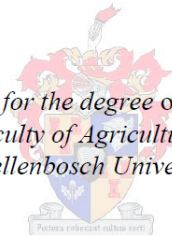


***In Situ* Denitrification of Nitrate Rich Groundwater in South Africa**

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ABSTRACT

South Africa is a water scarce country and in certain regions the quantity of surface water is insufficient to provide communities with their domestic water needs. In many arid areas groundwater is often the sole source of water. This total dependence means that groundwater quality is of paramount importance. A high nitrate concentration in groundwater is a common cause of water being declared unfit for use and denitrification has been proposed as a potential remedy. In many areas of South Africa nitrate levels exceed the recommended maximum concentration of 40 mg/L NO_3^- as N. Concentrations of 100 mg/L NO_3^- as N or even greater than 200 mg/L NO_3^- as N are found in various places. Water with nitrate concentrations exceeding 40 mg/L NO_3^- as N, belongs to the category of “dangerous” drinking water quality (“purple”, i.e. Class IV) according to DWA (1996, 1998) water quality guidelines. Concentrations in this range have been reported in case studies to cause conditions like methaemoglobinaemia (“blue baby syndrome”), spontaneous abortions, stomach cancers and livestock deaths,

The purpose of the study includes laboratory experiments to compare the denitrification efficiency, reaction rates and reaction mechanisms between woodchips, biochar and a mixture of woodchips and biochar. Further work included modelling of denitrification using the PHREEQC-2 1D reactive transport model. Field implementation of a denitrification technique was tested at a site which previously experienced some NH_4NO_3 spills, to determine the lifespan of the woodchips used during the experiment based on available data. The underlying intended purpose of this research is to contribute to the wellbeing of rural South Africans in areas where groundwater is plentiful, but elevated nitrate levels prevent the use of this water.

The purpose of the laboratory experiment was to establish the efficiency of carbon sources and compare their rates, sorption properties and processes by which they react. Laboratory experiment consisted of three leaching columns containing two layers of building sand on either side of a carbon containing layer. The carbon containing layers were made of about 600g of woodchips, biochar and woodchip and biochar mixture respectively. Parameters analysed from the effluent from the columns included NO_3^- , NO_2^- , SO_4^{2-} , NH_4^+ , Alkalinity, DOC (dissolved organic carbon content) and Phosphate.

The purpose of the field experimental work was to install a barrier containing a cheaply available carbon source to treat groundwater and to monitor changes with time in order to determine the efficiency and life span of carbon source used for the experiment. Experimental work was done at a site in Somerset West (South Africa) that had experienced spills in the past from agrochemical storage factory premises. Somerset West normally receives about 568 mm of rain per year. It receives most of its rainfall during winter; it thus has a Mediterranean climate. It receives the lowest rainfall (10 mm) in February and the highest (96 mm) in June. The “reactor”/ tank with dimensions- 1,37m height, 2.15m diameter used for the experiment was slotted for its entire circumference by marking and grinding through the 5mm thick plastic material. The top section was left open to allow for filling and occasional checking of filled material during the experiment. The tank was packed with *Eucalyptus globulus* woodchips which was freely available at the site.

Concentrations of groundwater nitrate at the site were well over what could be expected in any naturally occurring groundwater systems, and would result only by major anthropogenic activities in unconfined aquifer areas of South Africa. Nitrate levels in monitoring boreholes at the site ranged from about 20 mg NO_3^- -N/L at background boreholes up to about 600 mg/L NO_3^- -N. Woodchips used to denitrify groundwater in the field experiment were sampled after 27 months and 35 months of being active in the treatment zone. Various depths of samples were collected namely the top section, bottom of the tank and a full core sample of the tank.

Main results from the laboratory studies showed that biochar on its own as a carbon source for nitrate removal would not be viable, however, the presence of biochar in the mixture of woodchips and biochar increased the rate of denitrification. Biochar on its own was able to remove some nitrate, but results showed incomplete denitrification and limited reactivity. The results also confirmed that different processes were in play, while the redox reaction of denitrification was taking place in woodchips and biochar and woodchip mixtures, the biochar treatment followed a physical process and had only a small percentage of incomplete denitrification. This was confirmed by sulphate reduction and increased alkalinity in the woodchips and biochar and woodchip mixture treatments. Rates deduced from the data also showed that the woodchip and biochar mixture would take a shorter period to affect total denitrification.

Main results from the field work showed that nitrate was totally removed at the treatment zone and surrounding boreholes, and even sulphate and NH_4^+ were removed during the experiment. This shows that the woodchips were successful in affecting denitrification for 35 months. Data also shows that boreholes further

downstream from the tank had reduced NO_3^- , SO_4^{2-} and NH_4^+ levels. This would relate to higher permeability flow paths possibly present on the downstream side of the treatment zone. This became evident when pumping boreholes during sampling and noting that upstream boreholes had to be allowed for a recovery period, while downstream boreholes could be pumped continuously for 30 minutes without any reduced yields. This shows that not only did the treatment zone work at removing nitrate, but migration of excess available carbon from the tank may have further treated nitrate rich areas on the site.

During monitoring on the site, woodchips were sampled and analysed for their components at time period 27 months and 35 months of the experiment respectively. Results showed that woodchips were considerably more degraded than a) woodchips of the same species of tree that had undergone natural degradation on the floor and b) un-degraded woodchips of the same tree species. Comparing data from the two time series samples, a rate of woodchip degradation could be calculated. Using the available biodegradable carbon for the woodchips based on its composition, a barrier lifespan could be determined. The results of calculations show that the barrier would be effective for at least another 6.9 years from the period of the last sampling date. A total lifespan of about 10 years can thus be estimated. These calculations are tree species composition specific and rate specific.

PHREEQC-2 modelling was used to estimate the use of carbon in the experiment by adding incremental moles of carbon to the influent composition. Saturation indices from PHREEQC-2 showed that mineral phases of iron may precipitate from solution during the experiment. Experimental data were plotted against results of intermittent carbon reactions in PHREEQC-2 and it was found that initial rates in the experiment were higher and agreed with up to 100mg/L of carbon consumption when a 24 hour

residence time was used while later stages agreed with about 37.5 mg/L carbon consumption, where a 72 hr residence time was used.

It was concluded that biochar and woodchips combined are more effective than woodchips on their own at denitrifying groundwater. Also woodchips successfully denitrified groundwater at the Somerset West site for 35 months, with added removal of sulphate and NH_4^+ . Barrier life span calculations show that the barrier could remain active for an additional 6.9 years which relates to a total period of about 10 years of denitrification should the rates remain constant. It was concluded that nitrate removal and barrier lifespan would be extended by testing variable lignin content in different tree species prior to use in a denitrification barrier as lignin is unlikely to degrade in an anaerobic environment.

It was recommended that implementation or field test should be done using a biochar and woodchip mixture. Improved results may be achieved by analysing wood or plant material for comparative lignin content, cellulose content and hemicellulose contents. Wood types or plant species with higher lignin content would be more resistant to degradation in anaerobic conditions.

OPSOMMING

Suid Afrika is 'n waterarm land en in sommige gebiede is die beskikbare bogrondse water te min om aan plaaslike gemeenskappe se huishoudelike vereistes te voorsien. Grondwater is in hierdie gebiede die enigste bron van drinkwater. Dit is dus baie belangrik dat die grondwatergehalte van sodanige aard is dat dit met die minimum behandeling geskik sal wees vir mens en dier. Dit is egter so dat hoë nitraatvlakke in baie gevalle die algemene rede is waarom grondwater ongeskik verklaar word vir huishoudelike gebruik. As gevolg hiervan word in-situ denitrifikasie van grondwater voorgestel as 'n moontlike oplossing vir hierdie probleem. In baie gebiede in Suid Afrika is nitraat vlakke hoër as die aanbevole maksimum nitraat vlak van 40mg/L NO_3^- as N. Nitraat vlakke van ongeveer 100 mg/L en meer as 200 mg/L is al in verskeie gebiede gevind. Grondwater met nitraat vlakke hoër as 40 mg/L word as “gevaarlik” beskou volgens die WGO en Departement van Waterwese se riglyne. Gekonsentreerde vlakke in hierdie reeks is deur gevallestudies aangemeld wat metheamoglobinaemia, maagkanker en spontane aborsies en sterftes by lewende hawe veroorsaak.

Die doel van hierdie studie was om

- 1) laboratorium eksperimente uit te voer om die doeltreffendheid van 'n koolstofbron vir denitrifikasie, die reaksietempo en die meganismes te vergelyk tussen hout stukkie, houtskool en 'n mengsel van houtskool en houtstukkies
- 2) Modelling van denitrifikasie in PREEQC-2 te doen,
- 3) Veld toepassing van 'n denitrifikasie tegniek, die eerste van sy soort in Suid Afrika wat getoets was, op 'n area wat voorheen besoedel was.

- 4) om die lewensduur van die houtstukkies wat in die eksperiment gebruik word te bepaal. Die onderliggende doel van die navorsing is om 'n positiewe bydra te lewer vir ver afgeleë Suid Afrikaners waar daar volop grondwater beskikbaar is, maar hoë nitraat die gebruik van die water verhoed.

Laboratorium eksperiment bestaan uit drie kolomme waarvan twee lae bousand aan beide kante van die koolstof laag geplaas is vir logging. Elke koolstof laag het bestaan uit 600g houtstukkies, houtskool, asook 'n kombinasie van die twee onderskeidelik. Die uitvloei is ontleed vir NO_3^- , NO_2^- , SO_4^{2-} , NH_4^+ , alkaliniteit, DOC (opgeloste organiese koolstof) en fosfaat.

Die veld eksperiment is gedoen in 'n besmette area (Somerset Wes, Suid Afrika) waar agrichemikalië voorheen in 'n fabriek gestoor was. Die hoogste reënval word gedurende die winter maande in hierdie area ontvang en Somerset Wes het 'n gemiddeld van 568 mm per jaar. Dit het 'n Mediterreense klimaat waar die laagste reënval in Februarie 10mm en hoogste reënval in Junie 96mm is. Die reaktor/ tenk met hoogte 1.37m en deursnee van 2.15m is gebruik vir die eksperiment. Die omtrek van die 5mm dik plastiek tenk was verdeel in gelyke dele waarvan elk sowat 2mm breed was. Die boonste gedeelte van die tenk was onbedek sodat die houtstukkies daarin geplaas kon word asook om gereelde opvolg besoeke toe te laat. Die tenk is opgevul met *Eucalyptus globulus* houtblokkies wat vrylik in die area beskikbaar is.

Daar is bevind dat die konsentrasie van grondwater nitraat ver bo die natuurlike nitraat vlakke in grondwater bronne was, en kan vergelyk word met areas waar antropogeniese aktiwiteite op onbeperkte ondergrondse waterbronne, plaasvind. Nitraat vlakke het gewissel van ongeveer 20 mg/L tot 600mg/L by boorgate.

Monsterneming van houtstukke wat gebruik was in die veld eksperiment het na 'n tydperk van onderskeidelik 27 maande en 35 maande plaasgevind. Monsters is op verskeie dieptes geneem, dit het die boonste gedeelte, die onderste gedeelte en 'n volledige profiel van die tenk ingesluit.

Hoofresultate van die laboratoriumstudie het getoon dat die houtskool op sy eie nie effektief was as 'n koolstofbron nie, alhoewel dit die effektiwiteit van die houtstukkies verbeter het waar dit in die mengsel was. Houtskool het 'n klein hoeveelheid nitraat verwyder, maar resultate dui daarop dat dit onvoltooide denitrifikasie veroorsaak het en beperkte reaktiwiteit getoon het. Die resultate dui ook aan dat daar definitief verskillende meganismes van reaksie plaasgevind het. Terwyl houtstukkies en die houtstukkies- houtskool mengsel via redoks reaksies gedenitrifiseer het, het houtskool 'n meer fisiese proses gevolg, en 'n klein persentasie nitraat nie totaal verwyder is nie. Dit was bevestig deur sulfaat reduksie en 'n verhoging van alkaliniteit in die houtstukkies en houtstukkies en houtskool mengsel. Reaksietempo resultate van die navorsing toon dat houtstukkies en houtskool mengsel in 'n verkorte periode wel totale nitraat verwydering getoon het.

Hoofresultate van die veld toepassingseksperiment dui daarop dat nitraat totaal verwyder was in die reaksiesones en boorgate rondom die reaksiesones. Sulfaat en NH_4^+ was ook in die tydperk verwyder. Dit dui aan dat houtstukkies suksesvol aangewend is as 'n koolstofbron vir denitrifikasie gedurende die 35 maande wat die eksperiment gemoniteer was. Die data dui ook aan dat boorgate, verder stroomaf van die tenk, verminderde NO_3^- , NH_4^+ , en SO_4^{2-} vlakke getoon het. Dit dui op 'n area

van hoër deurlaatbaarheid aan die stroomaf gedeelte van die reaksiesones. Dit het duidelik geword gedurende die grondwater monsternemingsprosedure waartydens boorgate aan die stroomaf gedeelte van die studie area vir 30 minute aanhoudend gepomp kon word sonder om minder water te lewer, terwyl boorgate wat stroomop geleë is gepomp kon word met 'n herstel periode omdat water langer geneem het om die boorgat te bereik. Dit dui aan dat die reaksiesones suksesvol gewerk het, en ook dat ongereageerde opgeloste koolstof wel van die reaksiesones af kon versprei in die stroomaf rigting.

Monsterneming van houtstukke het plaasgevind na sowat 27 en 35 maande, en ontleding van uiteensettings produkte van houtstukke was gedoen. Resultate dui aan dat die houtstukke uit die reaksiesones aansienlik meer afgebreek het in vergelyking met 1) houtstukke wat onder natuurlike toestande afgebreek het en 2) natuurlike *Eucalyptus globulus* monster. 'n Reaksietempo vir afbreek van houtstukke kon bepaal word deur die data van elke monster van dieselfde posisie te vergelyk vir die verandering in konsentrasie oor die tydperk. Die bio-afbreekbare koolstof kon bepaal word met die beskikbare data vir die houtstukke. Die lewensduur van die reaksiesones kon bepaal word met die reaksietempo en beskikbare bio-afbreekbare koolstof vlakke. Die resultate dui aan dat die reaksiesones vir ten minste nog 6.9 jaar effektief kan wees na die 35 maande tydperk. Dit dui aan dat hierdie eksperiment vir ongeveer 10 jaar suksesvol kan opereer voordat houtstukke in die reaksiesones nie verder kan afbreek nie. Hierdie bepaling is egter spesie spesifiek en reaksie spesifiek.

Gevolgtrekkings van hierdie werk is 1) die houtskool en houtstuk mengsel behandeling meer effektief is as 'n koolstofbron vir denitrifikasie vergeleke met net houtskool. 2) Houtskool alleen is nie effektief as 'n koolstofbron vir denitrifikasie nie. 3) Houtstukke het suksesvol grondwater gedenuitruis vir 'n tydperk van 35 maande, met addisionele verwydering van sulfaat en NH_4^+ . Houtstukke wat gedurende hierdie projek gebruik was kan vir nog 6.9 jaar suksesvol denitruiseer.

Dit was aanbeveel dat toekomstige werk dalk die gebruik van die houtstuk en houtskool mengsel in die veld toets. Vir beste resultate met houtstukke, word dit aanbeveel dat 'n verskeidenheid van plantspesies ontleed word. Plantmateriaal of houttipes met hoër lignin vlakke sal minder afbreekbaar wees, en dalk 'n beperkte lewensduur hê in vergelyking met plantspesies wat laer lignin vlakke het.

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List of Abbreviations and Acronyms

- HIV Human immune virus
- AIDS Aquired immune deficiency Syndrome
- IX ion exchange
- RO reverse Osmosis
- ED electro dialysis
- POU point of use
- TDS total dissolved solids
- EC electrical conductivity
- PRB permeable reactive Barrier
- ABS Absolute value (excel function)
- DOC dissolved organic carbon

CHAPTER 1: CURRENT STATE OF RESEARCH ON DENITRIFICATION PROCESSES¹

1 Introduction

Since the 1970's, nitrate (NO_3^-) contamination of groundwater has become a significant environmental problem in many parts of the world (Rivett *et al.*, 2008). The European approach to the problem has increasingly recognised the need for integrated protection and management of water resources (Rivett *et al.*, 2008). Mitigation is difficult due to the long-term, diffuse and continuing nature of the problem (Hiscock *et al.*, 2007). The proportion of groundwater with mean nitrate concentrations above 25 mg/L NO_3^- in 2003 was reported as being 80% in Spain, 50% in the UK, 36% in Germany, 34% in France and 32% in Italy (Rivett *et al.*, 2008). Nitrate is a pollutant that has been reported in most countries due to various activities including mining, farming, feedlots at farms, improper sanitation practises such as unlined or unprotected pit latrines, unlined waste dumps and cemeteries, as well as industrial wastes from fertilizer producing factories and other industries. In

¹Publications related to this chapter include:

Israel, S., Tredoux, G., Engelbrecht, P., Wilsenacht, J., Germanis, J., Jovanovic, N., 2012. Nitrate removal for groundwater supply to rural communities, WRC report No. K5/1848

Tredoux, G., Engelbrecht, JFP., and **Israel, S.**, 2009. Nitrate in Groundwater, Why is it a hazard and how to control it? WRC report No. TT410/09

Israel, S., 2007. MSc thesis Stellenbosch University, *In Situ* denitrification of nitrate rich groundwater in Marydale, Northern Cape

Maherry, A.; Tredoux, G.; **Clarke, S.**; Engelbrecht, P., 2010. State of nitrate pollution in groundwater in South Africa, CSIR 3rd Biennial Conference: Science Real and Relevant, CSIR International Convention Centre, Pretoria

certain parts of the world it also occurs naturally as a product of chemical weathering of nitrogen containing rocks or leaching from accumulated layers in soils (Tredoux and Talma, 2006).

Regional work pertaining to nitrate concentrations and distribution in groundwater used isotopes as well as chemical analyses to identify sources of nitrate within sub Saharan Africa. High nitrate levels occur in groundwater in a variety of geological settings and a diversity of environmental conditions. Naturally occurring high nitrate levels were found in geological formations such as the Ganzi Group in Botswana, and its equivalent (the Nosib Group in Namibia), the Stormberg Basalt in the Springbok Flats (South Africa) and its equivalents (e.g. the Kalkrand Basalt in Namibia) and were attributed to the secondary characteristics of the geological formation and associated factors allowing the enrichment with nitrogen derived from other sources (Tredoux and Talma, 2006). In most cases, the occurrence of high nitrate in groundwater is due to contamination related to anthropogenic activities.

In unconfined aquifers, nitrate concentrations can be highly variable over short periods as they are directly affected by recharge processes (rainfall, infiltration etc.) as well as nitrate polluting activity. Feedlots and dairy farming areas have a large potential for nitrate pollution if waste materials are not managed adequately. Such activities should be restricted to areas of aquifers which have impermeable layers to protect the groundwater resources. Inappropriate on site sanitation at rural villages and towns frequently lead to groundwater pollution by nitrate and the abandoning of well fields. Low soil organic contents in the interior of South Africa limits the occurrence of natural denitrification, hence the persistence of nitrate in semi-arid and arid environments in southern Africa (Tredoux, 1993).

Nitrate and health effects thereof will not form part of this study, however, studies in countries other than South Africa show cases where any adverse effects or cases of methaemoglobinaemia are only found when nitrate concentrations are above 20 mg/L NO_3^- as N, while concentration classes below this constitute only 2.3% (0-10 and 10-20 mg/L NO_3^- as N) of all reported methaemoglobinaemia cases in the USA and the largest percentage of cases occur above 100 mg/L NO_3^- as N (43%), while ranges between 20-50 and 50-100 mg/L NO_3^- as N constitute 16.8 and 37.8 % of the total amount of reported cases in the USA respectively (Addiscott and Benjamin, 2004). Many cases are documented from all over the world where cases of fatal poisoning of cattle and even babies are recorded. In areas where HIV and AIDS are prevalent and groundwater is a sole source of water, a further complication of elevated nitrate put infants at risk as mothers are recommended to breast feed their babies (Colvin *et al.*, 1999). Where concentrations are already high, boiling of water, however important to kill bacteria, may concentrate nitrate levels more. Statistical data for cases of nitrate poisoning or nitrite poisoning are not available for South Africa. Cattle deaths have been recorded in certain parts (Tredoux *et al.*, 2004).

Nitrate ions are not easily filtered. Nitrate is water-soluble, colourless, odourless, and tasteless and is a macro-nutrient that is an essential part of proteins manufactured by bacteria and algae in water (US Department of Interior, Bureau of reclamation, 2009). Nitrogen is a naturally occurring gas in the earth's atmosphere, at approximately 78% by volume. Natural sources of NO_3^- in waters include direct fixation of nitrogen gas by algae and bacteria, photochemical fixation, electrical discharge and oxidation of ammonia and nitrite by nitrifying bacteria (US Department of Interior, Bureau of reclamation, 2009). Nitrate is used by bacteria to form amino acids used in the synthesis of proteins for all plants and animals. There is a large

variety of nitrate removal methods available. The best method to use is often dictated by the budget, skilled work force in the area where the remediation needs to occur, level of education involved in the method, level of sophistication, safety, and number of and nature of by-products or side reactions if any (Gavascar, 1999).

This study considers *In situ* biological denitrification, which refers to processes of enhancing the natural system's ability to denitrify water. The method is capable of denitrifying groundwater, waste water, treated effluent from waste water works, and other polluted water containing high nitrate concentrations (Schipper *et al.* 2004, Schipper and Vovodic-Vukovic 1998, 2000, Robertson and Cherry 1995, 1997, Robertson *et al.* 2000). It requires the addition of a suitable substrate normally a carbon source if heterotrophic denitrification is desired. Autotrophic denitrification takes place when reduced sulphur compounds, ferrous iron or hydrogen is added to the subsurface (Mateju *et al.* 1992; Mercado *et al.*, 1988). Permeable reactive barrier walls are constructed by digging a trench of suitable size and configuration perpendicular to the groundwater flow direction, and mixing aquifer material with organic matter, e.g. sawdust, woodchips, which acts as a carbon source to stimulate denitrification (Schipper *et al.* 2004, Schipper and Vovodic-Vukovic 1998, 2000, Robertson and Cherry 1995, 1997, Robertson *et al.* 2000).

1.1 Nitrate concentration distribution in South Africa

In many areas of South Africa, nitrate levels exceed the recommended maximum concentration of 40 mg/L NO_3^- as N (Tredoux *et al.* , 2000). Concentrations of 100 mg/L NO_3^- as N or even greater than 200 mg/L NO_3^- as N is commonly found in

various places. Water with nitrate concentrations exceeding 40 mg/L NO_3^- as N, belongs to the category of “dangerous” drinking water quality (“purple”, i.e. Class IV), DWAF (1996, 1998). Concentrations in this range have been reported in case studies to cause conditions like methaemoglobinaemia (“blue baby syndrome”), spontaneous abortions, stomach cancers and livestock deaths (Stadler, 2004 and 2005, and Adiscott and Benjamin, 2004). High nitrate levels occur in groundwater in a variety of geological settings and under a diverse set of environmental conditions. Naturally occurring high nitrate levels found in geological formations were attributed to the secondary characteristics of the geological formation and associated factors allowing the enrichment with nitrogen derived from other sources (Tredoux and Talma, 2006). Examples of these include accumulation in the soil profile and flushing by high intensity rainfall events.

Naturally occurring high nitrate levels were found in geological formations such as the Ganzi Group in Botswana, and its equivalent (the Nossib Group in Namibia), the Stormberg Basalt in the Springbok Flats (South Africa) and its equivalents (e.g. the Kalkrand Basalt in Namibia) and were attributed to the secondary characteristics of the geological formation and associated factors allowing the enrichment with nitrogen derived from other sources (Tredoux and Talma, 2006).

Nitrate concentrations in South and southern Africa have been studied for decades (Tredoux and Talma, 2006, Tredoux *et al.*, 2004). A nitrate distribution map was produced and published during 2001. The extent to which nitrate occurs and the levels were known as far as the data obtained allowed (Tredoux *et al.*, 2001). Table 1 shows the guideline values for nitrate concentrations for South Africa. Figure 1 shows the results of the interpolation using an Inverse Distance Weighting method in ARC GIS. The resultant map is very similar to that produced by Tredoux *et al.*

(2001). Differences were noted in areas of Northern Cape where a lack of new data was evident, while areas in the Western Cape were showing new areas with more elevated concentrations. Figure 1 shows the distribution of nitrate across South Africa after (Israel *et al.*, 2012).

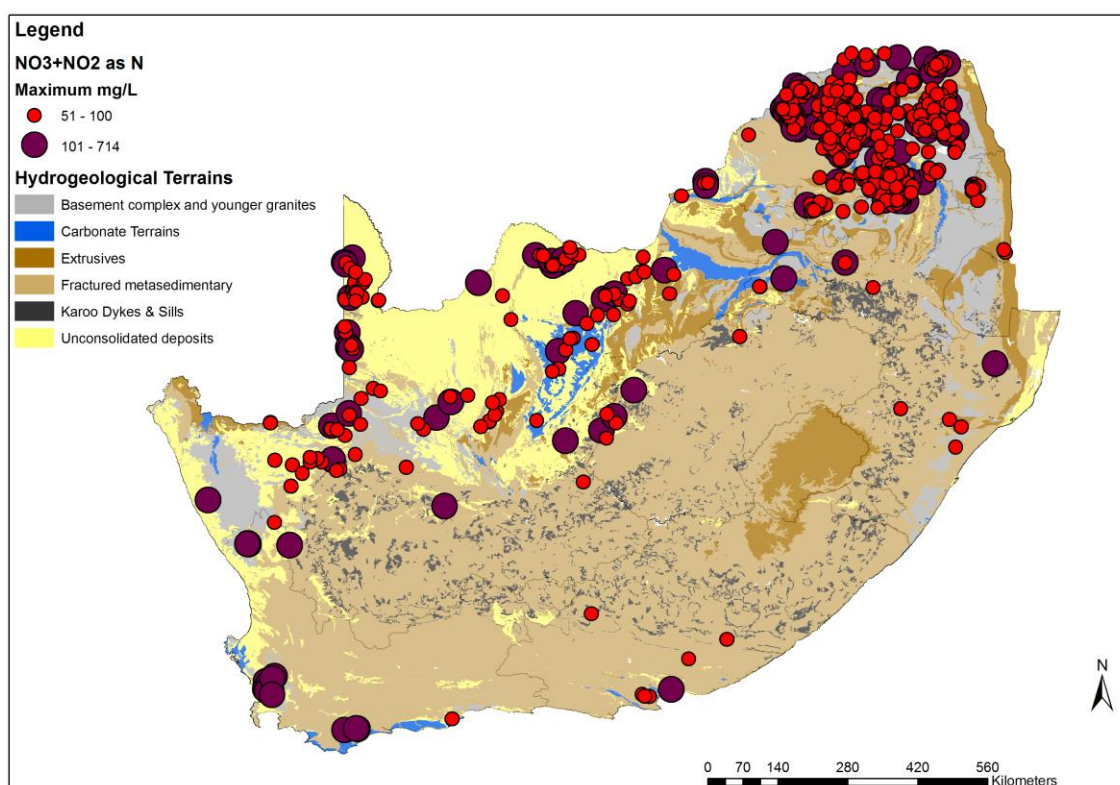


Figure 1: Maximum NO₃⁻+NO₂⁻ as N concentrations greater than 50 mg/L per hydro-terrain

This map highlights areas which may contain high nitrate concentrations; however this map must be used with caution for local scale interpretation. It represents a general picture of the concentrations over the past decade rather than specific concentrations and locations. The serious shortfall of databases, with respect to number of data points, frequency of sampling and the extent to which monitoring programmes have diminished in spatial distribution, may prove detrimental to proper representation of the state of nitrate or any other species' concentrations in

groundwater. Table 1 shows the guideline values for South African potable water and livestock watering.

Table 1: South African guideline values for potable water use and livestock watering (Tredoux and Talma, 2006)

Use	As N	As NO ₃ ⁻	Comments
Drinking water class			
Nitrate plus Nitrite (mg/L)			DWAF (1998)
Ideal	<6	<26	Negligible health effects
Acceptable	6-10	26-44	Insignificant risk
Marginal	10-20	44-89	Slight chronic risk to some babies
Poor	20-40	89-177	Possible chronic risk to some babies
Unacceptable	>40	>177	Increasing acute health risk to babies
Livestock watering			
Nitrate(mg/L)	0-90.3	0-400	DWAF (1996)
Livestock watering			
Nitrite (mg/L)	0-12.3	0-40	DWAF (1996)

The hydrogeological terrains for the country was lain over nitrate concentrations using ArcGIS. Table 2 shows the distribution of average nitrate and nitrite concentrations per hydrogeological unit.

Table 2: Distribution of average nitrate plus nitrite concentrations per hydrogeological unit, after Maherry (2010).

Hydrogeological -terrain	Average NO_3^- + NO_2^- as N	Average of Max NO_3^- + NO_2^- as N	Average min NO_3^- + NO_2^- as N
Basement Complex	12.6	13.3	12.1
Carbonate Terrains	7.4	7.9	7.1
Extrusives	18.9	20.4	17.7
Fractured metasedimentary	5.9	6.5	5.6
Karoo Dykes and Sills	6.8	7.1	6.6
Unclassified	3.6	4.3	3.3
Unconsolidated deposits	13.1	13.7	12.8

National land cover was used to assess which land use zones displayed elevated nitrate plus nitrite concentrations. The average nitrate plus nitrite concentrations for the Extrusive terrains are significantly higher in comparison to the other lithologies (Maherry *et al.*, 2010). Conversely, the Karoo Dykes and Sills, Fractured metasedimentary and Carbonate terrains have lower nitrate values (Maherry *et al.*, 2010). It was concluded previously that geological formations are not generally the source of nitrate and that it was rather physical features and other characteristics of the overburden and the bedrock that allow enrichment of nitrate in the groundwater where a pollution source is available (Tredoux, 1993). The “black cotton soil” derived from basalt is prolific in binding nitrogen and the generation of nitrate as demonstrated in the Springbok Flats. Table 4 shows the average nitrate plus nitrite concentrations per land cover class.

Table 3: Average nitrate and nitrite values per National Landcover 2000 class, (Maherry *et. al.*, 2010)

NLC2000 Landcover Classes	Average $\text{NO}_3^- + \text{NO}_2^-$ as N	NLC2000 Landcover Classes	Average $\text{NO}_3^- + \text{NO}_2^-$ as N
Bare Rock and Soil (erosion : dongas / gullies)	4.1	Mines & Quarries (underground / subsurface mining)	40.8
Bare Rock and Soil (erosion : sheet)	8.8	Shrubland and Low Fynbos	8.7
Bare Rock and Soil (natural)	3.2	Thicket, Bushland, Bush Clumps, High Fynbos	9.9
Cultivated, permanent, commercial, dryland	15.3	Unimproved (natural) Grassland	6.6
Cultivated, permanent, commercial, irrigated	3.9	Urban / Built-up (residential)	7.9
Cultivated, permanent, commercial, sugarcane	3.9	Urban / Built-up (residential, formal suburbs)	5.1
Cultivated, temporary, commercial, dryland	14.4	Urban / Built-up (residential, formal township)	18.5
Cultivated, temporary, commercial, irrigated	6.8	Urban / Built-up (residential, hostels)	0.0
Cultivated, temporary, subsistence, dryland	12.3	Urban / Built-up (residential, informal squatter camp)	6.8
Cultivated, temporary, subsistence, irrigated	3.4	Urban / Built-up (residential, informal township)	13.0
Degraded Forest & Woodland	16.2	Urban / Built-up (residential, mixed)	3.3
Degraded Shrubland and Low Fynbos	6.2	Urban / Built-up (rural cluster)	18.9
Degraded Thicket, Bushland, etc	9.6	Urban / Built-up (smallholdings, grassland)	2.9
Degraded Unimproved (natural) Grassland	4.2	Urban / Built-up (smallholdings, shrubland)	8.0
Forest (indigenous)	2.4	Urban / Built-up (smallholdings, thicket, bushland)	8.8
Forest Plantations (Acacia spp)	0.4	Urban / Built-up (smallholdings, woodland)	9.6
Forest Plantations (clearfelled)	2.1	Urban / Built-up, (commercial, education, health, IT)	7.2
Forest Plantations (Eucalyptus spp)	3.1	Urban / Built-up, (commercial, mercantile)	5.8
Forest Plantations (Other / mixed spp)	0.6	Urban / Built-up, (industrial / transport : heavy)	5.4
Forest Plantations (Pine spp)	1.3	Urban / Built-up, (industrial / transport : light)	2.4
Herbland	2.9	Waterbodies	9.4
Improved Grassland	4.5	Wetlands	12.6
Mines & Quarries (mine tailings, waste dumps)	3.9	Woodland (previously termed Forest and Woodland)	10.9
Mines & Quarries (surface-based mining)	8.7		

Elevated levels of nitrate plus nitrite concentrations can be seen in the Mines and Quarries land cover class with an average in excess of 40 mg/L. Urban areas have elevated levels of nitrate, in particular the rural cluster, formal and informal townships. Indigenous forests and forest plantations have low nitrate concentrations in groundwater. Woodland has higher nitrate concentrations, while degraded forest and woodland have even higher nitrate levels. Elevated levels of nitrate are also commonly associated with agricultural lands, particularly in areas where permanent, temporary commercial and temporary subsistence dryland farming is practiced. Although it would seem obvious that the elevated nitrate has to be related to the application of fertilizer to land Conrad *et al.*, (1999) found that the nitrate had the isotopic character of soil nitrogen and not of fertilizer. Thus it was concluded that the tilling of the soil caused nitrification of the soil nitrogen and leaching of nitrate into the subsurface in dryland farming areas they studied.

Elevated nitrate levels in South Africa are associated with mining areas, urban areas, in particular the rural cluster, formal townships and informal townships. Elevated nitrate concentrations occur and are typically associated with the agricultural sector, namely, permanent and temporary commercial dryland, and temporary subsistence dryland farming. Nitrate pollution and elevated nitrate concentration in South Africa still persists. The extent and distribution would seem to be increasing with new areas being affected. The lack of data in certain parts of the country may be obscuring the actual extent of the state of nitrate pollution in South Africa.

1.2 Nitrate removal technologies employed internationally

A large variety of nitrate removal methods are available (Table 4). The best method to use is often determined by the budget, skilled work force available, level of sophistication, safety and nature of by-products or side reactions (Gavascar, 1999).

USEPA has recognized only ion exchange (IX), reverse osmosis (RO), and electro dialysis (ED) water treatment unit processes as best available technology treatment techniques for nitrate removal. Point of use (POU) technologies using RO, NF, distillation, and Ion exchange can also be used to remove nitrate. Others have found that nitrate can be removed using either by chemical or biological denitrification, either above ground in tanks or wetlands (*ex-situ* treatment) or below ground in the soil/water matrix (*in-situ* treatment). Technologies used with their inherent advantages and disadvantages are listed in (Table 4).

RO technology, a well-known technology in South Africa, has been applied in Nzava, Limpopo for nitrate removal (Schoeman and Steyn, 2003). It has been very effectively applied for water desalination. Nitrate removal by means of biological denitrification is usually the preferred solution for nitrate removal because it is transformed into gaseous nitrogen with a very high yield and low process cost. Biological denitrification, however, has some drawbacks in process control and output water quality. Schoeman and Steyn (2003) demonstrated that the RO process could be very effectively applied for water denitrification in a rural area. Nitrate as N could be reduced from 42 mg/L to less than 1 mg/L (98% removal). The RO brine is very saline, and suitability for stock watering needs to be evaluated should the

conditions for stock watering be met in terms of nitrate as N nitrogen concentration, TDS and other constituent concentrations. Table 4 and

Table 5 show nitrate technologies and results achieved internationally.

Table 4: Nitrate removal methods used, modified from Schoeman and Steyn (2003), ITRC (2000), and US Bureau of reclamation (1999)

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 NO ₃ ⁻ removal, pressure, temperature, and pH requirements to meet membrane tolerances. may be chemically sensitive	50-96%
Bioremediation Permeable Reactive Barriers, 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%
Electrodialysis	electrochemical process in which ions migrate through an ion selective semi-permeable membrane	EDR can operate without fouling or scaling, or chemical addition; suitable for higher TDS sources, Low pressure requirements; typically quieter than RO, Long membrane life expectancy, EDR extends membrane life and reduces maintenance	EDR can operate without fouling or scaling, or chemical addition; suitable for higher TDS sources, ED cannot remove nonionic dissolved species or microbes, Not suitable for high levels of Fe and Mn, H ₂ S, chlorine, or hardness, Limited current density; current leakage; back diffusion At 50 percent rejection of TDS per pass, process is limited to water with 3000 mg/L TDS or less	30-50%
Pump and treat	Impacted ground	Plume containment, mass removal, re-use of clean	Long-term engineering cost, water rights issues, treatment system potentially expensive, hazardous	50-90%

	water pumped and treated	water, injection of clean water	concentrated waste stream	
Method	Basic methodology	Advantages	Disadvantages	Removal efficiency
Denitrification in combination with other contaminants	During anaerobic bioremediation of other contaminants, nitrates serve as an electron acceptor	Fortuitous nitrate reduction in the presence of other organic contaminants if nitrate is present in an organic contaminant plume, and conditions are anaerobic, denitrification most likely will occur	Reducing conditions must be present, a carbon source must be present, monitoring to determine, denitrification must be ascertained	70-95%
Distillation	Boiling, collecting steam free of contaminants	Removes most impurities from water including viruses, less expensive than bottled distilled water	Best suited for municipal water; rural waters of high mineral content will cause excessive scaling and increase maintenance, receiving containers may be contaminated again, regular cleaning and de-scaling of the elements of the boiler are required, produces flat tasting water devoid of all minerals, expensive to purchase and maintain, system is large and bulky, and not portable, slow production of water (water must be stored) meaning that without careful planning, water could run out.	90-98%

Table 5 provides an overview of operational biological denitrification sites known at this stage and their experiences. These methods have the potential for significant cost savings on expenses such as training and salaries for operators who would otherwise be required on site all the time when compared to process control in more sophisticated nitrate removal techniques. Rural areas in South Africa require treatment technologies that are robust and low cost and require minimum maintenance.

In situ biological denitrification refers to processes of enhancing the natural system's ability to denitrify water. The method is capable of denitrifying groundwater, waste water, treated effluent from waste water works, and other polluted water. It requires the addition of a suitable substrate normally a carbon source if heterotrophic denitrification is desired. Autotrophic denitrification takes place when reduced sulphur compounds, ferrous iron or hydrogen is added to the subsurface (Mateju *et al.* 1992; Mercado *et al.*, 1988).

Permeable Reactive Barriers (PRB) walls are constructed by digging a trench of suitable size and configuration perpendicular to the groundwater flow direction, and mixing aquifer material with organic matter, e.g. sawdust, woodchips, which acts as a carbon source to stimulate denitrification (Schipper *et al.* 2004, Schipper and Vovodic-Vukovic, 2000, Robertson and Cherry 1995, Robertson *et al.* 2003, Robertson *et al.* 2000). Slight variations of this principle are also in use, where site specific system configurations have been used. Table 4 and

Table 5 describe the performance of field and pilot scale studies.

Table 5 : Permeable reactive barrier test site performance data (after Tredoux *et al*, 2004)

Treatment method	Nitrate concentration (initial)	Aquifer type	Carbon substrate	% NO₃⁻ removed
PRB, Canada	5-57mg/L	Primary	Sawdust/woodchips	58-91
PRB, New Zealand	5-15 mg/L	Unconfined, sandy	Sawdust	95+
Electrokinetics/ wall, USA	Fe- Controlled amounts	Primary/ Secondary	None: Abiotic	84-87
NitrEI Canada	system, Up to 1000 mg/L (as N)	Primary/ unsaturated zone	None: electrochemical electrodes	levels down to 0.1 mg/L

Table 5 shows that many countries explored removal of nitrate using various methods. The testing of denitrification in an *ex situ* manner by RO is the only case of nitrate removal on field/ pilot scale in South Africa (Schoeman and Steyn, 2003). Other works are mainly confined to laboratory studies: Column experiments testing the rate of nitrate removal under varying flow conditions and feed nitrate concentrations (Greiben *et al.*, 2004), and *In situ* batch experiments testing various carbon sources as well as C: N ratios for denitrification (Israel, 2007). Biological treatment is preferred for large plants. Processes based on IX, RO and ED have a lower efficiency if compared with biological denitrification, but they seem to be very interesting for medium and small applications (Schoeman and Steyn, 2003). The testing of biological denitrification on field/pilot scale could prove invaluable to South African communities as it is effective in removing nitrate, but does not have the added complication of concentrated by-products which could inevitably pollute the water again. Some field and pilot scale denitrification studies have been recorded as references Table 4 and

Table 5.

As with any other technique or method, problems are bound to arise while the technology is growing and changing over time to obtain optimum conditions for various situations or sites. Literature identified most of the potential problems and eliminated or prevented them during configuration of a site or even a laboratory denitrification wall. Some problems were easier to detect and remedy than others. Despite the fact that there are many successfully operated sites worldwide, many started out being failures and became successful with some improvement, while newer sites have failed for reasons that are still under investigation. The sections below will highlight all the identified problems experienced during laboratory or field operations and what has been done to remedy the problems if anything has been suggested or even tried by scientists at their respective sites. Denitrification wall construction and monitoring is site specific. Not all problems will occur at all sites; however it will be useful to monitor for all possible problems as a precautionary measure.

The efficient functioning of a reactive barrier can often depend on the proper placement of the actual barrier and its effectiveness at allowing flow of source water be it groundwater or waste water. Many studies have shown successful denitrification all over the world. However, some of the sites were not always as successful, and often scientists who have successfully denitrified their source water through a permeable reactive barrier in one location have had failures in other areas using similar techniques. Successful denitrification of groundwater has been practiced for more than a decade in New Zealand (Schipper and Vodovic-Vokovic, 1998, 2000, 2001, and 2004), The latest attempted denitrification of non-point sources of nitrate from shallow groundwater failed due to hydraulic constraints

on the performance of the denitrification wall (Schipper *et al.*, 2004). Denitrification walls are most successful and effective at protecting downstream water quality when as much groundwater as possible is intercepted by them (Schipper *et al.*, 2004, Barkle *et al.*, 2008 and Robertson *et al.*, 2003). Hence the hydraulic properties of both the wall and aquifer are integral properties to be monitored and assessed throughout the life of an operation (Barkle *et al.*, 2008). Despite the success of denitrification walls in stimulating denitrification, factors such as the type, quantity, and particle size of organic amendments on the rates of denitrification, remain poorly understood (Greenan *et al.*, 2006).

Schipper *et al.* (2004) examined the behaviour of a denitrification wall in a shallow sandy aquifer consisting of coarse sands. In their study, they analysed samples from upstream of the wall, from within the wall and downstream from the wall. Their findings were alarming. The nitrate concentrations upstream ranged from 21 to 39 mg/L, while in the wall it was 0 to 2 mg/L, and downstream concentrations were 19 to 44 mg/L. They followed this with two tracer tests to investigate flow patterns. They found that only 4% of the flow through the aquifer was actually passing through the wall. After testing, they determined that there was a big contrast between the hydraulic conductivities of the aquifer (65.4 m/day) and the wall (0.48 m/day). This implied that during construction, most of the aquifer hydraulic conductivity was lost so that groundwater flowed under the wall rather than through it. In this study (Schipper *et al.* 2004) unlike their previous successful studies Schipper and Vovodic-Vukovic (1998, 2000), Robertson and Cherry (1995, 1997, Robertson *et al.* 2000) the wall acted as a flow barrier to the existing groundwater flow system.

The probable causes of the decrease in hydraulic conductivity as explained by Schipper *et al.* (2004):

1. Higher porosity but lower conductivity in the wall due to changes in the proportions of connectivity of pores transmitting groundwater during the mixing process
2. The addition of sawdust may have plugged pore spaces decreasing connection between pores
3. Fine clay and silt lenses may have resettled during mixing to form a well graded and less permeable soil

Other studies that showed changes in hydraulic conductivity owed it to biomass build-up and gas bubble formation as well as liquid carbon sources occupying pore spaces (Mercado *et al.*, 1988, Hunter, 2001). These are important parameters to consider when running a denitrification wall for remediation of nitrate.

Li *et al.*, (2005) considered the effect of mineral fouling on wall hydraulic conductivity. Their study considered zero valent iron walls (autotrophic denitrification). With the use of reactive transport modelling, they simulated the effects of corrosion and precipitation reactions for their specific environment. Their results showed a decrease in porosity and hydraulic conductivity over time as well as a redistribution of flow pattern or path in response to the fouling of pore space. According to Li *et al.*, (2005), the rate of change within a PRB is directly proportional to the rate at which mineral forming ions reach the PRB. They also add that when the PRB is more permeable than the aquifer, the median Darcy flux does not change much over time as the flow is controlled by the aquifer. Adverse effects of mineral fouling of pore

spaces include increased seepage velocity within the PRB, decreased residence time and possibly bypassing of the wall and flow reduction if fouling becomes extensive. Li *et al.*, (2005) and Zhang and Gillham (2005) did column tests using iron PRBs to investigate long term reactivity of iron and permeability as critical factors in the performance of PRBs. Since we are considering heterotrophic denitrification, their results concerning the reactivity of iron is not very relevant to this study, however, the production of gases into the system is indeed a phenomenon that occurs during denitrification using carbon sources as well. The main impacts of produced gases trapped in pore spaces include; reduced porosity; reduced permeability and reduced reaction rates due to smaller available surface area for reaction with aqueous solution

Zhang and Gillham (2005) in their laboratory study concluded that even though their method had much higher flow rates than what would occur in the field, they found that gas accumulation was about 10% of the initial porosity and hydraulic conductivity within their columns decreased by an order of magnitude.

Subsequent to work by Schipper *et al.* (2004), Barkle *et al.* (2008) published work that tested the various results found by Schipper *et al.* (2004). The construction technique was tested by mixing aquifer material without the addition of a carbon substrate, as well as testing the effect of grain or carbon substrate particle size in the change of hydraulic conductivity. The causes of the decrease in hydraulic conductivity experienced in previous studies were investigated using the same site. They found that the aquifer and mixed wall (only aquifer material mixed no organic substrate) had similar total porosities that were considerably lower than that of the biochip wall (coarse organic substrate mixed with aquifer material). The greater

porosity was attributed to the decrease in bulk density when introducing the wood chip material in the biochip wall. Mixed aquifer material under saturated conditions showed a tremendous loss in hydraulic conductivity due to re-settling or mixing technique used (Barkle *et al.*, 2008). This led to the conclusion that it was indeed the mixing technique rather than the addition of organic substrate that caused the decrease in hydraulic conductivity in a previous failed experiment (Schipper *et al.*, 2004; Barkle *et al.*, 2008). Flow bypassed both the biochip wall (aquifer material mixed with wood chips, and other materials coarser than sawdust) as well as the mixed wall (mixed aquifer material) (Schipper *et al.*, 2004). So even though the addition of the biochip to the aquifer increased the total porosity, it did not increase the hydraulic conductivity to much higher than that of the mixed wall (mixed aquifer material). Particle size within the aquifer is an important parameter to evaluate, and more importantly so, the redistribution thereof during construction. Repacking of particles caused the change in hydraulic conductivity which rendered the wall ineffective. Laboratory models predicted an 87% loss in hydraulic conductivity, which should be an alarming outcome, and a definite indication of potentially ineffective denitrification walls (Barkle *et al.*, 2008).

Waste water, although it is a separate problem, has been treated to remove nitrate at household scale, at trailer park scale, at an inn, and in a community in Canada (Robertson *et al.*, 2003). After 29 months of full scale operation, two systems were blocked. The top 15cm of the reactive barrier material had been degraded to the extent that permeability was reduced (Robertson *et al.*, 2003). The degraded material constituted about 10% of the reactive media present. Relatively consistent rates of biologically available carbon release and microbial biomass presence was measured in a sawdust wall (Schipper and Vojvodic-Vukovic, 2001). Later studies

revealed barrier by-pass to be potentially problematic to remediation (Schipper *et al.*, 2004). Increased DOC, Fe²⁺ and Mn²⁺ concentration may result from the remediation, and hence require monitoring (Robertson and Cherry, 1995).

There is a multitude of methods available and currently used to denitrify water of various sources. Each method has its advantages and disadvantages as well as specific requirements for implementation. One needs to take into consideration specific site conditions as well as budget and available time for reaction or experiment.

Ex situ methods currently used are not necessarily very specific to denitrification or nitrate removal, but rather remove nitrate as a secondary process. The tested reverse osmosis method used in rural South Africa yielded positive results for nitrate removal, however, the brine produced as a result is very concentrated, which presents further problems with respect to disposal.

Most literature points to biological treatment using a carbon source as electron donor for denitrification as being widely accepted in the world as well as being cheaply implemented and requiring minimum maintenance.

