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A catchment-scale method to simulating the impact of historical nitrate loading from agricultural land on the nitrate-concentration trends in the sandstone aquifers in the Eden Valley, UK

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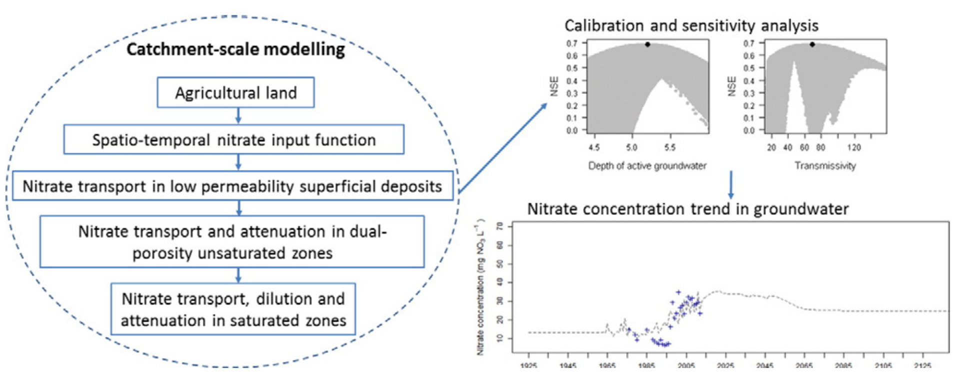
HIGHLIGHTS

- An approach to modelling groundwater nitrate at the catchment scale is presented.
- It considers nitrate transport in glacial till and dual-porosity unsaturated zones.
- The impact of historical nitrate loading on groundwater quality is better understood.
- The modelled results are valuable for evaluating the nitrate legacy issue.
- The method is transferable and requires a modest parameterisation.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrate water pollution, which is mainly caused by agricultural activities, remains an international problem. It can cause serious long-term environmental and human health issues due to nitrate time-lag in the groundwater system. However, the nitrate subsurface legacy issue has rarely been considered in environmental water management. We have developed a simple catchment-scale approach to investigate the impact of historical nitrate loading from agricultural land on the nitrate-concentration trends in sandstones, which represent major aquifers in the Eden Valley, UK. The model developed considers the spatio-temporal nitrate loading, low permeability superficial deposits, dual-porosity unsaturated zones, and nitrate dilution in aquifers. Monte Carlo simulations were undertaken to analyse parameter sensitivity and calibrate the model using observed datasets. Time series of annual average nitrate concentrations from 1925 to 2150 were generated for four aquifer zones in the study area. The results show that the nitrate concentrations in 'St Bees Sandstones', 'silicified Penrith Sandstones', and 'non-silicified Penrith Sandstones' keep rising or stay high before declining to stable levels, whilst that in 'interbedded Brockram Penrith Sandstones' will level off after a slight decrease. This study can help policymakers better understand local nitrate-legacy issues. It also provides a framework for informing the long-term impact and timescale of different scenarios introduced to deliver water-quality compliance. This model requires relatively modest parameterisation and is readily transferable to other areas.

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1. Introduction

Excessive nitrate concentrations in water bodies can cause serious long-term environmental issues and threaten both economy and human health (Bryan, 2006; Defra, 2002, 2006a; Pretty et al., 2000; Thorburn et al., 2003; Ward, 2009). Nitrate in freshwater remains an international problem (European Environment Agency, 2000, 2007; Hinkle et al., 2007; Rivett et al., 2008; Sebilo et al., 2006; Thorburn et al., 2003; Torrecilla et al., 2005; Wang et al., 2012a; Wang and Yang, 2008; Yang and Wang, 2010). Elevated nitrate concentrations in groundwater are found across Europe. For example, the European Environment Agency (2007) reported that the proportion of groundwater bodies with mean nitrate concentration >25 mg L^{-1} (as NO_3) in 2003 were 80% in Spain, 50% in the UK, 36% in Germany, 34% in France and 32% in Italy. Despite efforts made under the EU Water Framework Directive (Directive 2000/60/EC) by 2015 to improve water quality, there is still a continuous decline in freshwater quality in the UK. For example, nitrate concentrations are exceeding the EU drinking water standard (50 mg L^{-1} (as NO_3)) and have a rising trend in many rivers (Burt et al., 2008, 2011) and aquifers (Smith, 2005; Stuart et al., 2007). It is estimated that about 60% of all groundwater bodies in England will fail to achieve good status by 2015 (Defra, 2006b).

Agricultural land is the major source of nitrate water pollution (Ferrier et al., 2004; Thorburn et al., 2003; Torrecilla et al., 2005). Point source discharges have been estimated as contributing <1% of the total nitrate flux to groundwater in the UK (Sutton et al., 2011). Agricultural yields are increased by the addition of nitrogen (N) in fertilisers, but this leads to nitrate leaching into freshwaters (groundwater and surface water). Nitrate concentrations in groundwater beneath agricultural land can be several to a hundred-fold higher than that under semi-natural vegetation (Nolan and Stoner, 2000). During the last century, the pools and fluxes of N in UK ecosystems have been transformed mainly by the fertiliser-based intensification of agriculture (Burt et al., 2011). In response to this growing European-wide problem, the European Commission implemented the Nitrates Directive (91/676/EEC) to focus on delivering measures to address agricultural sources of nitrate.

In the freshwater cycle, nitrate leached from soil is subsequently transported by surface runoff to reach streams or by infiltration into the unsaturated zone (USZ – from the base of the soil layer to the water table). Nitrate entering the groundwater system is then slowly transported through the USZs downwards to groundwater in aquifers. Recent research suggests that it could take decades for leached nitrate to discharge into freshwaters due to the nitrate time-lag in the USZs and saturated zones (Ascott et al., in press; Burt et al., 2011; Howden et al., 2011; Jackson et al., 2007; Wang et al., 2012a, 2016). This may cause a time-lag between the loading of nitrate from agricultural land and the change of nitrate concentrations in groundwater and surface water. For example, Dautrebande et al. (1996) found that the anticipated decrease in nitrate concentrations in the aquifer following the reduction of nitrate loading from agricultural land was not observed. However, current environmental water management strategies rarely consider the nitrate time-lag in the groundwater system (Burt et al., 2011; Collins et al., 2009).

The Eden catchment, Cumbria, UK (Fig. 1) is a largely rural area with its main sources of income being agriculture and tourism (Butcher et al., 2003; Daily et al., 2006). The Environment Agency's groundwater monitoring data show that some groundwater exceeds the limit of 50 mg L^{-1} (as NO_3) in the Eden Valley (Butcher et al., 2005). In recent years, the increasingly intensive farming activities, such as the increased application of slurry to the grazed grassland, have added more pressures on water quality in the area (Butcher et al., 2003, 2005). Efforts have been made to tackle agricultural diffuse groundwater pollution in the area. For example, the River Eden Demonstration Test Catchment (DTC) project (McGonigle et al., 2014) was funded by the Department for Environment, Food & Rural Affairs (Defra) to assess if it is possible to cost-effectively mitigate diffuse pollution from agriculture whilst maintaining agricultural productivity (http://www.edendtc.org.uk/). The Environment Agency defined Groundwater Source Protection Zones (SPZs) (http://apps.environment-agency.gov.uk/wiyby/37833.aspx) in the Eden Valley to set up pollution prevention measures and to monitor the activities of potential polluters nearby. However, without evidence of the impact of nitrate-legacy issues on groundwater quality, it is difficult to evaluate the effectiveness of existing measures or to decide whether additional or alternative measures are necessary. So a key question for nitrate-water-pollution management in the area is how long it will take for nitrate concentrations in groundwater to peak and then stabilise at an acceptable level (<50 mg L^{-1} (as NO_3)) in response to historical and future land-management measures. Therefore, it is necessary to investigate the impacts of historical nitrate loading from agricultural land on the changing trends in nitrate concentrations for the major aquifers in the Eden Valley.

Wang et al. (2013) studied the nitrate time-lag in the sandstone USZ of the Eden Valley taking the Bowscar SPZ as an example. Outside of the study area, efforts have been made to simulate nitrate transport in the USZ and saturated zone at the catchment scale. For example, Mathias et al. (2006) used Richards' equation (a nonlinear partial differential equation) to explicitly represents fracture–matrix transfer for both water and solute in the Chalk, which is a soft and porous limestone. Price and Andersson (2014) combined a simple USZ nitrate transport model with fully-distributed complex groundwater flow and transport models to study nitrate transport in the Chalk. These catchment specific models, which require a wide range of parameters and are computationally-demanding, are of limited value for application to catchment-scale modelling for nitrate management. There is a need to develop a simple but still conceptually feasible model suitable for simulating long-term trend of nitrate concentration in groundwater at the catchment scale. In addition, the nitrate transport in low permeability superficial deposits has rarely been considered in existing nitrate subsurface models. Low permeability superficial deposits, however, overlay about 20.7% of the major aquifers in England and Wales (BGS, 2015a, 2015b), and 54% of the Permo-Triassic sandstones in the Eden Valley (Section 2.1).

Based on a simple catchment-scale model developed in this study, the impact of historical nitrate loading from agricultural land on the nitrate-concentration trends in sandstones of the Eden Valley was investigated. By considering the major nitrate processes in the groundwater system, this model introduces nitrate transport in low permeability superficial deposits and in both the intergranular matrix and fractures in the USZs. Nitrate transport and dilution in the saturated zone were also simulated using a simplified hydrological conceptual model.

2. Methodologies

2.1. Site setting

The Eden Catchment (2308 km^2) lies between the highlands of the Pennines to the east and the English Lake District to the west. The River Eden, which is the main river in the catchment, runs from its headwaters in the Pennines to the Solway Firth in the north-west. The area is mainly covered by managed grassland, arable land and semi-natural vegetation.

