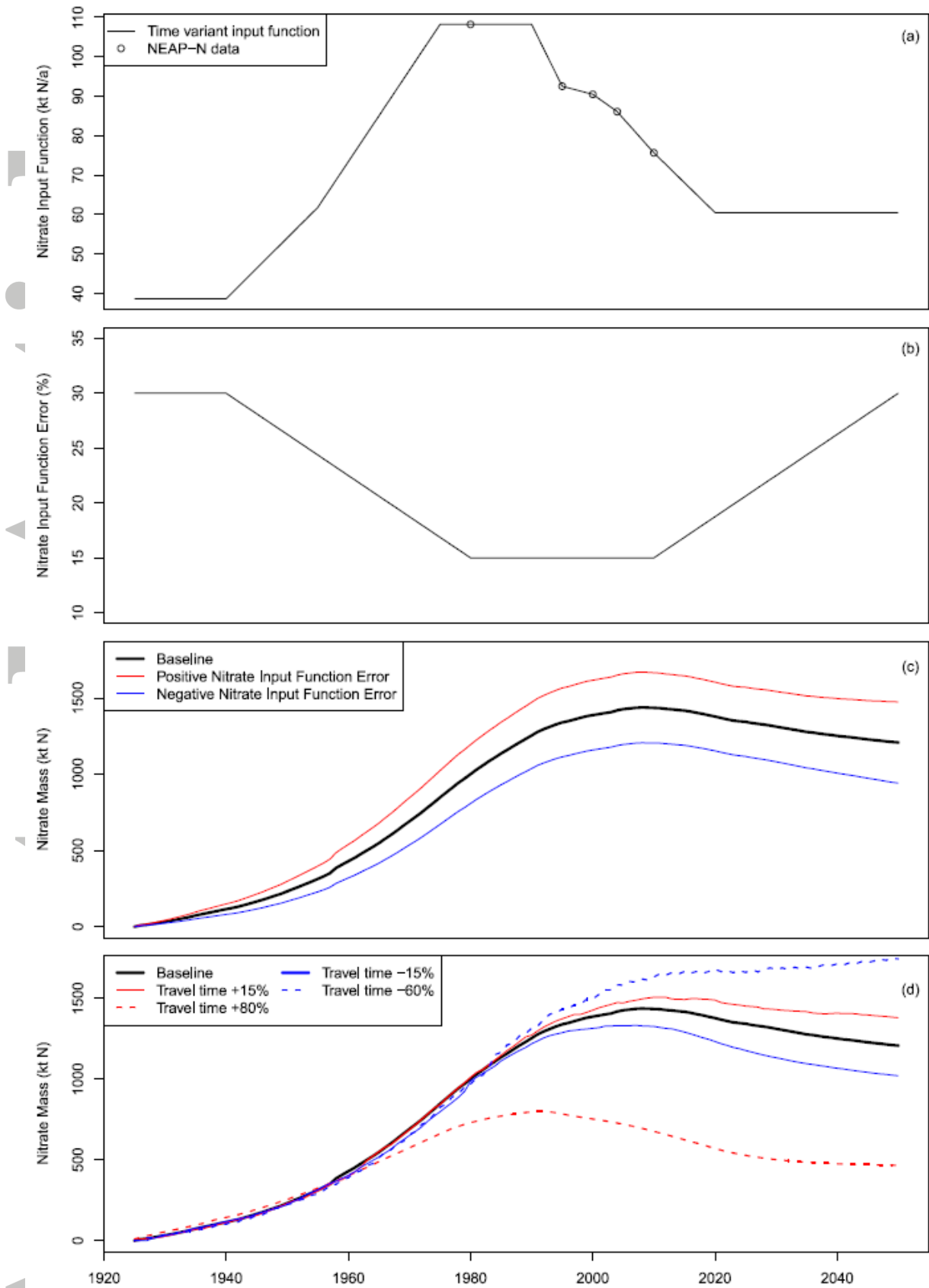


Figure 4: (a) Time variant nitrate input function, (b) nitrate input function error, (c) vadose zone nitrate mass considering input function uncertainty and (d) vadose zone nitrate mass considering travel time uncertainty.

