Science of the Total Environment 542 (2016) 694–705

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

The changing trend in nitrate concentrations in major aquifers due to historical nitrate loading from agricultural land across England and Wales from 1925 to 2150

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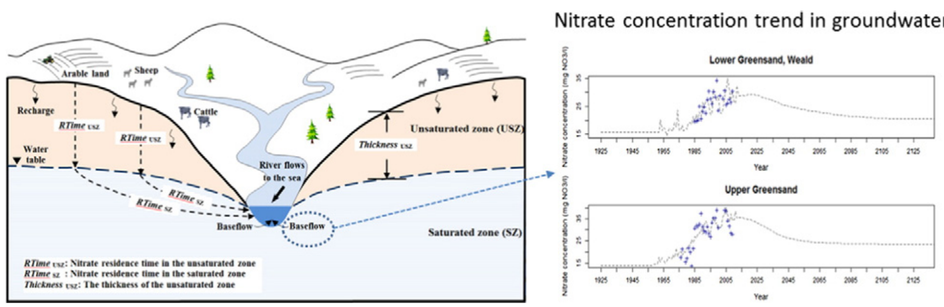
HIGHLIGHTS

- An approach to modelling groundwater nitrate at the national scale is presented.
- The long time-lag for nitrate in the groundwater system is considered.
- The impact of historical nitrate loading on groundwater quality is better understood.
- Areas of high groundwater nitrate input to surface water are delineated.
- The method is transferable and requires a modest parameterisation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 September 2015
Received in revised form 26 October 2015
Accepted 26 October 2015
Available online 4 November 2015

Editor: D. Barcelo

Keywords:
Nitrate
Groundwater quality
Unsaturated zone
Saturated zone
Time-lag

ABSTRACT

Nitrate is necessary for agricultural productivity, but can cause considerable problems if released into aquatic systems. Agricultural land is the major source of nitrates in UK groundwater. Due to the long time-lag in the groundwater system, it could take decades for leached nitrate from the soil to discharge into freshwaters. However, this nitrate time-lag has rarely been considered in environmental water management. Against this background, this paper presents an approach to modelling groundwater nitrate at the national scale, to simulate the impacts of historical nitrate loading from agricultural land on the evolution of groundwater nitrate concentrations. An additional process-based component was constructed for the saturated zone of significant aquifers in England and Wales. This uses a simple flow model which requires modelled recharge values, together with published aquifer properties and thickness data. A spatially distributed and temporally variable nitrate input function was also introduced. The sensitivity of parameters was analysed using Monte Carlo simulations. The model was calibrated using national nitrate monitoring data. Time series of annual average nitrate concentrations along with annual spatially distributed nitrate concentration maps from 1925 to 2150 were generated for 28 selected aquifer zones. The results show that 16 aquifer zones have an increasing trend in nitrate concentration, while average nitrate concentrations in the remaining 12 are declining. The results are also indicative of the trend in the flux of groundwater nitrate entering rivers through baseflow. The model thus enables the magnitude and timescale of groundwater nitrate response to be factored into source apportionment tools and to be taken into account alongside current planning of land-management options for reducing nitrate losses.

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http://dx.doi.org/10.1016/j.scitotenv.2015.10.127

1. Introduction

Nitrate (NO_3) is essential for living matter by acting as a source of nitrogen (N) that forms the building blocks of molecules. Man has benefited from the application of chemical nitrogen fertilisers to gain increased agricultural productivity. However, any excess nitrate applied can be leached from the soil into freshwater, depending on the timing, rate and method of fertiliser application. Nitrate concentrations in groundwater beneath agricultural land can be several- to a hundred-times higher than that under semi-natural vegetation (Nolan and Stoner, 2000). Nitrate-contaminated water can cause long-term environmental damage and threaten both economic and ecosystem health (Bryan, 2006; Defra, 2002; Mayer et al., 2002; Pretty et al., 2000; Sebilo et al., 2006; Thorburn et al., 2003; Ward, 2009).

Agricultural land is the major source of nitrate water pollution (Ferrier et al., 2004; Thorburn et al., 2003; Torrecilla et al., 2005). In England, over 70% of nitrate in groundwater and surface water has been shown to be derived from agricultural land (Foster, 2000; Hunt et al., 2004; Defra, 2006). Although legislation has been introduced to reduce nitrate water pollution, this remains an international problem (Campbell et al., 2004; European Environment Agency, 2000; Ferrier et al., 2004; Mayer et al., 2002; Rivett et al., 2007; Sebilo et al., 2006; Thorburn et al., 2003; Torrecilla et al., 2005; Wang et al., 2013; Wang and Yang, 2008; Yang and Wang, 2010; Yue et al., 2014). The EU Nitrate Directive, an integrated part of the EU Water Framework Directive (Directive 2000/60/EC), is implemented through a statutory instrument that sets rules (Action Programme rules) for best agricultural practices within Nitrate Vulnerable Zones (NVZs). These are designated areas where land drains and contributes to the excess nitrate found in contaminated groundwater and surface waters. However, the degradation of freshwater quality due to nitrate remains a problem in the UK. In many areas, nitrate concentrations are more than 50 mg NO_3 L^{-1} with a rising trend in both rivers (Burt et al., 2008, 2011) and aquifers (Smith, 2005; Stuart et al., 2007). However, evidence of some improvements in groundwater nitrate (*e.g.* Smith et al., 2010) is beginning to emerge.

