Groundwater Nitrate Bioremediation of a Fractured Rock Aquifer System in South Africa

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Abstract

Due to the importance of groundwater in South Africa, the University of the Free State has successfully developed a zero waste bioremediation technology to treat nitrate pollution in water. Groundwater nitrate pollution of a fractured rock aquifer arose due to the storage of fertilizer effluent in unlined quarries. Numerical model simulations indicates that the proposed remediation removes the nitrate from the aquifer in a shorter timescale than the predicted natural attenuation. Treating the polluted water on site with the zero-waste bioremediation technique, and then re-injecting the treated water into the aquifer provides a holistic and sustainable solution to nitrate pollution.

Keywords: bioremediation, groundwater, fertilizer effluent, numerical groundwater model, nitrate

Introduction

The use of bioremediation, especially denitrification, to remove site contaminants such as nitrate (without the use of filters or ion exchange) is a very complex process with multiple variables. Figure 1 displays the nitrogen cycle with the pathways of interest, namely the anammox, nitrification, ammonification, nitrogen fixation and denitrification. Even though leaching, mineralization, immobilization and volatilization forms part of the nitrogen cycle, it is not the main focus of this report as this system only focus on water treatment. These pathways are driven by various factors including biological, physical and physiological factors. Research has demonstrated that microorganisms have the ability to survive, adapt, and eventually thrive in almost every environment (Stevens et al. 1993; Phelps et al. 1994; Fredrickson & Onstott 1996; Colwell et al. 1997; Onstott et al. 1998; Pedersen et al. 2000; Moser et al. 2003; Kieft et al. 2005; Gihring et al. 2006; Onstott et al. 2009; 2011; Ragon et al. 2013; Lau et al. 2014; Rajala et al. 2015).

Nitrate reduction is a naturally occurring process, which is performed by a large group of heterotrophic facultative anaerobic bacteria, such as *Paracoccus denitrificans, Rhodobacter sphaeroides* and *Pseudomonas spp.* The ultimate by-product is nitrogen gas (N_2) which follows the following reduction pathway: nitrate (NO_3^-) → nitrite (NO_2^-) → nitric oxide (NO) → nitrous oxide (N_2O) → nitrogen gas (N_2) (fig. 1).

The groundwater nitrate pollution arose due to the storage of fertilizer effluent in two unlined dolerite quarries. This resulted in the degradation of the groundwater quality of the underlying fractured rock aquifer. Nitrate may enter groundwater with ease and migrate over large distances from the source due to the high solubility of nitrate, and because soils are largely unable to retain anions (fig. 2).