Some researchers have used specific strains of bacteria to enhance the denitrification process e.g. (Geben, 2004); however this is not a desired process as it would alter the ecosystem immensely.

Field and pilot scale studies show very promising results and testing of denitrification in the field in a South African field scale site is definitely a required progression. An important issue that came across from reviewing the methods used is that budgets play a big role in the construction and implementation time and sophistication.

Some sites made use of dosage control injection methods which use liquid carbon sources. This is a rapid denitrification due to immediate availability of the carbon source, however, the level of sophistication and hence education and budgets need to be higher to ensure successful operation.

The aim for this study was to use cheaply available carbon sources which lasts longer and effectively denitrifies groundwater with the least side reactions or undesirable outcomes. Previous laboratory work (Israel, 2007, Israel *et. al.* , 2009) comparing different carbon sources showed that sawdust was slowly degradable and had little negative side reactions as compared to other carbon sources used.

1.3 Site characterization methodologies

The behaviour of aquifer material, groundwater, geology, and geochemical changes under natural conditions are important to determine prior to site scale barrier construction. This determines the type and frequency of monitoring that may be required at a specific site. A good understanding of the site conditions, bench-scale column testing, and a conceptual model for the site should form the basis for the design and construction of permeable reactive barriers for groundwater remediation at various sites (Gavascar, 1999).

In general, four aspects of site characterization should be evaluated before implementing a PRB:

- Hydrogeology: Lithologies present and their properties, groundwater flow direction and velocity. Stratigraphic variations in permeability, and fracturing

- Contaminant loading: Contamination source location, plume location and extent, and contaminant concentrations
- Geochemistry, this includes any geochemical data available for the site to aid in the barrier design; and when possible
- Microbiology, this is routinely measured at all sites. But where available it can be used to indicate the presence and growth of bacteria in the system.

The plume must not pass over, under, or around the PRB and the reactive zone must reduce the contaminant to concentration goals without rapidly plugging with precipitates or becoming inoperable. The PRB design, location, emplacement methodology, and estimated life expectancy are based on the site characterization information, therefore insufficient or incorrect data could jeopardize the remediation effort (USEPA, 1998).

A conceptual site framework is a system of tasks (ITRC, 2005). It includes a site walk about investigation as well as evaluating old reports and interviewing people to:

- Identify potential contaminants on the site: predominantly from historical or recent data that is available for the site.
- Identification and characterization of the source or sources of contaminants: this can be done during a site inspection or from historical reports or interviews with people in and around the area of interest
- Delineation of potential pathways through various parts of the environment: this can be evaluated at the study site by walking about to inspect the links between different parts of the environment

- Establishment of background areas for contaminated areas: background areas are typically upstream from the source of contamination
- Identification of potential environmental receptors- (humans, animals, plants, rivers etc.
- Determination of the system or study area boundaries and limits

The complexity of the work should be comparable to the complexity of the study area and available data. It should be an iterative process (ITRC, 2005).

1.3.1 Hydrogeological characterization

To attain a “passive” remediation system, the Permeable Reactive Barrier PRB must be placed in a location that allows the plume to move through the reactive zone under the natural groundwater gradient; i.e., the gradient must do all the work (USEPA, 1998 and ITRC, 2005). Flow must be gravity driven. The piezometric surfaces (if a confined aquifer) or flow gradient (unconfined aquifer), the hydraulic conductivity, porosity, and the usual hydrologic parameters typical of a careful and complete subsurface characterization need to be determined (ITRC, 2005).

Changes in flow direction and flux due to processes such as rainfall, recharge or pumping at the site should be taken into consideration while designing a PRB as these have effects on flow velocity and direction. The stratigraphy and lithology of the site will determine the type of PRB design that is suitable for a particular site (USEPA, 1998 and ITRC, 2005). A low-permeability clay layer at the base of the aquifer is described as ideal to prevent contaminant underflow (Robertson and Cherry, 1995, USEPA, 1998, ITRC, 2005). Stratigraphic and lithological features (e.g. buried rock) might limit the ability to perform certain installation procedures. Understanding the vertical variation in stratigraphy is also important for choosing the stratigraphic zone(s) that the PRB will intersect. If the contaminant plume is moving through a highly permeable layer amidst less permeable layers, the PRB should be placed vertically to encompass this high permeability layer. Impermeable materials, such as clays, should not be “smeared” by the installation techniques across the permeable aquifer zone that is expected to provide flow into the PRB. A careful evaluation of the stratigraphic variability at the location of the PRB, and the continuity of the stratigraphy with respect to the up-gradient plume, will provide confidence in

the design and installation. If the plume comes into contact with zones of fractured rock, some flow diversion into the fractures is possible and some fraction of the contaminant could be short-circuited around the PRB. This could give the appearance that the remediation within the PRB is incomplete when, in fact, the PRB simply fails to intersect all the potential flow paths of the contaminant. Where fractures are identified at the site, reactive media can be placed into the fractures to intercept the contaminant migration pathways (USEPA, 1998).

Methods for determining hydraulic conductivity include field measurement such as pump tests, slug or bail test and hydraulic interference. Laboratory measurements of the same parameter can be done using a falling head permeator or a constant head permeator or even empirical determination using grain size (ITRC, 2005). Porosity is based on the grain size distribution and soil description (Table 6) of material present in the aquifer (ITRC, 2005).

Table 6: Standard porosity tables (ITRC, 2005)

Sediment type	Porosity range %
Well sorted sand or gravel	25-50
Sand and gravel mixed	20-35
Glacial till	10-20
Silt	35-50
Clay	33-60

Hydraulic gradient is estimated or measured using water table or potentiometric maps for the study area. Sufficient measurements should be taken to delineate localized and seasonal variations in the flow field. At some sites, it may be necessary

to evaluate both the lateral and vertical hydraulic gradients. If available, multiyear variations in the potentiometric surface should be evaluated. The hydraulic gradient for the area surrounding the proposed location of the PRB should be used during the design. Provision should be made in the design for temporal and seasonal variations of flow velocity and direction, temperature, aquifer heterogeneity in terms of hydraulic conductivity and porosity experienced at the site (ITRC, 2005).

1.3.2 Contaminant characterization

Information about contaminant concentrations at the site is necessary for any successful remedial operation (USEPA, 1998). The remediation technique must be effective up to the maximum concentrations and the total mass of contaminant that will be encountered at the treatment point. In PRBs, once emplaced, changing the thickness of the reactive zone becomes a challenge if the concentration of reactive media was miscalculated. Design must also eliminate the possibility that portions of the plume could flow around the barrier in any direction (USEPA, 1998 and ITRC, 2005). The extent of the plume, its width, depth, length, contaminant concentrations within these spatial dimensions, and how these can be expected to change over time is therefore important to understand (USEPA, 1998). PRBs are generally placed down-gradient of the plume, therefore it is important that the barrier be designed to accommodate the higher up-gradient concentrations (USEPA, 1998, and ITRC, 2005).

It is also good to know whether the plume is moving down-gradient over time or whether natural attenuation is occurring. If steady-state plume boundaries have been

achieved, the PRB could be designed to transect and attenuate only the lower down-gradient concentration(s) (USEPA, 1998). Barriers have been applied to plumes that are as wide as 304 m and as deep as 15.24 m.

1.3.3 Geochemical characterization

Field measurements of EC, pH, oxidation-reduction potential (ORP), temperature, and DO should be completed. Samples should be collected and analysed for inorganic parameters, including Ca^{2+} , Fe (total), K^+ , Mg^{2+} , Na^+ , Si, Cl^- , SO_4^{2-} , NO_3^- alkalinity, total organic carbon (TOC), and DOC (Dissolved Organic Carbon). Characterization of additional constituents (e.g. high levels of dissolved metals) may be necessary on a site-specific basis (ITRC, 2005). Precipitation onto the reactant surfaces may occur, potentially reducing the reactivity and permeability of the reactive zone over time (USEPA, 1998).

1.3.4 Microbial aspects

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. Native microbial consortia are often responsible for natural plume attenuation processes and could be beneficial for enhanced contaminant degradation within or down-gradient from the PRB (USEPA, 1998). Most studies make use of heterotrophic plate count and *Escherichia Coli*

counts as indicators of microbial activity (Robertson *et al.*, 2003, Israel, 2007, and Israel, 2009).

1.3.5 Design and construction of permeable reactive barriers (PRBs)

All known information about the site should be assessed prior to field characterization. Historical records, the memories of current or former workers, and surface features to obtain at least a general idea of the location of the source term(s). This information should be used to understand the plume and its behaviour over time. General information such as aquifer locations and thickness, yields and water table depths, water quality, stratigraphy, recharge areas, drainage basins should be obtained. Although this information might not be sufficient at the smaller scale of the contaminated site for affecting a complete remedial design, it can be very helpful in designing the site characterization (USEPA, 1998).

There are a multitude of configurations for permeable reactive barriers depending on the site conditions as well as the available budget. Laboratory testing prior to field testing is recommended by other studies (Robertson *et al.*, Gavascar, 1999, ITRC, 2005 and USEPA, 1998), to grasp the time period required to reduce concentrations to the desired concentrations within a controlled setting. This will help when doing calculations for field operational settings. Figure 2 shows a few possible field set-ups that have been used.

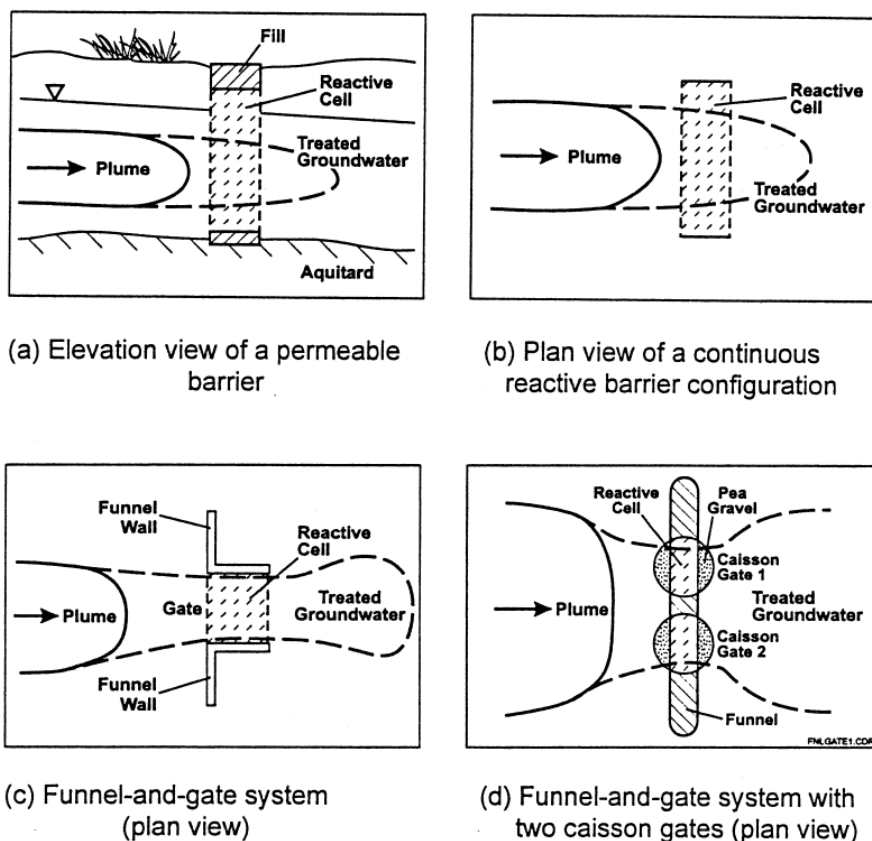


Figure 2: Possible lay outs depending on the site specific conditions and budget, from Gavascar, 1999.

An optimal design for a permeable reactive barrier can be achieved by a comprehensive examination of the site that includes reaction rates of the contaminants and the site hydrogeology. Depth of the installation is the main factor that drives the selection of a construction technique for permeable barriers. A geochemical evaluation based on the inorganic constituents of the aquifer and long-term monitoring of the barrier can be done to evaluate the longevity of the barrier.

The selection of a construction technique for a permeable barrier depends mainly on site characteristics such as:

- *Depth to aquitard or bedrock*- This can be the determining factor for construction technique selection. Depth also is an important driver of construction cost,

with most shallow installations costing less than deeper ones. Deeper installations generally involve more specialized equipment, longer construction time, and higher cost.

- *Geotechnical considerations*- The presence of cobbles or highly consolidated sediments may impede some construction technique. The presence of subsurface utilities or closeness to aboveground structures, such as buildings or fences, may also determine the type of construction technique selected and the degree of difficulty involved.
- *Waste generation*- Some construction techniques generate more waste than others do. This can be a consideration from the perspective of waste handling and disposal costs
- *Health and safety*- Construction techniques that involve entry of personnel into excavations may require more precautionary measures and oversight. Use of environmentally toxic materials is generally avoided during construction.

Digging techniques include backhoe excavation, clamshell excavation and caisson excavation. Backhoe digging is commonly used to dig trenches. Digging depths can vary from about 7m up to a maximum of 24m, but becomes more expensive with depth. Clamshell excavation can be used for digging up to 45m. Clamshells have a lower production rate than a backhoe and are relatively more expensive to use. Any rocks encountered may have to be broken up for the clamshell to operate efficiently (Gavascar, 1999). Caissons are load bearing enclosures that are used to protect an excavation. Caissons may have any shape in cross-section and are built from common structural materials. A vibratory hammer can be used to drive the caisson into the desired position. Cobbles and or highly consolidated sediments are the main reasons for caisson sinking being impeded.

1.4 Study site selection

A study site criterion to test in situ field scale remediation was developed by Israel *et al.* (2012). A national map of nitrate concentrations shows the spatial distribution of nitrate in South Africa, while, literature highlighted the best suitable conditions that the methods may work. The following was decided upon as a criteria for suitability of South African sites:

- An area with elevated nitrate concentration- from the distribution map (Figure 1) it was evident that a band of high nitrate concentrations occur across the northern provinces of South Africa, while other provinces (western Cape) had smaller areas that show high nitrate concentrations.
- A primary aquifer- most case studies found were done in primary aquifer settings. Since the method needed to be tested for the first time in situ in South Africa we selected an aquifer setting that has shown positive results.
- A shallow aquifer- A shallow aquifer was selected as a criterion as installation or implementation costs increase with depth.
- A confining layer/ clay layer at the bottom of the aquifer-this criterion represented the ideal from case studies. The clay layer serves to prevent underflow of the barrier.
- Logistically suitable (petrol, accommodation costs, etc.)- this criterion was purely driven by costs of travelling related to the sampling frequency and installation time etc.

Regions selected as priority areas for potential remediation include (Figure 1):

- Western Cape (west and south east coastal areas)
- Northern Cape and the northern provinces

The site characterisation for the selected site occurs in (CHAPTER 4: FIELD IMPLEMENTATION STUDY). Considering the distribution map of high nitrate concentrations, areas in the Western Cape, Northern Cape and northern provinces were highlighted. The Western Cape was selected as being more suitable on the basis of location. Permissions had to be obtained from land owners to test the methodology. An industrial area was selected for testing of the *in situ* field denitrification as it was made available by landowners and they were looking for a method to reduce their nitrate levels on the site

1.5 Effects of various parameters or factors natural or design related on denitrification

1.5.1 Electron acceptors

A variety of electron acceptors may be present in aquifers, including organic carbon compounds, as well as inorganic species e.g. iron, manganese, sulphide etc. (Rivett *et al.*, 2008). Denitrification in aquifers can be heterotrophic or autotrophic. Heterotrophic denitrification refers to bacteria using organic carbon as their energy source and source of cellular carbon (Rivett *et al.*, 2008). Organic carbon is usually preferentially oxidized with the electron acceptor that supplies the most energy to the micro-organisms, namely oxygen. With an excess of organic carbon, aerobic bacteria use dissolved oxygen until it is depleted, other electron acceptors subsequently becomes energetically favourable, in other words the energy input required for the reaction is equal to or less than the output of energy from the

reaction. Once oxygen is depleted, facultative anaerobes use nitrate as an electron acceptor. When nitrate becomes depleted, iron and manganese oxides, then sulphate, then hydrogen and carbon dioxide become favoured, until finally generating methane. This redox reaction sequence is commonly seen along groundwater flow paths in aquifers. In practice, systems seldom have strict redox zone boundaries as a number of redox reactions could be occurring simultaneously in the aquifer, including micro-scale redox reactions in pore spaces (Rivett *et al.*, 2008).

1.5.2 Nitrate concentration

Greben *et al.*, (2004) showed that the best denitrification results in their study were achieved when the nitrate concentration in the feed water was 200 mg/l, the available Chemical Oxygen Demand (COD) levels were sufficient and the hydraulic retention time was maintained at 24 hours. They ran experiments using 100mg/L and 200mg/L nitrate concentrations using variable flow rates and hydraulic retention time. Greben *et al.*, (2004) explained that when a higher concentration nitrate is available for the denitrifying organisms, these bacteria will out-compete the methanogenic bacteria for the available COD, which is used by both groups as the carbon and energy source. A similar result was obtained by Israel, (2007), where soil with higher initial nitrate concentration showed higher denitrification rate. According to Rivett *et al.*, (2008) excess nitrate concentrations affect the denitrification process by inhibiting the formation of N₂ gas and causing denitrification to terminate with the formation of N₂O, however, this may be case specific.

1.5.3 Different carbon sources

Electrons needed to affect denitrification can originate from the microbial oxidation of organic carbon. Lack of organic carbon to provide energy to heterotrophic microorganisms has been identified in many studies as the limiting factor to denitrification rates (Jacinthe *et al.*, 1998). Many factors affect the complex reactivity of organic matter towards oxidants e.g. temperature, pH and oxidant concentrations (Rivett *et al.*, 2008). The rate of denitrification is most often linked to the amount of dissolved organic carbon (DOC) rather than the solid fraction that may be present in the geological unit or strata at a site. Expected natural concentrations of dissolved organic carbon in aquifers is relatively low <5mg/L DOC, this can only react with small amounts of dissolved oxygen and nitrate (Rivett *et al.*, 2008). The actual quantity of and bioavailability of DOC is thus important or critical to the occurrence of denitrification in subsurface systems.

A large variety of organic carbon substrates have been tested as amendments to soil and groundwater systems to accelerate denitrification in the subsurface systems (Robertson and Cherry, 1995, Gibert *et al.*, 2008, Israel, 2007, Schipper and Gill, 2008, Robertson *et al.*, 2003, Greenan *et al.* 2006, Mercado *et al.*, 1988, Khan and Spalding, 1998 and Greben *et al.* , 2004). Greenan *et al.*, (2006) evaluated wood chips, woodchips amended with soybean oil, cornstalks, and cardboard fibres as carbon sources. In their study, cornstalks effected rapid denitrification, but they concluded that woodchips and amended woodchips would probably continue denitrifying longer than cornstalks. The addition of soybean oil to woodchips also

significantly increased nitrate removal compared to woodchips alone. Gibert *et al.*, (2007) evaluated seven organic carbon sources for denitrification. They tested softwood (branches and bark), hardwood (coarse woodchips small branches stems and leaves), coniferous mulch (mixture of woodchips, shredded bark and topsoil), willow (willow woodchips), compost (biological decomposition of organic waste-wood trimmings, leaves, rotten vegetables and fruits and food scraps), and leaves (freshly fallen beech leaves). The best performing substrate in their experiments was softwood in terms of extent and rate of denitrification. Hardwood, conifers and mixture also showed substantial denitrification and would be good for denitrification using a permeable reactive barrier. However other sources were ruled out for insufficient nitrate (soil), insufficient nitrate removal (willow and mulch), excessive release of nitrate that would likely be considered a source of contamination (compost), also excessive reduction of nitrogen to NH_4^+ and not to N_2 (willow and mulch).

Israel, (2007) considered the use of methanol, glucose, maize meal and sawdust as carbon sources for denitrification. It was found that liquid sources of carbon are more readily available to denitrification, while solid sources lasted longer during experimentation. Sawdust was selected for further work as it displayed the least side reactions and had the greatest percentage nitrate removal. It was observed that liquid sources may require dosage control that presents some technological challenges, while a simplistic system was desired. Organic substrates such as ethanol, methanol, acetic acid, glucose and sucrose were used for injection in liquid form into wellpoints or boreholes in nitrate contaminated areas (ITRCWG, 2000; Bates and Spalding, 1998, Deng *et al.*, 1998; and Nuttall *et al.*, 2001). A plant located at Bisamberg, Vienna (Austria) has been operating successfully for more

than 2 decades (Jechlinger *et al.*, 1991). It uses ethanol as the carbon substrate and the process is regulated to ensure that the raw water nitrate, which exceeds 15 mg/L, is reduced to approximately 9 mg/L in the product water.

In field studies, Mercado *et al.* (1988) used an aqueous solution of sucrose as substrate to treat the aquifer around an unused old well with estimated depth of 90-100 m and nitrate content in the order of 14 mg NO₃⁻/ L⁻¹.

Healy *et al.*, (2006) did a laboratory study examining various wood materials as carbon sources in horizontal flow filters. They used sawdust (*Pinus radiata*), sawdust and soil, sawdust and sand, and medium wood-chippings and sand in their experiment. They found that the wood-chippings and sand mixture performed the best yielding 97% nitrate removal at steady state conditions.

Cameron and Schipper (2012) in their work found that carbon substrate and temperature were more influential on nitrate removal rate than hydraulic conductivity of the media. They used 9 different carbon media including 5 different grain sizes of wood particles at two different temperatures.

Depending on the desired operational conditions and available budget, a range of solid or liquid carbon sources may be used to effectively reduce nitrate levels to within guideline concentrations for the prevailing site conditions.

1.5.4 Temperature

Griffiths *et al.* (1998) measured denitrification at 25°C. Carrera *et al.* (2003) working with wastewater treatment reactors, used varied temperatures to measure the rate of denitrification at these temperatures. The temperature ranged from 6°C to 25°C. Rates of denitrification were lowest at 6±0.5°C and highest at 25±0.5°C (Carrera *et al.*, 2003). The rate of denitrification generally increased with an increase in the temperature at which the reactions were run. According to Wild (1988), nitrate loss can double with a temperature increase of 10°C over a range from 10 to 35°C. In the lower temperature ranges such as 0 to 5°C, denitrification rates are low but measurable, and more nitrous oxide than di-nitrogen is produced. Wild (1988) also mentions that denitrification is typically favoured by warm wet soil conditions where little O₂ is present. Amatya *et al.*, (2005) varied temperature of denitrification from 10 to 30°C at 2°C intervals. Significant impacts on denitrification process were observed above temperatures of 16°C. As the temperature increased, nitrate nitrogen removal was found to be higher in the biological denitrification process, (Amatya *et al.*, 2005). Greben *et al.*, (2004) used temperatures of 30°C and room temperature for their experiments. Results indicate that the reactor temperature and pH had no direct influence on the denitrification process. This is an important finding as it means when this technology is applied in the field, the reaction will occur when neutral, nitrate rich ground water is fed to the reactor at an ambient temperature of 20-22°C. Cameron and Schipper (2012) used two different temperatures to compare 9 different carbon media in terms of nitrate removal performance. They found that carbon availability and temperature was more influential on nitrate removal rates than hydraulic conductivity of the media. Primary porosity of the media was found to be higher in higher temperature treatments (23.5°C) than in the lower temperature treatments (14°C) using maize cob and wood, and inversely correlated to the secondary

porosity of the media. Primary porosity refers to the pore space volume calculated from the difference in volume between influent water and water that drains from a column, while secondary porosity refers to the difference in wet and dry weight of the solid carbon media removed from the column. They attributed this to contraction of media with increasing temperature which is attributed to the movement of water from the cellulose to the surrounding water phase as temperature increases.

1.5.5 Rainfall events

Laboratory experiments were conducted to investigate the effects of water input properties on the movement of nitrate in three different porous media. Rainfall events of 4mm to 26mm were applied in 10minute durations over variable soil profile combinations (Sugita *et al.*, 2005). Findings show that nitrate and chloride concentrations were similar in homogenous sand media, while in the layered media (soil overlying fine sand) the nitrate concentration decreased with time which they interpreted as degradation of nitrate. Another interesting finding of their study was that high nitrate remained in the topsoil layer under light (4mm) to intermediate (13mm) rains in their two layered soil profile experiments. Under intermediate rainfall, large vertical spread of nitrate and nitrate infiltration occurred. Under high rainfall (26mm), they observed double peaks, this was said to indicate two pathways of flow/infiltration, one by preferential pathways and the other via the matrix. Their conclusions were that heterogeneity of the porous media resulted in large dispersion under intermediate to heavy rain, and denitrification under light rains. The onset of macropore flow depends on rainfall intensity while the rate of macropore flow depends on the rainfall intensity and duration (Sugita *et al.*, 2005). This is supported

by their results where cumulative rainfall of a few 13mm events caused infiltration and hence a change in the $\text{Cl}^-:\text{NO}_3^-$ ratio in the upper layers of soil. Stadler *et al.*, (2012) did a study involving Namibia, Botswana, and the Northern Provinces in South Africa. They found that in exceptional rainfall events, extraordinary rainfall amounts were some 240 to 365% of the long-term means for those same months in their study area. This caused a groundwater level rise of about 15m within a matter of weeks. A resultant peak in nitrate levels and subsequent cattle deaths were reported. Veterinarians diagnosed nitrate poisoning from high nitrate drinking water. Hence, big rainfall events caused infiltration of nitrate stored in the soil profile to the groundwater table. The study by Stadler *et al.* (2012), although rainfall events are more extreme and sporadic, compares favourably to the work done by Sungita *et al.* (2005). Stadler *et al.* (2012) also developed conceptual models for nitrate input to the subsurface. They discuss two types of recharge of nitrate levels. One where fast flow through exists (calcrete layers or preferred pathways) where during exceptional rainfall events, rapid recharge occurs. The other type of setting is where slow recharge occurs, and infiltration takes a longer time. Big rainfall events here also result in accumulated nitrate in the soil, vadoze and unsaturated zones infiltrating to the groundwater table, however with deeper saturated zones or slow infiltration. The time scale is very different to the first model.

1.5.6 Flow rate

Different field sites present variability in porosity, permeability and hydraulic conductivity. Hence the flow rate and direction plays a role in denitrification reactions. Residence time in the treatment zone and reduction or removal of nitrate may depend on the flow rate in the aquifer unit or soil zone. Laboratory studies have

been done to establish the effects of different flow rates for denitrification (Greben *et al.*, 2004 and Greenan *et al.*, 2009). Greben *et al.*, (2004) showed that a shorter hydraulic residence time (HRT) of 12hours and hence faster flow rate was not beneficial for the biological NO_3 removal. Three days after starting the reactors at a HRT of 12hours, the denitrification process ceased in both reactors. Their result is based on the fact that denitrifying bacteria as well as carbon source (COD or DOC) were washed out at a faster feed/flow rate. Groundwater flow rates are naturally slow, unless pumping is used as part of a treatment option. Greenan *et al.*, (2009) did tests using mean flow rates of 2.9, 6.6, 8.9 and 13.6 cm. d^{-1} . They achieved 100% nitrate removal with 2.9 cm. d^{-1} flow rates, 64% removal at 6.6 cm. d^{-1} , 52% removal at 8.9 cm. d^{-1} and 30% removal at 13.6 cm. d^{-1} . Their findings agree with that of Greben *et al.*, (2004) that denitrification will occur at higher flow rates, but efficiency may decline as insufficient concentrations of denitrifying bacteria and carbon source may result at higher flow rates.

1.5.7 Processes competing for available carbon or inhibiting denitrification

The denitrification process is less favourable energetically than the reduction of oxygen. In a system that contains oxygen, nitrate and carbon, the oxygen will be the preferred electron acceptor. Denitrification will only occur once dissolved oxygen reaches a low threshold level. Rivett *et al.*, (2008) said that denitrification will probably occur at dissolved oxygen concentration levels of below 2 or 1 mgO_2/L .

The presence of heavy metals, pesticides and pesticide derivatives can inhibit denitrification, Rivett *et al.*, (2008). Excess concentrations of organic compounds to

such an extent that they are toxic to denitrifying bacteria would also inhibit denitrification. Israel, (2007) during testing of denitrification with methanol observed a few days delay in reaction. This was owed to the possible toxicity to denitrifying bacteria. An order of toxicity of heavy metals to denitrifying bacteria was described as Cd>Cu>Zn>Pb. However, Labbe (2003) states that the presence of trace metals such as manganese enhances the rate of denitrification.

Denitrifying bacteria require carbon, phosphorous, sulphur and micro-nutrients such as boron, copper, iron, manganese, molybdenum, zinc and cobalt for effective metabolism, Rivett *et. al.* , (2008). Phosphorous may be a key limiting factor in certain aquifer systems due to its lower mobility relative to nitrate, Rivett *et. al.* , (2008).

High salinity as in industrial waste or waste waters is known to inhibit denitrification, but not entirely arrest the process, Rivett *et. al.* , (2008). The few studies that have been done show that sodium chloride concentrations above 5g/L may reduce the denitrification efficiency by about 10%, Rivett *et. el.*, (2008).

A lead time for microbial populations to adapt to new or different conditions e.g. additional carbon source or high nitrate concentration can be expected in most laboratory and field experiments. In certain environments, denitrifying enzymes or bacteria are readily available and affects denitrification as soon as oxygen is consumed, while in others, populations may synthesise the required enzymes for denitrification.

1.5.8 Longevity and hydraulic conductivity

The length of time that a denitrifying barrier remains effective is not known (Robertson *et al.*, 2008). Two factors are likely to affect the period of time during which a denitrification layer remains effective. One of these is the continued supply of readily available carbon to denitrifying bacteria, and the other managing the hydraulic conductivity of the barrier (Schipper *et al.*, 2010). Modelling done (Brenner *et al.*, 2001) showed that changing the K value (hydraulic conductivity) has an effect on the amount of flow that occurs through the barrier. Hence, when hydraulic conductivity diminishes within a barrier, flow convergence and overall flux through the barrier declines. This will impact on the lifetime of the barrier.

Work by Robertson and Cherry (1995) and Robertson *et al.*, (2008) shows that a barrier had been successfully operating for about 15 years, while Schipper *et al.* (2005) had a 7 yr operational barrier that became nitrate limited. An example of issues of longevity and changes in hydraulic conductivity occurred in Barkle *et al.*, (2008) where in situ mixing and re-settling of sediments lead to decreased K for the barrier and by-passing of the barrier. Robertson *et al.*, (2009) used coarse wood chip particles in the core of their wood particle reactor which maintained its hydraulic conductivity over 7 years of operation. They showed that coarse wood particle can deliver stable nitrate removal rates and remain highly permeable over a number of years. Robertson *et al.* (2009) in their study showed that finer wood particles (sawdust) had a 70 times lower hydraulic conductivity than their initial fresh sawdust, while coarser core layers composed of course wood chips, maintained an extremely high hydraulic conductivity and showed no deterioration with age. Jaynes *et al.* , (2008) in their study showed at least 5 years of successfully denitrifying agricultural drainage using woodchips as a carbon source. Robertson (2010) observed that reaction rates were approximately 50% lower in “older” reactive media when testing

woodchip media of varying age. Results for aged woodchips compared favourably to removal rates of woodchips that had been used in walls in longer term field trials.

Cameron and Schipper (2012) looked specifically at hydraulic properties, hydraulic efficiency and nitrate removal of organic carbon. The relationship between hydraulic efficiency and nitrate removal of different media was investigated. They found that primary porosity of wood media increased with temperature. They also found that larger grain sizes were less hydraulically efficient than smaller grain sizes, however the difference was small. An increase in porosity of 4% with time was noted in all media by Cameron and Schipper (2012). They owed it to the loss of carbon from the media to the denitrification reaction and microbial decomposition. Robertson *et al.*, (2009) concluded that coarse wood particles enhance permeability without compromising reactivity.

1.5.9 Treatment of other contaminants by redox processes

Laboratory studies using different C: N ratios and variable carbon sources (Israel, 2007) shows that when nitrate is depleted in the system, sulphate is reduced. This was also found in other studies (Robertson and Cherry, 1995). Robertson *et al.*, (2009) found that their denitrification medium could also reduce other redox sensitive species such as perchlorate. This was found previously in a wood particle layer (Robertson *et al.*, 2007). Bacteria in aquifers and soil obtain energy from oxidation of organic and inorganic compounds present in their environment. They either use organic carbon as an electron acceptor and a source of cellular carbon, or use inorganic form of carbon HCO_3^- (Rivett *et al.*, 2008). In nature, there exists a

sequence in which electron donors will be consumed. This is based on their availability as well as the energy required to consume them. Organic matter is oxidized, while electron donors are reduced. The first electron donor that is consumed during the oxidation of organic matter is free oxygen. Once dissolved oxygen is depleted, bacteria capable of growing with or without oxygen use nitrate as an electron acceptor. In laboratory and field studies (Israel, 2007, Robertson and Cherry, 1995, and many others) reduction in sulphate concentrations are reported as monitoring data becomes available. According to the known redox sequence (Appelo and Postma, 2005, McBride, 1994, Rivett *et al.*, 2008) iron and manganese reduction precedes sulphate reduction. Rivett *et al.* (2008) also reports that systems do not display strict redox boundaries and that it is possible if conditions allow for redox reaction to occur simultaneously in a system. Some of these reactions may occur in microsites, while others occur at a larger site scale.

1.5.10 More factors that inhibit or affect denitrification

Denitrification is likely to be inhibited by the presence of heavy metals with Cd>Cu>Zn>Pb being the relative inhibitory ability of the metals, Rivett *et al.*, (2008). In most cases, denitrification is not immediate as a “lead time” may be required for bacteria capable of mediating denitrification to establish (Rivett *et al.*, 2008, Israel, 2007, Robertson and Lombardo, 2003). Very important to denitrification is availability of carbon. Thus any microbial process that out-competes denitrifiers for available carbon is most likely to reduce the removal of nitrate (Schipper *et al.*, 2010). Dissolved oxygen in groundwater or influent water allows aerobes to out-compete

denitrifiers. Initially poor nitrate removal in work by Healy *et. al.* (2006) was attributed to high dissolved oxygen in the system. Sulphate can also be present and act as an alternate electron acceptor in more reducing conditions. According to Appelo and Postma (1994) denitrifiers normally out-compete sulphate reducing bacteria and sulphate reduction only occurs after most nitrates are already depleted. Thus retention times that are too high or carbon substrates that are in excess of that required for denitrification may lead to hydrogen sulphide production (Israel, 2007, Robertson, 2010).

1.6 Properties of wood and wood degradation

Dry wood and cellulose absorbs water when exposed to an atmosphere containing water vapour and under constant conditions, reach an equilibrium water content which depends on the relative humidity of the atmosphere or relative vapour pressure of water (Browning, 1963). In partially dried materials, changes in the quantity of hygroscopically-bounded water induced by variations in relative humidity govern many mechanical and physical properties and the amount of swelling and shrinking (Browning, 1963).

1.6.1 Composition and chemical reactions of wood

The largest part of wood is composed of materials of high molecular weight, described by Browning (1963) as an interpenetrating system of high polymers. The main constituents of wood include carbohydrates, phenolic substances, terpenes, aliphatic acids, alcohols, proteins, and inorganic constituents. The carbohydrate

group of cellulose which is mainly cold water insoluble and includes hemicelluloses, starch, pectic substances as well as water soluble polysaccharides such as arabinogalactans. This normally makes up about 50% of mature wood weight. Sugars occur in the sap and in developing tissues. The breakdown of cellulose in its component by hydrolysis yields D-glucose units. The greater part of phenolic compounds is comprised of lignin. The major parts of wood are composed of polysaccharides and lignin (Browning, 1963). Wood also contains extractives, which are soluble in cold water or neutral organic solvents. Figure 3 below shows an outline of wood components.

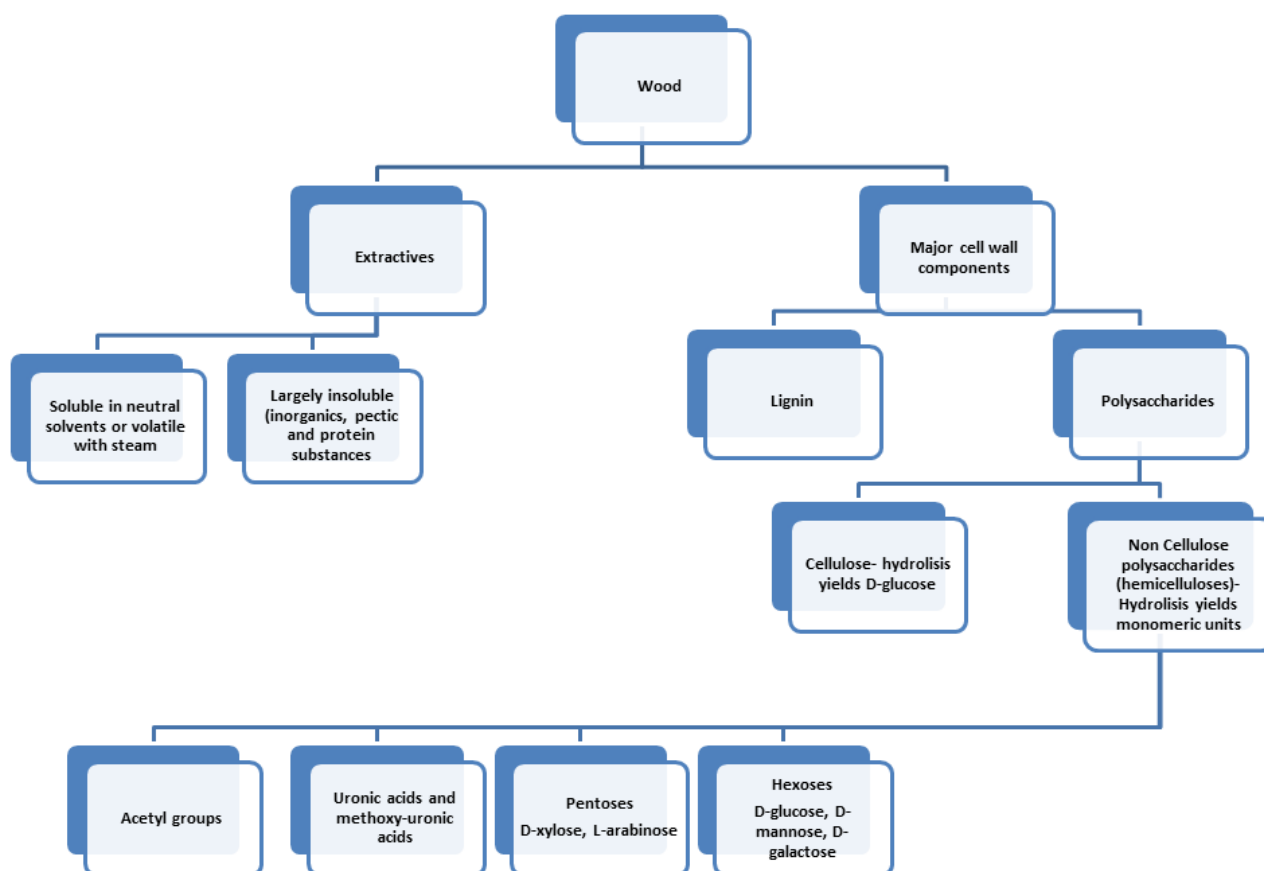


Figure 3: The idealized components of wood, after Browning 1963

Figure 3 shows, that once extractives are removed from wood, its composition is limited to major cell wall components lignin and polysaccharides, both cellulose and hemicelluloses. Extractives; which are soluble in water and neutral organic solvents, include fats and resins. Wood is resistant to the action of solvents and chemicals. This is due to its complex structure of associated high polymers; hence a chemical or solvent attacking one part of its structure may have no effect on another.

Neutral organic solvents and cold water leave the wood structure unattacked and are able to dissolve only the constituents of wood classified as extractives. The extraction process is affected by diffusion processes which govern the transfer of soluble materials from the solid wood to the solvent. Extraction is relatively rapid if grain size of wood is finer, and the amount of material dissolved does not increase significantly upon prolonged contact with fresh portions of solvent. The amount of material from the wood dissolved by water increases significantly as the temperature of the water and the time increases. This is due to the effect of hot water hydrolysing the acetyl groups to acetic acid and hence reacting like a weak acid solution on the wood. In essence, hotter water will dissolve larger proportions of the wood structure due to the decrease in pH produced from the weak acids formed in solution by acetic acid being released from the wood. During hot water action on wood, breakdown or degradation products of lignin appear in extracts. Cellulose is more resistant than other wood components, however it is hydrolysed and partially dissolved by water at temperatures in the range of 100 to 225°C at low acidities i.e. pH 5-8 (Browning, 1963).

Dilute acids have little effect on wood at normal temperature, while stronger acids are able to rapidly dissolve wood, and weak acids can dissolve wood components at high temperatures. Sulphuric, hydrochloric and phosphoric acids are used in the

process of hydrolysing wood to isolate lignin or to produce sugars. Solutions of strong bases (sodium, potassium, or calcium hydroxides) dissolve a considerable quantity of wood substances even at ordinary temperatures. The major attack occurs on the carbohydrates, of which the less resistant are dissolved. Aqueous solutions of neutral salts have similar effects on wood from ordinary temperatures to 100°C of water. Acid salts such as calcium or zinc chlorides produce acid by hydrolysis and lead to hydrolytic deterioration. Atmospheric oxygen is without effect on wood at ordinary temperature and in the absence of decay wood particles remain unaltered for thousands of years. The action of oxidizing agents e.g. chlorine consists of reactions with lignin to form soluble chlorinated oxidation products. Wood is generally reactive towards strong oxidizing agents. The reactions are not confined to lignin as the carbohydrates are partially oxidized with the formation of carbonyls and carboxyl groups, and with simultaneous depolymerisation. Reducing agents are used primarily in the pulp industry to alter the colours of the wood surfaces by the reduction of carbonyl groups and reacting with the colouring matters of wood (Browning, 1963).

The swelling of cellulose may be termed intercrystalline or intracrystalline. The most familiar case of swelling is the case of swelling of cellulose in water. If cellulose is exposed to water or water vapour, cross sectional swelling of the fibre begins as soon as adsorption of water begins. The diameter is likely to increase by up to 25% once immersed in water. Cellulose swelling compounds significantly enhance the reactivity toward chemical reagents, and more or less homogenous derivatives can be prepared from them. The reason for greater reactivity is that hydrogen bonds have been broken during the swelling and molecules of the swelling agent have been introduced into the cellulose structure instead. Chemical reagents can thus

diffuse freely into the cellulose structure and react with hydroxyl groups. This allows for addition reactions to occur readily across the C-OH bond in the cellulose structure. Oxidative and microbial degradation are both very relevant to reactions that may occur during *in situ* denitrification. Cellulose is very sensitive to oxidizing agents and the extent of the resulting degradation depends on the nature of the reagent and the conditions under which oxidation occurs. Microbial degradation is very similar to hydrolytic degradation, except that the large molecular size of the enzymes does not allow diffusion into the cellulose molecule and the attack is thus a localized one. This means that even though a loss in strength occurs as the degradation takes place; the degree of polymerization is not affected to the same extent (Immergut, 1963).

1.7 Research needs identified

Cameron and Schipper (2012) in their recent work concluded that future research regarding nitrate removal performance should focus on carbon availability of the substrate and increasing temperature rather than identifying hydraulically efficient media. According to Cameron and Schipper (2012) the changes in primary porosity due to temperature may be important when considering hydraulic retention time of media. The relationship between temperature, change in porosity due to temperature change and its effect on hydraulic retention time may have to be considered in future. Field scale research is needed to establish the suitability of alternate carbon sources considering efficiency, costs and factors controlling NO₃ removal and denitrification, (Schipper *et al.*, 2010). Design manuals should be

developed to address site evaluation and a suitable amount of background data that should be available for a particular site. Determining linkages between hydrological flow paths, retention time in walls/bioreactors and NO_3^- removal efficiency in an integrated manner including specialist engineers, hydrogeologists, biogeochemists and land manager, (Schipper, 2010). Studies testing the effects of rainfall on nitrate levels show that scenarios that results in higher frequency heavy rainfall could cause increased nitrate leaching. Increased heavy rainfall in heterogenous porous media could cause large dispersion and hence preferred pathway of nitrate leaching under heavy rainfall. Only light rain would promote denitrification (Sugita and Nakane, 2007). It seems to be established and re-iterated in many papers that coarse wood chips are successful at denitrifying groundwater of a range of concentrations but that different types of wood may yield slightly different results. The work by Robertson (2008) shows a barrier/wall being operating successfully for 15 years, and another being tested for 8 years already.

In this research, laboratory and field denitrification using *Eucalyptus globulus* woodchips of variable grain size will be tested for South African conditions to evaluate its applicability as a treatment technology to apply in rural areas of Southern Africa. The barrier material longevity will be evaluated based on data collected for the duration of the field experimental work. Denitrification rates, carbon availability, and predominant mechanism of reaction will be evaluated during laboratory experiments. The effects of prevailing local natural conditions e.g. rainfall and temperature on the field denitrification will be evaluated based on data collected during the field experiments.

1.8 Problem statement

Extensive research on permeable reactive barriers has taken place in countries like Canada, Australia, Austria, the USA and New Zealand on laboratory and field scale. Work in South Africa is limited to about 5 studies mainly in laboratories and one pilot scale study (Israel, 2007, Israel, 2012, Tredoux et al., 2009, Schoeman and Steyn, 2003, Greben *et al.*, 2004). With many areas of the country being classified as arid and semi-arid, groundwater presents an alternative water source. However there are areas where this available resource is not fit for drinking due to elevated nitrate concentration either from natural or anthropogenic sources.

Objectives of this study are to focus on nitrate removal from groundwater in an industrial area which represents the worst case scenario for natural and polluted groundwater in the country. To investigate the relationship between barrier thickness/concentration, retention time, flow paths and nitrate removal efficiency in barriers using data obtained in field and laboratory experiments as well as fundamental equations and available derived data or equations from other studies. Inevitably, to determine the barrier lifetime, or an approximate length during which woodchips can be used and is likely to be effective.

1.9 Structure of work

Background information and previous work on denitrification research has been discussed in this chapter. Chapter two will discuss laboratory column studies. Chapter 3 will consider a laboratory flow through tank experiment. Chapter 4

considers site characterisation and field implementation work. Chapter 5 will address the degradation and nitrate removal efficiency of woodchips used during the field experiment. Chapter 6 is considers main conclusions and recommendations for future work.

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2 CHAPTER 2: COLUMN DENITRIFICATION TESTS²

2.1 Background

Laboratory treatability studies were done as part of a Masters study (Israel, 2007), where sawdust, methanol, glucose and maize meal were used as carbon sources for denitrification. Results showed that sawdust was the most desirable carbon source in terms of criteria for field implementation in a rural area. Among the characteristics assessed were side-reactions, nitrate reduction rate, lag time of reactions, level to which nitrate was reduced, longevity of reactive material. Sawdust effectively denitrified water used for the experiment. Other carbon sources lead to sulphate reduction (maize meal), and lag time at the start of the experiment (methanol). It was desired that the carbon source for denitrification be slowly degradable and hence last longer, glucose and methanol were liquid sources which were more readily available and hence would deplete under field conditions and also require dosage control. Hence sawdust was selected for further study. Laboratory column and flow-through experiments were then proposed as pre-field implementation pilot scale work to establish the effects of flow and barrier thickness on denitrification efficiency.

A review of the role of sawdust in the removal of unwanted materials from water was done by Shukla *et al.*, (2002). They looked at the role of sawdust in removing dyes

² Publications related to this chapter:

Israel, S., 2007. MSc thesis Stellenbosch University, *In Situ* denitrification of nitrate rich groundwater in Marydale, Northern Cape

Israel, S., Engelbrecht, P., Tredoux, G., Fey, M.V., (2009) *In Situ Batch Denitrification of Nitrate-Rich Groundwater Using Sawdust as a Carbon Source-Marydale, South Africa, Water Air and Soil Pollution*, 204:177-194, DOI 10.1007/s11270-009-0036-6

and heavy metals. They considered studies on adsorption properties of sawdust, adsorption mechanisms, factors that influence adsorption of metals and favourable conditions. It is also compared to other agricultural by products such as barley, tree bark and moss peat. They recorded many studies that showed the usefulness of woodchips in its natural form and slightly modified in removing heavy metals (copper, lead, metal sulphides) and nitrate. Sawdust treated with phosphates has removed chromium, while copper-impregnated sawdust has removed arsenic (III). Sawdust and woodchips have been tested in the removal of many hazardous constituents of various spheres of the environment. In this section we test it in its removal ability for high nitrate groundwater, where concentrations are in the order of industrial processes which represent the extreme of what would be found in natural groundwater and soil systems. Work by Rivett *et al.*, (2008) state that denitrifying bacteria are essentially ubiquitous in the subsurface, hence adding of a particular strain of bacteria for denitrification is not necessary. Critically limiting factors to denitrification in the subsurface is thus not presence of suitable bacteria, but rather oxygen and electron donor concentration and availability, while other conditions e.g. nitrate concentration, nutrient availability, pH, temperature appear to be less important and have only secondary effects on denitrification. In using sawdust for denitrification, the electrons needed for denitrification can originate from the microbial oxidation of organic carbon. Lack of organic carbon to provide energy to heterotrophic bacteria is usually identified as a major limiting factor to the process of denitrification, Rivett *et al.*, (2008).