Carboniferous limestones fringe much of the Eden Catchment (Fig. 1) and have very low porosity and permeability, thus making a negligible contribution to total groundwater flow. Therefore, their storage and permeability rely almost entirely on fissure size, extent and degree of interconnection (Allen et al., 2010). They only constitute an aquifer due to the presence of a secondary network of solution-enlarged fractures and joints (Jones et al., 2000). Ordovician and Silurian intrusion rocks form the uplands of the Lake District and can also be found in the south-east of the catchment (Fig. 1).

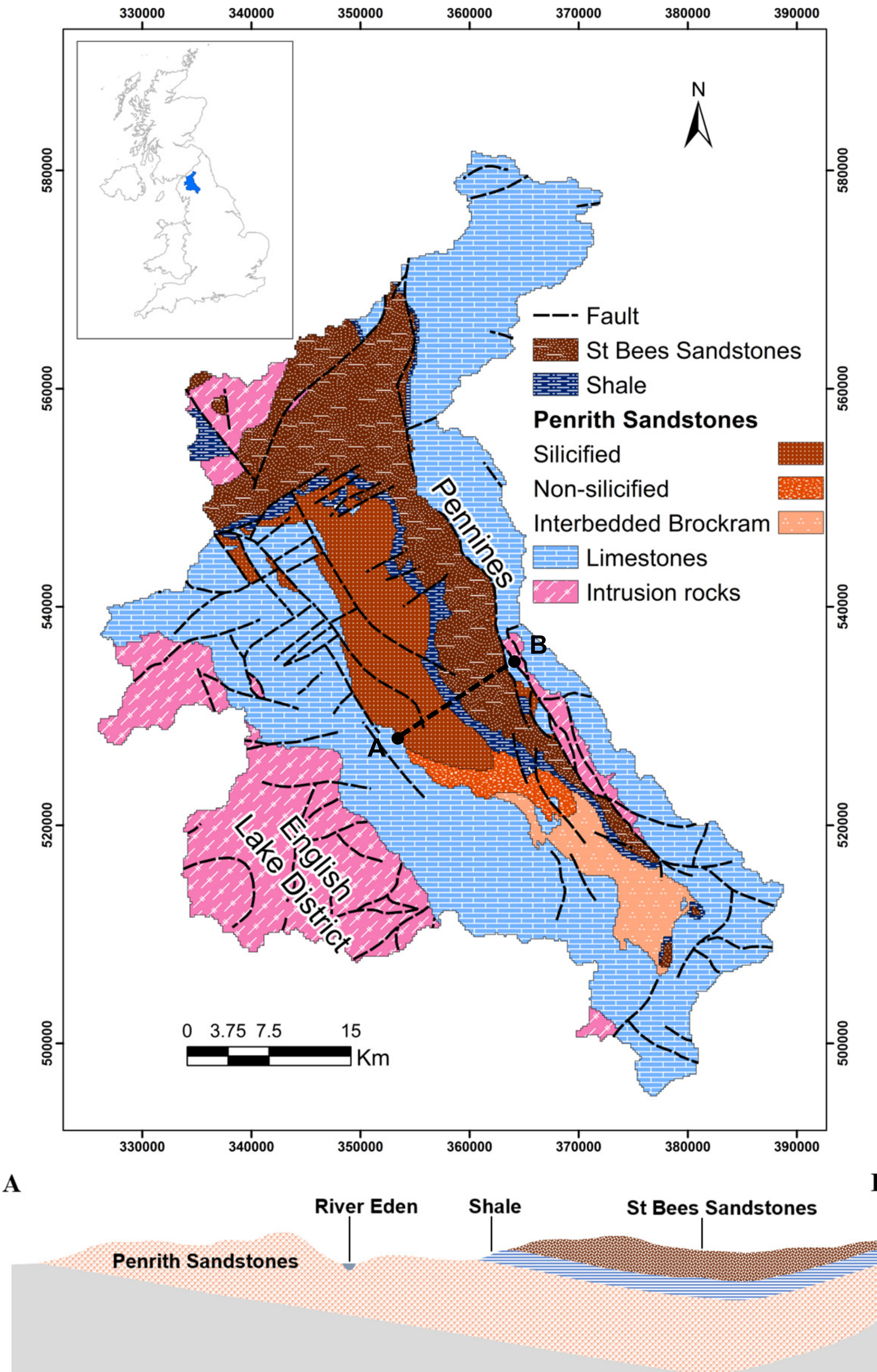

Fig. 1. Bedrock geology of the Eden Catchment, UK and a schematic geological cross-section. Derived from BGS 1:250 000 bedrock geological map (BGS, 2015a).

The Eden Valley in the central part of the catchment consists of thick sequences of the Permo-Triassic sandstones, i.e. St Bees Sandstones and Penrith Sandstones (Fig. 1). The early Permian Penrith Sandstone Formation (up to 900 m thick) dips gently eastwards and is principally red-brown to brick red in colour with well-rounded, well-sorted and medium to coarse grains (Allen et al., 2010; Butcher et al., 2003). According to Waugh (1970), these Penrith Sandstones, which were deposited as barchans sand dunes in a hot and arid desert environment, can be divided into three zones, i.e. 'silicified Penrith Sandstones', 'non-silicified Penrith Sandstones' and 'interbedded Brockram Penrith Sandstones' (Fig. 1). The sandstones in the northern part of the formation are tightly cemented with secondary quartz, occurring as overgrowths of optically continuous, bipyramidal quartz crystals around detrital grains. The sandstones in the rest of the formation are not silicified, but the sandstones in the southern part are interbedded with calcite-cemented alluvial fan breccias (brockrams). The study of Lafare et al. (2015) showed that the borehole hydrographs within the 'silicified' zone are characterised by small amplitudes of seasonality in groundwater levels. This indicates that silicified sandstones prevent the aquifer responding efficiently to localised recharge. However, the non-silicified sandstones in the middle and southern parts of the Penrith Sandstone show a greater relative variability of the seasonal component.

The Eden Shale Formation mainly consists of mudstone and siltstone and is an aquitard that confines the eastern part of the Penrith Sandstone aquifer. St Bees Sandstone formation conformably overlies the Eden Shale Formation and occupies the axial part of the Eden Valley syncline. The formation consists of very fine to fine-grained, indurated sandstone (Allen et al., 2010). The borehole hydrographs in the St Bees Sandstones showed that they are more homogeneous than the Penrith Sandstones and tend to act as one aquifer unit (Lafare et al., 2015). This study focused on these Permo-Triassic sandstones that form the major aquifers in the catchment. The ranges of transmissivity, storage coefficient and porosity of the Permo-Triassic sandstones are 8–3300 (m^2 day^{-1}), 4.5×10^{-8}–0.12 and 5–35 (%) respectively in the study area (Allen et al., 1997).

>75% of the bedrocks in the Eden Catchment are covered by Quaternary superficial deposits (Butcher et al., 2003, 2008, 2009). Only the Lake District and escarpment of the Northern Pennines have extensive areas of exposed bedrock. Glacial till is the most extensive deposit in the catchment. It is typically a red-brown, stiff, silty sandy clay to a friable clayey sand with pockets and lenses of medium and fine sand and gravel and cobble grade clasts (Butcher et al., 2009). The presence of glacial till has the potential to cause increased surface runoff and reduced groundwater recharge (Butcher et al., 2009; Jones et al., 2000). According to BGS 1:250 000 bedrock and superficial geological maps (BGS, 2015a, 2015b), glacial till covers about 46% of the Eden Catchment and 54% of the Permo-Triassic sandstones (679 km^2) in the Eden Valley.

2.2. The nitrate time bomb model (NTB)

The NTB model was initially developed to simulate nitrate transport in the USZs and to estimate the time and the amount of historical nitrate arriving at the water table at the national scale (Wang et al., 2012a). It requires the datasets of a uniform nitrate-input-function, estimated USZ thickness, and lithologically-dependent rates of nitrate transport in the USZs. More details about the NTB model are provided by Wang et al. (2012a). However, the NTB model was extended in the following ways to simulate the average nitrate concentration in an aquifer zone for the catchment-scale study.

2.3. Spatio-temporal nitrate loading from agricultural land

The single nitrate-input-function derived in the study of Wang et al. (2012a) has been validated using mean pore-water nitrate concentrations from 300 cored boreholes across the UK in the British Geological Survey (BGS) database (Stuart, 2005). It reflects the trend in historical and future agricultural activities from 1925 to 2050 (Wang et al., 2012a). For example, a rapid rise of 1.5 kg N ha^{-1} $year^{-1}$ (1955–1975) nitrogen loading was caused by increases in the use of chemical-based fertilisers to meet the needs of an expanding population. The nitrate loading in the UK peaked in 1980s and then started to decline as a result of restrictions on fertiliser application in water resource management. It was assumed that there would be 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} loading rate (Wang et al., 2012a). However, this single-input-function only generated a national average, rather than a spatially distributed input reflecting historical agricultural activities across a region. Therefore, a spatio-temporal nitrate-input-function was introduced for this catchment-scale study to represent nitrate loading across the Eden Valley from 1925 to 2050.

The NEAP-N model (Anthony et al., 1996; Environment Agency, 2007; Lord and Anthony, 2000), which has been used for policy and management in the UK, predicts the total annual nitrate loss from the agricultural land across England and Wales. It assigns nitrate-loss-potential coefficients to each crop type, grassland type and livestock categories within the June Agricultural Census data to represent the short- and long-term increase in nitrate leaching risk associated with cropping, the keeping of livestock and the spreading of manures. The NEAP-N data in 1980, 1995, 2000, 2004 and 2010 from the Department for Environment, Food & Rural Affairs were used in this study. The trend of nitrate loading from the single nitrate-input-function was used to interpolate and extrapolate the data for the years other than the NEAP-N data years. The section of results shows some examples of the spatio-temporal nitrate-input-functions derived in this study.

