In-situ nitrate removal from groundwater to supply rural communities: experimental work and modelling

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Abstract

With the increasing demand on limited resources, groundwater will have to serve more people in southern Africa, especially in remote rural areas. The situation is becoming more precarious with the projected change in rainfall and climate patterns. Concurrently, nitrate pollution of groundwater would seem to be on the increase. This makes the remediation of high nitrate groundwater by low cost and robust methods a much-needed intervention.

Three methods that have shown potential for full-scale application are reverse osmosis, ion exchange, and biological denitrification. Biological denitrification is specific in the removal of nitrate and is thus the most versatile approach being studied. In situ denitrification, i.e. within the aquifer, is an attractive alternative due to relative simplicity and low investment and maintenance costs.

Research needs identified include minimisation of nitrite accumulation, optimisation of reaction conditions, inhibitory effects of reaction intermediates and by-products, and optimisation of measuring and control systems. This work presents a laboratory model set up using a 2200 x 350 x 350 mm column for denitrifying high nitrate groundwater. The column contains seven ports which stretch along the entire column like observation boreholes and can be used either for sampling or injecting during the experiment. The sampling/injecting ports are at 300, 500, 700, 1000, 1200, 1500, and 1700 mm distance respectively. Hence the reactions can be studied over the total length of the column. An unconfined primary aquifer will be simulated. Flow, pH, EC and initial conditions will be as close as possible to field conditions. Monitoring will include nitrogen species (organic N, NO_2^-, NO_3^- and NH_4^+), pH, EC, Eh, as well as indicator microbiological species (e.g. heterotrophic plate count). Hydraulic properties and

flow rate will also be monitored with time. Modelling using PHREEQC and an excel based model will be done using the data from the experiment.

Results describe the comparison between Phreeqc modelling and batch experiments for in-situ groundwater denitrification using sawdust as an electron donor and carbon source with respect to changes in system performance with time.

Keywords: nitrate pollution, denitrification, experimental work, modelling of denitrification.

1 Introduction

An overview of the nitrate distribution in groundwater in South Africa was prepared by [1] (fig. 1). This shows a distinctive belt of high nitrate concentrations along the Northern provinces of South Africa, with a few isolated point type areas with high concentrations along the south west coast.
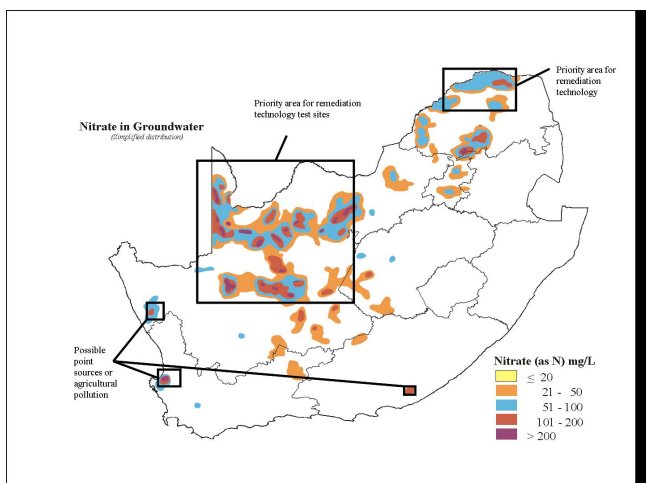

Figure 1: Map showing distribution of nitrate concentrations as N mg/L in groundwater across South Africa, after [2, 9].

A recent project re-examined the nitrate concentration for South Africa (fig. 2) with specific emphasis on more recent data [3]. The most recent data shows that the number of points being monitored nationally has diminished considerably, and that a large percentage of the country is either not monitored or the data is not held within a single database.

