



# An integrated pressure and pathway approach to the spatial analysis of groundwater nitrate: A case study from the southeast of Ireland



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## HIGHLIGHTS

- A methodology is introduced for evaluating parameters affecting groundwater nitrate.
- Investigation is at a regional scale using existing national spatial datasets.
- The results of statistical analysis support the results of the presented methodology.
- Pathway parameters are important in understanding groundwater nitrate.

## ARTICLE INFO

### Article history:

Received 18 February 2013

Received in revised form 18 December 2013

Accepted 18 December 2013

Available online 31 January 2014

### Keywords:

Groundwater

Hydrogeology

Nitrate

Water Framework Directive

Diffuse pressure

Pathway parameters

## ABSTRACT

Excess nitrogen in soil, aquatic and atmospheric environments is an escalating global problem. Eutrophication is the principal threat to surface water quality in the Republic of Ireland. European Union Water Framework Directive (2000/60/EC) water quality status assessments found that 16% of Irish groundwater bodies were 'at risk' of poor status due to the potential deterioration of associated estuarine and coastal water quality by nitrate from groundwater. This paper presents a methodology for evaluating pressure and pathway parameters affecting the spatial distribution of groundwater nitrate, investigated at a regional scale using existing national spatial datasets. The potential for nitrate transfer to groundwater was rated based on the introduced concepts of Pressure Loading and Pathway Connectivity Rating, each based on a combination of selected pressure and pathway parameters respectively. In the region studied, the South Eastern River Basin District of Ireland, this methodology identified that pathway parameters were more important than pressure parameters in understanding the spatial distribution of groundwater nitrate. Statistical analyses supported these findings and further demonstrated that the proportion of poorly drained soils, arable land, karstic flow regimes, regionally important bedrock aquifers and high vulnerability groundwater within the zones of contribution of the monitoring points are statistically significantly related to groundwater nitrate concentrations. Soil type was found to be the most important parameter. Analysis of variance showed that a number of the pressure and pathway parameters are interrelated.

The parameters identified by the presented methodology may provide useful insights into the best way to manage and mitigate the influence of nitrate contamination of groundwater in this region. It is suggested that the identification of critical source areas based on the identified parameters would be an appropriate management tool, enabling planning and enforcement resources to be focused on areas which will yield most benefit.

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## 1. Introduction

### 1.1. Background and aims

Excess nitrogen in soil, aquatic and atmospheric environments is an escalating global problem. In some situations, groundwater represents a

significant pathway for nutrient transport to surface water. Therefore excess nitrogen in groundwater can lead to ecological disturbances in receiving surface waters (Puckett et al., 2008; Tesoriero et al., 2009). Additionally, elevated concentrations of nitrate in drinking water can affect human health (Fan and Steinberg, 1996).

The concentration of nitrate in groundwater is highly variable (Burrow et al., 2010). The overall increase in nitrogen fertiliser during the intensification of agriculture in the UK during 1950–70 has previously been linked to higher nitrate concentrations (e.g. Foster,

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2000). However, it is sometimes difficult to link high nitrate concentrations in groundwater directly to nitrogen inputs. Groundwater nitrate is affected by complex physical and chemical processes within the soil, subsoil and aquifer. These processes mean that some areas are more vulnerable to nitrate contamination than others. To understand where and how nitrate concentrations become elevated requires an understanding of the sources of nitrate and the factors that control how nitrate moves through the hydrogeological system. This in turn can aid the development of effective management practices for the most vulnerable areas (Burow et al., 2010).

This paper presents a methodology for evaluating the factors affecting the spatial distribution of groundwater nitrate using pressure parameters (including land cover, fertiliser application rates, livestock and septic tank density) and pathway parameters (including soils, unconsolidated deposits, bedrock geology and climate data). Selected pressure parameters were combined into a single Pressure Loading (kgN/ha/yr). Similarly, selected pathway parameters were combined into a single Pathway Connectivity Rating. The potential for nitrate transfer to groundwater at each MP was then rated based on the calculated Pressure Loadings and Pathway Connectivity Rating. This regional scale evaluation, in the south east of Ireland, uses data available to policy makers, i.e. monitoring point data from the Irish EPA's groundwater quality monitoring network for the E.U. Water Framework Directive (2000/60/EC) (WFD) and pressure and pathway data from national spatial datasets. The results of statistical analysis of these datasets were compared to the results of the presented methodology. The majority of studies investigating the factors affecting the spatial distribution of groundwater nitrate are at a plot or farm scale (e.g. Tesoriero et al., 2009; Baily et al., 2011; Jahangir et al., 2012a; Premrov et al., 2012) or at a catchment scale (e.g. Jones and Smart, 2005; Benson et al., 2006; Floyd et al., 2009). This study is at a regional scale, similar to studies like Gardner and Vogel (2005), Roy et al. (2007) and Burow et al. (2010). Unlike other regional studies the pressure and pathway parameters for this study were compiled for the zone of contribution (ZOC) of each monitoring point, rather than at the monitoring point or for a fixed radius around it. Using the ZOC allows confidence that the pressure and pathway parameters are in the zone that influences the concentration of dissolved substances in the groundwater. The parameters identified by this methodology may provide useful insights into the best way to manage and mitigate the influence of nitrate contamination of groundwater in this region by allowing the critical source areas to be identified. This will provide a useful basis for policy makers tailoring mitigation measures to achieve WFD objectives in this region.

