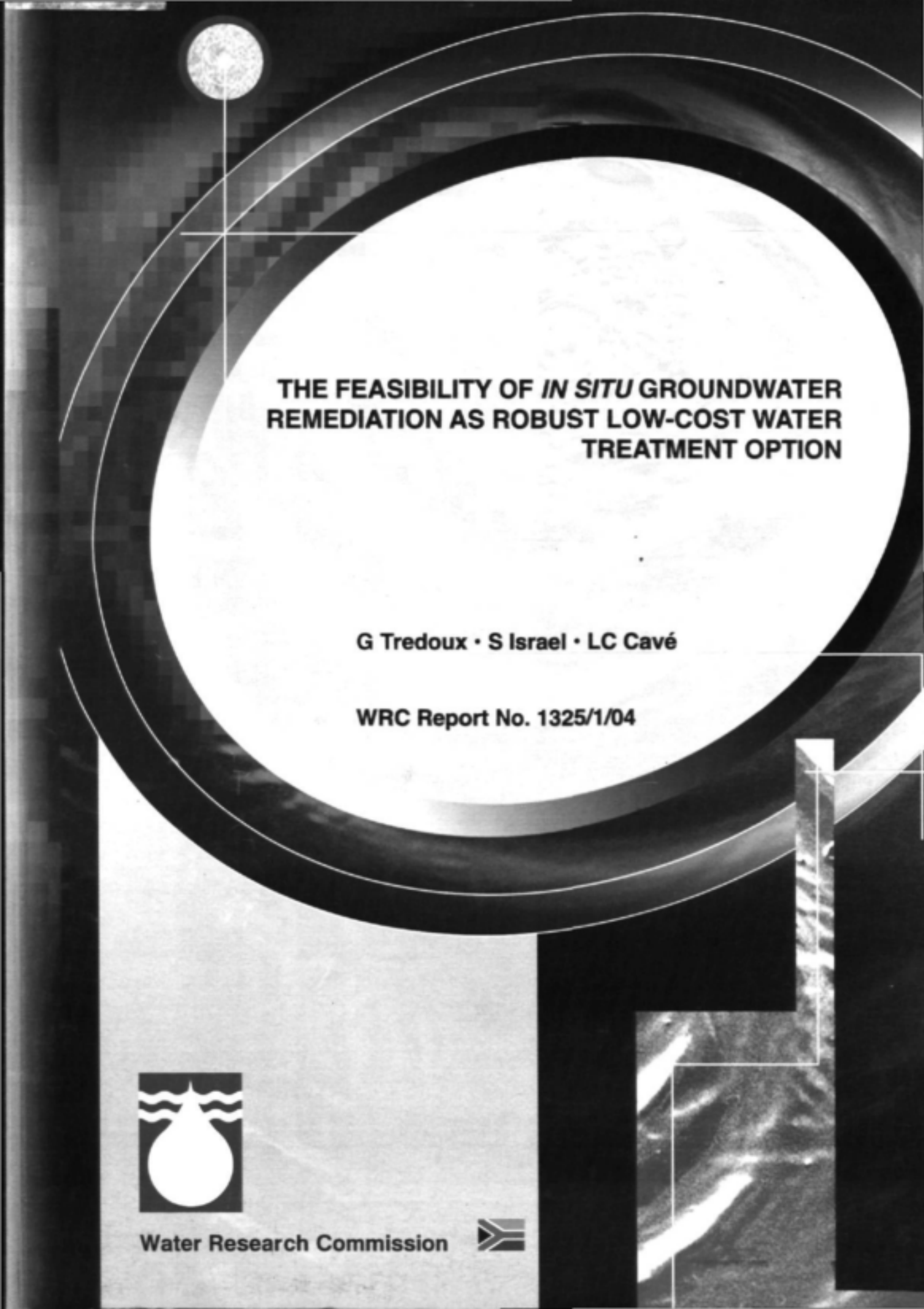

THE FEASIBILITY OF *IN SITU* GROUNDWATER REMEDIATION AS ROBUST LOW-COST WATER TREATMENT OPTION

G Tredoux · S Israel · LC Cavé

WRC Report No. 1325/1/04

Water Research Commission

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Report to the

Water Research Commission

By

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EXECUTIVE SUMMARY

Groundwater pollution is a worldwide phenomenon and the wide ranging consequences are gradually being realized. Research into methods of groundwater cleanup or remediation has increased and various techniques have been developed and applied. "*Ex situ*" pump-and-treat systems have been used widely, particularly in the United States of America. However, the success of such approaches has been questioned, considering the high costs involved. As an alternative, *in situ* treatment techniques, that remove contaminants while the groundwater resides in the aquifer, are being developed.

Objectives

This report presents information gained from literature and contacts with researchers abroad on the application of *in situ* treatment techniques. The present investigation represents an initial phase of the original proposal and the following objectives formed the core of the research:

- To identify from the literature and scientific contacts abroad, groundwater treatment processes that are (hydro)chemically suitable for *in situ* application.
- To obtain an overview of the mechanics of *in situ* treatment, the relationship to aquifer properties, and the intricacies of chemical injection for subsurface dosing, gas and treatment product control.
- To identify the factors controlling the economic feasibility of *in situ* groundwater treatment.
- To indicate potentially viable *in situ* treatment options for other troublesome groundwater constituents (e.g. iron, manganese, and fluoride).

Later phases of the research would entail the design, construction, operation and evaluation of a prototype *in situ* groundwater denitrification system, which will be to the benefit of the community and the derivation of design criteria for such systems. This, however, does not form part of the present project.

The present investigation focuses to a large extent on the removal of nitrate and, therefore, more detailed information is recorded on denitrification than on other treatment processes.

Nitrate removal

Most methods of nitrate removal that have been applied for *in situ* groundwater treatment are based on chemical and/or biological denitrification. The methods apply redox reactions, often with biological catalysis, to reduce nitrate to nitrogen gas. The appeal of using denitrification reactions for *in situ* application lies mainly in the fact that the main products of the reactions are gaseous and do not accumulate as hazardous by-products in the subsurface. Some of the techniques also do not require highly sophisticated technology.

A series of factors influence the denitrification reactions and the most important ones for biological denitrification are listed below:

- *Temperature, preferably near 35°C;*
- *pH, preferably neutral to alkaline;*
- *Organic carbon present as substrate for bacteria;*
- *Carbon:nitrogen ratio of 1:25;*
- *Presence of other nutrients such as phosphate;*
- *Presence of sufficient denitrifying bacteria;*

- *Low oxygen content, i.e. anoxic or anaerobic conditions;*
- *High soil water content;*
- *Control over anthropogenic activities disrupting the chemical equilibria, e.g. by disturbance of the soil.*

The efficiency of denitrification may not be of too great concern for *in situ* treatment systems, as long as the product water complies with drinking water specifications. Porosity and permeability in the aquifer are additional system related factors that affect the efficiency of denitrification.

Ion exchange, reverse osmosis and electro-dialysis have also been used in nitrate treatment plants, but have not been developed for *in situ* application. These methods remove anionic nitrate without the need for redox conversions, but they result in concentrated water treatment wastes that need to be disposed of.

Review of *in situ* groundwater treatment

Although *in situ* groundwater treatment is still being researched and developed, it has shown potential for the removal of a large range of inorganic contaminants, including arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), selenium (Se), technetium (Te), uranium (U), vanadium (V), nitrate (NO_3^-), phosphate (PO_4^-), and sulphate (SO_4^{2-}). Organic compounds can also be removed by *in situ* treatment methods.

Treatment methods

The most important *in situ* groundwater treatment methods for nitrate and many other contaminants can be divided into the following three main groups:

- *Permeable Reactive Barrier (PRB) methods*
- *Biological methods*
- *Electrochemical methods*

Permeable Reactive Barrier (PRB) techniques (also called "passive treatment walls") involve the physical placement of a barrier, consisting of reactive material, into a trench excavated in the aquifer. In other cases, a chemical reagent (e.g. a reducing agent) is injected into the aquifer to create the reactive barrier. This technique is called *In Situ* Redox Manipulation (ISRM). The barrier created with ISRM can be placed at much greater depths in the aquifer than with a trench-filled PRB. For these methods to work efficiently, especially for remediation operations, a primary aquifer is needed with well-defined, impermeable lower boundary.

PRB techniques, specifically zero-valent iron walls, are widely used for aquifer cleanup operations in preference to pump-and-treat methods. A wide range of contaminants, including arsenic, cadmium, chromium, copper, mercury, iron, manganese, molybdenum, nickel, lead, selenium, technetium, uranium, vanadium, nitrate, phosphate, and sulphate, can be removed in this way. Field studies of *in situ* treatment using PRBs have been completed for most of these contaminants.

With regard to biological methods, this study concentrated on denitrification and did not investigate the wide range of organic compounds that may also be treated by this method. *In Situ* Biological Denitrification (ISBD) methods generally require the introduction of a carbon source into the aquifer that serves as a substrate for the bacteria. This may be in the form of methanol, ethanol, glucose or even sawdust or wood chips injected via one or more boreholes. The Nitredox method is a special case of ISBD, involving the introduction of a carbon source and later oxidation of iron and manganese by-products.

Biological methods are widely used for removal of nitrate and degradable organic compounds. This treatment method is a viable option when the rate of contaminant biodegradation is faster than the rate of contaminant migration.

Electrochemical methods are more complex than PRB or biological methods, but are considered here because they are reputed to be applicable to fractured aquifer environments. Various electrochemical systems, applying enhancements such as electrokinetics and electro osmosis, have been described for groundwater treatment. These systems generally use an electrical current, applied via two *in situ* electrodes to control the movement and redox chemistry of ions and water in the subsurface. Electrochemical methods can be used as an enhancement of other PRB systems, e.g. by combining electrodes with iron walls to remediate nitrate contaminated groundwater and soils abiotically.

Electrokinetic methods appear to have been developed with a focus on remediating spills or leaks of organic chemical products. Much of the emphasis is on mobilising contaminated pore water and there is an expectation that the abstracted water would require additional ex *situ* treatment. It was stated in the literature that nitrate removal could be improved by coupling the electrokinetic method with an iron wall. However, no information was provided comparing the efficiency of electrokinetics on its own, or that of a coupled system, with non-electrical methods.

Advantages of in situ *treatment*

In situ treatment of contaminated groundwater uses the aquifer as a subsurface "treatment plant" to improve the quality of groundwater supplies. This has several advantages over conventional *ex situ* treatment technologies (pump-and-treat systems), including:

- *Cost and time savings on capital expenditure, maintenance, operator expenses, etc.*
- *Exposure to chemical reagents, where these are used, is limited.*
- *Many of the systems can operate for long periods (anything from 5 to 30 years) without need for reagent/substrate addition i.e. they are extremely low maintenance.*
- *Less stringent control of operating conditions is needed, which simplifies management of such systems.*
- *The systems are more robust and require less plumbing than surface-based treatment plants.*
- *Redox-based systems can often remove other contaminants e.g. chromate and organic chemicals, if these are also present.*
- *Abstracted water can be used directly with minimal or no extra treatment.*
- *The natural filtration processes in the aquifer provide additional water quality improvements.*

Side effects of in situ *treatment*

Some *in situ* treatment methods for removing groundwater contaminants may cause undesirable side effects, of which the most common problem is clogging in the subsurface. In the case of removal of organic compounds, the products of the treatment reaction may cause clogging of the aquifer due to biofilm build-up. If metals are removed by precipitation, the solid precipitates in the aquifer matrix may reduce the permeability of the aquifer over the long term. The specific hydrogeological conditions and the contaminant load will determine the extent of these phenomena. Side effects need to be managed to maintain the efficiency of the scheme and increase the treatment lifetime.

Depending on the environmental conditions, denitrification reactions may not always run to completion, i.e. nitrate nitrogen is not always fully converted to nitrogen gas. This can lead to the accumulation of other undesirable nitrogen species, such as nitrite or ammonium, in the groundwater. Nitrogen immobilisation may also retard the appearance of nitrate, but will not remove the nitrogen source from the aquifer and nitrate may re-develop at a later stage. Where potentially toxic reagents (e.g. dithionite, methanol) are introduced to the subsurface and not fully recovered or consumed by the reactions, groundwater quality may be adversely affected.

Possible side effects of *in situ* nitrate removal methods include clogging or loss of effective permeability in the aquifer as a result of factors such as:

- *Biofilm build-up in the aquifer, e.g. in biological systems.*
- *Mineral precipitates forming during the redox processes, e.g. iron or manganese oxides.*
- *Gas bubbles from nitrogen and carbon dioxide generation.*

Design criteria

For the design of any treatment system, both the hydrodynamics of the flow system and the source of the pollution need to be exceptionally well characterised to optimise the system.

The nature of the pollution source will affect the choice of system design. Where a single point source of pollution is affecting a water supply borehole, a simple porous barrier, single ISRM or ISBD injection borehole can be constructed along the flow path between the source and production borehole. If non-point sources are responsible for pollution, production boreholes must be protected by a surrounding gallery of treatment systems e.g. the daisy configuration for ISBD, the Nitredox system, multi-electrode arrangement or a circular barrier wall.

Trench and fill barrier methods are only suitable for shallow flow systems where the barrier can be constructed down to the impermeable bedrock. In deeper flow systems, treatment barriers can be created by borehole injection. *In situ* treatment methods are more likely to be successful in primary aquifers, where hydrodynamics are more easily understood and greater control over the treatment zone can be exercised than in fractured flow environments.

For nitrate removal systems, management of nitrogen inputs to the subsurface is still required, as treatment of the nitrate in the aquifer does not remove the contamination source. Although the treatment systems generally have a long lifetime, it is still important that the source of contamination be eliminated wherever possible.

Pilot and full-scale in situ *denitrification systems worldwide*

Most of the field scale *in situ* groundwater treatment systems use the PRB type technique. In Canada and New Zealand, sawdust and woodchips are used as carbon substrate in PRB systems. Biological denitrification plants in the USA, France and elsewhere, generally use ethanol or methanol as carbon substrate. In one pilot plant in Israel, sucrose was used for this purpose.

One full-scale denitrification plant has been in use for more than a decade. This is the one at Bisamberg, which supplies denitrified water to Vienna, Austria. The plant uses the Nitredox method. Iron and manganese that are mobilized from the aquifer during the denitrification process are re-precipitated in the oxidation step. The capacity of the plant is 60 L/s.

For the purpose of comparison, brief information on certain ex situ treatment systems is also provided in the report.

Potential for *in situ* treatment applications in South Africa

The literature review shows that *in situ* groundwater treatment has significant potential for application in South Africa. Internationally, researchers are enthusiastic about the potential of *in situ* treatment for addressing various problems regarding chemical constituents found in pollution situations but also those in natural groundwater environments. *In situ* treatment systems for iron and manganese removal have been used successfully for many decades while *in situ* nitrate removal has been in place for approximately two decades.

The countrywide distribution of nitrate levels in groundwater was compared with the various hydrogeological terrains of South Africa and the towns or rural communities where groundwater constitutes the sole water supply source. This assessment has indicated that there is some agreement between high nitrate concentrations, sole source areas and hydrogeology. High nitrate concentrations are fairly well correlated with aquifers composed of unconsolidated deposits, weathered basalts, and dolomites over an area extending from the Northern Cape Province all the way to northern Mpumalanga, including parts of North West and the Limpopo Province. Areas that are sole source areas with high groundwater nitrate concentrations have priority over other areas for remediation. These include towns such as Marydale, Leliefontein, Reivilo, Rietfontein in the Northern Cape, and others, largely located in the rural parts of Northwest and Limpopo Provinces.

Iron and manganese, occurring naturally in groundwater, may cause significant clogging problems in boreholes when redox conditions change and iron bacteria start multiplying. In primary aquifers, *in situ* treatment by oxygenation may provide a viable solution, e.g. by using the Vyredox process. This can be applied at Atlantis, where even persistent low levels of iron cause significant borehole clogging problems.

Regulatory requirements

Regulatory requirements for *in situ* treatment methods are not specifically covered in South African law. However, any *in situ* groundwater treatment system will be subject to the stipulations contained in the National Water Act (No 36 of 1998) and the National Environmental Management Act (No 107 of 1998). As a minimum, an impact assessment study will have to be carried out for any proposed full-scale *in situ* treatment scheme. The potential impact on the environment, socio-economic conditions and cultural heritage of all activities that require permission by law must be considered, investigated and assessed before implementation. Compliance with pollution prevention regulations require authorisation from DWAF before any reagents/substrates would be allowed to be injected into an aquifer as well as for the management of any waste products produced if any. However, it is believed that with a thorough approach, the legislative requirements can be fulfilled.

In this regard it may be of great value to learn from the approach in the USA and extracts of regulatory issues that are being addressed in that country are included in the report.

Cost comparison for different treatment methods

For the purpose of assessing economic feasibility, a desk study was conducted for denitrification of the groundwater at the rural town of Marydale. Three different *in situ* methods and one *ex situ* were considered. The capital investment for the *ex situ* plant was between three and seven times higher than for the *in situ* systems. The largest difference, however, was in the operating costs. Whereas the *in situ* methods had virtually no operating costs, the *ex situ* costs each year were nearly as high as the initial capital costs. The permeable reactive barrier system should have the lowest capital costs.

Even if these estimates have certain incorrect assumptions, it is evident from the calculations that it is impossible to have an *ex situ* treatment system that will be more economical than an *in situ* system such as the PRB. This also explains why *in situ* methods have already gained wide acceptance abroad.

Recommendations

The analysis of existing methods and systems worldwide, together with the preliminary cost analysis, shows that in many instances *in situ* groundwater treatment methods will provide a viable, cost-effective alternative to ex situ water treatment. In view of the success abroad, it is strongly recommended that such systems be tested both at field scale and full scale in South Africa. Particularly those systems that require a low capital investment, low running costs and limited know-how should be tested and installed without delay. For each potential site a feasibility study should be undertaken and cost estimates calculated. Three to five sites should be developed as demonstration units, for technology transfer and obtaining local experience with this technique.

It is recommended that all four methods, i.e. permeable reactive barriers (PRB), *in situ* redox manipulation (ISRM), *in situ* biological denitrification (ISBD) and electrokinetics are tested at suitable locations. All methods are suitable for groundwater denitrification, but also for the removal of other contaminants such as heavy metals or organic compounds. All four methods would be viable in the town water supply context but only some of them, e.g. PRBs, would be compatible with the rural setting. The availability of infrastructure and technical know-how would make the Nitredox and Vyredox methods viable for nitrate, iron and manganese removal in town water supply applications.

Local testing of PRBs for the remediation of contaminants such as heavy metals (e.g. chromium) or organic compounds is strongly recommended. In the USA and other countries many PRB remediation systems are successfully in operation. The cost advantages involved make these methods attractive for remediation of spills and other pollution problems and it is recommended that the methods be applied locally to develop the local expertise for wider application. *In situ* remediation could, for example, be tested at Springbok, where chromium was allegedly spilled into an alluvial aquifer. Whereas PRBs are applicable to shallow alluvial and other porous aquifers, ISRM techniques are recommended for testing on deeper porous aquifers. More details on each are provided below.

Recommended denitrification systems

Permeable reactive barriers (or "treatment walls"): PRBs can be constructed from cheap, readily available materials and would be relatively simple for communities to install with limited training. They provide long-term treatment without maintenance and no power source is required. By-products of the sugar industry could be investigated as a more readily degradable carbon source, for example in rural KwaZulu-Natal, in addition to the more conventional wood chip/sawdust barriers.

In situ redox manipulation: ISRM should be tested for deeper primary aquifers in South Africa. The dithionite chemical reagent should be readily available, since it is used in the pulp and paper industry. Laboratory testing would be recommended for the first phase followed by field-testing for those instances with promising test results. This method can be tested in the Kalahari in areas where the aquifers are not too deep. It could also work in basalt aquifers with sufficient porosity.

In situ biological denitrification: Internationally ISBD is probably the most widely used *in situ* treatment method for the removal of nitrate from groundwater. The configuration of the injection and abstraction boreholes is flexible and can be adapted to suit the specific treatment problem. Various conventional and organic substrates and cheaper locally available options could be tested for potential application in rural treatment systems. The injection of microbes would not be recommended at this stage.

Electrokinetics: Various electrochemical techniques might be useful as an enhancement for the first two methods above, as the electrochemical techniques do not appear to be completely efficient for nitrate removal on their own. More information would need to be collected on the electrode composition and installation, applied voltages, etc. and extensive testing conducted before electrokinetics could be applied in the field. The electrokinetic method is, however, the only one found that has been claimed to be suitable for fractured rock environments, which would make it worth testing for South Africa. This is the main reason why this method is recommended for testing despite the higher levels of technical skill and know-how that is required.

Nitredox: The Nitredox denitrification method is more complex and possibly too expensive for rural water supply application. However, based on its long successful record at Bisamberg, Austria, it is recommended that this technique be tested in a primary aquifer where the large number of injection and observation points can easily be created by the installation of well points. It is, however, essential to investigate whether the licensing costs in terms of registered patents may prohibit its application. Nitredox denitrification may be considered for town water supply application following a thorough evaluation of the costs involved.

Recommendations for iron and manganese removal systems

Vyredox: Iron and manganese removal is imperative in many high volume abstraction situations to avoid or minimise borehole clogging effects. At towns such as Atlantis, the beneficial effects of iron and manganese removal will offset the costs of implementing *in situ* treatment. It is recommended that a system similar to the Vyredox system be tested on a South African primary aquifer.

Recommendations for contaminant remediation systems

PRB: These can be constructed from cheap, readily available materials such as foundry wastes or furnace slag. They would be relatively easy to install at mining and industrial sites and would provide a low-cost, long-term treatment option.

ISRM: The ISRM technique is practically as effective and maintenance free as the PRB method but as ISRM can be installed at greater depth it can be applied to a larger range of primary aquifers.

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Mr E van Wyk	Department of Water Affairs & Forestry (DWAF)
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List of Acronyms and Abbreviations

BTEX	Benzene, toluene, ethylbenzene and xylenes
CERCLA	Comprehensive Environmental Response, Compensation & Liability Act
DCE	1,1-dichloroethylene
DC field	Direct Current field
DDT	Dichlorodiphenyltrichloroethane
DOD	US Department of Defence
DOE	US Department of Energy
EISBD	Enhanced In Situ Biological Denitrification
EPA	US Environmental Protection Agency
HCB	Hexachlorobenzene
ISBD	*In Situ* Biological Denitrification
ISRM	*In Situ* Redox Manipulation
ITRC	Interstate Technology and Regulation Cooperation Work Group
MTBE	Methyl tertiary butyl ether
NEMA	National Environmental Management Act
NWA	National Water Act
PCE	Perchloroethylene
PRB	Permeable Reactive Barrier
RCRA	Resource Conservation Recovery Act
TCE	Trichloroethylene
US	United States (of America)
VOC	Volatile Organic Compounds
WSA	Water Services Act

1. INTRODUCTION

Groundwater pollution is a worldwide phenomenon and the consequences are gradually being realized. Presently rural water supply is being extended and improved with great urgency to provide water to previously disadvantaged peoples in remote areas. This puts considerably more emphasis and pressure on groundwater as a resource with the result that groundwater pollution, also in the remote areas, is being drawn into the spotlight.

Research into methods of groundwater cleanup or remediation has been intensified and various techniques have been developed and applied. "Pump-and-treat" systems have been used widely, particularly in the United States of America. However, the success of such approaches has been questioned, considering the excessive costs involved (Simon *et al.*, 2001). As an alternative, *in situ* treatment techniques are being developed for removing contaminants while the groundwater resides in the aquifer or during groundwater abstraction.

As set out in the project proposal, the research focused mainly on nitrate as a prime candidate for the application of *in situ* remediation but it was undertaken to record information on other constituents that could be removed in a similar way. The main reason for the emphasis on nitrate is that the occurrence of high nitrate levels in groundwater is a widespread phenomenon. This is ascribed to both natural and anthropogenic causes. Ingested nitrate causes methaemoglobinaemia and this can be fatal for infants and livestock. At sub-lethal levels, methaemoglobinaemia can still be detrimental to children and livestock. It can also cause spontaneous abortion (Davison *et al.*, 1964). In most parts of the world 10 mg/L of nitrate (as N) is regarded as the upper limit for public water supplies, but in Europe the aim is presently to provide drinking water with less than 6 mg/L of NO_3-N.

The maximum permissible level of nitrate in drinking water in South Africa is 20 mg/L (as N). This value has been used as a cut-off for the identification of problem areas for water supply and it has also been used as the lower limit to simplify mapping of groundwater nitrate (see Figure 1). Groundwater over the greater part of South Africa has nitrate levels of below 20 mg/L. However, in the three northern provinces, occurrences of groundwater sources with 20-50 mg/L, as well as higher concentrations are widespread. Rural villages and small towns from the Northern Cape to the far northeast of Limpopo Province are severely affected by these high nitrate concentrations, (Tredoux *et al.*, 2000). Concentrations range from 50-100 mg/l and even well above 100 mg/l in some towns, while in the southern Kalahari concentrations of up to 500 mg/l of nitrate occur in more saline areas (Tredoux *et al.*, 2000).

Natural sources such as ammonium-bearing rock minerals can contribute nitrate through leaching by groundwater followed by oxidation when redox conditions allow (Cave, 1999). However, large tracts of land in arid to semi-arid areas are affected by nitrate, which naturally accumulates in groundwater under certain conditions. This natural groundwater nitrate is derived from soil organic nitrogen (Heaton, 1984). Tilling of the soil will also mobilize the natural soil nitrogen in the form of nitrate (Heaton, 1985; Conrad *et al.*, 1999). In addition to the natural accumulation of nitrate in the groundwater, nitrate pollution via point and diffuse sources has become a serious problem in South Africa. It is, therefore, imperative that treatment technologies be developed or improved to benefit communities suffering from conditions caused by high levels of nitrate in their groundwater supplies. In many parts, groundwater serves as the sole source of water. Problems arise where this sole source becomes unfit for use due to constituents such as fluoride and nitrate (Marais, 1999).

Since the high nitrate concentrations have not gone undetected, treatment methods have been employed in certain areas of Southern Africa. These include the northern parts of Limpopo Province, the Springbok Flats, as well as Namaqualand. In the rural village nZava in Limpopo, ion exchange is used to reduce the nitrate level in the groundwater.

