A FEASIBILITY STUDY OF IN-SITU IRON REMOVAL IN THE ATLANTIS PRIMARY AQUIFER, WESTERN CAPE PROVINCE, SOUTH AFRICA

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DECLARATION

I, Kate Robey, hereby declare that this dissertation, submitted for the MSc (Geohydrology) degree in the Faculty of Natural and Agricultural Sciences, Institute for Groundwater Studies, University of the Free State, Bloemfontein, South Africa, is my own work and has not previously been submitted by me at another University/Faculty.

I declare that all sources cited or quoted are indicated and acknowledged by means of a list of references.

I further cede copyright of the dissertation in favour of the University of the Free State.

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Kate Robey

30 June 2014

ACKNOWLEDGEMENTS

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LIST OF ACRONYMS AND ABBREVIATIONS

As^{3+}	arsenic ion
AWRMS	Atlantis Water Resource Management Scheme
AWWA	American Water Works Association
BCHT	Blended Chemical Heat Treatment
C/Co	ratio of final solute concentration divided by initial solute concentration
CDT	constant discharge test
CGS	Council for Geoscience
Cl^-	dissolved chloride ion
Cl_2	chlorine gas
ClO_2	chlorine dioxide
CoCT	City of Cape Town
CSIR	Council for Scientific and Industrial Research
DO	dissolved oxygen
DOC	dissolved organic carbon
DWA	Department of Water Affairs
DWAF	Department of Water Affairs and Forestry
EAW	Electrochemically Activated Water
EC	electrical conductivity
E.N.	electro-neutrality
EPA	Environmental Protection Agency
Fe^{2+} or Fe(II)	ferrous iron
Fe^{3+} or Fe(III)	ferric iron
HAAs	haloacetic acids
HOCl	hypochlorous acid
HS^- or H_2S	dissolved hydrogen sulphide ion or hydrogen sulphide gas
H_2O_2	hydrogen peroxide
ICP-MS	Inductively Coupled Plasma Optical Mass Spectrophotometer
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrophotometer
ICRC	Inorganic Contaminants Research Committee
ISIR	*in-situ* iron removal
ISRRI	In Situ Remediation Reagents Injection
K	hydraulic conducivity
KKRWSS	Klein Karoo Rural Water Supply Scheme
$KMnO_4$	potassium permanganate
mamsl	meters above mean sea level

meq/ℓ	milli-equivalent/litre
MIC	microbial-induced corrosion
Mn^{2+} or Mn(II)	bivalent manganese
Mn^{4+} or Mn(IV)	quadrivalent manganese
MnO_4^-	permanganate ion
NEMA	National Environmental Management Act (Act 107 of 1998)
NH_4^+	ammonium
NWA	National Water Act (Act 36 of 1998)
OH^-	hydroxyl free radical
O_3	ozone gas
pe	redox potential
pers. com.	personal communication
PO_4^{3-}	phosphate ion
PVC	polyvinyl chloride
Q	abstraction rate
redox	reduction-oxidation
SANAS	South African National Accreditation System
SANS	South African National Standards
Sc	specific capacity
SiO_2	silica
Sr	strontium
Sw	drawdown
Sy	specific yield
T	transmissivity
THMs	trihalomethanes
TMG	Table Mountain Group
TOC	total organic carbon
V	abstracted volume
Vi	injected volume
V/Vi	removal efficiency
WHO	World Health Organisation
WRC	Water Research Commission
WTP	water treatment plant
WWTW	Wastewater Treatment Works

CHAPTER 1.   INTRODUCTION

South Africa is largely a semi-arid country, rated among the top twenty water-stressed countries globally (Maclear, 1995). It relies primarily on surface water, but there is increasing pressure to supplement the already stressed surface water resources in the future. The problem is compounded by a limited capacity for new dam development, climate change, rapid urbanisation, industrial development, as well as government programmes aiming to provide adequate potable water and sanitation to millions of previously disadvantages South Africans (Turton, 2007; Hassan *et al*., 2008). Since an unreliable, restricted water supply is a limiting factor on the socio-economic growth of any country (Vegter, 1995) groundwater development has recently been identified as an important mitigation strategy by the Department of Water Affairs (DWA, 2011).

The groundwater strategy follows from actions initiated by the National Water Act No. 36 of 1998 (NWA; Republic of South Africa, 1998a), which recognised the significance of groundwater in the national water cycle and the importance of the evaluation of its status as a water resource. This strategy outlines action plans encouraging the preference of groundwater over surface water and advocates a greater contribution of groundwater through implementation of groundwater development programmes (Woodford *et al*., 2006). In South Africa, groundwater has been underutilised and underinvested, contributing no more than 15% to the overall water consumption in the last two decades (DWAF, 1986; Vegter, 1995; Woodford *et al.,* 2006). To date, irrigation comprises the lion's share of the national groundwater use (Figure 1; DWA, 2011). This is because groundwater was viewed as a secondary, augmentation option in South Africa due to the general misunderstanding and misuse of the resource, resulting in the assumption that it is unreliable (van Vuuren, 2011).
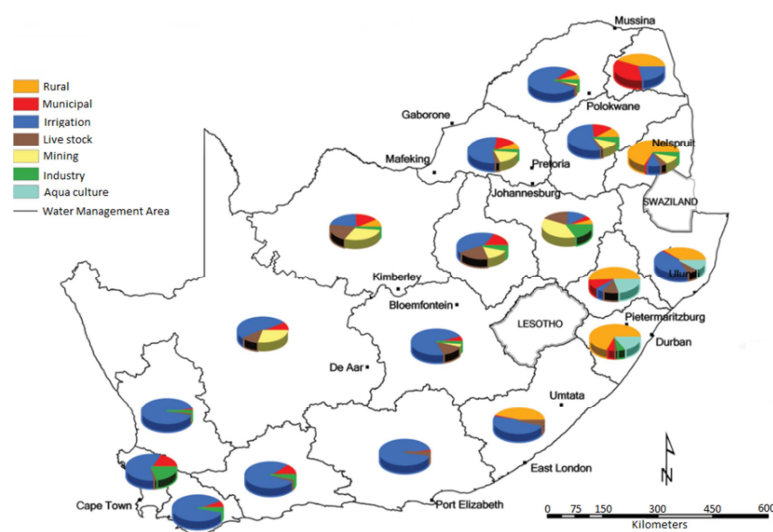
Figure 1: South Africa's groundwater use per Water Management Area (DWA, 2011)

