Measurement of Denitrification Rates in Groundwater: a collaborative New Zealand – Korean initiative

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ABSTRACT: Nitrate contamination of groundwater is a wide-spread problem in both New Zealand and South Korea and has lead to eutrophication of receiving lakes and rivers. Denitrification in groundwater has the potential to reduce inputs of N to these receiving waters but quantification of the amount of denitrification taking place is difficult. A series of denitrification measurements have been carried out in the field at selected groundwater locations in New Zealand using a recently developed re-circulating well technique to increase sensitivity. This is an ongoing project and the methodology and sites are described and some preliminary results discussed. An overview of the collaborative research programme on in-situ groundwater processes (in which this denitrification project is a component) is provided.

1 INTRODUCTION

Groundwater contamination, particularly from non-point sources, is a significant and growing issue in many countries, including New Zealand and South Korea. Contaminated groundwater can negatively impact surface waters. The research project described in this paper looks at the natural in-situ remediation processes in groundwater and how they might be managed to improve the removal of nitrogen and reduce the impact on receiving waters. The key research questions are: To what extent is denitrification occurring in the presence of natural biofilms in groundwater?; How much does the amount of naturally occurring denitrification in groundwater affect estimates of N loading to receiving waters?; What are the factors controlling denitrification in groundwater?; and Can we use this understanding to enhance the removal of nitrate in groundwater?

Denitrification considered in this paper is a microbially-mediated process whereby nitrate (NO_3) is reduced to N_2O and N_2 gases and an electron donor, such as organic carbon or Fe^{2+}, is oxidised. The rate of denitrification is influenced by groundwater chemistry, such as pH and redox status, substrate availability for the microbes, and biomass and type of microbes present in the system. Denitrifying microbes are fairly ubiquitous in the environment and it is usually assumed that these microbes will grow and function provided that the suitable environmental conditions, such as low oxygen levels, available substrate and nitrate, are present.

This research project is providing new knowledge about the mechanism of natural denitrification in actual aquifers. The validated computer model will provide a useful tool to design efficient remediation systems and to predict the effect of non-point source nitrogen leaching on groundwater and surface water quality. The related key question for Korea is the in-situ remediation of a range of groundwater contaminants, which includes nitrogen. This research will assist more integrated management of groundwater and non-point source contamination inputs by local and central government agencies.

The project is still being carried out so this presentation focuses on the design and methodology aspects. In the next section an overview of the whole research programme is provided and then the work on measurement of denitrification rates in groundwater is presented, beginning with the methodology and site selection, then discussing some preliminary results.

2 OVERVIEW OF THE COLLABORATIVE RESEARCH PROGRAMME

This research programme focuses on the characterisation of two groundwater processes, naturally occurring biofilms, and permeable reactive barriers, for the transformation of nitrogen species and common industrial contaminants. Experiments will be carried out at the laboratory and pilot scale and modelling of carbon and nitrogen species in groundwater systems will extend this to the sub-catchment scale. The project is divided into a number of objectives, which examine different aspects of this work.

In the first objective biofilms are being collected from a range of groundwater systems using natural and artificial substrates. Biofilms are also being grown in the laboratory using natural & spiked groundwater. The biomass and biofilm activities are being quantified using biochemical tests such as DAPI, crystal violet assay and protein for biofilm biomass estimations and selected enzyme assays to estimate biofilm activity. Confocal laser scanning microscopy (CLSM) is being used to visualise and determine biofilm structure. The denitrification potential of biofilms grown in the laboratory and on natural substrates in the groundwater system will be assessed using ^{15}N isotope analyses and measurement of disappearance of $^{15}N\text{-}NO_3$ and appearance of $^{15}N\text{-}N_2O$ and $^{15}N\text{-}N_2$ gases.

Denitrification rates under various reaction conditions are being determined using a column reactor at Hanyang University. The data & rate constants will be used for modelling denitrification in groundwater. The microbial consortia responsible for the denitrification are being identified. Denitrification rates are also being measured directly in a range of groundwater systems. The field measurement of denitrification rates is the focus of the remaining sections of this paper.