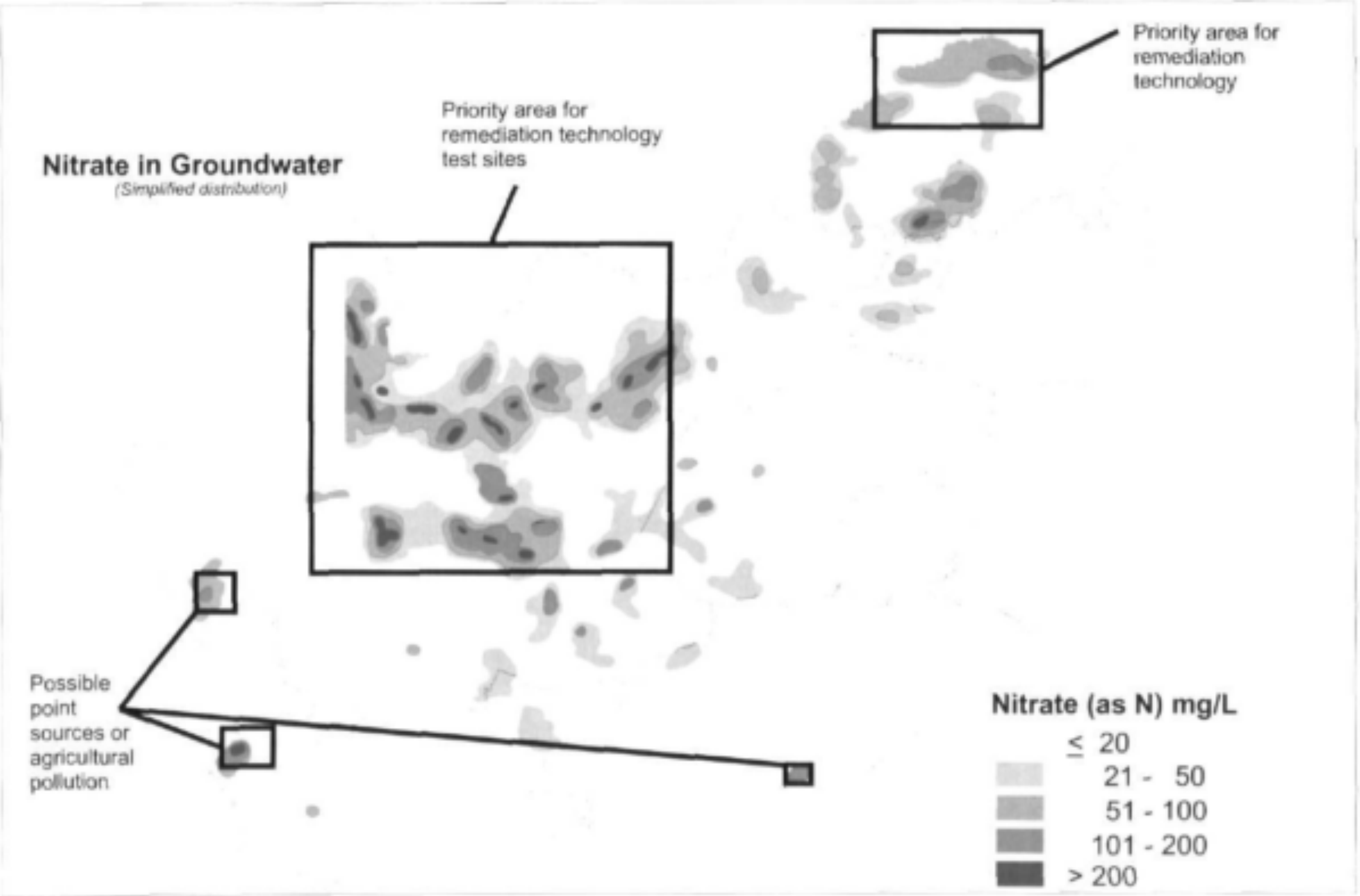


Figure 1: Groundwater nitrate distribution in South Africa *(after Tredoux et al., 2001)*

A farmer, Semmelink, residing in the Springbok Flats, used molasses to reduce the nitrate concentration in the groundwater used for stock watering (Anonymous, 1985). This *ex situ* method was somewhat similar to a flow-through or batch treatment system and used biological denitrification as discussed below. The system reduced the nitrate concentration to acceptable levels for consumption by livestock and although the product water was not aesthetically pleasing the livestock thrived. In Namaqualand reverse osmosis desalination is used but it is not specifically directed at denitrification. Several countries in Europe, the United States and Canada and other parts of the world, specifically apply denitrification to comply with strict nitrate guideline levels for potable water. The denitrification systems mainly use biological and sometimes ion exchange processes. In the USA, Permeable Reactive Barriers are the main *in situ* method applied. Most of these treatment plants are specific for nitrate removal and hence achieve optimum results in this regard.

In situ treatment refers to the removal of a groundwater constituent, while the water resides within the aquifer, whereas *ex situ* treatment entails abstraction of the groundwater, followed by treatment at surface. *In situ* treatment methods potentially provide a viable alternative to the highly sophisticated *ex situ* drinking water treatment systems used abroad. The reason is that *in situ* processes do not require capital-intensive water treatment plants. Later sections will highlight other comparisons between *ex situ* and *in situ* methods.

This literature review considers the currently practised *in situ* treatment methods and their applicability to rural areas and towns in Southern Africa. It also compares treatment methods (*in situ* vs *ex situ* as well as different *in situ* methods) and considers results achieved in other countries where full-scale treatment methods are already in use. The operating principles of the various methods and schematic sketches are included.

1.1 Objectives

The following objectives formed the core of this research project:

- ☐ To identify from the literature and scientific contacts abroad, groundwater treatment processes that are (hydro)chemically suitable for *in situ* application.
- ☐ To obtain an overview of the mechanics of *in situ* treatment, the relationship to aquifer properties, and the intricacies of chemical injection for subsurface dosing, gas and treatment product control.
- ☐ To identify the factors controlling the economic feasibility of *in situ* groundwater treatment.
- ☐ To indicate potentially viable *in situ* treatment options for other troublesome groundwater constituents (e.g. iron, manganese, fluoride, and organics).

Future research will entail the design, construction, operation and evaluation of a prototype *in situ* groundwater denitrification system. Such a prototype system will be operated to the immediate benefit of the affected community and for deriving design criteria for other full-scale systems. The necessary institutional arrangements will be made and support from funding agencies obtained. The appropriateness of the technology will be confirmed and acceptance thereof in all spheres of impact ensured. This did not form part of the present project but it is envisaged as an ensuing study applying the findings of this project.

Treatment processes such as reverse osmosis and ion exchange will also remove nitrate from groundwater. The specific removal of nitrate from water is based on oxidation-reduction reactions, which may be facilitated by bacterial action. In this project, the study of oxidation-reduction reactions had the highest priority and iron and manganese were the only other natural "nuisance constituents" in water that received attention. *In situ* treatment is widely applied for groundwater remediation as cost-effective alternative to pump-and treat schemes, particularly in the United States of America. Therefore, reference is also made to the application of certain techniques to the removal of these other pollutants from groundwater.

1.2 Structure of report

Following the introduction, the first chapter sets out the objectives of the research project and the structure of the report. Chapter 2 concentrates on nitrate and provides the theoretical background to the study, where the principles of nitrate reduction are discussed, as well as the conditions that favour or inhibit denitrification.

Chapter 3 discusses *in situ* groundwater treatment methods. These are subdivided into Permeable Reactive Barrier (PRB) techniques, biological processes, and electrochemical applications. A series of subsections cover the operating principles, applicability and a discussion of the efficiency, advantages and disadvantages of each of the methods. A section on iron and manganese removal by an oxygenation method is also included.

Chapter 4 specifically deals with nitrate and highlights other treatment methods that are suitable for nitrate removal. These are applied in *ex situ* treatment systems, but have not been adapted for *in situ* application at this stage. The principles of these methods are explained briefly for comparison with the *in situ* methods.

Chapter 5 lists all the operational sites worldwide that the authors are aware of and gives an overview of the applicability of *in situ* treatment. Most of these plants were specifically constructed for nitrate removal, although some do remediate chromate and organic constituents derived from the petroleum industry.

Chapter 6 covers the regulatory requirements of implementing an *in situ* treatment system; this discusses the National Water Act and the National Environmental Management Act. An approach to the legal requirements from a case study in the USA was also incorporated into this chapter as a potential guideline for developments in South Africa.

Chapter 7 provides cost information based on a hypothetical denitrification system at the rural town of Marydale. The methods discussed in Chapter 3 of the report were used to derive an initial estimate of the costs in the South African context as most documents consulted had recorded the cost information in dollars or sterling for other countries. This summarizes the information from the case studies while providing an overview and comparison of costs of the methods discussed.

Chapter 8 gives a general discussion and draws conclusions based on advantages, disadvantages and side effects of *in situ* treatment. A brief discussion of the applicability to South Africa's various groundwater environments is included this chapter.

Chapter 9 recommends promising treatment systems, which warrant further investigation. In this regard systems more suitable for rural water supply and those applicable to town supply are identified.

A brief cost estimate was carried out for the construction of a field scale *in situ* groundwater treatment system at the rural village of Marydale using the treatment methods highlighted in this report. The cost study, presented in Appendix A, contains a breakdown of costs involved in setting up different *in situ* treatment options and provides a comparison of these costs. Details of the full-scale Nitredox denitrification plant at Bisamberg near Vienna are provided in Appendix B. The description is illustrated with pictures taken during a visit in 1993. Appendix C contains a description of various denitrification systems tested at Broichhof.

2. BACKGROUND: PRINCIPLES OF NITRATE REMOVAL

Nitrate is highly mobile in the soil and groundwater environment. As all nitrates are soluble, they cannot be removed from solution by precipitation. Nitrate is also not adsorbed significantly onto the matrix under aquifer conditions, which leaves reduction as the only means for *in situ* nitrate removal from groundwater (Appelo and Postma, 1996). The methods discussed here are all based on the fundamental process of chemical and/or biological denitrification, in which the nitrate anions are reduced to nitrogen gas in a reaction with the reducing agent. This type of reduction also forms part of the natural nitrogen cycle (see Figure 2).

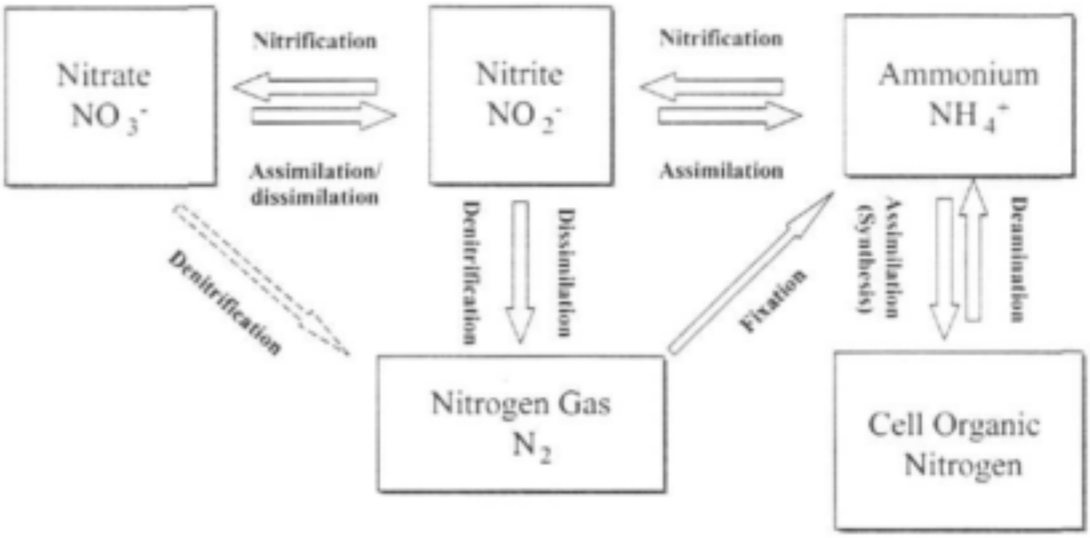


Figure 2: The nitrogen cycle, with emphasis on denitrification

The overall half-reaction for denitrification is:

$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_{2\,(g)} + 6H_2O \ldots\ldots\ldots\ldots\ldots\ldots E^0_{h\,(volts)} = 1.245 \qquad (1)$$

Denitrification requires the transfer of five electrons per nitrogen atom and proceeds through a complicated reaction pathway in which several intermediates such as nitrite and nitrous oxides are involved, before final conversion to nitrogen gas. The intermediates are sometimes found in groundwater in low concentrations, but the process predominantly proceeds to the final product, i.e. N_2 gas (Appelo and Postma, 1996).

Chemical denitrification requires electron donors such as reduced iron or sulphur species to be present in the groundwater or the aquifer. Nitrate reduction by Fe^{2+}, H_2S and CH_4 is thermodynamically favourable and will proceed spontaneously, although the kinetics of the reaction may be slow.

In cases of high nitrate loading, however, the reducing capacity of dissolved species is often exceeded. For significant denitrification to occur, the reducing agents must be present in the aquifer matrix, in the form of organic matter or minerals such as pyrite or iron (II) silicates, rather than in the groundwater (Appelo and Postma, 1996). The energy yield for reactions between nitrate and organic matter or pyrite can be evaluated from the following reactions:

$$\underset{\text{graphite}}{5C} + 2H_2O + 4NO_3^- \longrightarrow 2N_{2\,(g)} + 4HCO_3^- + CO_2 \qquad (2)$$

ΔG^0_r = - 458.06 kJ/ mol of NO_3^-

$$\underset{\text{pyrite}}{2FeS_2} + 2H_2O + 6NO_3^- \longrightarrow 3N_{2\,(g)} + 2FeOOH + 4SO_4^{2-} + 2H^+ \qquad (3)$$

ΔG^0_r = - 415.84 kJ/ mol of NO_3^-

These negative ΔG^0_r values show that the reactions are likely to proceed to the right. Since the energy yield is larger for the organic matter than for pyrite, nitrate reduction by organic matter should proceed before reduction by pyrite, Appelo and Postma (1996).

Biological denitrification is catalysed by bacteria, which utilise the redox reactions as an energy source. Microorganisms use the NO_3^- ion as a terminal electron acceptor in a complex set of reactions to oxidise organic carbon to CO_2 by reactions such as (Drever, 1997):

$$5C_{organic} + 4NO_3^- + 4H^+ \rightarrow 2N_{2\,(g)} + 5CO_{2\,(g)} + 2H_2O \qquad (4)$$

Such reactions are important in anaerobic environments where NO_3^- accepts the electrons generated by organic matter decay after oxygen has been depleted.

Denitrifying bacteria are biochemically and taxonomically very diverse, utilising a wide range of substrates. Most are facultative anaerobes, i.e. they are able to function in the presence or absence of oxygen (Korom, 1992). Both heterotrophic bacteria, which require an additional source of organic carbon, and autotrophic bacteria, which utilise inorganic carbon such as carbon dioxide or bicarbonate ions, are capable of reducing nitrate to nitrogen gas (Darbi *et al.*, 2002).

The biogeochemical reactions above form the basis of engineered denitrification systems for *in situ* removal of nitrate from groundwater. *In situ* methods are considered as viable alternative to *ex situ* methods, as they generally require less maintenance, less exact operational control, and running and capital costs are not as high.

In situ methods for nitrate removal involve the addition to the aquifer of an organic carbon source, denitrifying microorganisms, metallic iron or combinations of these. Biological methods require a carbon source to be added, with or without addition of microbes. The reagents can be introduced through injection into boreholes or excavation and construction of permeable barriers in shallow aquifers. Barrier placement methods generally involve filling a trench with a carbon substrate (e.g. sawdust) or iron (e.g. zero valent iron filings) to enhance or stimulate denitrification. Electrokinetic techniques may be used to enhance denitrification in conjunction with any of the above methods. These methods will be discussed in more detail in Chapter 3.

2.1 Factors that influence denitrification

The successful operation of any denitrification method is dependent on certain parameters that affect the denitrification reaction. These include factors such as:

2.1.1 Temperature:

Denitrifying bacteria perform optimally within certain temperature ranges. Ying-Feng Lin *et al.*, (2000) showed that a drop in temperature from 20 to 10°C caused a decrease in the rate of denitrification, while a later rise in temperature to 19°C marked the return of normal rates of denitrification in their experiment. Work by Mohn *et al.*, (2000) shows that temperature is indeed a controlling factor for the denitrification reaction. This is explained in two ways, either directly due to stimulation of microbial communities or indirectly due to greater amounts of C, NO_3^- and NH_4^+ becoming available at elevated soil temperatures. At low temperatures, nitrate and carbon accumulate and are not consumed by bacteria (Mohn *et al.*, 2000). According to Wild (1988), nitrate reduction 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 dinitrogen is produced. Wild (1988) also states that denitrification is typically favoured by warm, wet soil conditions where little O_2 is present.

2.1.2 pH:

An increase in pH to slightly above neutral pH, results in an increase in NO_3^- reduction to N_2 (Stevens *et al.*, 1998). This was shown in an experiment during which the pH was gradually increased to observe the products of nitrate reduction. It was found that nitrite accumulated at pH 8 when soil moisture content was high. Observations during this experiment revealed that the maximum flux of N_2O was at pH 6.5 while the minimum fluxes occurred at pH 6 and 8. Agronomic practices affecting the soil pH e.g. liming thus also affects the dominant reactions occurring at any given time (Stevens *et al.*, 1998). Fey (2002) showed that nitrate levels are highest in acidic conditions at depth in the soil profile. The surface charges are positive under acid conditions and nitrate can hence act as an anion for adsorption, this is however a site-specific case.

2.1.3 Organic carbon:

Organic carbon serves as a substrate for bacterial communities, which facilitate and enhance the denitrification reaction. High total organic carbon concentrations are desired for optimum occurrence of the denitrification reaction. It is often deemed necessary to add organic matter to soils deficient of humic substances to promote denitrification. Ying-Feng Lin *et al.*, (2000) demonstrated the effects of external carbon sources and organic carbon in general on the denitrification reaction. Addition of readily degradable carbon sources rich in N will enhance denitrification, while organic sources not readily degradable may enhance immobilization by converting NO_3^- to NH_4^+ on exchange sites. Carbon sources used by different researchers include glucose, sucrose, ethanol, methanol, acetic acid, and lactic acid. It is not clear from the literature which of these is more effective in terms of rate of denitrification, but cost and availability of the selected substrate should also be taken into account in the selection of a suitable external carbon source, (Carrera *et al.*, 2003).

2.1.4 Carbon:nitrogen ratio and aquifer material:

Baker (1998) found that a critical C:N ratio of 1:5 was needed to attain complete denitrification using plant carbon in nitrate polluted water. This represents ideal situations that can be simulated in a laboratory. In reality, most plant organic matter is consumed under aerobic conditions. Bates and Spalding (1998) varied the C:N ratio in experiments with NO_3^--N concentrations of to 2.5 to 5 mg/L. The most efficient nitrate removal occurred at the ratio of 1.25, where all nitrate was removed after 40 hrs in a lab experiment. The carbon content of the aquifer material as well as organic carbon dissolved in the groundwater affect the C:N ratio and the denitrification rate.

2.1.5 Oxygen content and redox potential:

The oxygen content is important in the sense that denitrification takes place under anoxic or anaerobic conditions, and the presence of O_2 may inhibit the denitrification reaction. Work by Mohn *et al.* (2000) also showed that the redox potential affects denitrification. In their experiments, redox potentials (mean values) ranging from 659±7 mV to 259±15 mV was measured. They correlated this with the O_2 content and the denitrification rate. The highest redox potential values coincided with well-aerated soils on a drained mound where the measured denitrification rate was low. Where the redox potentials were low, i.e. in waterlogged depressions, which indicated anoxic conditions, the denitrification reaction proceeded to completion yielding dinitrogen gas. Microbial communities prefer oxygen to nitrate as an electron acceptor; hence oxygen inhibits the denitrification reaction from occurring. Oxygen entering a denitrification system affects the reaction metabolically as well as kinetically due to the inhibitory effect of oxygen on denitrification (Plósz *et al.*, 2003). This inhibitory effect of oxygen on denitrification becomes larger with greater amounts of oxygen entering the anoxic environment (Plósz *et al.*, 2003). A small amount of oxygen entering the system and reacting with organic matter present will have a negligible effect on denitrification.

2.1.6 Microbial activity:

Microbes are known to accelerate reactions. Denitrifying bacteria use nitrogen oxides as terminal electron acceptors in the absence of free oxygen. The presence of these denitrifying bacteria is essential for the denitrification reaction. Temperature, pH, C:N ratio, redox potential and total organic matter are important factors for the denitrifying bacteria to operate. The extent to which carbon addition to the subsurface enhances bacterial denitrification depends on the carbon source used and its potential toxicity to the bacterial community. Bates and Spalding (1998) ascribed a decrease in denitrification rate to toxicity of the carbon substrate used (in their case ethanol) to the bacterial community. Denitrifying bacteria operate in the absence of free O_2 by reducing NO_3^- and NO_2^- to N_2, Firestone (1982). The general requirements for denitrification include: the presence of bacteria possessing the appropriate metabolic capacity; an energy source (organic carbon, reduced S compounds, or molecular hydrogen) and terminal electron acceptors (N oxides). According to Firestone (1982) the capacity to denitrify has been shown in about 23 genera of bacteria. Most denitrifying bacteria are chemotrophs, using chemical energy and not light energy, and using organic carbon as a source of electrons and cellular carbon, rather than CO_2 gas.

2.1.7 Water content of soils:

Paavolainen *et al.* (1999) used sprinkling filtration as a form of artificial groundwater recharge in southern Finland. This caused an increase in the pH of the humus layer of the soil from about 5 to 6.5. They also found that high soil moisture favours denitrification. This can also be explained by low oxygen content or reducing conditions. An increase in denitrifying enzyme activity often followed an increase in soil water content (Griffiths *et al.*, 1997). When soils are flooded, nitrate is mobilized and may limit the occurrence or the rate of denitrification (Firestone, 1982). Jacinthe *et al.* (2000) used water table management as a technique to stimulate denitrification. They increased the saturation of the upper part of the soil profile hence replacing O_2 with water in pores and generating an anoxic environment. They encountered a problem with N_2O evolution during their experiments, which may contribute to global warming. An interesting point raised by Jacinthe *et al.* (2000) was that a prolonged period of anoxic conditions, due to a high water table would decrease the mole fraction of N_2O in the nitrogenous gases emitted.

2.1.8 Permeability and porosity:

Permeability and porosity relate to the flow, pore spaces and their interconnectivity, in the soil and aquifer matrix. Soil and aquifer material of high permeability results in rapid leaching of mobile ions such as nitrate into the groundwater during rainfall events. It is essential to know the magnitude these properties when considering filtration of water through soil or aquifer material. Whereas these properties indirectly affect denitrification, they more directly affect recharge of the aquifer. The water content of the aquifer, impacts directly on denitrification as it exercises a degree of control over the oxygen content of the aquifer.

2.1.9 Effects of anthropogenic activity:

Anthropogenic activity refers to any disturbance of the natural processes by man. This includes tillage, agricultural activities, wastewater disposal, sludge deposition, feedlots, pit latrines, etc. These all contribute to increase the nitrogen content in soils and ultimately also the nitrate concentration in the groundwater. Besides their contribution of nitrogenous substances, they disturb the equilibrium of the nitrogen cycle. Nitrogen gas is released into the atmosphere when ploughing occurs, and this also disturbs the reaction equilibria. Additions of nitrogen containing fertilizers, wastewaters and sludge further disturb the chemical equilibria. Denitrification may be enhanced by certain anthropogenic activities e.g. when readily degradable carbon is added to the subsurface, e.g. at wineries (Fey, *Pers. Comm.*, 2003).

2.1.10 Presence of other nutrients:

Phosphate is an essential microbial nutrient, and supplemental phosphate may be needed during *in situ* denitrification, when treating soils or aquifer material with high-phosphate retention or other low phosphate waters (Hunter, 2003). Soils that retain or bind phosphate are common in the western United States (Lewis *et al.*, 1950). Movement of phosphate through soils or aquifers is much slower than that of nitrate (Gonzales-Pradas *et al.*, 1993), and low levels of phosphate may limit denitrification in deep soils and underlying aquifers, even when the overlying soils are contaminated with high levels of both phosphate and nitrate. This situation might be relatively common beneath livestock pens located on phosphate-binding soils.

If *in situ* treatment methods are to be of use in areas with phosphate-poor groundwater, then a long-lasting phosphate source must also be provided. Care would need to be taken to ensure that the phosphate source used does not leach undesirable levels of phosphate into the groundwater downstream of the barrier. Rock phosphate or calcium phosphate might prove to be an adequate phosphate source for *in situ* remediation projects (Hunter, 2003).

The recent paper by Hunter (2003) is apparently the first to report nitrite accumulations from the reduction of nitrate when phosphate is limiting. Factors that influence the growth rate of microorganisms have been shown to cause the accumulation of nitrite by denitrifying microorganisms. Blaszczyk (1993) observed that nitrite accumulations by *Paracoccus denitrificans* correlated with growth rate as controlled by the nutrient content of the growth medium. When *P. denitrificans* was grown in a nutrient-poor medium, growth was slow and a large amount of nitrite accumulated, but when *P. denitrificans* was grown in a rich medium, the growth rate was fast and a lesser amount of nitrite accumulated. Blaszczyk (1993) suggests that the cause for the accumulation of nitrite in media with a small nutrient content is due to a delayed synthesis of nitrite reductase relative to nitrate reductase.

3. IN SITU GROUNDWATER TREATMENT METHODS

Several *in situ* groundwater treatment methods have been developed. The applicability of each of these depends on the particular contaminant characteristics, the aquifer matrix properties and its chemical composition. The treatment methods can be divided into the following main groups:

- ☐ Permeable reactive barrier (PRB) methods
- ☐ Biological methods
- ☐ Electrochemical methods

The methods will each be discussed in more detail in the sections below. The costing of the various treatment methods is explained in Chapter 7, and further details provided in Appendix A.

3.1 Permeable Reactive Barrier (PRB) methods

This entails the placement of a permeable physical or chemical "barrier" in the flow-path of the pollution plume. The configuration of the barrier varies depending on the type of pollution source and the aquifer properties. The chemically reactive part of the barrier also varies depending on the actual contaminant being treated. For the purposes of this project the main emphasis will be placed on the various barriers that have been used for nitrate removal. The feasibility and potential of applying these techniques to South African aquifers are reviewed. In the paragraphs below, two types of barriers are discussed. In the first type, i.e. *In Situ* Redox Manipulation (ISRM), the aquifer material is chemically modified to serve as a chemical redox barrier. The second type, i.e. Permeable Reactive Barriers (PRB), involves the construction of a physical barrier consisting of chemically reactive material.

3.1.1 *In Situ* Redox Manipulation:

In Situ Redox Manipulation (ISRM) is a process that is based on chemical manipulation of natural redox processes to change the mobility or form of contaminants (Innovative Technology, 2000). In the case of nitrate, removal by ISRM involves chemical denitrification by reduced species of iron.

3.1.1.1 Operating principle

ISRM creates a permeable treatment zone by injection of chemical reagents into the subsurface, down gradient of the contaminant source. The type of reagent is selected according to its ability to alter the oxidation/reduction state of the aquifer materials and groundwater to such an extent that it will allow the destruction or immobilization of specific contaminants. The method is based on creating a permeable reactive barrier, placing optimum treatment capacity in the most permeable part of the subsurface.

Unconfined aquifers are usually oxidizing environments and many of the contaminants in these aquifers are mobile under oxidizing conditions. However, appropriate manipulation of the redox potential can result in the immobilization of redox-sensitive inorganic contaminants and the destruction of organic contaminants. This technique requires the presence of iron in the aquifer, which can be reduced from its oxidized state in the aquifer sediments to serve as a long-term reducing agent. Figure 3 below depicts the ISRM concept.

To create a treatment zone, sodium dithionite (along with pH buffers) is injected into the aquifer through a well and allowed to react with the aquifer material for approximately 18 hours. Water containing the reaction by-products and any remaining reagent is abstracted, tested for hazardous constituents, and disposed. Placement of the redox treatment zone is designed in such a way that contaminated groundwater flows naturally through the zone allowing the contaminants to react with the reduced iron in the sediment.

Sodium dithionite ($Na_2S_2O_4$) is a bleaching agent widely used in the paper industry. The dithionite ion dissociates easily into sulfoxyl radicals (SO_2^-). The sulfoxyl radical is a strong and highly reactive reducing agent. The reducing agent reacts as follows with the naturally occurring iron in the sediments:

$$SO_2^- + Fe\ (III) + H_2O \leftrightarrow SO_3^{2-} + Fe\ (II) + 2H^+ \quad (5)$$

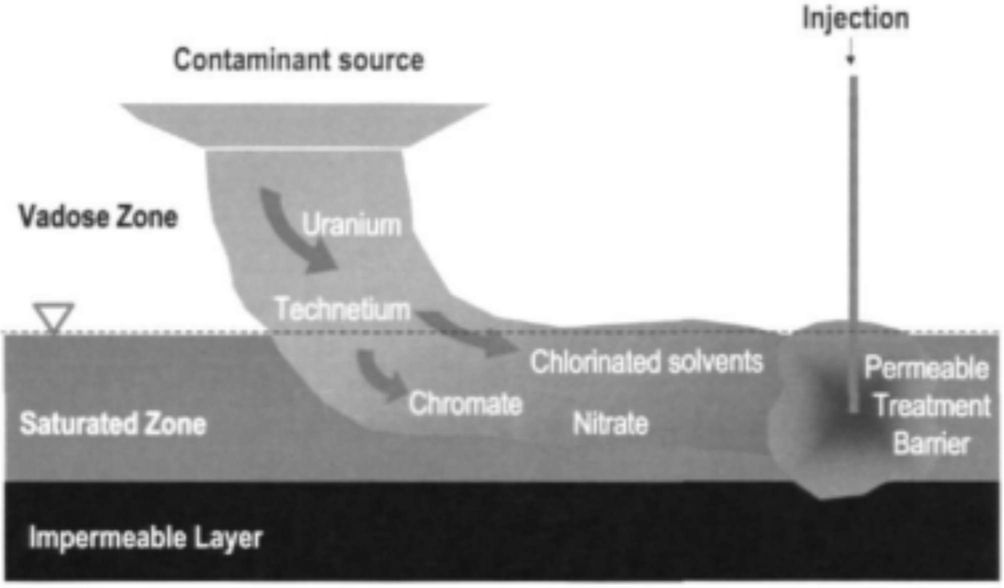


Figure 3: ISRM concept *(after Innovative Technology, 2000)*

The reduced Fe (II) then acts as a reducing agent for various contaminants in the groundwater. In the case of nitrate removal, denitrification occurs by the reaction of nitrate with the ferrous iron.