## 1.2. Factors which influence spatial distribution of groundwater nitrate

Leaching of nitrate occurs in soils, when crop uptake is low relative to the available nitrogen and excess water percolates through the soil column by matrix or macropore flow. This transports nitrogen compounds below the rooting zone, where plants can no longer utilise them. In particular, nitrate ions are readily mobile in the soil due to their negative charge. In temperate regions, optimum conditions for leaching often occur during wetter, colder months, making nitrate leaching a common winter phenomenon (Stark and Richards, 2008). The amount of nitrate lost is determined by soil and environmental factors, such as nitrification rate, soil texture and structure, soil permeability and water holding capacity, drainage volume, nitrogen fertilisation level and crop type as well as crop yield and rainfall (Stark and Richards, 2008). Previous studies have calculated leaching losses from agricultural land. For example, Goulding (2000) observed leaching losses of between 20 and 300 kg N/ha/yr in the UK; Bartley and Johnston (2006) measured 10–305 kg N/ha/yr from individual urine patches under different soil types in Ireland; Hansen et al. (2007) measured 3–327 kg N/ha/yr from spring barley crop in Denmark with and without

undersown catch crops and Hooker et al. (2008) calculated 161 to 194 kg/ha/year under spring barley systems in the South East of Ireland.

The principal mechanism for the depletion of nitrate concentrations in groundwater is microbial denitrification. Denitrification is the process whereby nitrate is converted, via a series of microbial reduction reactions, to nitrogen gas (Buss et al., 2005). The organisms that contribute to denitrification tend to be ubiquitous in surface water, soil and groundwater (Beauchamps et al., 1989; Rivett et al., 2008); they are found at great depths in aquifers (e.g. Francis et al., 1989). Anaerobic ammonium oxidation (anammox), using nitrite and nitrate as electron acceptors, is an important component of the global nitrogen cycle and may play an important role in nitrogen losses observed in soils and aquatic sediments (Robertson et al., 2012). Nitrate can also be reduced to nitrite and nitrous oxide gas by abiotic reactions, but in the subsurface these reactions are minor in comparison with biological denitrification (Buss et al., 2005).

In the soil zone most denitrification probably occurs in the uppermost 10–15 cm, where organic carbon concentrations are greatest from plant degradation and root exudates, and becomes less significant with depth (Burt et al., 1999). Poorly drained soils provide favourable conditions for denitrification (e.g. Gambrell et al., 1975; Lake et al., 2003). Denitrification rates in agricultural soil are highest in the autumn, when soil is moist but still warm (Addiscott, 1996).

Recent studies (e.g. Jahangir et al., 2012b) have shown that subsoils could have large potential to attenuate nitrate that has leached below the root zone if available carbon is not limiting. Gooddy and Darling (2009) found that low permeability subsoils such as Boulder Clay attenuates nitrate concentrations in groundwater by restricting the downward movement of recharging rainwater and promoting denitrification both in terms of redox conditions and time of exposure to them. Denitrification in the unsaturated zone of many aquifers is not commonly observed, except where exchange of air is limited by low permeability lithologies or where there are very high concentrations of electron donors such as organic waste (Buss et al., 2005). Additionally, where large fractures represent the predominant flow pathway in a formation, as in Ireland, there will be a small surface area for microbial growth relative to the fracture volume, and a comparatively short hydraulic residence time within the fractures. Consequently, the rate of biodegradation activity in a fracture flow system will be low compared to an intergranular system (Mather, 1989). The reduced biodegradation potential of organic contaminants during fracture flow is well-known (for example, Wealthall et al., 2001) and denitrification rates can be expected to be significantly less in such systems. As denitrifying bacteria are essentially ubiquitous in the subsurface, the critical factors are oxygen and electron donor concentration and availability (Rivett et al., 2008). Therefore the Geological Survey of Ireland (GSI) has compiled a list of bedrock formations with the potential for denitrification which contain oxidisable available electron donors in the aquifer matrix, namely organic carbon and sulphide (usually as pyrite) (EPA, 2012a).

## 2. Study area

### 2.1. Reason for investigating nitrate spatial distribution in this region

Eutrophication is the principal threat to surface water quality in the Republic of Ireland (Environmental Protection Agency, 2012b). In some situations, groundwater represents a significant pathway for nutrient transport to surface water. One way to measure the impact of groundwater nitrate on surface water quality is via the WFD water quality status assessments. These assessments were carried out by the Irish EPA in 2008. The Estuaries Surface Water Nitrates test found that 16% of groundwater bodies were 'at risk' of poor status due to the potential deterioration of associated estuarine and coastal water quality by nitrate from groundwater (Fig. 1). This risk assessment focuses on estuarine and coastal water bodies as nitrate is usually the limiting

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