This is despite South Africa's abundance of groundwater and its relative purity in comparison to many surface water resources, which enable approximately 315 towns to use it as their sole supply (Figure 2; Tredoux *et al.,* 2004; DWA, 2011). Furthermore, it is easier to protect groundwater against pollution and climate change and is generally cheaper, faster and more environmentally friendly to implement in comparison to surface water supply schemes (Sharma, 2001; van Vuuren, 2011). For example, the town of Atlantis, in the Western Cape, experiences low rainfall (< 460 mm/annum) and no readily available surface water resources, whereas groundwater with integration of artificial recharge has successfully supplied its water needs for more than three decades (DWA, 2010).
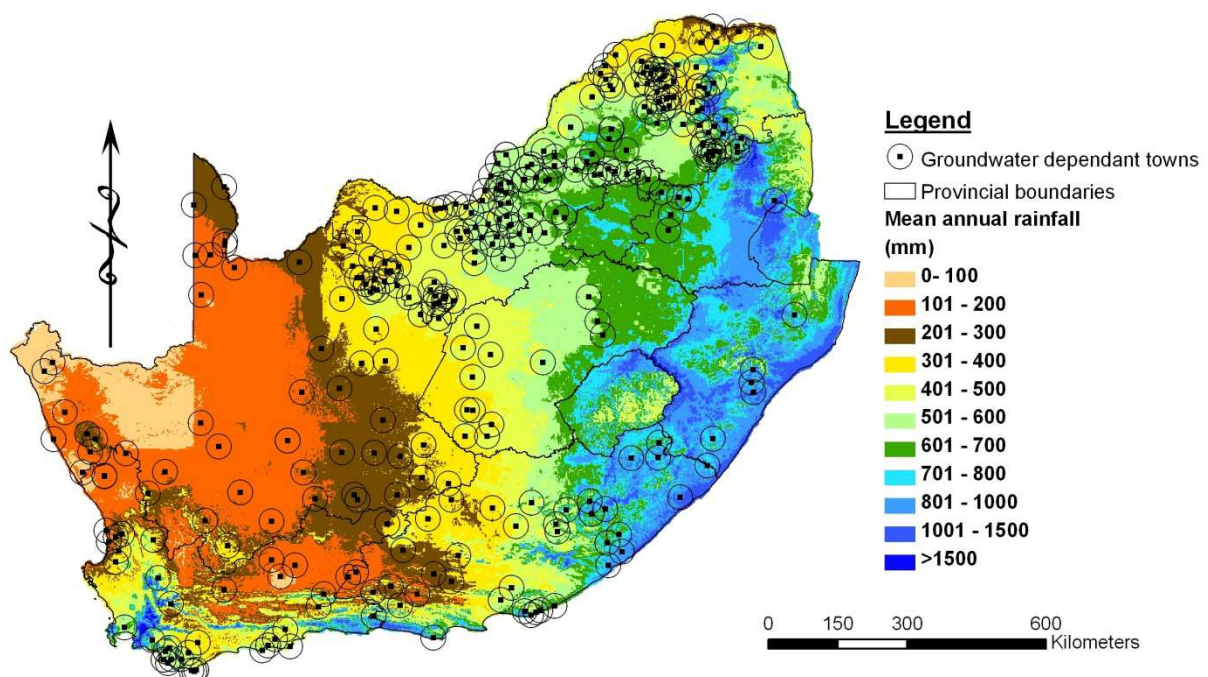
Figure 2: South Africa's distribution of mean annual rainfall and towns dependent on groundwater (data from Middleton and Bailey, 2009; DWA, 2011)

With the development of groundwater supply schemes on the increase, the two issues of utmost importance are the protection of groundwater quality and the planning and maintenance of this resource to sustain these schemes (DWA, 2011). In addition, potable water can be made accessible to more people if costs on production and treatment are kept low (Rajagopaul *et al.*, 2008). However, the long-term sustainability of many groundwater supply schemes, such as Atlantis, is currently threatened by operational and water quality problems caused by excess iron and manganese in the groundwater.

Jolly (2002) has identified the following main contributing factors to the failure of groundwater supply schemes:

- Water quality changes, which make water unsafe for consumption and/or use;

- The production boreholes cannot sustainably deliver the volumes the scheme was designed for;

- Water levels drop to such a degree that pumping becomes uneconomical.

The presence of elevated concentrations iron and manganese in groundwater is a potential threat to such schemes because they can contribute to all three causes of failure.