2.2 Natural redox processes in soils

When soils are saturated or submerged, the availability of oxygen is limited or depleted (Patrick, 1982). Nitrogen transformations are very different in this type of setting compared to a drained soil; this affects the amount of nitrogen available for biological activity. The presence of a thin aerobic soil layer in close proximity to an anaerobic layer has important effects on nitrogen transformations. Nitrate is not readily denitrified in the aerobic layer but is denitrified in the anaerobic layer, while $\text{NH}_4^+\text{-N}$ will be converted to $\text{NO}_3^-\text{-N}$ in the aerobic layer but not in the anaerobic layer. As long as oxygen is present in a soil, nitrogen and other oxidized components of soil water are not likely to undergo biological and chemical reduction, (Patrick, 1963). After oxygen is no longer present, the need for electron acceptors for facultative and true anaerobic organisms result in the reduction of nitrate, higher oxides of manganese, iron, sulphate and even carbon dioxide. Many scientists have produced evidence of this sequential reduction of oxygen, nitrate, manganese, iron, sulphate and carbon dioxide by organic matter present in soils (Patrick and Turner, 1968, Mc Bride, 1994). Often one component is not completely removed before the reduction of the next commences. In other words, nitrate reduction can start taking place while oxygen is still present in small quantities in a system; similarly, sulphate reduction can start while nitrate reduction is not yet complete. Under natural conditions, oxygen and nitrate reduction is rapid and they are often totally removed shortly after water logging, (Patrick, 1982). Where pollution or excess concentrations are present, the denitrification process would proceed until such time that the system is nitrate or carbon limited, and then proceed to the next oxidized electron acceptor available. The reaction for nitrate reduction by organic matter is bacterially catalysed and can be written as an overall reaction:



Equation 1 shows that one can expect an increase or elevated concentration of HCO_3^- or alkalinity should nitrate reduction by organic matter occur.

2.3 Sorption

The concept of sorption of inorganic ions has been studied extensively for a range of sorbents. Particular interest has been given to cases where woodchips, biochar and similar sorbents have been used particularly for nitrate removal. The term sorption refers to pollutant removal by surface bonding or by incorporation into the sorption media. When testing the sorption capability of certain media, one can use equations (Langmuir and Freundlich) to predict the nutrient removal value of a certain sorbent, Barrow, (2008).

Sorption occurs when the solution (liquid phase) condenses onto the solid phase (sorbent). One can measure sorption or amount of a particular ion removed from solution by using a known initial solution concentration and a known mass of sorbent as well as a known sorbent to solution ratio. A sorption isotherm indicates the maximum amount of pollutant that can be removed with a particular sorbent (Wanielista and Chang, 2008). The sorption process, unlike denitrification by organic material, does not require a period during which bacteria acclimatize to conditions, hence it is likely that media acting predominantly using a sorption mechanism would perform better in the initial phases of experimentation. There are generally three types of adsorption, physical, chemical and exchange adsorption (Sawyer *et. al.* , 1994). Physical adsorption is relatively non-specific and is due to weak forces of attraction between molecules e.g. Van Der Waal's forces. Chemical adsorption is the

result of much stronger forces. Adsorbed material forms a layer over the surface. Exchange refers to the replacement of an ion from the surface by an ion from the solution.

Equations:

Sorption using the Langmuir equation is expressed as follows:

$$\mathcal{J} = \mathcal{J}_{\max} \frac{Kc}{1+Kc} \quad \text{Equation 2}$$

Where K = Langmuir equilibrium constant, c = aqueous concentration, \mathcal{J} = amount sorbed, and \mathcal{J}_{\max} = maximum amount adsorbed as c increases.

Langmuir linear regression is as follows:

$$\frac{c}{\tau} = \frac{c}{\tau_{\max}} + \frac{1}{K \tau_{\max}} \quad \text{Equation 3}$$

A plot of $\frac{c}{\tau}$ versus c yields a slope = $1/\tau_{\max}$ and an intercept = $\frac{1}{(K \tau_{\max})}$.

The freundlich isotherm equation is,

$$\text{Log } Q = \text{Log } K + \frac{1}{n} \text{Log } C \quad \text{Equation 4}$$

Here Q represents the sorbed concentration, K represents the measure of capacity of the media, C = aqueous concentration. A plot of $\log Q$ vs $\text{Log } C$ gives a slope of $1/n$ and an intercept = $\text{Log } K$. Adsorption when plotted using this equation should

yield a straight line. The Freundlich isotherm is an empirical equation that can be used for heterogeneous systems with interaction between the molecules adsorbed. The n parameter, known as the heterogeneity factor, can be used to indicate whether the adsorption is linear ($n = 1$), whether it is a chemical process ($n < 1$), or whether a physical process is favourable ($n > 1$). On the other hand, the values of $1/n < 1$ and $1/n > 1$ indicate a normal Langmuir isotherm and cooperative adsorption, respectively, (Wan Azina Wan Ab Karim Ghani *et al.*, 2013).

2.4 Reaction Rates

Reaction rates can be used to determine the rate at which a process occurs. A first order reaction rate can be used to calculate the rate constant k (hr^{-1}) from the slope of a plot of $\ln C_0/C$ vs. the reaction time. While a second order rate of reaction can be found by plotting $1/C$ vs. time. Integration of the rate equation: the first order rate equation

$$\frac{dC}{dt} = k[C] \quad \ln \left[\frac{C}{C_0} \right] = -kt \quad \text{Equation 5}$$

The second order rate equation as follows:

$$\frac{dC}{dt} = k[C][H^+] \quad \frac{1}{[C]} = \frac{1}{[C_0]} + kt \quad \text{Equation 6}$$

Most existing or completed studies use low concentrations of NO_3^- -N e.g. 5 to 20 mg/L of NO_3^- -N (Powers, 2012), 0.5 to 5 mg/L (Wanielista and Chang, 2008), 17 to

37 mg/L (Robertson, Ford and Lobardo, 2005) and many other similar studies of nitrate removal. NO_3^- -N removal efficiency using biochar, biochar and woodchips mixed (50/50) and woodchips as carbon sources and sorption media will be discussed using influent NO_3^- -N concentrations ranging from 213 to 276 mg/L NO_3^- -N in the sections that follow. The high nitrate concentration in this study was used to have comparable rates, sorption capacities and carbon availability to field conditions. Samples were taken from a field site selected for field experimentation.

The aims of this experiment were

1. To compare the efficiency of nitrate removal between the 3 treatments used and to establish what is the effect of combining biochar and woodchips.
2. To determine a suitable residence time for which total denitrification would occur with minimal NO_2^- production
3. To consider the removal rate, sorption capacity, and possibly mechanism of reaction

2.5 Materials and methods

2.5.1 Reactant materials and properties

Woodchips were sampled from an existing field denitrification experiment. Sample preparation included overnight oven drying and sieving to establish particle size before use in the laboratory experiment.

Table 7 shows some properties and concentrations of components of woodchips and biochar used in the experiment.

Table 7: Properties and concentrations of components of materials used during the experiment

Material	Grain size range	Age	Moisture	Ash	Extractives/ Volatiles	Fixed carbon/ lignin (wood)
Woodchips ¹	0.45-0.60 mm	27 months	7.52%	7.84%	4.309%	31.39%
Woodchips ¹	0.45-0.60 mm	35 months	6.79%	13.69%	5.65%	30.33
Biochar	Fines		2.61 %	3.04%	19.9%	74.45%

¹Refers to full core samples of woodchips taken from the field experiment at 27 months and 35 months.

Treatments used were Woodchips (0.450-0.60mm woodchips), mixed woodchips (0.450-0.60 mm) and biochar (fines), and biochar only. The amount used was calculated using the carbon required (using acetate to nitrate and nitrite) based on the stoichiometric relationship for denitrification. Acetate was assumed to be the first breakdown product to participate in denitrification. The calculated amount took into consideration slow flow rate of 0.045 m/d and an operation period of 30 days (Table 8).

Table 8: Calculations to determine sawdust load required to denitrify groundwater in column experiments

1

<i>Experimental set-up</i>	Woodchips	Biochar	Mixture	
Area	0.173	0.173	0.173	m ²
Flow velocity	0.045	0.045	0.045	m/d
Flow rate	0.0078	0.0078	0.0078	m ³ /d
Inlet Nitrate	276	213	222	gN/m ³
Eff Nitrate	20	20	20	gN/m ³
N removal	256	193	202	gN/m ³
N removal rate	1.993	1.502	1.572	gN/d
N removal rate	0.071	0.054	0.056	molN ₂ /d
Nitrite removal rate	0.142	0.107	0.112	molN/d
Acetate (Nitrit) removal rate	0.107	0.080	0.084	mol Ac/d
Nitrate removal rate	0.142	0.107	0.112	molN/d
Acetate (Nitrat) removal rate	0.071	0.054	0.056	mol Ac/d
Acetate (tot) removal rate	0.178	0.134	0.140	mol Ac/d
Sawdust requirement	0.119	0.090	0.094	mol sawdust/d
Operation period	30	30	30	d
Sawdust load g	608	458	479	g sawdust
Sawdust load kg	0.607554896	0.457775	0.479121676	kg sawdust

Calculations in Table 8 takes into consideration the mole transfer during processes of nitrification, denitrification, cellulose degradation, and uses acetate as the first available carbon compound able to participate as a carbon sources in the reactions of denitrification. Example calculation: Find the area of the site/column/tank, note the flow velocity,

Flow rate = area * flow velocity;

$$0.173 * 0.045 = 0.0078$$

Required N removal rate gN/d = Flow rate * N removal required

$$0.0078 * 256 \text{ mg/L (required N removal)}$$

$$= 1.993 \text{ g N/d}$$

N removal rate in mol of nitrogen gas produced simply uses the molar mass of nitrogen (14) to convert the g N₂/d into mol N/day. Nitrite removal rate takes the

nitrate removal rate and multiplies it by the metabolic rate coefficients for nitrite conversion to N₂ gas as follows:

$$\text{Nitrite removal rate} = \text{ABS}(\text{mol N removal rate} * S_{\text{NO}_2} / S_{\text{N}_2})$$

$$= 0.071 \text{ mol N}_2/\text{day} * (-1.4/0.7)$$

$$= 0.142 \text{ mol N/day}$$

$$\text{Acetate removal rate N} = \text{ABS}(\text{Nitrite removal rate} * S_{\text{NO}_2} / S_{\text{acetate}})$$

$$= 0.142 \text{ mol/day} * (-1.05/-1.4)$$

$$= 0.107 \text{ mol Ac/day}$$

$$\text{Acetate (mol) for Nitrate removal} = \text{ABS} (\text{Nitrate removal rate} * S_{\text{acetate}}/S_{\text{NO}_3})$$

$$= 0.142 * (-1.05/2.1)$$

$$= 0.071$$

$$\text{Sawdust requirement in moles} = \text{Acetate (total$$

$$\text{removal}) * (S_{\text{gluc}}/S_{\text{Acetate}}) * (S_{\text{cellulose}}/S_{\text{glucose}}) * (X_{\text{sawdust}}/S_{\text{cellulose}})$$

$$= 0.178 * (-.88/2.1) * (-1/1) * (-1/0.622378)$$

$$= 0.119 \text{ moles of sawdust required}$$

$$\text{Sawdust grams required} = \text{operation period} * (\text{moles sawdust required} * \text{molar mass})$$

$$= 30 * 0.119 * (\text{average (cellulose+hemicellulose molar mass)})$$

$$= 30 \text{ days} * 0.119 \text{ g} * 170 \text{ mol/g}$$

$$= 606.9 \text{ g}$$

Figure 4 shows the breakdown of sawdust and reaction pathways that the calculation takes into account.

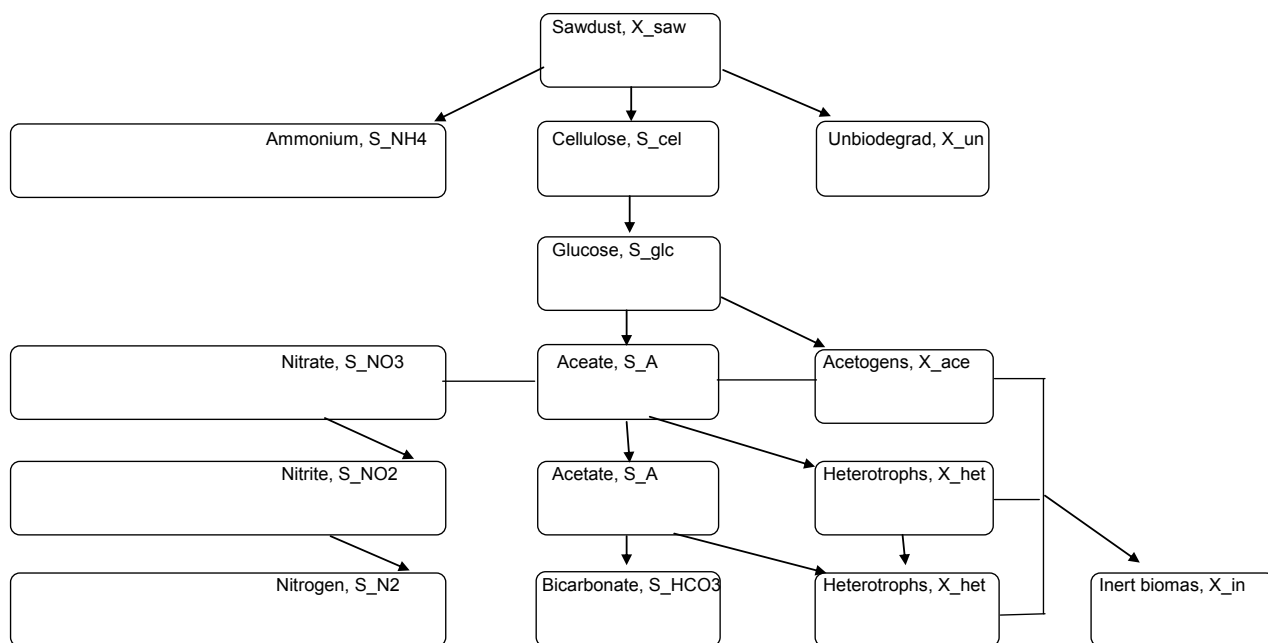


Figure 4: Sawdust/Woodchip breakdown and reactions taking place. Principle behind calculations in Table 8

Materials were packed in vertical columns with height of 0.5m and volume of 0.173m³. The woodchips used during this experiment had been used in a field denitrification experiment from July 2010 to July 2012 and October 2010 to June 2013, a 27 and 35 month period respectively. Wood samples collected from the field testing site at time 27 months and 35 months were analysed by the Stellenbosch wood science department using standard wood methods of analyses (ASTM, 2013). Ash content, moisture content, cellulose, lignin, hemicellulose breakdown products such as arabinose, cellobiose, glucose, and arabinose were measured based on a

species specific composition to be expected. Figure 6 shows the results of the analyses of the woodchips.

Biochar used during this experiment was analysed by Sika, (2012). The moisture content was 2.61% by mass, ash content was 3.04%, volatiles were 19.9%, and fixed carbon content was 74.45% (Table 7). The fixed carbon here refers to the portion of biochar that consists of condensed aromatic rings (black C) and is likely to persist in soils, whereas the volatile component is more easily degraded by soil microorganisms, depending on its physical accessibility (after Sika, 2012, from Keiluwiet *et al.*, 2010). In the case of biochar, one would envisage that the volatiles would be able to participate in a denitrification reaction.

Figure 5 shows the results of analysing the breakdown sugars of wood. Samples were collected from the top 20cm called (topsection), an augered sample of the entire tank (full core) and a sample from the lower part of the tank (lower) also woodchips that were from the same species and location that was not in the tank. Figure 6 shows the lignin, cellulose, extractives and ash content of wood used during the experiment.

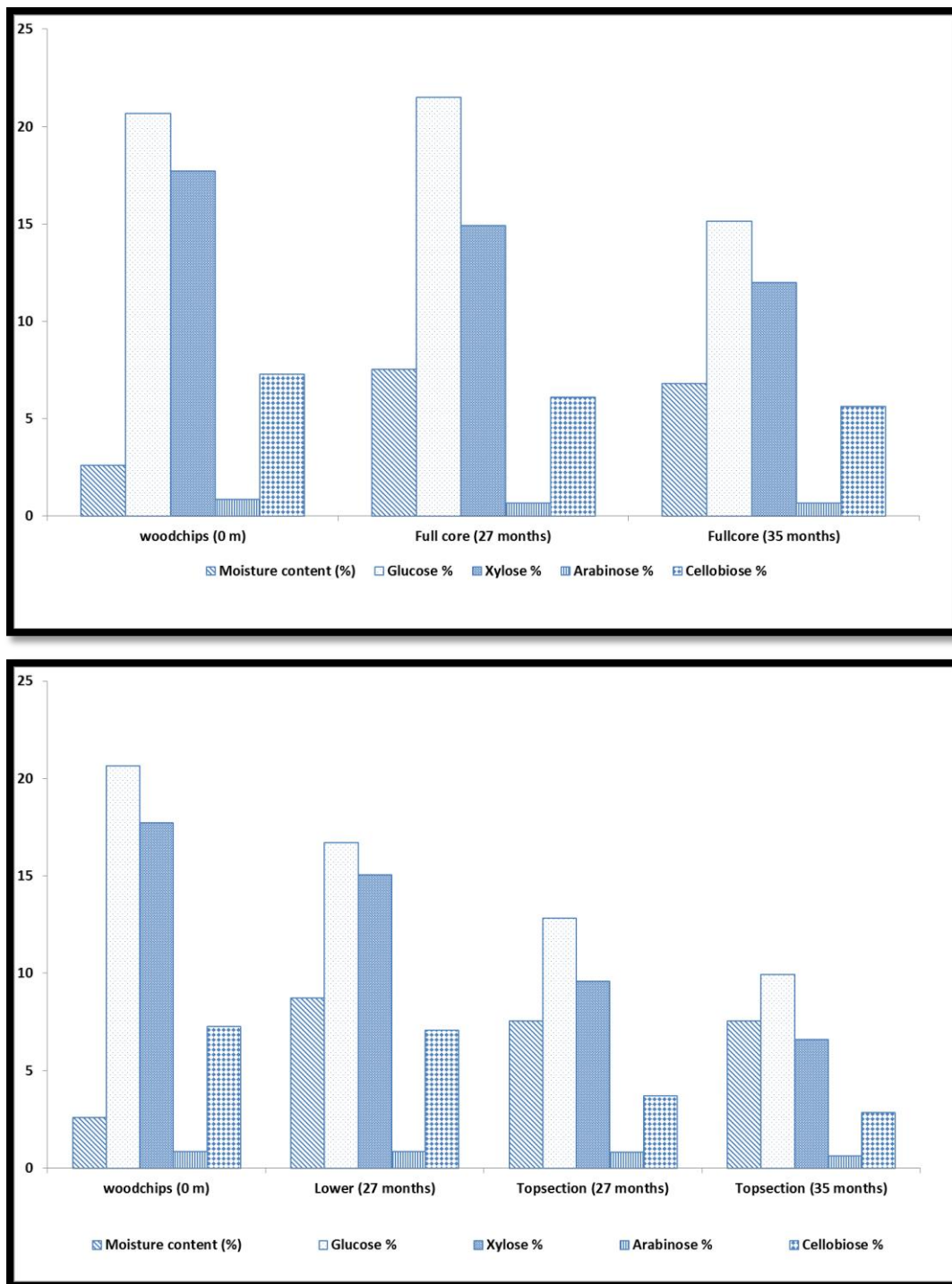


Figure 5: Results of analyses of wood samples from the top part of the tank, lower part of the tank, and the full composition of the tank installed in the field experiment. The top graph shows the breakdown sugars in the full core samples, the bottom shows the composition in the lower and top section. Both graphs are compared to the woodchips that were of the same species and location but not reacting in the tank.

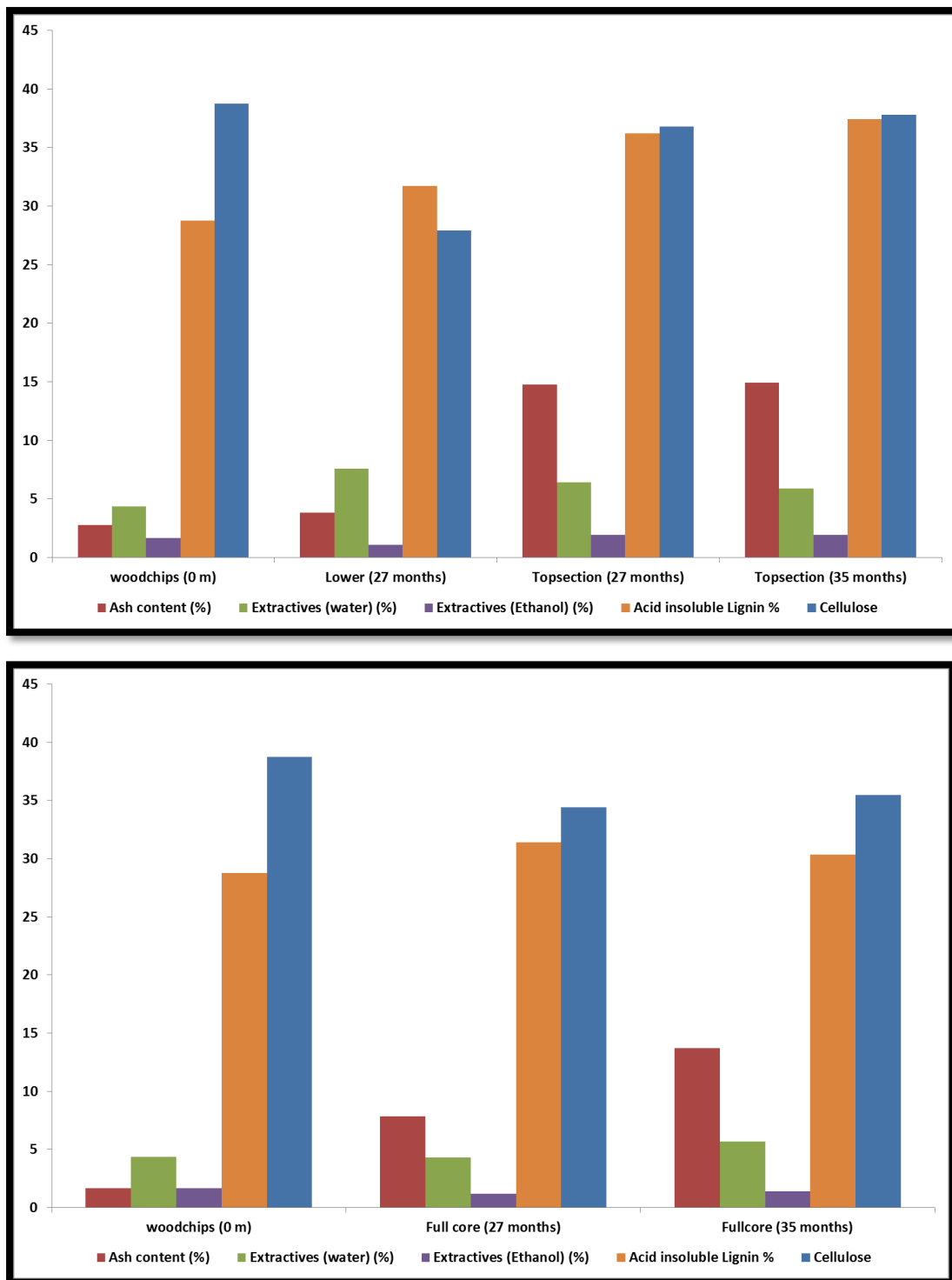


Figure 6: Results from wood content analyses for fresh wood chips, woodchips that was actively used in denitrification for 27 and 35 months respectively. Woodchips (0m) represents woodchips exposed to natural degradation processes for the duration of the experiment. Top section represents woodchips from the top 20cm of the tank, lower represents samples collected from the bottom of the tank, and fullcore represents samples that were collected with an auger which covered the entire depth of the tank.

Figure 7 shows the columns packed with woodchips, woodchip and biochar mixture and biochar respectively. The layer thickness was comprised of approximately 0.600kg of carbon. Figure 7 and Figure 8 shows the composition of the columns used during the experiment.



Figure 7: Pictures of columns packed with sand, woodchips (35 month) (left), woodchips (27 month) and biochar (middle) and biochar only (right)

Figure 8 shows the experimental set-up where 25 L tanks were connected to the columns using hose clamps and small adjustable plastic irrigation taps. Taps were marked according to measured flow rates and could hence be adjusted accordingly. Three measurements were taken per marking and the average used as the flow rate for that particular marking. The nitrate concentration of water collected in the field was 375 mg NO_3^- -N/L. This was diluted by mixing 15L of sample with an average of

375mg/L NO_3^- -N with 10L of tap water. Three separate mixes was made for each tank and poured into the 25 L tanks. A sample from each tank was then analysed for its nitrate concentration. The results showed that the influent water tank used for the woodchip treatment had 276 mg/L NO_3^- -N, the biochar and woodchip mixture's source water tank had 222 mg/L NO_3^- -N and the biochar only treatment's source water tank had 213mg/L NO_3^- -N. Dilution was made using tap water as it would compare more favourably to rainwater in composition than distilled water. These concentrations were used as the initial NO_3^- -N concentrations for the respective columns.

All columns were saturated with water from the 25L tanks and allowed a period of initial rest of 24 hours. During day 2, a slow influent rate of 15ml/min was used, however, high pressure on the system seemed to result in a high potential for leaks. A decision to alter the methodology to focus more on residence time in the column was taken. All columns were saturated and flow switched off for 24 hours. After 24 hours, a sample of water was collected by allowing flow to take place at the highest rate possible, hence displacing the volume of water that had been held in the tank for 24 hours. The new volume was then allowed to remain in the tank for 24 hours, after which the same procedure was followed for 7 days. The sampling frequency was then decreased to 72 and 96 hours for another 7 sampling events. Samples were analysed for NO_3^- , PO_4^- , DOC, NH_4^+ , NO_2^- , and Alkalinity. Figure 8 shows a schematic of the experimental setup.

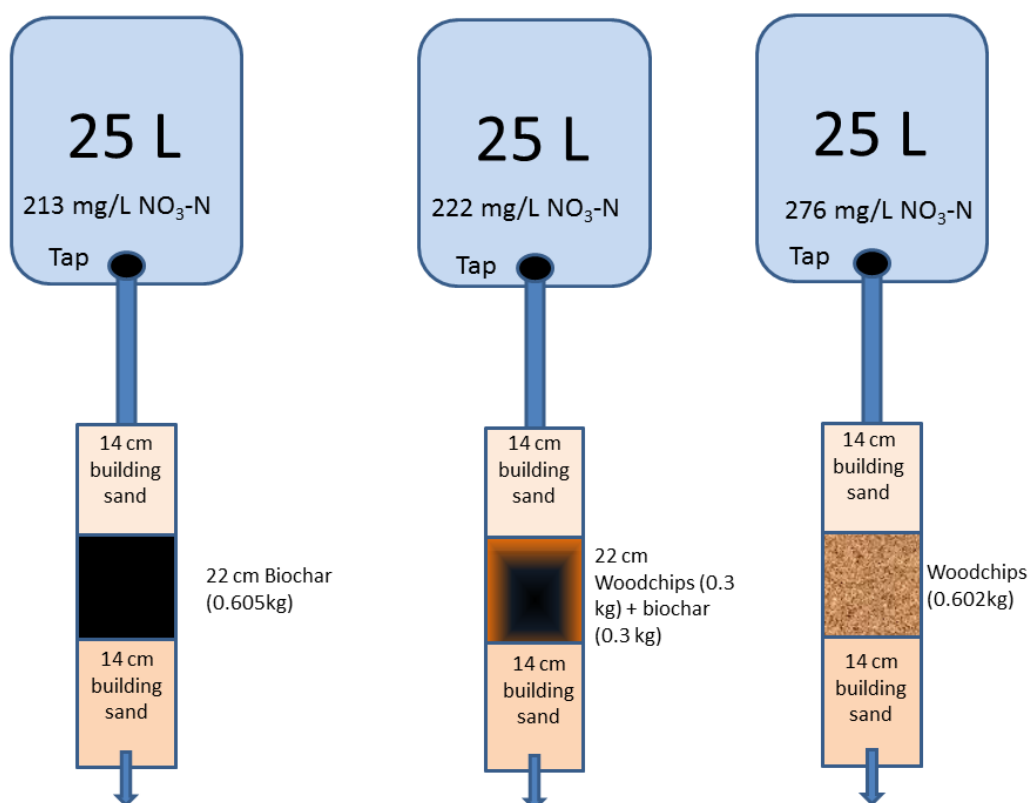


Figure 8: Experimental setup for nitrate removal using woodchips, woodchip and biochar mixture and biochar.

2.5.2 Sampling and analyses

Samples were collected for times 0, 24, 48, 72, 96, 120, 168, 240, 336, 408, 504, 672, 744 and 840 hours. Samples were analysed for NO₃⁻+NO₂⁻ as N, NO₂⁻, NH₄⁺, PO₄⁻, Alkalinity, DOC. Ammonium, soluble phosphate, and nitrate and nitrite were measured using flow injection colorimetry. Alkalinity was measured using a potentiometric titration, and dissolved organic carbon was measured using thermo catalytic oxidation. Data was assessed using equations or relationships outlined in Equations 2 to 6.

2.6 Results and discussion

The removal efficiency of woodchips, biochar and a 50:50 percent ratio of woodchip and biochar mix treatments is plotted in Figure 9. Appendix A contains all data collected during this laboratory experiment.

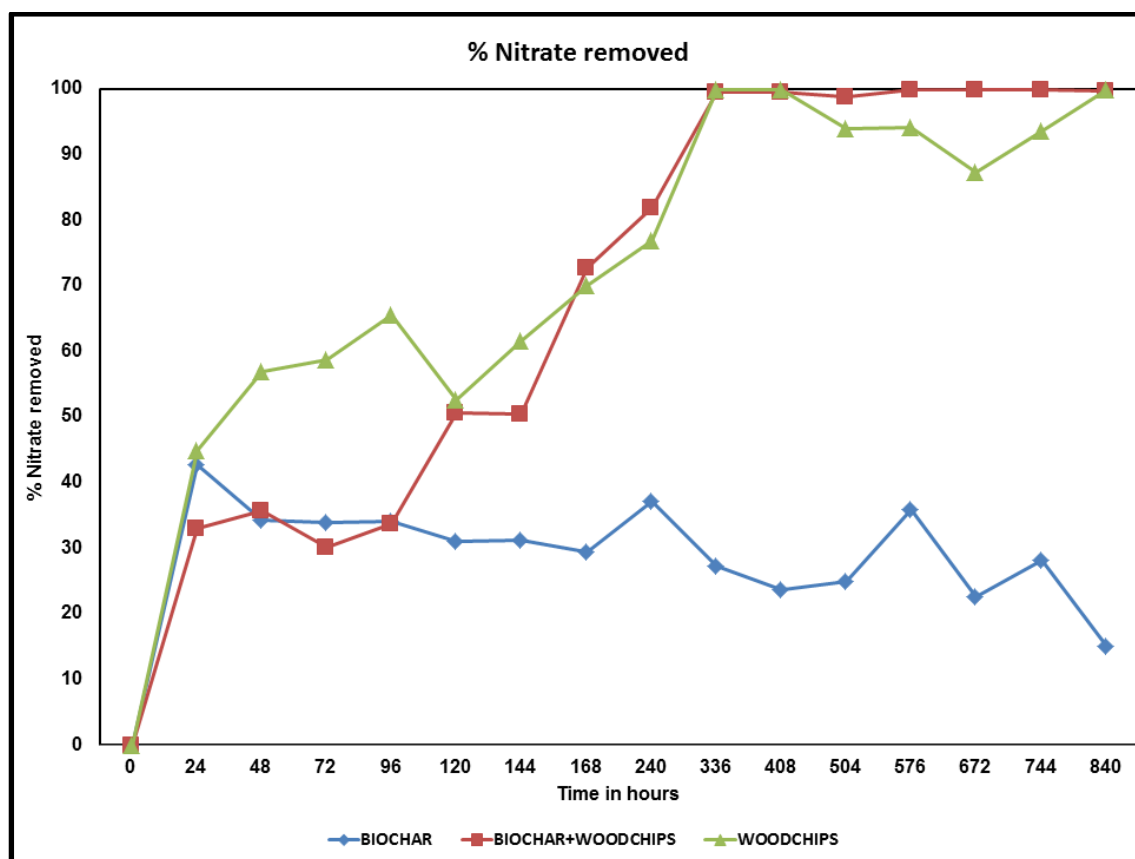


Figure 9: Nitrate percentage removed from solution over time for the treatments used.

Figure 9 shows that for the first 24 hour period, all the treatments removed between 30 and 45% of nitrate present in the initial solution. This would relate to a rapid rate of removal within that first 24 hours, however, samples were only collected every 24 hours for the first period of the experiment. The biochar removal rate shows a decrease over time, while the woodchip and 50% biochar and woodchip mixture

shows continued increased removal percentages. A residence time of one day was selected as previous work showed total removal of nitrate within 7 days (Israel, 2005), and residence times of 1 to 10 days (Robertson *et. al.* 2005). The period from time 0 up to time 240 hours was used to establish a rate of reaction for the woodchip, and woodchip and biochar mixture. Time 240 hours was selected as the woodchip only treatment and 50% woodchip and biochar mix treatment seemed to have passed the point of complete denitrification within the 72 and 96 hour saturation periods. Figure 9 shows that the woodchips only treatment remove the highest percentage of NO_3^- -N in the first period of the experiment, while a longer residence time (saturated period) results in the 50% mix of woodchips and biochar being more effective in removing nitrate. Biochar on its own seems to lack efficiency in removing these high nitrate concentrations. Powers (2012), using 6mg/L NO_3^- -N, concluded that reactors with 10% biochar by mass outperformed bioreactors with only woodchips. Wanielista and Chang (2008) achieved 95.36%, 81.34% and 65.68% for 0.5mg/L, 2.5mg/L and 5mg/L respectively using a media mix.

The rate of reaction was found using both equations 5 and 6 for all treatments using data for nitrate concentrations from time 0 up to time 240, as this period shows a gradual change in the nitrate concentration prior to total removal, which would represent completion of the reaction. Figure 10 shows the first order rate expression plot for the three treatments on the same axis. Woodchips and the 50% mix of woodchips and biochar curves has a steep slope with the woodchip and biochar mix having a greater slope or k value. All plots show a high value for R^2 . Biochar on its own shows a negative rate of reduction in concentration for the full duration of the experiment.

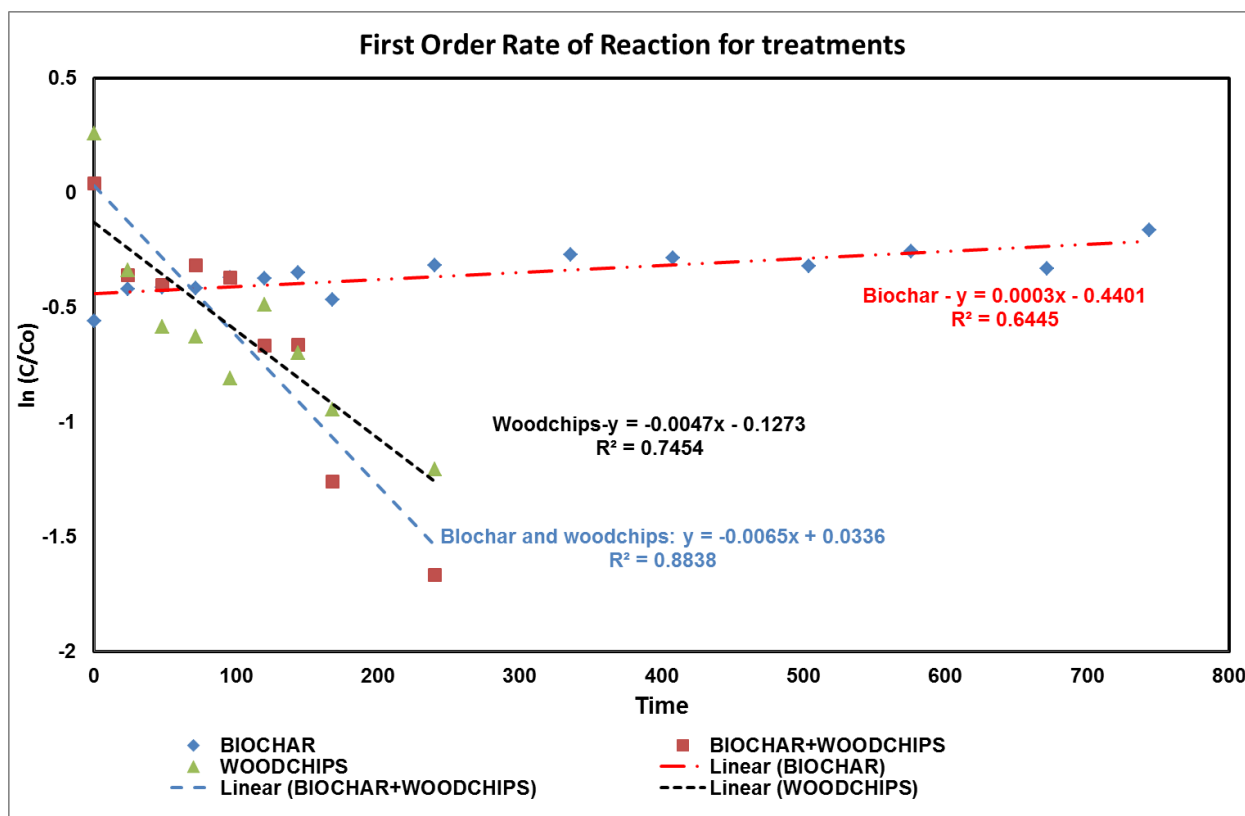


Figure 10: Data plotted as \ln of the ratio of the initial concentration and the concentration at a point in time C_t vs. time for the biochar, woodchips and biochar and woodchip 50/50 mixture, this would be representative of a first order rate of reaction. Trend lines are displayed for each treatment, with resulting equations and R^2 values

Figure 11 shows the 2nd order rate constant expression plot for the data over the same time period.

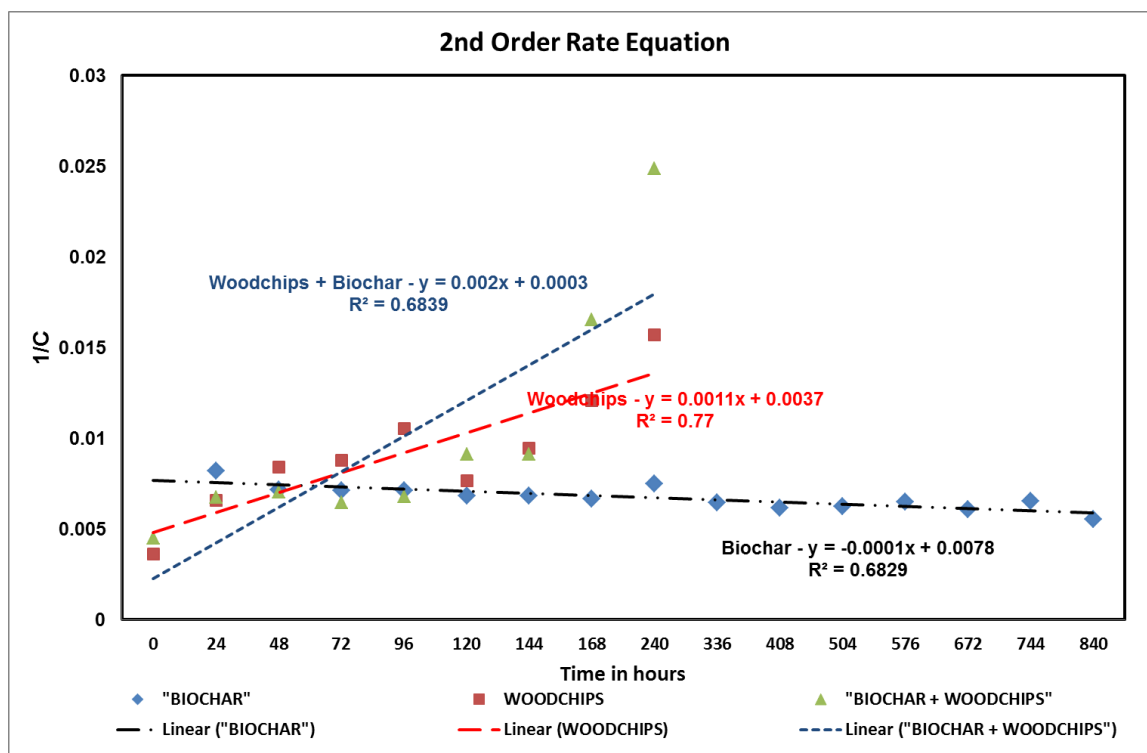


Figure 11: Shows the plot of the 2nd order rate expression for biochar, woodchips and 50/50 biochar and woodchip mixture. The x-axis shows the time, while the y-axis shows the reciprocal of the concentration. Trend lines, their equations and R^2 values are shown on the plot.

The trend line in Figure 10 and Figure 11 shows that even though biochar was able to remove nitrate (Figure 9) from solution, the rate of removal declined with time. A study by Mizuta *et al.* (2004) using bamboo powder charcoal and commercial activated carbon showed that bamboo powder charcoal was more effective than activated carbon at adsorption, however other studies with biochar 10% and woodchip 90% showed positive results. Mizuta *et al.* (2004) worked in very low concentration ranges of 0-10mg/L. Table 9 shows a summary of R^2 values and k values for the respective rate plots Figure 10 and Figure 11. Healy *et al.* (2006) used 60mg/L NO_3^- concentrations in their synthetic wastewater denitrification experiment, and achieved 97% reduction of NO_3^- -N in their 166 day experiment.

Their experimental set-up was a horizontal flow sand woodchip mixture similar to that used in Israel *et. al.* (2012). Table 9 shows the results from rate plots.

Table 9: Summary data from plotting nitrate concentrations using first order and second order rate equations. R^2 as well as k values (slope) from plots are recorded here

First order rate plot		
Treatment	R^2	K= Slope
Biochar Treatment	0.77	0.0003
Woodchips	0.754	0.0047
Woodchip and biochar	0.8838	0.0073
Second Order rate Plot		
Treatment	R^2	K= Slope
Biochar Treatment	0.6829	-0.0001
Woodchips	0.77	0.0011
Woodchip and biochar	0.68	0.002

The rate of nitrate removal from groundwater can be described as a combination of first and second order for woodchips and woodchip and biochar mixture, while first order for the biochar based on the fits of the plots. In the biochar treatment the reaction is independent of the available carbon content. In the woodchips and 50% mix of woodchips and biochar the reaction in the start-up time is limited by available carbon while in the latter period it is more limited by nitrate concentration (Figure 9, Figure 10, and Figure 11). This has been demonstrated (Figure 12) by previous work by (Israel, 2007), where the hourly data was collected during the first 24 hours.

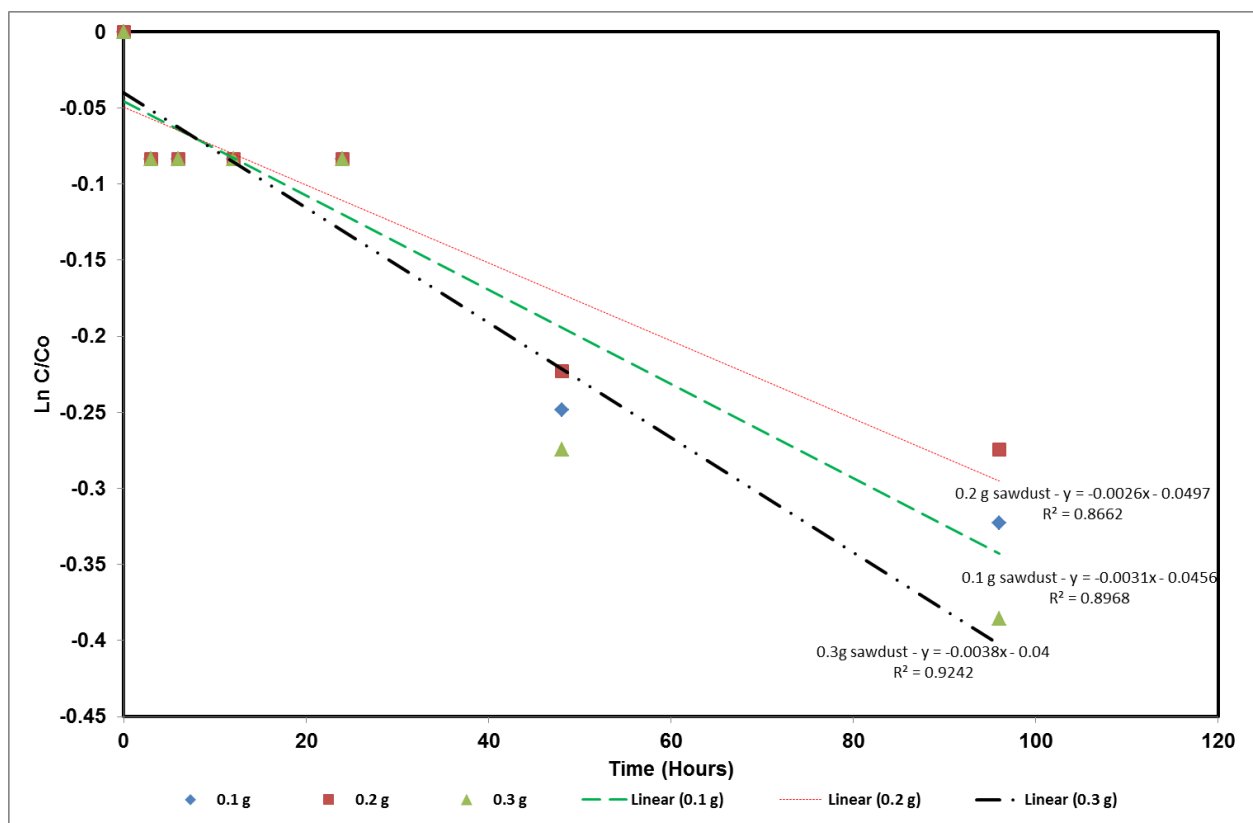


Figure 12: The rates of the first 96 hours of reaction using different carbon to nitrogen ratios. 0.1 g woodchips (12.6:1 C: N), 0.2 g woodchips (24:1 C: N), 0.3 g woodchips (34:1 C: N), data from Israel, (2007).

Figure 12 shows that from time 0 to 24 hours almost no nitrate is removed, this due to the dependence of available carbon as DOC to the denitrification reaction.

Using the results in Table 9, one can substitute the value for k into equation 5 to find how long it would take for the reaction to consume an amount of nitrate when a 24 hour residence time is used, e.g. how long would it take for the concentration of NO_3^- as N to be within acceptable concentrations for drinking water using the biochar and woodchip mix? Using the relationships in equation 5 and the plot of experimental data, Table 10 shows the time it would take to reduce the nitrate concentrations to within the SANS241 (2005) acceptable limits of 10 mg/L.

The rates determined in this experiment are somewhat lower than that determined by Wanielista and Chang (2008) who did similar experiments using lower concentrations.

Table 10: Determination of the time it would take for the reaction to proceed to a concentration of 10mg/L, the acceptable nitrate concentration using a 24 hour residence time, using the rates determined from data in first order rate plot (Figure 10)

Treatments	1st order rate k	C ₀	C _t	- k	t (hours)	T (days)
Biochar Treatment	0.0004	213	10	-0.0004	7646.77	318.62
Woodchips	0.0047	276	10	-0.0047	705.92	29.41
Woodchip+ biochar	0.0073	222	10	-0.0073	424.67	17.69

Figure 13 shows the time series plot of one of the treatments that best demonstrates the dependency on concentration of NO₃⁻ and availability of DOC.