This leads one to believe that the picture portrayed by the data is one that is an underestimation of reality. The particular interest in nitrate as a constituent of groundwater stems from its potential health effects to humans as well as livestock. Many cases of cattle deaths have been reported in certain areas where high nitrate groundwater prevails, [4]. Methaemoglobinaemia or "blue baby
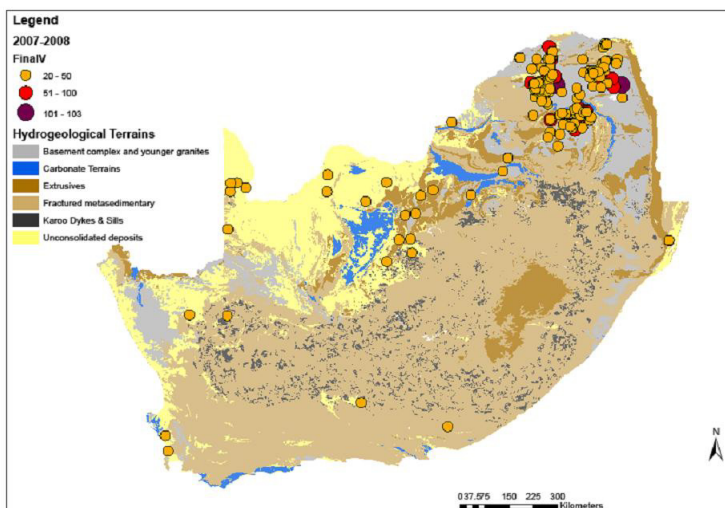
Figure 2:   Map showing nitrate concentration data and geology across South Africa for the period 2007 to 2008, prepared by [3].

syndrome" as it is otherwise known has also been owed to high nitrate and nitrite concentrations. Debate about the actual links between the high nitrate concentrations and some health conditions such as spontaneous abortion, cancer and death by asphyxiation is ongoing as definitive proof is not available for all conditions. Reports on actual cases of blue baby syndrome in the US showed that most occurred at concentrations above 20mg/L as N [5]. It is also argued that a combination of high nitrate and nitrite and bacterial pollution is more likely to cause such conditions rather than nitrate on its own.

Remediation or treatment of nitrate can be done in a variety of ways depending on the area and available budget. Different skill levels are required for different techniques. The three most referred to techniques for nitrate removal include ion exchange, reverse osmosis and bioremediation (table 1).

Many bacteria are capable of growing anoxically by reducing nitrogenous oxides to gaseous products. The bacteria use nitrogenous oxides instead of oxygen as an electron acceptor and the process results in the release of ATP and is termed denitrification or dissimilatory nitrate reduction. The organisms involved thus gains energy from the process and can then synthesis cell mass and or maintain existing cell mass.

Some detailed studies have raised a view that denitrification can only occur under anoxic conditions, but it has since been shown that it can indeed occur on the presence of oxygen [6]. The interactions of native microbial populations, contaminants, and reactive barrier materials are likely to be quite complex, and have the potential for either beneficial or detrimental effects on the remediation [7]. The hazard of high nitrate concentrations and probable causes thereof is discussed in more depth [8].

Table 1: Most popular methods used to remove nitrate, basic methods, advantages and disadvantages and removal efficiency [11].

Method	Basic methodology	Advantages	Disadvantages	Removal efficiency
Ion exchange	Ions from a resin is exchanged for ions in feed water	Ease of operation; highly reliable Lower initial cost; resins will not wear out with regular regeneration, Most effective and most efficient; widely used Suitable for small and large installations	Does not completely eliminate all NO_3^-, IX cannot remove nonionic dissolved species or microbes, Requires frequent monitoring for nitrate removal, Requires salt storage, Strongly basic anion resins are susceptible to organic fouling; reduced life; thermodynamically unstable	80-99%
Reverse Osmosis	Physical process directing purer water through a semi-permeable membrane	Produces highest water quality Can effectively treat wide range of dissolved salts and minerals, turbidity, health and aesthetic contaminants, and certain organics; some highly maintained units are capable of treating biological contaminants, Low pressure (<100 psi), compact, self-contained, single membrane units are available for small installations	Relatively expensive to install and operate, Frequent membrane monitoring and maintenance; monitoring of rejection percentage for NO3- removal, Pressure, temperature, and pH requirements to meet membrane tolerances. May be chemically sensitive	50-96%
Bioremed iation PRBs, injection etc.	Impacted ground water amended to stimulate biochemical reaction to convert nitrate to nitrogen gas	Cheap, very fast, natural process complete plume remediation, new technology	impact to geochemistry, regulatory concerns, biomass build up	70-95%