1.1   Water Quality Problems

The groundwater quality issues associated with iron and manganese mainly manifest as aesthetic and potable water problems. The factors that negatively affect the water quality and subsequently limit its use include (DWAF, 1996; Sharma, 2001; Alchin, 2008; WHO, 2008):

- The presence of these elements impart an astringent, metallic taste to the water at iron concentrations exceeding 0.3 mg/ℓ and 0.1 mg/ℓ for manganese;

- Aesthetic problems, i.e. reddish-brown or greyish-black water discolouration, which results in the staining of laundry, pumping fixtures, household appliances, walls and cooked food at concentrations as low as 0.3 mg/ℓ for iron and 0.2 mg/ℓ for manganese;

- At concentrations as low as 0.1 mg/ℓ both soluble ions can be oxidised in the presence of oxygen to form oxide coating on water pipelines that may later slough off and subsequently clog pumping fixtures, sprinklers and geysers;

- The presence of iron interferes with water treatment methods, such as the softening treatment of hard water since iron binds irreversibly on the ion exchange resins and is regarded as a common cause of softening plant failure;

- Iron and manganese cause problems in some industrial wet processes used in the textile, dyeing, white paper and beverage industries.

To circumvent the abovementioned problems, the World Health Organisation (WHO) recommends the removal of iron and manganese before distribution to concentrations below 0.3 mg/ℓ and 0.1 mg/ℓ, respectively (WHO, 2008).

The conventional water treatment approach to remove iron and manganese to the desired concentrations is well understood and requires above-ground water treatment after abstraction by a process that involves oxidation, followed by coagulation/flocculation, sedimentation and then sand filtration (Driscoll, 1986; Mackintosh and de Villiers, 2002). However, this approach is successful in developed settings such as cities, which have technical support but is often impractical and expensive for small-scale water schemes that are commonly located in rural areas (Andersson and Johansson, 2002; Mackintosh and de Villiers, 2002; Tredoux *et al.*, 2004). This is because the water treatment plant (WTP) facilities require large capital investments, expert management, operation by skilled staff, handling and storage of chemicals and generally have high operation and maintenance costs associated with periodic backwashing or filter rejuvenation, as well as proper disposal of the large volumes of generated sludge (Mettler *et al.*, 2001; Mackintosh and de Villiers, 2002).

1.2   Water Supply Problems

The main consequences of abstracting groundwater with elevated iron concentrations (and to a lesser extent manganese) are the operational problems associated with iron-related clogging. The clogging of production boreholes is a result of the ingress of atmospheric oxygen and pressure changes induced during pumping. This causes a shift in the reduction-oxidation (redox) equilibrium between the borehole and aquifer and results in the oxidation of the soluble ions (i.e. Fe^{2+} and Mn^{2+}) and precipitation of Fe(III)-oxyhydroxide and Mn(IV)-oxide in the borehole gravel pack and surrounding aquifer or forms coatings on the production borehole screen and pump (Tredoux *et al.*, 2004). The abiotic oxidation processes are often accompanied by the growth of iron-related bacteria, which exploit the oxidation of Fe^{2+} and Mn^{2+} in their metabolic processes, resulting in the development of slimy biofilms (Cullimore, 2008). Clogging in production boreholes has been observed where concentrations are as low as 0.5 mg/ℓ for iron and 0.05 mg/ℓ for manganese (Cullimore, 2008).

Over time, the build-up of oxides and biofilm can lead to severe clogging of the production borehole equipment and the aquifer in close vicinity (Driscoll, 1986; Cullimore, 2008). This leads to a reduction in borehole yield and transmissivity, which decrease the available drawdown in the borehole and increases production costs (Jolly, 2002; Deed and Preene, 2013). Ultimately, the submersible pump often burns out, further increasing operational costs. Apart from the need to replace failed equipment and lowered water production to the WTP due to borehole failure, there is also increased pressure on the other production boreholes, which leads to over-abstraction (Flower and Bishop, 2003; Deed and Preene, 2013).

Oxides and slimy biomass can be transported to the surface by the abstracted water, discolouring the abstracted water and clogging the flow meters and distribution pipelines requiring further treatment (Figure 3; Driscoll, 1986). The microbiological processes can produce odours, which deteriorate the water quality further and in cases of advanced stage of biofilm growth can cause microbial-induced corrosion (MIC) of the borehole screen and pump, which often would require replacement and in extreme cases, the drilling of a new borehole (Cullimore, 2008). This has been experienced in Botswana, where iron- and sulphate-related bacteria has caused such significant clogging and corrosion of the production boreholes, such that pumping equipment is required almost annually (Riekel and Hinze, 2002).

Figure 3: Iron-related clogging experienced at the Atlantis Aquifer of a borehole distribution pipeline between 15-20 mm thick (left) and flow meter (right) (More Water cc., 2002)

Iron-related clogging of production boreholes is a worldwide water-use problem impacting domestic water supply, agricultural and mining operations (e.g. Walter, 1997; Engelbrecht, 1998; More Water cc., 2002; Flower and Bishop, 2003; Timmer *et al.*, 2003; Karakish, 2005; Cullimore, 2008; Anderson *et al.*, 2010; Deed and Preene, 2013). Iron-related clogging is rated as one of the five main causes of production borehole failure (Driscoll, 1986) and manifests itself in South African groundwater supply schemes in both primary and fractured-rock settings.