3.1.1.2 Applications of ISRM

The method has been applied to chromate plumes in a field study, and bench scale tests show that ISRM is also effective for removal of dissolved trichloroethylene (TCE) and uranium in groundwater (Innovative Technology, 2000).

The ISRM method is well suited for sand or sand and gravel aquifers which have sufficient hydraulic conductivity to allow injection and significant migration of dithionite solution before it reacts to form sulphate, thiosulphate, and sulphide (Innovative Technology, 2000). Low permeability aquifers and fractured rock aquifers are not suitable for this method.

The method can be applied to sites where groundwater contamination by redox sensitive metals, such as chromium, uranium, and technetium, inorganic ions, radionuclides or chlorinated hydrocarbons are dispersed over large areas and are deeper than 10 metres below the surface (Innovative Technology, 2000).

3.1.1.3 ISRM vs. other technology

Compared to other methods, e.g. pump and treat, the ISRM method requires minimal operational and maintenance staff and hence lower costs. Permeable reactive treatment barriers are a similar method, however the ISRM can be used at greater depths than trench-and-fill reactive barriers, which are best suited for applications less than 12 metres below ground surface. Vapour stripping, air sparging, and bioremediation are also technologies competing with ISRM in the organic contaminant treatment field (Innovative Technology, 2000).

3.1.1.4 Efficiency

The method was tested at the US Department of Energy's decommissioned nuclear reactor site at Hanford in Washington. These tests were conducted to investigate the principle of ISRM and the treatability of various redox-active groundwater contaminants. The method is able to reduce aqueous concentrations of chromate in the groundwater from starting concentrations of 46 to 71 ppb to near the 2 ppb detection limit within four months (Innovative Technology, 2000). Less time is required to achieve results with the ISRM method as compared to other treatment technologies. Most of the dithionite solution used for creating the barrier, as well as mobilized trace metals, can be removed from the subsurface during the abstraction phase directly after the aquifer conditioning (Innovative Technology, 2000). Monitoring of a test site showed that the treatment zone remained anoxic and the contaminant remained below detection limits for two years after establishment of the ISRM barrier. The treatment zone lifetime is estimated at 7 to 13 years (Innovative Technology, 2000).

3.1.1.5 Other advantages/disadvantages

The treatment zone remains active in the subsurface where it can treat contaminants seeping to the water table and into the flow path even if the contaminant source is not removed. It is a relatively safe method as all reagents, as well as the modified matrix materials, remain in the subsurface where the reactions take place, and the inhabitants of a particular area are not exposed to any of the materials. The reactive barrier is renewable and dithionite can be re-injected once treatment requirements are no longer met.

The ability of the method to succeed is dependent on the hydraulic properties of the aquifer. The quantity of iron naturally present in the soil and the aquifer affects the reducing capacity. In the case of low iron content, the reducing capacity of the barrier will be small, while in the case of high iron content, the dithionite may be consumed before it has travelled far enough and reached the intended placement position in the aquifer.

3.1.1.6 Discussion

ISRM provides an innovative approach to cleaning up or retarding the migration of contaminant plumes through the aquifer. However, information on possible undesirable side effects appears to be lacking.

Although the method has been claimed to be successful, for example in decreasing concentrations of chromium, the addition of dithionite to the aquifer may increase dissolved iron concentrations, which can cause other problems relating both to water quality and to stability of aquifer materials. Where iron oxides form a major component of the primary aquifer, the permeability of the formation may be affected in the immediate vicinity of the injection borehole. Long term testing has yet to be conducted.

Dithionite is an irritant and may be harmful by absorption, ingestion or inhalation in high concentrations. Should a small amount of residual dithionite remain in the water after aquifer treatment it is not expected to have severe toxic or carcinogenic health effects. However, the actual application of the sodium dithionite may be hazardous, because of its flammability and its tendency to heat spontaneously in contact with moisture and air (Mallinckrodt Baker Inc., 2001). There are regulatory restrictions on injecting chemicals into a water resource under the pollution prevention policies of the National Water Act (1998), see Chapter 6.

3.1.1.7 Hydrogeological requirements for ISRM

The following aquifer characteristics are essential for the successful application of ISRM:

- High permeability, porous primary aquifers
- Appreciable natural iron (hydr)oxides, preferably iron-coated sands
- A simple, well characterised subsurface flow system
- Impermeable bedrock
- Injection borehole(s) between contaminant source and abstraction borehole

3.1.1.8 Potential limitations:

- Cost of dithionite and other reagents
- Hazardous material handling
- Only applicable in certain hydrogeological environments, particularly not in fractured rock systems
- Long term performance as yet unproven
- The dithionite ISRM system has been patented by the US company Battelle Pacific Northwest National Laboratory (July 1998) and royalties might be payable for its application.

3.1.1.9 Application in Southern Africa

It may be possible to investigate the applicability of this method in the following primary aquifers:

- Kalahari
- Weathered granite aquifers, e.g. Namaqualand granite-gneiss complex, Halfway House granite, etc.
- Primary aquifers: sites include: Chloorkop, Modderfontein, Sasolburg / Secunda

3.1.2 Permeable Reactive Barriers (PRB)

Permeable Reactive Barriers (PRB) are also referred to as "passive treatment walls" and "*in situ* reactive barriers" and have been tested over a long period from bench scale to full-scale implementation plants (Blowes *et al.*, 2000; Robertson and Cherry, 1995, 2000; Schipper, and Vojvodic-Vukovic, 2000). Laboratory studies show that the methods can be used for the treatment of many inorganic contaminants including arsenic, cadmium, chromium, copper, mercury, iron, manganese, molybdenum, nickel, lead, selenium, technetium, uranium, vanadium, nitrate, phosphate, and sulphate. Cadmium, chromium, copper, iron, nickel, lead, nitrate, phosphate, and sulphate have also been treated in field studies (Blowes *et al.*, 2000). Examples of PRB systems suitable for treating some of the other potential contaminants mentioned are discussed briefly, while those for nitrate are described in more detail.

O'Hannesin (1998) lists the various types of contaminants that can be treated and the reactive materials that have been used to treat these contaminants.

Table 1: Contaminants and reactive materials used for treatment *(modified from O' Hannessin, 1998)*

Contaminant	Reactive Material
Halogenated Organics (CCl_4, HCB, DCE, TCE, etc.)	Fe(0), bimetallic materials, Al, Fe, Zn, Mg, Sn.
Metals	Fe(0), organic carbon
Acid mine drainage	Organic carbon
Gasoline/petrol derivatives	Oxygen releasing compounds
Nitrate	Organic carbon or mixed organics + bacteria
Phosphorous	Metal oxides, limestone
Cr(VI), Cr	Fe(II) in aquifer material, Fe(0)

Permeable Reactive Barrier technology has been studied extensively and over 100 references testify to its usefulness in ridding groundwater from the above listed contaminants (See for example websites http://www.rtdf.org/public/permbarr/barrdocs.htm or http://www.prb-net.org). Its application extends to the USA, Canada, Austria, Australia, New Zealand and Russia with operational and test sites at industries, water works, municipal well fields, homes and wastewater treatment plants.

3.1.2.1 Operating principle

Permeable reactive barriers are constructed in the path of a migrating plume of contaminated groundwater. The porous treatment wall is constructed below the water table, perpendicular to the groundwater flow (Schipper and Vojvodic-Vukovic, 2000). They are typically designed as a continuous trench, filled with permeable, reactive material or a funnel-and-gate configuration, which includes impermeable sections, directing the groundwater flow through the permeable "gates".

PRB systems can be applied for the removal of anions, cations, organic compounds and inorganic compounds and utilise various processes such as reduction and precipitation, adsorption and precipitation, and biologically mediated reduction and precipitation (Blowes *et al.*, 2000). Various processes have been employed in different configurations and the system design is generally both site- and contaminant specific.

3.1.2.2 Treatment walls for inorganic anions

This includes:

- Reduction using zero-valent iron (iron metal) walls;
- Biologically mediated reduction and removal using organic carbon walls; and
- Adsorption and precipitation of inorganic anions.

The first two methods listed above, i.e. reduction using zero-valent iron and biologically mediated reduction, are suitable for nitrate removal. The third method applies mainly to phosphate and other non redox-active anions that are not suitable for removal by reductive or oxidative processes (Blowes *et al.*, 2000). This method is not appropriate for nitrate removal, since nitrate does not form insoluble salts and it is generally very weakly adsorbed on surfaces, (Blowes *et al.*, 2000; Robertson and Cherry, 1995; 2000; Schipper and Vojvodic-Vukovic, 2000).

3.1.2.2a Reduction using zero-valent iron walls

This method is applied mainly to chromium, arsenic, technetium and selenium (McRae *et al.*, 1997; 1999). It can, however, be used for other redox-active oxyanions or for simultaneous treatment of organic and inorganic contaminants (Blowes *et al.*, 2000). Reductive precipitation of anion-forming elements, using zero-valent iron as a reducing agent, has been investigated at laboratory scale, field pilot scale and in large-scale demonstrations.

Preliminary results showed that Tc (VIII), U (VI), and NO_3^- are removed by the zero-valent iron treatment walls (Blowes *et al.*, 2000). In contrast to the metallic species, however, nitrate is removed by conversion to N_2 gas, rather than immobilised by precipitation. Chemical data for existing permeable reactive barriers show that site-specific results vary in terms of pH, alkalinity, precipitate types and microbial activities (Liang *et al.*, 2000). One consistent variable is oxidation-reduction potential (Eh), which is between -400 and -600 mV within the Fe (0) medium (Liang *et al.*, 2000).

3.1.2.2b Denitrification walls with organic carbon

Treatment of nitrate may also be achieved by adding a slowly degrading carbon source, such as sawdust or woodchips, to the matrix of the permeable wall, instead of zero-valent iron. The carbon acts as an electron donor, promoting an anaerobic environment and providing an energy source for denitrifying bacteria (Schipper and Vojvodic-Vukovic, 2000). Biological denitrification is the main mechanism of nitrate removal in these systems.

This method has been applied to primary aquifers and shallow groundwater systems (Schipper and Vojvodic-Vukovic, 2000). Robertson and Cherry (1995) showed that denitrification walls effectively removed nitrate from groundwater with a known pollution point source (septic tank system).

Schipper and Vojvodic-Vukovic (2000) used the following equation to calculate nitrate removal rates using a denitrification wall:

$$\text{N removal} = \frac{q \times A \times \Delta\,[NO_3 - N]}{\text{Soil volume}} \qquad (6)$$

The numerator is the mass of nitrate removed in the wall, where q = groundwater flow rate (m day^{-1}); A = cross sectional area conducting groundwater (1 m^2 × the porosity); and $\Delta\,[NO_3 - N]$ ($g.m^{-3}$) = the difference between the nitrate concentration entering the denitrification wall and that arriving at the borehole. The denominator is the volume of the matrix in the wall that the nitrate passes through (Schipper and Vojvodic-Vukovic, 2000).

Factors that may affect the performance of the wall, or denitrification/nitrification rates include competing biological reactions such as dissimilatory nitrate reduction to ammonium and nitrogen immobilisation (Schipper and Vojvodic-Vukovic, 2000).

3.1.2.3 Requirements for the denitrification walls

- ☐ The site should have a shallow water table, preferably in a primary aquifer.
- ☐ Aquifer parameters should be well understood.
- ☐ Wellpoints should be constructed within the wall and on either side of it in order to monitor any change in concentrations as the groundwater passes through.

Before constructing a denitrification wall, both the soil and the groundwater should be sampled. Determination of groundwater flow rates in the aquifer is also an important part of the process that precedes emplacement of the wall. In simple, saturated flow systems, flow rates can be determined using Darcy's Law and measurements of hydraulic gradients, porosity and saturated conductivity at the site (Schipper and Vojvodic-Vukovic, 2000).

3.1.2.4 Case studies:

a) Five years of operation of a denitrification wall
Nitrate removal, denitrification and carbon dynamics were monitored in a pilot scale denitrification wall for 5 years (Schipper and Vojvodic-Vukovic, 2000).

Results of the monitoring exercise showed:

- The wall continuously removed more than 95% of the incoming nitrate in the groundwater.
- No decrease in the total carbon was detected in the system over the 5-year period.
- Available carbon decreased after the first 200 days of operation of the system, after which it remained fairly constant.
- Carbon availability was not limiting the size of the microbial population.
- A large decrease in the number of denitrifying bacteria occurred over time, as indicated by a decline in enzyme activity.
- The denitrification rate was still high enough to remove nitrate from groundwater and was limited by nitrate rather than by carbon availability.

The lessons learnt from the monitoring exercise were:

- Denitrifying bacteria use simple organic compounds, and are thus reliant on other organisms to degrade the sawdust into these compounds. Schipper and Vojvodic-Vukovic (2000) found that potential rates of denitrification were always greater than initial measured rates. They used this as an indication that denitrification was limited by nitrate concentration, rather than the carbon availability.
- Predicting the lifetime of the wall is not an easy task, due to the slowly changing carbon content. However, 40 m^3 of sawdust in a 35 x 1.5 x1.5 m trench has been calculated, to contain a sufficient amount of carbon to last approximately 15 years, using organic degradation with NO_3^- or SO_4^{2-} as electron acceptors (Robertson and Cherry, 1995).
- The longevity of the sawdust in the denitrification wall is estimated using stoichiometric equations with nitrate as the sole electron acceptor. It is possible that the lifetime of a denitrification wall might be over-estimated by this method, as only the rate of consumption of simple carbon compounds is considered. The calculation does not take into account that the initial rate of anaerobic degradation is limited by the initial cleavage of the polymeric carbon molecules.
- Oxygen intake by soil or the wall should be minimized, as oxygen directly attacks and thus consumes organic matter, affecting the efficiency of the wall.

b) *In situ* denitrification wall field trials

Robertson and Cherry (1995) ran field tests at three sites over approximately one-year periods, during which they monitored flow and change in concentration of species throughout the wall. They also calculated the longevity of the wall based on the measurements taken during the year of operation. Figure 4 shows the concentration changes in the wall with depth after 370 days of operation.

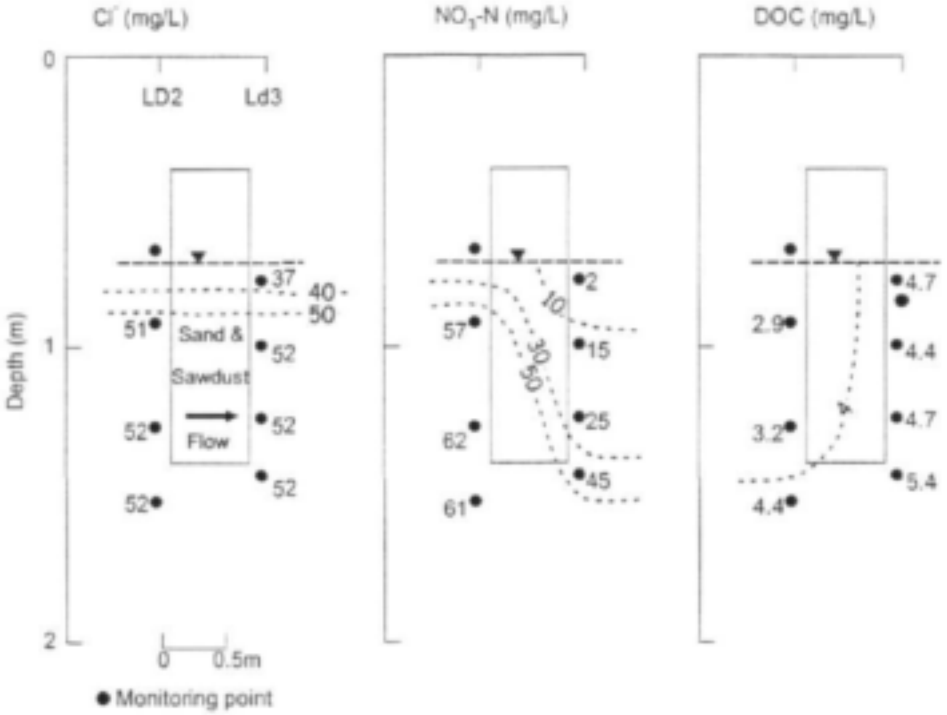


Figure 4: Results of monitoring a denitrification wall, operating for 370 days. Chloride, nitrate and DOC data are shown up and down-gradient from the wall *(from Robertson & Cherry, 1995)*

At another two sites where the testing was conducted, chemical profiles of the wall were measured after a year. The results for the two soils are presented in Figure 5.

3.1.2.5 Barrier longevity and undesirable side reactions

According to the following general equation for heterotrophic denitrification,

$$5CH_2O + 4NO_3^- \rightarrow 5CO_2 + 2N_2 + 3H_2O + 4OH^- \qquad (7)$$

56 kg of NO_3 - N requires about 60 kg of carbon for complete denitrification. This indicates that the carbon mass in the 40 m^3 of sawdust used in the wall in the tests performed by Robertson and Cherry (1995) could last up to 200 years. The longevity of the wall may, however, be grossly overestimated using only the denitrification reaction, since various other reactions can also remove organic carbon. For example, organic carbon is consumed or decreased by sulphate reduction and excess DOC leaching, as well as reaction with oxygen that enters the system.

Nevertheless, Robertson and Cherry (1995) showed that organic carbon consumption by oxygen and sulphate in their experiment was negligible compared to that by denitrification as the molar quantities of SO_4^{2-} and dissolved O_2 were less than that of the $NH_4^+ + NO_3^-$. Their calculation suggests that denitrification walls can provide effective denitrification for a considerable number of years without maintenance costs associated with replacing the carbon source.

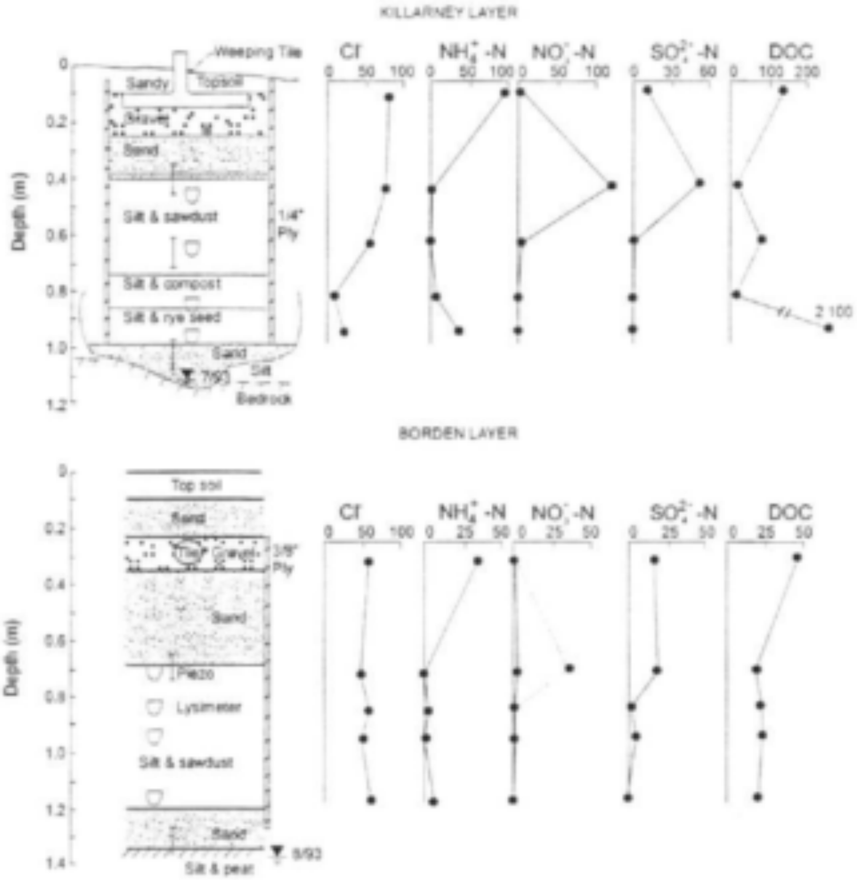


Figure 5: Denitrification walls showing chemical profiles (mg/l) after one year of operation (410-424 days after start-up) *(Robertson & Cherry, 1995)*

3.1.2.6 Applicability and efficiency of PRBs

The following factors may affect the applicability and effectiveness of permeable reactive barriers:

- ☐ Treatment walls may lose their reactive capacity over time, hence requiring replacement of the reactive medium.
- ☐ Biofilm formation or chemical precipitation of mineral salts may decrease the permeability of the treatment wall or surrounding aquifer.
- ☐ The depth and width of the barrier may be a limiting factor in its treatment capability.
- ☐ PRB treatment is limited to a subsurface lithology that overlies either impermeable bedrock or a continuous aquitard, at a depth within the vertical limits of trenching equipment.

3.1.2.7 Discussion

Denitrification walls are appealing for use in rural areas because:

- ☐ The walls can be constructed from inexpensive, non-hazardous, readily available materials such as sawdust or woodchips.
- ☐ Construction and filling of the trenches may provide employment for relatively unskilled labourers.
- ☐ The passive wall may have a long treatment lifetime without requiring maintenance.

This method could be applicable where groundwater for rural supply is sourced from alluvial aquifers overlying bedrock at relatively shallow depths (e.g. less than 10 m).

Denitrification walls could be constructed as a PRB between on-site sanitation and water supply boreholes in rural and peri-urban settings. Field trials would be recommended to show that the walls are effective for nitrate removal under local conditions.

3.1.2.8 Carbon sources

The solid organic carbon source used in the walls may limit the rate of denitrification, since complex organic molecules such as lignin and cellulose must first be broken down into simpler compounds before they are available to denitrifying bacteria. The C:N ratio and oxidisability of the organic matter have been found to be important parameters in denitrification (Dodds and Fey, 1995). Readily oxidisable, carbon-rich substrates such as sucrose or glucose promote rapid denitrification, while straw, grass and wood chips are less effective over the short term, but may provide a slow-release form of nitrogen for long-term applications. The *in situ* biological denitrification methods, discussed below, use liquid sources of organic carbon, such as alcohols, as a source of carbon which is readily available to the microorganism populations for rapid denitrification.

3.1.2.9 Potential limitations of the method

PRB systems are not suitable for all hydrogeological settings. The requirements of a shallow water table and impermeable bedrock at shallow depth will not be met by many of South Africa's fractured rock aquifer systems. Maintaining the anoxic conditions that promote denitrification may also be problematic in shallow groundwater environments.

The oxidation of organic matter tends to solubilise organic carbon compounds and increases the dissolved organic carbon content of the groundwater. This may cause undesirable side effects, such as disinfection by-products when the water is chlorinated.

3.1.2.10 Application in South Africa

Due to the requirements of the permeable reactive barrier methods as well as the need for groundwater remediation, the following areas have been noted as possible areas for application:

- Cape Flats, Atlantis and other sandy aquifers
- PE, Swartkops/Uitenhage alluvial aquifer
- Zululand coastal aquifer: Isipingo, Richards Bay Industrial Area
- Alluvial aquifers
- Marydale in the Northern Cape
- Mining areas

3.2 Biological methods for treatment of contaminants

Biological denitrification utilises bacteria to denitrify aqueous nitrates in the absence of oxygen. Biological treatment methods, also referred to as "bioremediation" by many consulting companies and researchers, are also used to treat BTEX, VOCs, MTBE, PCE, DDT and free products from fuel oil (http://www.ebsi-inc.com). For this purpose, specific microbes are added that consume the contaminants.

The denitrifying bacteria are heterotrophic (more correctly chemoheterotrophic), i.e. they require an energy source, either in the form of organic carbon, carbon dioxide or sulphur. These denitrifying bacteria are anaerobic respirators that can use nitrate and/or nitrite as electron acceptors for the oxidation of organic compounds when oxygen is absent, producing nitrogenous gases (N_2, NO, and N_2O). The list of denitrifying bacteria in Table 2 below includes 13 genera which have been documented to be capable of denitrification.

Table 2: Genera of bacteria capable of denitrification *(modified from Firestone, 1982; Rott & Lambert, 1991)*

Genus	Hydrogen Donor	Important characteristic of species
Alcaligenes spp.	Cl-compounds	Commonly isolated from soils
Agrobacterium		Some species are plant pathogens
Azospirillum		Capable of N_2 fixation, commonly associated with grasses
Bacillus	Cl-compounds	Thermophilic denitrifiers reported
Flavobacterium		Denitrification species recently isolated
Halobacterium		Requires high salt concentrations for growth
Hyphomicrobium		Grows on one-carbon substrates
Paracoccus denitrificans	Hydrogen	Capable of both heterotrophic and lithotrophic growth
Propionibacterium		Fermentors capable of denitrifying
Pseudomonas spp.	Cl-compounds	Commonly isolated from soils
Rhizobium		Capable of N_2 fixation in symbiosis of legumes
Rhodopseudomonas		Photosynthetic bacteria
Thiobacillus	Reduced S compounds	Generally grow as chemoautotrophs
Achromobacter spp.	Cl-compounds	
Thiobacillus thioparus	Reduced S compounds	
Thiomicrospira denitrificans	Reduced S compounds	
Thiosphera pantotropha	Reduced S compounds	
Pseudomonas pseudoflava	Hydrogen	

3.2.1 *In Situ* Biological Denitrification (ISBD)

This treatment method is a viable option when the rate of contaminant biodegradation is faster than the rate of contaminant migration. Rates are dependant on the type of contaminant, the microbial community, and the subsurface hydrogeochemical conditions. Treatment techniques are focussed on optimising the conditions that support natural denitrifying microorganisms.

3.2.1.1 Operating Principle

Several techniques for nitrate removal rely on natural microbiological reactions, which convert nitrate into other forms of nitrogen, particularly nitrogenous gases. For ISBD, substrates containing organic carbon are added as an energy source to enhance the activity of the microorganisms. The principle behind the technique is similar to the addition of carbon sources in denitrification walls (Section 3.1.2), except that the high molecular weight carbon sources in the wall have a slow-release action, whereas those used for ISBD are readily available, low molecular weight compounds. The reagents such as ethanol, methanol, acetic acid, glucose or sucrose are usually injected in liquid form into wellpoints or boreholes in the affected area (ITRCWG, 2000; Bates and Spalding, 1998). If there is no resident population of suitable microbial communities, microorganisms may also be artificially introduced.

The influx of oxygen into the system inhibits denitrification, and depletion of natural oxygen may cause delays in the reaction of microbes, which then become insufficiently fast to contain contaminants (ITRCWG, 2000). Lack of a sufficiently large size microbial population may also limit the clean-up rate. The size of a microbial population is, in turn, affected by the environmental conditions prevailing in the area. Often conditions of slightly high or low pH, organic carbon availability or the ambient temperature can enhance or inhibit growth, depending on the optimum conditions for growth of a specific microbial population. Salinity is also an important control on microbial activity.

3.2.1.2 Requirements for in situ *biological denitrification*

- ☐ Sufficient quantities of the carbon source should be available.
- ☐ The size of the microbial community should be large enough for a suitable rate of denitrification.
- ☐ Environmental conditions e.g. pH, temperature, salinity, enzyme activity should be suitable for growth of denitrifying bacteria.

3.2.1.3 Applications of ISBD

Smith *et al.* (1991) tested a microbial denitrification method using the denitrifying bacteria, *Hyphomicrobium X*. Their experiments were carried out in the form of batch tests and column tests in the laboratory. The column tests were also scaled up to small bioreactor columns for use as rural water treatment systems. Although these were intended for nitrate removal after the groundwater had been abstracted, it is possible that the technique could be modified so that the denitrifying microorganisms are injected into the subsurface for *in situ* nitrate treatment.