2 Laboratory setup and modelling

The denitrification reaction was studied in batch experiments using nitrate in groundwater, soil, and a carbon source as an electron donor and energy source for indigenous bacteria. No bacteria are added to the reaction as resident heterotrophic bacteria should be present to facilitate the reaction [9]. Sawdust /woodchips are used as a carbon source based on previous experiments which considered glucose, methanol, maize meal and sawdust [9]. Sawdust was selected for its slow release and potentially longer period of operation without maintenance [10]. Process modelling was done using excel. This is based on the stoichiometric relationships of the reactions and breakdown products (fig. 3) shows the conceptualization of the processes considered.

Using the data from batch experiments [9], Phreeqc was used to model the sandbox chemistry with time and distance within the column (fig. 4). Dissolved organic carbon was used to represent the available carbon for reaction. The influent water composition represents groundwater, while the cells labelled 1 to
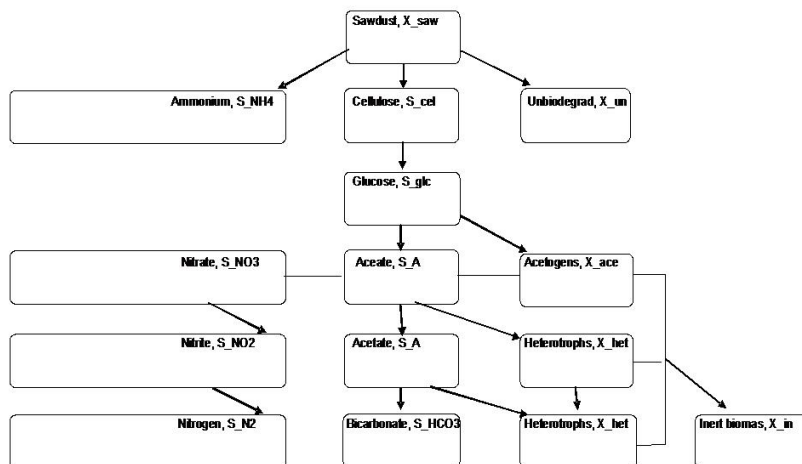
Figure 3:   Conceptual model for sawdust breakdown and denitrification [3].
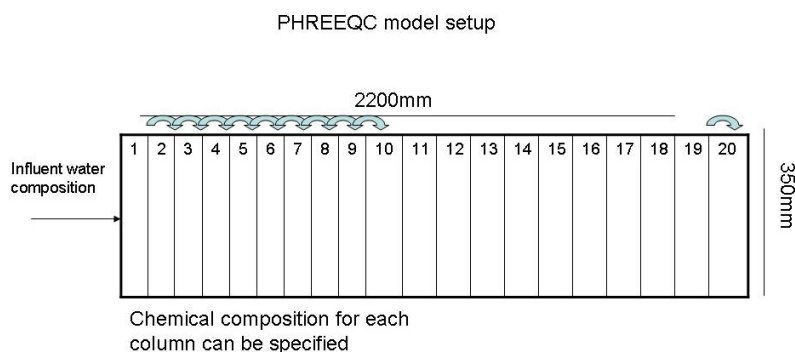
PHREEQC model setup

Figure 4:   Sketch to outline the operation of PHREEQC.