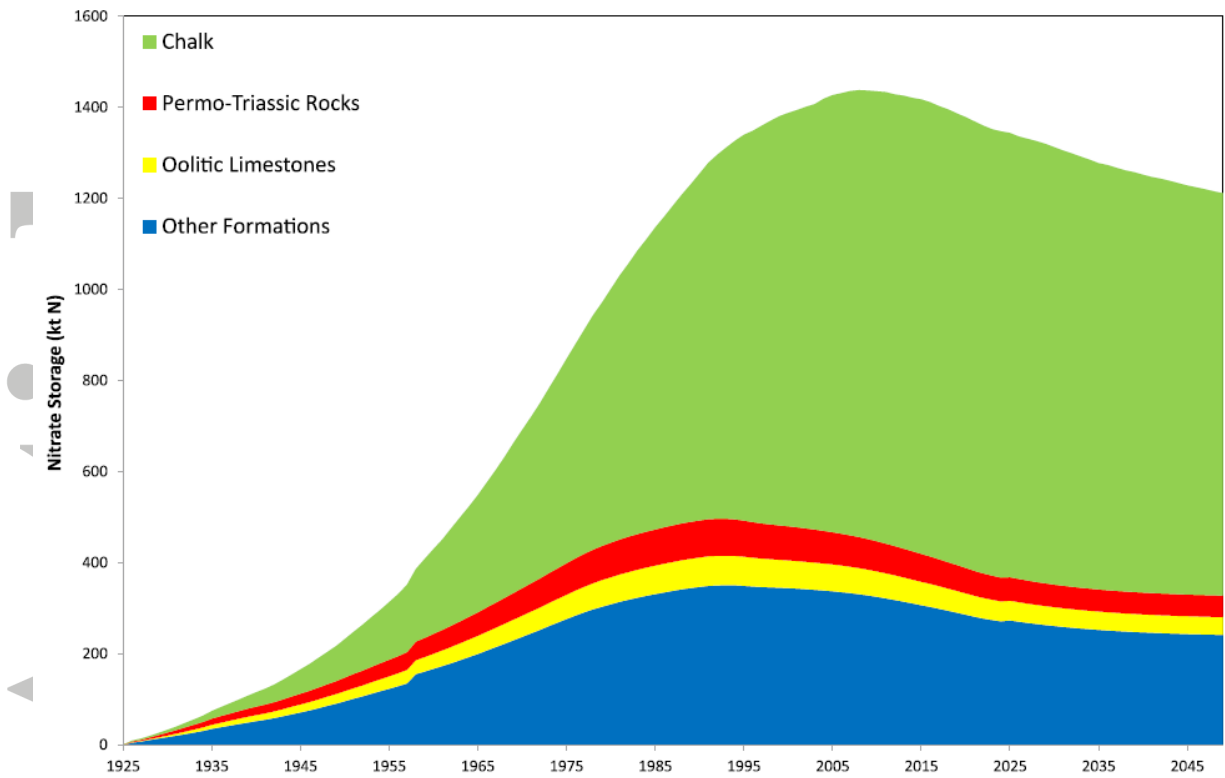


Figure 5: Change in vadose zone nitrate storage for 1925 – 2050 for moderate and highly productive aquifers.

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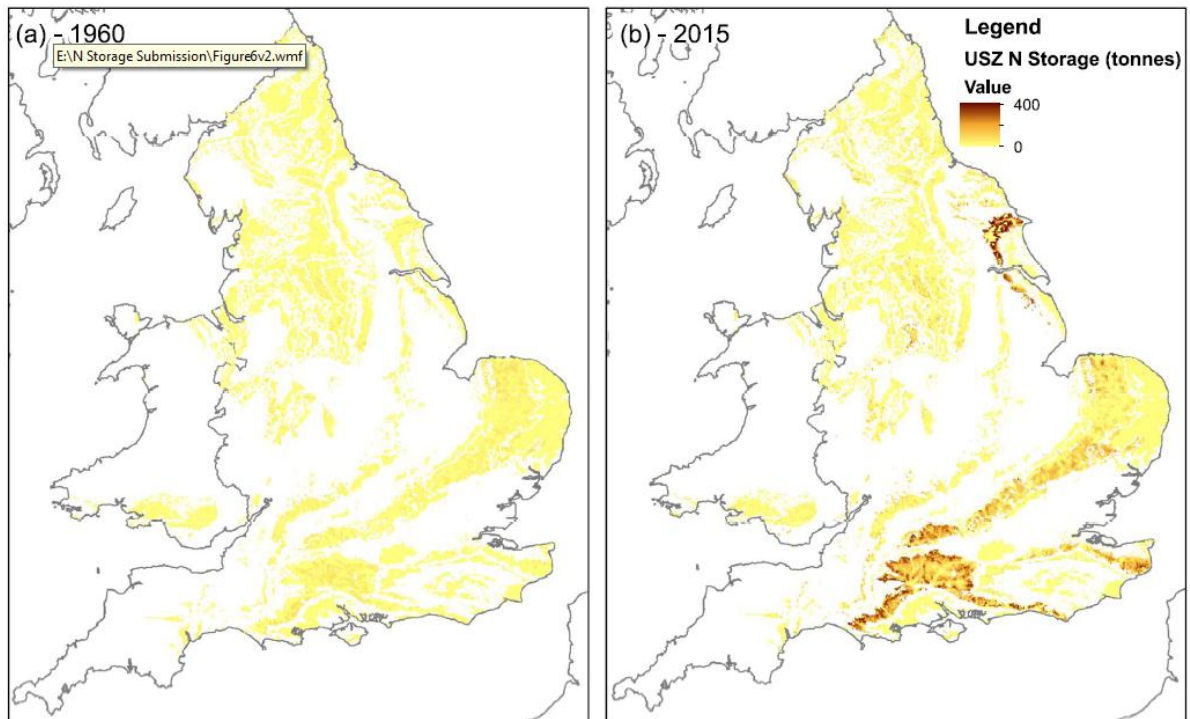


Figure 6: Spatial distribution of total vadose zone nitrate mass (as tonnes N per 1 km grid cell) in England and Wales in (a) 1960 and (b) 2015.