Storage of nitrate in porewater and consequent slow vertical migration through the unsaturated zone of major aquifers was first recognised in the 1970s (Foster and Crease, 1974; Young et al., 1976). The importance of this for nitrate management was highlighted by Dautrebande et al. (1996). The anticipated decrease in nitrate concentrations in the aquifer following the implementation of protection measures was not observed.

In the unsaturated zone (USZ), *i.e.* from the base of the soil layer to the water table, pore-water pressure is sub-atmospheric, and hence the fractures and matrix of rock may be only partially saturated. Therefore, hydraulic pathways within, and between rock matrix and fractures may be restricted (Ireson et al., 2009). In addition, the water and pollutants held by capillary tension on fracture walls could be an important means of storing soluble pollutants in the USZ (Price et al., 2000; Sorensen et al., 2015). Thus, the historical nitrate loading could, in some cases, stay in the USZ for a long time before reaching the saturated zone or aquifer. Through recent research, it has become increasing clear that it could take decades for leached nitrate from the soil to discharge into freshwaters (Jackson et al., 2007; Burt et al., 2011; Howden et al., 2011; Wang et al., 2012a; Allen et al., 2014). This may cause a long time-lag between improvements in agricultural practices or targeted land-use change and the reduction of nitrate concentrations in interconnected groundwater and surface water (*e.g.*, Burt et al., 2008; Allen et al., 2014). Current environmental management strategies rarely consider the nitrate time-lag, but rely instead on the predictions of a relatively rapid response of water quality to land-management practices (Smith and Lerner, 2008; Collins et al., 2009; Burt et al., 2011). Therefore, models or tools are needed to simulate nitrate storage and time-lag in groundwater system and thus support better-informed water resources management.

Catchment-scale models have been developed to simulate water and nitrate transport in both the USZ (*e.g.*, Jackson et al., 2007; Ireson et al., 2009) and the saturated zone (*e.g.*, Harbaugh et al., 2000; Jackson et al., 2006). Most of these models are catchment specific as a wide range of factors affects nitrate transport and fate in the groundwater system. At a regional or national scale, it is necessary to use a more generic methodology with an appropriate level of conceptual complexity to predict changes in average behaviour. Wang et al. (2012a) developed the national-scale parsimonious process-based "Nitrate Time Bomb" (NTB) model to produce maps showing whether the peak nitrate loading has arrived at the water table for different aquifers in Great Britain. The results helped to understand the trend in the amount of nitrate arriving at the water table and entering groundwater due to the historical nitrate loading from arable land. It was also useful for groundwater resource management to designate areas where the historical nitrate burden in the USZ is high. However, the NTB model developed for that original work needed to be extended to include a saturated zone component to make it useful for wider applications, such as estimating trends in groundwater nitrate concentrations. Another limitation of the original NTB model is that it used a single historical nitrate input function.

The purpose of this study was therefore to simulate the long-term trend in nitrate concentrations in the major aquifers of England and Wales, based on an extended NTB model which incorporates:

- a national-scale hydrological conceptual model of nitrate transport and dilution in groundwater
- estimates of nitrate velocity in the USZ based on readily available recharge values and aquifer properties
- a spatially distributed nitrate input function which reflects the historical agricultural loadings at different locations on the ground surface.

2. Methodologies

The NTB model simulates the nitrate transport in the USZ and estimates the time and the amount of historical nitrate arriving at the water table (Wang et al., 2012a). This used nitrate concentrations in porewater from 300 cored boreholes, and nitrate velocity estimates in USZs from both field data for the major aquifers of the Chalk, Permo-

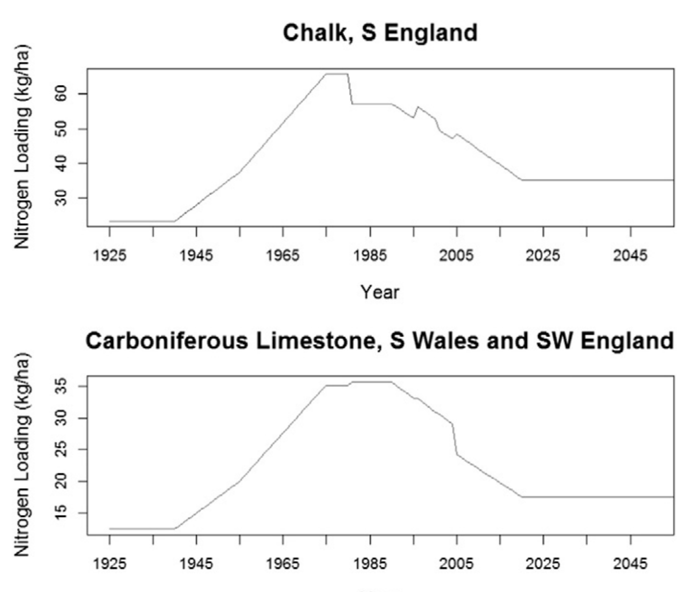

Fig. 1. Derived nitrate-input-functions at two locations in England and Wales, using a combination of NEAP-N predictions and the single nitrate-input-function.