20 represent aquifer material or soil material with respect to chemistry and exchange surfaces.

Based on stoichiometric relationships and experimental conditions several parameters were determined using a spreadsheet model (table 2). The spreadsheet model is useful to predict requirements based on stoichiometric relationships as well as flow characteristics and rate constants. Phreeqc uses a sequential method of calculating resultant concentrations of parameters using chemical compositions of constituents of the system, reaction mixtures, kinetics and ion exchange as well as transport over the specified period. One can thus calculate the concentration at any cell at a specific time and compare the concentration at all cells at a specific time. Initial solutions were influent

groundwater with nitrate concentration of 80mg/L and hardly any dissolved organic carbon present (1.0mg/L). Heterotrophic plate count data was used as an estimate of a starting concentration of bacteria of 20 in the form of plate count for groundwater and a lower concentration by two or so orders of magnitude was used for the soil. Soil nitrate was more elevated than the groundwater (230mg/L), while it was amended with carbon with an available dissolved organic carbon of 50mg/L was used. Alkalinity was higher for groundwater (345mg/L) than in the soil (140mg/L). Soil pH was 9, while groundwater pH was near neutral 7.2. Trace metals iron manganese and zinc were not present in the groundwater solution, but in low concentrations in the soil (Fe-2.5mg/L, Mn-0.04, Zn-0.05).

3   Results and discussion

Using the spreadsheet model and dimensions of the column used in the experiment as well as the respective volumes and concentrations of materials, a list of variables or parameters (table 2) could be determined using a set time period (90 days) for running of the experiment. Half saturation constants, yield coefficients, and stoichiometric relationships used in the spreadsheet model were used as input parameters in PHREEQC during the definition of the denitrification rate and kinetics blocks. Monod kinetic equations were used for denitrification and carbon consumption. Biomass growth was defined as a function of the rate of consumption of organic substrate. Saturation indices of various possible minerals are calculated with every step, so one could pre determine the probability that a mineral may or may not precipitate in a system based on the reactions and initial concentrations as well as the changes the system undergoes during reaction.

Table 2:   Dimensions, volumes and flow scenarios calculated from spreadsheet model.

Dimensions, volumes and flow scenarios from spreadsheet model

Experimental set-up		
Area	0.123	0.123 m2
Flow velocity	0.5	2.5 m/d
Flow rate	0.061	0.306 m3/d
Inlet Nitrate	40	40 gN/m3
Eff Nitrate	20	20 gN/m3
N removal	20	20 gN/m3
N removal rate	1.225	6.125 gN/d
N removal rate	0.044	0.219 molN2/d
Nitrite removal rate	0.088	0.438 molN/d
Acetate (Nitrit) removal rate	0.066	0.328 mol Ac/d
Nitrate removal rate	0.088	0.438 molN/d
Acetate (Nitrat) removal rate	0.044	0.219 mol Ac/d
Acetate (tot) removal rate	0.109	0.547 mol Ac/d
Sawdust requirement	0.073	0.366 mol sawdust/d
Operation period	90	90 d
Sawdust load	1120	5602 g sawdust

Concentration changes with time for the PHREEQC simulation (cell 5 of the column) is consistent to that of treatment where 24:1 C:N (fig. 5) was used for denitrification. The initial concentration of the soil-water mixture is more elevated for the solutions used in PHREEQC than that of the measured solutions.

