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Predicting groundwater redox status on a regional scale using linear discriminant analysis

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ABSTRACT

Reducing conditions are necessary for denitrification, thus the groundwater redox status can be used to identify subsurface zones where potentially significant nitrate reduction can occur. Groundwater chemistry in two contrasting regions of New Zealand was classified with respect to redox status and related to mappable factors, such as geology, topography and soil characteristics using discriminant analysis. Redox assignment was carried out for water sampled from 568 and 2223 wells in the Waikato and Canterbury regions, respectively. For the Waikato region 64% of wells sampled indicated oxic conditions in the water; 18% indicated reduced conditions and 18% had attributes indicating both reducing and oxic conditions termed "mixed". In Canterbury 84% of wells indicated oxic conditions; 10% were mixed; and only 5% indicated reduced conditions. The analysis was performed over three different well depths, <25 m, 25 to 100 and >100 m. For both regions, the percentage of oxidised groundwater decreased with increasing well depth. Linear discriminant analysis was used to develop models to differentiate between the three redox states. Models were derived for each depth and region using 67% of the data, and then subsequently validated on the remaining 33%. The average agreement between predicted and measured redox status was 63% and 70% for the Waikato and Canterbury regions, respectively. The models were incorporated into GIS and the prediction of redox status was extended over the whole region, excluding mountainous land. This knowledge improves spatial prediction of reduced groundwater zones, and therefore, when combined with groundwater flow paths, improves estimates of denitrification.

1. Introduction

Nitrate is a key groundwater contaminant in New Zealand and many other parts of the world. Increases in land use intensity with associated increases in fertiliser use and grazing animals, particularly dairy cows, have resulted in increasing levels of nitrate in groundwater systems and impacts on receiving waters such as streams, rivers and lakes (PCE, 2013). In New Zealand these concerns have led to the setting up of a Land and Water Forum (2010, 2012), reforms in freshwater management including a National Policy Statement for Freshwater Management and legislative framework that will require the setting of limits in fresh water for nutrients including nitrate (MfE, 2014). World-wide there are many researchers looking at the factors controlling the distribution of nitrate in groundwater (Kaown et al., 2007; McMahon et al., 2008; Fenton et al., 2009) and the importance of denitrification and redox status to the levels of nitrate observed in different groundwater environments (Thayalakumaran et al., 2008; Hinkle and Tesoriero, 2014).

In the context of meeting limits for environmental protection, a key removal process for nitrate is denitrification.

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

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Denitrification requires four conditions, namely anoxic or low oxygen conditions; provision of a suitable electron donor; microbial consortia capable of carrying out denitrification; and sufficient nitrate (Korom, 1992). Microbes capable of denitrification are considered ubiquitous in the environment (Rivett et al., 2008) and the first two conditions are linked in that if there are suitable electron donors such as carbon, 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 the groundwater provides a good indicator of where denitrification can occur. 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 potentiality occur in groundwater systems would assist water resource managers with assessment of where reductions in nitrate leaching loads may occur within the subsurface prior to the fluxes reaching receiving waters. At present knowledge is limited to where groundwater can be sampled and analysed from existing wells and characterised with respect to redox state. What is needed is a method to take these point assessments of redox state and be able to extrapolate them to the remainder of the region.

Discriminant analysis is a method used to distinguish between two or more groups and fits the requirements for this study. Linear combinations of discriminating variables that measure characteristics on which the groups are expected to differ, are formed and provide a model for extrapolation to the remainder of the region. Linear discriminant analysis (LDA) has been used previously in New Zealand hydrological studies to distinguish between groups of rivers at base flow condition (Close and Davies-Colley, 1990), to discriminate between clusters of rivers sites in the National River Water Quality network (Maasdam and Smith, 1994), and for estimation of age for a set of groundwater monitoring wells (Daughney et al., 2010). Discriminant analysis has been used to investigate the distribution of nitrate in groundwater (Kim et al., 2012; Melo et al., 2012) but only a few studies have used LDA to discriminate between zones of differing redox status. Hsu et al. (2010) and Lee et al. (2008) both used LDA to examine how redox zones influenced arsenic and nitrogen groundwater concentrations for two different catchments in Taiwan. Previous research by our team on determining the occurrence and potential rates of denitrification in small New Zealand catchments (Stenger et al., 2008; Clague et al., 2015) has led to the need for this study to predict subsurface redox status on a regional scale to permit improved assessment of denitrification at the catchment and regional scales.

Our hypothesis is that this spatial knowledge of subsurface redox status, when combined together with knowledge of groundwater flow paths, should significantly improve estimates for the potential for denitrification to occur within a catchment. The aims of this study were to classify the redox status for wells in two contrasting regions of New Zealand, develop models using LDA to distinguish between the groundwater redox states and to provide a prediction of redox status for groundwater within the two regions of Waikato and Canterbury using GIS tools.

2. Methods and materials

2.1. Regional study areas

The methodology was developed and demonstrated using groundwater monitoring data from two large, contrasting agricultural regions in New Zealand (Figs. 1 and 2). Groundwater resources are significant in both these regions and there are many wells with good quality monitoring data that have been collected by the regional councils. The Waikato region is located in the central North Island and covers an area of 25,000 km^2. It contains much of the Taupo Volcanic Zone and its geology is dominated by volcanic rocks and sediments. The highest elevations are in the south around the Central volcanic plateau and water flows northward, initially through subcatchment groundwater systems and then via the Waikato River and its tributaries. The Canterbury region is located on the east coast of the South Island and covers an area of 45,346 km^2. The hydrogeology is dominated by the Southern Alps along the western boundary of the region and significant aquifers occur in the alluvial gravel outwash plains that have formed over many glacial sequences.

The Canterbury and Waikato regions were selected for this study as groundwater use and quality are very important to both regions as a source of water for drinking, food and other industrial processing, and irrigation. Additionally both regions had large (>500) data sets of good quality (standardised sampling protocol and analysed for relevant parameters) groundwater chemistry that allowed robust models to be developed and tested for the assignment of groundwater redox status. The regions have contrasting hydrogeological conditions with Canterbury having large alluvial gravel aquifers consisting of greywacke eroded from the Southern Alps and Waikato having aquifers derived from volcanic material. There were 2223 wells with data suitable (NO_3, DO and Mn — see Section 2.2) for redox assignment from Canterbury and 568 wells with data suitable for redox assignment from Waikato. These wells also had available data for the predictive parameters used in the LDA model development.

2.2. Assignment of redox status

The principles and method used for the assignment of redox status is set out in McMahon and Chapelle (2008). Briefly there is a series of redox reactions that occur in groundwater systems that successively utilise O_2, NO_3, Mn(IV), Fe(III), SO_4, and CO_2 as electron acceptors. There is a decrease in energy available to the microbes from each successive electron acceptor so they will be utilised in the above order, provided that the system is in equilibrium. It is acknowledged that is not a strictly linear process with considerable overlap occurring. These assumptions provide a framework for assigning the redox status depending on which of the electron acceptors and the accompanying reaction products, such as Mn(II) or H_2S, are present. McMahon and Chapelle (2008) used O_2, NO_3, Mn(II), Fe(II) and SO_4 in their framework, as these parameters are relatively easy and inexpensive to measure and are commonly included in regional water quality monitoring programmes. These authors derived thresholds for each parameter based on concentrations typically found for particular redox environments for a range of studies; the thresholds were designed to