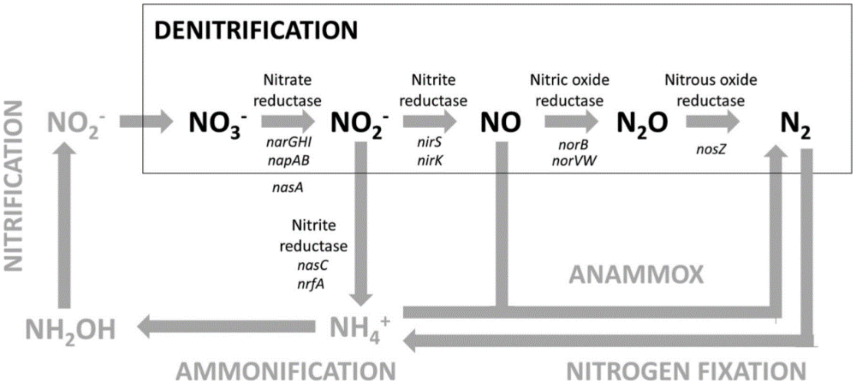

Figure 1 *The Nitrogen Cycle (Taken from Alvarez et al. 2014).*

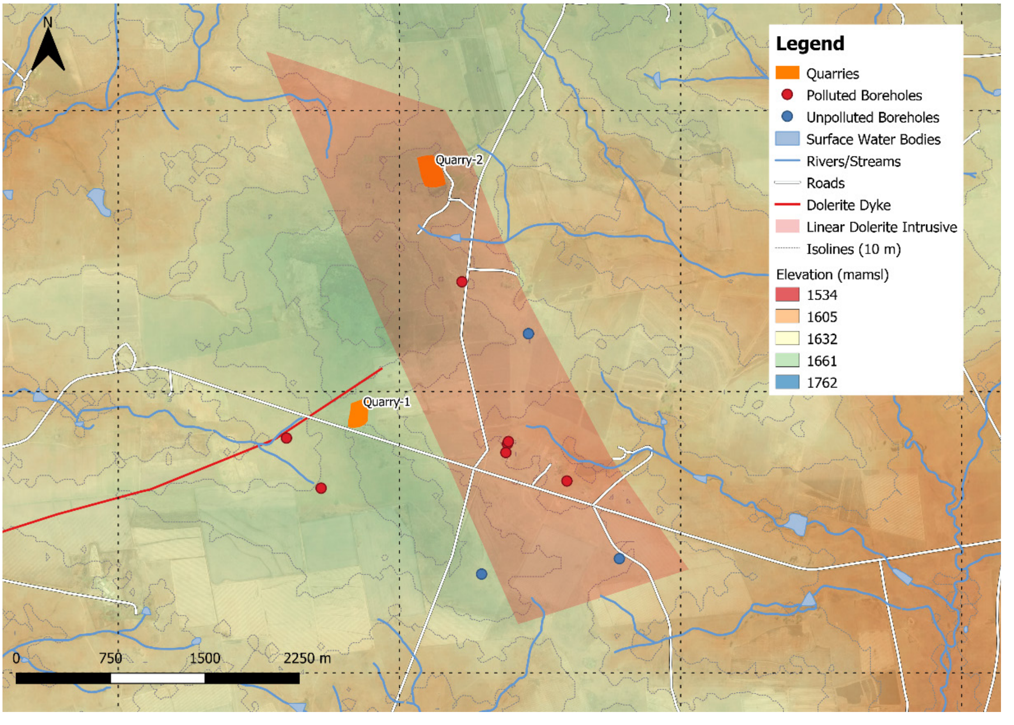

Figure 2 *Study Site Layout Map.*

Materials and Methods

Bioremediation – Proof of Concept

A customary nitrate reduction column was prepared according to standard operating procedures used in the TIA/SAENSE platform. The column consisted of 110 mm PVC pipe with a height of 1 m, containing dolomite as a solid matrix and sealed at both ends to create an anoxic environment. The column was equipped with In/Out valves and connected to a peristaltic pump with silicone tubing. The drainage volume of the column was measured, which was used to calculate the hydraulic retention time (HRT) of the column. Influent water containing an electron donor was introduced at the base of the column at the determined HRT. Before the nitrate contaminated water was added, the column was seeded with the microbial community that consisted of known nitrate reducers and the column was closed until optimal Oxidation Reduction Potential (ORP) conditions for nitrate reduction (± -150 mV) was reached. Once optimal ORP conditions were obtained, the column ran at a HRT of 24 hours.

The added donor will allow the microbial community to deal with higher amounts of nitrate and this relates to an increased Biological Oxygen Demand (BOD) and will enhance growth. To have maximum growth and denitrification, the electron donor is stoichiometrically balanced with the electron acceptors (oxygen, to promote anaerobic conditions and nitrate, for denitrification). The system therefore creates anoxic conditions by controlling the oxidation reduction (redox) state. Other factors that have an influence on denitrification such as temperature, pH and HRT was also controlled throughout the laboratory column experiment. The column effluent (treated water) was sampled intermittently and analysed for pH, DO, ORP, Temp, EC, NO_3-N, NO_2-N and NH_3-N. These parameters were used to determine if any working conditions could be changed in the column to ensure maximum nitrate reduction. Due to the high concentration of nitrates present in the water, the column first ran on diluted water for 60 days. Thereafter the dilution factor was decreased in order to identify the highest concentration of nitrate that the microbial consortium could tolerate while still reducing nitrate to levels below the SANS 241 class 1 limits.

Groundwater Quality Interpretation

Quarterly groundwater monitoring data for the study site was available from 2015 to 2018. This data was analysed statistically as well as over time to determine the groundwater response of specifically the nitrogen compounds, i.e. nitrate and ammonia in the groundwater.

Groundwater Numerical Modelling

A numerical groundwater model was developed for the study site to achieve the set objectives and the form the base for the numerical groundwater transport models. The FEFLOW software programme (Version 7.1) was used for the numerical groundwater model. The software applies the Finite Element method to approximate differential equations and simulate fluid flow and transport of dissolved constituents in the subsurface with reactive components.

The purpose of the model was to simulate contaminant transport in the groundwater system and to evaluate the remediation strategy for the site. To achieve this aim, modelling scenarios were performed using the developed, calibrated numerical groundwater model.

Remediation Strategy/Approach

The remediation strategy is to pump treated water from a bioremediation plant to the two quarries that initially contained fertilizer effluent water that polluted the underlying aquifer/groundwater. These two quarries are situated on a topographic high (water divide), thus if the quarries are filled with water, it will generate an artificial hydraulic head, recharging the underlying aquifer. The treated water will this be used to flush the underlying aquifer to dilute the nitrate concentrations within the groundwater. It is likely for this treated water to enter the same preferential flow paths of that of the fertilizer effluent initially dumped in the quarries.