The actual concentrations from previous experiments are compared to PHREEQC simulation results.
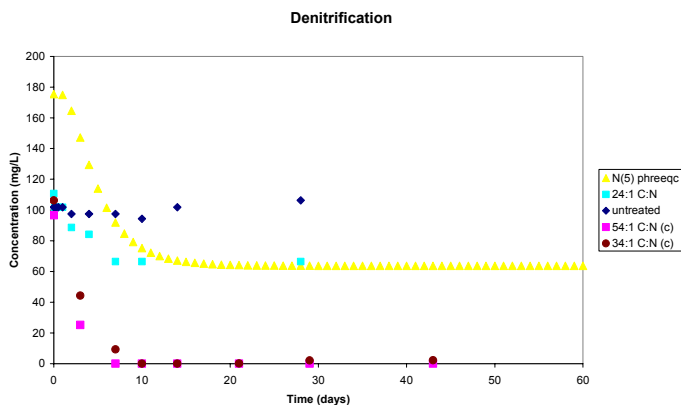

Figure 5:   Nitrate concentration changes with time.
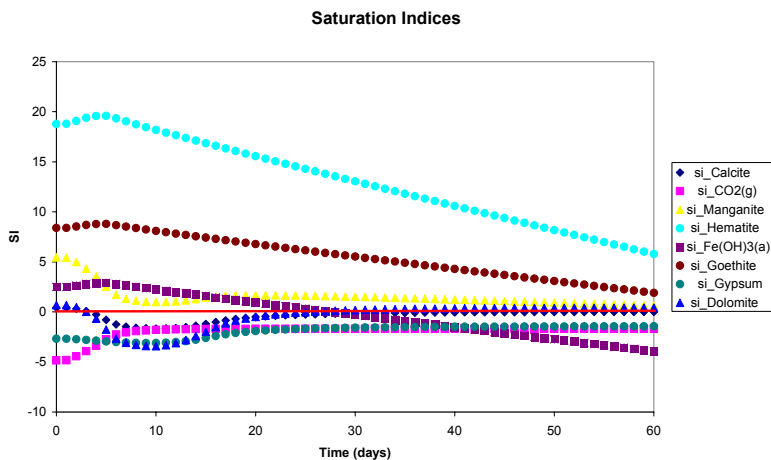

Figure 6:   Saturation indices as calculated by Phreeqc.

Greater C:N effects rapid denitrification in a short period of time. The PHREEQC simulation may be a carbon limited system. Saturation indices were determined in PHREEQC for iron, manganese, carbonate and sulphate containing minerals. Results from previous experiments showed the presence of iron in solution, however infrequent analyses makes it impossible to compare

here, however, its occurrence in solution where it was not present for the measured data confirms the probability of dissolution or precipitation at certain concentration ranges.

The graph shows over saturation of most iron containing minerals, and hence a possibility of precipitation of iron minerals. This presents some limitations to the longevity of remediation barriers. Monitoring of hydraulic conductivity or maintenance of low rates of deposition of iron containing minerals by limiting the oxygen in the system and hence maintaining iron in reduced form is a key to successful management of remediation.

Changes in pH affect the carbonate equilibrium causing it to move toward dissolution and become saturated again after the pH stabilized in the system. Comparison of the simulation pH and actual measured pH values during denitrification follows. Note that the initial pH values of mixed samples for measured results is lower than the resultant pH of mixing for PHREEQC.
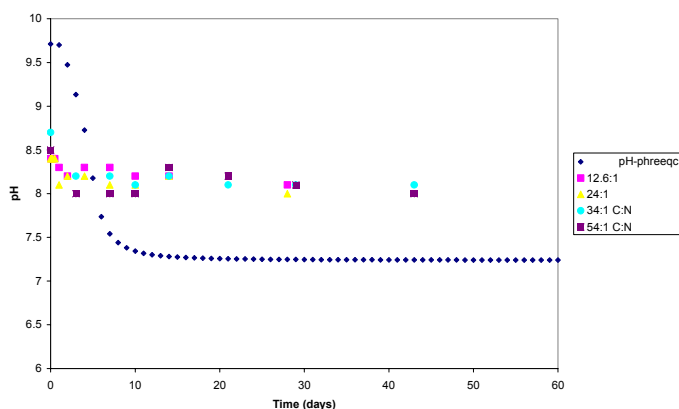

Figure 7:   Comparison of pH measured to calculated by Phreeqc simulation.