Mercado *et al.* (1988) applied ISBD to phreatic coastal aquifers in Israel with lithological units varying from sand dunes to heavy soils. They found that the unconsolidated aquifer formations serve as integrated bioreactors and filters for contaminants (Mercado *et al.*, 1988). In this case, ISBD was used for the treatment of nitrate-rich wastewaters infiltrated from the surface, rather than *in situ* treatment of nitrate-rich groundwater. The contaminated water was artificially recharged, along with an organic substrate and the aquifer used as a subsurface bioreactor to denitrify the wastewater. Nitrate free water could then be recovered from the aquifer after treatment.

The denitrification system operates on the same general principles as other *in situ* treatment systems i.e. an organic substrate is injected into the aquifer to introduce the carbon source (electron donor), which is required for denitrification. Phosphate is also injected with the carbon source to stimulate microbial growth. Anoxic conditions develop at the injection well, creating a natural bioreactor where nitrate is reduced to nitrogen gas.

Mercado *et al.* (1988) tested two main configurations for their ISBD treatment system:

- ☐ Denitrification in a single dual-purpose borehole
- ☐ Substrate injection through a battery of small diameter boreholes surrounding a production borehole

The single- and multi-well denitrification systems are illustrated in the following figures. In these drawings, the anoxic part of the aquifer is labelled Zone I. Zone II serves as a sand filter, in which turbidity and suspended solids are removed. Zone III is the area of nitrate free water, which can be recovered from the aquifer.

In the single well system (Figure 6), the same borehole is used for recharge (injection) and abstraction. This requires intermittent operation of the borehole, which needs to be equipped with both injection and pumping equipment or, alternatively, needs to be re-equipped each time its function changes. Nitrate polluted water and methanol substrate is injected into the borehole. After denitrification, a zone of nitrate free water is obtained around the borehole and this is later abstracted from the same borehole (Mercado *et al.*, 1988).

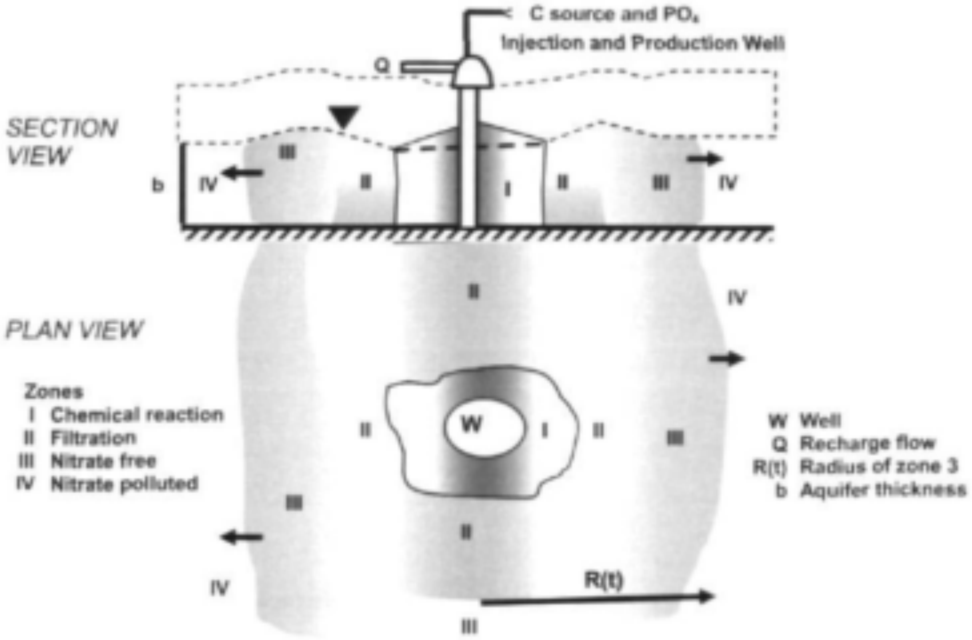


Figure 6: Schematic cross section (above) and plan view (below) through a single well denitrification system *(after Mercado et al., 1988)*

Figure 7 shows another configuration for a biological denitrification system. In this case, two piezometers of different depths were installed in the same borehole. The shallower one is used for injection of nitrate-polluted water and organic substrate and the deeper one is used to recover denitrified water from the aquifer. A drawback of this method is that severe clogging can occur due to gas generation and biomass accumulation (Kruithof *et al.*, 1985).

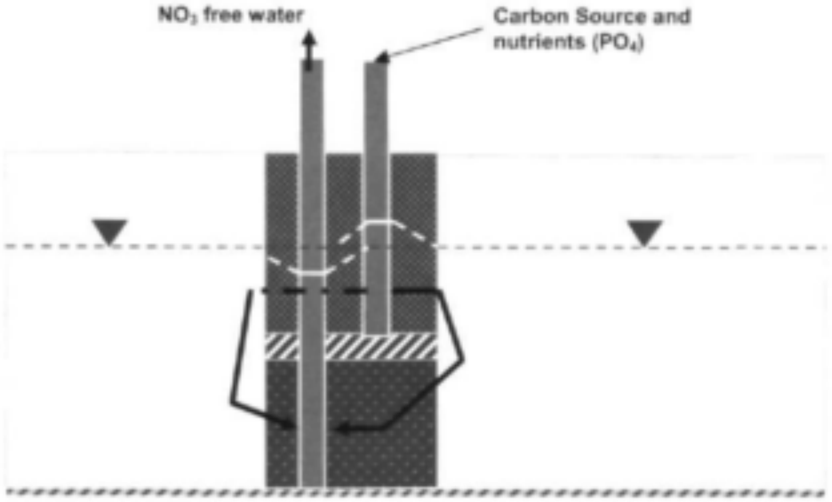


Figure 7: Schematic depiction of a vertical doublet denitrification system *(after Mercado et al., 1988)*

Figure 8 shows a horizontal doublet system. This system operates on the same principle as the previous two systems, with the bioreactor forms horizontally between the two wells.

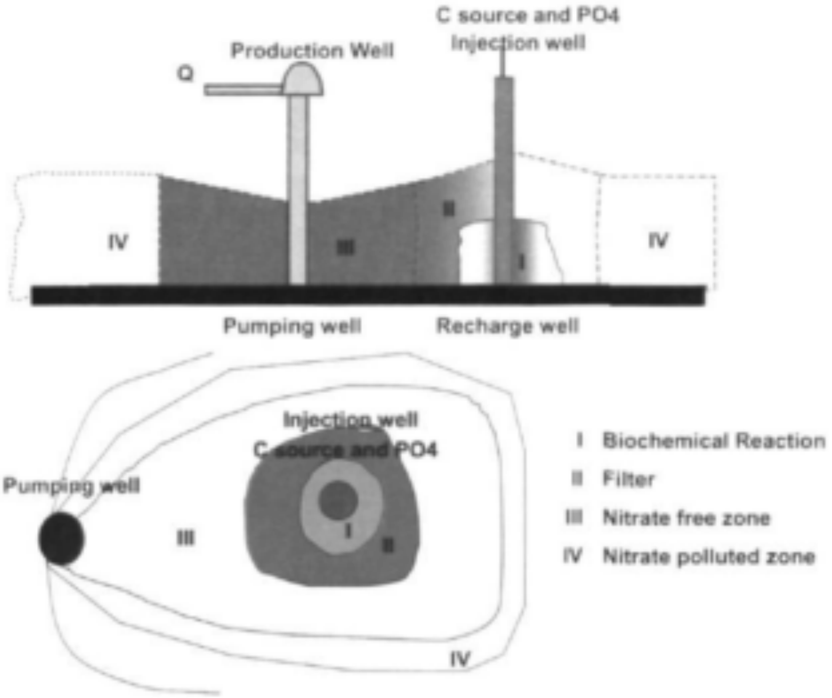


Figure 8: Schematic depiction of the horizontal doublet system *(after Mercado et al., 1988).*

The aquifer typically serves as the reaction vessel and filter. In this case zone I indicates the area where biochemical reactions are most likely to occur, the aquifer material in zone II acts as a filter, while the treated water in zone III can be abstracted for use. Zone IV represents the area of the aquifer containing groundwater polluted with nitrate. A multi-well configuration is the "daisy" denitrification system shown in Figure 9.

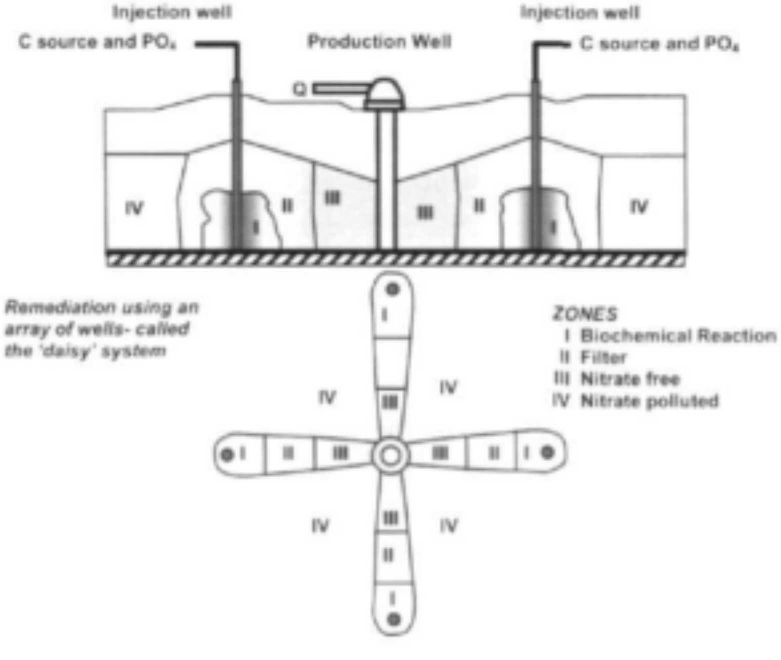


Figure 9: A schematic representation of the daisy system *(after Mercado et al., 1988)*

It involves a circular battery of small-diameter injection boreholes, surrounding the central production borehole. An organic substrate and phosphorus are introduced into the aquifer through the injection boreholes. Mixing, dilution and denitrification occur along the flow path towards the It involves a circular battery of small-diameter injection boreholes, surrounding the central production borehole. An organic substrate and phosphorus are introduced into the aquifer through the injection boreholes. Mixing, dilution and denitrification occur along the flow path towards the production borehole.

Field experiments conducted by Mercado *et al.* (1985), showed the Daisy System to have several advantages over the other system configurations. These include the fact that only one pumping borehole is required. The denitrified water also remains in contact with the untreated water, and is not completely depleted of oxygen. The oxygen concentration can be controlled by the number of injection wells and their sequence of operation. This means that the discharge rate of the production borehole can be changed without affecting the rate of nitrate removal (Mercado *et al.*, 1985).

3.2.1.4 Discussion

The effectiveness of ISBD is governed by the presence or availability of chemical species such as carbon, oxygen containing species (e.g. nitrate) and the environmental conditions, which affect microbial activity. If bacterial regeneration is inhibited, the denitrification rate will decrease and eventually stop as bacteria die off.

The oxygen influx in the system is an important controlling factor. A large amount of free oxygen in the system inhibits the denitrification process, since the bacteria will prefer to use oxygen for the oxidation of organic carbon rather than the nitrate. Oxygen influx is described as a probable cause for nitrite accumulation in systems studied by Smith *et al.* (1991). On the other hand, if aerobic bacteria are the most active denitrifiers in a system, nitrate removal may be retarded when the environment becomes completely anoxic and can no longer support these microorganisms. This may be a temporary effect until an anaerobic colony becomes established.

3.2.1.5 Limitations

Partial denitrification to nitrite is uncommon, but can be problematic in biological denitrification applications, since nitrite is more toxic than the original nitrate. Hunter (2003) reported nitrite accumulation when phosphorus was limiting. Some of the carbon sources that are used for ISBD e.g. methanol, are also toxic and can cause contamination problems if the dosage is too large and the compounds are not fully degraded in the aquifer. These factors all directly affect the success of the denitrification process.

3.2.1.6 Application in South Africa

In situ biological denitrification by Mercado's method due to it's multitude of configurations could be applied to a range of hydrogeological settings. It was applied in a coastal aquifer in Israel, so Southern Africa's coastal regions would be a good starting point if the treatment is required. These include:

- ☐ Atlantis
- ☐ Richards Bay
- ☐ Uitenhage coastal area

This method would in all likelihood also be applicable to alluvial and aeolian settings, it would thus include areas such as:

- ☐ Marydale, Northern Cape
- ☐ Swartkops area, Port Elizabeth
- ☐ Langebaan aquifer

3.2.2 The Nitredox method

The Nitredox method is a modified configuration of the biological denitrification technique, designed for *in situ* treatment of nitrate (Braester and Martinell, 1988). It involves injection of an organic substrate to enhance denitrification, but also includes an additional phase of injection with aerated water once the nitrogen is removed.

3.2.2.1 Operating principle

The system consists of one pumping borehole located at the centre of two concentric circles of injection boreholes (Figure 10 and Figure 11). Glucose or ethanol is injected into the boreholes in the outer ring to form a reduction zone where nitrate is reduced. At the inner ring, which acts as an oxidation zone, aerated water is injected and iron and manganese oxides are precipitated. The groundwater recovered from the central production borehole is partly free of nitrate and free of iron or manganese by-products (Braester and Martinell, 1988).

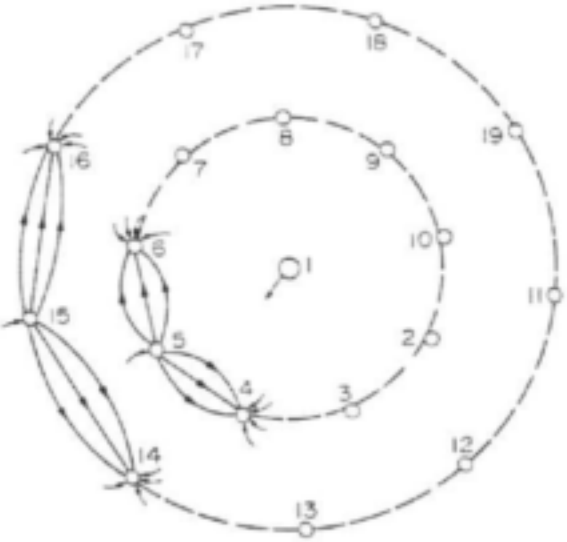


Figure 10: The Nitredox treatment method, plan view. 1 = production borehole, 2 – 10 = injection boreholes on the oxidation ring, 11– 19 = injection boreholes on the reduction ring *(Braester & Martinell, 1988)*

The injection boreholes are operated on a cyclic rotation such that on each circle only one borehole is injecting at a time. During injection, the two boreholes on either side of the injection borehole are pumped. The water pumped from the inner circle is sent through a degassing system to remove the nitrogen gas created by denitrification, so that the build up of gas in the subsurface does not decrease the effective permeability of the aquifer.

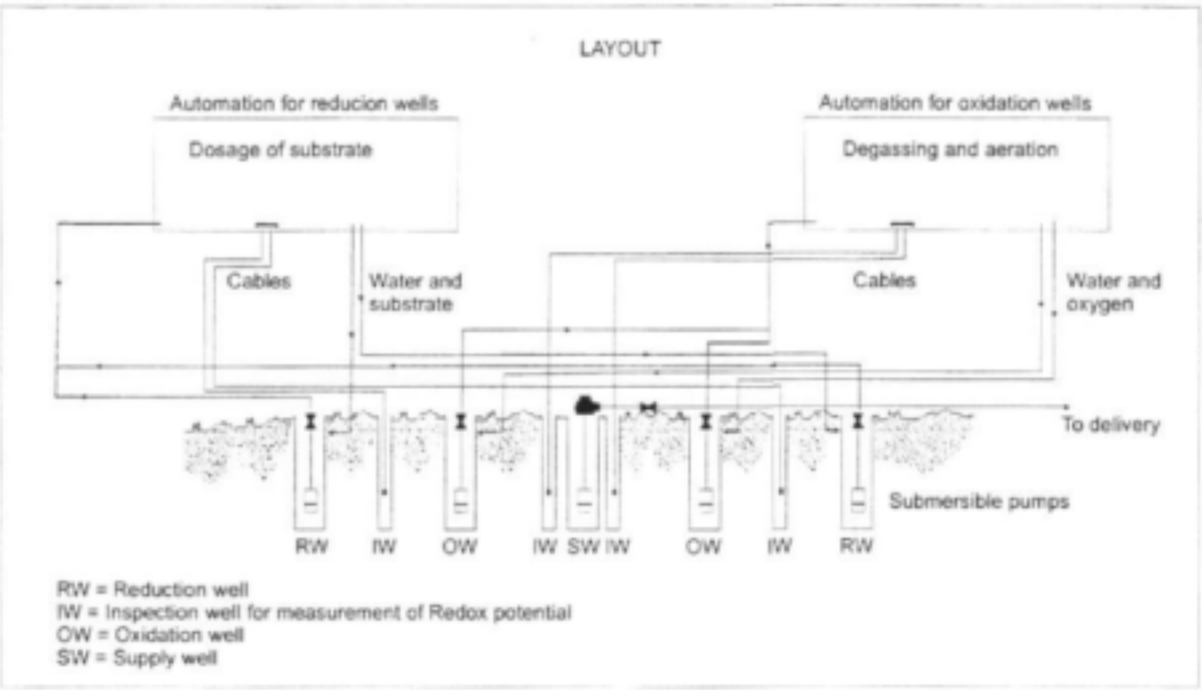


Figure 11: The Nitredox treatment method, cross-section and process diagram *(Braester & Martinell, 1988)*

Monitoring boreholes are positioned between the reduction and oxidation rings and between the oxidation ring and the production borehole to monitor redox potential and changes in chemistry as the process continues. Microorganisms may also be injected if there is no suitable resident community of denitrifying bacteria.

3.2.2.2 Discussion

The main problems arising from the use of this method is the precipitation of iron and manganese oxides, which may lead to clogging problems in the aquifer. The aim of the oxidation phase is to produce groundwater that is free of dissolved iron and manganese, but it may be more appropriate in some cases to remove these metals by *ex situ* treatment after abstraction. This method is complex, requires considerable expense on infrastructure and requires a skilled operator.

However, the largest full-scale *in situ* denitrification plant uses the Nitredox principle. This plant is located at Bisamberg, Vienna (Austria) and has been operating successfully for more than a decade (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.

From 1983 to 1987 in situ and ex situ biological denitrification tests were carried out in parallel at Broichhof, Neuss, Germany (Wibbe *et al.*, 1986). Based on the outcome of these, a full scale *ex situ* biological denitrification plant was constructed in 1989 (undated brochure published by the city of Neuss, Germany). The main problem experienced with the in situ tests was clogging by the biomass developing during denitrification. More details are provided in Appendix C. However, the exact details of the clogging problem need to be established in order to prevent this from occurring. Differences between the full scale plant at Bisamberg and the pilot scale at Broichhof need to be understood.

3.2.2.3 Application in South Africa

The Nitredox method is successfully applied in Austria to sand and gravel aquifers. Southern Africa's sand and gravel aquifers requiring treatment include the following:

- The Cape flats aquifer
- The Langebaan aquifer,
- The Atlantis aquifer
- Marydale alluvial aquifer
- Swartkops alluvial aquifer, Port Elizabeth
- Uitenhage coastal aquifer
- Weathered granites

This method can be used in many settings in Southern Africa. Its application is limited by financial implications of running such a treatment operation. This method would probably be more suited for the more affluent regions in the country.

3.3 Electrochemical methods

Various electrochemical systems have been described for groundwater treatment, applying enhancements such as electrokinetics and electroosmosis of pore water. These systems generally use an electrical current, applied via two *in situ* electrodes to control the movement and redox chemistry of ions and water in the subsurface. Electrochemical methods can be used as an enhancement of other PRB systems, e.g. by combining electrodes with iron walls to remediate nitrate contaminated groundwater and soils abiotically (Chew and Zhang, 1998).

Electrochemical treatment techniques involve the installation of an anode and a cathode within the zone of contamination. An electrical potential is applied across the two electrodes and the voltage initiates several processes including:

- Movement of water at a faster rate than that expected from hydraulic heads alone.
- Removal of contaminants through pore water/water films faster than that of the water phase.
- Development of an acid front that moves through the treatment zone.

3.3.1 Electrokinetic methods

Electrokinetics is more useful in enhancing other *in situ* treatment methods than when it is applied on its own and, according to Jacobs and Loo (1994), it can be applied in both porous and fractured aquifer media. Figure 12 presents a schematic diagram of the process.

Bench scale tests performed by Chew and Zhang (1998), using a soil sample artificially contaminated with 100 mg/L NO3 -N solution, showed that improved nitrate transformation could be achieved by combining electrode methods with an iron PRB wall (see Figure 13).

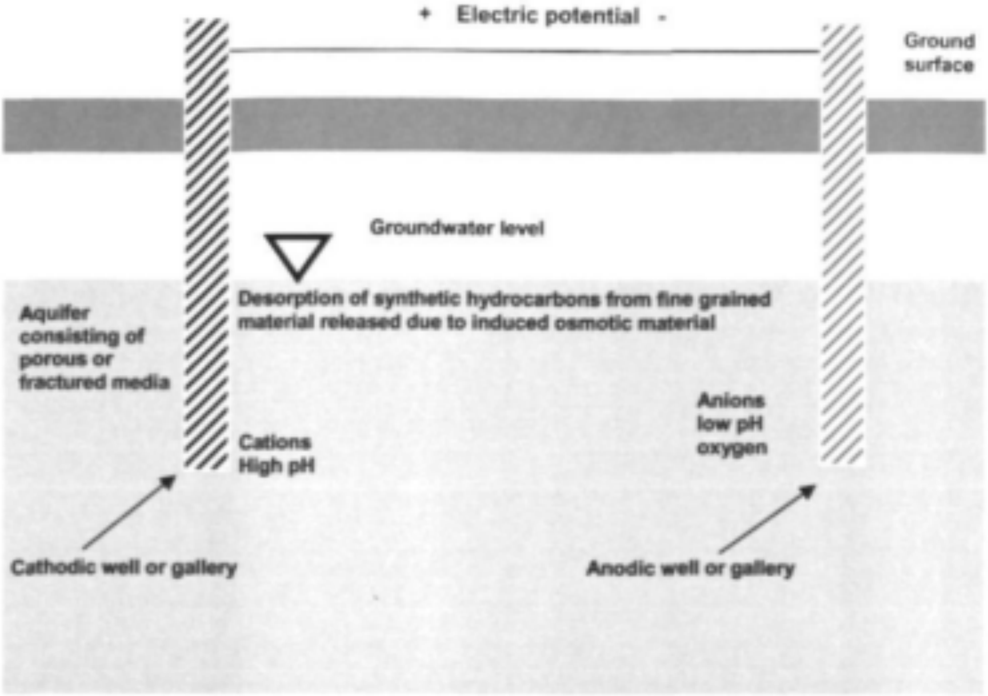


Figure 12: **Schematic diagram of electrokinetics** *(after Jacobs & Loo, 1994)*

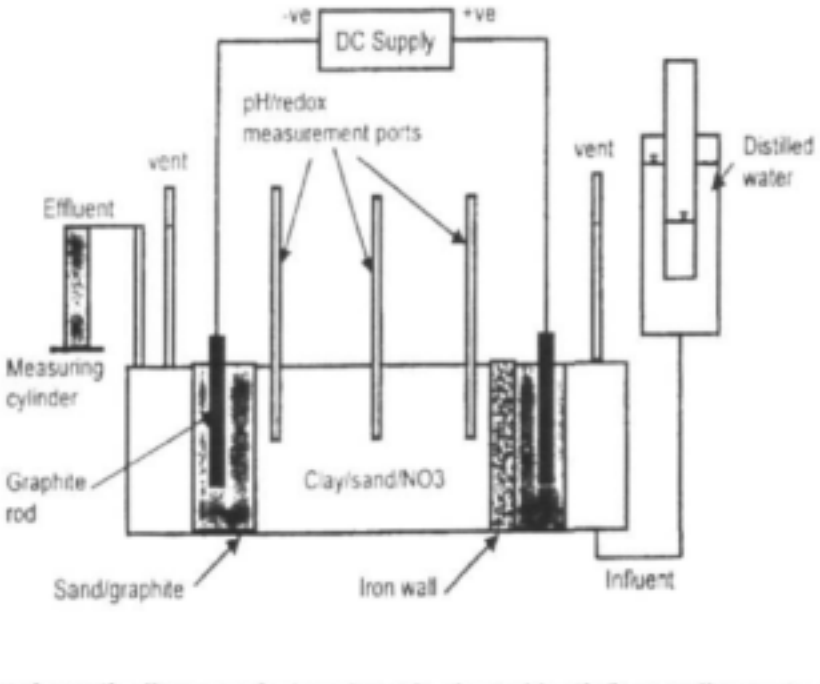


Figure 13: **A schematic diagram of a bench scale electrokinetic/iron wall experiment** *(Chew & Zhang, 1998)*

This is in essence a combination of two methods, the PRB or iron wall method and electrokinetic methods. It is recorded by Chew and Zhang that greater reduction in nitrate levels are achieved when the two methods are combined than when the electrokinetic method is used alone.

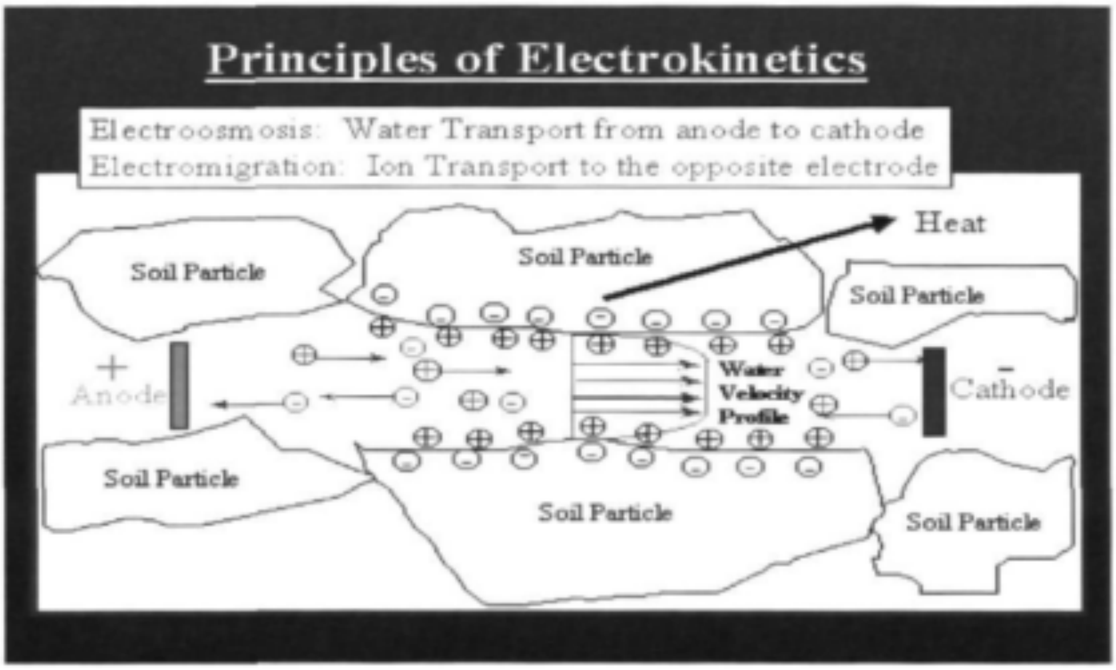
3.3.2 Principles of electrokinetics

Soil minerals generally have a negative surface charge that arises from cation substitutions in the mineral lattice. In solution, the negative surface charge is balanced by cations in the liquid phase positioning themselves all along the soil surface (double layer theory).

The bulk water also contains cations and anions in proportions that balance to give an overall neutral charge. The double layer effect, however, causes the total cations to exceed total anions in the soil pore water near mineral surfaces. When an electrical current is applied, the cations at boundary move toward the cathode, dragging the bulk pore water along with them. The anions in the bulk fluid move toward the anode, but are counterbalanced by the movement of cations in the bulk fluid. The process of ion migration under an applied current (electromigration) is, therefore, accompanied by migration of water molecules, termed electroosmosis (Figure 14).

Heat is also generated during this process, due to electrical resistive heating, which enhances the treatment of volatile organic contaminants. The increase in temperature may also affect the rate of biological denitrification by enhancing (or inhibiting) the performance of denitrifying bacteria. In general, higher temperatures should favour increased biological activity and increase denitrification rates.