2.4. Nitrate transport and dilution in the groundwater system

A simplified hydrogeological conceptual model was developed to simulate nitrate transport and dilution processes in the groundwater system at the catchment scale (Fig. 2) as follows:

- Water and nitrate are transported by intergranular seepage through the matrix and by possible fast fracture flow in the USZs
- Groundwater recharge supplies water to the Permo-Triassic sandstones as an input
- The thickness of glacial till affects the amount and timing of recharge and nitrate entering the groundwater system
- Groundwater in the Permo-Triassic sandstones flows out of the Eden Valley via rivers in the form of baseflow as an output
- Groundwater is disconnected from rivers where glacial till is present
- The year by year total volume of groundwater (Vol_{total}) for an aquifer in a simulation year is the sum of the groundwater background volume ($Vol_{background}$) and the annual groundwater recharge reaching the water table ($Vol_{recharge}$). Groundwater recharge and baseflow reach dynamic equilibrium whereby the amount of recharge equals that of baseflow in a simulation year
- Nitrate entering the Permo-Triassic sandstones is diluted throughout the Vol_{total} in a simulation year
- The velocity of nitrate transport in the Permo-Triassic sandstones is a function of aquifer permeability, hydraulic gradient and porosity
- The transport length for groundwater and nitrate can be simplified as the three-dimensional (3D) distance between the location of recharge and nitrate reaching the water table and their nearest discharge point on the river network.

More details about nitrate transport and dilution in the groundwater system will be described in the following sub-sections.

2.4.1. Nitrate transport in low permeability glacial till

Low permeability superficial deposits not only control the transfer of recharge and soluble pollutant to underlying aquifers but also affect the

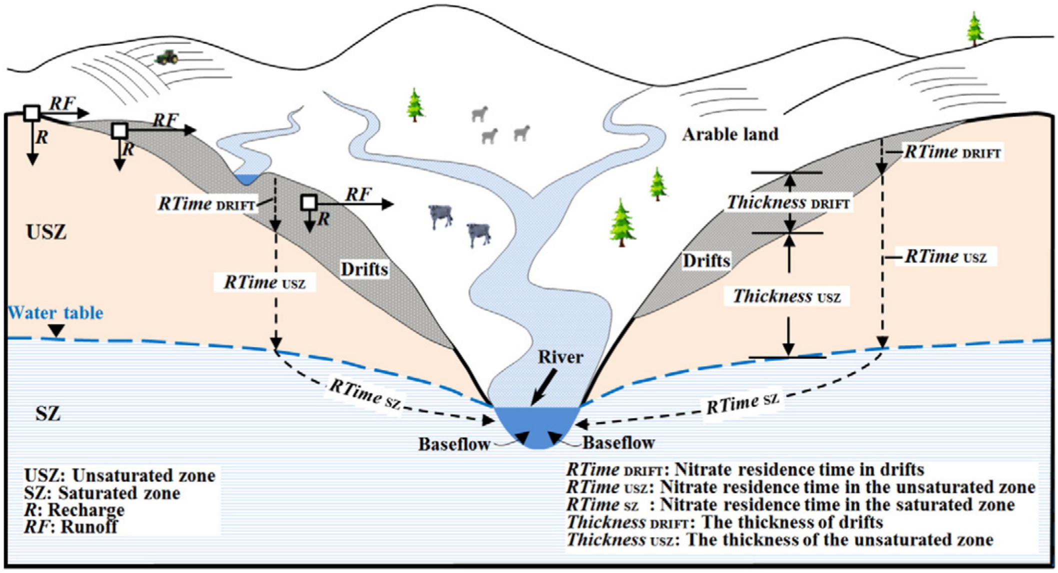

Fig. 2. The conceptualisation of nitrate transport in glacial till, unsaturated zones and saturated zones.

locations of groundwater discharge to surface waters (e.g. Butcher et al., 2008, 2009). It was assumed in the original NTB model (Wang et al., 2012a) that the presence of low permeability superficial deposits stops recharge and nitrate entering aquifers. This simplification is sensible to reduce the number of parameters for a national-scale study. However, field experiments in the Eden catchment undertaken by Butcher et al. (2009) showed that the thickness of low permeability glacial till affects the amount of water and nitrate entering the groundwater system. It was found that glacial till can be relatively permeable when its thickness is <2 m, within which the superficial deposits are likely to be weathered and fractured. Therefore, the spatial distribution of the thickness of glacial till exerts a strong influence on groundwater recharge processes to the underlying USZs in the study area (Butcher et al., 2009). In the study area, more than half of the Permo-Triassic sandstones are overlain by glacial till as described above. According to Lawley and Garcia-Bajo (2009), about 59% of glacial till has a thickness <2 m. Therefore, it is important to consider the water and nitrate transport in glacial till for this catchment-scale study, rather than have the same assumption as the national-scale study of Wang et al. (2012a).

The thicker the glacial till, the less water can transport through glacial till thus reducing recharge rates; and the reduction of recharge will be diverted to surface runoff (Butcher et al., 2008, 2009; Jones et al., 2000). The following sub-section describes how the reduction of recharge is estimated.

2.4.1.1. Estimating the reduction of recharge. A soil-water-balance model SLiM (Barkwith et al., 2015; Wang et al., 2012b) was used to estimate distributed recharge (1961–2011) in this study using the information on weather and catchment characteristics, such as topography, land-uses and baseflow index. Based on the BGS database of the spatial distribution of the thickness of superficial deposits (Lawley and Garcia-Bajo, 2009), glacial till was divided into five thickness classes, i.e., 0–2 m, 2–5 m, 5–10 m, 10–30 m, and >30 m. A parameter (*RRch*) was introduced into the soil-water-balance model to represent the reduction of recharge (percentage of the amount of recharge at the base of the soil that cannot enter the groundwater system) or the increase of runoff for five thickness classes of glacial till. Monte Carlo (MC) simulations were undertaken to calibrate the recharge model for this study. The parameter of reduction of recharge was randomly sampled within 0–100% for each thickness class; and the modelled results were compared with the surface component of observed river-flow data for 19 gauging stations in the study area. Scatter plots for *RRch* against the performance of the recharge model from MC simulations were produced to identify the reduction of recharge for each thickness class of glacial till. The results section (Section 4) provides more details. The reduction of recharge affects the amount of both water and nitrate entering the groundwater system as described below.

2.4.1.2. Estimating the amount of water and nitrate transport through glacial till. The presence of low permeability glacial till reduces the amount of water and nitrate entering the underlying unsaturated zones as mentioned above. Therefore, where the glacial till is present, the amount of nitrate entering the groundwater system can be expressed as:

$$M_{\mathrm{DRIFT},i}(t) = M_i(t - RTime_{\mathrm{DRIFT},i}) \cdot (1 - RRch_i/100) \tag{1}$$

$$RTime_{\mathrm{DRIFT},i} = \mathrm{Thickness}_{\mathrm{DRIFT},i}/V_{\mathrm{DRIFT},i} \tag{2}$$

where $M_{\mathrm{DRIFT},i}(t)$ (mg NO_3) is the amount of nitrate travelling through the glacial till into the USZs at cell i in the year of t; $RTime_{\mathrm{DRIFT},i}$ (year) is the nitrate-residence time in glacial till at cell i (Fig. 1); $M_i(t - RTime_{\mathrm{DRIFT},i})$ (mg NO_3) represents the amount of nitrate loading from the base of the soil at cell i in the year of $t - RTime_{\mathrm{DRIFT},i}$; $\mathrm{Thickness}_{\mathrm{DRIFT},i}$ is the thickness of glacial till at cell i (Fig. 2); $V_{\mathrm{DRIFT},i}$ (m year^{-1}) is the nitrate-transport velocity in glacial till; and $RRch_i$ (%) is the reduction of recharge at cell i where glacial till exists. $RRch_i$ was assigned to be zero where no glacial till is present in this study.

2.4.2. Nitrate-transport velocity in the Permo-Triassic sandstone USZ

The groundwater recharge rate, aquifer porosity and the storage coefficient are key factors affecting pollutant velocity of transport in the USZs (Leonard and Knisel, 1988). The spatially distributed nitrate velocity in the USZs and hence the residence time can be expressed as equations below (Rao and Davidson, 1985; Rao and Jessup, 1983):

$$V_{\mathrm{USZ},i} = \frac{q_i}{Sr_{\mathrm{aquifer}} \cdot Rf_{\mathrm{aquifer}}} \tag{3}$$

$$RTime_{\mathrm{USZ},i} = \mathrm{Thickness}_{\mathrm{USZ},i}/V_{\mathrm{USZ},i} \tag{4}$$

where $\mathrm{Thickness}_{\mathrm{USZ},i}$ is the USZ thickness at cell i (Fig. 2); $V_{\mathrm{USZ},i}$ (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 representing how much water remains in the rock after it is drained by gravity. $Sr_{aquifer}$ is the difference between porosity and specific yield of aquifers.

2.4.3. Groundwater available for nitrate dilution

Aquifers are discretised into equal-sized cells for numerical modelling purposes. The total volume of groundwater $Vol_{total}(t)$ (m^3) in a simulation year t can be expressed as:

$$Vol_{total}(t) = Vol_{background} + Vol_{recharge}(t) \tag{5}$$

$$Vol_{background} = \sum_{i=1}^{n} A_i \cdot D_{aquifer} \cdot Sy_{aquifer} \tag{6}$$

where A_i (m^2) is the area of the 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.

