Journal of Hydrology 556 (2018) 611–624

Contents lists available at ScienceDirect

Journal of Hydrology

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

Research papers

Applying linear discriminant analysis to predict groundwater redox conditions conducive to denitrification

S.R. Wilson [a,*], M.E. Close [b], P. Abraham [b]

[a] Lincoln Agritech Ltd, PO Box 69-133, Lincoln 7640, New Zealand
[b] Institute of Environmental Science & Research, PO Box 29-181, Christchurch 8540, New Zealand

ARTICLE INFO

Article history:
Received 12 December 2016
Received in revised form 7 August 2017
Accepted 23 November 2017
Available online 26 November 2017
This manuscript was handled by L. Charlet, Editor-in-Chief, with the assistance of Ewen James Silvester, Associate Editor

Keywords:
Nitrate
Redox status
Statistical modelling
New Zealand

ABSTRACT

Diffuse nitrate losses from agricultural land pollute groundwater resources worldwide, but can be attenuated under reducing subsurface conditions. In New Zealand, the ability to predict where groundwater denitrification occurs is important for understanding the linkage between land use and discharges of nitrate-bearing groundwater to streams. This study assesses the application of linear discriminant analysis (LDA) for predicting groundwater redox status for Southland, a major dairy farming region in New Zealand. Data cases were developed by assigning a redox status to samples derived from a regional groundwater quality database. Pre-existing regional-scale geospatial databases were used as training variables for the discriminant functions. The predictive accuracy of the discriminant functions was slightly improved by optimising the thresholds between sample depth classes. The models predict 23% of the region as being reducing at shallow depths (<15 m), and 37% at medium depths (15–75 m). Predictions were made at a sub-regional level to determine whether improvements could be made with discriminant functions trained by local data. The results indicated that any gains in predictive success were offset by loss of confidence in the predictions due to the reduction in the number of samples used.

The regional scale model predictions indicate that subsurface reducing conditions predominate at low elevations on the coastal plains where poorly drained soils are widespread. Additional indicators for subsurface denitrification are a high carbon content of the soil, a shallow water table, and low-permeability clastic sediments. The coastal plains are an area of widespread groundwater discharge, and the soil and hydrology characteristics require the land to be artificially drained to render the land suitable for farming. For the improvement of water quality in coastal areas, it is therefore important that land and water management efforts focus on understanding hydrological bypassing that may occur via artificial drainage systems.

1. Introduction

Nitrate is a key groundwater contaminant in New Zealand (MfE 2017) and many other parts of the world (Spalding and Exner, 1993). In New Zealand, increasing land use intensity, particularly in the dairy sector, has led to increasing levels of nitrate in groundwater systems and impacts on receiving surface waters such as streams, rivers and lakes (PCE, 2013, Mfe 2017). These concerns have led to the establishment of a Land and Water Forum (Land and Water Forum, 2010, 2012), reforms in freshwater management including a National Policy Statement for Freshwater Management, and a legislative framework that will require the setting of limits in fresh water for contaminants including nitrate (MfE, 2014).

In the context of meeting limits for environmental protection, a key natural attenuation process for nitrate is denitrification. The ability to predict the distribution of reducing conditions in the subsurface is essential for predicting the fate of nitrate along groundwater flow paths. Previous approaches for estimating the subsurface distribution of denitrification at the regional scale can be broadly divided into vulnerability mapping, and statistical prediction methods. The vulnerability mapping approach involves the analysis and integration of geochemical, geological, and hydrological datasets (Hansen and Thorling, 2008; Hojberg et al., 2017), and can incorporate geophysical survey data (Refsgaard et al., 2014). Vulnerability mapping relies on the availability of large datasets with good spatial coverage across the region being studied. To predict the presence of reducing conditions in areas where there

Abbreviations: LDA, Linear discriminant analysis; DO, dissolved oxygen.

* Corresponding author.
E-mail address: scott.wilson@lincolnagritech.co.nz (S.R. Wilson).

https://doi.org/10.1016/j.jhydrol.2017.11.045
0022-1694/

is lesser data availability and determine the key controlling variables, statistical models are used (Nolan et al., 2002; Gurdak and Qi, 2012; Tesoriero et al., 2015; Close et al., 2016; Rosecrans et al., 2017). However, both the vulnerability and statistical approaches are premised on understanding the relationship between the redox status of groundwater samples, and local environmental variables such as geology or soil drainage.

For denitrification to occur, four environmental conditions need to be present; anoxic or low oxygen conditions; the presence of a suitable electron donor; sufficient nitrate to act as an electron acceptor, and denitrifying microbes to mediate the reduction reaction (Korom, 1992; Böhlke, 2002, McMahon and Chapelle, 2008; Rivett et al., 2008). The most important electron donor minerals in groundwater systems are organic carbon, pyrite, and the ferrous iron associated with iron oxides (Pedersen et al., 1991; Korom, 1992; Rodvang and Simpkins, 2001; Appelo and Postma, 2005).