The next objective of the research focuses on the development of the groundwater model FEMWATER-N for parallel processing, which will enable larger, more complex groundwater systems to be simulated much more rapidly using high performance parallel computers. A solver that operates in both parallel and serial modes has replaced the existing code. Testing of the new version has shown that the system works well for small and medium sized model domains but for large domain with a number of rivers and streams there were stability issues caused by groundwater-surface water interactions. The computer code for the river module has been re-engineered, which has improved the accuracy of the model and this version is currently being tested. This model will be used with the denitrification rate information obtained from other sections to determine the likely impact of denitrification on estimates of nitrate loading from a catchment into a receiving surface water body.

The final objective uses zero-valent iron (ZVI) and modifications of ZVI to degrade two common industrial groundwater contaminants, pentachlorophenol (PCP) and trichloroethylene (TCE). A limitation was identified in that PCP, unlike many other chlorinated chemicals, was not fully degraded by ZVI. However, a modification using nickel with ZVI to form bimetallic ZVI/Ni completely degraded PCP as well as being cheaper than other bimetallic compounds that have been reported in the literature. The use of iron reducing bacteria for the regeneration of ZVI has been investigated. The degradation of TCE has been enhanced by encapsulating the bacteria responsible for the degradation in a polymer pellet to increase their survival and effectiveness. Both hydrophilic and hydrophobic polymers are being investigated in this research.

3 MEASUREMENT OF DENITRIFICATION RATES IN GROUNDWATER

Rates of in situ reaction processes, including denitrification rates, in groundwater are often measured using the push-pull test (Istok et al., 1997). This is a practical and economical alternative to the approach of using large-scale natural gradient tracer tests with multiple wells. A significant disadvantage of the push-pull test is that it is not suited to groundwater systems where reaction rates are slow and groundwater velocities are fast. In these conditions the injected tracer tends to move beyond the recapture zone before a significant amount of reaction has taken place. A re-circulating well technique has recently been developed (Burbery & Wang, 2009) to overcome this limitation, whereby the injected tracer (and sometimes nitrate) is retained within a re-circulation cell for a sufficient length of time so that the denitrification rate can be estimated.

The technique is described in detail by Burbery and Wang (2009) and is briefly summarised here. A re-circulating, or dipole, flow cell is set up in the groundwater by pumping from a down-gradient well and injecting the pumped water into an up-gradient well, as shown in Fig. 1. The action of the dipole cell mixes the solutes within the cell and isolates the solutes within the dipole from the surrounding regional flow, thus providing a prolonged residence time within the testing zone. The shape of the re-circulation cell is dependent on the distance between the wells, the regional flow rate, and the well pumping rate. After the pumping has equilibrated a conservative tracer is injected as a pulse and the concentrations of tracer and nitrate are monitored in the re-circulating flow. Provided the rate of mass loss from the dipole is smaller than the effective rate of denitrification, the tracer and nitrate breakthrough curves can be used to estimate the denitrification rate. The mathematical procedure for analysing the breakthrough curves is given by Burbery and Wang (2009) and is not reproduced here.

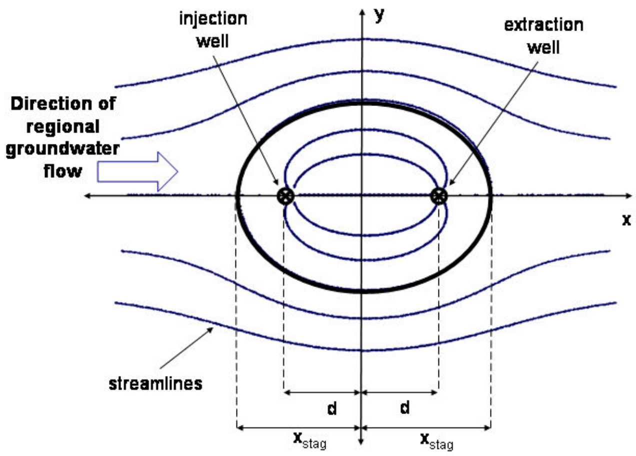

Fig. 1. Schematic of the re-circulating flow cell in a homogeneous, isotropic aquifer, where d is half-distance between the wells and x_{stag} is the stagnation point for the dipole flow cell.

4 SITE SELECTION AND DESCRIPTION

Six sites have been selected in three different aquifer settings throughout New Zealand and their locations are shown in Fig. 2. Two sites are located in coarse alluvial gravel aquifers, two are located in pumice sand aquifers with fine to coarse sand layers and the other two sites are located in an Oruanui Ignimbrite formation, which is an un-welded fine sand aquifer in the Taupo region.