According to the 'piston-displacement' mechanism (Headworth, 1972; Price et al., 1993), water and nitrate are displaced downwards from the top of the USZs. Therefore, instead of travelling through the USZs, water and nitrate reaching the water table are displaced from the bottom of the USZs. This explains why observations show that the water table responds to recharge events at the surface on a time-scale of days or months, whilst the residence time for pollutant fluxes in the USZs is in the order of years (Headworth, 1972; Lee et al., 2006; Wang et al., 2012a).

In the USZs, water and nitrate could be transported through both the intergranular matrix and fractures in dual-porosity strata (Headworth, 1972; Jackson et al., 2007; Smith et al., 1970). The ratio of fracture flow (*RFF*) was introduced in this study to represent the amount of water that is transported through the fractures in the USZs, thereby having a limited time-lag. Therefore, the volume of recharge entering an aquifer $Vol_{recharge}(t)$ (m^3) in the simulation year t can be represented as:

$$Vol_{recharge}(t) = \sum_{i=1}^{n} A_i \cdot \left[q_i\left(t - Rp_q\right) \cdot (1 - RFF/100) + q_i(t) \cdot RFF/100\right] \tag{7}$$

where t is time (year); Rp_q (year) is the water-table-response time to rainfall events; RFF(%) is the percentage of fast flow travelling via fractures in the USZs; $q_i(t - Rp_q) \cdot (1 - RFF/100)$ (m $year^{-1}$) is the annual recharge that enters aquifers as piston flow at cell i at time $t - Rp_q$; and $q_i(t) \cdot RFF/100$represents the amount of water entering aquifers via fractures in the USZs in the year t.

According to the study of Lee et al. (2006), the value of $Rp_q$is controlled by several factors, such as the thickness of the USZs, moisture content and fractures in the USZs, and rainfall densities. The way of identifying Rp_qwill be described in the model construction section (Section 3.1).

2.4.4. The velocity of nitrate transport in aquifers

The average velocity of nitrate transport in an aquifer VS_{mean}(m $year^{-1}$) can be calculated using the equations:

$$VS_i = \frac{365 \cdot T_{aquifer} \cdot G_i}{D_{aquifer} \cdot \Phi_{aquifer}} \tag{8}$$

$$G_i = \frac{GWL_i - RL_i}{Dist_i} \tag{9}$$

$$VS_{mean} = \frac{\sum_{i=1}^{n} VS_i}{n} \tag{10}$$

where $T_{aquifer}$ (m^2 day^{-1}) is the transmissivity of the aquifer; G_i (—) and $Dist_i$ (m) are, respectively, the hydraulic gradient and horizontal distance between cell i and the nearest point where groundwater is discharged into the river; GWL_i (m) is the groundwater level for cell i; RL_i (m) is the river stage at the nearest river point to cell i; $D_{aquifer}$ (m) is the depth of active groundwater in an aquifer; $\Phi_{aquifer}$ is the porosity of an aquifer zone; VS_i (m $year^{-1}$) is velocity of nitrate transport for cell i; and n is the total number of modelling cells in the aquifer zone.

Eqs. (8)–(10) were used only when an aquifer cell does not overlap with a river cell. If aquifer cells spatially overlap with river cells, the nitrate travel time in them was assigned to be zero without using these equations.

2.4.5. Annual nitrate concentration in groundwater

Annual nitrate concentration $Con_{aquifer}(t)$ (mg L^{-1} (as NO_3)) for an aquifer in year t can be represented as:

$$Con_{aquifer}(t) = \frac{\sum_{i=1}^{n} M_{DRIFT,i}(t - RTime_{NONDRIFT,i}) \cdot (1 - ATT/100)}{Vol_{total} \cdot 1000} \tag{11}$$

$$RTime_{NONDRIFT,i} = RTime_{USZ,i} + RTime_{SZ,aquifer} \tag{12}$$

$$RTime_{SZ,aquifer} = \frac{\sum_{i=1}^{n} Dist_{3D,i}/VS_{mean}}{n} \tag{13}$$

where $M_{DRIFT,i}(t - RTime_{NONDRIFT,i})$ (mg NO_3) is the amount of nitrate loading from the base of glacial till into the USZs at cell i in the year of $t - RTime_{NONDRIFT,i}$; $RTime_{NONDRIFT,i}$ (year) is the residence time for nitrate to travel through the USZs and aquifers at cell i (Fig. 2); $RTime_{USZ,i}$ (year) is the nitrate-residence time at cell i in the USZs; $RTime_{SZ,aquifer}$ (year) is the average residence time for nitrate dilution and transport in the aquifer; $Dist_{3D,i}$ is the 3D distance between cell i and its nearest discharge point on a river; and ATT(%) is the attenuation factor representing the percentage of nitrate mass that is attenuated in the USZs. $ATT$was assigned to be zero in this study by assuming that nitrate is conservative in the groundwater system as described in the section of discussion.

3. Modelling procedure

3.1. Model construction and data

Based on BGS 1:250 000 bedrock geological map (BGS, 2015a), the Permo-Triassic sandstones in the Eden Valley were divided into four aquifer zones, i.e. 'St Bees Sandstones', 'silicified Penrith Sandstones', 'non-silicified Penrith Sandstones' and 'interbedded Brockram Penrith Sandstones' as described previously. These aquifer zones were then discretised into 200 m by 200 m cells. The St Bees Sandstone formation is separated from the Penrith Sandstones by impermeable Eden Shale Formation. Since the groundwater flow in the study area is dominated by flow to the River Eden (Butcher et al., 2003; Daily et al., 2006), the groundwater-flow direction in the Penrith Sandstones is almost parallel to the boundaries between aquifer zones of the Penrith Sandstones. This indicates that the groundwater interaction between aquifer zones is limited and can be ignored in this study.

In order to determine the water-table-response time to rainfall events Rp_q, the cross-correlation method, which is a time series technique, has been adopted in this study. Cross-correlation has been used to reveal the significance of the water-table response to rainfall (e.g. Lee et al., 2006; Mackay et al., 2014). Datasets used for this calculation include 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 in the Skirwith Borehole in the study area. Rp_q was set to the period of time over which there is a correlation between groundwater level and rainfall at the 95% confidence level, assuming that it is homogenous in the study area. Fig. 3 shows that the vertical bars are above the 95% confidence level for 15 months, thereby indicating that it takes 15 months for the groundwater level in the Permo-Triassic sandstones in the study area to fully respond to the monthly rainfall event.

The information on glacial till thickness $Thickness_{DRIFT,i}$ was derived using the BGS 1:250 000 superficial deposits geological map (BGS, 2015b) and BGS database of the thickness of superficial deposits (Lawley and Garcia-Bajo, 2009). According to the field experiments undertaken by Butcher et al. (2008, 2009), the nitrate velocity in glacial till $V_{DRIFT,i}$ is 0.6 m year^{-1} whilst nitrate travels, on average, 3.5 m year^{-1} in the USZs of the Permo-Triassic sandstones.

The river network derived from the gridded Digital Surface Model (NextMap DSM) was used to calculate the distance to river points for each cell. BGS 1:250 000 superficial geological map (BGS, 2015b) was also used to identify the locations where aquifers are disconnected from rivers due to the presence of glacial till. These locations were not considered when calculating the distance to the river. The hydraulic gradient G_i was calculated using the long-term-average (1961–2012) groundwater levels GWL_i (Wang et al., 2013) and river levels RL_i derived from the NextMap DSM data in the study area. The USZ thickness $Thickness_{USZ,i}$ was calculated using GWL_i and the NextMap DSM data in the study area. The yearly distributed recharge estimates from the calibrated recharge model mentioned above were used to simulate nitrate-transport velocity in the Permo-Triassic sandstone USZs and the groundwater volume $Vol_{total}(t)$, respectively.

3.2. Calibration

Monte Carlo (MC) simulations were also undertaken to calibrate the extended NTB model developed in this study. In this study, MC parameters include $\Phi_{aquifer}$ (the porosity for an aquifer zone), $Sy_{aquifer}$ (specific yield), $Rf_{aquifer}$ (retardation factor for calculating the nitrate velocity in the USZs), $T_{aquifer}$ (transmissivity), $D_{aquifer}$ (depth of active groundwater) and *RFF* (the ratio of fracture flow in the USZs). These MC 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 of parameter were defined based on literature, observed results or expert judgment. For example, the aquifer properties of active groundwater depth, porosity, transmissivity and specific yield were based on the collation of Allen et al. (1997), assuming that they are homogenous in each aquifer zone. Performing MC simulations is a computer-intensive task especially when multiple 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. Parameters that can be identified or calculated based on existing datasets, methods and hydrogeological knowledge from hydrogeologists were fixed. These fixed parameters of this model include A_i (the area for a modelling cell i), q_i (the recharge value for

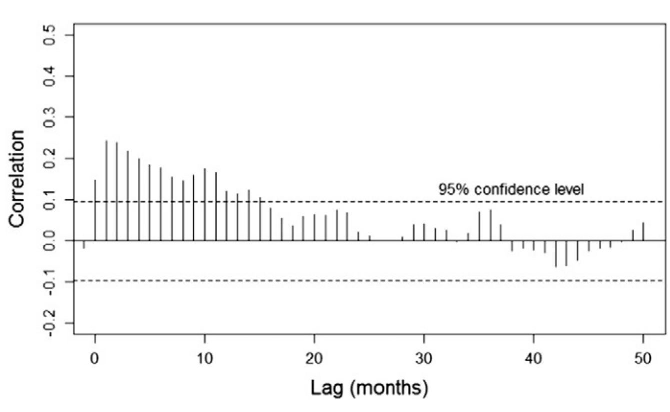

Fig. 3. Cross-correlation between rainfall and groundwater levels of the Skirwith Borehole in the Eden Valley, UK.

cell$i$), Rp_q (the water-table-response time to recharge events), GWL_i (the groundwater level for cell), RL_i (the river level for cell$i$), $Thickness_{DRIFT,i}$ (the thickness of glacial till at cell$i$), $V_{DRIFT,i}$ (the nitrate velocity in glacial till), $Thickness_{USZ,i}$ (the USZ thickness at cell i), G_i (hydraulic gradient), and etc. For example, the time-variant distributed recharge was estimated using the SLiM model (Section 2.4.1.1). The section of model construction describes the parameterisation of some of these fixed parameters.