Figure 14 and Figure 15 show schematic diagrams of the movement of ions and water under the influence of an applied direct current (DC) field.



Principles of Electrokinetics

Electroosmosis: Water Transport from anode to cathode
Electromigration: Ion Transport to the opposite electrode

Figure 14: Principles of electrokinetics *(after Athmer & Huntsman, 2001)*

Reactions that occur at the cathode and anode are as follows:

Anode:
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $E_o = -1.23$ volts (8)

Cathode:
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E_o = -0.83$ volts (9)

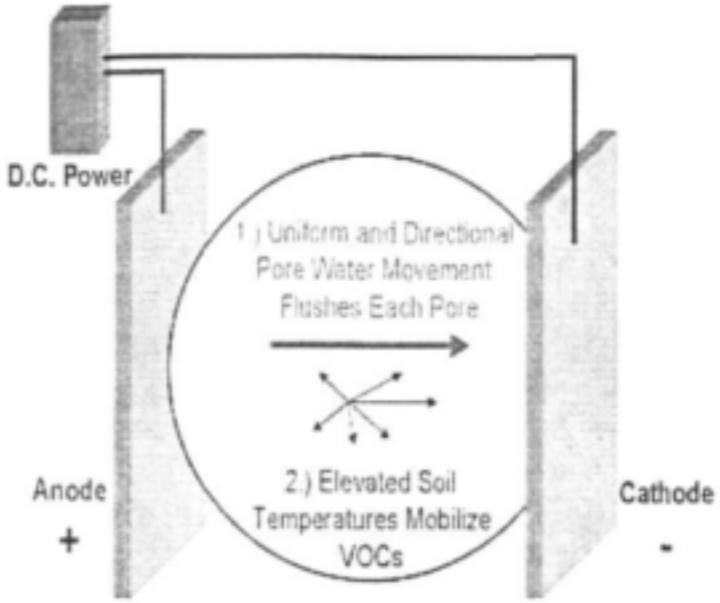


Figure 15: Electroosmosis effects applied to groundwater remediation of organic contaminants
(from Athmer & Huntsman, 2001)

3.3.4 Application of electrokinetics/electroosmosis

Electroosmosis can be adapted to many types of *in situ* and ex-situ treatment systems (Ho *et al.*, 1999; Athmer and Huntsman, 2001). When properly applied, the technique provides two main benefits over the conventional PRB methods (Athmer and Huntsman, 2001):

- ☐ Electroosmosis provides uniform pore water movement. Unlike hydraulic conductivity, electroosmotic flow rate is not sensitive to pore size.
- ☐ Electricity applied directly to the subsurface results in heating. This not only increases the mobilization of volatile organics, but also increases the apparent electroosmotic permeability by lowering the viscosity of the pore water.

The system can be set up in various configurations. Figure 16 provides an example where the extraction well is used as a cathode. A ring of anodes is installed surrounding the contamination plume. The electroosmotic flow of pore water is towards the extraction well.

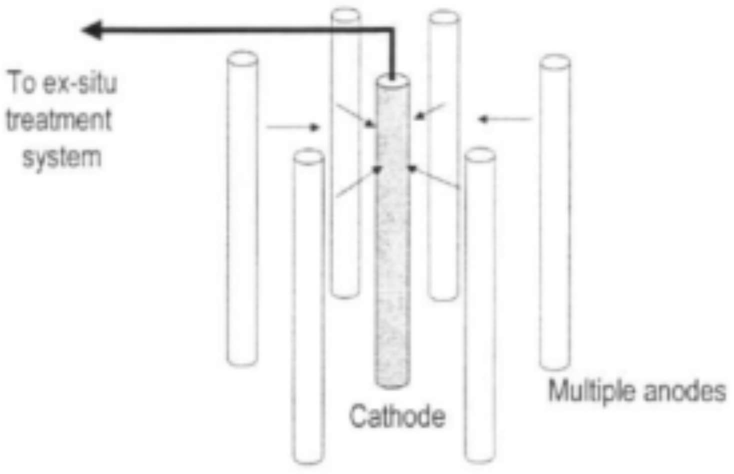


Figure 16: A ring of anodes around a cathode in the pumping well. Electroosmotic flow is induced toward the pumping well *(after Athmer and Huntsman, 2001)*

A review of all existing physical and chemical parameters including pH, permeability, lithology, water table depth, concentration of contaminants and alkalinity is required before designing an electrokinetic system for groundwater remediation. It is recommended that laboratory batch tests be run for 5-10 days before initiating field scale tests, to ensure smooth operation of the method (Jacobs and Loo, 1994; Loo, 2000)

3.3.5 Discussion

Electrokinetic methods appear to have been developed with a focus on remediating spills or leaks of organic chemical products. Much of the emphasis is on mobilising contaminated pore water and there is an expectation that the abstracted water would require additional *ex situ* treatment.

Chew and Zhang (1998) showed that nitrate removal was improved over that which could be obtained by electrokinetics alone by adding an iron wall, but do not give a comparison of the efficiency of electrokinetics and other, non-electrical methods of nitrate treatment. Their experiment showed that without the iron wall, only 25 to 37% of the nitrate was transformed to other forms of nitrogen using electrokinetics at various constant voltages. This could be improved to up to 88% removal when the iron wall was in place, suggesting that the PRB is an important component of the treatment system.

Where electrokinetic methods are used to enhance permeable reactive barrier technologies, they will be subject to similar advantages and limitations as PRB systems. They will, however, require additional infrastructure in the form of the electrodes, power sources and related control systems, and so will be more expensive to install and maintain.

Electrochemical methods also have several advantages over other treatment methods including requiring no chemicals before or after treatment, small treatment area and low investment costs (Koparal and Öğütveren, 2002).

3.3.6 Application in South Africa

An additional consideration for electrokinetic systems is the cost and availability of the power supply. It may be possible to investigate alternative power sources such as solar power for use in rural areas of South Africa, if the technology proves promising for contaminant removal.

Electrokinetic methods could be used anywhere in South Africa in conjunction with other in-situ methods. So this method could be used for both primary and secondary aquifers in South Africa.

3.4 Iron and manganese removal

Iron and manganese are often found in natural groundwater and several water quality problems, mainly aesthetic in nature, are associated with high dissolved concentrations of these elements. Iron concentrations are generally an order of magnitude higher than manganese. Both iron and manganese are easily oxidised when groundwater is abstracted, forming precipitates which may clog pipelines, irrigation nozzles and other infrastructure. Iron especially is also a cause of orange-brown staining on walls and laundry and is often the source of consumer complaints regarding water quality.

Iron and manganese can also be problematic within the aquifer. The ingress of oxygen during pumping disturbs the redox environment around boreholes and can trigger precipitation of iron and manganese oxides in the borehole and surrounding aquifer. This can lead to serious clogging of well screens and pumps, especially when accompanied by growth of iron bacteria and associated biofilm development.

The Vyredox method is an *in situ* groundwater treatment technique developed for the treatment of high iron and manganese concentrations in groundwater. It can also be modified for the treatment of hydrocarbons (Braester and Martinell, 1988). The method is based on a similar system to the Nitredox method, described in Section 3.2.2 and the Nitredox system, in fact, represents a modification of the Vyredox treatment technique. The first operational Vyrdox plant was built in 1969 and by 1988 more than 100 plants were constructed in over 10 countries (Braester and Martinell, 1988).

3.4.1 Operating principle

For both iron and manganese, the reduced forms (Fe(II), Mn(II)) are more soluble than the oxidised forms (Fe(III), Mn(IV)) which tend to precipitate as oxides or oxyhydroxides. The oxidation state of these elements is controlled by chemical equilibria which are very sensitive to the amount of dissolved oxygen in the water. Well-oxygenated groundwaters will seldom have iron and manganese problems, because the metals remain insoluble in the aquifer, but anaerobic groundwaters (e.g. under low permeability soils or high in organic matter) may encounter problems with increasing iron and manganese concentrations.

The principle of the Vyredox system is to control iron and manganese *in situ* by increasing the oxygen content of low-oxygen groundwaters. The natural filtering action of the aquifer is used to remove the iron and manganese precipitates before they reach the production borehole (Braester and Martinell, 1988).

Figure 17 shows the configuration of a typical Vyredox plant. Treatment is initiated when the monitored concentration of iron and manganese in the production borehole start to rise. Oxygen from the air is simply dissolved in the injection water, which is taken from another Vyredox treated borehole in the wellfield, or from a storage tank of iron- and manganese-free water. Injection takes place for 20 to 30 hours, followed by 4 to 10 hours of contact time. As for ISBD (Section 3.2), various arrangements of injection wells around the production borehole may be used to ensure an even distribution of the reagents (in this case oxygen).

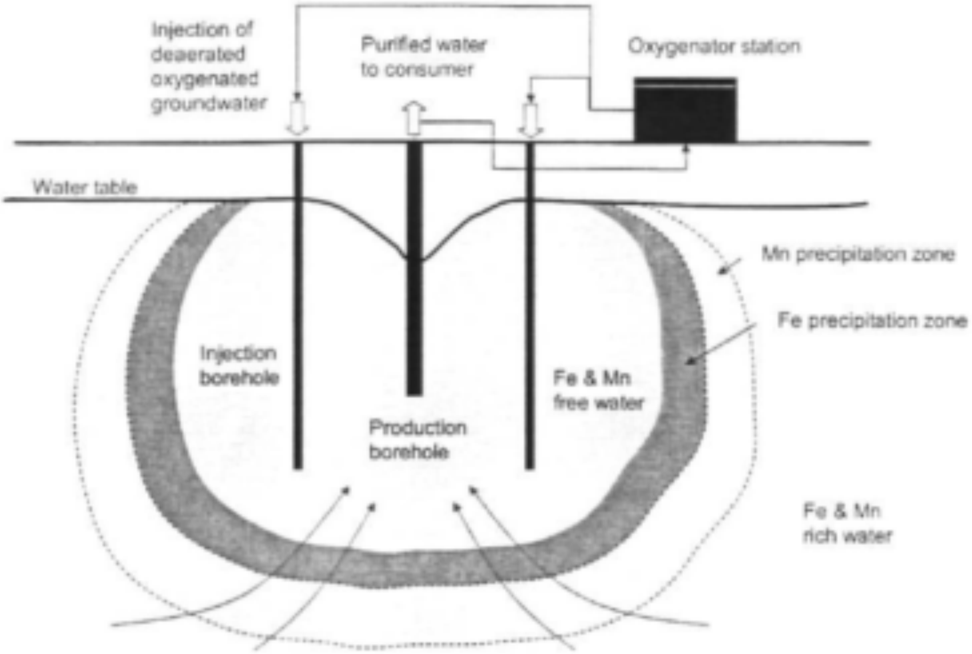


Figure 17: Arrangement of a typical Vyredox treatment system *(after Braester and Martinell, 1988)*

The injection of oxygenated water causes an oxidised zone to be established around the production borehole, stimulating the activity of natural iron and manganese bacteria. Iron and manganese precipitation occur in this oxidised zone. The groundwater is filtered through the zone around the production borehole during pumping so that the water that is abstracted is free of precipitated solids. Cycles of pumping and injection are used to manipulate the position of the redox gradient in the subsurface and so to distribute the iron and manganese precipitates throughout the oxygenated zone. This helps to minimise permeability losses in the aquifer (Braester and Martinell, 1988).

3.4.2. Discussion

The method is limited to situations where the groundwater pH is near neutral. Lower pH water requires increased oxygenation for treatment. In reduced waters with low pH, other oxidisable species, such as methane and hydrogen sulphide, are often present and it is difficult to set up the required redox gradient for precipitation. Manganese treatment is generally more difficult to achieve than iron treatment, especially at low pH.

The rate of iron and manganese removal is not constant over time and systems may require some time for optimum removal conditions to develop. Once iron and manganese precipitates start accumulating in the aquifer, these provide suitable surface for the adsorption of dissolved Fe^{2+} and Mn^{2+} ions under neutral pH conditions. Removal rates increase over time as the dissolved ions are now removed by the two phase process of adsorption and then oxidation.

The precipitation zone needs to be properly developed to obtain good iron and manganese removal efficiency by the Vyredox method. Often ten or more injection cycles may be needed to develop the zone. The size and shape of the zone may need to be manipulated by changing the configuration of the injection boreholes and altering pumping and injection routines for each and every production borehole in the wellfield. A good understanding of both the oxidation and precipitation kinetics may be needed to optimise the system. This requires a high level of geochemical understanding and technical know how, which may be a limitation for rural applications.

Experience from practical applications of the Vyredox method has reportedly shown that clogging is not as problematic as would be expected. Braester and Martinell (1988) claim that rather than rapidly clogging up the aquifer with iron and manganese precipitates, the Vyredox system may, in fact increase borehole efficiency over the first few months of operation. The Vyredox treated borehole is effectively protected by a "shield" of oxygenated water, which prevents the transport of reduced iron and manganese to the borehole, thereby preventing clogging of screens and pumping equipment.

If the oxygenation zone is properly developed and the plant is run correctly, the loss of pore volume will occur very slowly. Over time, the iron precipitates may mature to more stable forms, such as haematite, which have a smaller volume than the hydrated forms (e.g. ferrihydrite) first precipitated.

3.4.3 Application in South Africa

This method is applicable in areas where concentrations of Fe above that of drinking water standards have been detected in groundwater. These include:

- ☐ Dysselsdorp
- ☐ Calitzdorp
- ☐ Cape Flats
- ☐ Swartkops/ Uitenhage

The Dysselsdorp and Calitdsdorp areas are situated on the secondary TMG aquifer, while areas like the Swartkops/Uitenhage are situated on primary or alluvial aquifers. The successful treatment of iron and manganese is subject to the suitability of the selected areas in terms of their conditions such as pH (both change induced and natural pH). Areas like Atlantis and the Cape Flats primary aquifers would serve as good test sites as the aquifers are well understood. The Fe levels are not above drinking water standards.

4 *EX SITU* TREATMENT METHODS FOR NITRATE REMOVAL

Some additional options that are in use, or have been tested, for the treatment of nitrate in water are listed here. Most of these are *ex situ* methods that are applied in water treatment plants and would be difficult to adapt to *in situ* applications for groundwater treatment. Although these options and their attributes are mentioned for completeness, the details of operation are beyond the scope of this review.

4.1 Anion exchange

Treatment by an ion exchange resin replaces nitrate with another anion, generally chloride. The treatment affects the major anion composition of the water and increases chloride concentrations in solution. The resin may also retain some sulphate and bicarbonate. Ion exchange resins need to be regenerated periodically by flushing with a concentrated chloride solution. This produces a concentrated nitrate wastewater brine.

4.2 Electrodialysis and reverse osmosis

Reverse osmosis and electrodialysis are relatively expensive membrane-based techniques of nitrate removal and also produce concentrated waste solutions, which pose a problem for disposal.

4.3 Sulphur/limestone autotrophic denitrification

Nitrate is reduced by *Thiobacillus denitrificans* bacteria using elemental sulphur as an electron donor under anaerobic conditions. Limestone is used to maintain the pH (Darbi *et al.*, 2002).

4.4 Sorption on chitosan

Chitosan gel beads, manufactured from the shells of crustaceans, such as crabs and shrimps, have been demonstrated as a suitable medium for the sorption of nitrate (Jaafari *et al.*, 2001).

4.5 Bioreactor columns

Hyphomicrobium X bacteria have been immobilised on various porous media, ranging from polyurethane and polyvinyl acetate foams, glass beads, alginate beads, glass wool and river sand. Polyurethane and sand systems were used to develop small bioreactor columns that treat nitrate-rich waters by denitrification (Smith *et al.*, 1991).

4.6 Catalytic reduction

Platinum group elements have been used as catalysts for the chemical reduction of nitrate in laboratory tests. Testing of platinum, palladium and rhodium electrodes found that rhodium was most effective at removing nitrate, but the process is not efficient for total removal of nitrate (Reddy and Lin, 2000). Catalytic reduction cells could be used for *ex situ* treatment of groundwater.

4.7 Electrocoagulation

Nitrate can be removed by entrainment with the precipitation of iron hydroxides or other metal oxide flocs. Electrocoagulation was found to be more effective than catalytic reduction for nitrate removal, but is accompanied by the production of sludge waste (Kopara and Oğütveren, 2002).

5. OPERATIONAL IN SITU DENITRIFICATION PLANTS WORLDWIDE

Table 3 provides an overview of operational biological denitrification sites known at this stage and their experiences. These include ISBD and Nitredox methods in various configurations.

In South Africa only one case is known where a carbon substrate was used to denitrify groundwater for stock watering. This was, however, done *ex situ* and on a small scale. The system showed evidence of reduced nitrate concentrations after flowing through a carbon substrate of molasses (Anonymous, 1985). Other treatment methods used in South Africa include an ion exchange treatment plant in the rural village of nZava in the northeastern part of Limpopo Province (see Figure 18).

Figure 18: Desalination plant at nZava with power supply and storage tanks (left) and deionization unit (right) with operator

Figure 19: Deionization plant brine discharge point

The brine from the desalination plant is discharged into a watering trough (see Figure 19) located near a small river passing the village. Apparently the animals drink the water at certain times.

Table 3: Summary of pilot and field-scale *in situ* denitrification plant published information (*modified from Cartmell et al., 1999*).

Reference, treatment & location	Aquifer type	Carbon substrate	Operational details			NO_3^--N mg/l	% NO_3^- reduced	Miscellaneous operational and other details
			Injection regime	Injection boreholes	Abstraction rate			
Jechlinger *et al.* (1991), Nitredox, Bisamberg, Austria	sand & gravel	ethanol or methanol	cyclic pumping	16 boreholes at 18m radii from abstraction well	5 ML/d	23	75	The full-scale plant at Bisamberg has been successfully in operation for more than a decade.
Khan & Spalding (1998), daisy wheel ISBD, Nebraska, US	sand & gravel	ethanol	continuous & pulse (C&P)	8 boreholes at 12m depth and 12m radii, rate = 0.065 ML/d	6 ML/d	40	35=C 90-100=P	This operation has proved successful at pilot scale. The continuous (C) regime gave higher denitrification efficiency than the pulse (P) regime but it also led to complete biofouling after 10 days. This could perhaps have been prevented by recirculation of treated water through the system to dilute the high nitrate water. This system also used an inner oxidation ring at 6 m radius, (presumably to oxidise any residual nitrite).
Hamon & Fustec (1991), daisy wheel ISBD, Carbonne, France	shallow alluvial aquifer	ethanol	continuous & pulse (C&P)	15 boreholes at 25m radii	0.7 ML/d	23	70 for both C & P	This was a successful field demonstration, lowering local NO_3^- concentration to below the EC limit. Increasing the no. of boreholes increased homogeneity of the clean up. Clogging was limited by pulsing (P) carbon supply (1 hour on/1 hour off), or, when pumping was continuous (C), using limiting carbon concentration. Recirculation of some of treated water also ameliorated clogging risks.
Mercado *et al.* (1988), daisy wheel ISBD, Shivat Zion, Israel	heterogenous	sucrose	pulse	2 operational boreholes at 100m depth, 15-25m radii, rate = 0.048-0.1 ML/d	1.2-1.4 ML/d	14	10	Clogging was experienced in one of the wells, rendering it inoperable. However, local clogging of substrate injection wells could be reduced by intermittent substrate injection. Aquifer denitrification efficiency depended on hydrodynamic dispersion and local hydrogeological conditions. The authors recommended the use of more injection wells.
Janda *et al.* (1988), Vsetaty, Central Bohemia	fine gravel & sand	ethanol with 5 % methanol	continuous – with and without recirculation	4 boreholes at 17m depth and 12-15m radii	0.5 ML/d	25-27	20-30 no recirc. 30-50 with recirc.	Initially, this method was operated as a trial without the recirculation of groundwater. Under this regime, inadequate mixing was demonstrated with very high carbon concentration in some parts, causing breakthrough, whilst in other parts, groundwater was flowing through the system without any exposure to carbon at all. The change in operation to include the recirculation of some of the treated water through the aquifer improved overall efficiency. More boreholes were also recommended to further improve efficiency.
Kruithof *et al.* (1985), horizontal doublet design ISBD, Van Heek, Netherlands	phreatic	methanol	continuous & pulse (C&P)	min of 3 boreholes at 10-25m radii	-	19	30=C 50=P	This method was found to remove nitrate, but gave rise to an accumulation in nitrite. Also, clogging of aquifer was reported. Intermittent methanol dosing did not ameliorate clogging in this instance.
Chevron *et al.* ISBD, line of injection boreholes, Calais, France	chalk	ethanol	-	clusters of 3 boreholes, 3m apart	-	226-565	80	Natural *in situ* denitrification was evident prior to remediation in this instance, but was limited by carbon. The pulse injection regime used depended on the fissuring of the chalk. Denitrification was achieved in long time operation (450 days). Improvements to the system could have reduced this time period. Rates of denitrification were improved when trace metals were supplied in conjunction with the carbon substrate.

Many full-scale *in situ* treatment plants are in operation for removing contaminants other than nitrate. However, based on the information gained from the literature and from researchers, only one full-scale Nitredox denitrification plant is presently in operation. It is located at Bisamberg, Vienna, Austria (Jechlinger *et al.*, 1991). This plant (see Figure 20) has been in operation since 1987 and partially denitrified groundwater is abstracted at a rate of 60 L/s from the production well as part of the Vienna drinking water supply. The plant has been modified and improved on several occasions both to improve its efficiency and to prevent clogging of the aquifer (Dinhobl, *Pers. Comm.*, Vienna, 2003). A detailed description of this scheme is included in Appendix B.

Figure 20: Bisamberg *in situ* denitrification system, with abstraction well (EB) on the left

The field scale and full-scale *in situ* denitrification plants listed in Table 3 extend from the USA to Eastern Europe and the Middle East. Table 4 gives a brief list of the field trials of some permeable reactive barriers used for denitrification in other parts of the world. PRBs have been used for about ten years in countries like New Zealand, Canada and the USA. Many accounts of the performance of treatment walls are found in international journals.

Researchers currently practising the implementation of this technology confirm that it can be used for a range of situations from one borehole in a rural village to a system of boreholes in a town. The table only shows three examples of field trials specific to nitrate, although there are several accounts of PRBs used for the treatment of oil spills, TCE, chromium, and various other contaminants. For the purposes of this report, only a few examples were selected to illustrate that the method has been used successfully.

The PRB and the NitrEl systems require little or no maintenance. 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.

Table 4: Operational site information for *in situ* nitrate treatment methods *(after Robertson & Cherry, 1995; Schipper & Vojvodic-Vukovic, 2000; Blowes et al., 2000).*

Treatment method	Nitrate concentration (initial)	Aquifer type	Carbon substrate	% NO_3^- removed
PRB, Canada	5-57mg/L	Primary	Sawdust/woodchips	58-91
PRB, New Zealand	5-15 mg/L	Unconfined, sandy	Sawdust	95+
Electrokinetics/ Fe-wall, USA	Controlled amounts	Primary/ Secondary	None: Abiotic	84-87
NitrEl system, Canada	Up to 1000 mg/L (as N)	Primary/ unsaturated zone	None: electrochemical electrodes	Reduce levels down to 0.1 mg N/L

6. REGULATORY REQUIREMENTS

6.1 Legal requirements for South Africa

The implementation of a full scale or field scale *in situ* nitrate removal system in South Africa will be subject to the requirements of the National Water Act (Act No 36 of 1998) (NWA) (Van Wyk, E, DWAF, *e-mail communication*, January, 2004). Such a system will require a licence application according to the procedure set out in Section 41, subsections (2) and (3):

> (2) A responsible authority -
> - (a) may, to the extent that it is reasonable to do so, require the applicant, at the applicant's expense, to obtain and provide it by a given date with -
>   - (i) other information, in addition to the information contained in the application;
>   - (ii) an assessment by a competent person of the likely effect of the proposed licence on the resource quality; and
>   - (iii) an independent review of the assessment furnished in terms of subparagraph (ii), by a person acceptable to the responsible authority;
> - (b) may conduct its own investigation on the likely effect of the proposed licence on the protection, use, development, conservation, management and control of the water resource;
> - (c) may invite written comments from any organ of state which or person who has an interest in the matter; and
> - (d) must afford the applicant an opportunity to make representations on any aspect of the licence application.
>
> (3) A responsible authority may direct that any assessment under subsection (2)(a)(ii) must comply with the requirements contained in regulations made under section 26 of the Environment Conservation Act, 1989 (Act No. 73 of 1989).

Subsection (2)*(a)*(ii) describes the need for an assessment of the "proposed licence on the resource quality". Subsection (3) refers to the requirements contained in regulations made under section 26 of the Environment Conservation Act (Act No 73 of 1989)" (see below). It is concluded (Van Wyk, 2004) that the above is the most appropriate legislation to comply with and the licence could include the following conditions and requirements (but there may also be other site specific issues, which may need to be referred to DWAF Legal Services):

- ***Environmental Management Plan***, including monitoring plan & mitigation measures; and
- ***Emergency Procedures***.

The applicable section of the Environment Conservation Act (Act No 73 of 1989) provides important information regarding environmental impact reports and reads as follows:

> ***26. Regulations regarding environmental impact reports.*** *– The Minister or a competent authority, as the case may be, may make regulations with regard to any activity identified in terms of section 21 (1) or prohibited in terms of section 23 (2), concerning –*
>
> *(a) the scope and content of environmental impact reports, which may include, but are limited to –*
>
> *(i) a description of the activity in question and of alternative activities;*
>
> *(ii) the identification of the physical environment which may be affected by the activity in question and by the alternative activities;*

(iii) *an estimation of the nature and extent of the effect of the activity in question and of the alternative activities on the land, air, water, biota and other elements or features of the natural and man-made environments;*

(iv) *the identification of the economic and social interests which may be affected by the activity in question and by the alternative activities;*

(v) *an estimation of the nature and extent of the effect of the activity in question and the alternative activities on the social and economic interests;*

(vi) *a description of the design or management principles proposed for the reduction of adverse environmental effects; and*

(vii) *a concise summary of the finding of the environmental impact report;*

(b) *the drafting and evaluation of the environmental impact reports and of the effect of the activity in question and of the alternative activities on the environment; and*

(c) *the procedure to be followed in the course of and after the performance of the activity in question or the alternative activities in order to substantiate the estimations of the environmental impact report and to provide for preventative or additional actions if deemed necessary or desirable.*

[S. 26 amended by s. 15 of Act No. 79 of 1992 and by Proclamation No. R. 29 of 1995]

Other issues which are important include the pollution prevention regulations under the NWA Chapter 3 Part 4 Section 19 subsections (1), and (2), which suggest that authorisation from DWAF would be required before any reagents/substrates would be allowed to be injected into an aquifer as well as for the management of any waste products produced if any. Where relevant, the artificial introduction of microorganisms for denitrification may also be subject to legal controls and the impact of the transfer of genetic material may require special investigation. The statement about microorganisms is partly addressed by the National Environmental Management Act (NEMA, see below) where any change or possible altering of an environment needs to be investigated beforehand and submitted to authorities to evaluate the "environmental" feasibility of any treatment implementation.

It is clearly defined in the National Water Act that reasonable measures should be taken to avoid the probability that any activity performed or undertaken at any given time in an area would cause or would be likely to cause pollution to the water resource. The measures in the NWA, Chapter 3 Part 4: Pollution prevention, subsection 19 (2) include:

(2) The measures referred to in subsection (1) may include measures to:
- *(a)* cease, modify or control any act or process causing the pollution;
- *(b)* comply with any prescribed waste standard or management practice;
- *(c)* contain or prevent the movement of pollutants;
- *(d)* eliminate any source of the pollution;
- *(e)* remedy the effects of the pollution; and
- *(f)* remedy the effects of any disturbance to the bed and banks of a watercourse (NWA, 1998).

Some *in situ* methods produce wastes, which have to be discarded. The legislation guides the process by stipulating that it has to be discarded in such a manner that it does not cause any form of pollution to the environment as a whole.

In terms of the National Environmental Management Act (Act No 107 of 1998) (NEMA) Chapter 5 Section (24) under implementation, the potential impact on the environment, socioeconomic conditions and cultural heritage of all activities that require permission by law must be considered, investigated and assessed before implementation, and this should be reported to the body that grants permission or authorises the implementation. Procedures for investigation should consider the potential impacts of the activity as well as the cumulative effects on the environment. Mitigation measures to keep impacts to a minimum should also be investigated. According to the National Environmental Management Act, the coordination and cooperation of organs of state (in this case probably the Department of Water Affairs and Forestry (DWAF) and Department of Environment Affairs and Tourism (DEAT) should be ensured. Monitoring and management programmes for potential impacts should be investigated and formulated. Public participation and information is also stressed in the National Environmental Management Act.