The two paramount examples in South Africa impacted by the clogging problems include the Atlantis Water Resource Management Scheme (AWRMS) and Klein Karoo Rural Water Supply Scheme (KKRWSS). Both schemes are located within the Western Cape Province and have been developed in semi-arid areas, which lack a proximal surface water supply

(Flower and Bishop, 2003). The AWRMS was established in 1976 and targets the primary Atlantis Aquifer to supply the towns of Atlantis and Mamre as well as the Silwerstroom Resort (Flower and Bishop, 2003). The KKRWSS supplies the town of Dysselsdorp and the surrounding rural communities since 1986 from the fractured aquifers of quartz arenites in the Table Mountain Group (TMG) (Flower and Bishop, 2003). The iron-related clogging has resulted in significant operational problems for both schemes. For example by 2000, the production capacity at the Calitzdorp Wellfield of the KKRWSS declined by 77% from its original yield in 1987, with all 19 production boreholes having been impacted (Cavé and Smith, 2004; Smith and Roychoudhury, 2013). The boreholes currently operate at no higher than 20% of their originally assigned yield (Cavé and Smith, 2004; Smith and Roychoudhury, 2013). While the AWRMS used to supply all the water needed by Atlantis for over two decades, it is currently operating at only 30-40% of its capacity, resulting in surface water having to be brought in (DWA, 2011). To deal with the clogging problems in both groundwater supply schemes, a number of production boreholes have had to be reconstructed, pumping rate specifications lowered, costly chemical rehabilitation treatments were applied to recover lost yields and continuous lower rates rather than intermittent high pumping rates previously applied were implemented (Jolly and Engelbrecht, 2002; Smith, 2002; Flower and Bishop, 2003).

While these are prominent examples, the majority of towns in the Western Cape and Eastern Cape Province that exploited groundwater do so from the TMG aquifers, especially the Peninsula Formation and Nardouw Subgroup and have production boreholes that are severely affected by clogging due to the presence of iron often at concentrations less than 1.0 mg/ℓ (Mackintosh and de Villiers, 2002; Smart and Tredoux, 2002). Examples include the towns of Hermanus, Plettenberg Bay, Albertinia, Botrivier, Ceres, Waboomskraal, Cape Agulhas, Steytlerville, Cape St. Francis, the Arabella Country Estate near Kleinmond and the Clovelly Country Club in Cape Town (Jolly and Engelbrecht, 2002; Smart and Tredoux, 2002; Kgwaila *et al.,* 2011). Other notable occurrences of problematic iron-rich groundwater are in the Malmesbury Group rocks of the Western Cape, the Natal Group sandstones in the Kwazulu-Natal and alluvial deposits in the Eastern and Western Cape (Tredoux *et al.,* 2004).

Since iron, manganese and the bacteria involved in the clogging processes are ubiquitous in groundwater, furthermore the ingress of oxygen through pumping cannot be entirely prevented, the general mitigation approach is to control the rate of clogging of production boreholes through monitoring and maintenance protocols (More Water cc., 2002; Flower and Bishop, 2003). In severe cases, chemical rehabilitation by the patented Blended Chemical Heat Treatment (BCHT) or Electrochemically Activated Water (EAW) methods has been

applied (More Water cc., 2002; Smith, 2002; Smith, 2006). However, if not successfully managed, the iron-related clogging will ultimately return and continue in the vicious cycle of equipment failure, lowered production yields to the WTP and high operational and maintenance costs and in severe cases leads to stoppages or failure of the groundwater supply scheme (Deed and Preene, 2013). This is currently experienced in both the AWRMS and KKRWSS wellfields due to high water demands resulting in over-abstraction and thus the clogging re-occurs within a short period of time (Jolly 2002; Smith, 2002; Flower and Bishop, 2003; Smith and Roychoudhury 2013). This is not only a threat to the current groundwater supply schemes mentioned but is a concern for future groundwater developments, especially in the semi-arid Western Cape, where the TMG and Cape Flats Aquifers are currently targeted for investigation (Flower and Bishop, 2003).

1.3   Health Concern

Both iron and manganese are essential micronutrients for all living organisms (WHO, 2008) and there are no immediate health risks of iron in drinking water below 10.0 mg/ℓ, except for slight health risks expected in young children and sensitive individuals (DWAF, 1996). Toxic symptoms are only observed after an excessive intake (DWAF, 1996). Acute poisoning of young children (under the age of four years old) only occurs when iron concentrations exceed 10 mg/ℓ and chronic poisoning of adults occur due to years of excessive intake of iron on a daily basis of quantities between 40 to 70 mg/ℓ, but these situations are rare (DWAF, 1996; WHO, 2008). Since iron poisoning from water is rare there is no health-based guideline recommended by the WHO (2008). Manganese toxicity is more controversial due to the potential neurological damage it could cause in adolescents (Mettler, 2002; WHO, 2008; Bouchard et al., 2011). Generally, the greatest exposure of manganese is in food, but adverse neurological damage has been found as a result of extended exposure of manganese concentrations exceeding 0.6 mg/ℓ in drinking water sourced from groundwater (WHO, 2008). The health-based guideline recommended for manganese is 0.4 mg/ℓ by the WHO (2008), which can potentially render the groundwater unsuitable as a drinking water resource if not treated before distribution.

The South African drinking water authorities have to adhere to the aesthetic risk thresholds of $Fe \leq 0.3$ mg/ℓ and $Mn \leq 0.1$ mg/ℓ and chronic health risk limits to the $Fe \leq 2.0$ mg/ℓ and $Mn \leq 0.5$ mg/ℓ, set out by the South African National Standards (SANS) specification for domestic water supply, i.e. SANS 241:2011 (SANS, 2011). In certain parts of South Africa, groundwater iron concentrations are higher than these requirements (Figure 4). For example in Albertinia in the Western Cape, iron in groundwater from the TMG aquifers reaches concentrations of more than 20 mg/ℓ (Jolly and Engelbrecht, 2002). Unfortunately, the