4.1 Alluvial gravel aquifer sites

The Burnham experimental site (Fig. 2) is located on the Central Canterbury Plains alluvial gravel aquifer. The experimental site has 23 wells located within an area of 50 m by 100 m with an up-gradient injection well and 4 down-gradient monitoring well arrays. It has been characterised using tracer and pump tests (Pang et al, 1998; Dann et al, 2008). The groundwater velocities at the site are high with a mean of 60 m/day and the flow paths show significant heterogeneity and curvature (Pang et al, 1998).

A denitrification test using re-circulating wells was undertaken at this site as part of this project but the tracer was not retained within the re-circulation flow cell for longer than 1 hour after the injection was completed. The main reasons for the test failure were the high groundwater velocities and the significant level of heterogeneity at the site. The well pumping rate was restricted by the size of the available extraction well. This was a 150 mm diameter well but a larger well and pump would have been required for the high regional flow rates and heterogeneity observed at the site.

A second site in an alluvial gravel aquifer has been identified in Southland (Fig. 2). This site has a lower groundwater velocity of 3-6 m/day (Hughes, 2000) and a larger diameter pumping well (300 mm diameter) is available for the test. The denitrification experiment will be carried out later in 2009.

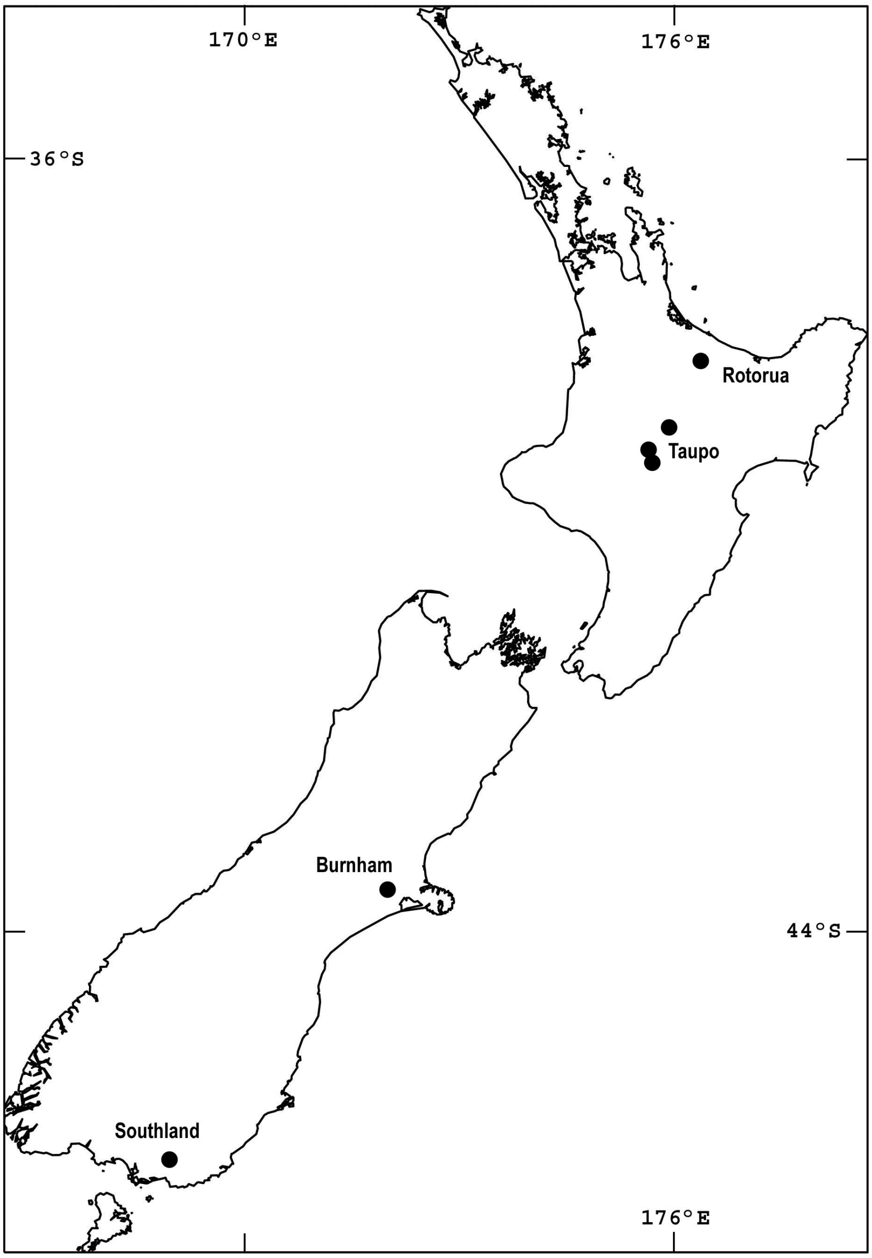

Fig. 2. Location of experimental sites within New Zealand.

4.2 Pumice Sand Aquifers

An experimental site has been set up near Rotorua (Fig. 2) to investigate the movement and attenuation of microbes in a coarse pumice sand aquifer (Wall et al., 2007). A total of 10 wells have been installed with an up-gradient injection well and 3 down-gradient well arrays. The groundwater velocity is approximately 0.6 m/day and the aquifer is reasonably homogeneous (Wall et al., 2007). This site was used for the denitrification experiment and the wells were 2 m apart. The second site selected in a pumice sand aquifer is located at Kuratau near Lake Taupo. The wells are 5.5 m deep and are located 2 m apart and are screened in an anoxic section of the aquifer. The denitrification rate experiment is currently underway at this site.