Two sets of MC simulations were conducted to calibrate the extended NTB model. The first one was to calibrate the model against the nitrate velocity value in the Permo-Triassic sandstone USZs, which was derived from measurements of porewaters from drill cores in the Eden Valley (Butcher et al., 2008, 2009). The second MC simulation was then conducted using the observed average nitrate concentrations from the Environment Agency for each aquifer zone. In the former, the bias (absolute difference) between simulated and observed nitrate velocity in the USZs was used to evaluate the model fit. In the latter, the Nash-Sutcliffe efficiency (*NSE*) score (Nash and Sutcliffe, 1970) was used to calculate the goodness-of-fit between observed and modelled nitrate concentrations, via:

$$NSE = 1 - \frac{\sum_{i=1}^{N} (Vobs_i - Vsim_i)^2}{\sum_{i=1}^{N} \left(Vobs_i - \overline{Vobs}\right)^2} \tag{14}$$

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

A zero *NSE*score indicates that modelled data are considered as accurate as the mean of the observed data, and a value of one suggests a perfect match of modelled to observed data. The model with the highest *NSE* score in a set of MC simulations is deemed to have the optimum parameter set. The *NSE* score was also used in calibrating the recharge model mentioned above.

In the second MC simulation, the observed nitrate concentrations were partitioned into two sets of 70% for MC simulation and 30% for validation. The average value of the *NSE* scores in the calibration of the NTB model for four aquifer zones (0.32–0.69) is 0.48, whilst that for aquifer zones in the validation (0.33–0.67) is 0.46. This indicates that the risk of overfitting in calibrating the NTB model is limited.

4. Results

4.1. Spatio-temporal nitrate-input-function

A spatio-temporal nitrate-input-function was derived using a combination of NEAP-N predictions and the single nitrate-input-function as mentioned above. It contains a nitrogen loading map for each year from 1920 to 2050. Fig. 4 shows some examples of time series of nitrate loading at locations randomly selected within the study area. The actual nitrate loading for a cell depends on land-use type, livestock density and the measures of farming activities at this location. In general, it shows that the improved grassland (fertilised grassland) and arable land-uses have higher nitrate loading than the woodland land-use type. The low nitrate loading between 1925 and 1940 reflect the pre-war low level of intensification with very limited use of non-manure-based fertilisers. The gradual rise of nitrate loading from 1940 to 1955 was the result of the intensification of agriculture during, and just after, World War II. Nitrate loading reached its peak value during the 1980s after a rapid rise (1955–1975) due to increases in the use of chemical based fertilisers, and then started to decline as a result of restrictions on fertiliser application. Fig. 5 shows the spatial distribution of nitrate loading in some years. Generally, the western part of the ‘silicified Penrith Sandstones’ and the eastern and northern parts of the ‘St

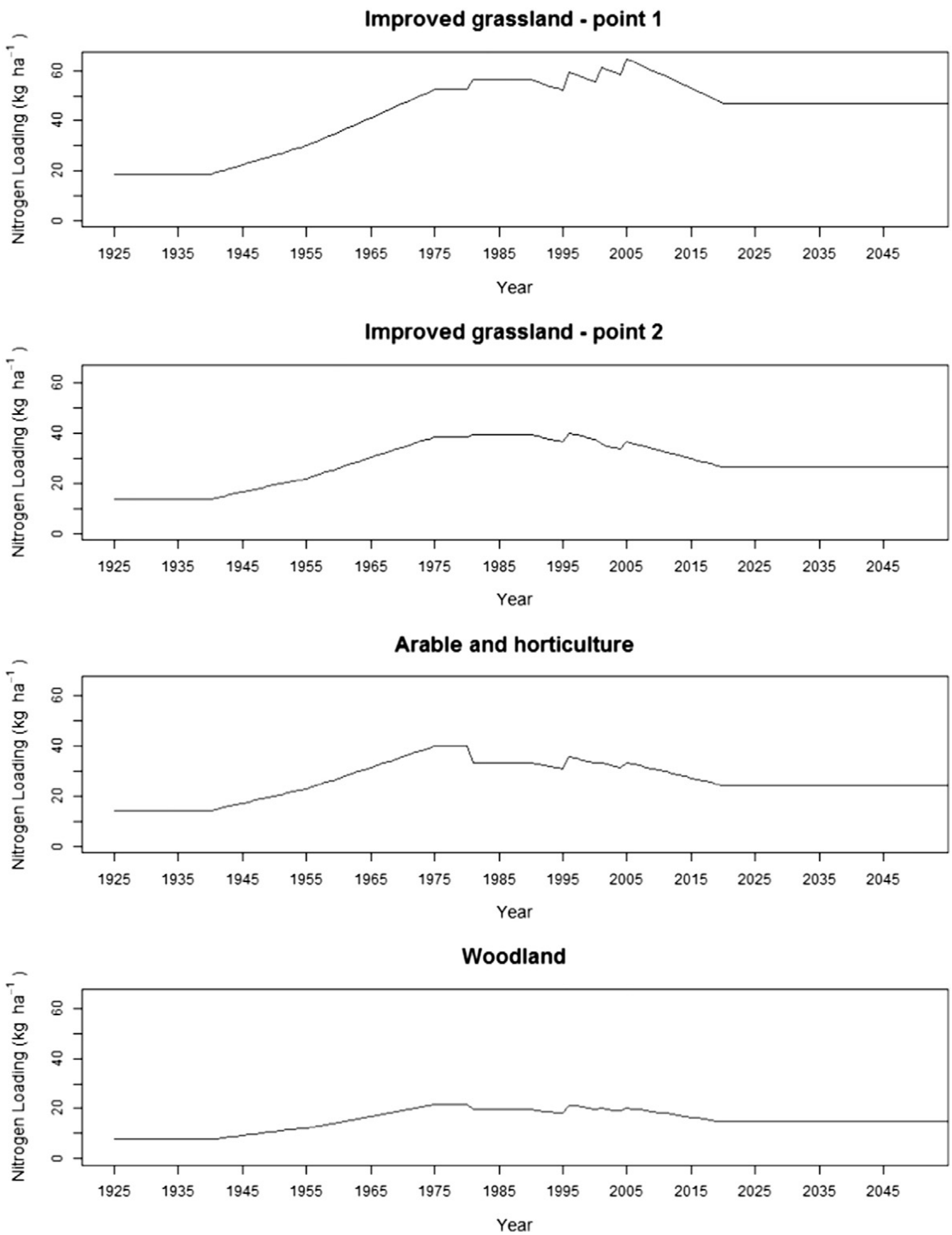

Fig. 4. Derived nitrate-input-functions at three locations randomly selected within the land-uses of 'improved grassland', 'arable and horticulture' and 'woodland' in the Eden Valley, UK.

Bees Sandstones' have higher nitrate loading than the rest of the study area (Fig. 5).

4.2. Sensitivity analysis

A sensitivity analysis was conducted when carrying out MC simulations to calibrate both the recharge model and the extended NTB model. The purpose was to determine which parameters contribute most to the model efficiency, and which of them are identifiable within a specific range linked to known physical characteristics of different hydrological or hydrogeological processes. Each MC run was plotted as a dot in the scatter plots to show the model performance of a MC run in the vertical axis when using a parameter value on the horizontal axis. In each scatter plot, many MC runs form a cloud of dots to represent a response surface that indicates how the model performance changes as each parameter is randomly perturbed.

As mentioned above, the reduction of recharge (*RRch*) was identified for each thickness class of glacial till through the MC simulations of the groundwater recharge model. It shows that the recharge model is sensitive to the parameter of *RRch* for all five thickness classes of glacial till.