existing data (i.e. Middleton and Bailey, 2009) only allowed for the distribution and identification of iron prevalence throughout South Africa, although since manganese behaves chemically similar to iron in solution, it may be assumed that high concentrations of iron is generally accompanied by relative high manganese concentrations (although this depends on local conditions).
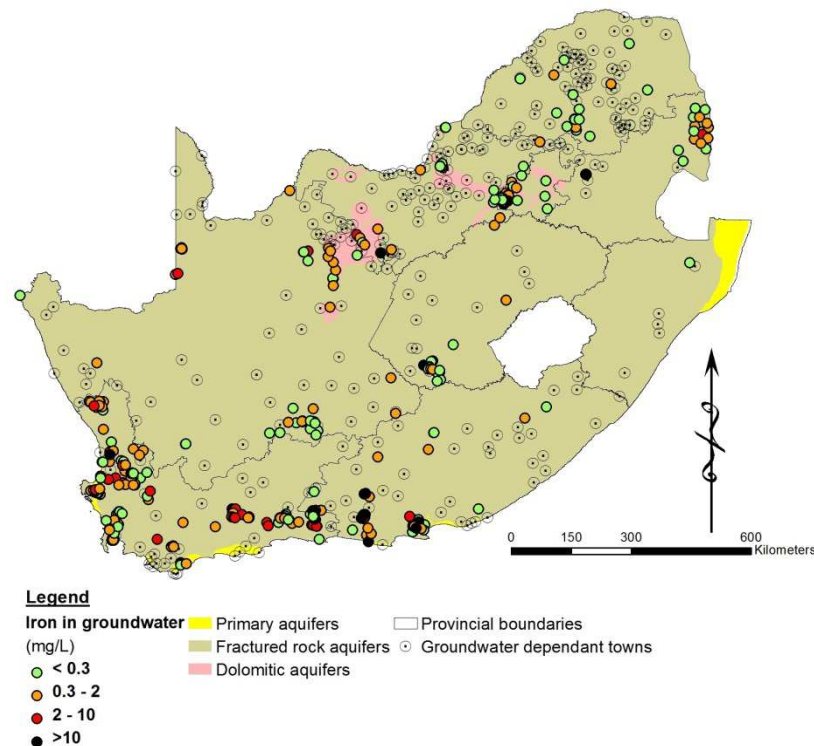
Figure 4: Distribution of the principal aquifer types and iron concentrations in South Africa (data from Middleton and Bailey, 2009; DWA, 2011)

Indirect health impacts can also occur through the presence of elevated iron and manganese concentrations, or through the *ex-situ* treatment, or by the clogged production boreholes and their rehabilitation treatment. For example, lack of water due to the failed clogged boreholes or aesthetic taste and undesirable appearance of the water due to high iron and manganese content could promote users, particularly in rural areas, to abandon the groundwater resource and use inferior or contaminated surface water instead, leading to incidents of cholera and typhoid (Sharma, 2001). This has been noted in South Africa in the rural Lowveld of Mpumalanga, where boreholes are often abandoned by communities due to high iron concentrations leading to staining of laundry and food (Andersson and Johansson, 2002). The presence of iron bacteria is not a health risk, but the periodic or continuous chlorination necessary to control the populations and remove the slimy biomass has potential health risks associated with the carcinogenic by-products from the chlorine-based chemicals used in above-ground water treatment and borehole rehabilitation (Cullimore, 2008).

1.4   Research Motivation

Despite the current knowledge and implementation of monitoring, maintenance and rehabilitation treatments more information is required to deal with the long-term prevention of iron-related problems in South African groundwater supply schemes. Other strategies proposed for overcoming these problems include:

- Finding other sources of water;

- Abandoning the borehole and drilling at new site;

- Investigating other methodologies.

Surface water resources are already stressed and new supply developments and subsequent surface water treatments may be overly expensive or unavailable in rural areas. Furthermore, the cost of installing new production boreholes and NWA licensing appears fruitless, especially in cases where the preventative monitoring and maintenance protocols are not currently being followed. Therefore, this study focuses on the third strategy mentioned above, namely investigating other methodologies, such as the *in-situ* iron removal (ISIR) method.

Globally, ISIR treatment has been successfully implemented in groundwater supply schemes for decades (e.g. Europe, United States of America and China) and was designed to reduce the amount of iron and manganese in the abstracted water, in order to decrease or obviate above-ground water treatment before distribution (Appelo *et al*., 1999). This is generally achieved by the periodic injection of oxygenated water into the anoxic aquifer, oxidising the soluble iron and manganese ions and precipitation of their respective oxides in the subsurface (Hallberg and Martinell, 1976). When abstraction is resumed, such groundwater then will have lower iron and manganese concentrations (Hallberg and Martinell, 1976). Another well-known benefit of this treatment method is the reduction of clogging in production boreholes due to the inhibition of iron and manganese oxidising processes occurring at the borehole interface with the aquifer (Mettler *et al.,* 2001; van Halem *et al*., 2011). In addition, the iron and manganese precipitates accumulate in the aquifer and stabilised over time into compact, crystalline minerals, which prevent iron and manganese mobilisation from the aquifer rocks, even when reducing conditions prevail again (Appelo *et al*., 1999; Mettler *et al.,* 2001; van Halem *et al*., 2011).

The experience abroad and in Africa as well has shown that ISIR is a robust and sustainable iron and manganese removal process, which has great potential in South Africa for the reasons that:

- It is a fast, simple and cost-effective approach to dealing with iron- and manganese-related problems in wellfields;

- It reduces the need for *ex-situ* treatment (which is costly and includes generation of sludge, high electricity and water usage) and improves production borehole longevity;

- It can be applied on both small and large-scales and can be designed to be mobile.