4.3 Oruanui Formation Fine Sand Aquifers

Two sites have been selected around Lake Taupo in the Oruanui formation. At both sites there is an oxic layer near the water table and then a deeper anoxic layer. The wells at one site are 1.5 m apart and at the other site are 2 m apart. The denitrification rate experiments are currently underway at these sites.

5 PRELIMINARY ANALYSIS OF RESULTS FROM ROTORUA SITE

A denitrification rate experiment was carried out at the Rotorua site and a preliminary analysis is given to illustrate the methodology. The pumping rate between the wells was 19.2 m^3/day and the duration of pumping was 12 days. A pulse of Br tracer (1.8 kg in 100 L) was injected over a 5 hour period and the Br and NO_3 concentrations were monitored in the re-circulating water. The dissolved oxygen level was 70% saturation and the DOC values ranged from 0.7 – 1.1 mg/L. The Br tracer and NO_3-N concentrations in the re-circulating water (Fig. 3) show that the Br tracer increased rapidly during the injection period and then decreased rapidly to around 120 mg/L after injection ceased, corresponding to the tracer concentration equilibrating within the flow cell. Thereafter the levels slowly decreased to around 50 mg/L after 12 days, reflecting the slow loss of tracer from the flow cell. This indicates that the re-circulating cell technique worked well with respect to the tracer and the establishment of the dipole flow cell. The NO_3-N concentrations in the surrounding well array prior to the experiment ranged from 10.6 – 12.2 mg/L. The increase in NO3-N concentrations in the re-circulating water (Fig. 3) probably reflects the mixing of water within the dipole flow cell. The NO3-N concentrations decreased over the 12 day experimental period but did not decrease below 10.7 mg/L, similar to some background concentrations. This indicates that little, if any, denitrification had taken place, which is not surprising given the high level of dissolved oxygen and low levels of DOC. More denitrification is expected at the sites around Taupo given the more anoxic conditions observed at those sites.

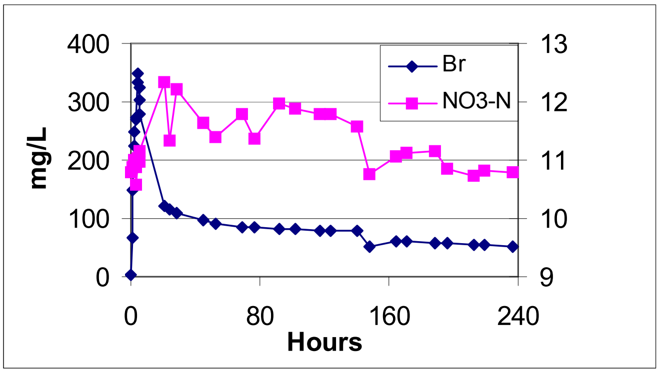

Fig. 3. Br and NO_3-N concentrations in the re-circulating water at the Rotorua site

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