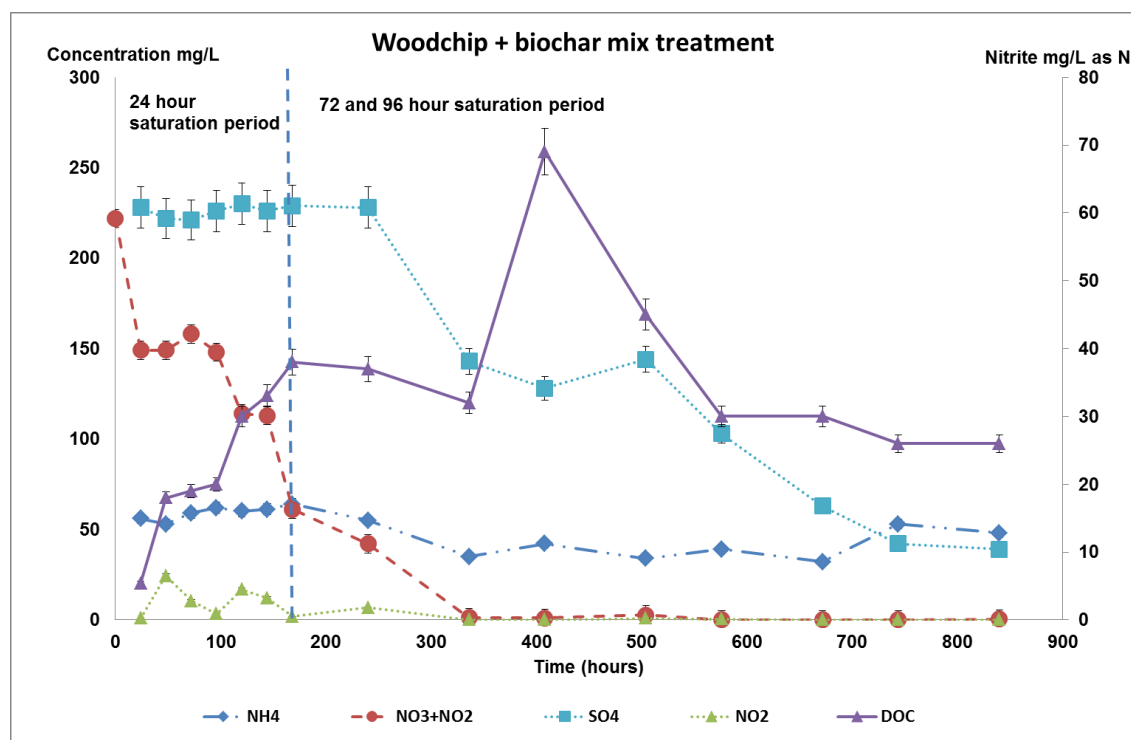


Figure 13: Times series plot of parameters analysed for during the experiment for woodchip and biochar treatment. The x- axis shows the time and the primary y-axis shows the concentration of NH₄⁺, NO₃⁻+NO₂⁻, and SO₄²⁻, the secondary y-axis shows the concentration of NO₂⁻ and DOC

Figure 13 at time 400 hours show a peak in DOC, which coincides with no available NO_3^- in solution as well as a small reduction in sulphate. This compares favourably to results found by Robertson (2010) during his column experiment using woodchips of varying age. During this phase using 72 hour residence time, the reaction becomes nitrate limited and sulphate reduction starts to proceed in the columns where woodchips are present. Robertson (2010) states that woodchips lose about 50% of their reactivity during their first year of operation as soluble organic compounds are leached out, but then relatively stable rates of nitrate removal may persist for a number of years thereafter.

The data was plotted using the Langmuir and Freundlich isotherm relationships to see to what extent sorption occurred and whether one could delineate differences in processes occurring in each treatment. Figure 14 shows the Langmuir, while Figure 15 shows the Freundlich plot of the data. The nitrate removal for each treatment was plotted using Equations 3 and 4. Since the concentration range for the initial solutions are similar, the curves were plotted on the same system of axes.

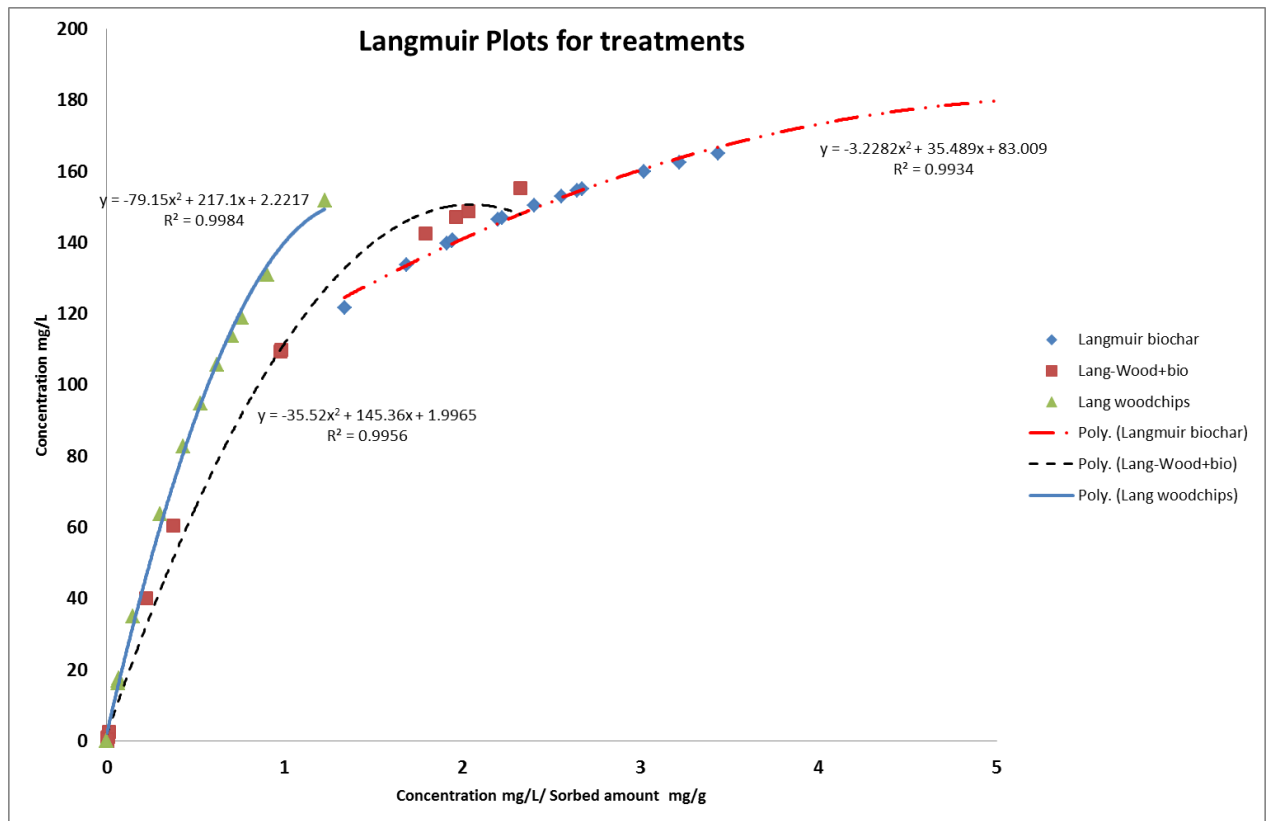


Figure 14: Langmuir plot for data collected during the experiment. The x axis shows the ratio between the solution concentration and the sorbed concentration and the y axis shows the solution concentration. Linear regression lines were made for each plot, and R^2 values are indicated for each plot

All plots have high R^2 values. Plotting the data on the same axes shows that the biochar and 50% mix treatment has overlap, as well as the 50% mix and the woodchips only treatment. This may be linked to different mechanisms of reaction, with biochar treatment having predominantly sorption and woodchips having predominantly redox reactions e.g. denitrification.

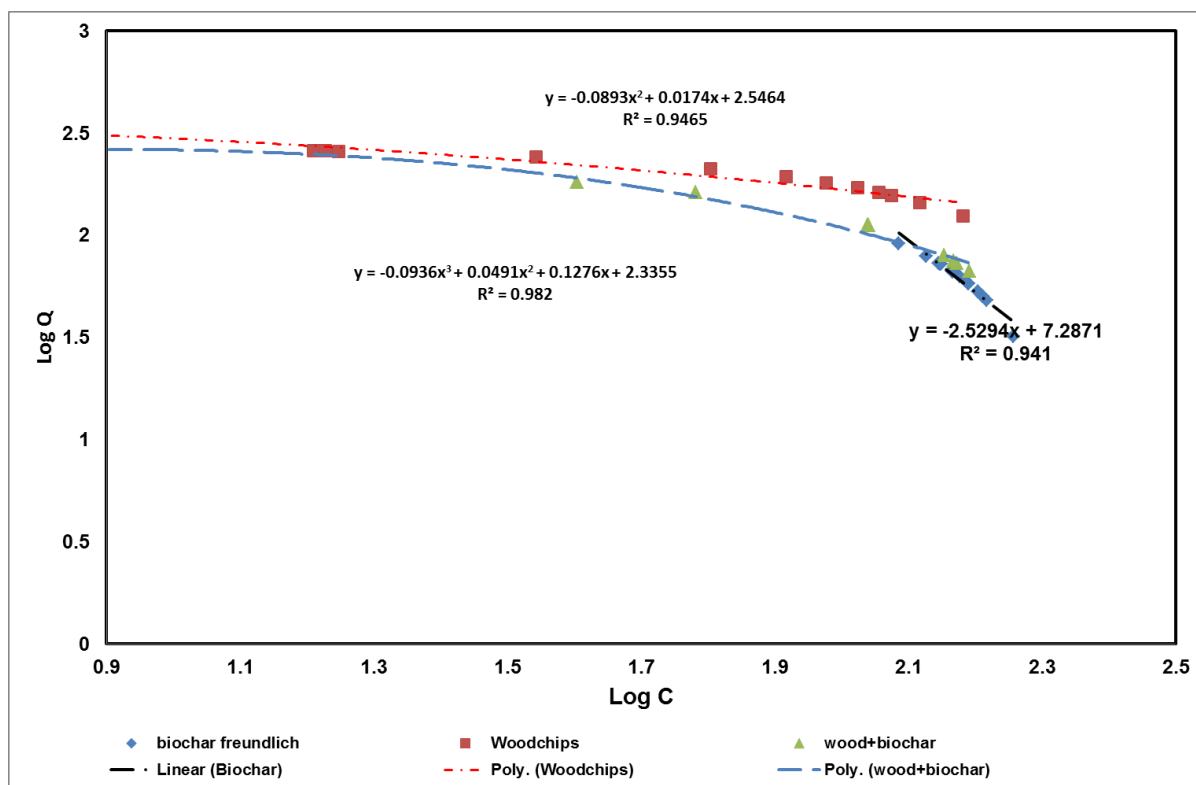


Figure 15: Freundlich plot of data collected during nitrate removal experiments. The x axis shows Log C (solution concentration) and the y axis shows Log Q (sorbed concentration). Linear regression curves, their equations and R^2 values are also shown.

Similarly to the Langmuir plot, the woodchip and biochar mix treatment plots overlap with both the plots of the woodchips only and biochar only plots. This could be linked to the fact that it possesses properties of both with respect to sorption and reaction mechanism. Due to the fact that data from time series experiments were merely fitted to the Langmuir and Freundlich relationships, these plots cannot be used to establish sorption coefficients, but rather indicate the type of sorption processes and the difference in processes for the different treatments. A plot using data from Israel (2007), where different carbon to nitrogen ratios were used follows Figure 16, and data that could be used to plot a sorption isotherm. This shows that larger C: N ratios lead to a greater reduction in nitrate concentration (Figure 16). The experiment used

various C: N ratios, the plot shows the removal at each ratio using initial concentration (C_o) and final concentration (C_e).

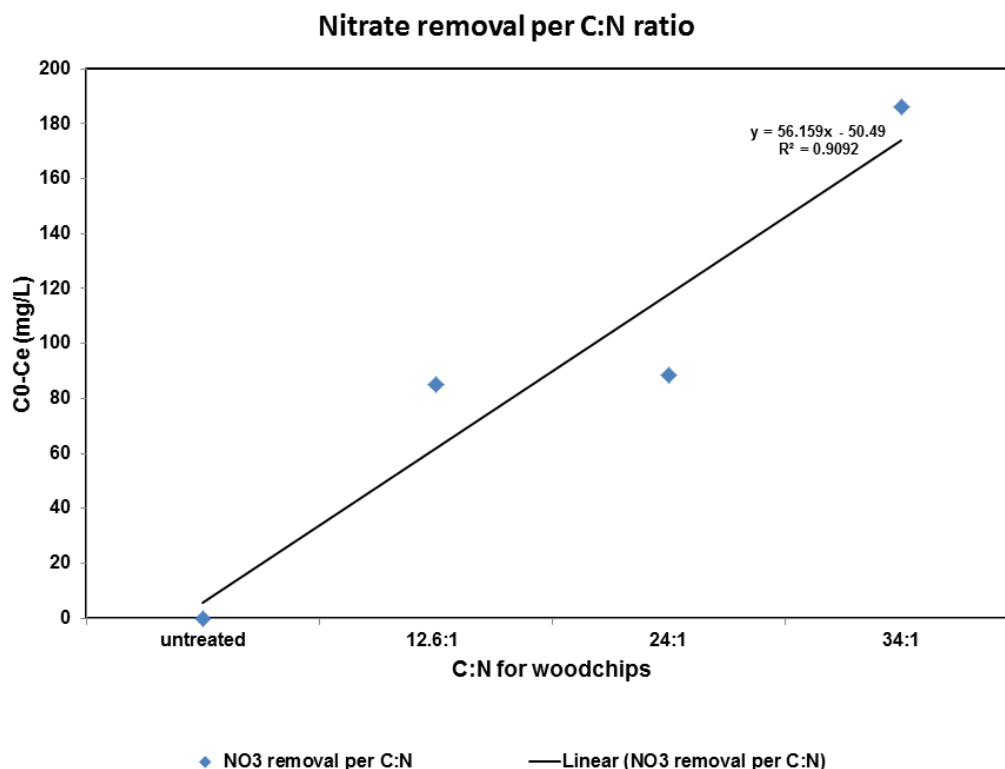


Figure 16: Nitrate removal per carbon to nitrogen ratio as used in Israel, (2007).

Figure 16 shows that greater C: N ratio removes a larger amount of nitrate from solution. Some supporting evidence to the difference in mechanisms by which nitrate is removed stems from other species analysed for during the experiment. Equation 1 in the background section shows that HCO_3^- is produced during the denitrification reaction where nitrate acts as an electron acceptor for organic carbon. Figure 17 shows a plot of Alkalinity for the three treatments for the last period of the experiment.

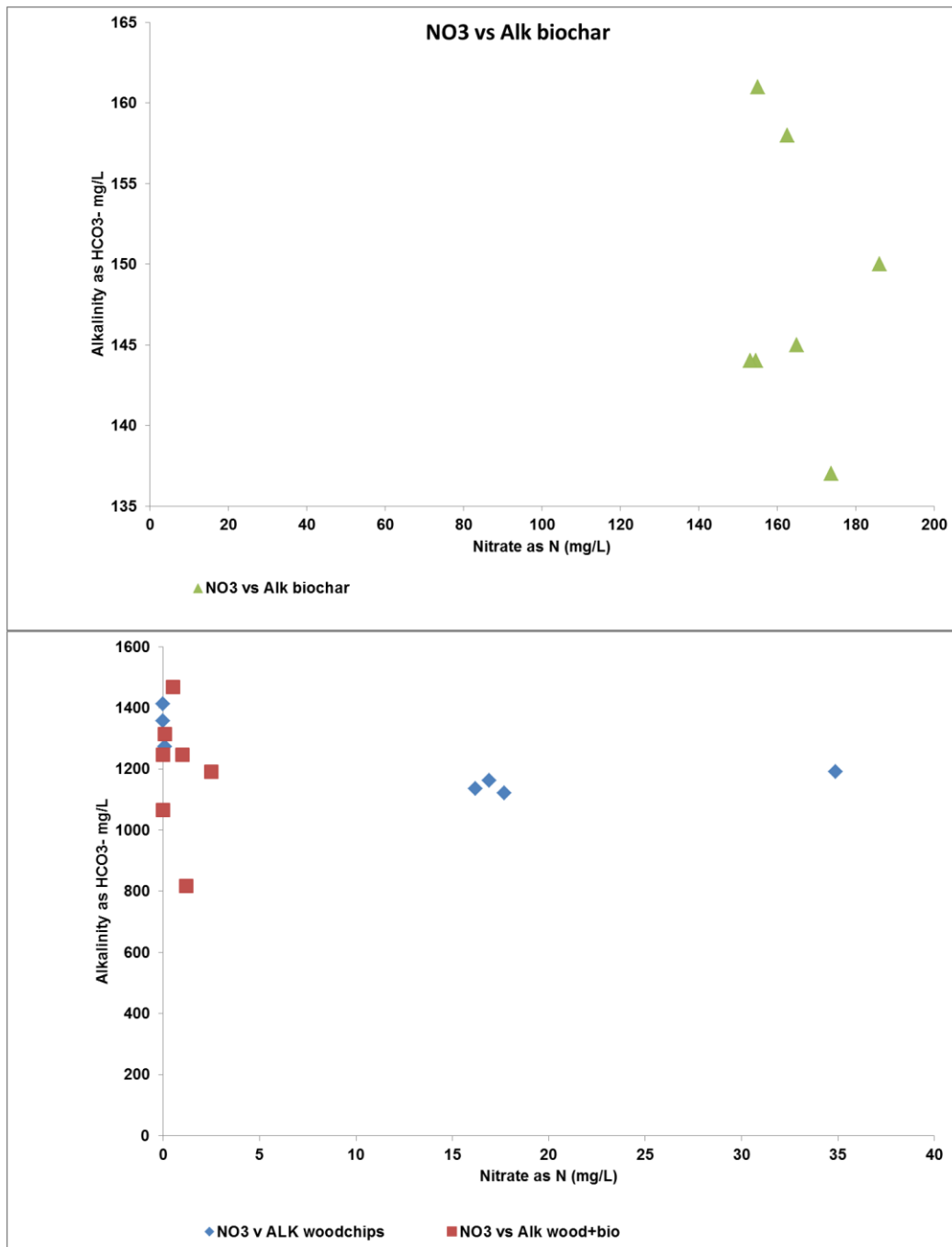


Figure 17: Alkalinity for the 3 treatments during the nitrate removal experiment. The x-axis shows nitrate as nitrogen concentration and the y-axis shows the alkalinity

Data for Figure 17 were obtained during the last part of the experiment, this due to insufficient sample volume for analysis during earlier stages. It shows that alkalinity is produced in the woodchip only and 50% woodchip and biochar mix columns, but not in the biochar only treatment. The alkalinity levels remain much lower in the

biochar treatment; small changes noted are due to the limited nitrate concentration changes. This shows that the removal of nitrate from biochar only treatment is most likely a physical sorption reaction or incomplete denitrification, while that in the woodchip and mixture may be a combination of sorption and predominantly denitrification. More supporting evidence of redox processes is shown in the sulphate concentrations during the latter part of the experiment when saturation periods exceed the required residence time for total nitrate removal. Figure 18 shows the sulphate vs. nitrate concentrations for the experiment.

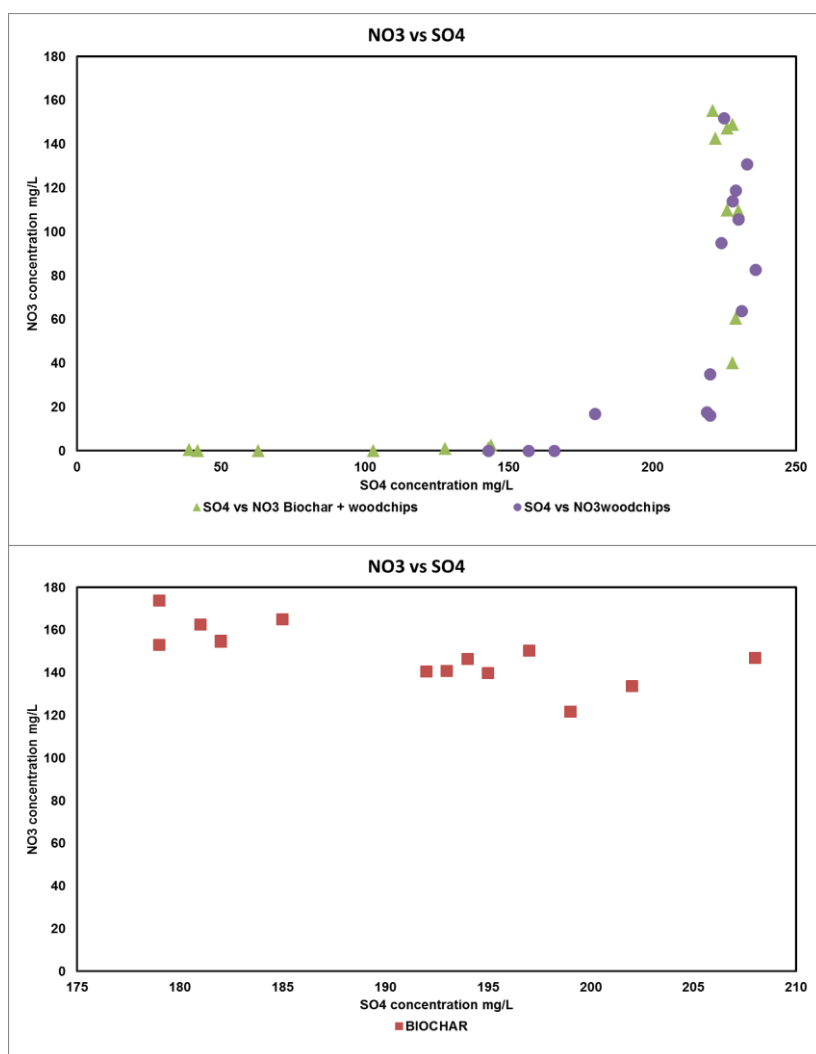


Figure 18: Plots of nitrate versus sulphate concentrations during the experiment. X axis shows the sulphate concentrations in mg/L, and the y-axis shows the nitrate concentrations in mg/L

Figure 18 shows that in the biochar treatment, the sulphate concentration shows limited change, while the woodchips and mixed treatments show a decrease in concentration of 100mg/L in the woodchip treatment with NO_3^- removal and even greater decrease in sulphate concentration in the mixed treatment. This confirms that the redox sequence for water logged soils as described in the background section is taking place in the woodchips and woodchip and biochar mixture, however, the process is somewhat enhanced in the mixed treatment due to a potentially larger surface area for the reaction. This could be due to the added sorption properties of the biochar in the treatment. The presence of the biochar in the 50/50 mixture can thus be said to enhance the efficiency of woodchips for nitrate removal. The total removal of all nitrate from woodchip and woodchip and biochar mixture agrees favourably to Hamona and Fustec (1991) who used similar hydraulic retention time of just under 1 day using ethanol and acetic acid (representative of immediately available carbon sources), influent concentrations of 100mg/L and achieved 100% removal within their first week of running column experiments. Robertson (2005) recommended 1-10 days residence time within which to get total nitrate removal. Robertson (2010) showed that woodchips used for 7 years had removal efficiency within 75% of woodchips used for 2 years in their field barriers. Although woodchips used for this experiments were 27 months (2 years and 3 months) and 35 months (2 years and 11 months), the removal efficiency remained high, showing that the woodchips still had hemicelluloses and possibly extractives available to affect quick availability of carbon. This is confirmed by the wood analyses Figure 6.

2.7 Conclusions

2.7.1 Removal efficiency

Nitrate removal efficiency from groundwater was greater in the woodchip and biochar mixed treatment during the second phase of the experiment when a longer period of saturation or residence time was used. During the first period, where residence time is 24 hours, the removal efficiency of woodchips only is greater. Biochar treatment removal efficiency was not comparable to the treatments containing woodchips. Within the first 10 days, 100% of nitrate was removed from both woodchips, and woodchip and biochar mixture. Biochar treatment did not achieve such success; however, the presence of nitrite shows that incomplete denitrification may have been occurring from the limited amount of organic carbon that was present in the biochar (Figure 61 in Appendix A). Removal rates were lower than other studies; e.g. Winlielista and Chang (2008); but was sufficient to effect total removal in a short period. First order rates of reaction for woodchips and woodchip and biochar mixture were an order of magnitude higher than that of biochar on its own. Biochar seems to have removed an amount of nitrate, as data shows the presence of nitrite which signifies incomplete denitrification. The biochar contained a smaller concentration of organic carbon in comparison to the woodchips and woodchip and biochar mixture that was insufficient to affect total removal of nitrate from the groundwater solution.

2.7.2 Reaction rates

Reaction rates, as compared to other experiments, were low, however, the results show that total removal of nitrate occurs within the 72 hour period when this is used as a residence time, while when using 24 hour residence time, nitrate removal to within acceptable drinking water standards (WHO, 1998 and DWA, 1998) will occur within 29.41 days for woodchips only treatment, and 17.69 days for woodchip and biochar mixed treatment, based on first order rate calculations. Previous work (Israel, 2007) shows that the reaction rate for the first few hours was 0 and owed this to the availability of dissolved organic carbon during the experiment. Hence, the rate of denitrification is carbon limited in systems where carbon has to be made available from a “solid” carbon source during the initial time of the reaction. While, where longer residence times or reaction “contact time” is used, the system can become nitrate limited. This supports the rate of denitrification being 2nd order as it depends not only on nitrate concentration, but also on availability of carbon for reaction.

2.7.3 Sorption

The data from the experiment was fitted to Langmuir and Freundlich equations. The plots show good fits for Langmuir plots, while Freundlich plots tend to show different processes for period 1 (when 24 hour residence time was used) and period 2 (where longer residence time was used). These plots also show separation of biochar and woodchip only treatments, and overlap between the biochar and woodchip mixed treatment with both the woodchips and biochar treatments separately. It was concluded that this is due to the different sorption properties of the respective treatments. Earlier data (Israel, 2007 and Israel 2009, Figure 16) shows that NO_3^-

removal increases with C: N ratio of woodchips. It was established that in fact the predominant reactions taking place in the woodchips and woodchip and biochar mixture is the typical redox sequence that one would see in water logged soils and anaerobic environments, while biochar, even though signs of incomplete denitrification are present with nitrite production, has predominantly physical sorption type reactions taking place. This also supports higher removal rates in the woodchips and biochar mixture with the redox and added sorptive capacity of the biochar.

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3 CHAPTER 3: HORIZONTAL FLOW THROUGH TANK EXPERIMENT³

3.1 Background

Batch and column experiments showed that various carbon sources are able to affect denitrification of high nitrate concentrations in groundwater (Israel, 2007, and chapter 2). This aided in understanding the rates of reaction, possible side reactions or by-products and for comparing the efficiency of different carbon sources under controlled conditions. Field experiments present a less controllable situation where oxygen levels, flow dynamics, and the effects of temperature and precipitation play a significant role in the resultant reaction rates and efficiency. A horizontal flow through test was done prior to field studies to try and closely approximate natural conditions and to observe the effects of some of the parameters that cannot be accounted for in column and batch experiments. Healy *et al.*, (2006) did a laboratory study examining various wood materials as carbon sources in horizontal flow filters. They used sawdust (*Pinus radiata*), sawdust and soil, sawdust and sand, and medium wood-chippings and sand in their experiment. They found that the wood-chippings and sand mixture performed best, yielding 97% nitrate removal at steady state conditions. Laboratory studies have been done to establish the effects of different flow rates for denitrification (Geben *et al.*, 2004 and Greenan *et al.*, 2009). Geben *et al.*, (2004) showed that a shorter HRT of (12 hrs.) and hence faster flow rate was not beneficial for the biological NO₃ removal. Three days after starting the reactors at

³ Publications linked to this chapter:

Israel, S., Tredoux, G., Maherry, A., Engelbrecht, J.F.P., Wilsenacht, J., Germanis, J., Jovanovic, N., (2012) Nitrate Removal for groundwater supply to rural communities, WRC Report No. K5/1848

a HRT of 12hrs, the denitrification process ceased in both reactors (Greiben *et al.*, 2004). Their result is based on the fact that denitrifying bacteria as well as carbon source (COD or DOC) were washed out at a faster feed/flow rate. Greenan *et al.*, (2009) did tests using mean flow rates of 2.9, 6.6, 8.9 and 13.6 cm. d⁻¹. They achieved 100% nitrate removal with 2.9 cm. d⁻¹ flow rates, 64% removal at 6.6 cm. d⁻¹, 52% removal at 8.9 cm. d⁻¹ and 30% removal at 13.6 cm. d⁻¹. Their findings agree with that of Greiben *et al.*, (2004) that denitrification will occur at higher flow rates, but efficiency may decline as insufficient concentrations of denitrifying bacteria and carbon source may result at higher flow rates.

The denitrification process is less favourable energetically than the reduction of oxygen. In a system that contains oxygen, nitrate and carbon, the oxygen will be the preferred electron acceptor. Denitrification will only occur once dissolved oxygen reaches a low threshold level. Rivett *et al.*, (2008) denitrification will probably occur at dissolved oxygen concentration levels of below 2 or 1mgO₂/L. A lead time for microbial populations to adapt to new or different conditions e.g. additional carbon source or high nitrate concentration can be expected in most laboratory and field experiments. In certain environments, denitrifying enzymes or bacteria are readily available and affect denitrification as soon as oxygen is consumed, while in others, populations may synthesise the required enzymes for denitrification. Dissolved oxygen in groundwater or influent water allows aerobes to out-compete denitrifiers. Initially poor nitrate removal in work by Healy *et al.*, (2006) was attributed to high dissolved oxygen in the system. The sections that follow describe the method, monitoring and results of a flow through tank experiment.

3.2 Methodology

A laboratory experiment using a 2200 mm x 350 mm x 350 mm tank (column) for denitrifying high nitrate groundwater was run for 3 months. The tank contained seven ports which stretched along the entire tank like observation boreholes and used either for sampling or injecting during the experiment. This tank was used for its versatility and possibility of sampling at any point along the flow path. Figure 19 below shows the scenario for the laboratory set up, linked to its representation in the field setting.

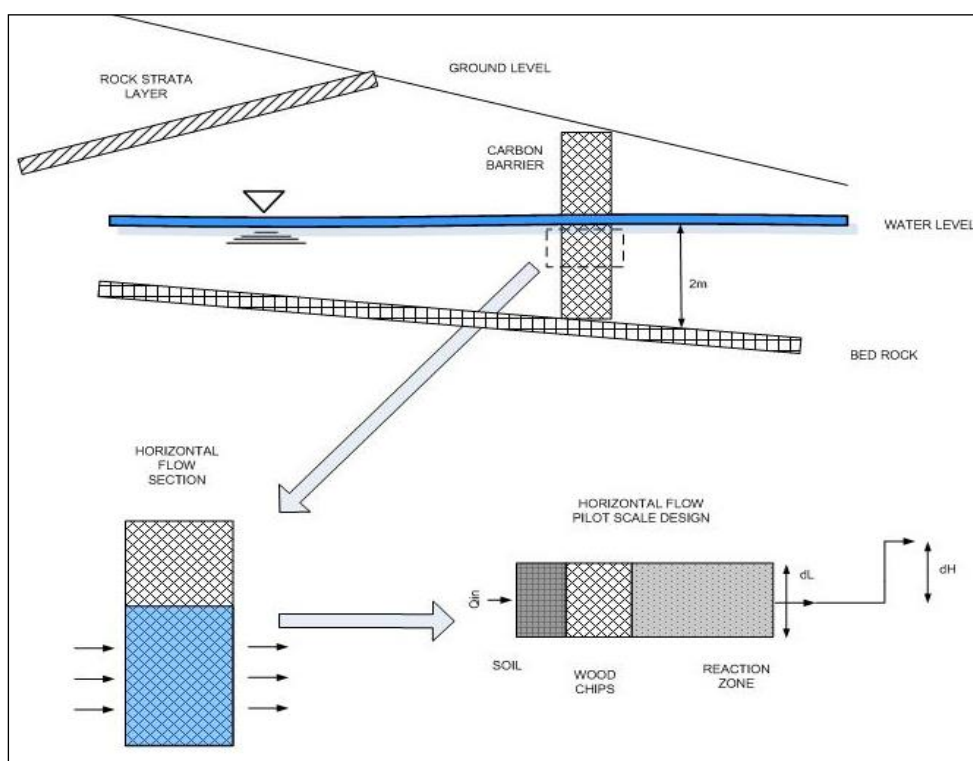


Figure 19: Scenario for laboratory tank set up, upper section of the figure represents the subsurface setting, the bottom left represents a zoomed in version of the blocked area which includes the aquifer material and carbon barrier, the bottom right represents the tank with flow.

The sampling ports (sampling pipes in Figure 20) were at 300 mm (horizontal), 500 mm (vertical), 700 mm (horizontal), 1000 mm (vertical), 1200 mm (horizontal),

1500 mm (vertical), and 1700 mm (horizontal) from the inlet of the tank. Hence the reactions could be studied over the total length of the column if desired. The tank represented an unconfined primary aquifer. Initial pH, EC, alkalinity, temperature and TDS were kept as close as possible to field conditions at the Somerset West site where the samples were collected. Monitoring included nitrogen species (NO_2^- , NO_3^-), pH, EC, Eh, DOC (dissolved organic carbon), and DO (dissolved oxygen). No microbial species were monitored. Sampling pipes (Figure 20) enabled sampling all along the tank at any point in time to track the progress of denitrification in the tank. Water was added through a thin transparent tube running from a barrel placed about 2 m above the tank to ensure gravity flow; the flow rate was regulated at the barrel to about 27 ml/minute equivalent to 4.5×10^{-3} L/sec. The influent water quality appears in Table 11.

Table 11: Influent water quality from BH 6 at the Somerset West site

Borehole	X	Y	Sample_Date	SO_4^{2-}	NO_3^-	$\text{NO}_3^- \text{-N}$	NH_4^+	$\text{NH}_4^+ \text{-N}$	EC	pH	PO_4^-	
BH6	18.065	34.09	2010/09/03	285	1230	278.28	160	124.4	360	6.8	0.1	
Borehole	X	Y	Sample_Date	Alkalinity	Na^+	Mg^{2+}	Ca^{2+}	K^+	Cu	Zn	Fe	Mn
BH6	18.065	34.09	2010/09/03	681	64	27.7	442	5.7	0.01	0.39	0	1.91

The tank was initially saturated with tap water to test the flow and the structure for leaking. The water from the influent tank was then added to the already saturated tank at a constant rate of 4.5×10^{-3} L/sec for the 90 day period.

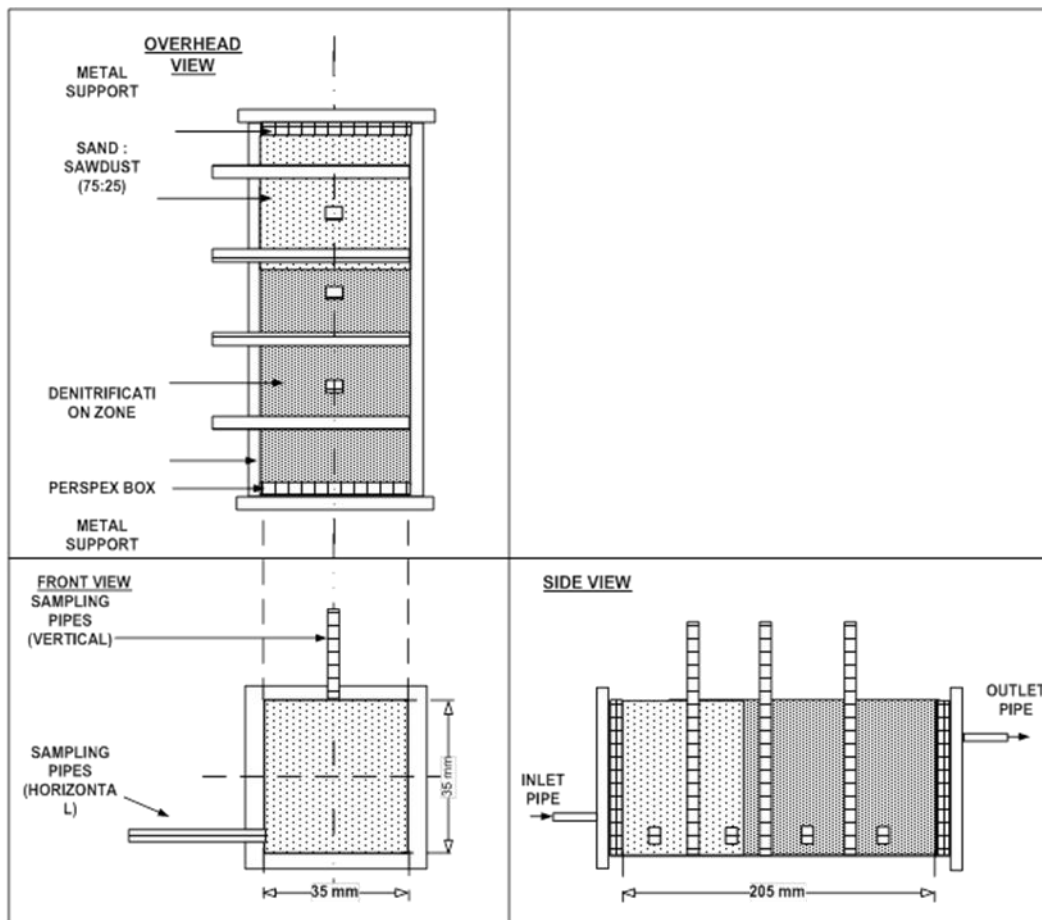


Figure 20: Tank showing the position of sampling or injecting ports (overhead view could also be “plan” view).

This laboratory scale denitrification served as a pre-cursor to field scale testing. Monitoring and sampling was done at regular intervals of 3-5 days for the duration of the experiment. The duration of the experiment was 90 days. The experiment took place from September 2009 up to and including December 2009. Samples were taken from the 4th horizontal sampling pipe from the inlet (1700mm). The carbon source selected for the experiment was sawdust, based on positive results achieved in previous laboratory studies performed, Israel (2007).

3.3 Results and discussion

Results of a three month experiment performed using an average flow rate of 27 ml/min is shown in the following section. Figure 21 shows the nitrate behaviour during the tank experiment.

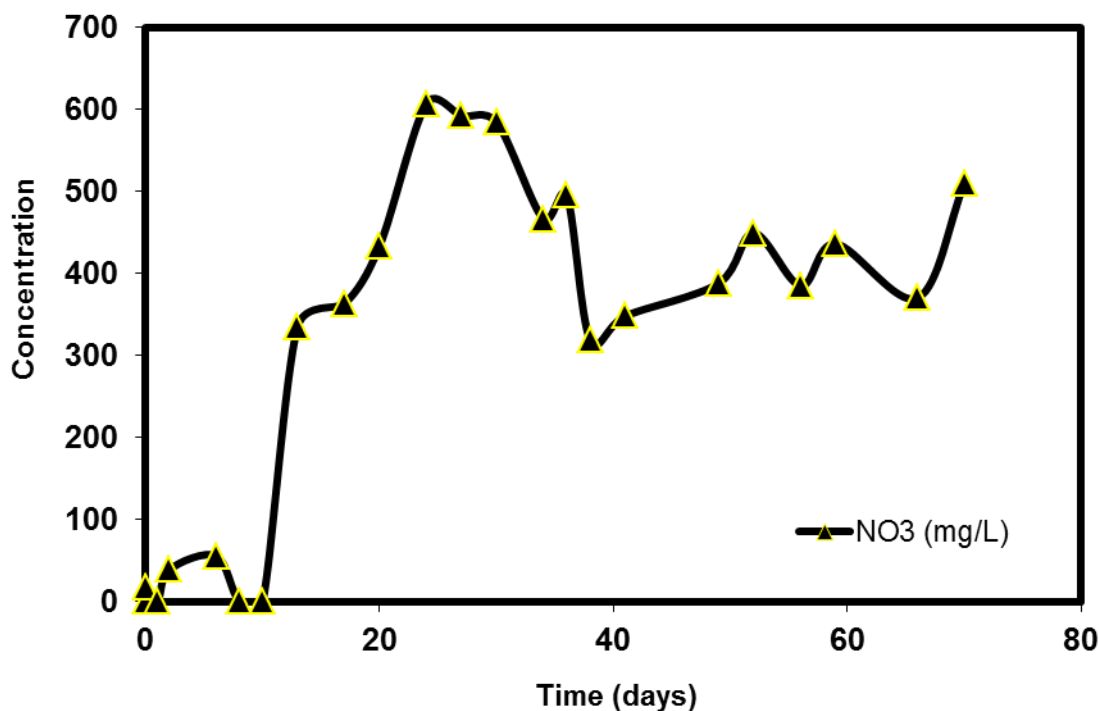


Figure 21: Nitrate concentration changes with time within the tank measured at sampling pipe 4.

Nitrate concentration showed an initial decrease after 10 days (Figure 21), this seems to be when nitrate may have been limiting. Considering the flow rate, as well as the fact that the tank had been saturated with tap water prior to the influent water being added, a small concentration of nitrate could possibly be denitrified in a short period of time as carbon may have been readily available for reaction. This was followed by an increase in nitrate level to a peak concentration of 607 mg/L as NO₃⁻ on day 24 (half the inlet water's concentration) of the experiment on the 16 October

2009, followed by a reduction to 319 mg/L as NO_3^- (a quarter of the inlet concentration) on day 38 of the experiment. Subsequent increases are either as a result of an increase in dissolved oxygen in the tank or from mixing of high nitrate influent water and tap water used to saturate the tank during the testing period. Figure 22 shows the dissolved oxygen behaviour for the duration of the experiment, while Figure 23 shows the nitrite behaviour.

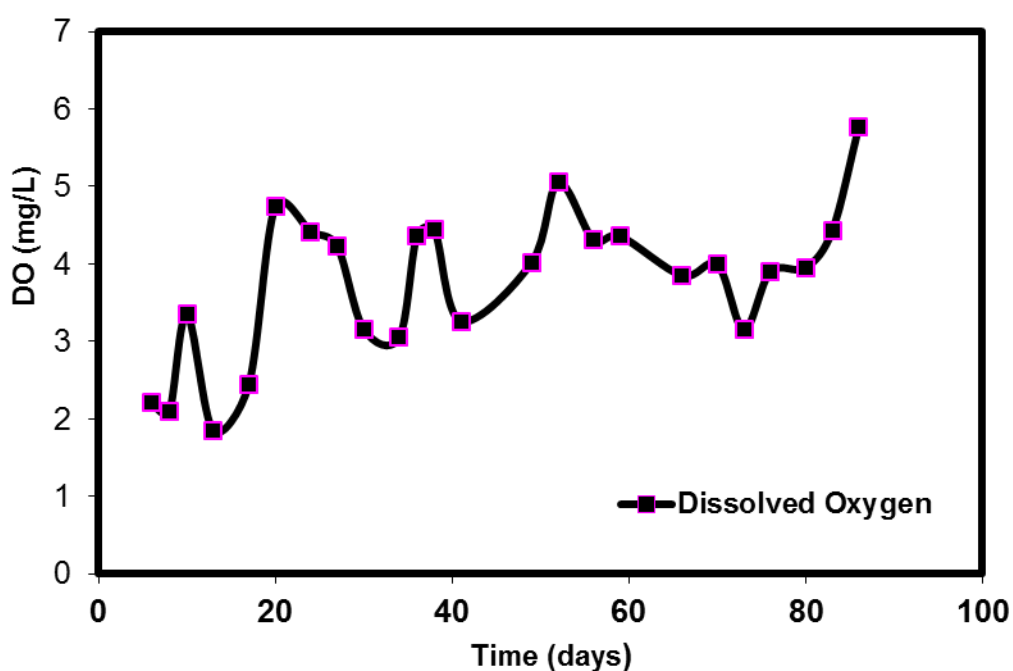


Figure 22: Dissolved oxygen measured with a hand held field meter for the duration of the experiment.

Fluctuation in the dissolved oxygen shows that the tank was not air tight. This would negatively impact denitrification. This compares favourably to results from work by Healy *et al.* (2006), where an initial low level of denitrification occurred and it was owed to the presence of oxygen in their experiment.

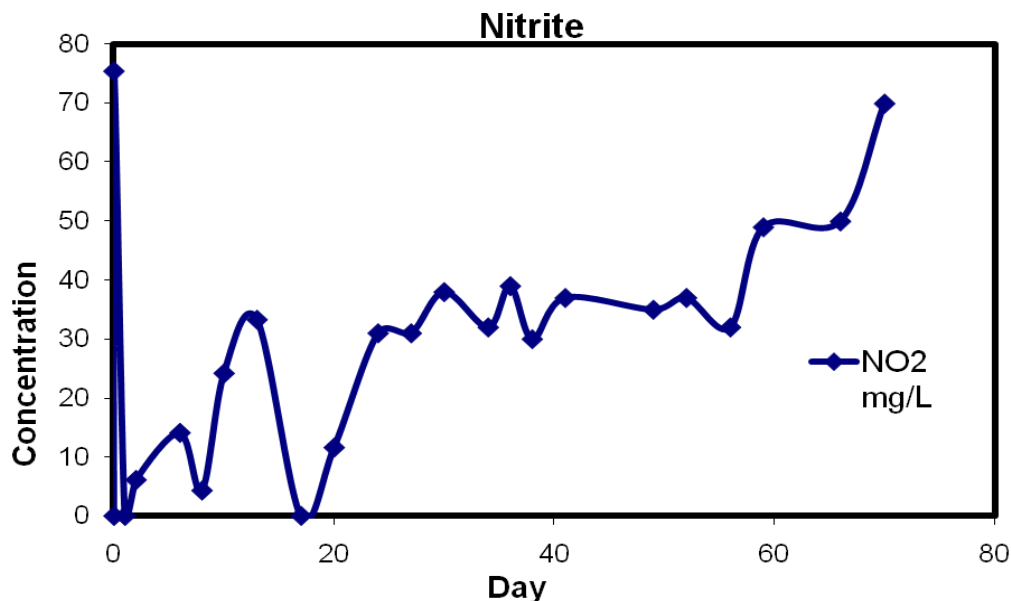


Figure 23: Nitrite concentration with time in the tank, measured at horizontal sampling pipe 4.

Nitrite is primarily formed as an intermediate during denitrification (Figure 23); it is hence an indication of incomplete reaction at a specific point in time. It was found in work by Robertson *et al.* (2000) and Israel (2007), that nitrite was detected as an intermediate to denitrification, a subsequent decrease and total denitrification occurred. This was not the case in this experiment as the influent dissolved oxygen levels increased with time to above the maximum of 2 mg/L referred to by Rivett *et al.* (2008) at which denitrification will still take place. The dissolved organic carbon content (Figure 24) shows an overall decline with time, with some intermittent increases during the experiment. A peak in DOC occurs after about 10 days of the tank experiment. This coincides with total removal of the nitrate that was present in the tank after the first few days of inlet water entering the tank. This type of occurrence has been reported by Robertson (2010) and found in the laboratory column tests (Chapter 2, Figure 13).

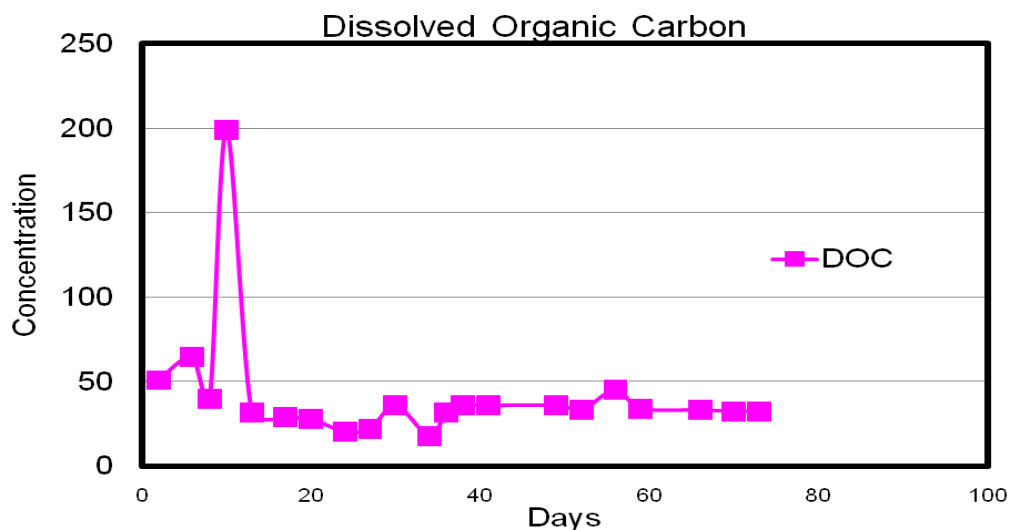


Figure 24: Dissolved organic carbon concentration with time for the tank measured at sampling pipe 4.

Figure 25 shows the alkalinity and EC behaviour for the duration of the experiment.