To date, ISIR has only been investigated from a theoretical point of view by DWA (Less, *pers. com.* 2012) or proposed by a number of hydrogeological consultants working on the iron-related clogging problems experienced at the AWRMS and KKRWSS (e.g. Jolly and Engelbrecht, 2002; Cavé *et al.*, 2004; Cavé and Smith, 2004; Tredoux *et al.,* 2004). Some of the reasons for the lack of ISIR investigation in South Africa include:

- The infancy of large-scale groundwater development and the lack of demand as economic impacts of iron-related problems were only recognised in the early 1990's;

- The lack of funding for feasibility studies as production borehole clogging is not an immediate threat to the water resource, as opposed to research in pollution-related problems such as acid mine drainage;

- ISIR has been successful applied in primary aquifers but literature on its application in fractured rocks is sparse, which is a limitation for its application in South Africa, which predominately exploits fractured aquifers;

- Other options such as wellfield management, maintenance and rehabilitation treatments have been investigated.

The research presented in this dissertation forms part of the capacity development for the WRC study entitled "*Preventing Production Borehole Clogging by In-Situ Iron Removal in South African Aquifers*", which is the first investigation into the feasibility of this treatment in a South African context. On recommendation from the WRC steering committee, the study area selected was the primary, intergranular Atlantis Aquifer due to iron-relate clogging jeopardising the sustainability of both its wellfields. The research findings will also be used by the City of Cape Town's Bulk Water Department (CoCT) and the Council for Scientific and

Industrial Research (CSIR) for the continual management of the Atlantis Aquifer in supplying water to the town of Atlantis.

1.5   Research Aim and Objectives

The aim of the project was to investigate the feasibility of the ISIR technique in the prevention of iron- and manganese-related problems (i.e. water quality and supply) in a South African primary aquifer. The objectives set out to achieve the abovementioned aim include:

- Site characterisation and preliminary evaluation of the study area to investigate the feasibility of ISIR application;

- Design and construct an ISIR prototype and methodology for the study site;

- Assess the effectiveness of Fe^{2+} and Mn^{2+} removal by the ISIR treatment at the study site.

CHAPTER 2.   LITERATURE REVIEW

2.1   Iron and Manganese in Groundwater

Iron and manganese are ubiquitous elements in the Earth's crust, with iron the fourth most abundant element, making up about 5%, while manganese comprises only 0.1% of the Earth's crust (DWAF, 1996; Howe *et al.*, 2004). As a result, they are found in most rock-forming minerals such as silicates, carbonates, sulphides and oxides (Appelo and Postma, 2005). Iron exists in one of two oxidation states, namely as ferrous iron (i.e. Fe(II) or Fe^{2+}) or ferric iron (i.e. Fe(III) or Fe^{3+}), which is found as either Fe(II)- or Fe(III)-bearing minerals or as ions dissolved in water (i.e. Fe^{2+} and Fe^{3+}) (Pérez-Guzmán *et al.*, 2010). Whereas manganese can occur in a number of different oxidation states in solid state ranging from Mn(III) to Mn(VII) but its occurrence in water is either as the bivalent (Mn^{2+}) or quadrivalent (Mn^{4+}) ion (Howe *et al.*, 2004). The prevalence of each oxidation state and thermodynamic stability of iron and manganese in minerals are controlled by the pH, redox potential (i.e. pe), temperature and the presence of sulphide and/or carbonate ions (Figure 5; Appelo and Postma, 2005).
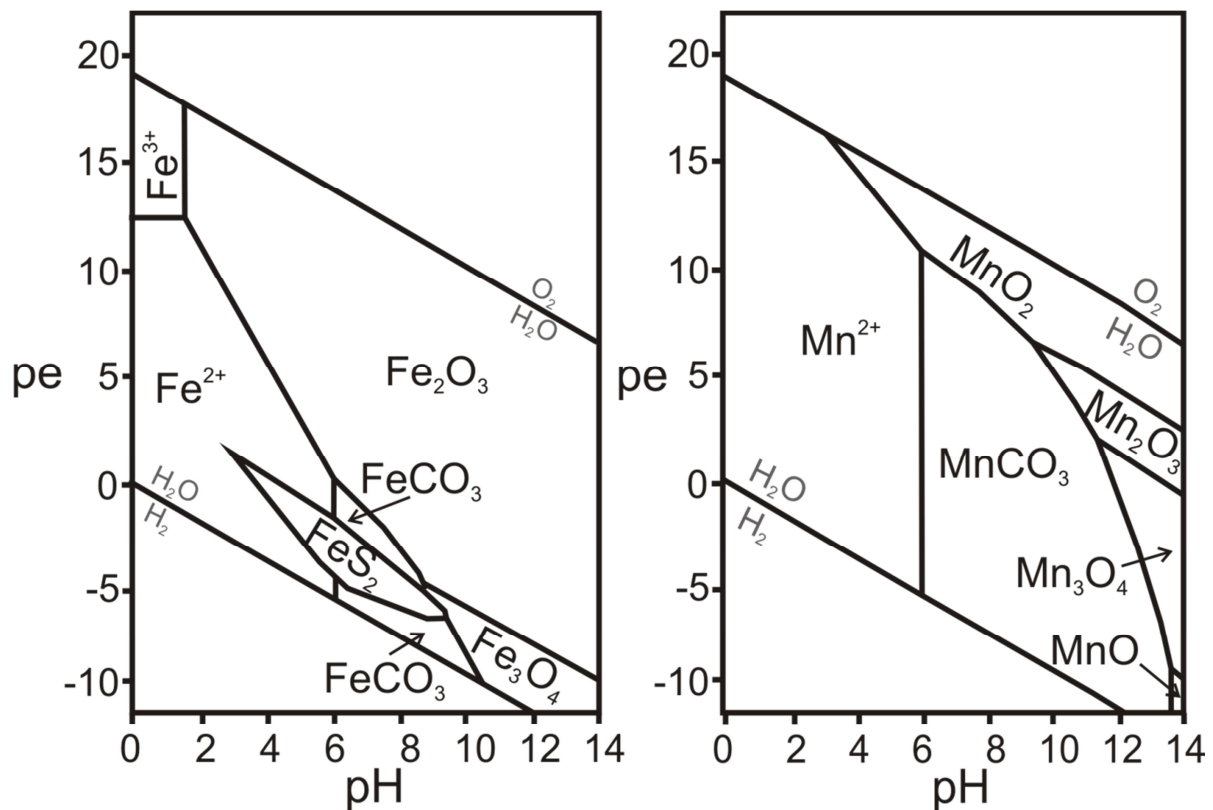
Figure 5: The pe-pH stability diagrams of iron (left) and manganese (right) in natural water (modified from Appelo and Postma, 2005)