The literature review revealed that the regulatory requirements for *in situ* groundwater treatment have not been specifically covered in South African legislation. The authorisation for addition of reagents to an aquifer and the management of waste products constitute the two most important legal aspects to be considered during the activities of an *in situ* treatment system.

6.2 Regulatory issues in the USA that may be relevant for use in South Africa

Nitrate contamination is pervasive, and regulatory enforcement of nitrate plumes has been limited. This section describes regulatory issues related to nitrate contamination and further identifies and describes regulatory issues specific to Enhanced *In Situ* Biological Denitrification (EISBD) in the USA. The following paragraphs were obtained and adapted from Chapter 8 of an Interstate Technology and Regulatory Cooperation Work Group document entitled, Technology overview: Emerging technologies for enhanced *in situ* bioremediation of nitrate-contaminated ground water (ITRCWG, 2000) with some comments on how these regulatory issues compare to South African legislature or a lack thereof in certain respects.

Excerpt from ITRCGW (2000):

6.2.1 Regulatory enforcement of nitrate contamination

> *Most state regulatory agencies in the USA have a difficult time dealing with nitrate-contaminated groundwater. State pollution prevention programs are aggressively pursuing "permitting" to prevent further nitrate contamination in ground water. However, once a site becomes contaminated with nitrates above standards, especially non-permitted facilities, the application of remediation practices to deal with nitrate contamination is lacking. In South Africa, nitrate is merely monitored. Treatment of nitrates is not specific and nitrate concentrations are partially reduced through ion exchange processes where these sites are in existence. There are various reasons for these phenomena:*

6.2.1.1 Perceived threat of nitrate contamination

> *Because nitrate-contaminated groundwater's only proven health affect, methaemoglobinaemia, is not perceived as a grave health threat compared to contamination by volatile organic compounds or certain metals, nitrate is not treated as a contaminant of highest concern. It should be emphasized that even if the previous statement is correct, the nitrate standard of 10 mg/l NO_3–N must be enforced according to federal and most state standards. Since the most common solution to nitrate contamination is to provide an alternative water supply, many regulators view the problem as resolved once this is accomplished. This does not deal with the nitrate plume that may persist, creating further problems in the future. Similarly in South Africa, the threat of nitrate contamination is not yet properly understood, due to a lack of anecdotal information linking high nitrate concentrations with any loss of life, except that of cattle. No specific treatment for the removal of nitrate is in place in South*

Africa. Alternate water sources have been available in the past; this is however becoming scarce in areas where high nitrate concentrations are problematic.

6.2.1.2 No real economic remediation technology

While pumping nitrate-contaminated groundwater and disposing of it in some fashion is the simplest remediation technology, nitrate in groundwater can be dealt with by means of treatment, such as reverse osmosis or ion exchange. However, the high cost and time involved in these efforts is a strong deterrence for regulators to require remediation.

Furthermore, most parties responsible for causing nitrate contamination do not have vast financial resources. Examples of this would be small population centres that have wastewater treatment systems that are improperly constructed or managed and small, privately owned animal operations. These "mom and pop" operations do not have the financial resources to support a long-term pumping remediation system. Those responsible parties that do have greater financial capabilities rarely pursue nitrate remediation on their own – often because of the low perception of threat mentioned above. This case is very similar to the South African scenario in that most areas affected by the high concentrations of nitrate are often rural areas where communities are totally dependant on the resource and alternate sources are not always available. Financial responsibility for remediation is often not affordable by communities and other organisations like government, consulting agencies and municipalities together often have to fund such remediation technologies.

Many nitrate-contaminated groundwater sites are the result of non-point sources. Examples of this would be areas in the Midwest where agricultural land has been over fertilized consistently, but no one field is the sole source of the nitrate contamination. Housing developments with septic tank leach-field treatment systems have also caused regional non-point source nitrate contamination. When this occurs, there is no single responsible party for regulators to pursue to require remediation. This leaves many states with contaminated groundwater and no allocated or available resources for remediation.

The sources of nitrate contamination in Southern Africa range from non- point sources like field irrigation and fertilization to point source pit latrines. The source can only be pin pointed through isotopic studies and distribution maps up to now do not distinguish between sources. It is known that naturally high nitrate concentrations also prevail in certain areas. Remediation technologies are not in place to treat nitrate specifically and responsible parties often do not realize the seriousness of nitrate contamination and the persistence of nitrate as a groundwater constituent.

6.2.1.3 No voluntary plume remediation

Many states have regulations or are in the process of developing regulations that allow responsible parties to voluntarily remediate groundwater contamination. These regulations are fairly recent and provide incentives for responsible parties to adequately deal with their environmental concerns. Prior to these regulations, most responsible parties rarely initiated cleanup of their problems unless there was some direct benefit. Again, since nitrate is not a contaminant of highest concern, voluntary remediation of nitrate contamination was unheard of and unexpected. However, with these new voluntary remediation regulations, the situation may change. South Africa is yet to deal with an issue such as voluntary plume remediation. The method that treats nitrate contamination in Southern Africa is ion exchange. This is an expensive technology and is only available where funding is adequate. Incentives for voluntary *remediation would probably be progress towards achieving cleaner and safer water in the areas where remediation is much needed.*

6.2.1.4 Non-RCRA or CERCLA constituent

Since nitrate is not a Resource Conservation Recovery Act (RCRA) or Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) constituent, these federal regulations have not applied to nitrate contamination. Those facilities that fall under RCRC and CERCLA regulations have not been required to deal with nitrate contamination. Only when nitro-aromatic contaminants have been present have RCRA or CERCLA facilities dealt with nitrate contamination. However, the situation may be changing with the new understanding and remediation technology of natural attenuation and the need for an electron acceptor. Nitrates act as an electron acceptor under certain conditions, and nitrate contamination might be addressed through natural attenuation of volatile organic compounds. DOE and DOD have shown an interest in dealing with nitrate contamination at some facilities and are very much interested in EISBD.

6.2.1.5 Impacts to public and domestic supply wells

A nationwide survey by EPA in the late 1980s gives a general indication of the extent of nitrate impact on public and domestic supply wells (EPA, 1992). These estimates are as follows:

- *Approximately 30 million people drink groundwater from about 9 900 000 domestic wells in the United States. About 450 000 of these individuals are infants under the age of one year.*
- *Approximately 136 million people drink groundwater from about 94 600 public water supply wells nationally. About 2 million of these individuals are infants under the age of one year.*
- *Of the population that obtains drinking water from domestic wells, approximately 1.5 million are estimated to be consuming water with at least 10 mg/L nitrate-nitrogen. Of the people exposed at this level, about 22 500 are estimated to be infants younger than one year and thus possibly at risk of developing methaemoglobinaemia.*
- *Of the population that obtains drinking water from community water supply wells, approximately 3 million individuals are estimated to be consuming water with at least 10 mg/L nitrate-nitrogen. Of these, about 43 500 are expected to be infants.*

Even though the above statistics show a considerable impact of nitrate on public water supplies, federal and state regulations are designed to help ensure that public supply wells meet standards. As these figures indicate, nitrate contamination has probably impacted more public supply wells than any other contaminant in the USA. Usually treatment occurs at wellhead, or a new public supply of water is provided. In many cases, regulators are quick to identify and rectify nitrate contamination at public supply wellheads.

A survey of nitrate concentration by Marais in 1999 revealed that most areas sampled had a large amount of boreholes with nitrate concentration greater than 45 mg/l. Figure 21 *is a summary of the outcomes of the survey.*

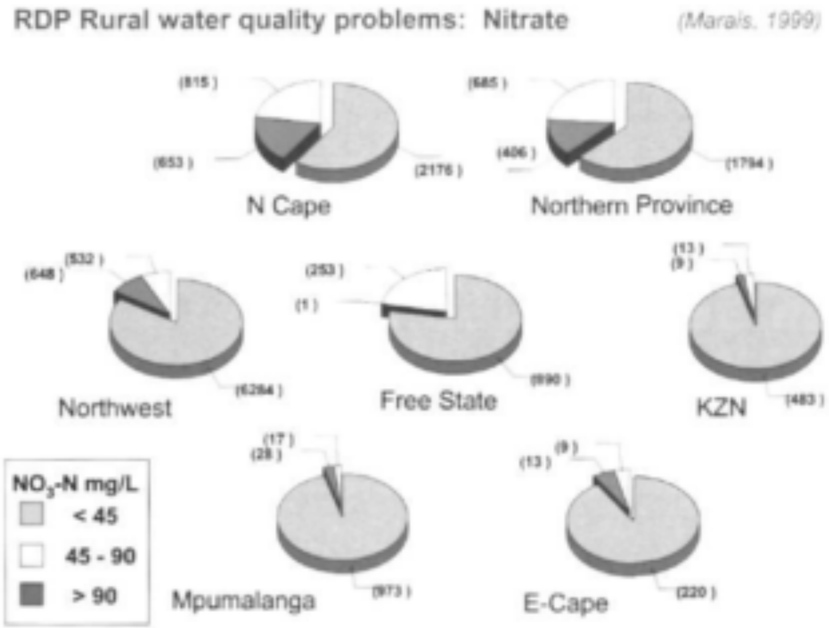


Figure 21: **Nitrate concentrations in rural areas of South Africa. The highest allowable nitrate concentration as documented in the water quality guidelines for drinking water/ domestic use in South Africa is 20 mg/l as N. The figure above shows that most of the sampled boreholes were above this standard** *(after Marais et al., 1999)*.

Many states in the USA do not have any regulatory standards for domestic supply wells. In New Mexico alone, more than 700 documented domestic supply wells have been impacted with nitrate contamination above standards. For those states that have ground water standards for nitrate, regulations may be in place to address the nitrate contamination. Unfortunately, as previously mentioned, little can be accomplished to deal with the nitrate plume except to provide a clean alternative water supply or make recommendations for the domestic well owner. These recommendations may include identification of the nitrate source, steps to prevent further nitrate contamination, and suggestions to deepen or move domestic wells beyond the nitrate contamination, if applicable.

South Africa has documents setting national guidelines for water quality. These are addressed in every region through the department of water affairs and forestry's monitoring networks. Remediation activities are however not as effectively in place as these guidelines. The issues of responsibility (polluter, government organisations, or NGO's) and impact (social, financial and environmental) are not dealt with explicitly in South African legislature. The water act does state that the polluter should pay, however, with nitrate contamination it is not always a simple task of pointing out polluters. South African legislature does not single out contaminants or give specific instructions on how to deal with them; it covers a large range of problems and is open to interpretation.

The water guidelines document does cover treatment options, and under nitrate and nitrite it recommends options to users. The paragraph states the following:
" Conventional water treatment and disinfection have no significant effect on nitrate or nitrite removal. Nitrites and nitrates are normally removed by strong base ion-exchange resins, although biological removal by anaerobic organisms provided with a carbon source such as ethanol may prove more cost effective in certain cases."

7. COMPARISON OF COST ESTIMATES FOR DIFFERENT TREATMENT METHODS

The EPA and other international institutions have implemented field scale denitrification plants and cost information is available for the USA situation. Using these data could provide a rough idea of the capital and operational costs, but these are based on a totally different value system. Cost information from international reports is likely to give a warped projection for the South African situation. For this reason, a desk study was undertaken using the hypothetical installation of a treatment system at Marydale in the Northern Cape Province.

The desk study involved a comparison of cost estimates for the implementation of three of the *in situ* treatment techniques at Marydale, as well as projected costs for an *ex situ* system of nitrate removal. Table 5 below presents a summary of the cost data obtained during the desk study for ease of comparing the methods. A detailed breakdown of the costs is provided in Appendix A. This compares the viability of implementing nitrate removal by means of the various methods and is based on a best estimate of actual costs, using South African based prices. The desk study highlights the steps taken in the process of obtaining the cost information as well as problems that arose during the process. A very simple economic model was used considering the capital, operating and maintenance costs of the proposed treatment methods.

Table 5 compares capital costs, maintenance costs and operating costs over a ten-year period for the four treatment options, based on *in situ* treatment of a primary aquifer and South African economic conditions.

Table 5: Summary of cost information generated during a desk study for the aquifer at Marydale, Northern Cape

Denitrification method	PRB	ISRM	ISBD	*Ex situ*
Capital investment	R 51 332	R 100 289	R 82 935	R 350 000
Operation and maintenance				R 2.00/m^3
Required m^3/ annum for 2005	142 287	142 287	142 287	142 287
Running cost over 10 yrs				R 2 845 740
Total cost over 10 yrs	**R 51 332**	**R 100 289**	**R 82 935**	**R 3 195 740**

The above summary table does not take into account human resource time. In some cases, additional costs, such as accommodation for operators would be required, but these variables were also not determined and have not been accounted for in the cost comparison.

The cost for the PRB method is based on a barrier size of 10 m deep x 10 m long x 1 m wide. This size is based on factors such as the maximum aquifer depth in the area. The ISRM method is based on emplacement of a 152 m^2 permeable barrier. The *in situ* biological denitrification and the *in situ* redox manipulation both require a number of boreholes to be drilled or well points to be installed. The chemicals required for these two methods were also included in the "capital cost".

The summary table shows that all the *in situ* methods are less costly than the *ex situ* method currently used in South Africa (reverse osmosis). Permeable reactive barriers seem to be the least expensive method by far, as ISRM and ISBD both require borehole drilling costs and establishment costs.

The running costs are the most important factor separating the *ex situ* method from the *in situ* techniques. *In situ* methods require monitoring, e.g. on a quarterly basis, but so does the *ex situ* method. Operating expenditure is almost non-existent for simple *in situ* treatment systems. In all the literature reviewed, only one PRB site required some maintenance after about 5 years of operation. This is, however, not a frequent occurrence and some *in situ* treatment methods often require no maintenance for at least ten years. Consultation with operators of *ex situ* sites showed that their requirement of electricity, chemicals, and membranes (in the case of ion exchange) contributed to the high running costs. In the above calculation for the *in situ* methods the applicable chemical costs were included with the capital costs. Another major advantage that the *in situ* methods have over the *ex situ* is the minimal exposure to chemicals during the treatment.

There are large differences in the costs involved with different *in situ* methods as well as with *in situ* vs. ex situ methods. According to the literature, significant cost savings can be achieved when comparing ISRM or PRB technologies with pump-and-treat *ex situ* systems. For example, cost calculations were performed to compare a full-scale 420 m long ISRM barrier with a conventional pump-and-treat system for treatment of a chromium contamination plume (maximum concentration 910 ppb) at a site in Hanford, USA. From the comparison it was evident that ISRM was 50 to 60% cheaper over the 30-year lifespan of the treatment system (Scott *et al.*, 1998; Innovative Technology, 2000). The capital outlay for ISRM and pump-and-treat options was comparable, but the pump-and-treat method required higher maintenance and operational costs.

8. GENERAL DISCUSSION AND CONCLUSIONS

Although *in situ* groundwater treatment is still being researched and developed, it has already been tested for the removal of a large range of inorganic contaminants including arsenic, cadmium, chromium, copper, mercury, iron, manganese, molybdenum, nickel, lead, selenium, technetium, uranium, vanadium, nitrate, phosphate and sulphate. In situ treatment of organic contaminants, e.g. solvents, such as TCE, is also possible and is gaining popularity at contaminated sites worldwide. Most of the research into in situ groundwater treatment has been conducted at laboratory scale, but field tests have also been completed successfully for a number of the contaminants listed above. Full scale treatment systems are also in place, of which the Nitredox denitrification plant at Bisamberg, Austria appears to be the most successful example.

The main types of treatment systems are permeable reactive barriers, biological methods and electrochemical methods. Permeable reactive barriers can be subdivided into two types of barriers, viz. those that are emplaced in a trench excavated in the aquifer and those that are created by chemically modifying the aquifer properties in a selected area. The second type is generally created at a strategic place in the aquifer by injecting a chemical, e.g. a reducing agent.

In the case of nitrate removal, most methods that have been applied for *in situ* groundwater treatment are based on chemical and/or biological denitrification. The methods apply redox reactions, often with biological catalysis, to reduce nitrate to nitrogen gas. The appeal of using denitrification reactions for *in situ* application lies mainly in the fact that the main products of the reactions are gaseous and do not accumulate as hazardous by-products in the subsurface. Some of the techniques also do not require highly sophisticated technology.

Ion exchange, reverse osmosis and electro-dialysis have also been used in nitrate treatment plants, but have not been developed for *in situ* application. These methods remove anionic nitrate without the need for redox conversions, but they result in concentrated water treatment wastes that need to be disposed.

8.1 Advantages

In situ treatment of contaminated groundwater uses the aquifer as a subsurface "treatment plant" to improve the quality of groundwater supplies. This has several advantages over conventional pump-and-treat systems, including:

- Cost and time savings on capital expenditure, maintenance, operator expenses, etc.
- Exposure to chemical reagents, where these are used, is limited.
- Many of the systems can operate for long periods (anything from 5 to 30 years) without need for reagent/substrate addition i.e. they are extremely low maintenance.
- Less stringent control of operating conditions is needed, which simplifies management of such systems
- The systems are more robust and require less plumbing than surface-based treatment plants.
- Redox-based systems can often remove other contaminants e.g. chromate and organic chemicals, if these are also present.
- Abstracted water can be used directly with minimal or no extra treatment.
- The natural filtration processes in the aquifer provide additional water quality improvements.

8.2 Drawbacks

Some *in situ* treatment methods for removing groundwater contaminants may cause undesirable side effects, of which the most common problem is clogging in the subsurface. In the case of removal of organic compounds, the products of the treatment reaction may cause clogging of the aquifer due to biofilm build-up. If metals are removed by precipitation, the solid precipitates in the aquifer matrix may reduce the permeability of the aquifer over the long term. The specific hydrogeological conditions and the contaminant load will determine the extent of these phenomena. Side effects need to be managed to maintain the efficiency of the scheme and increase the treatment lifetime.

Depending on the environmental conditions, denitrification reactions may not always run to completion, i.e. nitrate nitrogen is not always fully converted to nitrogen gas. This can lead to the accumulation of other undesirable nitrogen species, such as nitrite or ammonium, in the groundwater. Nitrogen immobilisation may also retard the appearance of nitrate, but will not remove the nitrogen source from the aquifer and nitrate may re-develop at a later stage. Where potentially toxic reagents (e.g. dithionite, methanol) are introduced to the subsurface and not fully recovered or consumed by the reactions, groundwater quality may be adversely affected.

Possible side effects of *in situ* nitrate removal methods include clogging or loss of effective permeability in the aquifer as a result of factors such as:

- Biofilm build-up in the aquifer, e.g. in biological systems.
- Mineral precipitates forming during the redox processes, e.g. iron or manganese oxides.
- Gas bubbles from nitrogen and carbon dioxide generation.

However, operational systems have shown that it is possible to manage the systems for successfully overcoming any side effects.

8.3 *In situ* treatment applications in South Africa

Based on the literature review and feedback received from various researchers, *in situ* groundwater treatment has a significant potential for application in South Africa for solving problems encountered in various natural groundwater environments and pollution situations.

The countrywide distribution of nitrate levels in groundwater was presented in Figure 1. This information may be compared with the hydrogeological terrains of South Africa and the towns or rural communities where groundwater constitutes the sole water supply source (Figure 22). High nitrate concentrations in groundwater appear to be fairly well correlated with aquifers composed of unconsolidated deposits, weathered basalts, and dolomites over an area extending from the Northern Cape Province all the way to northern Mpumalanga, including parts of North West and the Limpopo Province. Within these high nitrate areas, those communities that are sole source aquifer towns with high groundwater nitrate concentrations would have priority over other areas for nitrate removal systems. These include towns such as Marydale, Leliefontein, Reivilo, Rietfontein and others, largely in Limpopo Province.

Iron and manganese, occurring naturally in groundwater, may cause significant clogging problems in boreholes when redox conditions change and iron bacteria start multiplying. In primary aquifers, *in situ* treatment by oxygenation may provide a viable solution, e.g. by using the Vyredox process. This can, for example, be applied at Atlantis, where persistent low levels of iron cause significant borehole clogging problems.

8.4 Design criteria

For the design of any treatment system, both the hydrodynamics of the flow system and the source of the pollution need to be exceptionally well characterised to optimise the system.

The nature of the pollution source will affect the choice of system design. Where a single point source of pollution is affecting a water supply borehole, a simple porous barrier, single ISRM or ISBD injection borehole can be constructed along the flow path between the source and production borehole. If non-point sources are responsible for pollution, production boreholes must be protected by a surrounding gallery of treatment systems e.g. the daisy configuration for ISBD, the Nitredox system, multi-electrode arrangement or a circular barrier wall.

Trench and fill barrier methods are only suitable for shallow flow systems where the barrier can be constructed down to the impermeable bedrock. In deeper flow systems, treatment barriers can be created by borehole injection. *In situ* treatment methods are more likely to be successful in primary aquifers, where hydrodynamics are more easily understood and greater control over the treatment zone can be exercised than in fractured flow environments.

For nitrate removal systems, management of nitrogen inputs to the subsurface is still required, as treatment of the nitrate in the aquifer does not remove the contamination source. Although the treatment systems generally have a long lifetime, it is still important that the source of contamination be eliminated wherever possible.

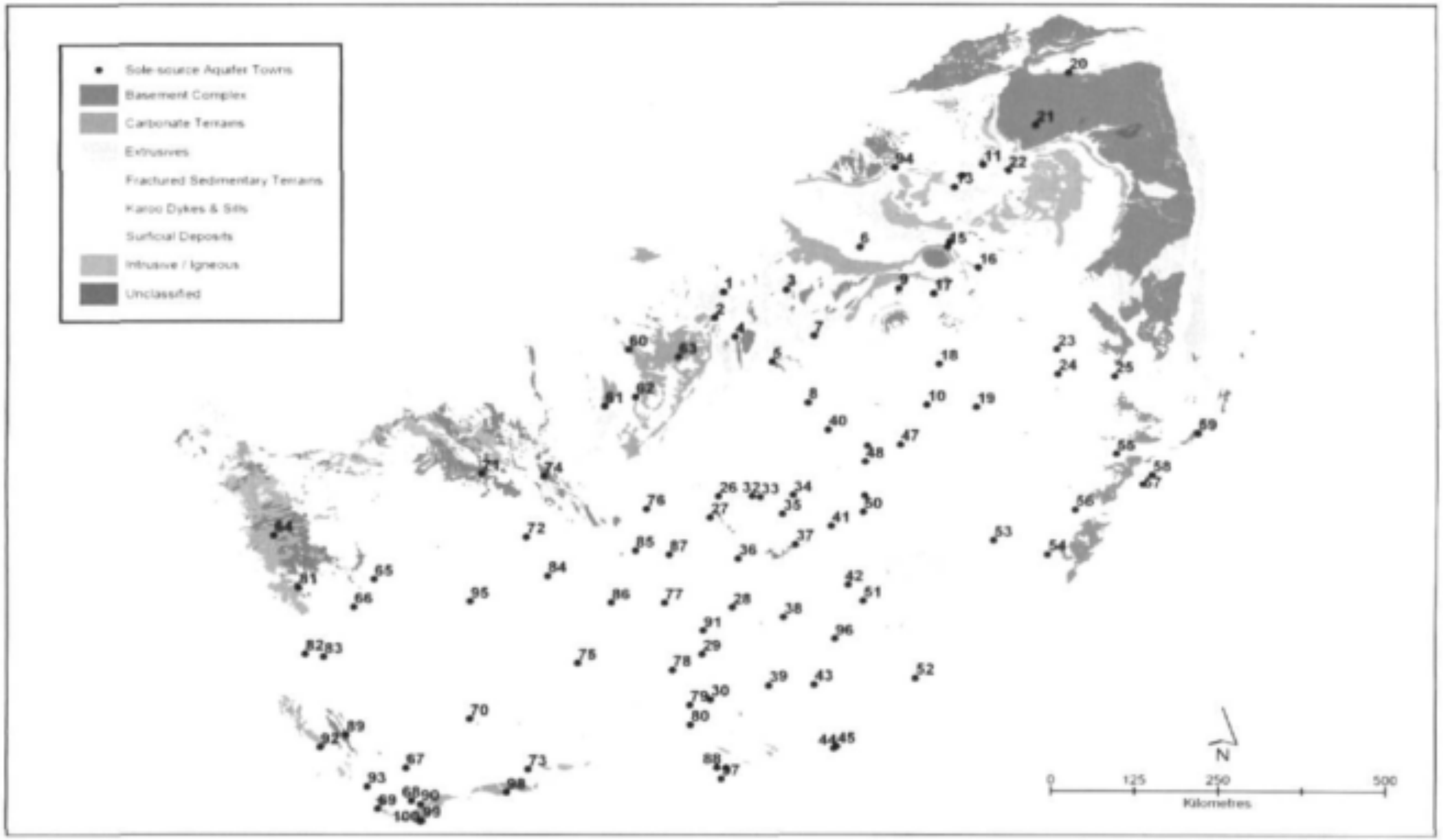


Figure 22: Hydrogeological regions of South Africa and towns solely dependent on groundwater *(see Table 6 for town names).*

Table 6: List of names of "sole source" towns shown in Figure 22

No	TOWN
1	Stella
2	Vryburg
3	Sannieshof
4	Amalia
5	Bloemhof
6	Koster
7	Leeudoringstad
8	Bultfontein
9	Fochville
10	Paul Roux
11	Naboomspruit
12	Nylstroom
13	Warmbaths
14	Pretoria
15	Verwoerdburg
16	Delmas
17	Meyerton
18	Petrus Steyn
19	Kestell
20	Louis Trichardt
21	Pietersburg
22	Roedtan
23	Volksrust
24	Newcastle
25	Vryheid
26	Luckhoff
27	Petrusville
28	Middelburg
29	Graaff-Reinet
30	Jansenville
31	Jeffreys Bay
32	Fauresmith
33	Jagersfontein
34	Edenburg
35	Trompsburg
36	Colesberg
37	Bethulie
38	Hofmeyr
39	Somerset East
40	Brandfort
41	Smithfield
42	Jamestown
43	Adelaide
44	Boesmansriviermond
45	Kenton on Sea
46	Excelsior
47	Clocolan
48	Tweespruit
49	Wepener
50	Van Stadensrus
51	Dordrecht
52	Komga
53	Cedarville
54	Harding
55	Kranskop
56	Richmond
57	Blythedale Beach
58	Zinkwazi Beach
59	Kwabonambi
60	Kuruman
61	Postmasburg
62	Danielskuil
63	Reivilo
64	Kamieskroon
65	Loeriesfontein
66	Nieuwoudtville
67	McGregor
68	Napier
69	Gansbaai
70	Laingsburg
71	Kenhardt
72	Vanwyksvlei
73	Herbertsdale
74	Marydale
75	Beaufort West
76	Strydenburg
77	Richmond
78	Aberdeen
79	Klipplaat
80	Steytlerville
81	Bitterfontein
82	Lambert's Bay
83	Graafwater
84	Carnarvon
85	Britstown
86	Victoria West
87	De Aar
88	Humansdorp
89	Riebeek-Kasteel
90	Bredasdorp
91	Nieu Bethesda
92	Atlantis
93	Botrivier
94	Thabazimbi
95	Williston
96	Thornhill
97	St. Francis
98	Stilbaai
99	Struisbaai
100	Agulhas

9 RECOMMENDATIONS REGARDING SYSTEMS FOR FURTHER INVESTIGATION

The analysis of existing methods and systems worldwide, together with the cost analysis, has shown the technical and economic viability of *in situ* groundwater treatment methods as cost-effective alternative to *ex situ* water treatment. It is recommended that such systems be tested at field scale and full scale. Due to the differences regarding infrastructure and levels of technological inputs, different systems are expected to be viable in the rural water setting compared to town water supply. The recommendations regarding these two situations are set out below for nitrate removal.

Furthermore, permeable reactive barriers should be tested for groundwater denitrification but also for other applications, particularly for remediation of contaminants such as heavy metals, e.g. chromium or for removal of organic compounds. A recommendation in this regard is also appended.