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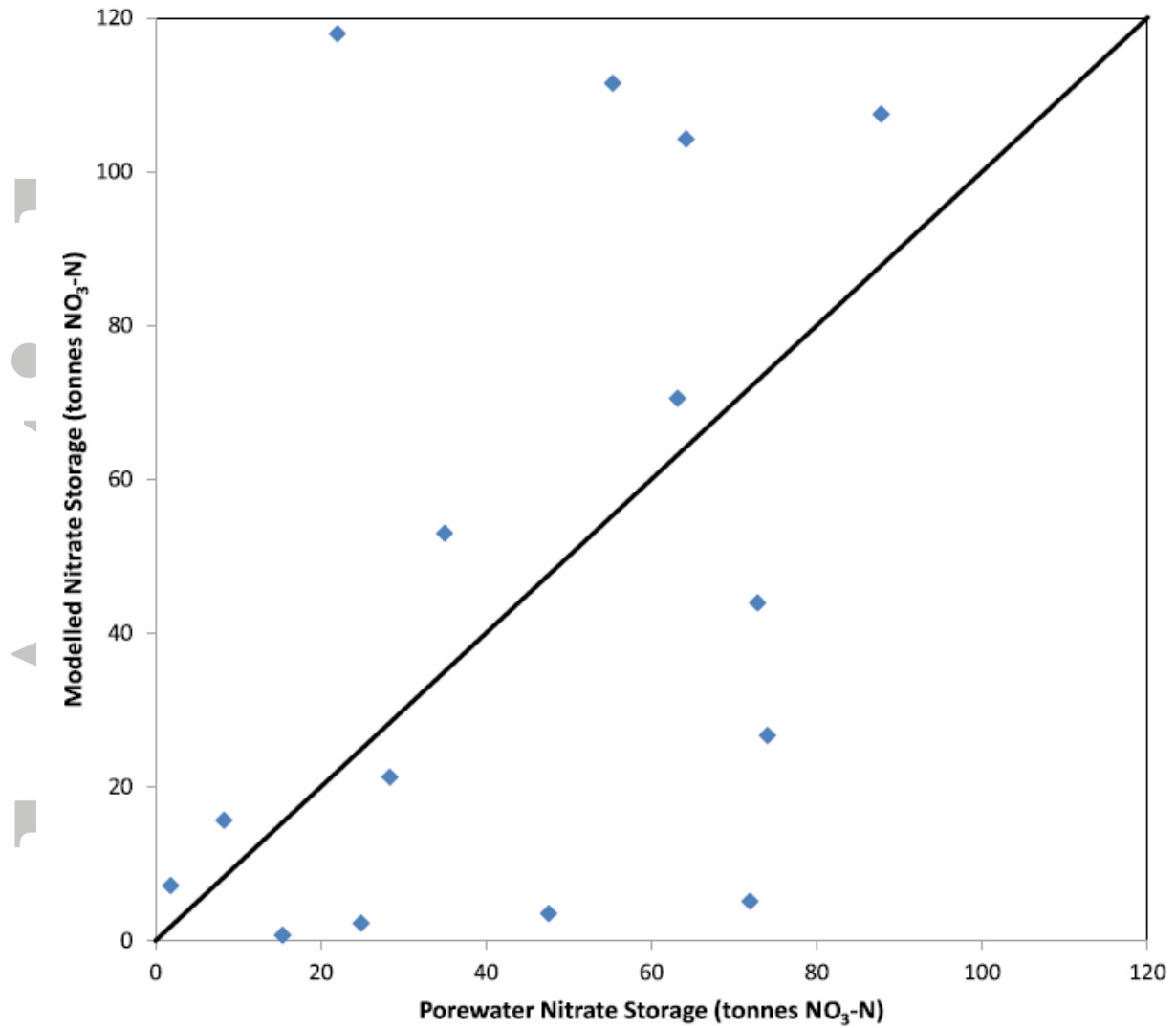


Figure 7: Nitrate storage in the vadose zone (tonnes NO<sub>3</sub>-N) for 1 km grid cells as derived from the model and observed porewater profiles for 15 borehole sites.

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