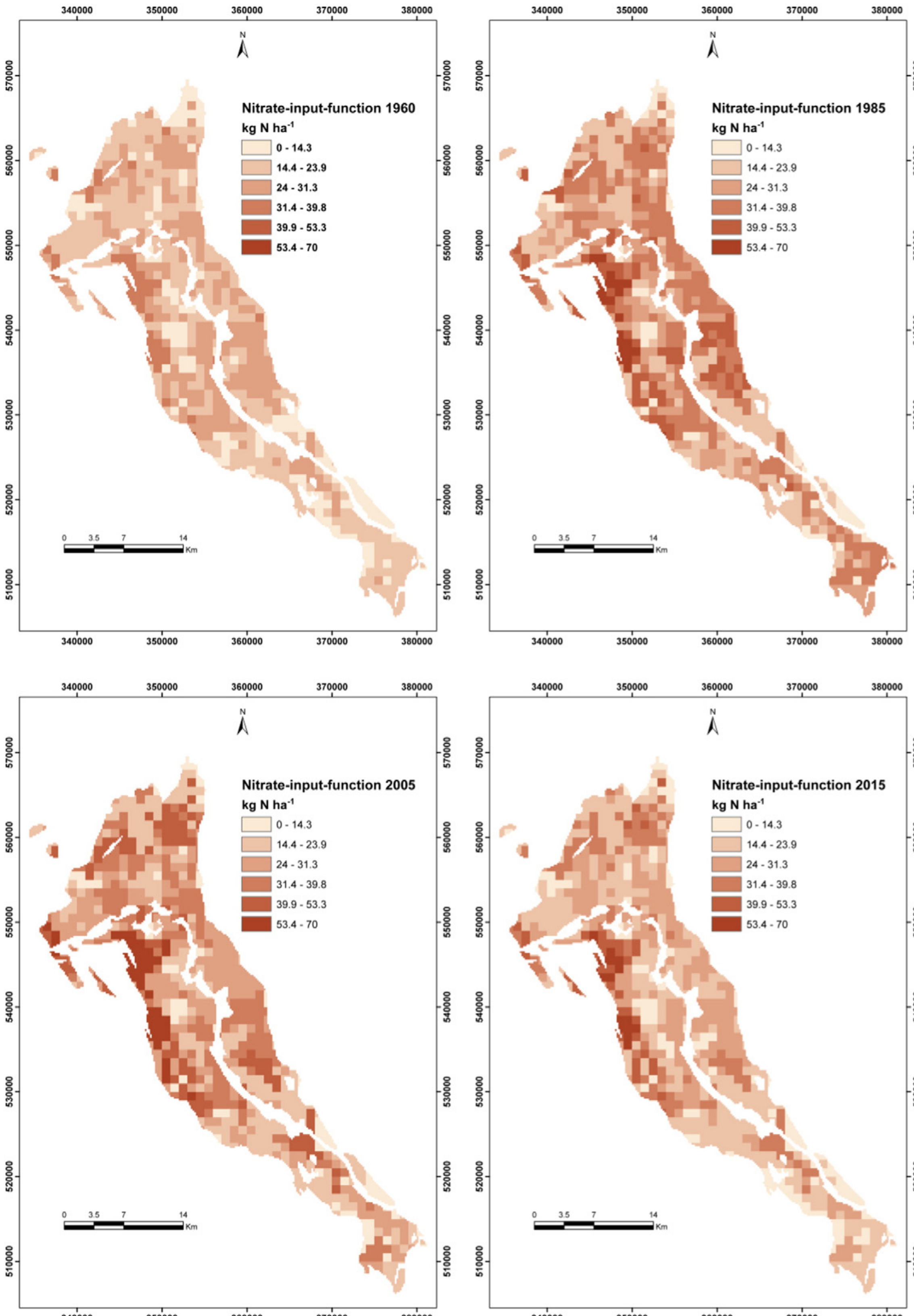

Fig. 5. The spatial distribution of nitrate loading in some years for the Permo-Triassic Sandstones in the Eden Valley, UK.

The performance of the recharge model reached its highest ($NSE = 0.853$) when *RRch* of the 0–2 m thickness class was set to 55.6%. However, the recharge model produced better results when *RRch* for rest of thickness classes, i.e. 2–5 m, 5–10 m, 10–30 m and >30 m, were close to 100%. This indicates that about 44% of water and nitrate can travel through the thin glacial till with a thickness of <2 m, whilst no water and nitrate enters the underlying Permo-Triassic sandstones when the thickness of overlying glacial till is larger than 2 m. This is consistent with the findings from the field experiments in the study area undertaken by Butcher et al. (2009).

In the first set of MC simulation (Section 3.2), specific yield Sy_{aquifer}, porosity Φ_{aquifer} and the retardation factor $Rf_{aquifer}$were initially varied together resulting in a group of behavioural runs (with bias <0.001 m year^{-1}). In order to clearly demonstrate parameter sensitivity, further MC simulations were undertaken by varying one parameter at a time whilst fixing the other two parameters (Fig. 6). The values of fixed parameters were determined by a set of parameter values chosen from one of the behavioural models from the initial MC runs. Fig. 6 shows that the extended NTB model is very sensitive to these parameters in all four aquifer zones. These parameters, therefore,

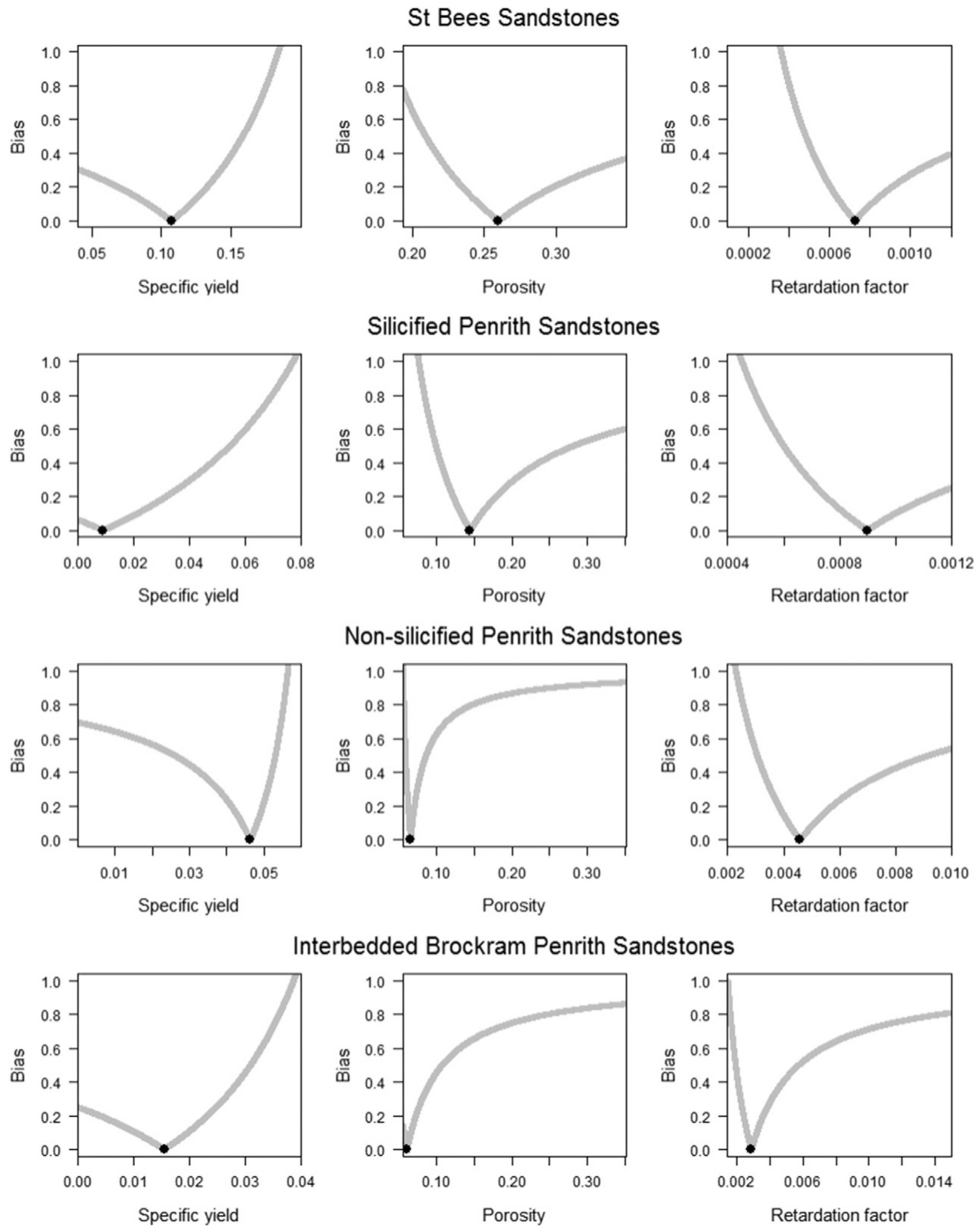

Fig. 6. Sensitivity scatter plots for parameter values in estimating the nitrate velocity in the USZs of four aquifer zones in the Eden Valley, UK. Grey dots indicate individual parameters from Monte Carlo runs and the black dot denotes the optimum parameter value.

can be easily identified based on the shapes of response surfaces in these scatter plots. The optimum parameter values, which are denoted by black dots, result in the minimum bias in the MC simulations. In the second set of MC simulations for calibrating the extended NTB model against the observed nitrate concentrations, it was found that the model is sensitive to the depth of active groundwater D_{aquifer} and transmissivity T_{aquifer}, but slightly less sensitive to the ratio of fracture flow *RFF* in the USZs (Fig. 7).