Microbes capable of denitrification are considered to be ubiquitous in the environment. As a result, the first two conditions are coupled in the presence of suitable electron donors such as carbon, since the microbes are usually able to reduce oxygen levels so that nitrate is the next electron acceptor and denitrification is able to take place. Thus the redox status of groundwater provides a good indicator of where denitrification can occur (Gurdak and Qi, 2012). This information on redox status can be combined with information on groundwater flow paths and nitrate concentrations to assess if denitrification is likely to occur in a particular groundwater zone. Due to difficulties in sampling in the subsurface there is considerable uncertainty as to the spatial and temporal distribution of reducing zones and even more uncertainty on how much denitrification is occurring. Knowledge of where denitrification can potentially occur in groundwater systems would assist water resource managers with assessment of where reductions in nitrate loads may occur within the subsurface prior to the fluxes reaching receiving waters.

Observations of subsurface redox conditions in New Zealand are limited to the availability of groundwater samples from wells, which can be characterised with respect to redox state. A method to extrapolate these groundwater data to the remainder of the region was proposed and applied by Close et al. (2016). The method used was linear discriminant analysis (LDA), a multivariate statistical method used to distinguish between two or more groups. LDA involves the formation of a model from linear combinations of discriminating variables representing physical characteristics for which the groups (redox classes) are expected to differ. The resulting model is then applied by extrapolation to the remainder of the region.

The method presented by Close et al. (2016) included a number of predictive parameters for elevation, slope, drainage class, carbon content, soil order, geology, geological age, and land use. Potential limitations of the approach were the exclusion of hydrological indicators of redox status, and the use of somewhat arbitrary depth thresholds. Close et al. (2016) also suggested that further work be carried out to test the appropriate scale for application of the LDA method. This paper refines the work of Close et al. (2016) by investigating some key aspects of the methodology and its application. Additional parameters have been included to represent depth to water table, and hydraulic conductivity as measures of waterlogging and groundwater flow potential respectively. The discriminating potential of land surface recharge estimates has also been tested within a subset of the region for which recharge data were available. This paper also assesses the depth for which the model predictions can be considered to be valid, and optimises the representative depth ranges to overcome the use of subjective depth thresholds. Finally, the effect that scale has on the predictive success of the model is tested to determine the number of samples required to have confidence in the model predictions.

2. Methodology

2.1. Study area

Redox assignment was carried out for existing groundwater monitoring data from the 29,800 km^2 Southland region of the South Island of New Zealand (Fig. 1). Sample data were supplied by the regional water management authority, Environment Southland.

The population of Southland is mostly settled on pastoral farms or rural communities, many of which rely on groundwater for a drinking water supply. A recent increase in dairy farming (Ledgard, 2013) and the resulting deterioration of water quality has led to groundwater quality being a particular important issue for the region (Rissmann et al., 2016).

Qualitative approaches to determine areas of denitrification potential have previously been carried out in the Southland region. Rissmann (2011) assigned geological units with a denitrification potential category (high to low) to produce a map of denitrification potential of Southland Aquifers. The classification was based on the expected denitrification potential of main-rock and sub-rock categories in the New Zealand 1:250,000 geological database (QMAP, Rattenbury and Heron, 1997). Areas of soil denitrification potential (SDP) were mapped by Killick et al. (2014) using a ranking system, with organic and gley soil classes having high SDP ratings. Soils with moderately high or high SDP were found to occur in areas of restricted drainage, suggesting a relationship between denitrification potential and soil drainage. Recently, these geology and soil-based studies have been combined to form a regional map of combined reduction potential (Rissmann et al., 2016). The classification provided by this approach involved a twelve fold categorisation of soil redox potential overlying geological redox potential (e.g. low over high).

2.2. Regional hydrogeology

The geology of the Southland region has a high spatial variability from relatively inert plutonic rocks to more reactive organic and volcaniclastic sediments. This variability prompted Rissmann (2011) to map five denitrification categories ranging from very low to very high based on main-rock and sub-rock characteristics in the QMAP geological database (Rattenbury and Heron, 1997).

The basement geology of the Southland Region is centred on the Southland Syncline, formed by indurated Mesozoic clastic and volcanoclastic sediments (Turnbull and Allibone, 2003). Basement geology to the northeast of the syncline consists of Permian to Triassic schist and semi-schist along the northern boundary of the region (Turnbull, 2000). The mountainous country in the western part of the region is known as Fiordland, which consists of mostly crystalline Mesozoic to Palaeozoic rocks (Turnbull et al., 2010). There are very few wells intercepting the basement geology, since the productivity of these rocks is low, even when fractured, and the associated terrane is typically unsuitable for high production pasture or cropping.

The basement rocks are overlain by a regional Paleogene to Neogene marine transgression sequence of conglomerate, sandstone, mudstone and limestone. These sediments host coal and lignite measures, as well as glauconitic sandstones which can provide electron donors for denitrification in areas where they occur.

Overlying the Paleogene to Neogene sandstones are sequences of Quaternary sediments with a complex depositional history determined by climatic and sea level fluctuations, tectonics, catchment vegetation, and the availability of and distance from sediment sources. As a result, the Quaternary sediments represent a diversity of lithologies emplaced within in a wide range of