The pH range for PHREEQC is greater than that of the actual measured pH levels. Biomass build-up based on heterotrophic plate count (HPC) measured was plotted and compared to modelled values. A limitation to the initial concentration using PHREEQC resulted in inability to use the initial measured heterotrophic plate count, but the closest number was use as an initial concentration.

The PHREEQC graphs represent different positions and hence a delay can be noted in the cell 20 graph as compared to e.g. cell 5. In comparison to measured values, the untreated values plot closest to the modelled values, this is due to the small initial biomass concentrations used in the input of PHREEQC. Measured data shows a peak growth and eventual die-off or start of die off, however the monitoring period was only 28 days and hence no further data was available for comparison.
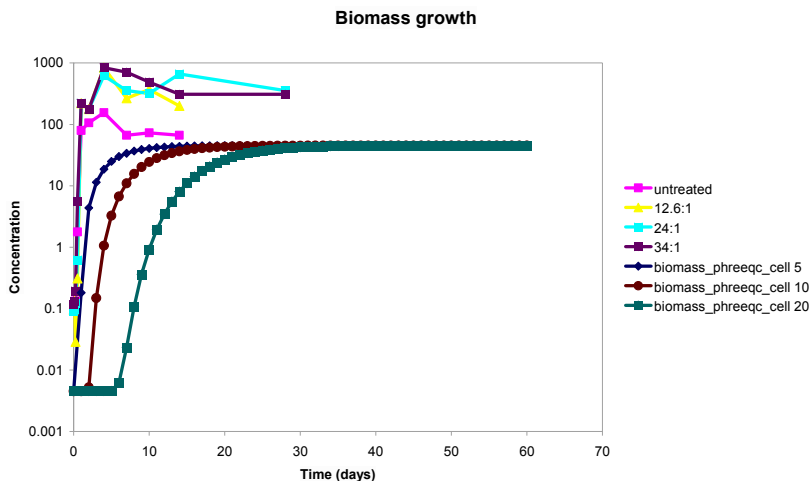
Figure 8:   Heterotrophic plate count or biomass concentration with time.

4   Conclusions

The PHREEQC simulation reaction is carbon limited as complete depletion of the carbon source occurs before the nitrate is used up, while the opposite relationship is true for the actual measured samples. This is due to the intermittent release of carbon during the laboratory experiment.

Both the measured and simulated experiments show a decline in the nitrate concentration with time coinciding with an increase in alkalinity.

Phreeqc calculates saturation indices for mineral assemblages, here many iron and manganese minerals may precipitate or be oversaturated, while carbonate containing mineral assemblages will dissolve with time. Carbon dioxide gas also becomes more saturated in the system, as it is a product of denitrification and many other redox and biological reactions.

The relationship between alkalinity and nitrate concentrations is consistent to the measured data. As is the biomass growth. Importantly, the biomass growth takes into account the rate of carbon consumption, but is greatly affected by the initial number of or amount of bacteria as well as the initial concentrations of carbon.

The saturation index gives one an indication of probability of precipitation or dissolution. The extent of precipitation may lead to eventual clogging in a barrier technology. It is thus useful to be able to calculate this but more important to measure parameters such as hydraulic conductivity or changes in flow rates to try and avoid it.

Initial concentrations of chemical constituents as well as biomass play an important role in the output concentrations. Transport in PHREEQC relates to a delayed response with time in the sandbox, due to the travel time of solutions.

5   Recommendations

Future experimental work and modelling should take into account changes in initial concentration per cell after carbon and nitrate is used up, instead of using the same initial conditions for each cell.

PHREEQC gives a good indication of saturation indices of minerals. One could use this as an indication of potential precipitate formation and possibly clogging if concentrations and amounts are sufficient.

Monitoring of parameters such as flow rate, porosity and hydraulic conductivity as well as changes in pH and Eh or pe with time could help prevent clogging and act as a early warning system for detection of potential.

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