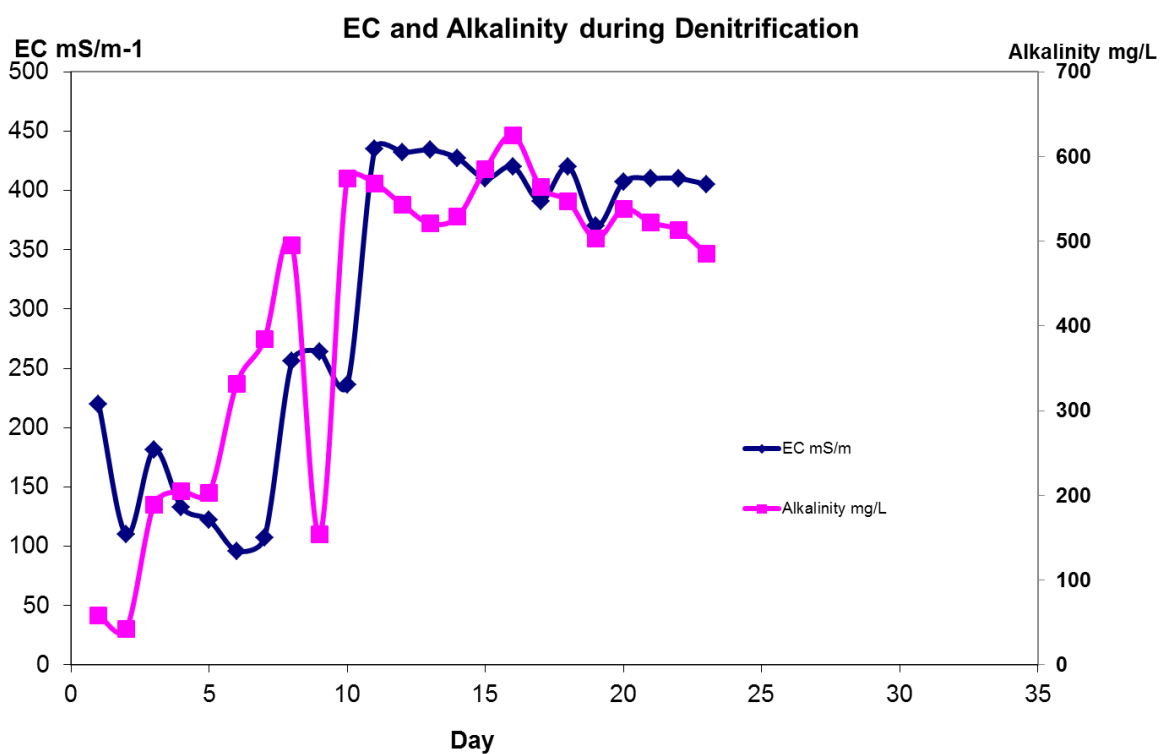


Figure 25: Alkalinity and Electrical conductivity during the flow through tank experiment.

Alkalinity is known to increase during denitrification as alkalinity is produced by bacterial activity; here Figure 25 shows a decrease in the alkalinity before the 20th day of the experiment. This could be as a result of precipitation or cation exchange of Ca^{2+} or Mg^{2+} containing minerals.

The barrier thickness of 630 mm used was sufficient to halve the concentration of NO_3 from a peak of 600 mg/L (half the influent concentration) to 319 mg/L (quarter of the influent water concentration) during the experiment. This indicates that the system was carbon limited. The experiment confirmed that denitrification can occur when dissolved oxygen concentration is low. Increases in dissolved oxygen coincide with increases in nitrate and sulphate concentrations. Nitrification may have been occurring in the tank. An overall increase in alkalinity indicates biological activity as well as high CO_3^{2-} mineral content. Nitrite production during the experiment indicates a period of incomplete denitrification which can be expected with a carbon loading insufficient for the nitrate concentration used. Calculations show that 8834 g of sawdust was required to reduce the nitrate concentration to within the 20 mg/L guideline value in the source water. This equates to a barrier of about three times the thickness of the barrier used during this experiment. Table 12 shows the actual calculation retrospectively calculated compared to the actual sawdust mass that was used.

The gradual increase in nitrate during the first period of the experiment can be due to nitrate that was attached to soil being released into solution or displaced off soil particles or nitrification taking place, similar to what would occur during infiltration of

rainfall where nitrate stores are present in soils (Stadler, 2005 and Stadler *et al.*, 2004 and Sungita and Nakane, 2007). High nitrate water constantly flowing into the tank may also be diluted and denitrified to an extent before reaching sampling tap no. 4.

Table 12: Calculation of actual requirement for tank experiment using model developed by Israel *et al.*, (2012).

Experimental set-up	Actual- retrospectively	
Area	0.123	0.123 m ²
Flow velocity	0.306	0.306 m/d
Flow rate	0.037	0.037 m ³ /d
Inlet Nitrate	278	100 gN/m ³
Eff Nitrate	20	20 gN/m ³
N removal	258	80 gN/m ³
N removal rate	9.660	2.995 gN/d
N removal rate	0.345	0.107 molN ₂ /d
Nitrite removal rate	0.690	0.214 molN/d
Acetate (Nitrit) removal rate	0.517	0.160 mol Ac/d
Nitrate removal rate	0.690	0.214 molN/d
Acetate (Nitrat) removal rate	0.345	0.107 mol Ac/d
Acetate (tot) removal rate	0.862	0.267 mol Ac/d
Sawdust requirement	0.577	0.179 mol sawdust/d
Operation period	90	90 d
Sawdust load	8834	2739 g sawdust

Another plausible explanation is the mixing of tap water used to test the tank with extremely high nitrate concentration from the industrial site (the influent water). The total removal of nitrate within the first ten days can be explained by readily available carbon being present before the first nitrate water entered the tank due to saturation of the tank during flow testing. Influent water of high nitrate concentration was constantly entering the tank, hence mixing with the material and water in the tank. This could explain the increased nitrate concentration after the initial carbon was consumed. Another possible explanation could be nitrification as oxygen was entering the system, at high oxygen concentrations denitrification would be inhibited. Nitrite concentration increased throughout the experiment. Nitrite is an intermediate of denitrification; hence incomplete denitrification was taking place. The spike in

DOC levels coincides with the period when the nitrate concentration was totally reduced in the initial period of the experiment.

3.4 Conclusions

The following conclusions were drawn for the laboratory flow through experiment:

- Denitrification took place successfully where industrial levels of nitrate of 1123 mg/L NO_3^- in the influent water was reduced to 600 mg/L NO_3^- and further to 317 mg/L NO_3^- within 14 days [day 24 to day 38 of the experiment] by the time it reached the 4th horizontal sampling tap. Influent water (1123 mg/L NO_3^-) was constantly added to the tank at 4.5×10^{-3} L/sec.
- Since the system was not air tight, oxygen entered the system and ranged from 1.84 mg/L initially to about 6 mg/L dissolved oxygen toward the last part of the experiment. This inhibited denitrification.
- Alkalinity showed an overall increasing trend.
- Initial denitrification took place during the first 10 days to remove the small concentration (55 mg/L) of nitrate from the influent water that initially passed through the barrier.
- Dissolved organic carbon shows an intermittent increase in concentration, which coincide with periods preceding reduction of nitrate concentration.
- After day 60 of the experimental no change in the DOC concentration is noted. This implies that either a steady state was established (carbon that becomes available = carbon consumed), or that no further DOC was made available from the sawdust.

3.5 Recommendations

Recommendation with respect to laboratory studies include ensuring the tank or column being used is air tight, or accounting for air entering the system if it occurs.

It is important to ensure that the carbon source concentration is at least sufficient to denitrify the maximum nitrate concentration that is present over the required experimental time.

Frequent monitoring is recommended as reaction rates may be rapid when carbon is already available for reaction.

3.6 References

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4 CHAPTER 4: FIELD IMPLEMENTATION STUDY⁴

4.1 Background

At the initial stages 2 sites were suggested for testing the field method; one site in the Milnerton,(Western Cape, South Africa) area which had an unconfined, primary aquifer setting and the other in Somerset West (Western Cape, South Africa) close to the coast which is also unconfined and a mixture of sand, clay and calcrete. The Milnerton site was ruled out as development was due to occur at the site within the period of testing.

The Somerset West site was a 3.6 ha area situated on an area that was previously the location of an ammonium nitrate warehouse. During 1995 a site investigation revealed that seepage of ammonium nitrate through the floor of the Ammonium Nitrate Warehouse occurred. The presence of open or damaged bags of calcium chloride was exposed to wind, rain, and atmospheric conditions. Installation of three groundwater monitoring wells (ANBH1, ANBH2, and ANBH3) in the immediate vicinity of the Ammonium Nitrate Warehouse at depths of 7.9 mbgl, 4.5 mbgl and 5.8 mbgl resulted. Rest water levels in these wells were reported at depths of 2.0-2.55 mbgl. Additional monitoring boreholes (ANBH4, ANBH5, ANBH6, ANBH7, ANBH9,

⁴ Publications related to this chapter:

Israel, S., Rozanov, A. , Tredoux, G., and Jovanovic, N.,2011. In situ nitrate removal from groundwater using freely available carbon material at an industrially polluted site, Groundwater Division International Conference, Durban South Africa, 19-21 September 2011

Israel, S., Rozanov, A., Tredoux, G., and Jovanovic, N.,2013. In situ nitrate removal from groundwater using freely available carbon material at an industrially polluted site, Chapter 15, IN:Assessing and managing groundwater in different environments, IAH selected papers, Eds. J. Cobbing, S. Adams, I Dennis, and K. Riemann, Taylor and Francis Group, London, UK

and ANBH10) were drilled to monitor the possible plume migration from the source area. Nitrate levels fluctuate seasonally at the site, with high concentrations originating from the area where the ammonium nitrate warehouse was previously located. During 2006, a consulting firm called SRK removed the top 1.5m of soil from the area to eliminate a large quantity of ammonium nitrate that was stored in the soil. They reported elevated levels of nitrate and ammonium down to 2m. This left residual ammonium nitrate in the soil profile which could reach the groundwater. On investigation of the site, dissolved carbon concentrations were low and deemed insufficient to affect natural denitrification in the groundwater.

4.2 Study site location

The site used for field testing is situated in the Somerset West area of the Western Cape Province (Figure 26). Historical reports for the site and available data were consulted. The surface elevation is approximately 6.5 m amsl. A water body (Paardevlei, Figure 26) is situated adjacent to the site and covers an area of approximately 50 ha (SRK, 2006). Natural drainage channels to the lake have been canalised away from it and over the years the walls have been raised.

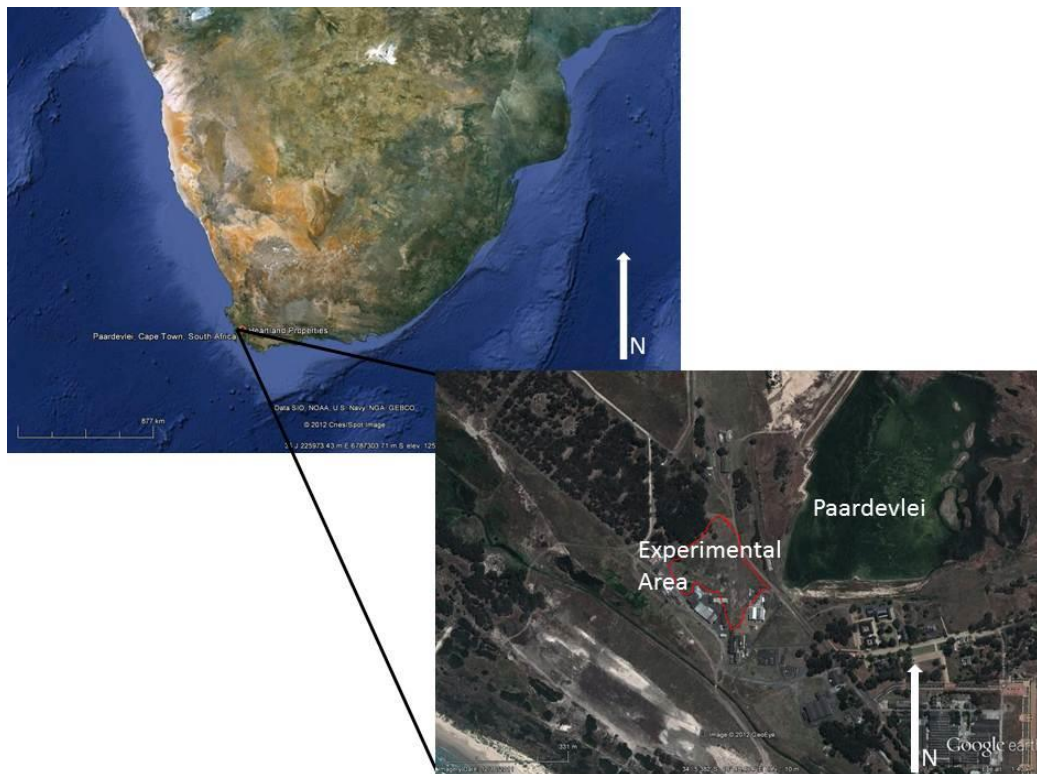


Figure 26: Location of the study site in Somerset West, Western Cape, South Africa

4.2.1 Site geology

The site is situated on coastal plain sand underlain by the Malmesbury Shale formation. Malmesbury rocks are comprised of dark green-grey shale, hornfels and quartzite and they are generally well fractured. Fractures, particularly in the vadose zone, are generally filled with very stiff, dark green-grey clay. The site is located in the interface zone between the Coastal Plain and Coastal Dune Belt. Quaternary sediments of the Langebaan geology occur at the site. The presence of calcrete boulders as well as coarse sand with white clays was noted during excavation at the site.

4.2.2 Climate

Somerset West normally receives about 568 mm of rain per year. It receives most of its rainfall during winter, it thus has a Mediterranean climate. It receives the lowest rainfall (10 mm) in February and the highest (96 mm) in June (SRK, 2006). The average midday temperatures for Somerset West range from 16.2°C in July to 26.1°C in February. The region is the coldest during July when the mercury drops to 7.2°C on average during the night. Figure 27 shows cumulative monthly rainfall figures recorded by Somerset West site from 2009 up to August 2013.

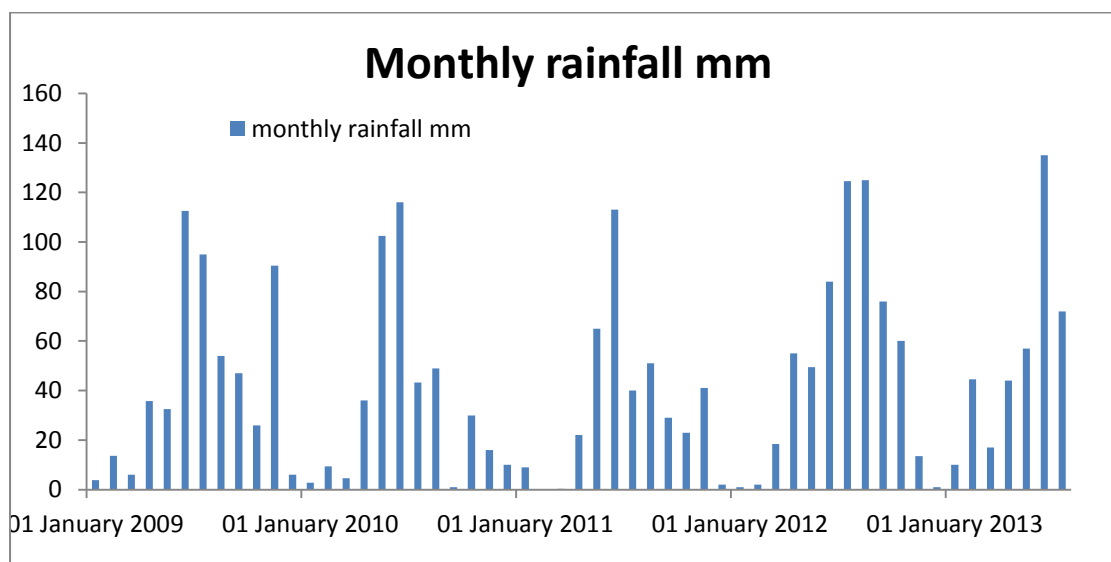


Figure 27: Cumulative monthly rainfall for the Somerset West site from 2009 up to August 2013, data from Somerset West site records.

Figure 27 shows that minimum and maximum rainfall experienced at the site since 2009 have increased, with highest rainfall occurring during June (100-140mm), and months having no rainfall e.g. January and February.

4.2.3 Land use and vegetation

The majority of the lowland area in Somerset West is heavily transformed by agriculture and urbanisation and there is minimal natural vegetation remaining but rather predominantly alien herbaceous vegetation (Holmes, 2002). The SOMERSET WEST SITE in particular have mainly bluegum (*Eucalyptus globulus*) trees as well as grasses across the site. A general soil profile (SRK, 2006) for the study site is presented in Table 13.

Table 13: Generalised soil profile for the Somerset West site during winter (July 2010) excavation

Strata	Depth (mbgl)	Description
Surface	0 – 0.3	Grassed surface dark grey to black soil
Transported/alluvium	0.3 – 0.6	Darker black soil, medium grained
Transported/alluvium	0.6 – 1.4	Water table depth encountered at 1.35mbgl, calcrete boulders occurring in brown medium grained soil
Transported/alluvium	1.4-3m	Moist – wet, cream clayey sand with fine-calcrete gravel concretion and coarse angular grained sand. Groundwater seepage encountered at this depth.

Sampling of groundwater using sampling method as specified by Weaver (2005) and soil samples were collected during excavation in the position where the tank was to be put in place. Water-level depth measurements were taken at the all boreholes surrounding the area selected for barrier emplacement at Somerset West site prior to installation of the treatment zone. Sampling and analyses of nitrate were carried out

to establish the distribution of nitrate concentrations across the area where the nitrate removal would be tested. Distances between points were measured and water-level data were used to construct contours of groundwater-level data and to determine groundwater-flow vectors, as recommended by Gavascar (1999).

Borehole locations, names and distances between boreholes and position of carbon source tank are shown in Figure 28.

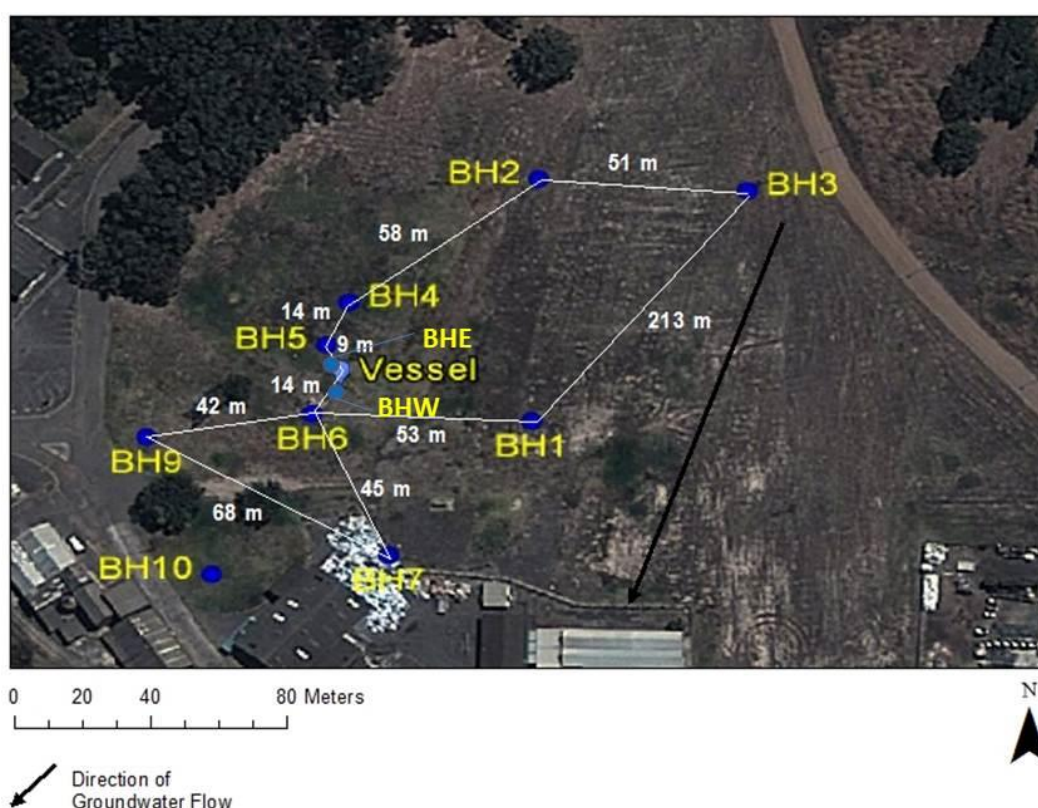


Figure 28: Location of boreholes and monitoring points on the site as well as the distances between points. General groundwater flow direction is shown by the arrow in the legend. It is based on water level contours for the site

Water-table elevation data were then interpolated and used to determine groundwater flow at the site based on groundwater-elevation gradients. Figure 29 shows the groundwater interpolated elevation map. Groundwater flow is from a high elevation toward a lower elevation.

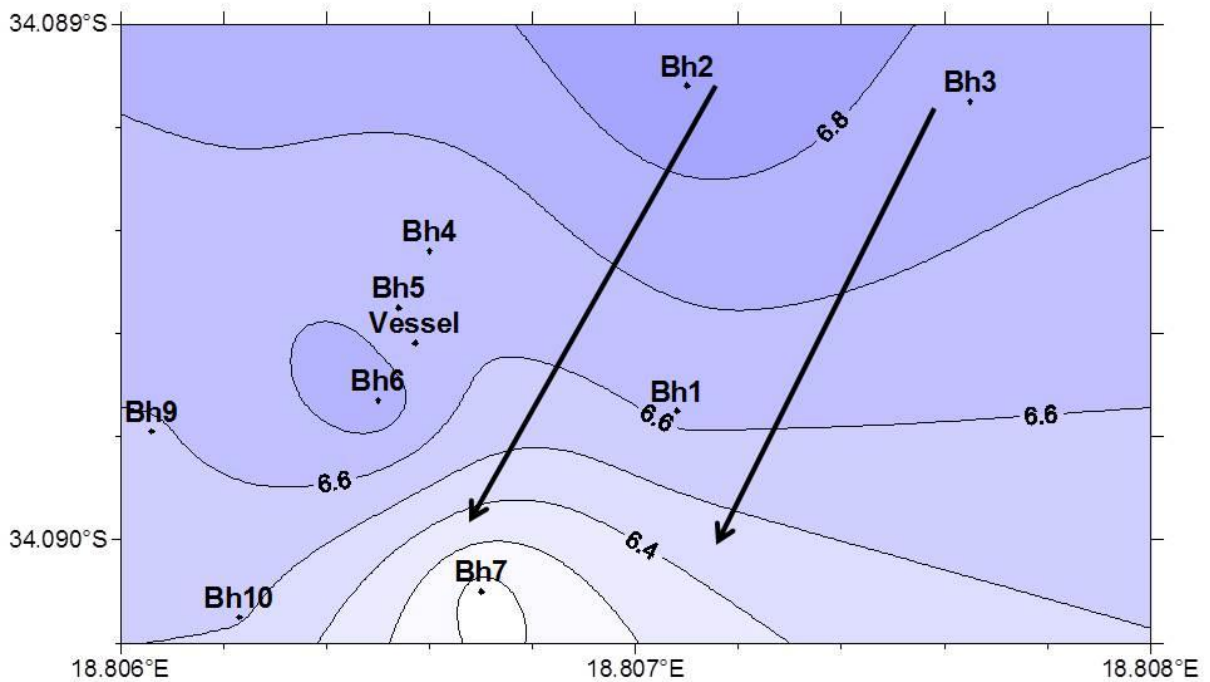


Figure 29: Groundwater table elevation contours for the site. Arrows show the general direction of groundwater flow

Figure 29 shows that flow occurs towards the coastal dune area just east of BH9, and measures were put in place to divert or channel flow away from the Paardevlei to the west. The carbon source tank was placed between BH5 and BH6 (labelled Vessel in Figure 28). Soil samples were collected during excavation. Figure 30 shows the results of soil analyses (also in Appendix B, Table 25, Table 26, Table 27, Table 28, and Table 29).

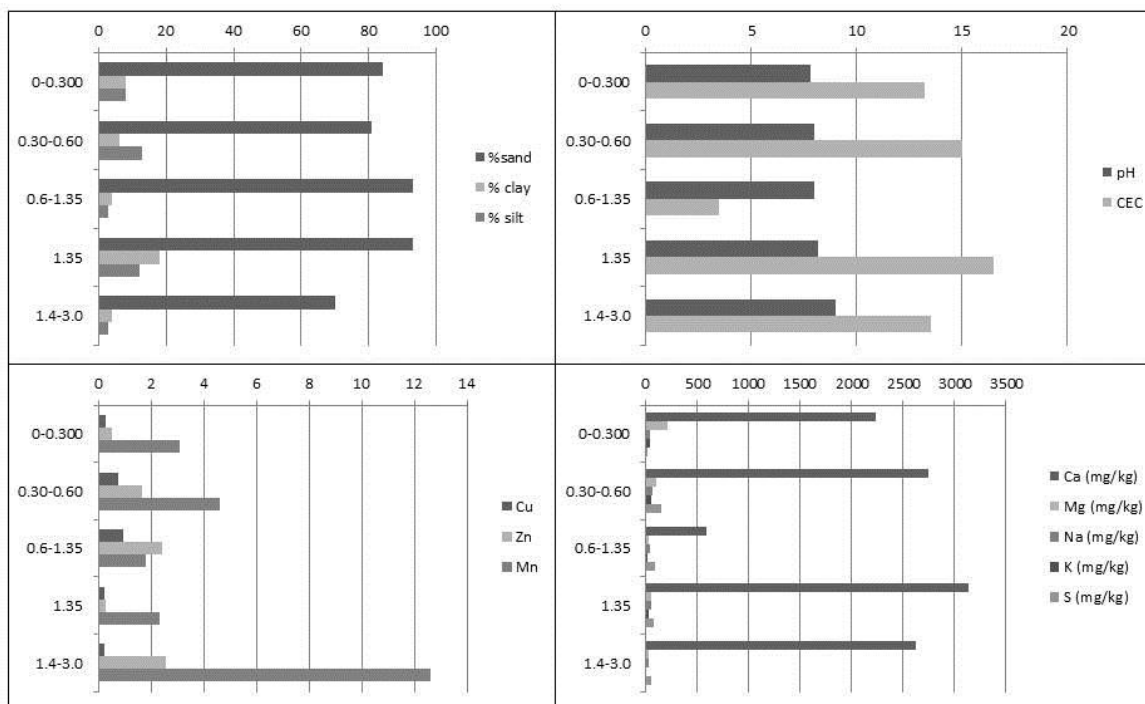


Figure 30: Soil data collected during the excavation for emplacement of the carbon source holding tank

The soil profile is composed of predominantly sand-sized particles, with the soil depth of 1.4m to 3m having the highest clay content of 10%. This relates to a higher cation exchange capacity for this depth as more charged surfaces are available in clay particles. The predominant soil texture of the aquifer was sandy and porosity is estimated to be about that of sand (20% to 35%) based on the particle sizes present.

Trace metals copper (Cu), zinc (Zn) and manganese (Mn) were analysed for as it is documented that the presence of trace metals can enhance denitrification rates at various concentrations (Labbé *et al.*, 2003). The groundwater level depth was at 1.35 m below surface at the area where excavating took place. It varies across the site as the elevations of points are slightly different. Results show that manganese is the dominant trace metal at most soil depths and it is particularly concentrated within the saturated zone below 1.35 m depth, while zinc is more concentrated just above the

water table. Manganese oxides are among the strongest naturally occurring oxidizing agents in the environment, having high sorptive capacities and participating in various redox reactions with both organic and inorganic compounds.

Exchangeable nutrients were analysed as an indication of availability in the soil environment. The results of the cations or exchangeable nutrients show that calcium is the dominant cation in the soil at all depths. The presence of calcareous boulders and calcrete nodules at some depths as well as the fact that the position of the excavation was at a contact between more clayey type geology and coastal calcareous sands supported the fact that calcium was the dominant cation at all soil depths. Sulphur is a redox sensitive species which may be affected by oxidation reduction processes and subsurface conditions. Figure 31 shows the percentage carbon along the soil profile. This was tested to evaluate the possible occurrence of natural denitrification and the available carbon in the subsurface.

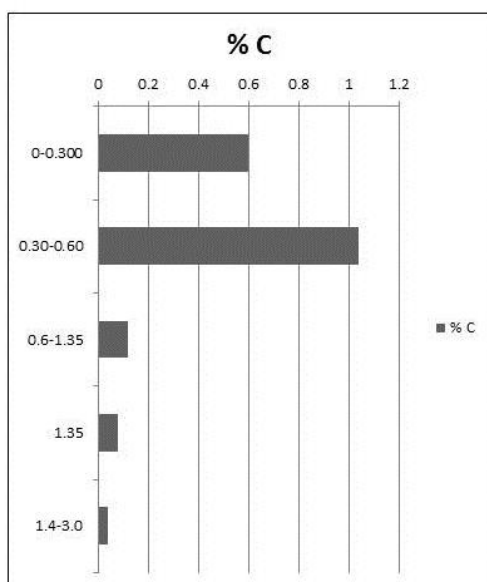


Figure 31: Percentage carbon along the profile dug during excavation

The percentage total organic carbon (TOC) results show that the maximum total organic carbon is just over 1% along the soil profile. This would result in a low likelihood for natural denitrification at the site, hence it was deemed necessary to amend the subsurface with a slowly degradable carbon source to enhance the natural process of denitrification. Historical reports for the site show that the area used for this experiment had been disturbed by removal of up to 1.5 and 2m of top soil to rid the site of historically spilled ammonium nitrate fertilizer material from the store that was previously at the location. Hence a formal new soil profiling was not done, other than that reported by the study team who did the excavating and data recording during excavation for the emplacement of the tank.

4.3 Methodology

4.3.1 Sampling and results prior to field implementation

Available data for the site was gathered prior to emplacing the barrier (Table 14). Water samples were collected at the site prior to selection of the area in which to place the tank. The results are displayed in Table 15.

Table 14: Available data for boreholes at the site

Borehole	BH4	BH5	BH6	BH7
Drilled depth	6 m	5.5 m	4.5 m	4.5 m
Rest WL	1.5 m	1.5 m	1.5 m	1.5 m
Winter WL	1.5mbgl	2.36 mbgl	2.6mbgl	2.4 mbgl
Summer WL	3.24 mbgl	3.47 mbgl	3.17 mbgl	No data available
BH diameter	63 mm	63 mm	63 mm	63 mm
Clay depth	0.5 m- 4 m	0.5 m-4 m	0.5 m-4.5 m	0.5 m-4.5 m
Sandy clay depth	4 m-6 m	4 m-5.5 m	Not penetrated	Not penetrated

Initial sampling of boreholes was completed during May 2010. Another sampling event took place during June and the results of these assessed. During June, a site visit followed to select a suitable location on the site to put in place a vessel to hold the carbon source amendment and increase denitrification within the groundwater system. Comparison of water levels as well as the site visit was used to select a most suitable area to emplace the treatment zone/ tank. Following further investigation by staff at the Somerset West site, it was found that some cables cross the site at the position selected for the tank. The position was thus shifted to prevent damages to cables or other infrastructure. Although not in the optimum position based on available data and site information, the tank was put in place about 2m east of its preferred point of insertion.

Table 15: Results from initial sample analyses from Somerset West site for June 2010

SAMPLE ID:	ANBH10. 1	ANBH10. 2	SOMERSET WEST SITE - BH 3	ANBH 1	ANBH 2	ANBH 5	ANBH 6	ANBH 7	ANBH 9
NH4 as N mg/L	3.7	3.0	<0.1	3.1	3.7	1.1	2.4	0.8	2.7
Alk as CaCO3 mg/L	466	466	47	290	56	320	330	295	344
NO3 +NO2 as N mg/L	29	23	38	346	180	177	326	167	348
DOC mg/L	3	4	6	9	6	9	5	3	7
EC mS/m (25°C)	119	117	151	435	190	235	365	245	475
pH (Lab) (20°C)	7.1	7.0	6.5	6.9	6.1	7.0	7.0	7.7	7
TDS (Calc) mg/L	762	749	966	2784	1216	1504	2336	1568	3040

Note that the boreholes in bold above were closest to the area where the tank was eventually put in place, hence concentrations in these ranges were used to determine / approximate the sawdust load that would be required to treat the nitrate present to within acceptable levels.

4.3.2 Barrier placement

The selected area was just about 2m from the originally desired point. Figure 32 shows the borehole positions.



Figure 32: Positions of boreholes (blue dots), and position of tank for treatment white dot)

Boreholes logs were obtained for drilled boreholes at the site. Borehole logs for BH5 and BH6 which are in close proximity to where the tank was put can be seen in Figure 33.

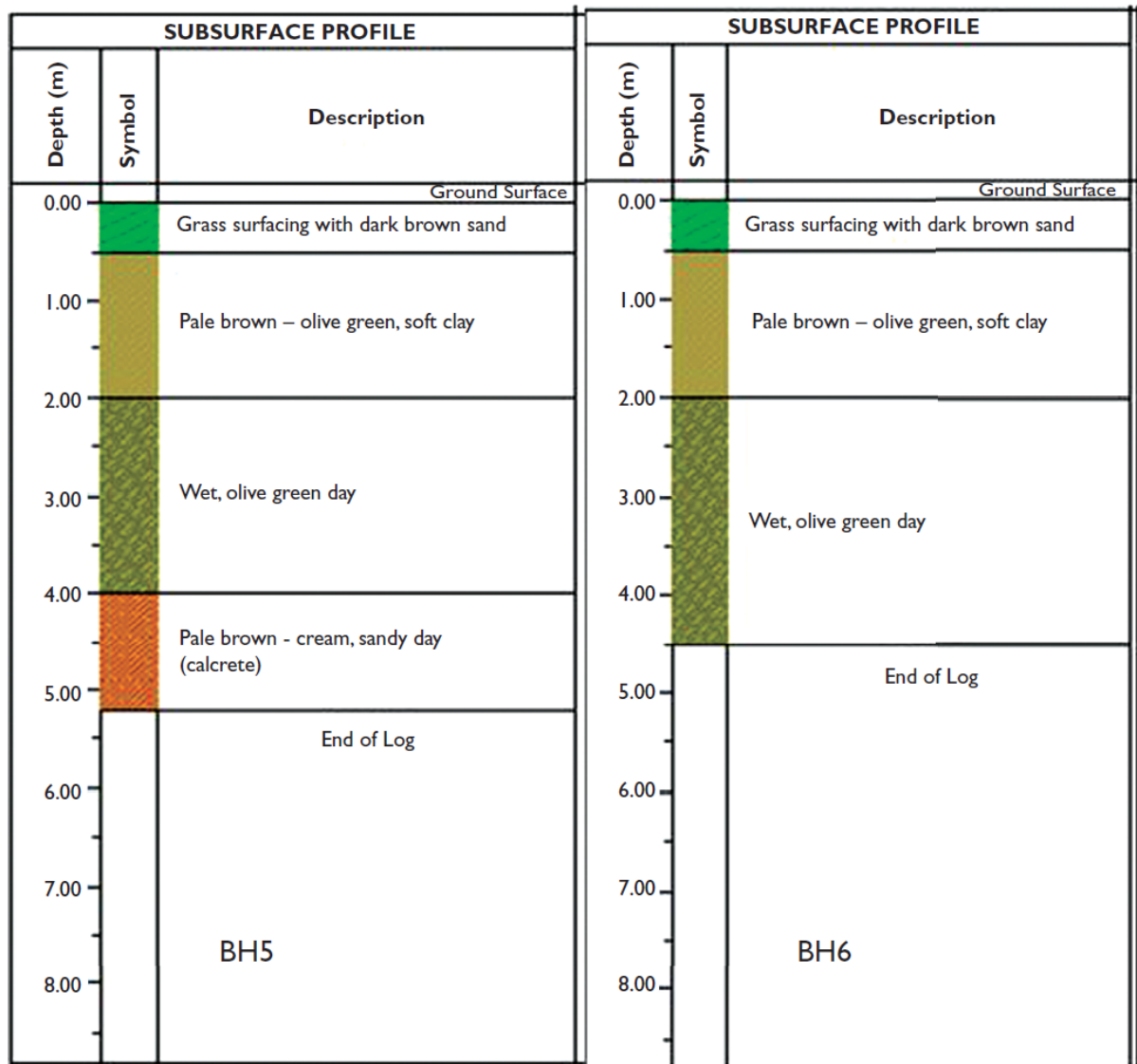


Figure 33: Borehole logs for boreholes 5 and 6 in close proximity to where the tank is located

An excavator was used for digging a large diameter excavation (Figure 34).



Figure 34: Excavator used for digging to below the water table.

The “reactor”/ tank with dimensions- 1,37m Height, 2.15m diameter used for the experiment was slotted for its entire circumference by marking and grinding through the 5mm thick plastic material. The top section was left open to allow for filling and occasional checking of filled material during the experiment. Figure 35 shows the tank being slitted prior to emplacement at the site.

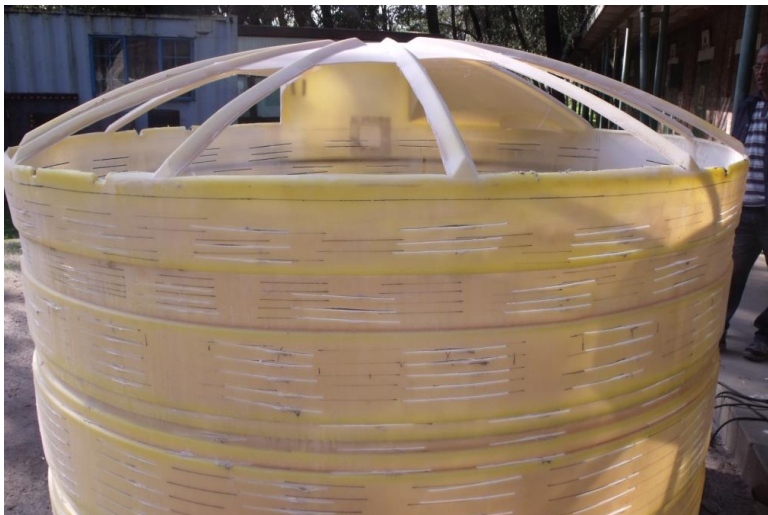


Figure 35: Tank that was used to house the woodchips during the experiment. Slits were grinded through the entire tank to ensure flow could occur through the tank

Calculations required for woodchip mass needed to remove nitrate was done using an excel model taking into account stoichiometric relationships and requirements for denitrification. Table 16 shows the results of calculating woodchip requirements for the field experiment, an example calculation in Chapter 2.

Table 16: Experimental design calculations based on stoichiometric relationships and site conditions

<i>Experimental set-up</i>	Scenario 1	Scenario 2	
Area	2400.000	2400.000	m ²
Flow velocity	0.002	0.01	m/d
Flow rate	4.800	24.000	m ³ /d
Inlet Nitrate	300	150	gN/m ³
Eff Nitrate	20	20	gN/m ³
N removal	280	130	gN/m ³
N removal rate	1344.000	3120.000	gN/d
N removal rate	48.000	111.429	molN ₂ /d
Nitrite removal rate	96.000	222.857	molN/d
Acetate (Nitrit) removal rate	72.000	167.143	mol Ac/d
Nitrate removal rate	96.000	222.857	molN/d
Acetate (Nitrat) removal rate	48.000	111.429	mol Ac/d
Acetate (tot) removal rate	120.000	278.571	mol Ac/d
woodchips requirement	80.337	186.497	mol sawdust/d
Operation period	365	200	d
woodchipsload g	4984916	6340891	g sawdust
woodchips load kg	4984.91573	6340.890851	kg sawdust

Furthermore, the mass to volume ratio of the woodchips needed to be determined prior to packing the tank with woodchips to be used in the experiment.

Method: Measuring the mass to volume ratio of woodchips/sawdust

1. A known volume of water was placed on a mass balance
2. The mass balance was then zeroed

3. Woodchips was then added to the known volume until the volume increased by e.g. 100mL
4. The mass in g was recorded from the balance
5. The mass in g is then equivalent to the volume added.
6. This procedure was repeated 3 times to ensure that the results were accurate

Table 17 shows the results of the small experimental procedure to determine the mass to volume ratio for the material used in the tank.

Table 17: Results of sawdust mass to volume assessment experiment, repeated in triplicate

	Volume of water	Volume of water added	Mass of sawdust/woodchips	Mass/volume ratio
1	200mL	50mL	50.08	1.0016
2	200mL	50mL	50.71	1.0142
3	500mL	200mL	202.1	1.0105

The results show that the weight to volume ratio of sawdust material used during this experiment is not much greater than 1. Hence the 5000L tank is likely to hold about 5000kg of sawdust, which according to calculations should last between 200 and 365 days depending on the flow rate and concentration changes over time.

The tank was then covered with geotextile to avoid soil particles from entering it during the experiment. Figure 36 shows the tank wrapped in geotextile prior to packing and emplacement to avoid the influx of fines into the tank while underground.



Figure 36: Biddum cloth placed around the tank to prevent larger grain sizes from clogging slits along the circumference of the tank

Soil samples were collected at various depths during the digging process. These were the top 0-30cm of the soil which was a dark grey to black layer with some vegetation cover. 30-60cm was a darker (black) soil, at around 60cm hard calcrete boulders occurred in the profile. The soil in this area was reddish brown and was collected for analysis. The water table was encountered at 1,4m where calcareous sand with some gravel sized calcrete nodules presents (Figure 37 and Figure 38). A percentage of clay was present within the layer as well. The aquifer material was sampled for further analysis.



Figure 37: Calcrete boulder encountered during excavation. Pebble and cobbled size calcrete nodules were also present in the profile



Figure 38: Resultant visual after reaching the water table. Water seeped from the side walls of the excavation at approximately 1.35 m below surface level.

Excavating continued up to 3m depth as the entire tank needed to be placed within the water table. Figure 39 shows picture of the profile where digging took place.



Figure 39: The top dark grey brown sand, while the bottom section of the soil displays a calcareous sand and clay type soil. The area that is smeared just above the calcareous layers marks the depth to water table

At 3m depth, the tank was lowered into the excavation using the bucket of the excavator (Figure 39). The tank was carefully lowered into the excavation and placed in the centre. Water seeped through the slits from all side walls of the excavation. Figure 40 shows the fitting of a piezometer to monitor the concentrations within the tank.



Figure 40: Lowering of the tank into the excavated area prior to filling and compacting of woodchips

Figure 41 shows the insertion of a 63mm PVC pipe to use as a monitoring point for the middle of the tank for the duration of the experiment.



Figure 41: Central monitoring point inserted into the circular opening in the tank

Woodchips were obtained from chopped down and chipped Eucalyptus trees on the site for the experiment. A few small experimental procedures were followed to calculate the required woodchip mass as well as to determine the mass/volume ratio for the woodchips used. This was then carefully put into the tank until it was full. The side of the excavation was filled for safety reasons. Workers at the site helped to distribute the woodchips evenly as well as to pack it by standing on it. Figure 42 shows the filling and compacting of the woodchips in the tank.



Figure 42: Filling and compacting of the woodchips in the tank

Two additional piezometers were placed on either side of the tank to monitor concentrations next to the tank which would show incoming and outgoing concentrations. Geotextile was then placed over the top of the tank to avoid sand particles from entering the tank. The excavation was then refilled. Figure 43 shows water in the excavation already filling the area prior to filling.



Figure 43: Filling of the excavated area, the picture on the left shows the groundwater that had already seeped into the tank while the emplacement and filling was taking place.

The system was allowed to settle and establish for 2 days. An initial groundwater sample was bailed from each piezometer after 2 days. A monitoring regime followed.

A biweekly sampling regime was followed from 2 days after the tank was put in place. Nitrate levels for the tank, and the two monitoring points adjacent to it showed almost immediate response to the carbon that was introduced to the system. Sampling frequency was later changed to monthly, then quarterly, then back to biweekly towards the end of the monitoring period.

4.3.3 Sampling the tank after more than 2 years

A digger loader was used to excavate the area adjacent to the tank, to a depth where the tank was visible. Figure 44 shows steps in the sampling procedure.



Figure 44: Excavation to the depth at the top of the tank for sampling of the woodchips within the tank.

Soil was collected from the unsaturated zone as well as the saturated zone and these were analysed for cations and anions, metals, pH and NO_3^- and NH_4^+ content. Woodchips were collected from the tank and submitted to the SGS laboratory for analyses of major cations and anions, metals, %C, and total Nitrogen. Woodchips were again sampled from the tank using a less disturbing technique after 35 months. An auger was designed to penetrate the full depth of the tank in order to remove the woodchips. Samples from 27 months, 35 months as well as woodchips from the source location that had been exposed to natural degradation was submitted to the University of Stellenbosch's Forestry department for analyses for all components of

wood. Wood component analyses were done on a species specific basis by the Stellenbosch Forestry department laboratory.

4.4 Results

Water level measurements were recorded as far as possible during the experimental period. Figure 45 shows the water table depth with time along with the monthly rainfall at the field site.

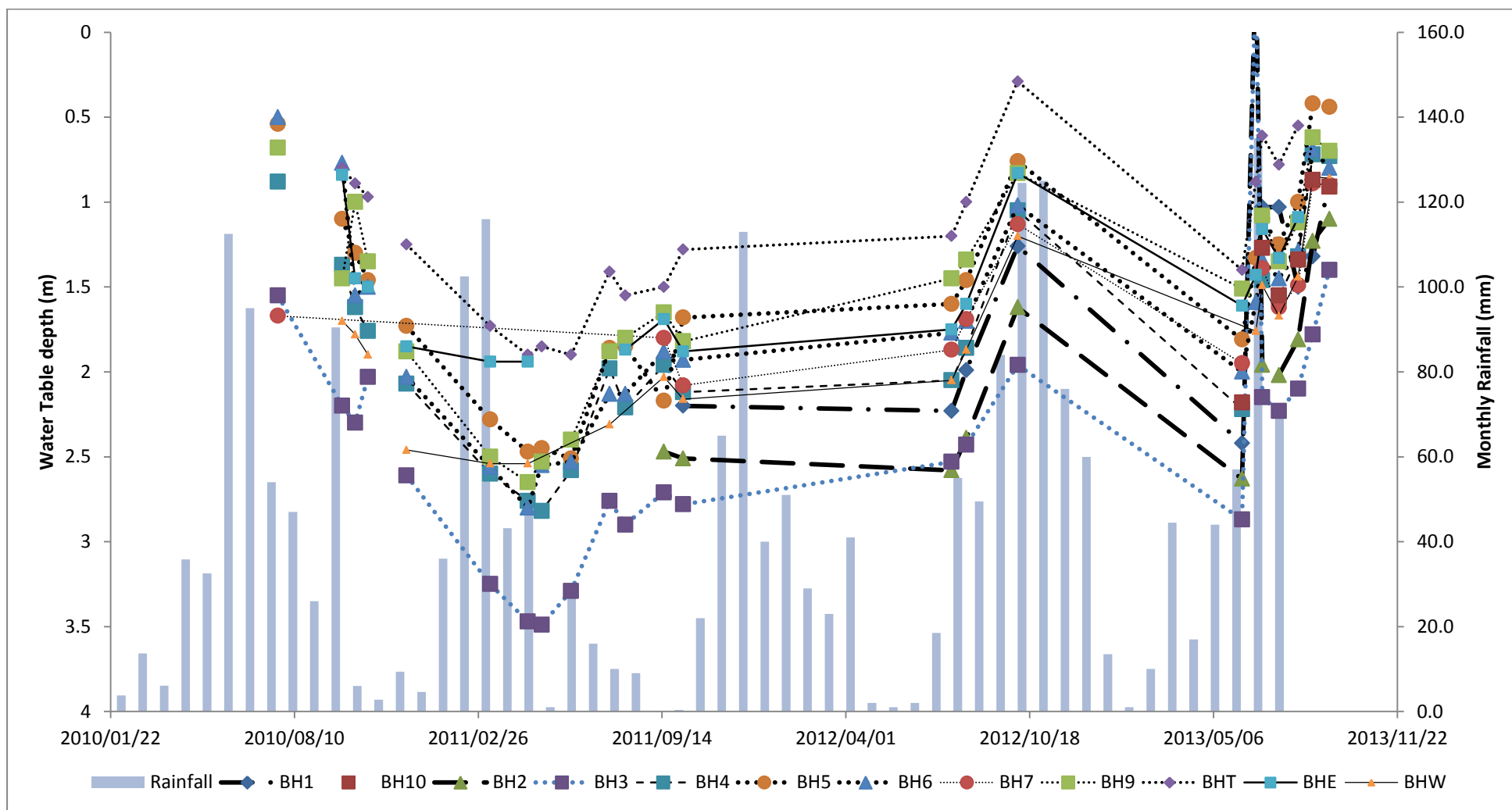


Figure 45: Monthly rainfall and water table depth from ground level at the Somerset West study site

Figure 45 shows monthly rainfall since 2010, prior to installation of the treatment zone, along with the changes in water table depth at the site since 2010. Peaks are representative of cumulative monthly rainfall. Figure 45 shows the impact of rainfall on water table depth at the site. Water table depth measurements were taken at all the boreholes at the site. Initially BH3, BH4, BH5, BH6, BH9, BHT, BHE, BHW water tables were measured (from July 2010), the rest were measured from late in 2011. Table 18 shows the minimum, maximum and average water table depths measured at the site, as well as the number of measurements taken at the respective points.