Favourable conditions for mobilisation of iron and manganese ions into groundwater occur under reducing and low pH conditions, in the absence of sulphide or carbonate ions (Smith, 2006). In most natural groundwater (i.e. pH range of 5.0 to 8.5 and pe values from -7 to +12) the dissolved iron and manganese ions are in the bivalent form, i.e. Fe^{2+} and Mn^{2+} (Figure 5; Sharma, 2001). In the presence of oxygen, the mobilised bivalent ions are oxidised into insoluble ions (i.e. Fe^{3+} and Mn^{4+}) and precipitate out of solution. Hence, the bivalent ions are only present as trace concentrations in surface water but commonly occur at elevated concentrations in anoxic groundwater (Appelo and Postma, 2005).

From the pe-pH diagrams it is suggested that the Fe(III)-oxides predominate in natural oxic waters at near-neutral pH (Figure 5; Appelo and Postma, 2005). However, in natural systems the precipitation of Fe(III)-oxyhydroxide is favoured, either as ferrihydrite in the presence of silica (SiO_2), phosphate (PO_4^{3-}) or dissolved organic carbon (DOC) or as lepidocrocite in aluminium-free waters with high Fe^{2+} (at least 10 mg/ℓ) and carbon dioxide (Sharma, 2001; Smith, 2006). The formation of goethite is favoured in the presence of aluminium and Fe^{3+} (Sharma, 2001; Smith, 2006). However, the oxidation of Fe^{2+} by oxygen also decreases when it occurs as complexes, formed with organic and inorganic ions such as DOC, SiO_2 or PO_4^{3-} (Sharma, 2001; Munter *et al.,* 2005).

In groundwater with pH below 8.5 abiotic oxidation of Mn^{2+} is much slower than that of iron (Howe *et al.*, 2004). The oxidation rates increase with higher pH or microbial activity (i.e. up to five orders greater than abiotic oxidation) or the presence of catalytic surfaces such as Mn(IV)-oxide (Rott and Meyerhoff, 1994; Howe *et al.*, 2004). The sequence of reactions involving the oxidation of Mn^{2+} and precipitation as Mn(IV)-oxide compounds involve its co-existence with other manganese forms, i.e. Mn(III)-hydroxide, Mn^{2+} adsorbed to particulates and Mn(II)-ligand complexes (Howe *et al.*, 2004). The individual concentrations of these species depend on the pH, temperature, time, sulphate, chloride, nitrate and inorganic or organic carbon content (Howe *et al.,* 2004). However, unlike iron, Mn(II)-organic complexation does not play as a major role in manganese solubility in natural waters, even in the presence of high DOC (Howe *et al.*, 2004).

In reducing conditions, the low solubility of siderite ($FeCO_3$) and pyrite (FeS_2) control mobility Fe^{2+} with siderite only being important when sulphate concentrations are low. For the Mn(IV)-oxide, rhodochrosite ($MnCO_3$) controls manganese solubility over a wider pe and pH range and more efficiently in waters of high alkalinity (Figure 5; Sharma, 2001; Howe *et al.*, 2004; Smith, 2006). In addition, Mn(II)-sulphide is not represented on the redox diagram as it is much more soluble than pyrite and therefore is extremely rare (Appelo and Postma, 2005).

The source mineral for Fe^{2+} and Mn^{2+} ions in groundwater of fractured aquifers depends on the various rock-forming minerals, whereas in primary, sedimentary aquifers the iron is most commonly found in the form of its oxides and hydroxides (Table 1; Smith, 2006). Other important Fe(II)-bearing minerals include pyrite, siderite and the rock-forming silicates (e.g. biotite, amphiboles, smectites, illite and pyroxenes). Major manganese deposits are of sedimentary origin and the most commonly occurring manganese-bearing minerals include pyrolusite (MnO_2), rhodochrosite ($MnCO_3$), rhodonite ($MnSiO_3$) and hausmannite (Mn_3O_4) (Howe *et al.*, 2004; Buamah, 2009). Other sources include Mn(II)-bearing minerals like alabandite (MnS), manganese phosphate (Mn_3PO_4), Mn(III)-oxyhydroxide (γ-MnOOH) or ferromanganese minerals such as micas and amphiboles (Howe *et al.*, 2004).