Results and Discussion

The results of the Nitrate Reduction Column Tests (fig. 3) are discussed below:

I. Stage One Results (inlet effluent diluted five times)

a. The average nitrate reduction was 88.4% during the first 60 days and was below the SANS241 standards for drinking water.
b. No nitrite or ammonium was produced, indicating that complete denitrification took place, with final concentrations of 0.049 mg/L and 1 mg/L, respectively.
c. The increase of the nitrate concentration in the outlet values during 31/01/2017 and 09/02/2017 happened, because feeding of the donor in the column was stopped to determine if the system (microorganisms) will be able to restore itself once introduction of the donor was again resumed. The system was able to restore itself as can be seen in the graph.

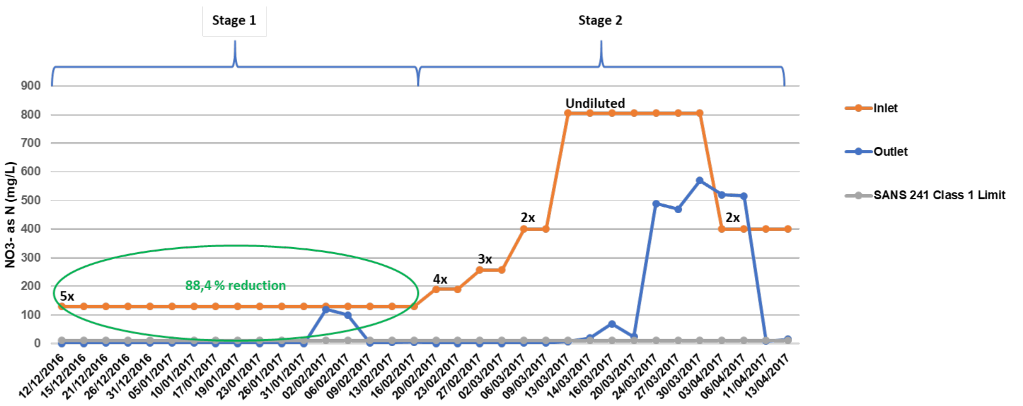

Figure 3 *Nitrate (as N) profiles for the influent and effluent water.*

II. Stage Two Results (stepwise increase of inlet effluent concentration):

a. On 16/02/2017 the dilution factor was decreased to four times (4×) to contain an inlet nitrate concentration of ~190 mg/L and for the following seven days, the nitrate reduction could be maintained below the SANS241 standards (1.3 mg/L as N, resulting in 99.3% removal).
b. On 23/02/2017, the dilution factor was again decreased to three times (3×) to contain an inlet nitrate concentration of ~258 mg/L and for the following seven days, the nitrate reduction could still be maintained below the SANS241 standards (0.9 mg/L as N, resulting in 99.7% removal).
c. On 02/03/2017, the dilution factor was again decreased to two times (2×) to contain an inlet nitrate concentration of ~400 mg/L and for the following seven days, the nitrate reduction could once again be maintained below the SANS241 standards. The nitrate outlet was 2.1 mg/L (as N), resulting in 99.5% removal. The nitrite and ammonium concentrations were 0.05 mg/L and 0.26 mg/L, respectively.
d. On 09/03/2017, the inlet was pumped undiluted into the column with an inlet nitrate value of 805 mg/L. During the following seven days, the nitrate outlet gradually increased to 24.3 mg/L, the nitrite increased to 3.92 mg/L and the ammonium increased to 0.75 mg/L.
e. From 24/03/2017 to 30/03/2017, the outlet values increased drastically, having nitrate and nitrite concentrations of 570 mg/L and 63 mg/L, respectively. The ammonium remained at 0.27 mg/L.
f. On 30/03/2017, the pump was stopped and the column was closed for five days. The inlet was again diluted two times (2×) to a nitrate concentration of ~400 mg/L before starting the column for another 14 days.
g. During the last week of the experiment (11/04/2017 – 13/04/2017) the outlet values decreased again for nitrate, nitrite and ammonium to 15.2 mg/L, 2.02 mg/L and 1 mg/L, respectively.
d. The highest nitrate inlet value observed in this study, that did not lead to incomplete denitrification, was two times (2×) diluted i.e. ~400 mg/L of nitrate, however nitrate concentrations between 400 mg/L and 800 mg/L remains to be tested.