4.3. Estimates of nitrate concentration

The annual nitrate concentrations from 1925 to 2150 for four aquifer zones in the Eden Valley were simulated based on the calibrated extended NTB model. The NTB-Model performance was evaluated using the simulated nitrate concentrations from the best model and all observed data (Table 1). The values of (Modelled mean − Observed mean)/Observed range show that the NTB model may overestimate or

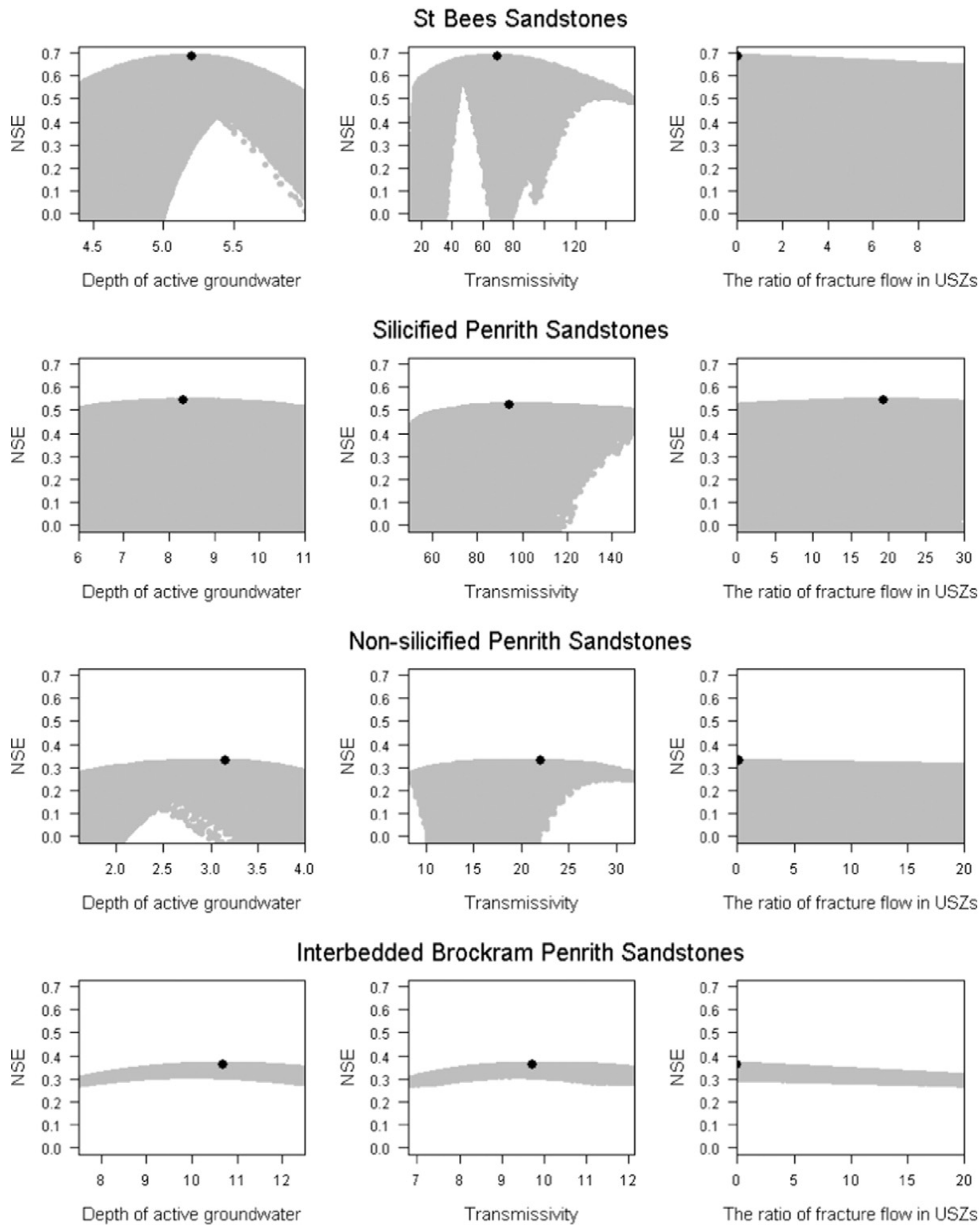

Fig. 7. Sensitivity scatter plots for parameter values in simulating the nitrate concentrations of four aquifer zones in the Eden Valley, UK. Grey dots indicate individual parameters from Monte Carlo runs and the black dot denotes the optimum parameter value.

Table 1
The NTB-model performance in four aquifer zones of the Eden Valley, UK.

Model performance evaluation method	St Bees Sandstones	Silicified Penrith Sandstones	Non-silicified Penrith Sandstones	Interbedded Brockram Penrith Sandstones
Modelled mean (mg L^{-1} (as NO_3))	20.7	26.2	32.4	30.1
Observed mean (mg L^{-1} (as NO_3))	19.3	29.2	34.1	29.7
Modelled range	23.1	25.8	30.9	20
Observed range	28.3	30.3	32.5	22.4
(Modelled mean − Observed mean)/Observed range (%)	4.9	−9.9	−5.2	1.8
Modelled median (mg L^{-1} (as NO_3))	20	25.1	30	28
Observed median (mg L^{-1} (as NO_3))	21.1	30	34.7	19.9
Root Mean Square Error (RMSE: mg L^{-1} (as NO_3))	2.8	3.5	5.9	4
RMSE/Observed range (%)	9.9	11.6	18.2	17.9
NSE	0.68	0.53	0.29	0.37

underestimate the nitrate concentrations. The NTB model produces the best performance in the 'St Bees Sandstones' with a NSE value of 0.68 and a Root Mean Square Error (RMSE) value of 2.8 mg L^{-1} (as NO_3), which is 9.9% of the range of observed nitrate concentrations (28.3 mg L^{-1} (as NO_3)). In the 'non-silicified Penrith Sandstones', the NSE and RMSE values are 0.29 and 5.9 mg L^{-1} (as NO_3) (18.2% of the range of observed data) respectively. The performance of the NTB model in other aquifer zones of the study area is in between that of these two. The visual inspection (Fig. 8) also shows that the modelled time series of nitrate concentrations are in good agreement with the observed data, and can well reflect trends in the observed data in the study area. Therefore, this is acceptable for such a modelling study that focuses on the long-term trends in the annual average nitrate concentrations in aquifer zones.

Spatially distributed recharge values between 1961 and 2011 were used in simulating nitrate concentrations. The spatially distributed long-term-average recharge values (1961–2011) were used for years outside of the period from 1961 to 2011, thus resulting in less fluctuation in the modelled nitrate concentrations from year to year.

The results show that the nitrate concentration in the 'St Bees Sandstones' keeps rising until the peak value of 36 mg L^{-1} (as NO_3) is reached at the nitrate-concentration-turning-point year 2021. It was estimated that the nitrate concentration in the 'silicified Penrith Sandstones' will have reached its peak value of 43 mg L^{-1} (as NO_3) in the year 2051. The nitrate concentration in the 'non-silicified Penrith Sandstones' is at its peak value that will last from 2015 to 2034. After reaching peak values, the nitrate concentrations in these three aquifer zones will decline to stable levels. It was also found that the nitrate concentration in the 'interbedded Brockram Penrith Sandstones' has passed it peak and started to level off after a slight decrease.

5. Discussion

5.1. Nitrate-concentration trends

An extended NTB model was developed in this study to assess long-term trends of nitrate concentrations in aquifer zones at the catchment scale. The extended NTB model fits the purpose of this study, and the modelled nitrate concentrations can well reflect the trends in the observed data of the s03tudy area (Section 4.3). The results show that the nitrate concentration in the 'interbedded Brockram Penrith Sandstones' has passed its peak value and is declining slightly. The nitrate concentrations in 'St Bees Sandstones' and 'silicified Penrith Sandstones' are rising until their nitrate-concentration-turning-point years are reached, whilst that in the 'non-silicified Penrith Sandstones' is at its peak value and will start to decrease from 2034. However, nitrate concentrations in all four aquifer zones will eventually level off with values below the EU drinking water standard (50 mg L^{-1} (as NO_3)). Although the nitrate-concentration trends in aquifers are controlled by many factors in each cell of the modelling area, such as recharge, nitrate loading, glacial till thickness, USZ thickness, USZ fracture flow, and aquifer properties. However, the thickness of UZSs may partially explain the different nitrate-concentration trends in these four aquifer zones. Since 'interbedded Brockram Penrith Sandstones' has an average USZ thickness of 2 m, which is much lower than that in 'St Bees Sandstones' (14.5 m), 'silicified Penrith Sandstones' (45 m) and 'non-silicified Penrith Sandstones' (12.9 m), its USZ has a much shorter nitrate time-lag than that in the other three USZs. Therefore, it will be easier for the peak nitrate loadings in 'silicified Penrith Sandstones' than that in 'silicified Penrith Sandstones' to reach the water table. These results are valuable for the management of both groundwater and surface water in the study area. Groundwater is essential for maintaining the flow of many rivers in the form of baseflow when rivers are connected with high permeability aquifers. Nine river gauging stations in the Permo-Triassic Sandstones in the Eden Valley have an average baseflow index of 43% (NERC, 2003). This indicates that the nitrate remaining in the Permo-Triassic Sandstones will affect the long-term quality of surface water and hence the ecological quality in the study area.

5.2. Fracture flow in the USZs

Since there is limited information about the fracture flow in the Permo-Triassic Sandstone USZs of the study area, MC simulations were undertaken to better understand the fracture flow in these USZs. As mentioned in the section of sensitivity analysis, the ratio of fracture flow in the USZs *RFF* is identifiable for each aquifer zone. It was found that the optimum *RFF* values for the USZs of 'St Bees Sandstones', 'silicified Penrith Sandstones', 'non-silicified Penrith Sandstones' and 'interbedded Brockram Penrith Sandstones' are 0.035%, 19.4%, 0.134% and 0.002% respectively. This indicates that 19.4% of water and nitrate travel through fractures in the USZ of 'silicified Penrith Sandstones', whilst >99.8% of water and nitrate is transported by intergranular movement through the matrix in the other three USZs. Fig. 1 shows that there are more faults cutting through the sandstones in the 'silicified Penrith Sandstones' than other aquifer zones where the density of faults is low or faults have developed along the aquifer boundary. This may partially explain why the 'silicified Penrith Sandstones' have higher values of *RFF* than other three aquifer zones.

5.3. Method transferability

The approach developed in this study can represent the major hydrogeological processes in the groundwater system using a simplified conceptual model. It can be used to investigate the impact of historical nitrate loading from agricultural land on the long-term trends of nitrate concentrations in aquifers at the catchment scale. Although it was demonstrated by its application in the Eden Valley, UK, the methods for preparing most of the model parameters have been described. Therefore, this simple approach is reproducible by other scientists to address nitrate-legacy issues faced by many countries.