Table 18: Count, Minimum, maximum, and average water table depth for Somerset West study site per borehole

Borehole	Water Table depth
BH1 count	10.
BH1 Min	0.9
BH1 Max	2.4
BH1 Average	1.6
BH10 count	6
BH10 Min	0.9
BH10 Max	2.2
BH10 ave.	1.4
BH2 count	11
BH2 Min	1.1
BH2 Max	2.6
BH2 Average	2.0
BH3 count	22
BH3 Min	1.4
BH3 Max	3.5
BH3 Average	2.5
BH4 count	22
BH4 Min	0.7
BH4 Max	2.8
BH4 Average	1.8
BH5 count	23
BH5 Min	0.4
BH5 Max	2.5
BH5 Average	1.5

depth	
BH6 count	23
BH6 Min	0.5
BH6 Max	2.8
BH6 Average	1.7
BH7 count	12
BH7 Min	0.9
BH7 Max	2.1
BH7 Average	1.5
BH9 count	22
BH9 Min	0.6
BH9 Max	2.7
BH9 Average	1.5
BHE count	17
BHE Min	0.8
BHE Max	1.9
BHE Average	1.5
BHT count	20
BHT Min	0.3
BHT Max	1.9
BHT Average	1.2
BHW count	18
BHW Min	0.9
BHW Max	2.5
BHW Ave.	1.8

Borehole	Water Table
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The maximum water table depths are representative of the period following summer, while the minimum water table depth typically represents the water table after the effects of cumulative rainfall events. The count in Table 18 represents the number of water table depth measurements taken at the respective monitoring point.

During sampling, it was noted that boreholes BH3, BH2, BH4, and BH5 (Figure 28) did not yield as much water and often the pump had to be switched off for the borehole to recover to continue pumping. While at boreholes BH6, BH7, BH10, BH9, BH1 (Figure 32) continuous pumping could be used. This showed that the site contained areas of higher porosity and permeability toward the coastal dunes. Also, water appeared milky, which was indicative of rich carbonate terrain. Considering the flow direction and position of the tank, groundwater movement was faster in the area towards the dunes hence impacting on monitoring boreholes further from the tank. Measurements of NO_3^- as N, NH_4^+ as N, electrical conductivity, sulphate, total dissolved solids and pH were taken from samples collected periodically at the site to evaluate the changes in concentration over time (box and whisker plots of concentration ranges can be seen in Appendix B). Time series plots of these parameters per borehole follow (Figure 46, Figure 47, Figure 48, and Figure 49). Sampling events took place biweekly initially (2010), followed by monthly (2011), then quarterly (2012), then biweekly sampling events for the last 3 months of the experiment (2013). Boreholes were grouped according to their location e.g. upstream from the tank, around the tank, and downstream from the tank. The least impact on quality can be expected upstream with certain of these boreholes (BH3) being situated behind the area where the ammonium nitrate warehouse was previously present at the site. Figure 46 show trends in concentration at up-stream boreholes from the position of the tank.

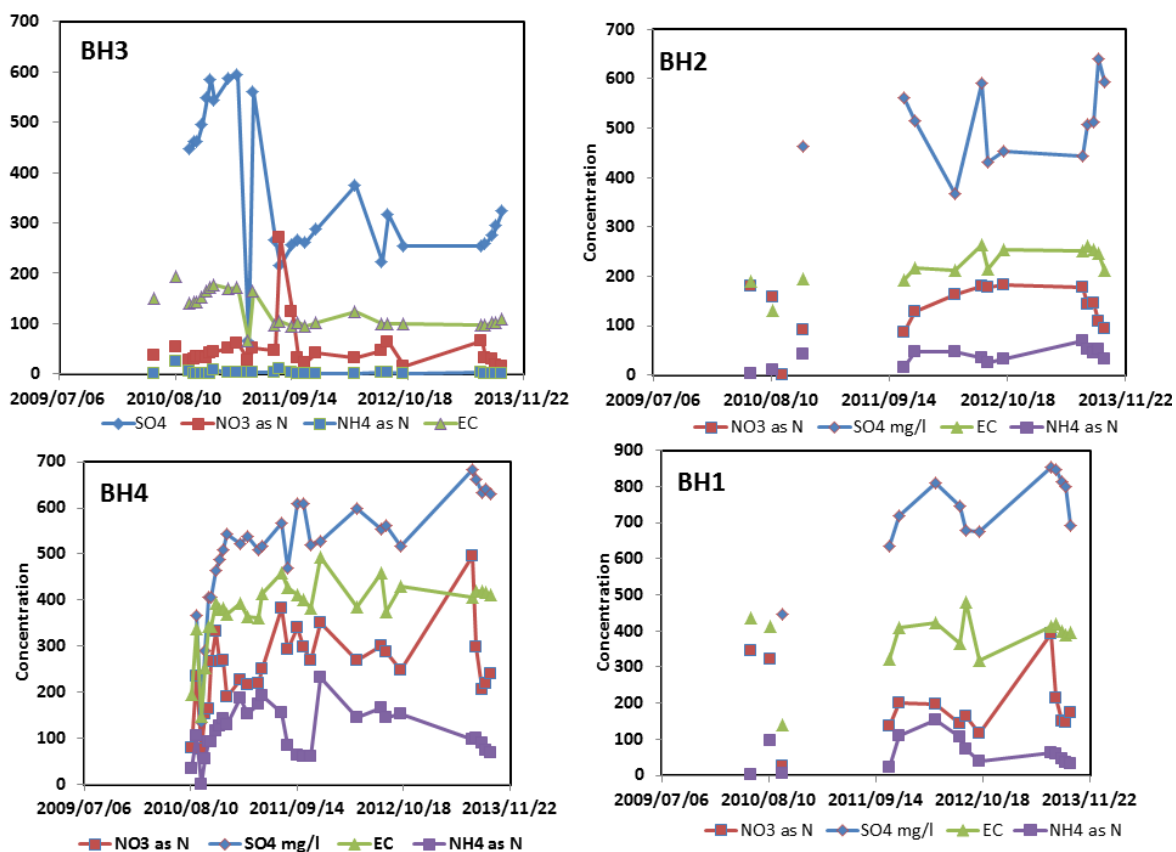


Figure 46: Time series view of NO₃⁻-N, NH₄⁺-N, EC and SO₄²⁻ for boreholes BH1, BH2, BH3, and BH4 at the Somerset West site.

Borehole BH3 is situated upstream from the area where an Ammonium nitrate warehouse was situated. It can thus be looked at as a borehole displaying background type concentrations for the site. Boreholes BH1, BH2, and BH4, are likely to indicate the result of historical spills at the site. Concentrations here may be elevated and affected by stored NO₃⁻ and NH₄⁺ in the soil. Removal of soil up to about 1.5 or 2m took place at the site in the past; however, nitrate and ammonium levels below this depth still showed elevated concentrations, (SRK, 2006). The soil could thus act as a store for elevated concentrations of anions and cations. Figure 47 shows the concentration trends at and around the tank for the duration of monitoring.

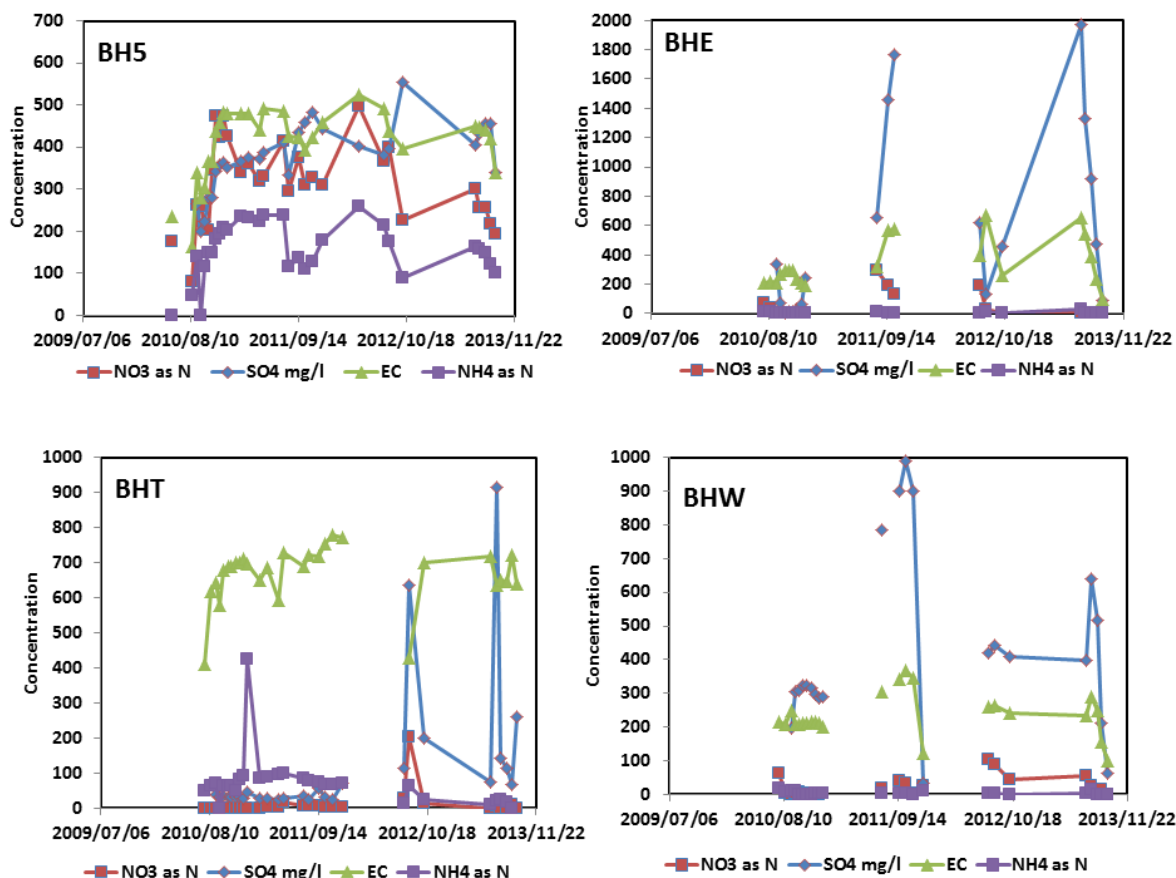


Figure 47: Time series plot of NO_3^- -N, NH_4^+ -N, EC and SO_4^{2-} for boreholes BH5, BHE, BHT and BHW. BH5 situated behind/upstream from the tank when considering the general flow direction of groundwater.

Figure 47 shows that NO_3^- as N levels remain low at the tank and boreholes around it. A spike in NO_3^- as N levels can be seen in most boreholes, and subsequent removal or reduction in NO_3^- levels is evident. Sulphate levels show reduction after all or most NO_3^- -N is removed at boreholes. This agrees with redox sequences described for waterlogged soils (e.g. Mc Bride, 2005 and Appello and Postma (2005)). Downstream boreholes are plotted in Figure 48. Results from BH5 show seasonal variation in nitrate levels as affected by rainfall events (either dilution or concentration from reaction with soil surfaces when residual spill materials are present), as well as an overall decreasing trend over the period of monitoring with respect to nitrate.

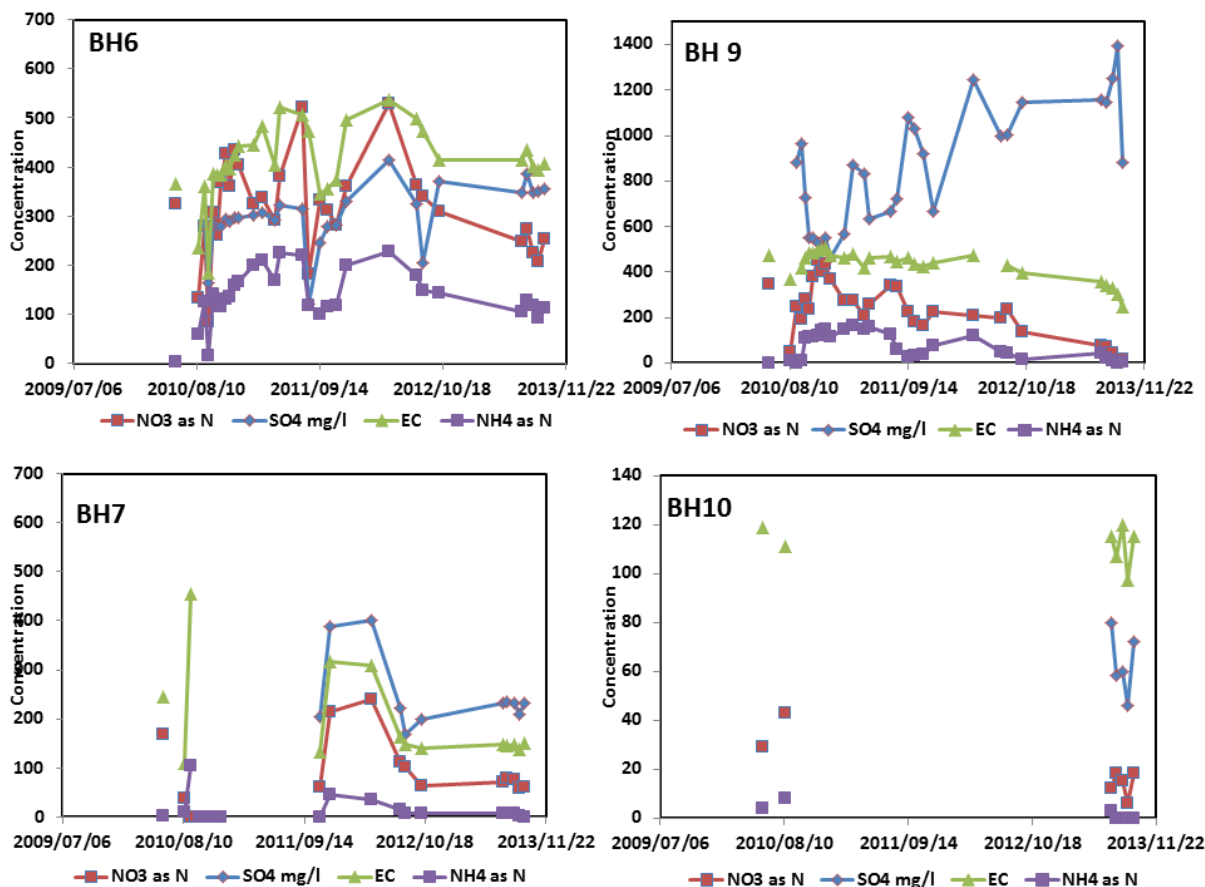


Figure 48: Time series plot of NO₃⁻-N, NH₄⁺-N, EC and SO₄²⁻ for boreholes downstream of the tank at the Somerset West site

Figure 48 shows that BH9 shows a dramatic increase in nitrate initially following a period of high rainfall and a gradual decline in its nitrate concentrations over time, and a subsequent reduction in sulphate levels toward the end of the monitoring when all nitrate was removed from solution. It also shows a decrease in the NH₄⁺ concentration over time. Boreholes BH7 and BH10 only have a short period of continuous monitoring data, however BH7 presents lower levels of NO₃⁻-N and NH₄⁺-N from 2012 to 2013. BH6 shows period decline in NO₃⁻ as N concentrations as well as NH₄⁺-N concentrations. Trend in pH was plotted for boreholes Figure 49.

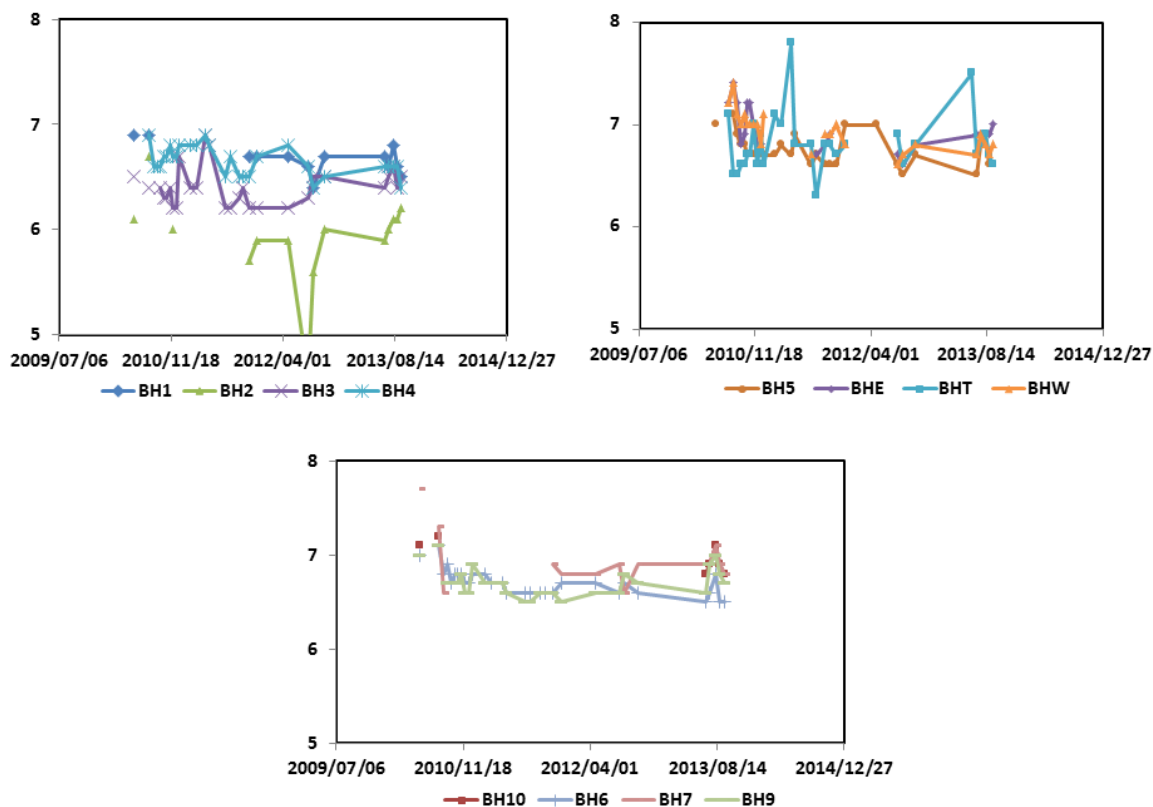


Figure 49: pH levels at boreholes for the duration of the experiment

Figure 49 show that pH is typically between 5 and 8 with lowest pH levels at BH2 at the site, which is upstream from the treatment zone. Furthermore, all other boreholes have pH above 6 and below 8. This shows that the aquifer has some buffering capacity.

Spatial plots of the NO_3^- -N, NH_4^+ -N, SO_4^{2-} and EC were done using surfer. The ordinary kriging technique was used to contour data. This gives a spatial view of the change in concentrations across the site.

Figure 50 shows the spatial distribution of nitrate levels at the site for the duration of the experiment. Here one can see that the borehole BHT, the piezometer in the centre of the tank containing the woodchips contains low or no nitrate for most of the time during the 3 years.

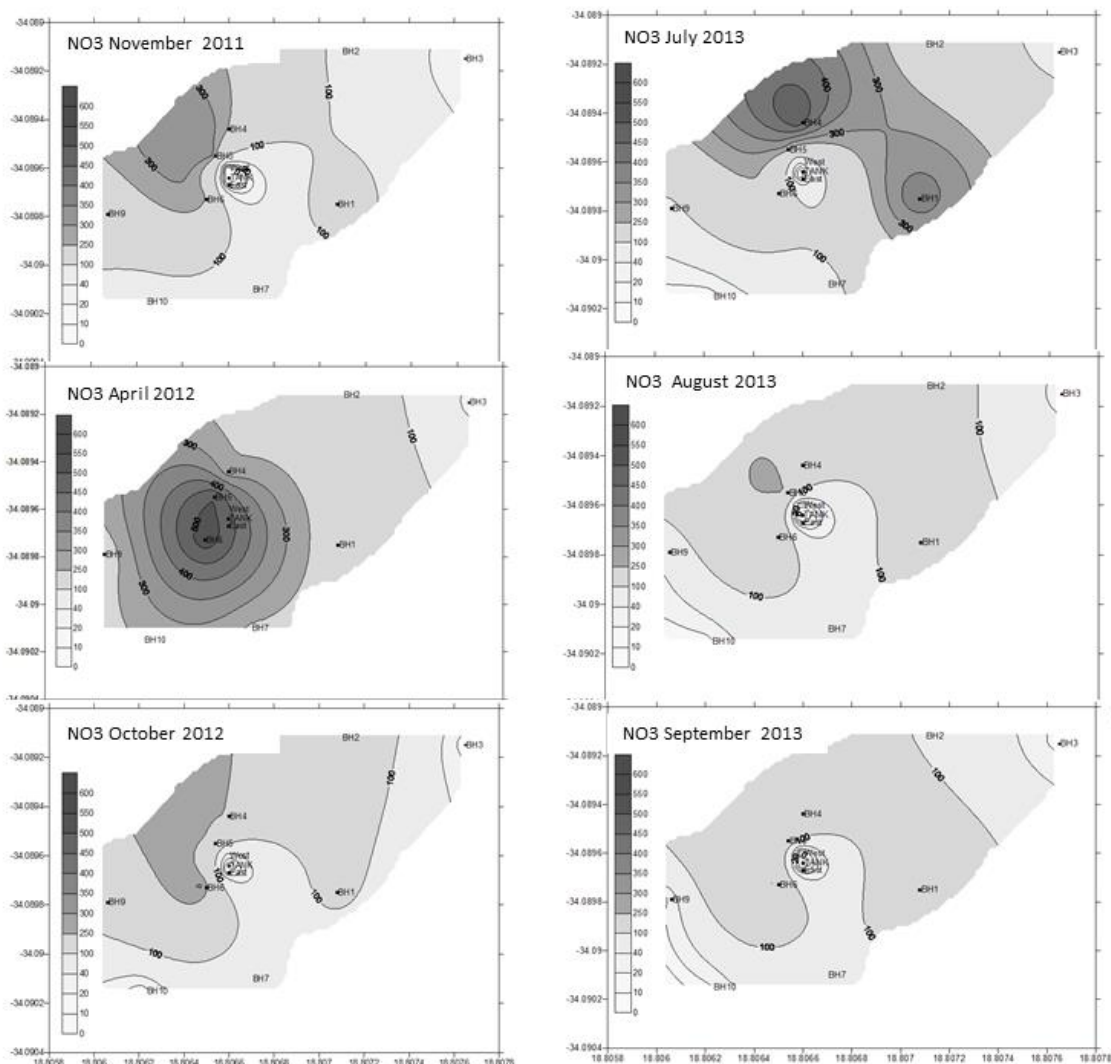


Figure 50: NO_3^- as N spatial distribution at various times during the 3 years of field testing of denitrification. Dark shades represent higher concentrations, while lighter shades represent lower concentrations and white represents a zero concentration.

However, during April 2012 and July 2013, nitrate levels were elevated at BHE, BHT, BHW, BH5, BH4 and BH6 (Figure 50). Subsequent field sampling events show that the zero nitrate levels were re-established in the tank BHT as well as adjacent piezometers BHE and BHW and that NO_3^- as N levels were reduced at boreholes around the tank BH6, BH5 and BH4 respectively. During year 3 (2013), A pulse of high nitrate during July (Figure 50) can be seen from BH2, BH4, and BH1. During August and September, these concentrations are considerably lower. This shows the effects of high rainfall (spike in nitrate due to leaching from the soil) and subsequent

denitrification and dilution of groundwater at the site (trend in EC, Figure 53). SO₄ distribution is shown in Figure 51.

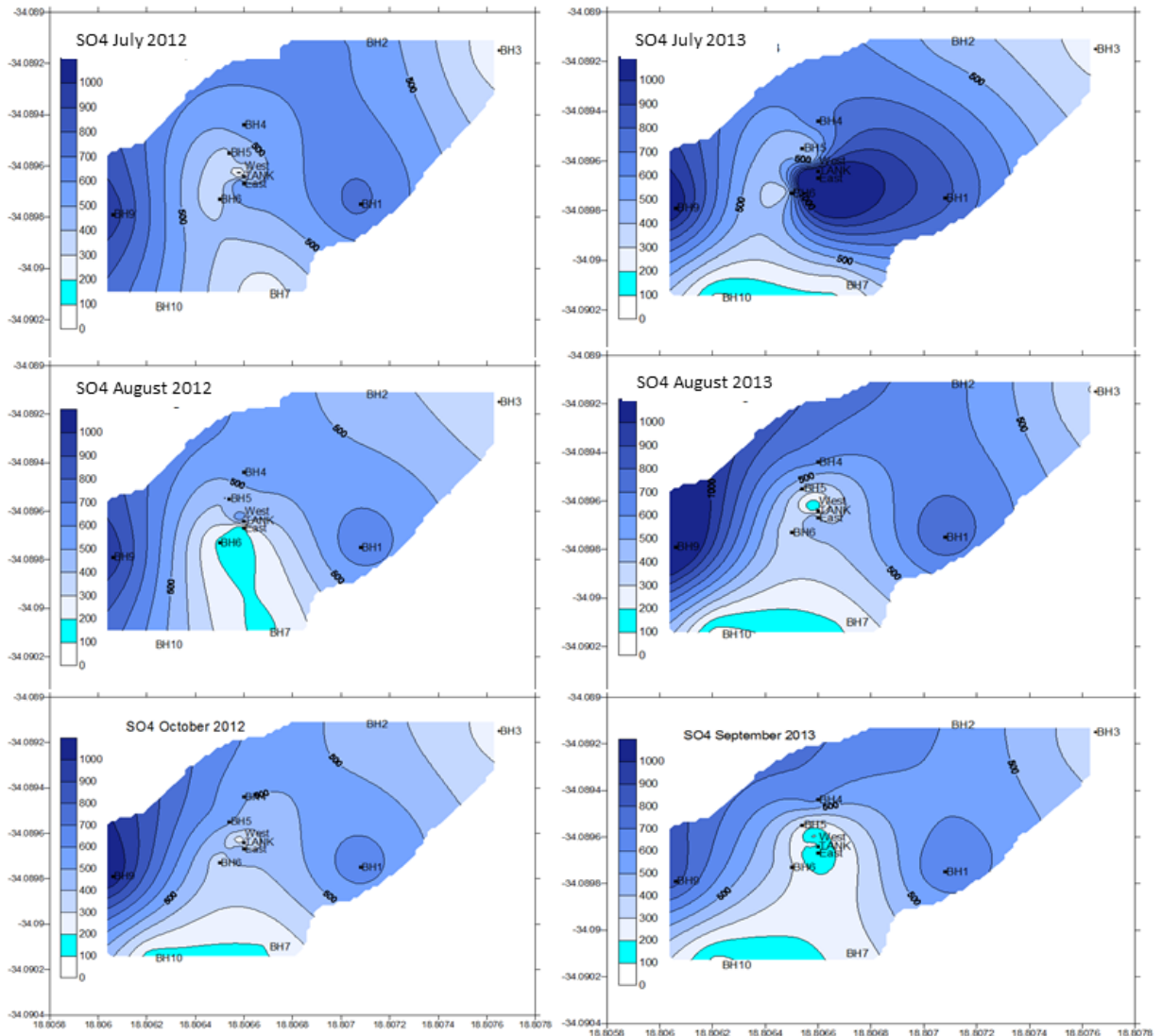


Figure 51: Spatial distribution of Sulphate (SO₄²⁻) concentration at Somerset West field denitrification site at different times over 3 year monitoring period. Darker shades of blue represent higher concentrations, turquoise represents the category 100 to 200 mg/L, lighter shades represent lower concentrations. Concentration ranges from 0 to 1000 mg/L at various times.

Figure 51 shows the distribution of sulphate across the site for the duration of the field experiment. Here one can see that sulphate levels are reduced at the tank and adjacent piezometers, as well as at other boreholes toward the end of the 3 years. In

exceptional rainfall events, dilution could decrease the concentrations of anions and cations in solution. However, the fact that sulphate levels decrease subsequent to nitrate levels in the tank, and adjacent piezometers, gives an indication of denitrification being complete, and sulphate reduction starting to be the dominant redox process. Figure 52 shows the $\text{NH}_4\text{-N}$ distribution over time.

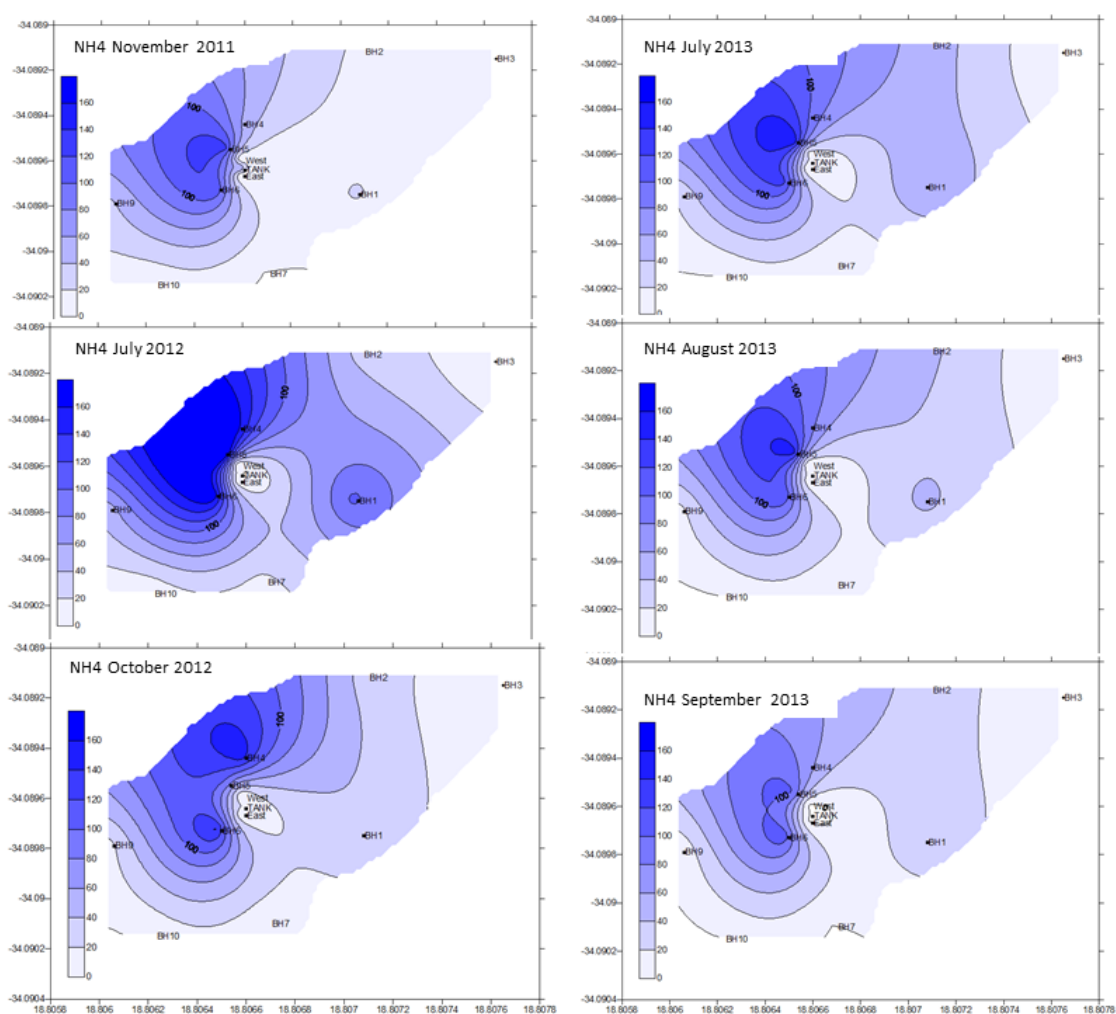


Figure 52: Spatial distribution of NH_4^+ at different times during 3 years of monitoring field denitrification. Darker shades of blue represent higher concentrations, while lighter shades and white represent lower concentrations

Figure 52 shows that ammonium levels at the tank and adjacent piezometers were reduced considerably over the 3 year period. BH 9 also shows a reduction in ammonium levels with time. Figure 53 shows the distribution of EC across the site.

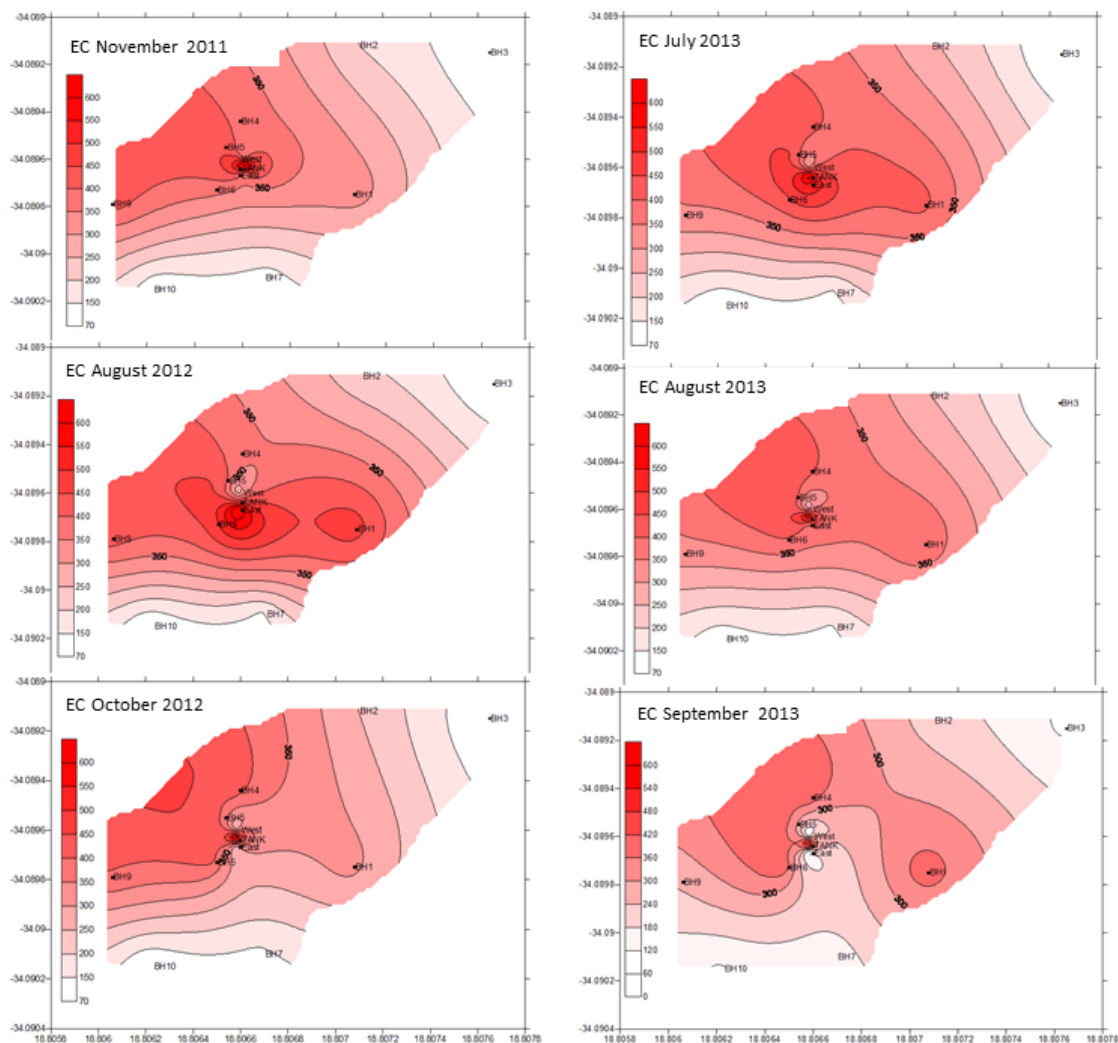


Figure 53: Spatial distribution of Electrical Conductivity (EC) at Somerset West during 3 year monitoring of field denitrification

Figure 53 shows that the EC remained higher in the tank than the surrounding areas on the site. Exceptional rainfall during 2013 reduced the EC across the site; however the tank EC remained elevated while the two adjacent points were close to zero. Figure 54 show the results of analysing the woodchips from the tank. Wood samples were analysed for all its components namely; lignin, cellulose, extractives, ash content and moisture content. Figure 54 also shows further breakdown products of non cellulose polysaccharide component of the woodchips, these components and their breakdown products are likely to participate in denitrification reactions.

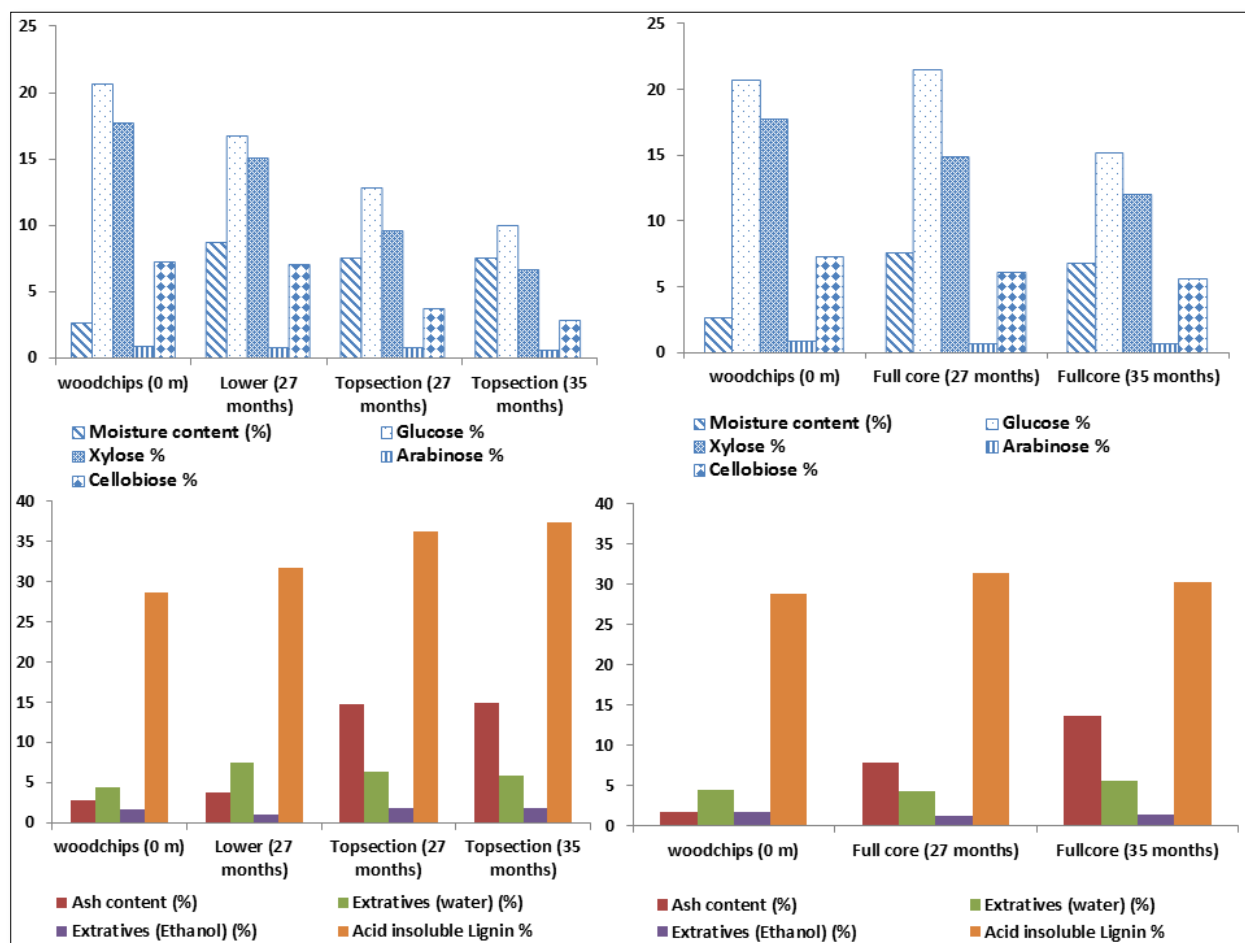


Figure 54: Results of wood chip analyses for samples collected at 27 months, 35 months and source material which remained in the natural environment

The moisture content in wood includes both water bonded to the wood, cell wall material and free water within the hollow of the cell lumens. The moisture content in the woodchips used for the field testing is elevated when compared to the sample of the original woodchips which continued to be exposed to the elements.

The percentage of extractives available was higher in the woodchips that were removed from the tank compared to woodchips undergoing atmospheric degradation, except in the sample that represented the tank woodchips after 27 months. Alkaline earth metals such as calcium, potassium, and magnesium account for up to 70% of ash content. “Older” woodchips with respect to time in the

subsurface contains higher levels of ash than the reference sample (woodchips (0m)) as well as those removed from the tank after 27 months. Even though the samples are of the same tree species, it appears that samples that were in the tank had higher lignin content than the sample that was exposed to atmospheric conditions for the top section samples, while the full core samples have similar % lignin. The lignin component of the top section samples showed greater % for samples that had been present in the tank for a longer period. This indicates that environmental exposure is required for lignin breakdown, while saturated or partially saturated conditions in the subsurface may have caused slower or negligible lignin breakdown.

Cellobiose is a disaccharide which contains two glucose molecules and can be hydrolysed enzymatically into glucose. This would thus represent a potential constituent which can be broken down and participate in denitrification. Comparing the cellobiose levels in Figure 54, it is evident that the samples exposed to the elements labelled woodchips (0m), contains higher levels of cellobiose than samples of woodchips that were in the tank for 27 and 35 months respectively. Figure 54 further shows the moisture content as well as the percentage of the breakdown products of hemicelluloses. Since the sugars represent breakdown products of constituents of wood, as well as substrates for denitrification, the result measured here shows the remaining levels as a result of breakdown of cellulose as well as consumption in denitrification and sulphate reduction in the tank. After 27 months in the tank, the sample representing a mixture/ full core of woodchips, the glucose levels in the wood is higher than that in the wood sample exposed to the elements. However, the lower and top sections of the tank for the same period show lower levels of glucose. The samples at 35 months have a lower glucose content than both

the 27 months and sample exposed to the elements. A similar trend is present for cellobiose, which evidently breaks down into glucose by hydrolysis. Low levels of arabinose were present in all woodchips. All sugars show a decreasing trend with respect to the length of time woodchips were in tank. This can be linked to consumption of breakdown products of wood during the denitrification reaction in the sub-surface.

4.5 Discussion

4.5.1 Rainfall and nitrate concentrations

Sugita and Nakane (2007) showed in laboratory experiments that water is likely to cause nitrate leaching at rainfall events of 26mm in both homogenous and layered soil media. Hence, larger magnitudes and cumulative rainfall will result in flushing of nitrogen found on soil particles surfaces during the infiltration process. Rainfall records for Somerset West from November 2006 up to August 2013 are presented in Figure 55.

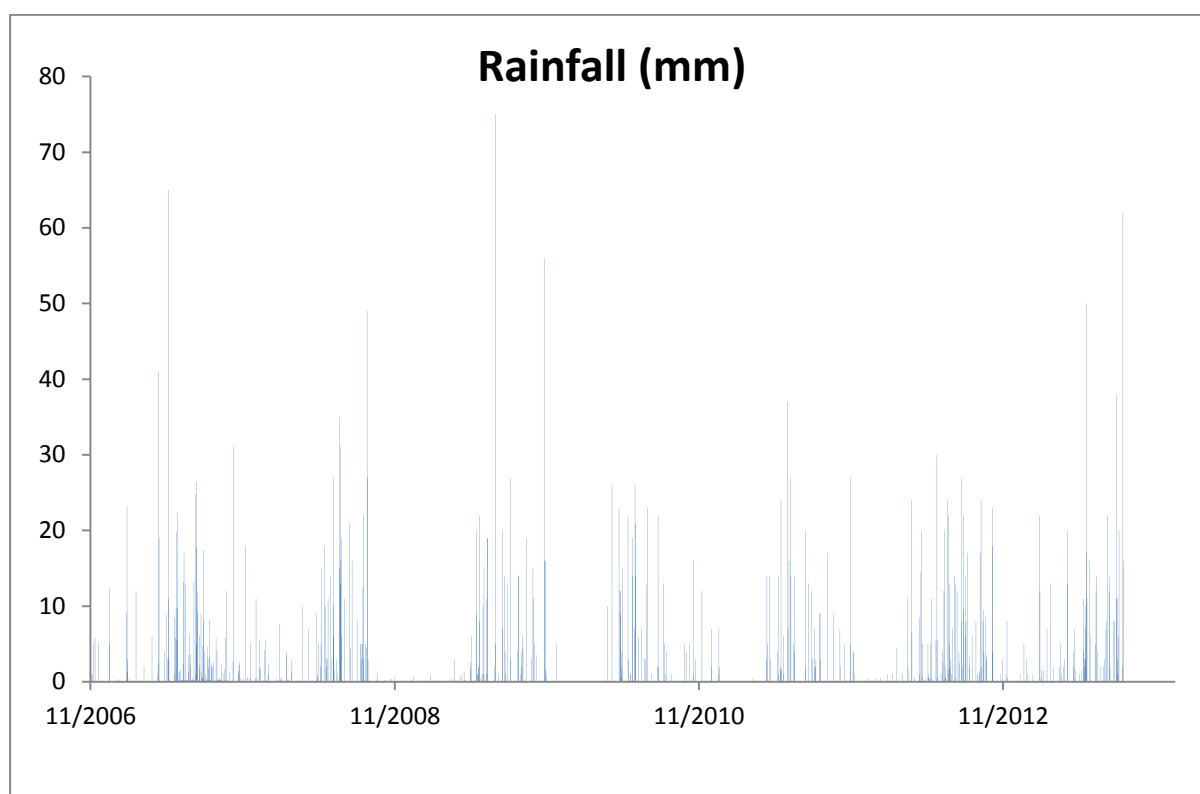


Figure 55: Daily rainfall records for Somerset West site recorded on site for the period 2006 to 2013.

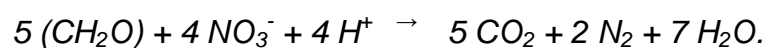
Figure 55 shows that the peak rainfall period in the Somerset West area is from May to November every year, with certain years having a few big rainfall events of 20mm/day and above. This would certainly be a potential mechanism for nitrate to be flushed from the soil profile into the groundwater as tested by Sugita and Nakane

(2007). Two periods during the field experiment shows a spike in the nitrate concentrations at all boreholes across the site (Figure 46, Figure 47, Figure 48, Figure 50) shortly after high cumulative rainfall events. A similar phenomenon of high nitrate containing pockets in the vadoze zone in arid and semi-arid regions of Southern Africa is discussed by Stadler *et al.*, (2012). Stadler *et al.*, (2012) describe a few scenarios of nitrate dynamics related to aquifer thickness or depth and type, as well as rainfall intensity and frequency. Deeper aquifers have nitrate-rich recharge water due to historic rainy periods and a resultant slow flow through, while in shallower aquifers, regular rainfall results in a low rate of nitrate reaching the water table, while episodic or storm events lead to rapid flow through and recharge containing high nitrate from that stored in the soil profile as the “nitrate pool”. This seems to explain to an extent the nitrate peak seen at the Somerset West site, where historical spills at a depth below 2m form the soil nitrate pool and during large rainfall events, mineralization and shallower water table result in detection of high nitrate levels at all boreholes at the site. This phenomenon can be seen in Figure 50 in this chapter, where elevated nitrate levels occur at all boreholes across the site in the vicinity where historical spills may have occurred.