The most polluted borehole, indicating the highest nitrate concentration over the monitoring period (maximum = 7 692 mg/L as NO_3^-) is also the closest borehole down gradient from Quarry1 along a dolerite dyke that acts as a preferential groundwater flow path for polluted water to flow from the quarry to the borehole. A plot of the time series data from 2015 to 2018 indicates a trend of decreasing nitrate concentrations with time (fig. 4).
A trend line of the average concentration changes throughout the monitoring history is also shown on fig. 4. This trend line can

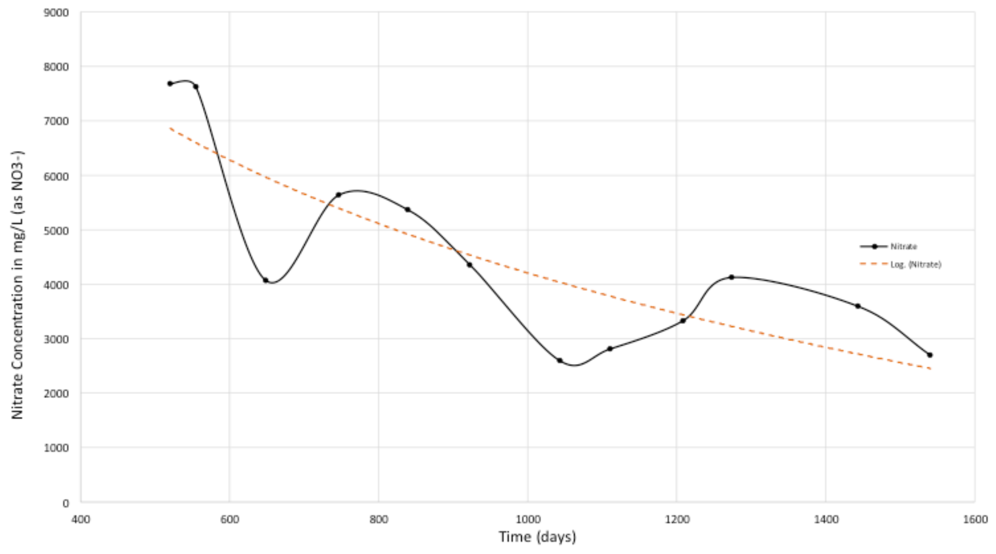

Figure 4 *Time Series data of nitrate concentrations in the most polluted borehole down gradient from Quarry-1.*

be described by the following mathematical expression:

$y = -4060 \ln(x) + 32\,253$

The equation expresses the average behaviour of nitrate concentration (as NO_3^-) over time, where time in fig. 4 is in days. Evaluation of this expression in conjunction with the time series data indicates that the rate of nitrate decrease is such that the nitrate concentration is projected to reach concentrations below the SANS 2015 drinking water limit of 50 mg/L (as NO_3^-) in the year 2024.

The simulations from the numerical model indicates that the proposed remediation removes the nitrate from the most polluted borehole in a shorter timescale (between the year 2021 and 2023) than the predicted natural attenuation (fig. 5).

The analysis above is based on the assumption that the source is totally removed and that the only nitrate present in the system is the nitrate in the groundwater itself.

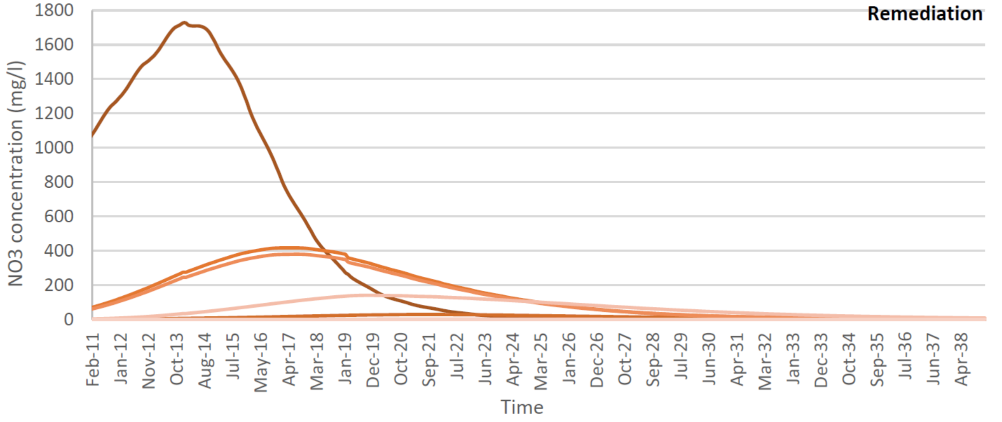

Figure 5 *Simulated nitrate concentrations (as N) with the implementation of the remediation strategy.*

Conclusions

The results obtained from the laboratory column test indicates that an effective bioremediation strategy can be developed for the complete nitrate reduction in the polluted water. The simulations from the numerical model indicates that a combined remediation strategy of pumping contaminate water, treating it on site with the zero-waste bioremediation technique, and then re-injecting the treated water into the aquifer can provide a holistic and sustainable solution to the nitrate pollution.

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