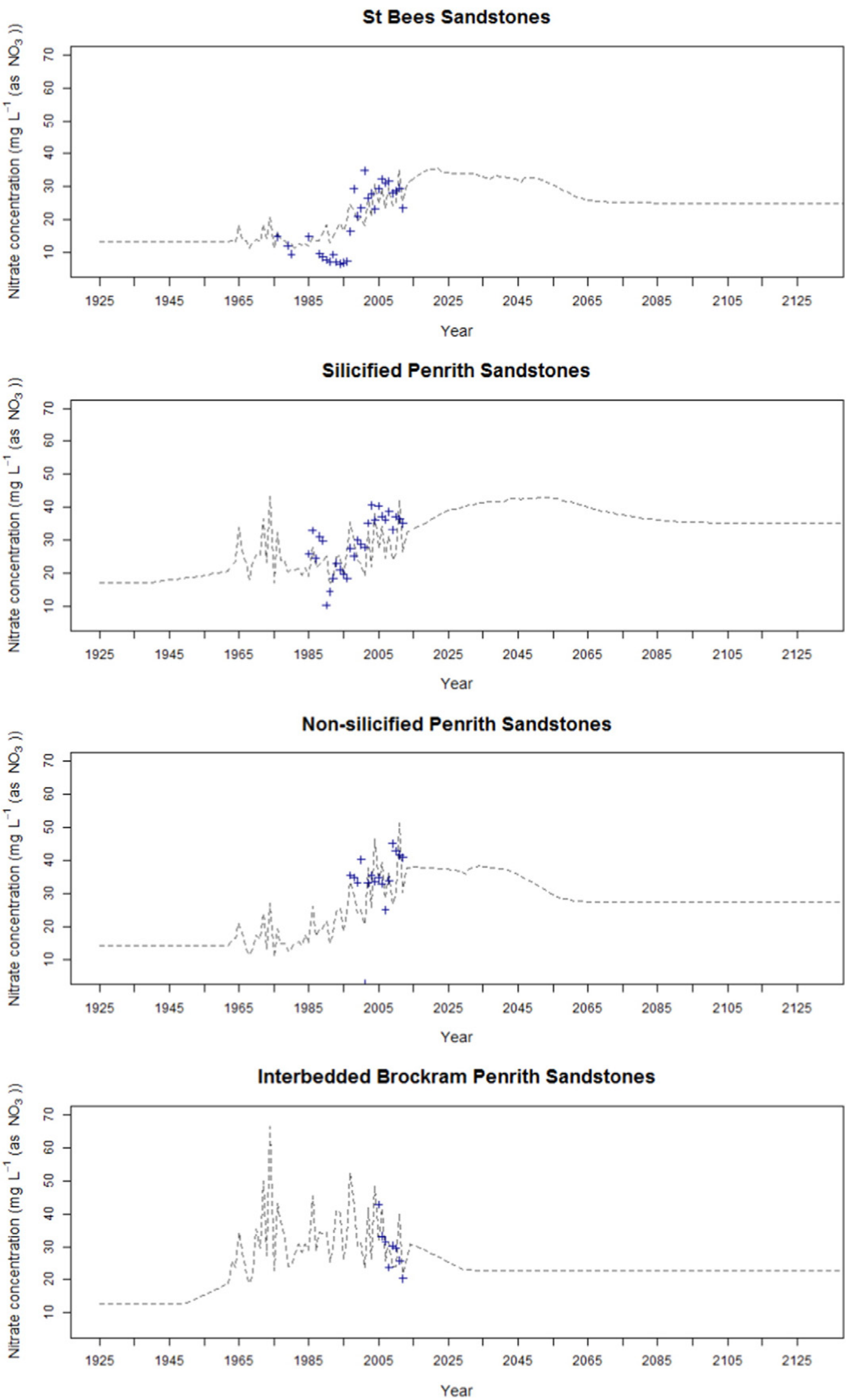

Fig. 8. Time series of modelled and observed nitrate concentrations of four aquifer zones in the Eden Valley, UK. The dashed lines are the modelled annual nitrate concentrations and the crosses are the observed values.

5.4. Limitations

However, a number of limitations should be considered when interpreting the modelled results in this study. First, the seasonal interactions between aquifers and rivers have been ignored in this modelling study with an annual time-step. The magnitude of water exchange between aquifers and rivers is governed by aquifer-river connectivity, the permeability of the riverbed, and the seasonal fluctuations of groundwater levels and river stages (e.g. Calver, 2001; Fleckenstein et al., 2006; Kirk and Herbert, 2002). Water and nitrate in rivers could infiltrate into aquifers via hyporheic zone due to the fast rise of river stage after storms in dry seasons. Doussan et al. (1997) found that nitrate concentrations are consistently reduced when river water infiltrates into the first few metres of bed sediments. The denitrification rates in hyporheic zones are affected by temperature, sediment grain size, and dissolved oxygen (Grimaldi and Chaplot, 2000). However, these detailed processes in hyporheic zones have been simplified in this study, which focused on the annual average nitrate concentrations in aquifer zones. In general, groundwater eventually flows to surface water and maintains the flow of many rivers. Groundwater flow in the study area is dominated by flow to the River Eden (Butcher et al., 2003; Daily et al., 2006). Therefore, groundwater recharge can be treated as the input of the groundwater system in the Eden Valley; and the output of the system is the baseflow entering the River Eden. It was assumed that the input and output of the Permo-Triassic sandstone aquifers in the Eden Valley reach a dynamic balance on an annual basis. As mentioned previously, the aquifers are disconnected from rivers where glacial till is present in the study area. This method, however, can be improved to represent the detailed water and nitrate interactions between aquifers and rivers when simulating seasonal or monthly nitrate concentrations in the future.

Denitrification, which is generally facilitated by the absence of oxygen, is a microbial process in which nitrate is progressively reduced to nitrogen gas. Denitrification is considered to be the dominant nitrate attenuation process in the subsurface system (Rivett et al., 2007, 2008). However, Rivett et al. (2007) suggested that denitrification only accounts for a loss of 1–2% in the USZs in general. Butcher et al. (2005) found no evidence for denitrification and concluded that denitrification is not a significant process controlling nitrate concentrations in the USZs and unconfined aquifers of the Permo-Triassic Sandstones in the Eden Valley. Furthermore, evidence from the porewater chemistry of the cored borehole in the study area showed that oxidation of ammonium to nitrite (nitrification) occurs instead in the USZs (Butcher et al., 2008). In spite of this, detailed information on the distribution of nitrification in the study area is unavailable. Therefore, it was assumed that nitrate is conservative and its biogeochemical processes in the groundwater system have been ignored in this study. However, the attenuation factor *ATT* has been introduced into the model and it can be parametrised when more information on nitrate attenuation in the groundwater system is available.

The long-term annual average recharge between 1961 and 2011 has been used to simulate nitrate concentrations in the future because the agreed future change scenarios were unavailable for this study. Consequently, nitrate concentrations estimated after 2011 should be treated with caution and are simply indicative of the most likely peak average nitrate concentrations. When future recharge values under different climate change scenarios become available, better simulations can be performed.

Since there were no time-variant groundwater-level data available for this study, it was assumed that the groundwater background volume $Vol_{\mathrm{background}}$ remains the same in each simulation year. When the information on time-variant groundwater flow in the study area becomes available in the future, the model can be improved to produce a better estimation of the time-variant total volume of groundwater (Vol_{total}) and hence the nitrate concentrations.

It was assumed that the future nitrogen-fertiliser-application rate will be reduced to the level in the mid-1950s, i.e. 40 kg N ha^{-1} (Wang et al., 2012a) when deriving the spatio-temporal nitrate-input-function (Figs. 4 and 5) using the NEAP-N data and the single nitrate-input-function. This explains the levelling off nitrate concentrations after passing their peak values in four aquifer zones of the study area. Once a set of agreed scenarios of future nitrate loading becomes available, the model is able to better estimate nitrate concentrations into the future. In addition, the lateral migration of nitrate in the USZs was ignored in this study due to the lack of information on this. Finally, hydrodynamic dispersion of nitrate in the unsaturated zones due to both mechanical dispersion and diffusion will occur, but was not accounted for in this study. All these simplifications, however, facilitated the modelling procedures for this simple approach, which requires relatively modest parameterisation but provides a framework for better informing land-management strategy that needs to take better account of nitrate-legacy issues.

6. Conclusions

This paper presents a catchment-scale approach to modelling the long-term trends in nitrate concentrations in aquifers. It requires relatively modest parameterisation and runs on an annual time-step. However, it considers enough hydrogeological processes at the catchment scale but in simplified ways. For example,

- the spatio-temporal nitrate loading from agricultural land has been derived
- the impact of low permeability superficial deposits on nitrate transport was considered
- a simple methodology was introduced to represent the nitrate transport via both the intergranular matrix and fractures in the USZs
- a simplified hydrological conceptual model was developed to simulate nitrate transport and dilution in aquifers.

The model provides useful estimates of present and future nitrate concentrations in aquifers. These results can help policymakers understand how the historical nitrate loading from agricultural land affects the evolution of the quality of groundwater and groundwater-dependent surface waters. It also helps develop time frames to assist in understanding the success of programmes of measures at the catchment scale. This model is also valuable for evaluating the long-term impact and timescale of different scenarios introduced to deliver water-quality compliance, such as the changes of land-use and fertiliser-application rate under future climate-change impacts. However, the assumptions of the model should be considered when using the modelled results to solve the localised nitrate problems. More complexities could be introduced into the model in the future when it is applied to other areas with complicated hydrogeological settings to better represent the nitrate processes in the groundwater system.

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