For iron and manganese, in situ removal, e.g. by the Vyredox or similar method, is recommended for avoiding borehole clogging in porous aquifers.

9.1 *In situ* treatment systems for rural water supply application

Systems that are recommended for rural groundwater denitrification, but also for the removal of other contaminants, e.g. heavy metals or organic compounds, include:

☐ ***Permeable reactive barriers (PRB)***

These can be constructed from cheap, readily available materials and would be relatively simple for communities to install with limited training. They provide long-term treatment without maintenance and no power source is required. By-products of the sugar industry could be investigated as a more readily degradable carbon source, especially for use in rural KwaZulu-Natal, in addition to the more conventional wood chip/sawdust walls.

☐ ***In situ redox manipulation (ISRM)***

In situ redox manipulation is recommended for the deeper porous aquifers in South Africa. The dithionite chemical reagent should be readily available, since it is used in the pulp and paper industry. Laboratory testing would be recommended for the first phase and field-testing only if the lab results look promising.

☐ **In situ *biological denitrification (ISBD)***

In situ biological denitrification is strongly recommended as it is probably the most widely used method internationally. The configuration of the injection and abstraction boreholes is flexible and can be adapted to suit the specific treatment problem. Various conventional and organic substrates and cheaper locally available options should be tested for potential application in rural treatment systems. The injection of microbes would not be recommended at this stage.

☐ ***Electrokinetics***

Various electrochemical techniques can be useful as an enhancement for the first two methods above, as the electrochemical techniques do not appear to be completely efficient for nitrate removal on their own. More information would need to be collected on the electrode composition and installation, applied voltages, etc. and extensive testing conducted before electrokinetics could be applied in the field. The electrokinetic method is, however, the only one found that has been claimed to be suitable for fractured rock environments, which would make it worth testing for South Africa. This is the main reason why this method is recommended for testing in rural areas, despite the higher levels of technical skill and know-how that is required.

9.2 *In situ* treatment systems for application in town water supply

It is recommended that the methods set out above are tested for town water supply where needed. All four methods will be viable in the town water supply context for the removal of nitrate and other contaminants from groundwater. In addition, the availability of infrastructure and technical know-how would also make the Nitredox method viable in these circumstances. Therefore, The Nitredox nitrate removal system should be considered for application following a thorough evaluation of the costs involved.

☐ ***Nitredox***

The Nitredox method is recommended for testing in a primary aquifer where a large number of injection and observation points can easily be obtained by installing well points. Its long successful record at Bisamberg, Austria provides a strong motivation for local application. As the technique is somewhat more complex it is better suited for town water treatment rather than for rural water supply application. It is necessary to investigate whether licensing costs in terms of registered patents will be applicable.

☐ ***Vyredox (or similar)***

Iron and manganese removal is imperative in many high volume abstraction situations to avoid or minimise borehole clogging effects. At towns such as Atlantis, the beneficial effects of iron and manganese removal will offset the costs of implementing *in situ* treatment. It is recommended that a system similar to the Vyredox system be tested on a South African primary aquifer. Recommended sites also include the Calitzdorp and Dysselsdorp areas where Fe is currently investigated as a most likely cause of clogging of aquifers in the Table Mountain Group aquifer.

9.3 *In situ* remediation of polluted groundwater

In the USA and other countries, many *in situ* remediation systems are successfully in operation at contaminated sites. The cost advantages involved make these methods attractive for remediation of spills and other pollution problems and it is recommended that the methods be applied locally to develop the local expertise for wider application.

In situ remediation could, for example, be tested at Springbok, where chromium was allegedly spilled into an alluvial aquifer. The two most important techniques that are recommended for application are PRB and ISRM techniques.

☐ ***Permeable reactive barriers (PRB)***

These can be constructed from cheap, readily available materials such as foundry wastes or furnace slag. They are recommended as they would be relatively easy to install at mining and industrial sites and would provide a low-cost, long-term treatment option.

☐ **In situ *redox manipulation (ISRM)***

The ISRM technique is practically as effective and maintenance free as the PRB method but as ISRM can be installed at greater depth it is recommended for application to a larger range of primary aquifers of greater thickness.

9.4 Recommended case study examples

☐ **Denitrification**

The widespread occurrence of high nitrate concentrations in groundwater poses a serious health risk for rural and town water supply in the northern areas of South Africa. This investigation showed that *in situ* denitrification is a technically and economically viable option and it is recommended that the technique be applied at field scale. Various possibilities are possible, but the preliminary calculation showed that installing a permeable reactive barrier in an alluvial aquifer, such as that at Marydale, is the preferable solution as it requires little subsequent maintenance. An alluvial aquifer in a defined river bed is preferred for ease of monitoring in this case. Relatively intensive monitoring is recommended for the initial units. This may be reduced once the operational parameters and logistics are well understood. Further field tests, preferably using *in situ* redox manipulation, should follow in the thicker primary aquifers. Subsequently, fractured aquifers should be investigated with the addition of the electrokinetics technique.

- **Iron and manganese removal**

In view of the extensive iron and manganese related clogging problems that occur in many aquifers, it is recommended that the technique be applied to a primary aquifer of which the aquifer dimensions, parameters and flow characteristics are well understood, and where clogging has become a problem, such as the one at Atlantis. In this case, the Vyredox or similar technique is the preferred option. Once the technique has been demonstrated in a primary aquifer, it should be extended to secondary aquifers.

- **Pollution remediation**

As in most countries, groundwater pollution is on the increase in South Africa and the installation of permeable reaction barriers for remediation is the widely applied solution abroad. It is recommended that the technique be tested, e.g. using a "iron wall" for example at Springbok where chromium pollution was found in alluvial aquifer. In this case, the test site should also have a clearly defined geometry for ease of monitoring. Field applications for the removal of other pollutants, such as organics should follow the successful initial test.

REFERENCES

Anonymous, 1985. Water denitrified with molasses. *SA Waterbulletin*, **Feb. 1985**, p.13.

Appelo, C.A.J. & Postma, D., 1996. *Geochemistry, groundwater and pollution*. A.A. Balkema, Rotterdam.

Athmer, C.J. & Huntsman, B.E., 2001. A case for electroosmosis remediation. Proceedings: Fourth Tri-Service Environmental Technology Symposium, San Diego, California, 18-20 June 2001.

Bates, H. K. & Spalding, R. F., 1998. Aquifer Denitrification as Interpreted from *In situ* Micrcosm Experiments, *J. Environ. Qual*, **27**, 174-182.

Blaszczyk, M., 1992. Comparison of denitrification by *Paracoccus denitrificans, Pseudomonas stutzeri* and *Pseudomonas aeruginosa*. *Acta Microbiol. Pol.*, **41**, 203-210.

Blaszczyk, M., 1993. Effect of medium composition on the denitrification of nitrate by *Paracoccus denitrificans*. *Appl. Environ. Microbiol.*, **59**, 3951-3953.

Blowes, D.W., Ptacek, C.J., Benner, S.G., McRae, C.W.T., Bennett, T.A. & Puls, R.W., 2000. Treatment of inorganic contaminants using permeable reactive barriers. *Journal of Contaminant Hydrology*, **45**, 123-137.

Braester, C. & Martinell, R., 1988. The Vyredox and Nitredox method *in situ* treatment of groundwater, *Wat. Sci. Tech.*, **20(3)**, 149-163.

Carrera, J., Vincent, T. & Lafuente, F.J., 2003. Influence of temperature on denitrification of an industrial high-strength nitrogen waste water in a two-sludge system. *Water SA*, **29(1)**, 11-16.

Cartmell, E., Clark, L., Oakes, D., Smith, S., Tomkins, J, 1999, Feasibility of In-situ Bioremediation of nitrate in aquifers systems, R & D Technical Report P277, WRc report number EA4683, Environment Agency

Chew, C.F. & Zhang, T.C., 1998. *In situ* remediation of nitrate contaminated ground water by electrokinetics/iron wall process. *Water Science and Technology*, **38(7)**, 135-142.

Conrad, J.E., Colvin, C., Sililo, O., Görgens, A, Weaver, J. & Reinhart, C. 1999. *Assessment of the impact of agricultural practices on the quality of groundwater resources in South Africa*. Report No. 641/1/99, Water Research Commission, Pretoria, South Africa.

Darbi, A., Viraghavan, T., Butler, R. & Corkal, D., 2002. Batch studies on nitrate removal from potable water. *Water SA*, **28(3)**, 319-322.

Dodds, H. A & Fey, M.V., 1995. *Decontaminating nitrate-polluted soil*. Contract report to Sastech R&D, Department of Geological Sciences, University of Cape Town.

Drever, J.I., 1997. *The geochemistry of natural waters*. Surface and groundwater environments 3rd edition. Prentice Hall, Upper Saddle River.

EPA, 1992. *Another look at: "National Survey of Pesticides in drinking water Wells"*, Phase 2 report, EPA Office of Water Publication # EPA 570/9-91-020, 166 plus appendices.

EPA, 1995. In situ remediation technology status report: Treatment walls. Report No. EPA/540/K-94/004. Office of Solid Waste and Emergency Response, US Environmental Protection Agency.

Firestone, M. K., 1982. Biological Denitrification, In: Stevenson, F.J. (ed.). *Nitrogen in soils*, Agron. Monogr., 22, ASA, CSSA and SSSA, Madison, WI

Gonzales-Pradas, E.M., Villafranca-Sanches, M. & Socias-Viciana, M., 1993. Phosphate and nitrate sorption on calcareous soils from Spain. *Arid Soil Res. Rehabil.*, **7(2)**, 181-190.

Hamon, M. & Frustec, E., 1991. Laboratory and field study of an *in situ* ground water denitrification reactor. *Res. J. Water Pollut. Control. Fed.*, **63(7)**, 942-949

Heaton, T.H.E., 1984. Sources of the nitrate in phreatic groundwater in the Western Kalahari. *J. Hydrol.*, **67**, 249-259.

Heaton, T.H.E., 1985. Isotopic and chemical aspects of nitrate in the groundwater of the Springbok Flats. *Water SA*, **11**, 199-208.

Ho, Sa V., Athmer, C.J., Sheridan, P.W., Hughes, B.M., Orth, R., McKenzie, D., Brodsky, P.H., Shapiro, A.M., Sivavec, T.M., Salvo, J., Schultz, D., Landis, R., Griffith, R. & Shoemaker, S., 1999. The Lasagna Technology for *in situ* soil remediation. 2. Large field test. *Environmental Science & Technology*, **33(7)**, 1092-1099.

Hunter, W. J., (2003) Accumulation of nitrite in denitrifying barriers when phosphate is limiting. *J. Contam. Hydrol.*, **66**, 79-91

Innovative Technology, 2000. *Summary Report: In Situ Redox Manipulation, Subsurface Contaminants Focus Area*. Prepared for US Department of Energy, Office of Environmental Management and Office of Science and Technology.

ITRCWG, 2000. *Technology Overview, Emerging Technologies for Enhanced In Situ Bioremediation (EISBD) of Nitrate-contaminated Ground Water*. Interstate Technology and Regulatory Cooperation Work Group, Enhanced *In Situ* Bioremediation Work Team.

Jaafari, K., Elmaleh, S., Coma, J. & Benkhouja, K., 2001. Equilibrium and kinetics of nitrate removal by protonated cross-linked chitosan. *Water SA*, **27(1)**, 9-13.

Jacinthe, P. A., Dick, W. & Brown, L. C., 2000. Bioremediation of nitrate contaminated shallow soils and waters via water table management techniques: evolution and release of nitrous oxide. *Soil Biology and Biochemistry*, **32(3)**, 371-382

Jacobs, J. & Loo, W.W., 1994. Direct push technology opens new remediation avenues. *Econ. Magazine*, December 1994, 36-37.

Janda, V., Rudovsky, J., Wanner, J., & Marha, K., 1988. *In situ* denitrification of drinking water. *Wat. Sci. Tech.*, **20(3)**, 215-219.

Jechlinger, G., Schöller, F., Seidelberger, F., & Zibuschka, F., 1991. *Denitrification In Situ*. In: Proceedings of I.W.S.A workshop: Inorganic nitrogen compounds and water supply. Hamburg, 27-29 November 1991,113-122.

Khan, I. A., & Spalding, R. F., 1998. *Denitrification using a daisy well system*. Presentation to National Sanitation Foundation International Symposium, Safe Drinking Water in Small Systems: Technology, Operations, and Econimics. Washington D. C., May 10-13

Kopara, A.S. & Oğütveren, Ü., 2002. Removal of nitrate by electroreduction and electrocoagulation. *J. Hazard. Mat.*, **B89**, 83-94.

Korom, S.F., 1992. Natural denitrification in the saturated zone: A review. *Wat. Res. Research*, **28**, 1657-1668.

Kruithof, J.C., Van Paasen, J.A.M., Hijnen, W.A.M., Dierx, H.A.L. & Van Bennekom, C.A., 1985. Experiences with nitrate removal in the eastern Netherlands. Proceedings: *Nitrates Dans les Eaux*, Paris 22-24 October.

Liang, L., Korte, N., Gu, B., Puls, R. & Charles, R., 2000. Geochemical and microbial reactions affecting the long-term performance of *in situ* 'iron barriers'. *Adv. Env. Research*, **4(4)**, 273-286.

Loo, W.W., 2000. Electrokinetic treatment of hazardous wastes. *Standard Encyclopedia of Environmental Science and Technology*, McGraw Hill, New York, p. 14.69-14.84.

Mallinckrodt Baker Inc., 2001. *Material Safety Data Sheet S3650, Sodium Hydrosulfite*.

Marais, S, 1999. *Dependency of communities on groundwater for water supply and associated nitrate and fluoride problems.* Paper presented at Workshop on Fluorides and Nitrates in Rural Water Supplies, Mafikeng, 9 - 10 March 1999.

Mercado A., Libhaber, M. & Soares, M.I.M., 1988. *In situ* biological groundwater. denitrification: Concepts and preliminary field test. *Wat. Sci. Tech.*, **20(3)**, 197-209.

Mohn, J., Schurmann, A., Hagedorn, F., Schleppi, P., & Bachofen, R., 2000. Increased rates of denitrification in nitrogen-treated forest. *Forest Ecology and Management*, **137(1-3)**, 113-119.

National Water Act, Act No. 36 of 1998. Republic of South Africa.

National Environmental Management Act, Act No 107 of 1998. Republic of South Africa.

O'Hannesin, S., 1998., *Groundwater Remediation using In situ treatment Walls*. Powerpoint presentation from EnviroMetal Technologies Inc.

Paavolainen, L., Fox, M., & Smolander, A., 1999. Nitrification and denitrification in forest soils subjected to sprinkling filtration. *Soil Biol. Biochem.*, **32(5)**, 669-678.

Reddy, K.J. & Lin, J., 2000. Nitrate removal from groundwater using catalytic reduction. *Water Research*, **34(3)**, 995-1001.

Robertson, W.D. & Cherry, J.A., 1995. *In situ* denitrification of septic system nitrate using reactive porous media barriers: Field trials. *Ground Water*, **33(1)**, 99-111.

Schipper, L.A., & Vojvodic-Vukovic, M., 2000. Nitrate removal from groundwater and denitrification rates in a porous treatment wall amended with sawdust. *Ecol. Engineering*, **14**, 269-278.

Schipper, L.A., & Vojvodic-Vukovic, M., 2001. Five years of nitrate removal, denitrification and carbon dynamics in a denitrification wall. *Wat. Res. Research*, **35(14)**, 3473-3477.

Scott, M.J., Metting, F.B., Fruchter, J.S. & Wildung, R.E., 1998. Research investment pays off. *Soil and Groundwater Cleanup*, **Oct. 1988**, 6-13.

Simon, S. G., Meggyes, T., Mc Donald, C., Tunnermeier, T., (18-19 October, 2001), In-situ barriers vs. Pump and Treat methods for Groundwater remediation, Report on a Workshop held at the Federal Institute for Material Research and Testing (BAM), Berlin, , European Science Foundation Grounwater Pollution Programme

Smith, G.D., Barnes, C.J., Lynch, R.M., Byrne, C.J. & Jacobson, G., 1991. *Possible denitrification technology for small settlement water supplies*. Technical Memorandum 91/12. Division of Water Resources, CSIRO, Australia.

Soares, M.I.M., Belkin, S. & Abeliovich, A., 1988. Biological groundwater denitrification: Laboratory studies. *Wat. Sci. Tech.*, **20(3)**, 189-195.

Stevens, R.J., Laughlin R.J., & Malone, J.P., 1998. Soil pH affects the process reducing nitrate to nitrous oxide and di-nitrogen, *Soil Biol. Biochem.*, **30(8-9)**, 1119-1126.

Tartakovsky, B., Millette, S., Delisle, S. & Guiot, S.R., 2002. Ethanol-stimulated bioremediation of nitrate-contaminated ground water. *Ground Water Monitoring and Remediation*, 78-87.

Tredoux, G, Talma, A. S., & Engelbrecht, J. F. P., 2000. *The increasing nitrate hazard in groundwater in the rural areas*. Paper presented at WISA 2000, Sun City, RSA, May 2000.

Tredoux, G, Talma, A. S., & Engelbrecht, J. F. P., 2001. Nitrate in groundwater in Southern Africa. In: Seiler and Wohnlich (eds). *New approaches characterizing groundwater flow*. Swets & Zeitlinger Publishers, Lisse, ISBN 90651 848 X.

Wibbe, H B, Wertz, A, Böckle, R, Rohmann, U, & Hunke, D, 1986. Großversuch zur Grundwassersanierung durch gesteuerte Denitrifikation und anschließende aerobe Behandlung im Untergrund. *DVGW-Schriftenreihe Wasser*, Nr 106, Eschborn, Germany, pp 181-202.

Wild, A., 1988. *Russul's Soil Conditions and Plant Growth, Eleventh Edition*, Department of Soil Science. University of Reading, John Wiley and Sons Inc., New York.

Ying-Feng Lin, Shuh-Ren Jing, Tze-Wen Wang, & Der-Yuan Lee, 2002. Effects of macrophytes and external carbon sources on nitrate removal from groundwater in constructed wetlands, *Environ. Pol.*, **119(3)**, 413-420.

Web Sites

***In Situ* Redox Manipulation:**
http://www.battelle.org/Environment/publications/EnvUpdates/winter99/article2.html

Permeable Reactive Barriers:
http://www.frtr.gov/matrix2/section4/4-41.html
http://www.prb-net.org/
http://www.rtdf.org/public/permbarr/barrdocs.htm

Electrokinetics:
http://www.ebsi-inc.com
http://www.fast-tek.com
http://www.terrancorp.com/techdocs/ektri/ektri.htm
http://spnr.ars.gov/BioD/Biod.htm

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APPENDIX A

COST ESTIMATES FOR IN SITU DENITRIFICATION OPTIONS FOR THE TOWN OF MARYDALE

S. Clarke, A. J. Hön & G. Tredoux

1. Introduction

This cost study was motivated by the fact that cost estimates for *in situ* groundwater treatment schemes were only available for overseas plants and could not be easily translated to the South African situation. Cost information acquired through literature for schemes in Europe and the USA was based on the first world economies of these countries and would be unrealistic if directly converted to South African currency. Contact with overseas researchers and operators indicated that costs for each component of the scheme (e.g. labour, chemical reagents, borehole installation, etc.) could not be extrapolated from international case studies, but would need to be sourced individually, based on South African market values.

The proposed treatment methods considered in the cost analysis included:

- permeable reactive barriers;
- *in situ* redox manipulation; and
- biological denitrification.

These methods with all their requirements as well as cost information are listed below, based on quotations received from South African companies. A reverse osmosis treatment plant was used for comparison as a potential *ex situ* treatment option. Reverse osmosis was selected as a treatment plant that could potentially treat nitrate contamination, although it is not specifically designed for nitrate removal.

Marydale was chosen as the site for the cost study on the grounds that it is a rural area in which inhabitants are dependant on groundwater for their everyday water supply. The quality of water extracted from the well field in the area is not always of good quality, often having nitrate concentrations over the maximum allowable by the WHO.

This cost study examines the breakdown of all costs involved in the installation and running of different *in situ* denitrification systems for the Marydale groundwater supply. Relevant service providers and organisations were contacted for the information required to do this.

2. Geological overview

The Marydale Group, named after the town of Marydale, is the major geological feature in the area. It occurs on the boundary between the Kaapvaal Craton and the Namaqua Metamorphic Belt. Metamorphic rocks, primarily quartzites, gneisses, and porphoritic gneisses of the Namaqua Metamorphic Province, occur south west of this boundary, (SACS, 1980). North east of the contact, the gneissic granites of the Kaapvaal Craton dominate.

Quaternary aeolian deposits occur in low lying areas between koppies or ridges of the more resistant rocks (Shand and VSA, 1997). These deposits are sands of the Kalahari group which have migrated. The Brakbosch fault is believed to pass through Marydale in a north-south direction. Lithological logging of boreholes of the Marydale well field revealed that the area consists of unconsolidated sands and silts, with sandstone, siltstone and calcrete and bedrock comprising quartzitic gneisses and granite gneisses.

3. Hydrogeology

Exploration boreholes drilled in the area revealed that a primary and a secondary aquifer are present in the area. The secondary fracture system is not well understood, but it is believed that the bed rock is not very permeable. The yield of the secondary aquifer is less than that of the primary aquifer (Shand and VSA, 1997).

The main water bearing unit is the alluvial cover of more or less 12 m thick, which occurs in the lower lying areas between the quartzite and granite ridges. The aquifer material consists of sedimentary layers containing primarily sand and silt. The texture grades from sub-rounded into course grained at the lower part of the profile to medium and fine grained at the top of the profile (Shand and VSA, 1997).

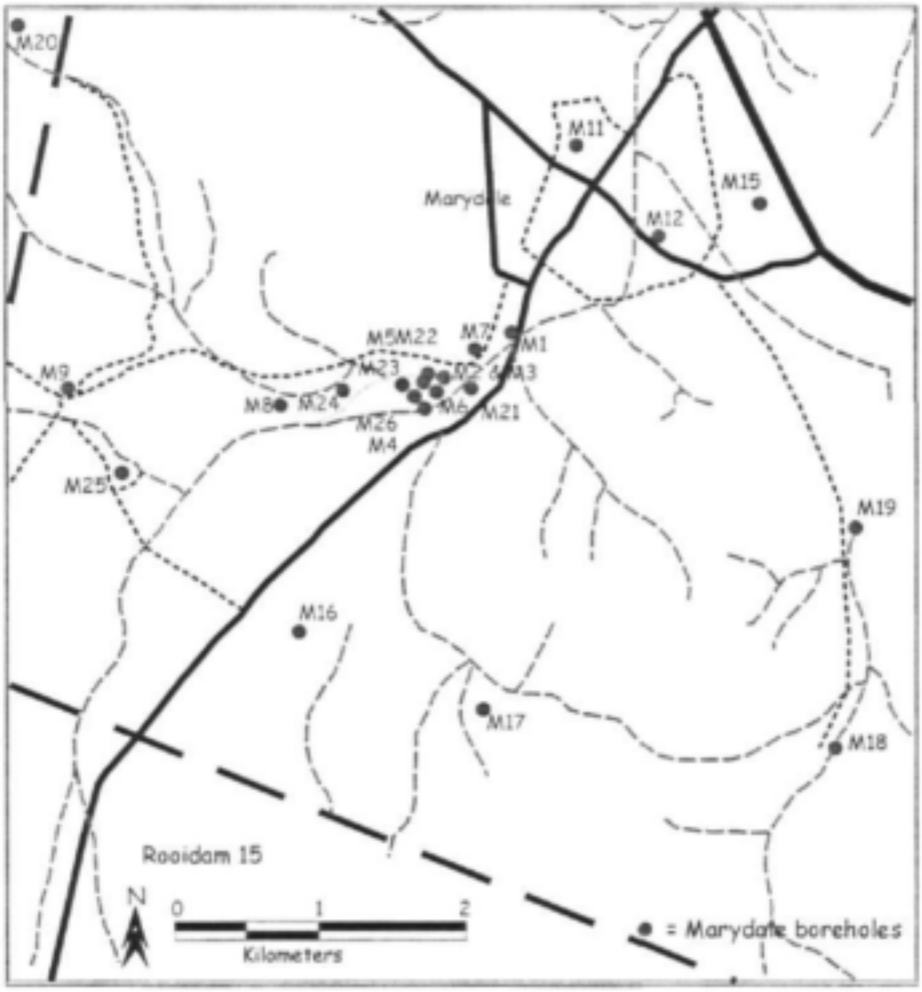

Figure A1: Marydale well field, placed in river bed *(Shand, 1997)*

The sediments are of aeolian origin. A weathered layer of 2 to 3m occurs in the bedrock, (Shand and VSA, 1997). Boreholes are drilled primarily in this alluvial cover, and it is suspected that the underlying quartzites are relatively impermeable to groundwater infiltration (Pers. Comm., 2003). Rest water levels vary from 5 to 25m below ground level. The deeper levels are measured in the secondary aquifer while the shallower measurements are found for the primary aquifer (Shand and VSA, 1997).

4. Hydrochemistry

A well field containing 10 boreholes is used as the town water supply. Of these wells, half produce groundwater of nitrate concentration above the maximum allowable 20 mg/l, (Hofmann, 1997). Microbiological sampling showed that coliform counts of 15/100ml in some boreholes were three times as much as the SABS limits (Hofmann, 1997). No faecal coliforms were detected. This serves as an indication that no human or animal waste reaches the boreholes. According to Hofmann (1997), "the Marydale well field may be described as microbiologically suitable or sound".

Samples collected in the Marydale area were primarily Na-Cl rich, with some samples showing no dominant chemical character. VSA Geoconsultants describe the water as being "very hard" and this due to its high Ca concentrations. These high concentrations of calcium present the possibility of scale formation on pipes and elements of electrical appliances. The calcium concentrations range from 360 to 710 mg/l as $CaCO_3$ in the area (VSA Geoconsultants, 1997).

Total dissolved solids are on average 1105 mg/l in the Marydale well field, with concentrations varying for other sampled points. The average TDS values for Marydale and Annex Kalkput is about 986 mg/l. High TDS values for Brulpan (1234 mg/l) and Rietfontein (2490 mg/l) indicate that the water is saline. Fluoride concentrations average at around 1,4 mg/l which may cause staining of teeth of sensitive users. Boreholes other than that in the Marydale well field have fluoride levels of 1.2 mg/L (Marydale/Annex Kalk Put), 1.0 mg/L (Brulpan), and 1.2 mg/L (Rietfontein).

The nitrate levels of 12.2 mg/l (as nitrogen) exceed the maximum allowable 10 mg/l NO_3-N. This presents a health risk to infants up to the age of six months old. Adults are also advised to avoid long term use. The average nitrate level (as nitrogen) for Marydale/Annex Kalkput is 8.3 mg/l, while Brulpan has concentrations of 3.5 mg/l and Rietfontein has concentrations of 5.3 mg/l (VSA Geoconsultants, 1997).

5. Cost estimates for in situ nitrate removal systems

5.1 Capital costs

5.1.1 Permeable Reactive Barriers

Companies and individuals were contacted regarding the prices of various equipment and services required to implement a permeable reactive barrier (See Annexure A). The results are tabulated below.

However time consuming a task; this approach rendered results based on South African goods and service fees, which eliminates the problem of having incomplete cost information based on the economies of foreign countries. The requirements under the activity column were matched as closely as possible to that of the systems used in other currently operating systems.

Table A1. Capital costs for a PRB system

Activity	Breakdown	Cost
Slurry wall	Material Wall size (10 m deep x 10 m length x 1 m width)	Bentonite Ca R2.10/kg Bentonite Na R2.15/kg 480 kg required = R1032 7520 L water = to be negotiated with the town water supply body
Treatment wall	Material	Suggestion to use alien vegetation in the region as a source of sawdust to remove the cost of transport and purchasing of sawdust in another province.
	Transport	R 3 /km x 100 km = R 300
	Installation	Dependant on worker wage: Approximately R 5000
Dewatering	Establishment	R 30 000
	Installation	R 5000
	Diesel and running	R 1000
	Supervision	R 2000 per day x 2 = R 4000
Contingencies	Expenses that may not be accounted for above	R 5000
Total capital costs		**R 51 332**

In the quest to find information, it was found that woodchips and sawdust are relatively cheap materials, but not so readily available in the vicinity of Marydale. It was also discovered by the investigating team that these materials are in considerable demand for the manufacture of secondary products such as chipboard, used to make cupboards etc. This would make obtaining large quantities of sawdust a difficult task, unless an arrangement is made with a relatively big company to support such a project.