4.5.2 Nitrate removal from groundwater

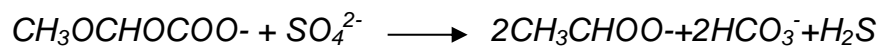
The fact that nitrate removal occurred in a short period of time where carbon was available e.g. BHT, BHW and BH around the tank and remained low throughout the experiment shows that denitrification using cheaply available wood material is effective. This is in agreement with work by Robertson *et al.*, (2008), Robertson and Cherry, (1995), Robertson (2010), Robertson *et al.* (2007), Greenan *et al.* (2009),

Schipper and McGill (2008), Robertson *et al.* (2009), Schipper and Vojvodic-Vukovic (2001), Schipper *et al.* (2005). Also, periods where high rainfall caused a spike in the nitrate levels across the site (Figure 50), and subsequent removal of all nitrate especially in and around the treatment zone of the tank confirms that the treatment zones removal of nitrate was effective. Borehole BH9, downstream of the tank (BHT), shows a steady decline in nitrate levels over the period of the experiment. During this experiment, NH_4^+ levels were also reduced over time. Work done by Robertson (2010) showed that the rate of nitrate removal within a woodchip barrier declined with time. He compared 7yr, 2yr and fresh samples. In chapter 2, a similar type experiment was done. Wood analyses showed that indeed the wood samples that were in the reaction zone for a longer period had lower concentrations of sugars. This may explain the nitrate removal and the reduction in rate of nitrate removal. Graphs for pH show that in general in and around or downstream from the reaction zone, pH remains near neutral, while upstream boreholes have pH levels as low as 4.5 occurred at BH2. This is in agreement with (Appelo and Postma, 1994 and Robertson and Blowes, 1995) which shows that pH is buffered by calcareous compositions of soil as well as other mineral phases where calcareous soils are not present, denitrification has the ability to raise the pH from low pH values to near neutral pH values (McQuarrie *et al.*, 2001).



The above equation shows that denitrification consumes acidity. Hence, it would increase the pH where low pH would otherwise have predominated. During excavation at the site, calcrete boulders were encountered. Groundwater

compositions for the site had Ca^{2+} as the dominant cation. Hence there would be a high inherent buffering capacity as well as that offered by the denitrification process. This would explain why pH levels didn't drop far below 6 in and downstream from the reaction zone/ BHT. Also the occurrence of sulphate reduction would produce further alkalinity to the system and provide even more buffering capacity to pH as follows:



Sulphate reduction occurred at several of the boreholes as can be seen in the time series as well as the surfer spatial concentration distribution diagrams (Figure 46, Figure 47, Figure 48, and Figure 51).

Rainfall frequency and intensity as well as the level and period of saturation within the reactive zone (BHT) played a key role in denitrification efficiency as well as wood degradation for the duration of the experiment. Despite the flushing of the soil nitrate pool to the groundwater level and high nitrate levels occurring across the site, a rapid denitrification occurred at the main reactive area (BHT) as well as at the monitoring points around it. This shows that the method was effective in reducing the nitrate levels from high levels of up to 202mg/L NO_3^- -N during the 2012 after a major rainfall event, down to 15mg/L NO_3^- -N within a period of about 2.5 months. Another finding was that the nitrate levels after rainfall events became progressively diminished comparing the cumulative rainfall for the period during which the experiment was running. The area around the reactive zone area showed rapid denitrification, while higher levels persisted upstream where the historical spills may have occurred, (SRK, 2006). The reduction of sulphate at the tank shows that nitrate was totally removed especially around the reactive area (BHT).

The use of coarse and mixed grain sizes of woodchips ensured that the area where the woodchips were installed had a higher porosity and permeability than the surrounding parts of the aquifer and vadoze zone. The coarse nature and variable sizes of the woodchips ensured that it had a much better hydraulic conductivity to its surroundings; it would thus have captured most of the water flowing towards it. In a paper by Robertson *et al.* (2005) they showed that the use of high K reactive media in the shallow water table zone that do not necessarily have to penetrate the full depth of the contaminant plume to be effective. Sampling at either side i.e. upstream and downstream, showed that the nitrate levels were reduced on the downstream side of the reactive zone (BHT) (Figure 50).

4.5.3 Woodchip degradation

The predominant type of wood found at the Somerset West site was Eucalyptus (*E. globulus*) species. The major components of wood in general are cellulose, hemicellulose, lignin, and extractives (Figure 54). These were analysed for further breakdown products of hemicelluloses such as glucose, xylose, arabinose and cellobiose (Figure 54). Literature was consulted to obtain the composition of Eucalyptus species. Based on literature, the range of % w/w for components of Eucalyptus species are as follows: Lignin 20.5-31.3%, Cellulose 41.3-50%, Extractives (ethanol) 1.72-4.46%, Ashes 0.17-0.53% (Evtuguin and Neto, 2007). Comparing these values to those obtained from the woodchips used during the experiment, one can establish in comparison how degraded the woodchips are. Table 19 shows the degree to which the samples removed from the tank and those

that were exposed to the elements differ in composition from a fresh sample of *Eucalyptus globulus* using the upper end of the composition range. This gives an indication of the effects of the environmental and physical conditions (pH, redox condition, degree of saturation, use/uptake during denitrification and position in the tank) on the degradation of woodchips. Table 19 shows the degree of degradation of woodchips in comparison to higher end composition from literature for a fresh/pristine eucalyptus *globulus* tree.

Table 19 : Degree of variation in composition of a fresh sample (degraded under natural conditions) vs samples from experimental work using the upper end of the range of Eucalyptis composition after Evtuguin and Neto, (2007).

Sample ID	Date of sampling	Ash content (%)	% difference	Extratives (Ethanol) (%)	% difference
woodchips (0 m)	21/06/2013	2.798	427.950	1.666	62.645
Lower (27 months)	11/10/2012	3.856	627.457	1.060	76.242
Topsection (27 months)	11/10/2012	14.774	2687.571	1.926	56.825
Topsection (35 months)	21/6/2013	14.949	2720.618	1.945	56.382
Full core (27 months)	11/10/2012	7.840	1379.305	1.200	73.099
Fullcore (35 months)	21/6/2013	13.693	2483.589	1.390	68.837
Eucalyptus Globulus	Pristine	0.530		4.460	
Sample ID	Date of sampling	Acid insoluble Lignin %	% difference	Cellulose	% difference
woodchips (0 m)	21/06/2013	28.750	8.147	38.750	22.5
Lower (27 months)	11/10/2012	31.720	-1.342	36.810	26.38
Topsection (27 months)	11/10/2012	36.210	-15.687	27.900	44.2
Topsection (35 months)	21/6/2013	37.410	-19.521	37.780	24.44
Full core (27 months)	11/10/2012	31.390	-0.288	34.440	31.12
Fullcore (35 months)	21/6/2013	30.330	3.099	35.470	29.06
Eucalyptus Globulus	Pristine	31.300		50.000	

The results in Figure 54 shows that the woodchips removed from the reactive zone after 35 months have much lower sugar content than that removed after 27 months. The periods of rainfall and hence saturation of the tank/reactive area would affect the degree to which and time during which the woodchips were under water and when they may have been dry. This would have an effect on the extent to which and duration of reactions within the tank can take place. In particular, the lignin results reflect a different trend to the sugars and their breakdown products with lignin content being more elevated in woodchip samples representing the longer period in

the tank. Some factors play a role here; lignin is known to be resistant to biodegradation and is degraded by white rot fungi, Perez *et al.* (2002). The reference sample which had been exposed to natural environmental conditions has lower lignin content than those in the tank. The conditions in the tank seem to have affected the degradation of lignin, with periods of saturation and anaerobic conditions or extremely low oxygen levels inhibiting the growth of white rot fungi and hence the degradation of lignin in the tank. The top section of the tank is more degraded as compared to an average of the full core of the tank. This can be explained by the fact that during summer seasons when the water table is lower, the lower part of the tank remains saturated while the top is exposed to higher temperatures and moist conditions. This would be more favourable for establishment of a fungal community able to degrade lignin at least for the few months while the tank water level is under-saturated. Table 19 shows that ash content is greater in samples that had been in the treatment zone for a longer period, it also appears that the position from which the sample was collected and its degree and time during which it was under saturated and reducing conditions impacts on the concentrations of wood breakdown products present. The percentage difference between the pristine composition of Eucalypt species and the wood used in the experiment gives an idea of how the woodchips have degraded, including the woodchips (0m) which was degraded under natural conditions. The lack of degradation of lignin in the anaerobic environment also increases its percentage of the total composition in the sample; hence a perceived increase in concentration may be an increase in relative % of total composition. Table 19 also shows that woodchips in the lower section of the tank are more degraded. This could be owed to longer periods of saturated conditions prevailing and favourable environmental conditions for reactions to take place.

4.5.4 Limitations of the field setting

The tank used was only 1.37 m in height while the winter water table was at about 1.4 m depth below ground level and the summer water table depth ranged from 1.8 (minimum depth) to over 3 m (maximum water table depth) in some boreholes. This means that the tank's location was limited to between 2.8 mbgl and 1.48 m. Uncertainty with respect to the ability to sample all points during summer, as well as summer reaction rates or occurrence exist. Certain boreholes have water levels below 2.8 m during summer. The bedrock was not encountered during the excavation hence there is uncertainty about underflow in the treatment zone as well as flow by-passing the treatment zone. The presence of disconnected clay lenses as well as calcareous sands in certain parts of the aquifer presented potential for areas or zones of variable flow. Monitoring was done bi-weekly using indicator parameters to accommodate the available budget; this limited the amount of data obtainable for the study area. Uncertainty with respect to distribution of clay lenses and calcrete boulders presented some limitation with respect to the local flow direction and velocity at the site. The area immediately around the tank had a rapid rate at which denitrification occurred. The presence of clay is not ideal, but not limiting either. It simply means that flow is much slower than desired in some areas of the site, and hence the denitrification will take place over a longer period in those areas. Despite all of these limitations, the experiment was a success.

4.6 Conclusions

4.6.1 Rainfall and nitrate concentrations

It was evident from the data that periods of exceptional rainfall as well as high cumulative rainfall resulted in nitrate levels being elevated at the test site.

This also relates to the soil becoming depleted with respect to nitrate stores with time, and hence may eventually lead to flushing of all $\text{NO}_3^-/\text{NH}_4^+$ from the upper soil layers into the groundwater table and subsequent movement towards an area of discharge from the aquifer.

The low flow rate across the site discussed in work by SRK (2006) as well as clay layers and calcrete nodules would play a role in retardation in the time that nitrate rich groundwater can move across or off the site.

4.6.2 Nitrate removal from groundwater

The field experiments showed that woodchips were effective at reducing nitrate levels as well as sulphate and even NH_4^+ in groundwater. Field experimentation showed that despite periods of high rainfall causing a spike of nitrate levels at all boreholes across the site, that nitrate levels are reduced in a short period. It also confirms that the woodchips used remained an effective source of carbon for the duration of the experiment. Additionally, pH buffering capacity at the field site was high as pH remained near neutral in and around the treatment area, with low pH only occurring upstream. The consumption of acidity during denitrification as well as the presence of calcrete and clay lenses serves as a buffering capacity at the site.

Intermittent release of available carbon from woodchips as well as large stores of available carbon, is indicative of the fact that denitrification is not carbon limited in this field experiment. This explains why sulphate reduction proceeded when nitrate was consumed at many boreholes across the site.

4.6.3 Woodchip degradation

The results of woodchip analyses showed that woodchips have been degraded with time. However, the degradation rate is slow and supports the use of woodchips as a carbon source for long term denitrification methods. Table 19 confirms that woodchips were partially degraded with duration of the experiment, however, a large percentage of carbon breakdown products still remain after the 37 months duration and hence the field experiment would be able to run for a much longer period.

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5 CHAPTER 5: INVESTIGATING THE RELATIONSHIP BETWEEN BARRIER THICKNESS/CONCENTRATION, RETENTION TIME, NITRATE REMOVAL EFFICIENCY AND BARRIER LIFETIME⁵

5.1 Background

Denitrification is defined as a microbially facilitated process of nitrate reduction (performed by a large group of heterotrophic facultative anaerobic bacteria) that may ultimately produce molecular nitrogen (N_2) through a series of intermediate gaseous nitrogen oxide products. Laboratory and field denitrification have been successfully tested in previous chapters. This chapter strives to use the data obtained to establish relationships between the respective parameters to better inform future work. The fundamental reaction of denitrification (Equation 1), pg. 70, shows that nitrate is consumed or reduced while organic carbon is oxidized.

Nitrate forms neither insoluble minerals that could precipitate, nor is it adsorbed significantly, Appello and Postma (2005). This is also shown in work done in chapter 2. In systems where available carbon supply exceeds that required for denitrification, reactions may proceed to further remove oxygen containing compounds such as SO_4^{2-} from solution as organic compounds are oxidized. In carbon deficient environments, natural denitrification is carbon limited and the denitrification reaction

⁵ Publications related to this chapter:

Israel, S.; Tredoux, G.; Engelbrecht, P.; Wilsenach, J.; Germanis, J.; Maherry, A., 2009. In-situ nitrate removal from groundwater to supply rural communities: experimental work and modelling, *Management of Natural Resources, Sustainable Development and Ecological Hazards, II*, Pages: 427-436 (Book chapter)

does not remove all nitrate and nitrite from the system. The gradual decreases in oxygen and nitrate with depth in aquifers indicates that reduction rates for oxygen and nitrate are slow. The reactivity of organic matter is probably the overall rate controlling factor, Appello and Post (2005).

5.2 Modelling of denitrification

Modelling of the denitrification has been done extensively in the waste water industry using Monod kinetics which relates growth of microbial population to the concentration of the substance limiting its growth. Modelling of processes involved in a tank sized experiment was documented by Israel (2009) using PHREEQC (Parkhurst and Appello, 1999) reactive transport modelling to include rates, kinetics, biomass growth and decay rates and exchange processes using varying concentrations and rates. Microbial growth and decay can also be included in the PHREEQC model, and is directly linked to the consumption of either the oxidant or the organic matter. Calderer *et al.* (2010) defined a mathematical model to describe nitrate, oxygen, and organic carbon consumption coupled with growth and decay of a heterotrophic microbial population using Simulink. Andre *et al.* (2011) modelled batch and flow through experiments.

PHREEQC uses speciation calculations based on the Debye Hückel equation as well as the extended Debye Hückel equation where ionic strength of solutions is high. Rate equations and reaction kinetics can be specified according to known literature values and stoichiometric relationships. The overall rate for a kinetic reaction of minerals and other solids is (Parkhurst and Appello , 1999):

$$R_{k=} r_k \frac{A_0}{V} \left(\frac{m_k}{m_{0k}} \right)^n \dots \dots \dots \text{Equation 7}$$

where r_k is the specific rate (mol/m²/s), A_0 is the initial surface area of the solid (m²), V is the amount of solution (kgw), m_{0k} is the initial moles of solid, m_k is the moles of solid at a given time, and $(m_k/m_{0k})^n$ is a factor to account for changes in A_0/V during dissolution and also for selective dissolution and aging of the solid. For uniformly dissolving spheres and cubes $n = 2/3$. All calculations in PHREEQC are in moles, and the factor A_0/V must be provided by the user to obtain the appropriate scaling.

Specific rate equations in PHREEQC have various forms, largely depending on the completeness of the experimental information. The Monod rate equation is commonly used for simulating the sequential steps in the oxidation of organic matter (Van Cappellen and Wang, 1996). A series of rate expressions can be developed in line with the energy yield of the oxidant; first O₂ is consumed, then NO₃⁻ and successively other, more slowly operating oxidants such as Fe(III) oxides and SO₄²⁻. The coefficients in the Monod equation can be derived from first-order rate equations for the individual processes. The combined overall Monod expression for degradation of organic carbon in a fresh-water aquifer is (Parkhurst and Appello, 1999):

$$R_c = 6 S_c \left(\frac{S_c}{S_{c0}} \right) \left\{ \frac{r_{max} m_{O_2}}{K_m + m_{O_2}} + \frac{r_{max} m_{NO_3}}{K_m + m_{NO_3}} \right\} \dots \dots \dots \text{Equation 8}$$

where the factor 6 derives from recalculating the concentration of S_c from mol/kg soil to mol/kg pore water. S_c represents the organic carbon content (mol/kg soil), S_c/S_{c0} represents a factor to take into account that certain parts of organic matter may not be degraded (e.g. lignin), r_{max} represents the maximum rate for a particular species, K_m is equal to the concentration where the rate is half r_{max} (i.e. half saturation

constant), and m_x represents the molality of the respective species in solution. Using PHREEQC, redox reactions can be modelled by adding carbon stepwise through an irreversible reaction to a mixture of water and sediment that contains oxidants. Figure 56 shows PHREEQC modelling of redox zones in waterlogged soil.

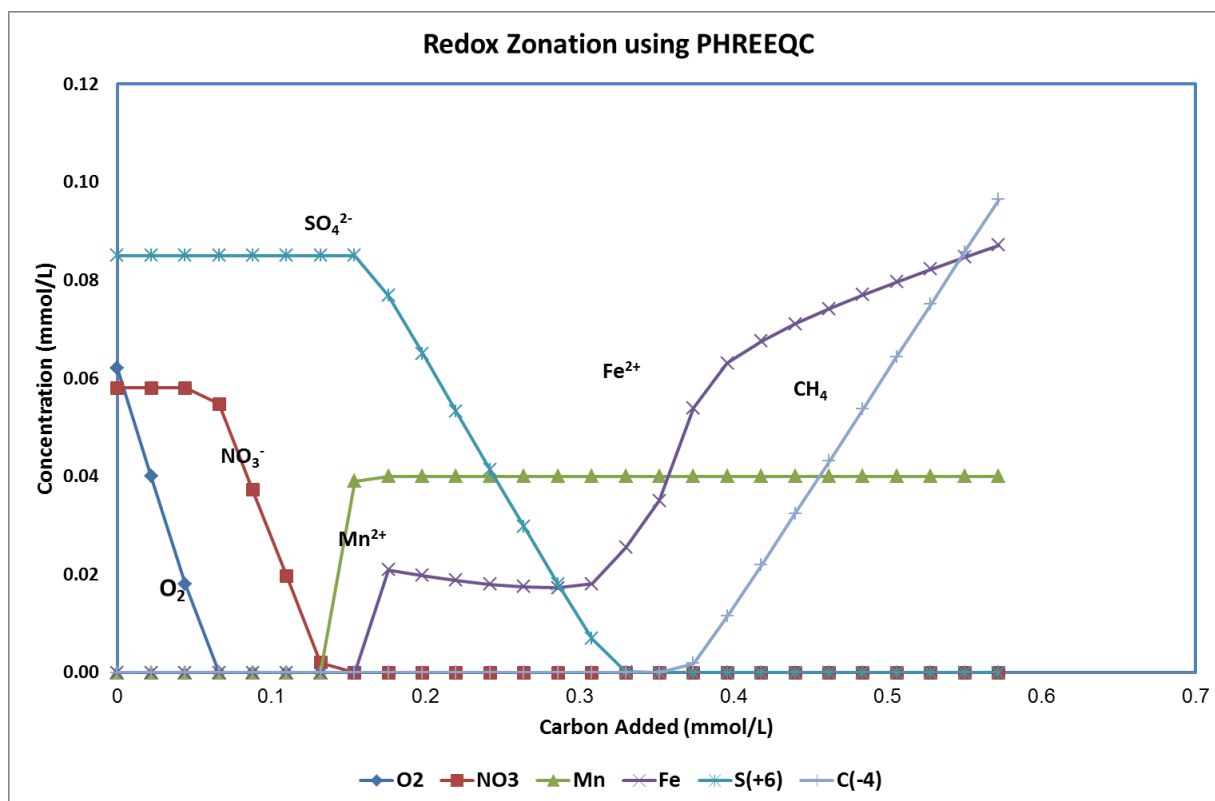


Figure 56: Development of redox zones modelled by PHREEQC using stepwise addition of carbon to oxidized sediment, after Appelo and Postma (2005)

Figure 56 describes the oxidation reduction sequence that is likely to occur in shallow groundwater systems or water logged soils. Modelling done by Israel (2009) shows that it is possible to predict the likelihood of a particular mineral phase to precipitate during the reaction. 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. Figure 57 shows the setup of a model used during Israel (2009) simulating the flow through tank

experiment (Chapter 3). Dissolved organic carbon was used to represent the available carbon for reaction. The influent water composition represents groundwater, while the cells labelled 1 to 20 represent aquifer material or soil material with respect to chemistry and exchange surfaces.

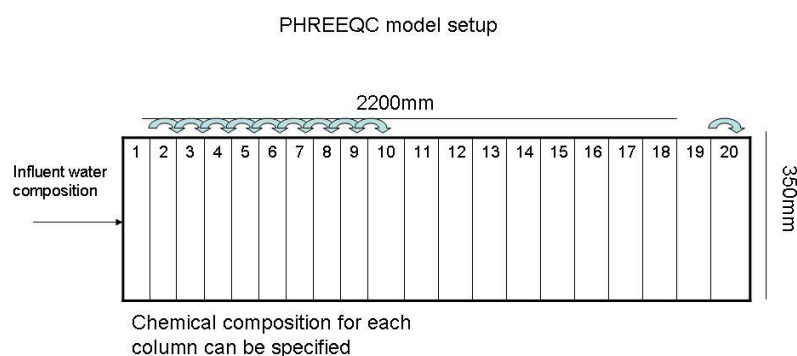


Figure 57: Phreeqc model set-up used by Israel (2009)

Initial input 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 (Heterotrophic Plate count) 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. 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). 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. Figure 58 shows the results of saturation indices as calculated by the PHREEQC model.

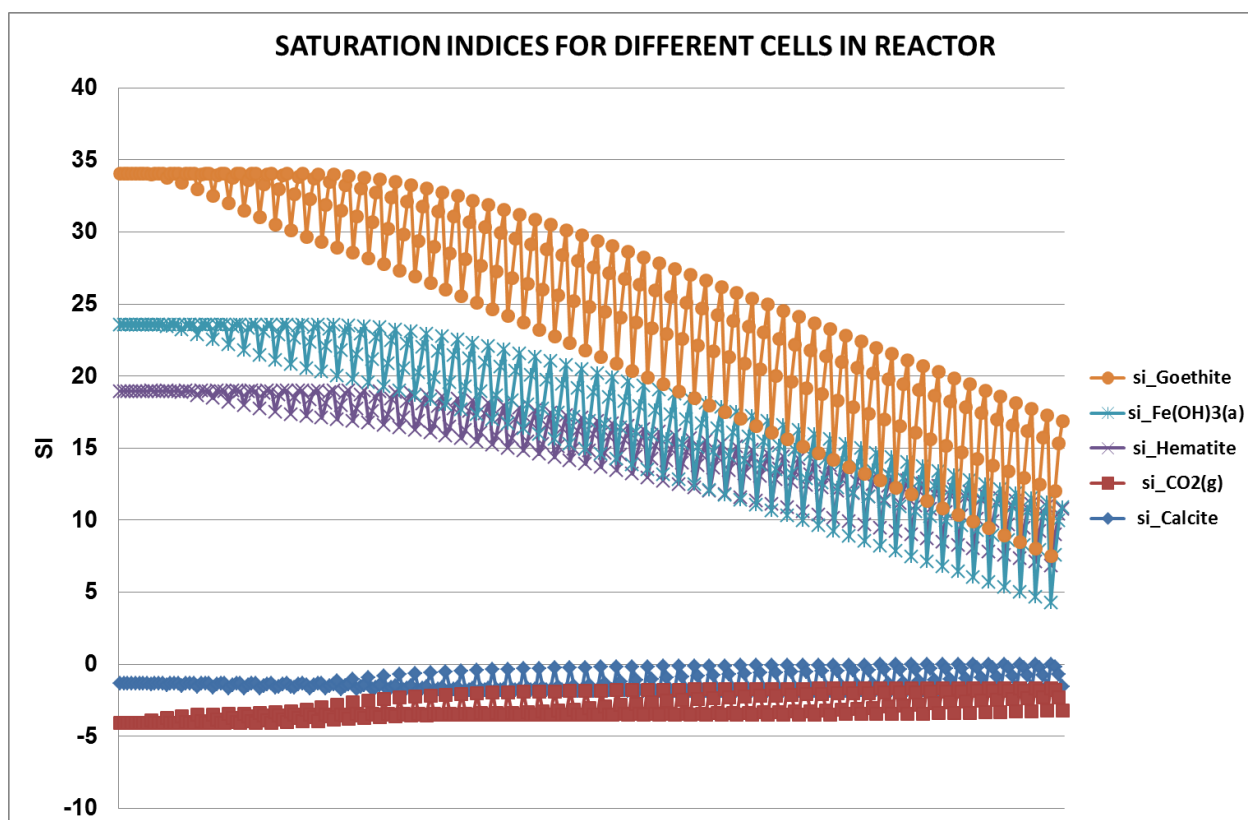


Figure 58: Saturation indices is as results from PHREEQC modelling done for the experimental conditions specified in this section, Israel (2009)

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. 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 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 importantly to measure parameters such as hydraulic conductivity or changes in flow rates to try and avoid it.

5.3 Methodologies

In chapter 2, we determined that the denitrification is predominantly a redox process, although the presence of biochar enhanced the rate of nitrate removal from solution. This is owed to the potential for carbon compounds to sorb to biochar surfaces and hence increasing the surface area for reaction. The redox process was confirmed by considering the redox zonation seen in Figure 56 in this chapter. Sulphate reduction occurring after nitrate reduction in the woodchip and woodchip and biochar treatments confirmed the redox sequence proceeding in these treatments. The increase of alkalinity as a by-product of microbial activity and a product of the denitrification redox reaction also confirmed this.

The PHREEQC-2 model was used to set up a model for the laboratory column experiment to see whether the redox sequence and its rate using woodchips as a carbon source can be simulated. According to literature (Appello and Postma, 1999 and Robertson, 2005) organic matter becomes less reactive with age. An external carbon source was used as groundwater and soil contained less than 1% organic carbon. Organic matter reactivity is also ultimately the driver of most redox reactions (Appello and Postma, 1999). Since lignin is largely resistant to degradation, carbohydrate degradation becomes the most important process aided by microbial organisms. Equilibrium thermodynamics have been used to model the denitrification reaction. A partial equilibrium model was proposed by scientists where organic matter fermentation provides the overall kinetic control, while subsequent oxidation steps approaches equilibrium was proposed in 1996 (Appello and Postma, 2005). The order of redox reactions in the thermodynamic model is derived from calculation using e.g. H_2 as an electron donor. In reality, the microbes are competing for the energy available from the oxidation of H_2 , acetate and formate. Microbial growth could thus be linked directly to availability and consumption of these species in solution.

Input concentrations from laboratory experiments were used to model the redox sequence that would be likely adding a varying number of moles of carbon to the system. Carbon was only available from woodchips present in the experiment. A series of different number of moles of carbon were added incrementally to the solution in separate simulations. Incremental additions ranged from 0.05 moles to 0.2 moles in 16 steps. The number of moles were divided into the number of steps and added at every point to the resultant solution of the previous step. The results of the simulations were plotted on the same system of axes with observed experimental

results (Figure 59). Figure 59 shows that the woodchip, and woodchip and biochar experiments agree closely to the 37.5 mg C/L incremental addition of carbon in the latter part of the experiment, while they plot closer to the 0.2 mole (150 mg C/L) increments in the start-up period of the experiment.

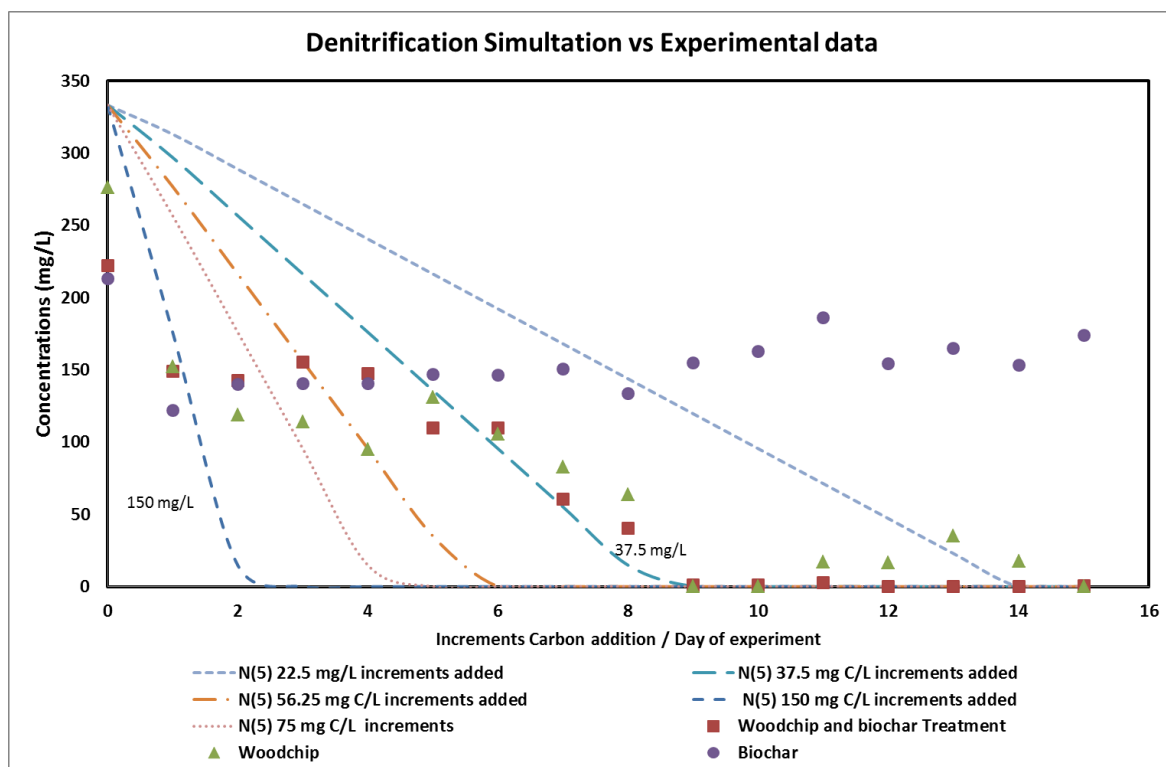


Figure 59: PHREEQC simulation of incremental carbon addition and experimental data from column experiments

This shows that a larger pool of carbon was required and used in the starting few days of the experiment, while smaller amounts are required in the latter part for denitrification. This could also relate to establishment of denitrifying or heterotrophic bacteria during the experiment. Variation from modelled data can be accounted for by considering lack of available carbon in the middle part of the experiment with gradual nitrate removal occurring. DOC removed from reaction by sampling will be

reviewed to establish this. Figure 60 shows the DOC measured in the laboratory for the duration of the column experiment.

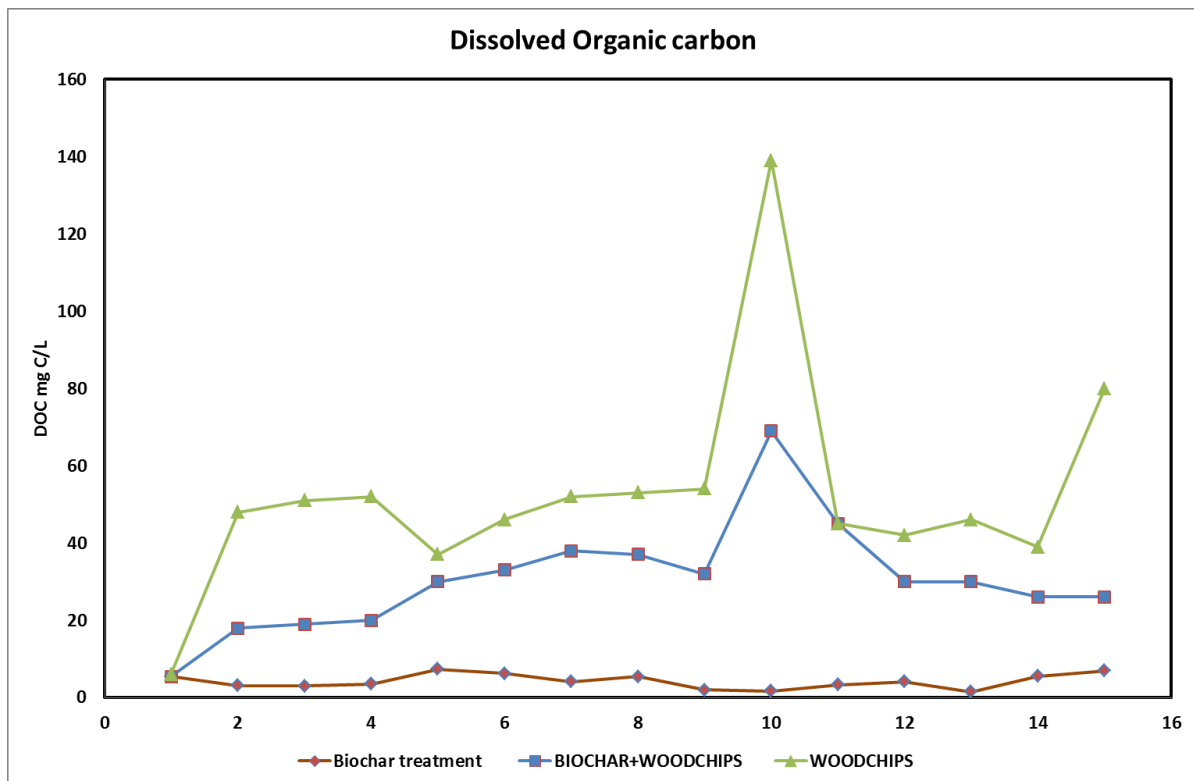


Figure 60: DOC mg/L for the duration of the laboratory column experimental work.

Figure 60 shows that in the start-up period of the experiment, DOC levels in solution are low, indicative when compared to Figure 59 that most of the available DOC was used up by the reactions taking place in the experimental set-up. After the 10th sample was removed, and all nitrates were already reduced, a spike in the DOC occurred in the woodchip and woodchip and biochar treatments. Robertson (2010) showed that DOC escalated to 22 mg/L only after nitrate was reduced to 0.1 mg/L during his study of woodchips of varying age. This marks the onset of sulphate reduction in the system.

5.4 Results and discussion: barrier lifespan

Rates of nitrate removal as determined by the model are steady and reach equilibrium within a determined period, while actual rate of removal during the experiment follow different modelled rates of carbon addition (Figure 59). This is confirmed by the DOC measurements recorded during the experimental procedure (Chapter 2 and Figure 60). Low initial DOC levels are due to large percentage of available DOC being removed by reaction. Figure 59 shows the removal of up to 100mg N/L within the first two sampling events. Sampling events 5 to 9 coincide perfectly with a 37.5 mg C/L incremental addition. Using data for this period, one can determine the total amount of DOC or C made available from the woodchips.

DOC measured during experimental procedure represents the excess of DOC after reaction with nitrate for the particular sampling event, hence one can compute the total carbon released from woodchips for that period to be the sum of incremental C additions and the DOC measured in solution. It is clear that the reaction is nitrate limited, however also that much larger nitrate concentrations can be removed with the amount of carbon that was available for this reaction. Stoichiometric determinations of carbon requirements are calculated based on the total available breakdown products, with the intermittent release of carbon not built into these calculations. Available DOC for reaction can be related to woodchip degradation as the woodchips are the only source of carbon in the experimental set-up. Woodchips were analysed for breakdown products at various times during field experiments (Chapters 2 and 3). The difference in available or excess DOC between the woodchip and woodchip + biochar treatments (Figure 60) can be owed to a smaller

amount of woodchips in the latter treatment as well as the potential for adsorption onto biochar.

Field experimental data showed that initial samples from groundwater contained below 1% organic carbon, hence the introduction of an external carbon source to affect denitrification in the field. Data clearly shows that the woodchips have degraded over the time that it was used in the experiment (Chapter 2 and 3, also Table 20, Table 21, and Table 22). The question is by how much, and what does this mean for the lifespan of slowly degradable carbon sources. DOC was not measured during the field experiment, as it was noted during the first few sampling events that DOC was consumed rapidly. This compares favourably with the results from the laboratory tests, however, it is suspected that once most of the nitrate is removed, or equilibrium is reached, that excess DOC may move across the site and also be oxidized by nitrate present across the site. This agrees with results from Robertson *et al.*, (2005).

As with redox reactions, breakdown of organic matter, in this case woodchips is sequential and has energy barriers to overcome. Microbes aid in the breakdown of woodchips and preferentially use the first available constituents that fall within their energy requirements. Since lignin is resistant to breakdown, carbohydrates become the most important breakdown products that partake in various reactions facilitated by a variety of microbes. A degradation rate can thus be established for woodchips by using samples taken at various times during the experiment. Rates are defined as a change in concentration over a time period. Hence the degradation rate for woodchips would be:

$$\mathbf{Rate} = \frac{\Delta y}{\Delta x} \dots \dots \dots \mathbf{Equation\ 9}$$

Where Δy represents the change in concentration of total carbon and Δx represents the duration over which the concentration change occurred. Since the degradation is likely to be sequential, and samples exposed to different conditions during the experimental procedure undergoing different processes, samples from the same depth/location taken at different times will be compared here. Rates were based on samples collected after 27 months and 35 months of reactivity in the field experiment (chapter 3). Data clearly shows that varying location and processes prevailing contribute to different concentrations (Table 20).

Table 20: Data from woodchip breakdown products analyses

Sample ID	Date of sampling	Ash content (%)	Extratives (Ethanol) (%)	Glucose %	Arabinose %
Lower (27 months)	11/10/2012	3.856	1.060	16.72	0.83
Topsection (27 months)	11/10/2012	14.774	1.926	12.84	0.8
Full core (27 months)	11/10/2012	7.840	1.200	21.49	0.67
Topsection (35 months)	21/6/2013	14.949	1.945	9.95	0.63
Fullcore (35 months)	21/6/2013	13.693	1.390	15.14	0.66
Sample ID	Date of sampling	Acid insoluble Lignin %	Cellulose	Xylose %	Cellobiose %
Lower (27 months)	11/10/2012	31.720	27.900	15.06	7.07
Full core (27 months)	11/10/2012	31.390	34.440	9.57	3.72
Topsection (27 months)	11/10/2012	36.210	36.810	14.92	6.1
Topsection (35 months)	21/6/2013	37.410	37.780	6.61	2.84
Fullcore (35 months)	21/6/2013	30.330	35.470	11.98	5.61

Table 20 shows that woodchips in the lower section of the tank are more degraded than the top section and full-core samples, also that samples from 35 months are more degraded than that collected at 27 months. Literature denotes Lignin to be resistant to biodegradation (Appello and Postma, 2005, Shah *et al.*, 1999, McCrady, 1991). Lignin degradation is primarily an aerobic process, and in an anaerobic environment lignin can persist for very long periods (Van Soest, 1994). For the purposes of finding a barrier lifespan, the lignin percentage will be subtracted from

the total carbon composition of the woodchips. So that biodegradable carbon represents only hemicelluloses and cellulose present and likely to degrade under the anaerobic conditions likely to persist in the field.

Biodegradable Carbon can thus be defined as:

Biodegradable C = (Extractives + Cellulose + Arabinose+ Xylose+ Cellobiose+Glucose+Lignin)

- Lignin.....Equation 10

This would represent the biodegradable fraction of the wood still present. Results of subtracting the lignin content from the total available carbon for degradation are shown in Table 23. The results from Table 21 and Table 22 show the rate of degradation using data for 2 sampling events for woodchip material used during the field experiment. Table 24 takes the results measured in Table 21, Table 22, and Table 23 to determine the length of time that the barrier will still be active for its current composition of available biodegradable carbon. These samples have already been degraded during the experiment as participating in the denitrification and other reactions over time. Table 21 and Table 22 display the results using equation 10 for all determinants of the woodchip analyses. Note here that rates per parameter vary between different samples e.g. the ash content is much higher in the full core sample than the top section which shows that it is more degraded.

Table 21: Rate of change in concentrations for determinants analysed from samples collected in the top section of the tank used in the field experiment. All results for wood components were reported in %; hence the rates calculated here are as % over time.

Top Section of Tank	Change in concentration Top Section	Time (Months)	Rate/month	Rate/day	Rate per hour
Ash content (%)	0.175	8	0.022	0.00073	0.000030
Extratives (water) (%)	0.529	8	0.066	0.00220	0.000092
Extratives (Ethanol) (%)	0.020	8	0.002	0.00008	0.000003
Acid insoluble Lignin %	1.200	8	0.150	0.00500	0.000208
Glucose %	2.890	8	0.361	0.01204	0.000502
Xylose %	2.960	8	0.370	0.01233	0.000514
Arabinose %	0.170	8	0.021	0.00071	0.000030
Cellobiose %	0.880	8	0.110	0.00367	0.000153
Cellulose %	-0.970	8	-0.121	-0.00404	-0.000168
Total Carbon change (excluding lignin)	6.439	8	0.805	0.02683	0.001118

Table 22: Rate of change in concentration for determinants from woodchip samples taken from the full profile of the tank used during the field experiment. All measurements were in %; hence the rates calculated here is % over time.

Full Core	Fullcore con. Change	Time (Months)	Rate/month	Rate/day	Rate per hour
Ash content (%)	5.8527068	8	0.73158835	0.02439	0.001016
Extratives (water) (%)	1.345670653	8	0.168208832	0.00561	0.000234
Extratives (Ethanol) (%)	0.190087158	8	0.023760895	0.00079	0.000033
Acid insoluble Lignin %	1.06	8	0.1325	0.00442	0.000184
Glucose %	6.35	8	0.79375	0.02646	0.001102
Xylose %	2.94	8	0.3675	0.01225	0.000510
Arabinose %	0.01	8	0.00125	0.00004	0.000002
Cellobiose %	0.49	8	0.06125	0.00204	0.000085
Cellulose %	-1.03	8	-0.12875	-0.00429	-0.000179
Total carbon change (excluding lignin)	7.224242189	8	0.903030274	0.03010	0.001254

Relative increase in cellulose and lignin is due to the degradation of other components of the total composition. Absolute values were used to determine the change of ash content and extractives, as these are expected to increase with time, while hemicellulose and cellulose are likely to decrease in concentration over time. Cellulose and lignin levels appear to show an increase over time. Wood science methods measure the relative % as opposed to actual concentration. It is hence possible that a perceived increase in concentration is actually an increase in relative

percentage composition as the % of breakdown sugars shows a decrease. The above rates as well as results of above calculation were used to determine the biodegradable carbon, accounting for lignin's resistance and impact on biodegradability of cellulose and hemicellulose. Bear in mind that the woodchips used have already been reactive in the system for 27 and 35 months respectively. Table 23 shows the results of calculating the biodegradable carbon content based on the results from woodchips analysed.

Table 23: Biodegradable carbon percentage based on species specific analyses of woodchips applying equations 6 and 7

Biodegradable Carbon	Full core (27 months)	Fullcore (35 months)	
Total Carbon %	114.52	106.23	
Lignin % cell wall	31.39	30.33	
Biodegradable Carbon %	83.13	75.90	
Biodegradable Carbon	Lower (27 months)	Topsection (27 months)	Topsection (35 months)
Total Carbon %	116.84	99.39	103.06
Lignin % cell wall	31.72	36.21	37.41
Biodegradable Carbon %	85.12	63.18	65.65

Table 23 shows that more than 60% of biodegradable carbon still remains in the barrier composition after 35 months of reactivity in the field. Hence, about 25 to 30% of degradation has occurred during the 27 and 35 months respectively. The calculation in Table 23 accounts for the lignin in the wood composition which is unlikely to degrade under anaerobic conditions. The results of Table 23 will be used, taking into account the data for wood chips analysed at 35 months as these would give an idea of the degradation possible after the last sampling event. Table 24 shows the result for the lifespan of the barrier determined by using results from calculation in the above tables.

Table 24: Barrier life span calculated based on rate of total carbon degradation and available biodegradable carbon accounting for lignin's unlikely degradation under anaerobic conditions

Degradation % per day	per day	Cbiodegradable % (after 35 months)	%/day	Years
Top section	0.027	65.65	2447.03	6.70
Full Core	0.030	75.90	2521.51	6.91

Lignin concentration of total carbon has a big impact on the degradability of wood chips. The woodchips analysed during this experiment had already been under anaerobic conditions and successfully affected denitrification for 27 and 35 months respectively. Woodchips have undergone some degradation since the time of emplacement as can be seen in chapter 3, where the ash content has dramatically increased in comparison to what is expected in a fresh sample of Eucalyptus wood. Table 24 shows that an additional period of 6.7 to 6.9 years can be expected for the woodchips to be active should the rate of degradation remain constant. Note that these calculations are species and environment specific; however, the method can be used for any tree species. In this experiment *Eucalyptus globulus* was used.

5.5 Discussion and conclusions

Comparing the results of PHREEQC thermodynamic modelling to laboratory results showed that observed rates denitrification and hence of carbon consumption in denitrification showed variability during the experiment. This could be due to a change in the residence/contact time between solution and available carbon (chapter 2) where different residence times were used. However, laboratory data compared favourably with modelled data when incremental carbon additions of about 35mg/l were used. A potential shortfall of the modelling exercise, compared to actual field

conditions is that PHREEQC does not allow for the reactivity of NH_4^+ while the denitrification is being modelled. In other words where conditions are suitable for both reactions to take place concurrently, the model would not be able to predict this simultaneously.

Due to the abundance of woodchips, the reactions were nitrate limited and subsequently sulphate reduction occurred. It was concluded that rates of reaction may vary between start up and completion according to availability of substrate, suitable microbial community as well as contact time. Although modelling of the reaction was a useful exercise for determining the carbon consumption rates in the different parts of the experiment, the use of actual data from the field experimental work with respect to carbon source degradation proved invaluable. The top section and a full core sample of the tank were taken at 27 and 35 months respectively. Results show that the overall rates of degradation are different depending on location in the tank. When considering individual breakdown sugars, the full core sample represents a more degraded composition, and hence shows a higher lignin percentage. Lignin had been described to be resistant to degradation in an anaerobic environment. It is evident that the lignin content of wood chips impacts on its degradability. This alludes to a comparative analysis of tree species composition prior to use as a carbon source for denitrification. Calculations to determine the lifespan of the woodchips used during the field experiment is based on the degree of degradation that had already taken place. It is evident that the position of the sample in the treatment tank; and the difference in conditions at different positions all contribute to the eventual barrier life span. Barrier life span is likely to be species or composition specific, as well as location specific. Results showed that woodchips in the lower part of the tank had been the most degraded, while the top section shows

the least degradation. According to calculations, the barrier can still last an additional 6.9 years before fresh carbon needs to be added to the system. This makes the barrier useful for a total period of up to 10 years before fresh woodchips would be required. These results are affected by the lignin content of the wood compared to the other more degraded components. This calculated life span compares favourably with Schipper *et al.* (2005) who had a wall operational for 7 years before requiring maintenance, but falls short of Robertson and Cherry (1995) and Robertson *et al.*, (2008) that showed a barrier to be operational for 15 years. Robertson *et al.*, (2009) also used coarse wood chip particles in the core of their wood particle reactor which maintained its hydraulic conductivity over 7 years of operation. Jaynes *et al.*, (2008) in their study showed at least 5 years of successfully denitrifying agricultural drainage by means of using woodchips. Robertson (2010) observed that reaction rates were approximately 50% lower in “older” reactive media when testing woodchip media of varying age.

Groundwater flow is very slow compared to most laboratory column setups, and although degradation rates show a relatively short period of barrier life, the DOC yielded from the woodchips is likely to move from the tank during rainfall periods to denitrify areas further downstream from the tank.

This work has demonstrated that coarse and mixed woodchips size successfully denitrified groundwater for a period of 37 months in the field. Degradation rate calculations, and subsequent life span calculations based on the composition after 37 months showed that the barrier can denitrify groundwater for an additional 6.7 to 6.9 years. A barrier life span of approximately 9.8 to 10 years can be expected for the particular degradation rate and woodchip composition.

5.6 Recommendations

The following is recommended for future field experimental work, comparative analysis of varying tree species to determine lignin content, as this represents the non-biodegradable fraction of the wood media and is not likely to degrade under anaerobic conditions.

Degradation of wood is sequential, and starts with hemicelluloses, celluloses and lignin remains as non-degradable fraction especially in an anaerobic environment. More time series samples of woodchip degradation would possibly yield better results, especially since laboratory experimental results showed different rates for different contact times.

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6 CONCLUSIONS AND RECOMMENDATIONS

This study investigated the relationship between barrier thickness/concentration, retention time, flow paths and nitrate removal efficiency in barriers using data obtained in field and laboratory experiments as well as fundamental equations and available derived data or equations from other studies. Inevitably, this study aimed to determine the barrier lifetime, or an approximate length during which woodchips can be used and is likely to be effective. This study was done bearing in mind that nitrate pollution is prevalent in some rural areas in South Africa. The methods selected was based on criteria of having low maintenance, robust and cheaply available carbon sources, which would likely occur or be available close to these rural areas.