Note on slurry wall construction:

Slurry walls are typically placed at depths up to 30 metres (100 feet) and are generally 0.6 to 1.2 metres (2 to 4 feet) in thickness. Installation depths over 30 m (100 ft) are implementable using clam shell bucket excavation, but the cost per unit area of wall increases by about a factor of three. The most effective application of the slurry wall for site remediation or pollution control is to base (or key) the slurry wall 0.6 to 0.9 metres (2 to 3 feet) into a low permeability layer such as clay or bedrock. This "keying-in" provides for an effective foundation with minimum leakage potential. An alternate configuration for slurry wall installation is a "hanging" wall in which the wall projects into the groundwater table to block the movement of lower density or floating contaminants such as oils, fuels, or gases. Hanging walls are used less frequently than keyed-in walls.

5.1.2 In Situ Redox Manipulation

Table A2. Capital costs for an ISRM system

Activity	Breakdown	Cost
Drilling Approximately 10-20 m deep Maximum requirements	5 injection/withdrawal wells	R 78 000
	5 multi-level monitoring wells	
	4 standard monitoring wells	
Reagents	Sodium dithionite	\$ 900 per metric ton
		R 32 per 500 g = R 6400
	Fe (if naturally occurring iron is not sufficient)	Naturally occurring iron high enough
	Mixing and storage tanks	1 m^3 = R 500
		2.5 m^3 = R 1090
		3 m^3 = R 1690
Injection pumps	Bank of 3 chemical dosing pumps to pump 2 L/s to 20 m below surface	R 500 000* ALDOSS Dave Hendriks 021 715 5051
	Centrifugal pump 2L/s at 2 bar	R 3389 excl VAT PUMPCO Harry v d Merwe
Tracer Tests	Reagent/chemicals (Cl, B)	Sodium chloride R144.56 / 5 kg
	Transport	R 3.00 per km x 1500 km = R 4500
Waste removal	K/Na sulphate extraction	R 3000
Contingencies		R 5000
Total capital costs		**R 100 289**

* Note: The chemical dosing pumps were considered too expensive for this application and were not opted for in the final cost summation.

The pumps selected are based on the rate of injection/withdrawal required. This, in turn, depends on the flow rate within the aquifer as well as the size or storativity and transmissivity of the aquifer. This was determined using a simple model and inputting the transmissivity, area, and calculating the values of K (hydraulic conductivity) and estimating the velocity of the groundwater flow. The effects of different injection rates were simulated to determine the area of influence of an injection rate with an injection time or residence time of 18 hours. It showed that an injection rate of 2 L/s would allow the substance being injected to cover an area of approximately 150 m^2, while 10 L/s injection would cover an area of about 456 m^2 and 30 L/s would spread over an area of 1245 m^2.

The amount of dithionite needed is dependant on its solubility and concentrations required. Dithionite is readily soluble in water and exhibits strong reducing action in aqueous solution.

"Operation of the barrier is relatively inexpensive because, after emplacement, external energy sources, management of large volumes of water, or management of secondary waste is not required. The ISRM process provides a permanent in situ solution for groundwater remediation. Once treated, the contaminant becomes less toxic and remains immobilized. Risk is also reduced through a reduction in human exposure to waste products. The barrier is

renewable and can be re-established, if needed, during the length of the project" (Pacific Northwest National Laboratory, operated by Battelle for the US Department of Energy).

5.1.3 *In Situ* Biological Denitrification

Table A3. Capital costs for an ISBD system

Activity	Breakdown	Cost
Borehole construction	Dependent on configuration of system	± R 78 000
Carbon substrate e.g. glucose, methanol, acetone, ethanol	2% by weight of soil in area being treated Glucose – R 154.67 / 5 kg Methanol – R 42.25 / 2.5 L Ethanol – R 187.22 /2.5 L Acetone – R 73.27 / 5 L	± R 1 546.70 (based on using 50 kg glucose)
Nutrients (phosphate)	(if needed)	Not included in costing
Injection pumps **Withdrawal pumps**	Centrifugal pump 2L/s @ 2 bar	R 3 389 excl VAT as for the above method
Contingencies		R 5 000
Total capital costs		**R 82 935**

5.2 Monitoring and maintenance costs for in situ methods

Permeable Reactive Barriers require maintenance costs for monitoring or when a barrier needs to be repaired or replaced. Examples of such technologies in Canada and New Zealand show that little or no maintenance was required over five and ten years of operation, respectively. Monitoring costs have been estimated considering that nine boreholes would be sampled each time. The costs include analyses, travelling and accommodation (see table below). Biological denitrification plants do not require any disposal or treatment of waste.

Table A4. Monitoring costs for *in situ* treatment systems

Activity	Breakdown	Cost
Monitoring	Time	R10 000
	Travel	R10 000
	Accommodation	R 500
Chemical Analyses	Major cations and anion	R 5850

6. *Cost estimates for reverse osmosis treatment system*

This is an ex situ method that is currently used in South Africa and should be able to remove nitrate along with other components.

Table A5. Capital costs for ex situ treatment by reverse osmosis system

Activity	Breakdown	Cost
Reverse osmosis plant	Material	R 150 000
	Construction 50 KL output plant	
Building and infrastructure	Material	R 200 000
	Construction	
	Transport of material	

Table A6. Operating costs for ex situ treatment by reverse osmosis system

Activity	Breakdown	Cost
Operational cost	Membrane costs	R 2 per KL
	Chemical costs	
	Electricity	
Operator salary	Human resource time	These costs are not included in the analysis
Skills maintenance	Capacity building for operator	Not included in cost analysis.

7. Discussion and Conclusions

It is evident from the above information that in-situ methods are by far more affordable to start up than ex-situ. This is probably mainly due to the large amounts of infrastructure used in ex-situ methods. In-situ methods use the sub-surface as a treatment vessel, eliminating the costs incurred by constructing of infrastructure.

The permeable reactive barrier method has the lowest capital costs and would thus be affordable for the poorer communities to sustain. ISRM and ISBD methods are more expensive to start up than the PRB method, but they also require fairly low maintenance. The in-situ redox manipulation (ISRM) method has additional costs for disposal of wastes produced during the initial injection. This introduces the problem of above ground waste disposal which potentially worsens the pollution problem.

The robust nature of in-situ methods contribute to its low running and maintenance costs. The fact that a minimum amount of training is required and exposure to chemicals is limited to initial phases of treatment provides additional advantages of in-situ treatment methods both in terms of costs and safety.

APPENDIX B

BISAMBERG *IN SITU* DENITRIFICATION PLANT, VIENNA, AUSTRIA

1. General

One of the production wells in the wellfield at Bisamberg, Vienna, has a relatively high nitrate concentration approaching the drinking water limit of 10 mg/L. In-situ groundwater denitrification according to the Nitredox principle has been applied successfully for approximately 15 years. EVN Wasser (formerly Nösiwag) operates the treatment plant.

Figure B1 Bisamberg in-situ denitrification plant

The details of this plant that are provided below were obtained from the EVN Wasser website (http://www.evnwasser.at/nitrat_bisamberg.html), Jechlinger *et al.* (1991), Braester & Martinell (1988), and a site visit in 1993.

2. Layout of the plant

2.1 Wellfield area

The treatment system consists of three concentric circles of wells surrounding the production well from which the denitrified water is abstracted. The first ring of 49 wells, representing the reduction zone, is located at a distance of 38 m from the production well. The wells have a diameter of 50 mm. All of these serve for chemical injection for the purpose of denitrification. This circle of wells is subdivided into 8 sectors consisting of 4 to 8 wells that are operated as a group. The second circle of wells, at the start of the oxidation zone, is located at a distance of 18 m from the production well. This circle of wells consists of 16 wells also with a diameter of 50 mm. The inner circle of wells, which ends the oxidation zone, is located at a distance of 10 m from the production well. These wells have a diameter of 150 mm. The wells of the two inner circles, at 18 m and 10 m, respectively are all equipped with pumps with a yield of 3.75 L/s. These pumps send the water through the oxygenator in the water treatment unit leading to an enrichment of oxygen in the water. The production well is located at the centre of the concentric circles and was constructed with a filter casing of 600 mm diameter. Inside this well there are three pumps, two of which have a yield of 30 L/s and are connected to the drinking water supply. The third pump located in the same well has a yield of 25 L/s and this water is used in the treatment process. All wells in the whole system have been installed to a depth of approximately 13 m.

Figure B2 Denitrification zone in foreground

2.2 Control station

The control station is located next to the wellfield and controls the whole operation, including the alcohol dosage and the oxygen enrichment for the water treatment process. All pipes and cables needed for the treatment process are linked to the control station.

Figure B3 Control room location and pipework (right)

3. Operation

3.1 Reduction zone

Denitrified water, abstracted from the production well at a rate of 25 L/s, is mixed with ethanol and injected into the outer concentric circle of wells located at a distance of 38 m from the production well. The circle of wells is subdivided into 8 sectors and at any given stage the alcohol water mixture is in injected into two opposite sectors. Each dosing cycle lasts three hours followed by half an hour rinsing without alcohol addition. The purpose of this procedure is to prevent clogging of the aquifer. Subsequently, injection commences in the next two sectors in a clockwise direction.

For each sector, three alcohol dosage pumps are available. Each of these can supply 0.4 L of alcohol per hour. The nitrate concentration in each of the oxidation wells is measured continuously and recorded in the control station. The alcohol dosage depends on the nitrate content of the groundwater in the oxidation well of the particular sector. As long as the average nitrate concentration is between 20 and 25 mg/L (as nitrate) only one alcohol dosage pump is in operation. When the concentration of nitrate is between 25 and 30 mg/L, two alcohol dosage pumps are used. All three dosage pumps for the particular sector are in use when the nitrate concentration lies between 30 and 35 mg/L. This means that the dosage of alcohol can range from 0.4 to 1.2 L per hour in any particular sector.

3.2 Oxidation zone

Both inner concentric circles of wells, at a distance of 18 m and 10 m from the production well, form part of the oxidation zone. Groundwater is abstracted at a total rate of 30 L/s from eight wells in the outer of these concentric circles and at a rate of 15 L/s from four wells in the inner circle. The water is enriched with oxygen in the oxygenators in the control room and injected into the other eight wells in the outer circle and the other four wells in the inner circle respectively to promote oxidation and precipitation of dissolved iron and manganese. The operating cycle is designed for each well to be used alternatively for abstraction or injection.

3.3 Production well

The production well is equipped with two pumps each abstracting 30 L/s for the city drinking water supply system. This means the treatment plant can yield denitrified product water at a rate of 60 L/s.

3.4 Disinfection

As a result of the biological treatment process, the growth of biomass in the subsurface is stimulated. The bacterial population of the product water is completely different from that of the raw water, mainly because a significantly more stable population forms during the denitrification activity. However, the possibility exists that re-infection of the water supply in the distribution system may happen more easily due to the more readily available substrate in the form of the somewhat increased biomass. Accordingly, the water is disinfected using chlorine dioxide. The Austrian regulations prescribe a chlorine dioxide concentration of 0.04 mg/L and this has to be maintained at the Langenzersdorf water supply reservoir. The concentration is measured at the reservoir and the dosage at the plant, usually between 0.6 and 0.7 mg/L, adjusted to maintain the required level.

4. Denitrification process

The plant operation is based on the chemical reduction of nitrate by the addition of an organic compound, in this case ethanol, as a carbon source (see Figure B 4). The bacteria use the available oxygen in the subsurface and once the free oxygen is depleted the oxygen from the nitrate molecule is utilised. In this way the nitrate is reduced to elemental nitrogen that is volatilised.

The injection of ethanol in the outer circle of wells and the associated bacterial processes create a reducing environment that also leads to the reduction of iron and manganese, which are present in the aquifer matrix. For this reason, the two additional circles of wells were introduced to form the oxidation zone. The oxygenated water that is introduced into these rings of wells ensures oxidation and precipitation of the iron and manganese in the aquifer. At the same time the oxygen level in the final product water is increased.

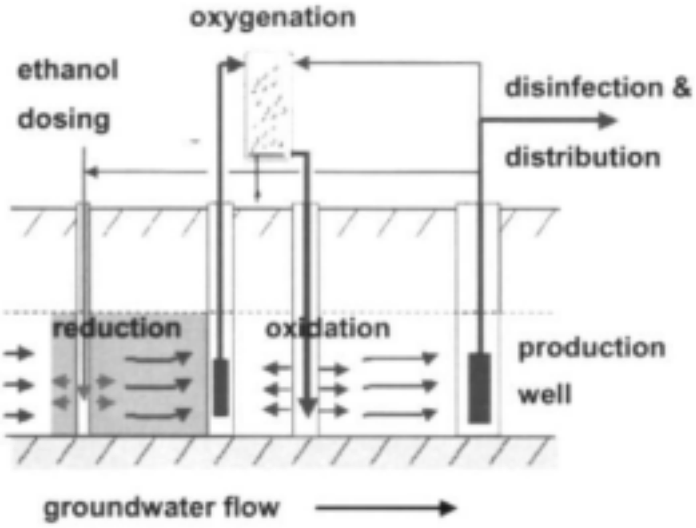

Figure B4: Schematic layout of nitrate removal by the Nitredox method at Bisamberg

5. Final note

As this denitrification plant is the first and, until now, the largest of its kind in Europe, no general operation manual is available from the manufacturer. For this reason, the operation has to be adapted from time to time for optimum production. This also varies according to the water consumption and the concentration of nitrate in the raw water.

APPENDIX C

BROICHHOF *EX SITU* DENITRIFICATION PLANT, NEUSS, GERMANY

1. Introduction

Agricultural activities in the catchment of the aquifer at Neuss, near Cologne, Germany, have led to high nitrate levels in the production wellfield. The European nitrate standard was being reduced in the 1980s and denitrification of the groundwater was essential to comply with the stricter guidelines. The Broichhof plant employs *ex situ* biological denitrification and came into operation in August 1989. The details of this treatment plant are included because parallel *in situ* and *ex situ* denitrification tests were carried before the current plant was chosen. The Engler-Bunte Institute at the University of Karlsruhe carried out the research that lead to the construction of this facility.

2. Treatment plant design

The raw water is abstracted from six wells at a rate of 50 m^3/h each, from the aquifer in Quaternary sediments. The slotted casing in the wells was placed relatively close to the surface as the groundwater with the highest nitrate concentration was found at a depth of 15 m and it decreased with depth (see Figure C1). The treatment plant consists of three parallel streams, each consisting of a biological denitrification reactor, a filter for clarification, and a trickling bed (see Figure C1). The denitrification reactor is filled with activated carbon. The substrate added to the denitrification reactor consists of acetic acid and phosphate. Clarification is required for removing the turbidity caused by bacteria biomass flushed from the reactor. A flocculating agent is added to aid the filtration. The nitrogen formed during denitrification is removed in the trickling bed, while the water is also simultaneously oxygenated.

3. Infiltration system

Following denitrification, the treated water is reintroduced into the aquifer up gradient of the final production boreholes. Artificial recharge takes place via a 300 m long trench excavated to a depth of 8 m.

4. In situ denitrification tests

Two types of *in situ* plants were tested, one using injection of acetic acid and phosphate, similar to the *ex situ* biological denitrification plant, while the other consisted of a reactive barrier type system with peat placed into boreholes.

4.1 Acetic acid dosage

The pilot scale *in situ* denitrification tests at Broichhof were carried out in parallel with the pilot scale *ex situ* treatment tests. The layout of the *in situ* substrate injection pilot plant for the field tests is shown in Figure C2. Groundwater abstracted from the aquifer was dosed with acetic acid (equivalent to a final DOC of 200 mg/L) and phosphate (20 mg/L) and injected into the aquifer. The main reason for using acetic acid was to reduce the clogging potential in the injection wells. As associated development of biomass during denitrification was considered to be the main cause of clogging, it was planned to reduce the denitrification rate in the injection boreholes. The lower the pH, the slower the rate of denitrification, therefore a high dosage of acetic acid was administered for 15 minutes every six hours.

This *in situ* biological denitrification system succeeded in reducing the nitrate concentration in the groundwater by at least 50 percent, which was sufficient to bring the nitrate concentration within the guideline levels for potable water.

4.2 Peat as 'reactive barrier'

The layout of this plant is shown schematically in Figure C3. Little is known about the success of this field test.

5. Final treatment system

Following all the *ex situ* pilot testing and *ex situ* field testing, it was decided to construct a full scale *ex situ* biological denitrification system, mainly because of the extensive biomass development experienced in this instance and the potential clogging of the aquifer. The denitrified product water is infiltrated into the subsurface at shallow depth up gradient of the main well field and blends with the untreated deeper groundwater before abstraction. The design of the plant is shown schematically in Figure C4. Further (unpublished) information has to be obtained regarding the reasons for the clogging problems.

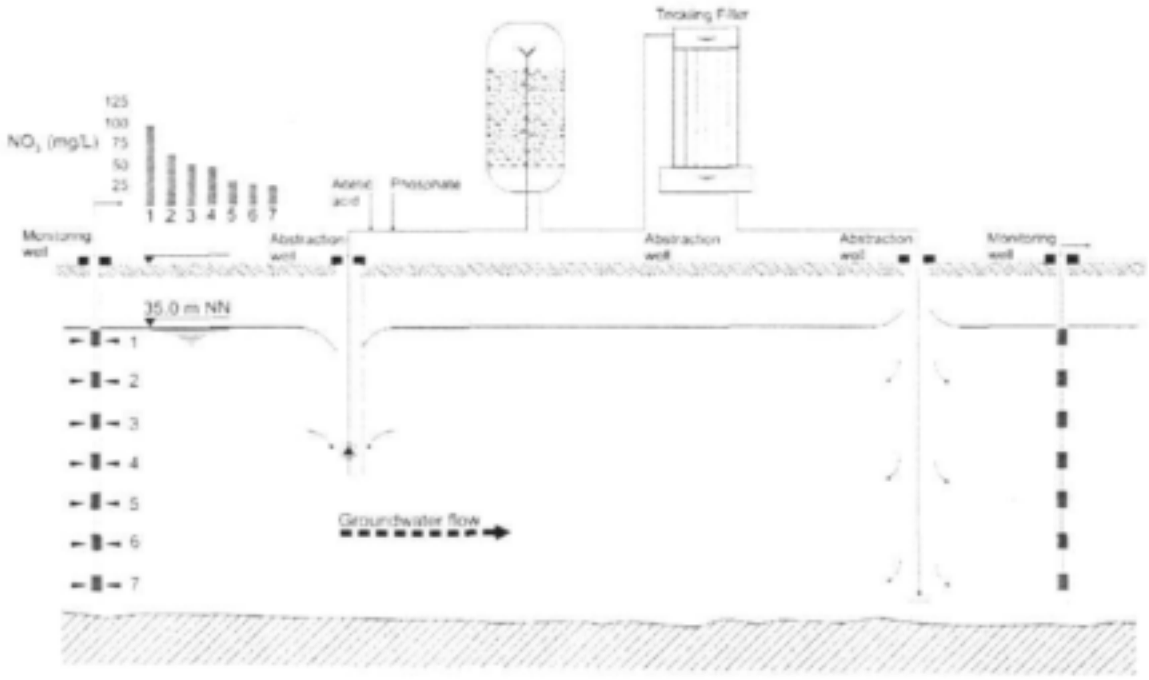

Figure C1: *Ex situ* biological denitrification tests at Broichhof, Neuss, Germany

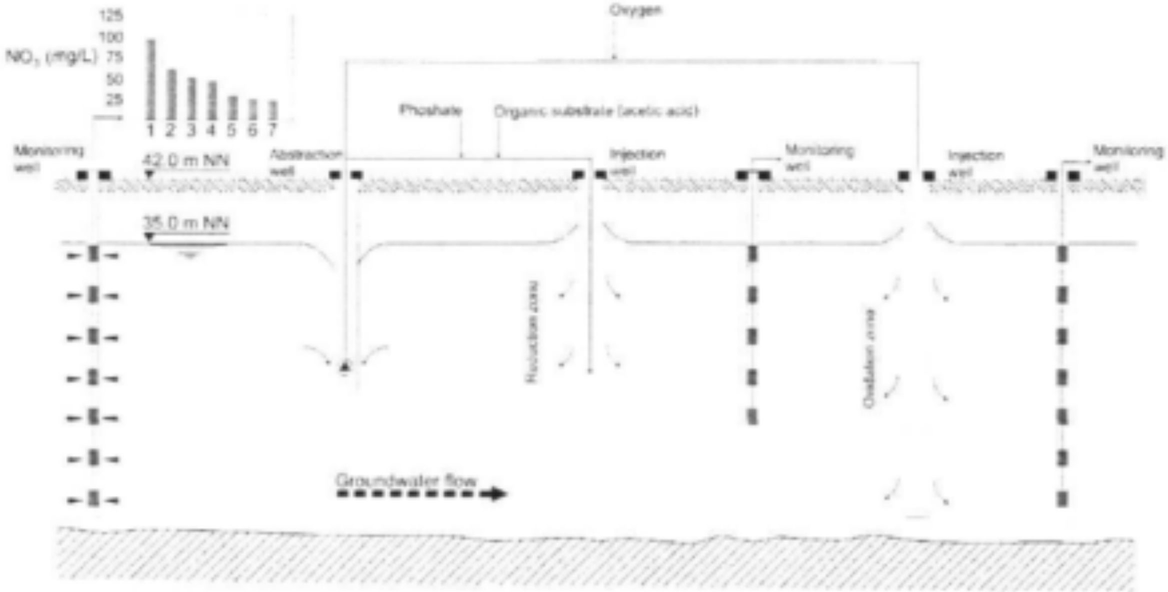

Figure C2: *In situ* biological denitrification tests at Broichhof, Neuss, Germany

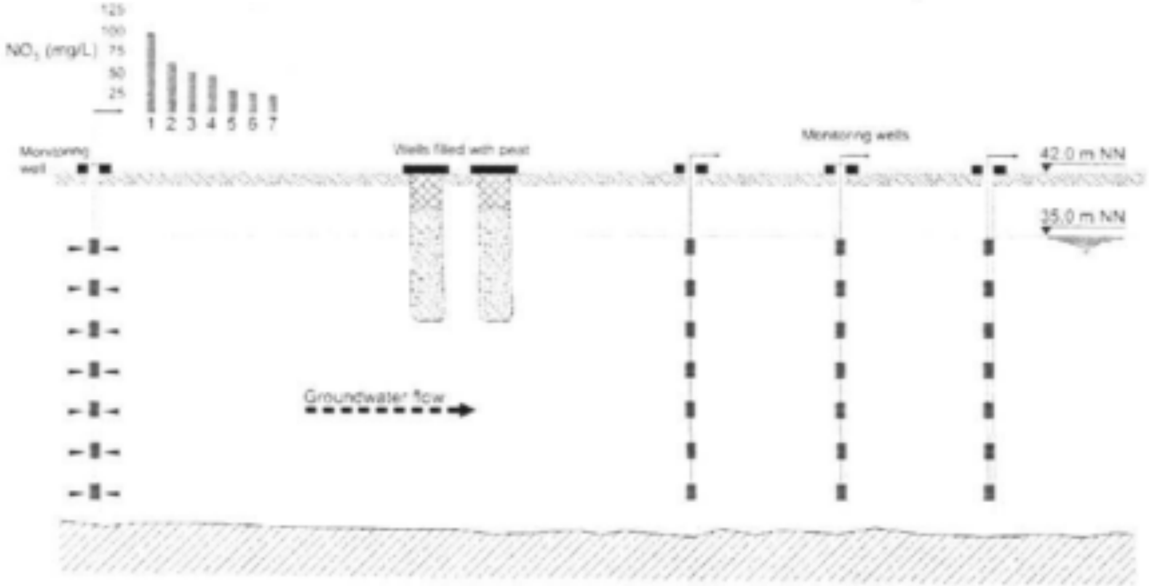

Figure C3: *In situ* biological denitrification using peat as organic substrate at Broichhof, Neuss, Germany

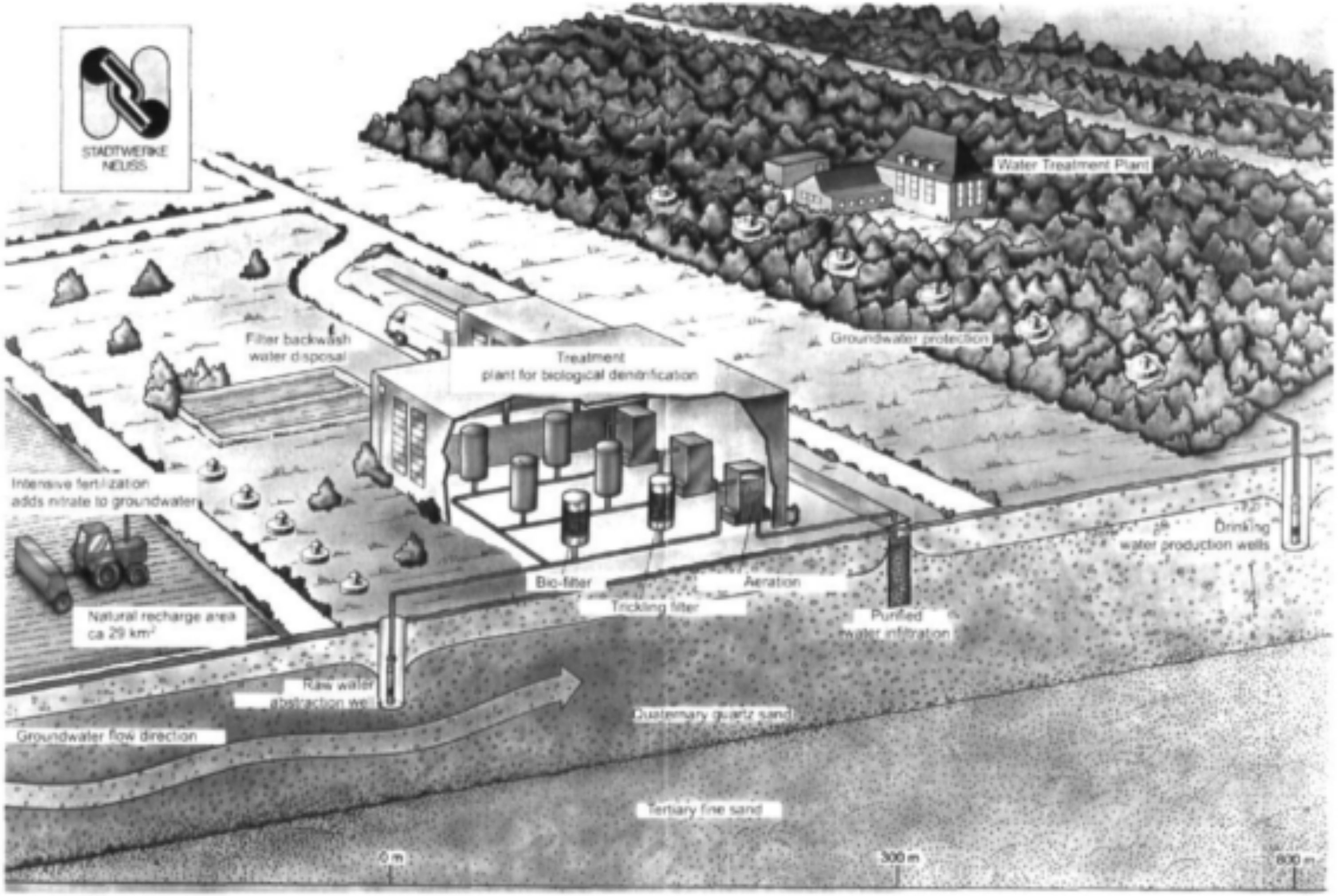

Figure C4: Biological denitrification systemas part of the water treatment process at Broichhof, Neuss, Germany

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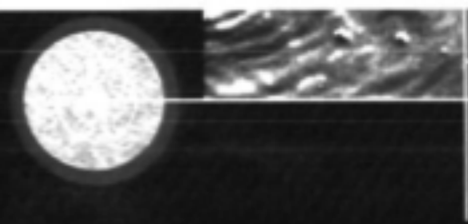

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