6.1 Laboratory studies

Laboratory studies were done using cheaply available carbon material (woodchips from *Eucalyptus globulus*) common at the site where the technology was tested in the field. The grain size was variable and allowed for high hydraulic conductivity and permeability. Sand was used in the layering in column experiments as it provides extra filtering capacity to pollutants, however, would not likely sorb to sand surfaces. Woodchips, Biochar and a mixture of woodchips and biochar were evaluated and compared in terms of their nitrate reducing ability, sorption/reactions and efficiency as carbon sources. The main results of this section showed that biochar on its own would not be a suitable carbon source for denitrification as its composition has only a 19.9% extractives, which would be available for reaction. Incomplete denitrification

occurred in the biochar treatment. Woodchips and the mixture of the biochar and woodchips were very effective at reducing nitrate within only 10 days of using a 24 h residence time. Sorption curves showed that there were definitely different mechanisms of reaction between the biochar and woodchips, with the mixture showing overlap with both treatments. Biochar mixed with woodchips increased the efficiency of nitrate removal, which may show some promise for use in future work, with regard to nutrient control in fields where this is required e.g. storm water nutrient loads, farming practises to prevent nitrate leaching to groundwater, or even waste water treatment. A contact time of 24 to 72 h seems to be sufficient to achieve a good rate of denitrification and even total removal of nitrate. Barriers should thus be designed taking this type of residence time into account. Flow through tank experiment showed that influent rate plays an important role in the degree to which water mixing and denitrification could occur. The initial denitrification during the first 10 days was due to available carbon in the tank, and low concentration of nitrate entering the tank. It was calculated that the required wall carbon concentration should have been about 3 times more to denitrify all water passing through the tank. The tank experiment also showed that the influx of oxygen can inhibit denitrification; however, denitrification can occur at low oxygen concentrations.

6.2 Field implementation studies

Excavation and emplacement of the barrier was done bearing in mind that the hydraulic conductivity of the tank and woodchips needed to be greater than that of the water-bearing lithologies to ensure flow towards and through the tank. The water-

bearing lithologies contained a mixture of coarse sand and clay material, hence porosity ranged between 25% and 60%. Even though the porosity of clays can be high, the permeability is not. The coarse sand present in the subsurface would most likely be preferred by fluid movement; the hydraulic conductivity of sand ranges between 10^{-2} and 10^{-7} m/s. During the 35 months of sampling at the site, it was noted that the borehole yield responses varied across the site, where boreholes upstream from the tank had to be pumped intermittently allowing the water to gather in the borehole, while downstream boreholes could be pumped continuously for 30 minutes without any problems with yields. This signifies that the permeability and hydraulic conductivity may be different for the area downstream or east of the emplacement position to that upstream or west of the tank. The main results from field work include some interesting findings for the site. Due to nitrogen stored in the soil, cumulative and or high intensity rainfall events caused a spike of nitrate across the site. What was even more interesting was the fact that nitrate levels at and close to the tank showed a rapid decline in nitrate levels shortly after these events (Figure 50, Chapter 4). This indicated that the treatment method was indeed working for the site. There were two high rainfall periods during the field experiment, and effective reduction in nitrate levels occurred after both. The system was however nitrate limited as the onset of sulphate reduction occurred after nitrate was removed. This was detected when the colour and smell of samples were characteristic of sulphate reduction. This was therefore included in the sampling and analyses regime. Similarly for iron and manganese, but these were quickly removed from solution as their concentrations were low in the groundwater. What was remarkable was that due to the higher rate of movement of water in the downstream area of the tank, water containing DOC could migrate from within the tank in the groundwater stream and reduce nitrate

further away from the tank. Some boreholes showed seasonal variations as well as an overall decreasing trend in nitrate concentrations. It was thus concluded that the woodchips of variable size was sufficient to affect denitrification at the site for the 35 months that it was monitored. Samples from the field experiment were used to determine the degree to which the woodchips were degraded as well as to determine what the possible lifespan of the barrier would be. Woodchips showed a degree of degradation compared to the composition of woodchips that were exposed to natural degradation as well as fresh woodchips with much higher ash contents showing the degree of degradation as well as reduced concentrations of glucose, arabinose, cellobiose, and xylose. The field experiment shows that the method could be applied successfully in rural areas with limited maintenance and at least monthly monitoring. With regard to barrier design, high permeability barriers show great promise with respect to ensuring flow occurs preferentially into the barrier. Penetrating the total depth up to bedrock was not achieved in this experiment; however, results were still positive overall. The coarse nature of the woodchips eliminated the potential for clogging with iron precipitates, also iron and manganese concentrations were fairly low at the start-up of the experiment.

6.3 Barrier lifespan and rates

In carbon deficient environments, natural denitrification is carbon limited and the denitrification reaction does not remove all nitrate and nitrite from the system. The gradual decreases in oxygen and nitrate with depth in aquifers indicates that

reduction rates for oxygen and nitrate are slow. The reactivity of organic matter is probably the overall rate controlling factor.

Models are useful in showing rates of reactions and likelihood that particular minerals would precipitate or dissolve under particular specified conditions. For the purposes of this work, modelling was used to indicate the reactive pathways that may be followed in the field as well as to relate mineral precipitation to monitoring regime. However, during actual field experience, iron and manganese were present in small quantities and would probably not lead to barrier degradation. This would however be useful to monitor should concentrations and stores in soil be large.

Bearing in mind that reactivity of organic matter is probably the overall rate controlling factor; one needs to establish the rate of degradation of the carbon source during field work to establish actual rates as well as to determine the barrier lifespan; as this is an overall control on the rate of reaction. The field measurement of degradation of carbon represents an overall rate for all processes that may have occurred. It was noted that the rate for particular sugars breakdown were higher and one would thus consider those to be the constituents that broke down first to participate in reactions within the treatment area. Determinations of rate of degradation was done comparing the concentrations for samples collected after 27 months of field experimental work and those collected after 35 months of field work. The degradation rate was taken as an overall carbon degradation rate. For the purposes of calculating barrier lifespan, the lignin content was subtracted from the total carbon content of the woodchips as according to literature; lignin is unlikely to degrade in an anaerobic environment. Degradation rate for samples from the top section of the tank was approximately 0.026 % per day and about 0.030 % per day for samples taken as a full core of the tank. These rates as well as the calculated

available biodegradable carbon were used to determine the lifespan of the woodchips in the treatment zone.

With about 65% and 75% biodegradable carbon remaining after 35 months, the calculated lifespan for the barrier was about 6.7 and 6.9 years respectively. This implies that this treatment method can be used for 9.8 years to 10 years. The removal or considerable lowering of NH_4^+ concentration at the site points to additional sorption mechanisms or conversion of NH_4^+ to NO_3^- when brief aerobic conditions occur during summer and potentially fresh recharge events (big rainfall events) and subsequent denitrification. If rates of reaction and degradation decline as implied in literature, then the lifespan of the barrier may be even greater than calculated.

Permeable reactive barriers have been tested in Canada, the US and Europe at various scales. The climatic conditions, soil composition and tree species and all processes controlled by these factors are unique to South Africa. This work thus represents testing field in situ denitrification for the first time in South Africa. Positive results were achieved at the site, with general trend in nitrate levels declining at the site.

Even though the reaction is nitrate limited at times, the method holds added benefits of reducing sulphate concentrations which may also be a potential impacting chemical compound in areas. The removal or reduction of the NH_4^+ concentration was not expected, however this holds promise for certain areas.

In field implementation, it is important to study the experimental site well in advance. Minimal available data for an area can affect the design and monitoring regimes.

Woodchip degradation can be monitored as a time series using non-disturbing techniques as digging may disturb the reaction zone and introduce oxygen into the environment.

This type of treatment method can be applied to storm water nutrient level controls as well as waste water treatment as demonstrated by a few researchers. It should also be suitable as a low cost robust technique require little maintenance for at least almost 10 years; however, monitoring is essential as rates may vary depending on the external parameters at a particular site.

Rainfall records, water levels, depth of treatment zone, specie of wood and its initial composition as well as water and soil compositions are important parameters in order to aid your understanding of the site.

This method is site specific, woodchip biodegradable carbon composition specific and environment specific. When testing it, a site characterisation is of utmost importance.

7 RECOMMENDATIONS AND FUTURE WORK

This field experiment was done on a small scale, a larger scale test using a horizontal wall intercepting plume water to a greater depth would be recommended for future work.

Limitations of this study included incomplete study site historical data for seasonal variations in concentrations and water table depth prior to the implementation of the barrier. At least one year of monitoring of the site prior to implementation of denitrification technology is recommended.

In addressing the needs of rural South Africans, this method showed great promise for nitrate, sulphate and ammonium removal at the test site. It is recommended that it be tested in a rural community where water is plentiful but currently not useable.

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**APPENDIX A:
DATA FROM LABORATORY COLUMN
EXPERIMENTS**

Sample ID	Sample_Date	NH ₄ ⁺	NO ₃ ⁻ +NO ₂ ⁻	NO ₂ ⁻	NO ₃ ⁻	DOC	SO ₄ ²⁻	PO ₄ ⁻ -P	Alkalinity
	24/07/2013		213	0	213				
Biochar treatment	25/07/2013	45	122	0.2	121.8	5.4	199		
Biochar treatment	26/07/2013	50	140	0.2	139.8	3.1	195		
Biochar treatment	27/07/2013	47	141	0.3	140.7	3	193		
Biochar treatment	28/07/2013	51	141	0.5	140.5	3.5	192		
Biochar treatment	29/07/2013	47	148	1.1	146.9	7.3	208		
Biochar treatment	30/07/2013	51	148	1.6	146.4	6.2	194		
Biochar treatment	31/07/2013	53	155	4.6	150.4	4.1	197	0.18	
Biochar treatment	01/08/2013	50	140	6.3	133.7	5.4	202	0.33	
Biochar treatment	2013/08/05	37	161	6	155	2	182	0.43	161
Biochar treatment	2013/08/08	50	165	2.5	162.5	1.7	181	0.42	158
Biochar treatment	2013/08/12	48	189	2.9	186.1	3.3	179	0.52	150
Biochar treatment	2013/08/19	41	160	5.5	154.5	4.1	182	0.77	144
Biochar treatment	2013/08/22	43	168	3	165	1.5	185	0.94	145
Biochar treatment	2013/08/26	45	157	3.9	153.1	5.5	179	0.51	144
Biochar treatment	2013/08/29	44	181	7.3	173.7	6.9	179	1.3	137
Water in tank	24/07/2013		222	0	222				
BIOCHAR+WOODCHIPS	25/07/2013	56	149	0.2	148.8	5.4	228	0	
BIOCHAR+WOODCHIPS	26/07/2013	53	149	6.5	142.5	18	222	1.4	
BIOCHAR+WOODCHIPS	27/07/2013	59	158	2.8	155.2	19	221	0.58	
BIOCHAR+WOODCHIPS	28/07/2013	62	148	0.9	147.1	20	226	0.4	
BIOCHAR+WOODCHIPS	29/07/2013	60	114	4.5	109.5	30	230	0.48	
BIOCHAR+WOODCHIPS	30/07/2013	61	113	3.2	109.8	33	226	0.38	
BIOCHAR+WOODCHIPS	31/07/2013	64	61	0.5	60.5	38	229	0.63	
BIOCHAR+WOODCHIPS	01/08/2013	55	42	1.8	40.2	37	228	0.47	
BIOCHAR+WOODCHIPS	2013/08/05	35	1.2	0	1.2	32	143	0.79	817
BIOCHAR+WOODCHIPS	2013/08/08	42	1	0	1	69	128	0.84	1246
BIOCHAR+WOODCHIPS	2013/08/12	34	2.7	0.2	2.5	45	144	0.76	1191
BIOCHAR+WOODCHIPS	2013/08/19	39	0.1	0.1	0	30	103	0.44	1246
BIOCHAR+WOODCHIPS	2013/08/22	32	0	0	0	30	63	0.51	1066
BIOCHAR+WOODCHIPS	2013/08/26	53	0.1	0	0.1	26	42	1	1315
BIOCHAR+WOODCHIPS	2013/08/29	48	0.5	0	0.5	26	39	1.1	1468
Water in tank	24/07/2013		276	0	276				
WOODCHIPS	25/07/2013	55	152	0.1	151.9	6	225	0	
WOODCHIPS	26/07/2013	55	124	5.2	118.8	48	229	1.8	
WOODCHIPS	27/07/2013	55	114	0.2	113.8	51	228	0.81	
WOODCHIPS	28/07/2013	47	95	0.1	94.9	52	224	1.1	
WOODCHIPS	29/07/2013	69	132	1.1	130.9	37	233	0.14	
WOODCHIPS	30/07/2013	60	106	0.3	105.7	46	230	1.2	
WOODCHIPS	31/07/2013	48	83	0.3	82.7	52	236	1.4	
WOODCHIPS	01/08/2013	42	64	0.3	63.7	53	231	1.3	
WOODCHIPS	2013/08/05	43	0	0	0	54	166	0.5	1357
WOODCHIPS	2013/08/08	47	0	0	0	139	143	0.44	1412
WOODCHIPS	2013/08/12	46	21	4.1	16.9	45	180	0.48	1163
WOODCHIPS	2013/08/19	36	18	1.8	16.2	42	220	0.48	1135
WOODCHIPS	2013/08/22	52	41	6.1	34.9	46	220	0.87	1191
WOODCHIPS	2013/08/26	42	18	0.3	17.7	39	219	0.9	1121
WOODCHIPS	2013/08/29	35	0.1	0	0.1	80	157	0.5	1274

Cells with 0 values mean that the parameter was below the detection limit of the analytical method.

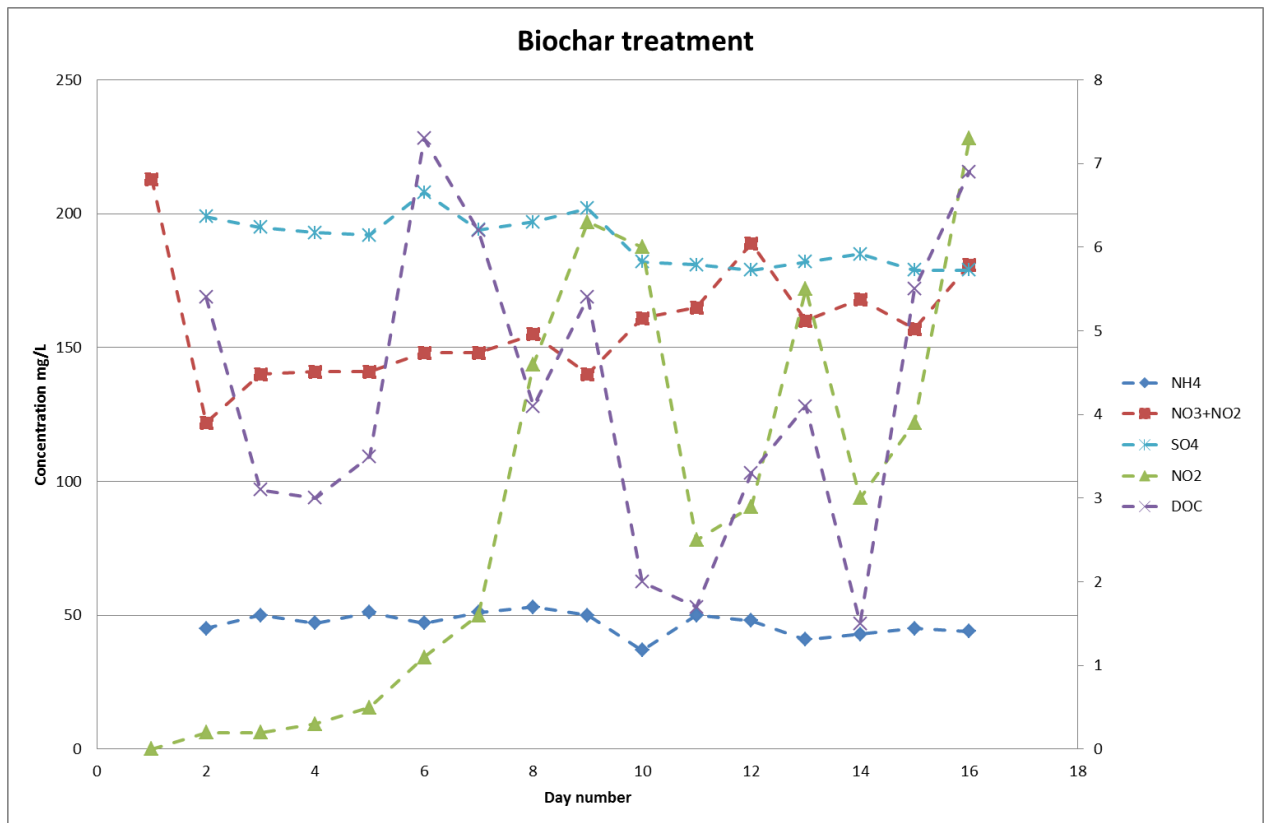


Figure 61: biochar treatment, showing incomplete denitrification with NO_2^- levels increasing in solution

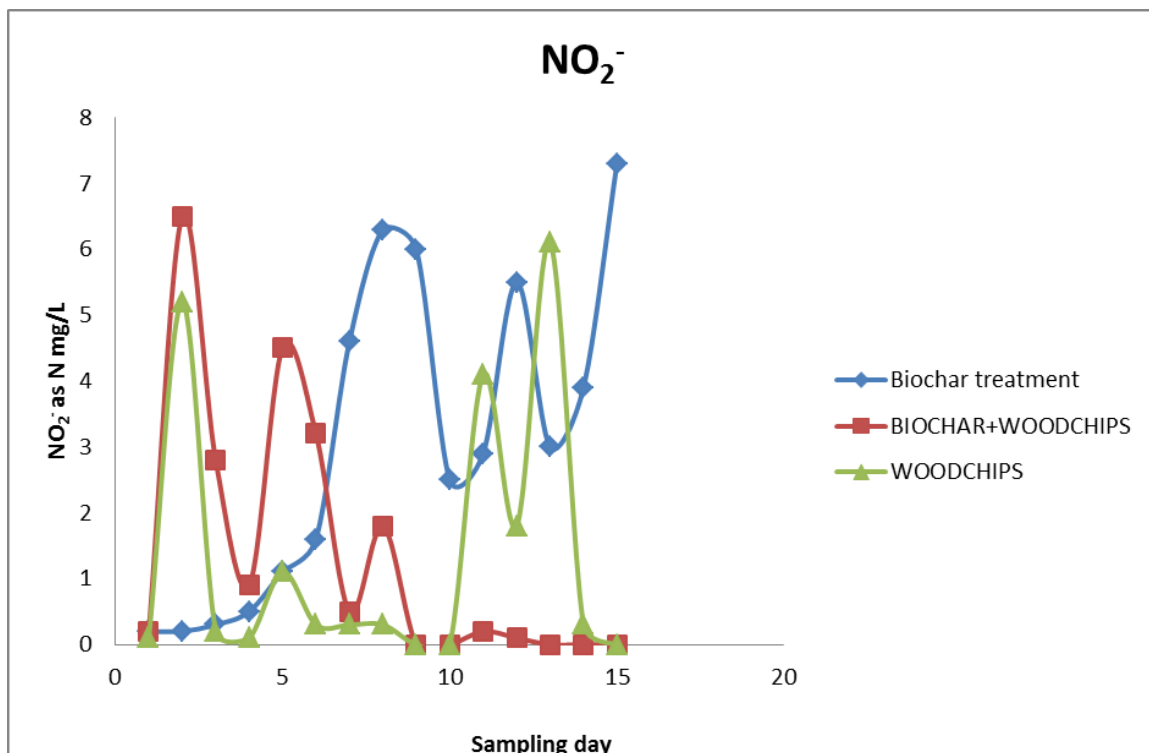


Figure 62: NO_2^- production in various treatments

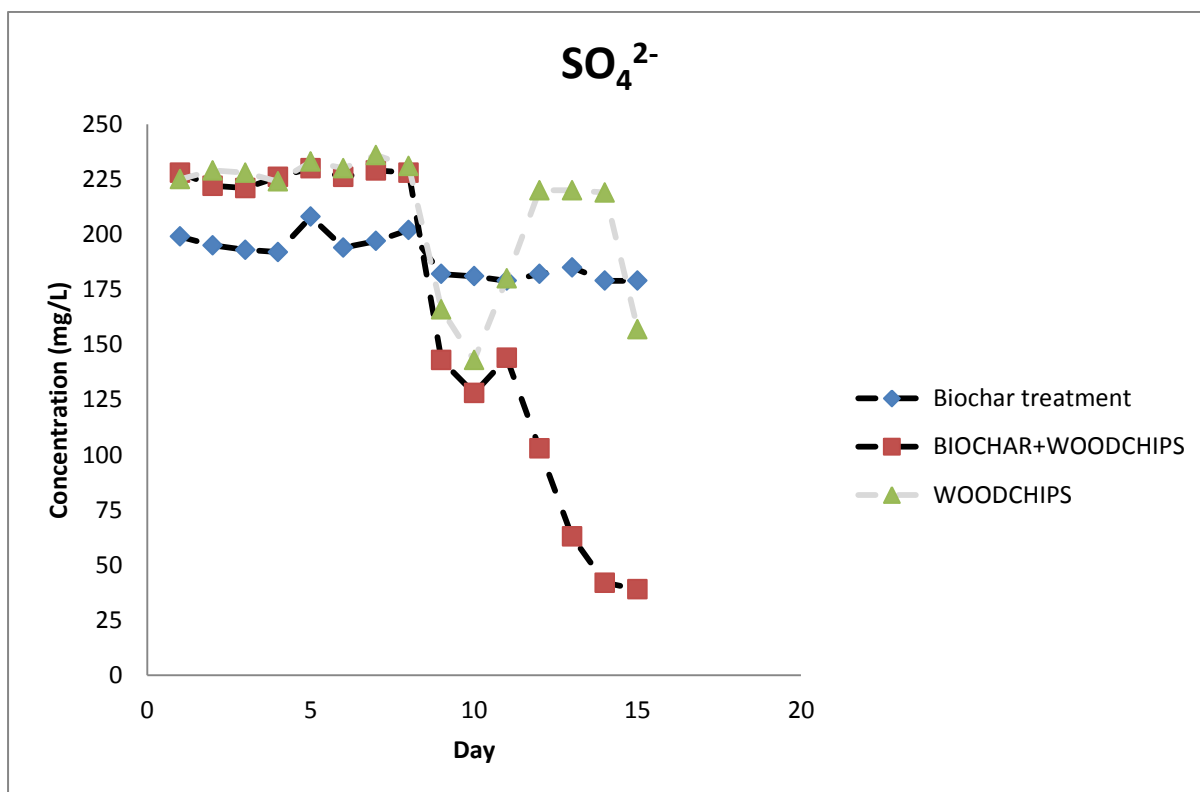


Figure 63: Sulphate concentrations in various treatments

APPENDIX

B:

Data collected during field experiments

Soil Chemistry - samples collected during excavation for tank emplacement

Table 25: Particle size distribution for soil at the tank emplacement area

Depth in m	%sand	% clay	% silt
0-0.300	84	8	8
0.30-0.60	81	6	13
0.6-1.35	93	4	3
1.35- 1.4	93	18	12
1.4-3.0	70	4	3

Table 26: Concentration of chemical species in the soil profile in mg/kg.

Depth in m	Ca (mg/kg)	Mg (mg/kg)	Na (mg/kg)	K (mg/kg)	S (mg/kg)
0-0.300	2238	209	40	46	19.3
0.30-0.60	2744	101	72	52	150.5
0.6-1.35	589	32	44	19	90.2
1.35-1.4	3141	62	57	30	77
1.4-3.0	2621	36	30	6	50.2

Table 27: Metal ion concentration in the soil profile at the location of the tank

Depth in m	Cu	Zn	Mn
0-0.300	0.27	0.52	3.1
0.30-0.60	0.72	1.65	4.6
0.6-1.35	0.92	2.39	1.8
1.35-1.4	0.21	0.29	2.3
1.4-3.0	0.24	2.56	12.6

Table 28: % Carbon in the soil profile at the location of the tank

Depth in m	% C
0-0.300	0.6
0.30-0.60	1.04
0.6-1.35	0.12
1.35-1.4	0.08
1.4-3.0	0.04

Table 29: pH and cation exchange capacity

Depth in m	pH	CEC
0-0.300	7.8	13.2
0.30-0.60	8	15
0.6-1.35	8	3.5
1.35	8.2	16.5
1.4-3.0	9	13.5

Initial Groundwater Samples for the site**Borehole Positions at Somerset West site**

BH name	X	Y
ANBH1	18.80708	34.08975
ANBH2	18.8071	34.8912
ANBH3	18.80765	34.08915
ANBH4	18.8066	34.08944
ANBH5	18.80654	34.08955
ANBH6	18.065	34.08973
ANBH7	18.8067	34.0901
ANBH9	18.80606	34.08979
ANBH10	18.80623	34.09015

Summary statistics per borehole for the duration of monitoring

	Unit	Max	Min	AM	Q25	Q50	Q75	# Exc	# ND	Standard deviation	Number of Samples
BH1											
SO ₄ ²⁻	mg/l	854	635	751.9	685.5	746	812	0	0	76.3	11
pH		6.9	6.4	6.7	6.6	6.7	6.7	2	0	0.142	13
Cond	uS/cm	480	319	398.7	389	410	418	0	0	43.7	13
NH ₄ ⁺	mg/L	155	3.1	64.5	36	58	97.2	0	0	42.5	13
NO ₃ ⁻	mg/L	393	117	207.7	145	175	213	13	0	88.7	13
BH10											
SO ₄ ²⁻	mg/l	80	46	63.2	58	60	72	0	0	13.2	5
pH		7.2	6.8	7	6.9	6.9	7.1	0	0	0.16	7
Cond	uS/cm	120	97	112	109	115	117	0	0	8	7
NH ₄ ⁺	mg/L	7.8	0	2.1	0	0	3.4	0	0	3	7
NO ₃ ⁻	mg/L	45	6	23.2	14.3	18	32.5	7	0	14.4	8
BH2											
SO ₄ ²⁻	mg/l	640	367	506.8	450.8	510	569.3	0	0	79.6	12
pH		6.7	4.6	5.9	5.9	6	6.1	13	0	0.455	14
Cond	uS/cm	265	130	221.2	198.5	216.5	253.5	0	0	37.6	14
NH ₄ ⁺	mg/L	69	3.7	36.3	26	37.8	48	0	0	18.3	14
NO ₃ ⁻	mg/L	183	0	134.6	101.5	146	179	14	0	51.1	15
BH3											
SO ₄ ²⁻	mg/l	594	67	364.6	259	305.5	487.3	0	0	145.4	26
pH		6.9	6.2	6.4	6.3	6.4	6.5	24	0	0.184	28
Cond	uS/cm	193	67	126.4	100	107.5	155.8	0	0	34.1	28
NH ₄ ⁺	mg/L	25.7	0	2.6	0	0.535	2	0	0	5.3	28
NO ₃ ⁻	mg/L	271	15	49.6	29.9	36.8	52	28	0	48.4	28
BH4											
SO ₄ ²⁻	mg/l	683	135	516.9	484	524	602.3	0	0	117.5	28
pH		6.9	6.4	6.7	6.6	6.6	6.8	7	0	0.138	29
Cond	uS/cm	494	149	378.2	365	392	416	0	0	72.6	29
NH ₄ ⁺	mg/L	233	0	114	75	105	152	0	0	52.6	29
NO ₃ ⁻	mg/L	496	76.5	256.8	220	265.3	297	29	0	84.4	29
BH5											
SO ₄ ²⁻	mg/l	555	200	377.3	343	378.5	433	0	0	78.9	28
pH		7.1	6.5	6.7	6.6	6.7	6.8	2	0	0.154	30
Cond	uS/cm	525	164	412.6	373.8	439	474.5	0	0	82.4	30
NH ₄ ⁺	mg/L	258	0	155.5	118.5	153	208.1	0	0	66.4	30
NO ₃ ⁻	mg/L	499	81.5	315	257	315.5	373.8	30	0	98	30
BH6											
SO ₄ ²⁻	mg/l	413	120	298.9	281.5	297.5	333.5	0	0	61.6	28
pH		7.1	6.5	6.7	6.6	6.7	6.8	3	0	0.14	30
Cond	uS/cm	536	184	411.4	383	405.5	466	0	0	75.6	30
NH ₄ ⁺	mg/L	228	2.4	136.6	115.4	128.5	169.3	0	0	55	30
NO ₃ ⁻	mg/L	529	85.5	315.4	264.2	319	363.3	30	0	97.8	30
BH7											
SO ₄ ²⁻	mg/l	400	168	247.5	205.5	231	233.5	0	0	75.4	11
pH		7.7	6.6	6.9	6.8	6.9	6.9	0	0	0.282	14
Cond	uS/cm	456	110	196.6	142.3	148	224.8	0	0	99.2	14
NH ₄ ⁺	mg/L	105	0	12.4	0	4.5	8.3	0	0	24.9	20
NO ₃ ⁻	mg/L	240	0	85.7	60	64	102	15	0	65.7	17
BH9											
SO ₄ ²⁻	mg/l	1396	462	854.5	619.3	875	1040.5	0	0	265.3	28
pH		7.1	6.5	6.7	6.6	6.7	6.8	3	0	0.153	29
Cond	uS/cm	505	250	430.9	411.8	454.5	475.3	0	0	64.8	28
NH ₄ ⁺	mg/L	164	0	73.2	16	55.5	122.2	0	0	58.3	30
NO ₃ ⁻	mg/L	451.3	11	229.7	169.8	232.8	321.3	30	0	122.4	30
BHE											
SO ₄ ²⁻	mg/l	1972	7	559.9	67.5	336	788.5	0	0	634.9	19

pH		7.4	6.6	6.9	6.8	6.9	7	0	0	0.203	21
Cond	uS/cm	668	95	340.7	216	296	395	0	0	165.9	21
NH ₄ ⁺	mg/L	28	0	5	0.2	3	6.5	0	0	6.5	21
NO ₃ ⁻	mg/L	293	0	45.9	0.05	1	35.1	7	0	84.1	21
BHT	Unit	Max	Min	AM	Q25	Q50	Q75	# Exc	# ND	Standard deviation	Number of Samples
SO ₄ ²⁻	mg/l	916	24	113.7	29.8	34.5	83	0	0	199.3	28
pH		7.8	6.3	6.8	6.6	6.8	6.9	3	0	0.294	30
Cond	uS/cm	779	412	667.8	643	691	720	0	0	83.6	29
NH ₄ ⁺	mg/L	423.9	0	66.9	24	64	79.3	0	0	74.1	30
NO ₃ ⁻	mg/L	202	0	10.3	0.133	0.825	5.8	5	0	36.7	30
BHW	Unit	Max	Min	AM	Q25	Q50	Q75	# Exc	# ND	Number of Samples	
SO ₄ ²⁻	mg/l	989	34	425.2	291	322	499.5	0	0	22	
pH		7.5	6.6	7	6.8	7	7.1	0	0	39	
Cond	uS/cm	369	101	234.8	208.5	214.5	260	0	0	24	
NH ₄ ⁺	mg/L	436.8	0	86.8	5	17	129	18	0	27	
NO ₃ ⁻	mg/L	21	0	4.9	0.193	2.6	6.5	0	0	24	

Where #Exc refers to the number of time the SANS241 standard is exceeded, and #ND refers to the number of non-detects.

Box and Whisker Plots for Site chemistry

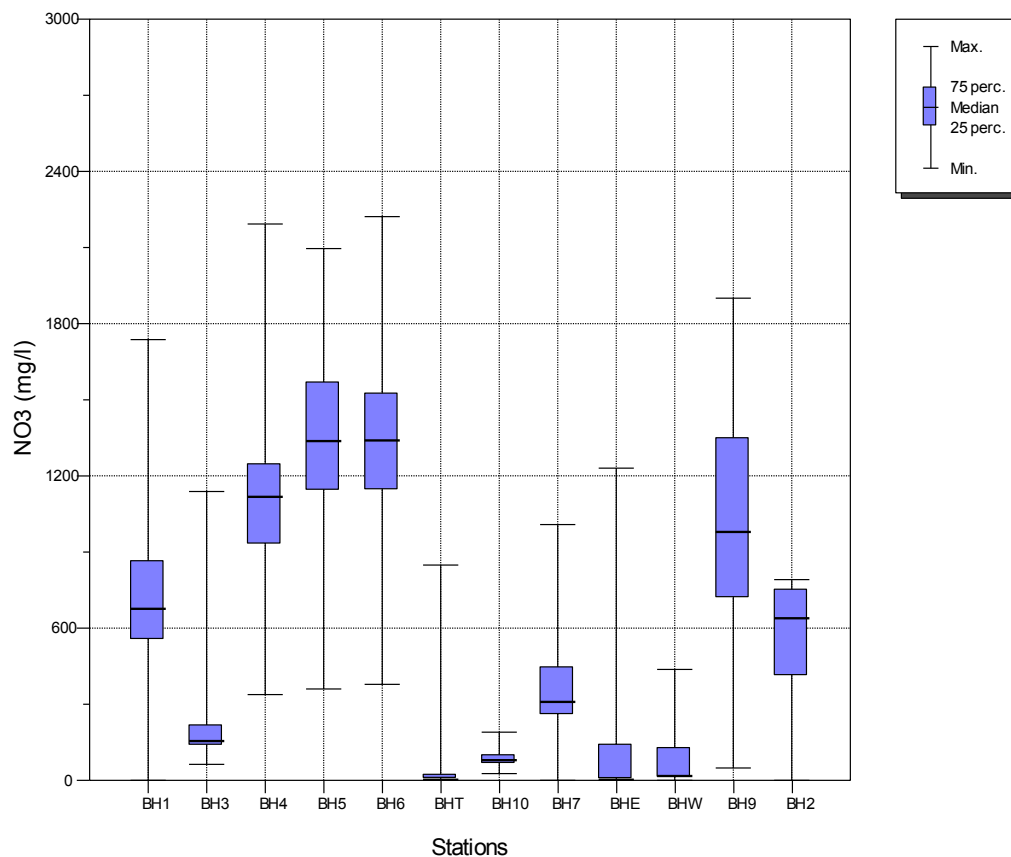


Figure 64: Box and whisker plots of nitrate concentrations at the Somerset West site for the duration of the experiment

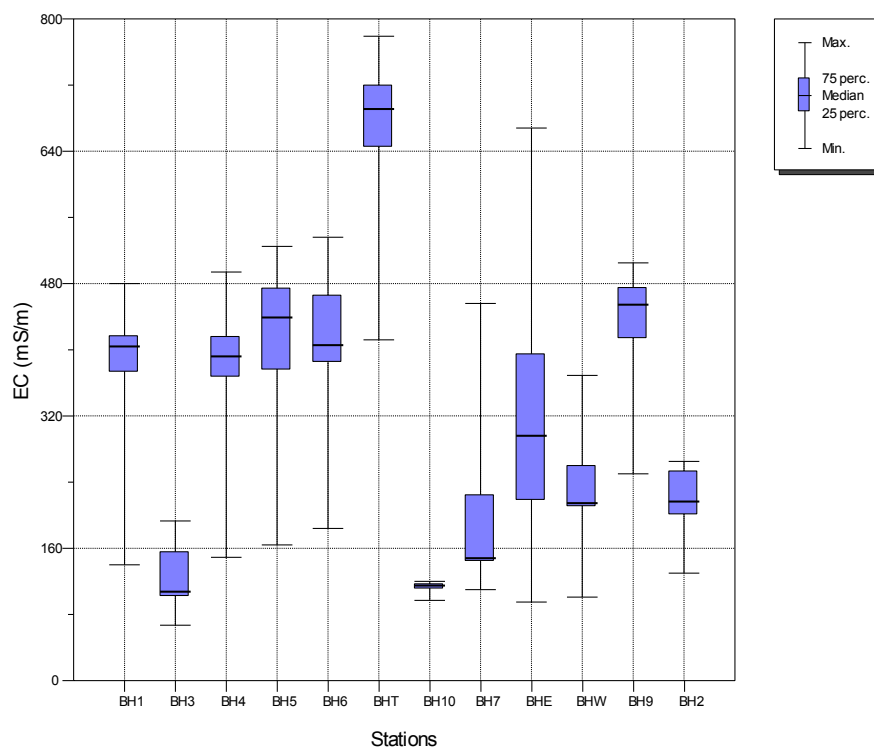


Figure 65: Box and whisker plots for EC at the Somerset West site for the duration of the experiment

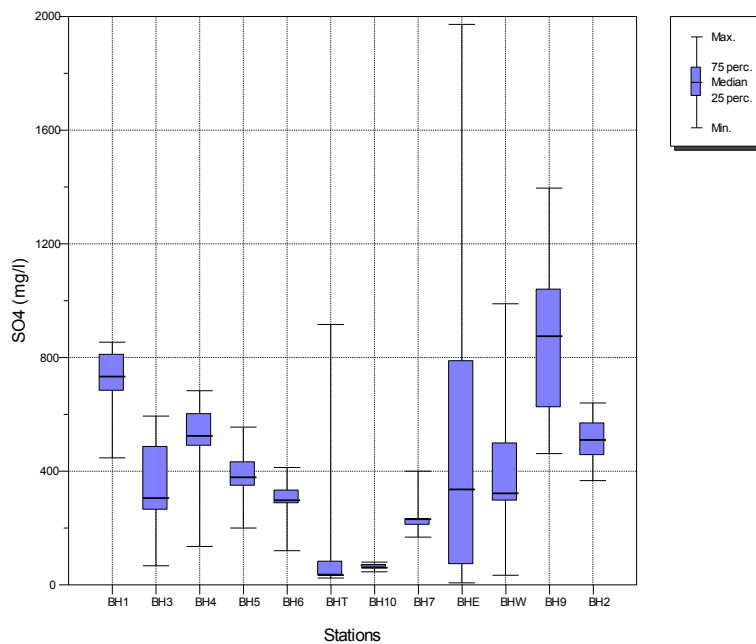


Figure 66: Box and whisker plots of Sulphate concentrations at boreholes at the Somerset West site

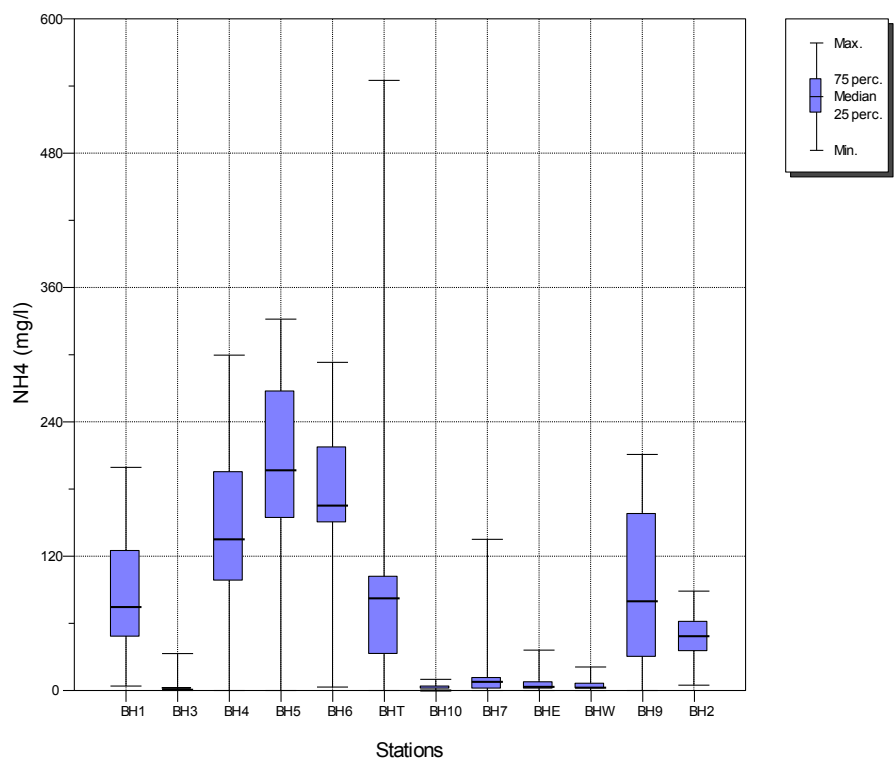


Figure 67: Box and whisker plots of NH_4^+ levels across the Somerset West site for the duration of the experiment

APPENDIX
Modelling with PHREEQC

C:

Conceptual model for woodchips breakdown

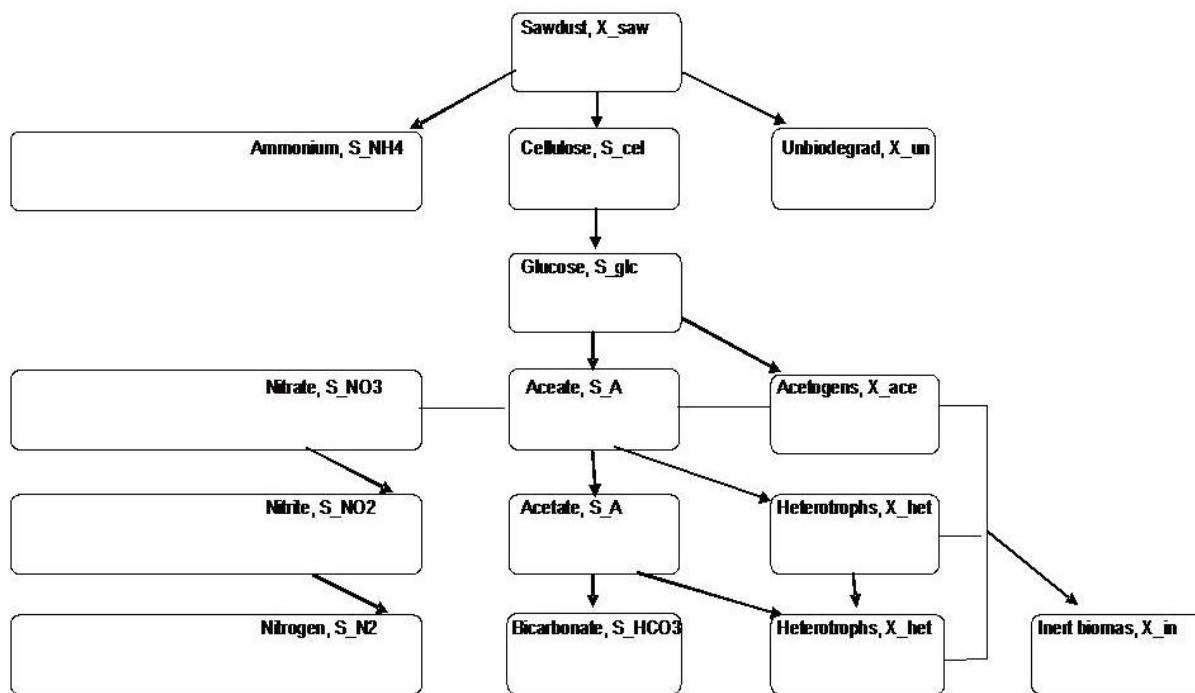


Figure 68: Conceptual model for woodchips breakdown, after Israel (2009)

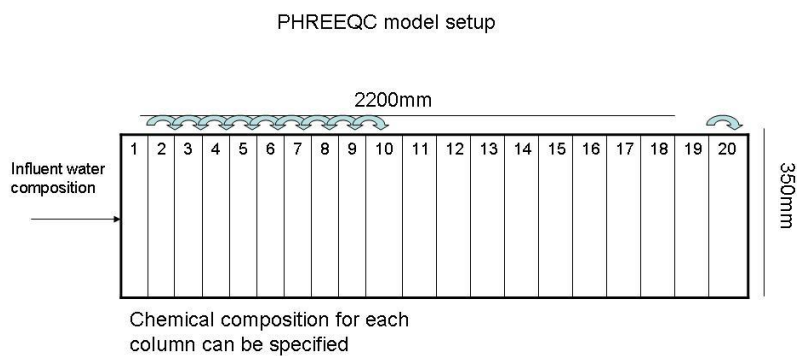


Figure 69: PHREEQC model set up (from Israel, 2009)

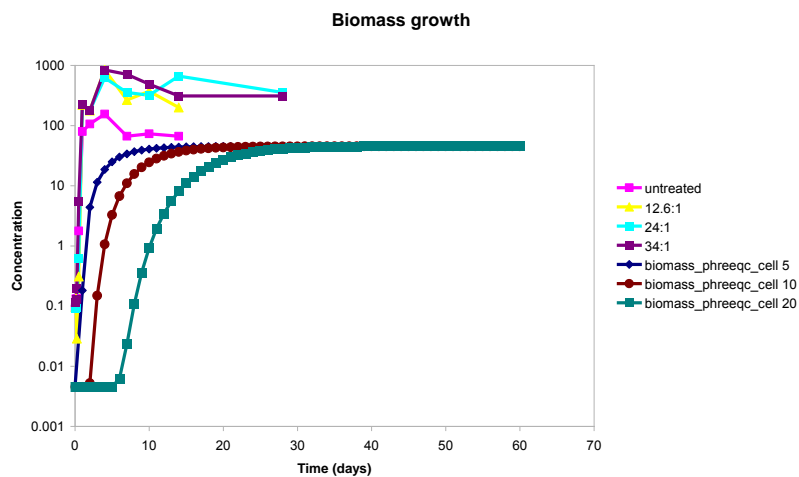


Figure 70: Biomass growth as modelled by PHREEQC compared to actual measurements during Israel (2007)

Example PHREEQC input file for simulation 1 using 0.03 moles of Carbon added over 16 steps

Solution 1

units mg/L

ph 6

Na 150

K 29

Mg 39

Ca 222

Cl 150

N(5) 222

Amm 56

S(6) 199

Alkalinity 320

O(0) 10

Fe 0.01

Mn 0.19

Reaction 1

C; 0.03 moles in 16 steps

INCREMENTAL_REACTIONS true

USER_GRAPH

headings C O2 NO3 Mn Fe S(+6)

axis_titles "Carbon added, mol/L" "Concentration, mol/L"

selected_output

file pHd0_03_in_16.csv

Totals N(5) N(3) Mn(2) Fe(2) S(6) Amm O(0)

units mg/L

-Alkalinity

-Ph

-Time

punch

increments

USER_GRAPH

-start

10 graph_x step_no

20 graph_y tot("O(0)"/2*1000, tot("N(5)")*1000, tot("Mn(2)")*1000, tot("Fe(2)")*1000,
tot("S(6)")*1000

-end

END

Example Output from PHREEQC

sim	state	soln	step	pH	pe	Alk	N(5)	N(3)	Mn(2)	Fe(2)	S(6)	Amm	O(0)
1	i_soln	1	0	6	4	0.006403	1.59E-02	0.00E+00	3.46E-06	1.79E-07	2.07E-03	3.11E-03	6.26E-04
1	react	1	1	6.05477	13.3797	0.007653	1.46E-02	7.35E-13	3.46E-06	5.92E-14	2.07E-03	3.11E-03	9.01E-09
1	react	1	2	6.11955	13.2584	0.009153	1.31E-02	8.56E-13	3.46E-06	6.02E-14	2.07E-03	3.11E-03	5.35E-09
1	react	1	3	6.17289	13.1649	0.010653	1.16E-02	9.12E-13	3.46E-06	6.04E-14	2.07E-03	3.11E-03	3.70E-09
1	react	1	4	6.2179	13.0858	0.012153	1.01E-02	9.30E-13	3.46E-06	6.08E-14	2.07E-03	3.11E-03	2.70E-09
1	react	1	5	6.25659	13.0154	0.013654	8.62E-03	9.16E-13	3.46E-06	6.18E-14	2.07E-03	3.11E-03	2.02E-09
1	react	1	6	6.29033	12.9502	0.015154	7.12E-03	8.75E-13	3.46E-06	6.34E-14	2.07E-03	3.11E-03	1.51E-09
1	react	1	7	6.3201	12.8871	0.016654	5.62E-03	8.06E-13	3.46E-06	6.58E-14	2.07E-03	3.11E-03	1.11E-09
1	react	1	8	6.34662	12.8224	0.018155	4.12E-03	7.04E-13	3.46E-06	6.96E-14	2.07E-03	3.11E-03	7.81E-10
1	react	1	9	6.37044	12.7493	0.019655	2.62E-03	5.62E-13	3.46E-06	7.58E-14	2.07E-03	3.11E-03	4.96E-10
1	react	1	10	6.39199	12.6451	0.021155	1.12E-03	3.52E-13	3.46E-06	8.97E-14	2.07E-03	3.11E-03	2.32E-10
1	react	1	11	6.4129	-2.86679	0.022747	0.00E+00	0.00E+00	3.46E-06	1.79E-07	1.84E-03	3.11E-03	0.00E+00
1	react	1	12	6.4347	-3.01782	0.02459	0.00E+00	0.00E+00	3.46E-06	1.79E-07	9.19E-04	3.11E-03	0.00E+00
1	react	1	13	6.44679	-3.15615	0.026115	0.00E+00	0.00E+00	3.46E-06	1.79E-07	1.57E-04	3.11E-03	0.00E+00
1	react	1	14	6.42958	-3.22567	0.026367	0.00E+00	0.00E+00	3.46E-06	1.79E-07	3.17E-05	3.11E-03	0.00E+00
1	react	1	15	6.40847	-3.23712	0.026399	0.00E+00	0.00E+00	3.46E-06	1.79E-07	1.61E-05	3.11E-03	0.00E+00
1	react	1	16	6.38791	-3.23534	0.026411	0.00E+00	0.00E+00	3.46E-06	1.79E-07	1.05E-05	3.12E-03	0.00E+00