Table 1: Common iron oxides in sediments (Appelo and Postma, 2005; Smith, 2006)

	Mineral	**Formula**	**Surface area (m^2/g)**
Fe(III)-oxides	Hematite	α-Fe_2O_3	50-120
Fe(II)-oxides	Ilmenite	$FeTiO_3$	-
Fe(II,III)-oxides	Magnetite	Fe_3O_4	-
Fe(III)-oxyhydroxides	Goethite	α-FeOOH	60-200
	Lepidocrocite	γ-FeOOH	-
	Limonite	FeO(OH).$n$$H_2O$	-
	Ferrihydrite	$5Fe_2O_3.9H_2O$ or as $Fe(OH)_3$	200-500

Since the biogeochemical properties of iron and manganese are similar, the occurrence of these two elements is a regular feature in groundwater of sedimentary aquifers. The concentration of these ions (i.e. Fe^{2+} and Mn^{2+}) in natural groundwater depends on their availability in the soils or rocks, the solubility of the hosting minerals and/or the bacterial activity where dissolution occurs (Appelo and Postma, 2005). However, manganese oxides are reduced at higher pe than iron oxides (Figure 5) and manganese often occurs at concentration an order of magnitude less than iron in sedimentary aquifers (Appelo and Postma, 2005). In some cases, however, the manganese concentrations are much higher than iron, for example in the clay-rich aquifers of deltaic areas such as the Nile Delta Aquifer in Egypt where manganese concentrations are almost double that of iron (Olsthoorn, 2000).

Although, Fe^{2+} and Mn^{2+} ions result from the dissolution of Fe(II)- and Mn(II)-bearing minerals under anoxic conditions, the slow dissolution rates of most minerals at near-neutral pH result in the Fe^{2+} and Mn^{2+} concentrations being generally low (Appelo and Postma, 2005). The main source of Fe^{2+} and Mn^{2+} is generally from reductive dissolution of their Fe(III)-oxyhydroxide and Mn(IV)-oxide within the aquifer under anoxic conditions and in the presence of reducing agents such as DOC, methane and hydrogen sulphide ion (HS^-) (Equation 1; Sharma, 2001; Howe *et al.*, 2004). These reactions may be abiotic (i.e. organic)

or microbial-mediated (Cavé *et al.*, 2004; Munter *et al.*, 2005). In microbial catalysis, the iron- and manganese-reducing microbes initiating this reaction must be in direct contact with the oxide surface, or excrete complex formers and reductants that enhance dissolution (Appelo and Postma, 2005).

Equation 1: $4FeO(OH) + CH_2O + 7H^+ \rightarrow 4Fe^{2+} + HCO_3^- + 6H_2O$
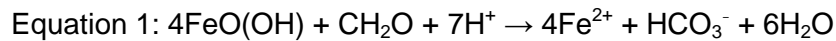
Anthropogenic activities also introduce conditions that favour the mobilisation of Fe^{2+} and Mn^{2+} in groundwater. These include the introduction of reducing substrates during *in-situ* nitrate removal or hydrocarbon pollution (Radčenko and Hauskrecht, 1982; Braester and Martinell, 1988; Tredoux *et al.*, 2004). In the case of hydrocarbon pollution plumes, the reduction of manganese- and iron-oxides in the aquifer is enhanced by the degradation of organic pollutants such as benzene, toluene, ethylbenzene and xylene (Christensen *et al.,* 2000). However, these redox reactions cause a buffer that may limit the spreading of the organic pollutants (Appelo and Postma, 2005). Another important source of Fe^{2+} is through the partial oxidation of pyrite, which is present in organic matter deposits such as peat (Equation 2), which could occur as a result of lowering the water table by pumping or through mining activities (Appelo and Postma, 2005).

Equation 2: $2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$
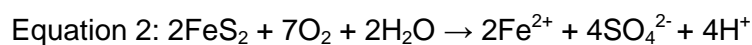
Municipal wastewater discharges, sewage sludge, or emissions from alloy and iron production are the most important anthropogenic sources of manganese and iron (Howe *et al.,* 2004; Karakish, 2005). In some cases, elevated Fe^{2+} concentrations in the groundwater in the borehole are not derived directly from the aquifer but through the disintegration of steel casings, pumps and piping from corrosive groundwater conditions or idle groundwater (Driscoll, 1986).

2.2   Iron and Manganese Treatments

Groundwater is an important source of water, especially for cities and rural areas in semi-arid areas with no proximal surface water resources (More Water cc., 2002). The presence of elevated concentrations of Fe^{2+} and Mn^{2+} in anoxic groundwater has several negative effects associated with its abstraction and subsequent use, which often requires treatment before distribution to the consumer and periodic production borehole maintenance. As a result of this, the treatment of groundwater and maintenance of production boreholes in municipal, agricultural, mining and domestic boreholes with elevated iron and manganese is a multi-million dollar industry worldwide (Sharma, 2001; Deed and Preene, 2013).

2.2.1 Above-ground removal treatments

Traditionally, the removal of iron and manganese from groundwater after abstraction is achieved by a treatment process train of oxidation, coagulation/flocculation and sedimentation in a settling tank and then filtration (Mackintosh and de Villiers, 2002). Atmospheric oxygen can be effective in the oxidation of Fe^{2+} and Mn^{2+} and precipitation of their oxides, but if the ions are complexed (e.g. DOC, SiO_2 or PO_4^{3-}) or the pH is low (Figure 6), aeration may not be satisfactory for their removal and chemical dosing may be used, with or without pre-aeration (Sharma, 2001). The alternative stronger chemical oxidants available include: chlorine gas (Cl_2) often as hypochlorous acid (HOCl), chlorine dioxide (ClO_2), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2) or ozone gas (O_3) (Table 2).

An increase in oxidant often resolves the reaction time if organics are present and should also be taken into account if oxygen-demanding ions such as ammonium (NH_4^+), HS^- and methane are present in the groundwater (Sommerfeld, 1999). In addition to the strength of the oxidant influencing the efficiency of iron and manganese removal, the pH is an important control and depending on the oxidant used, the pH must be adjusted such that removal is feasible (DWAF, 1996).
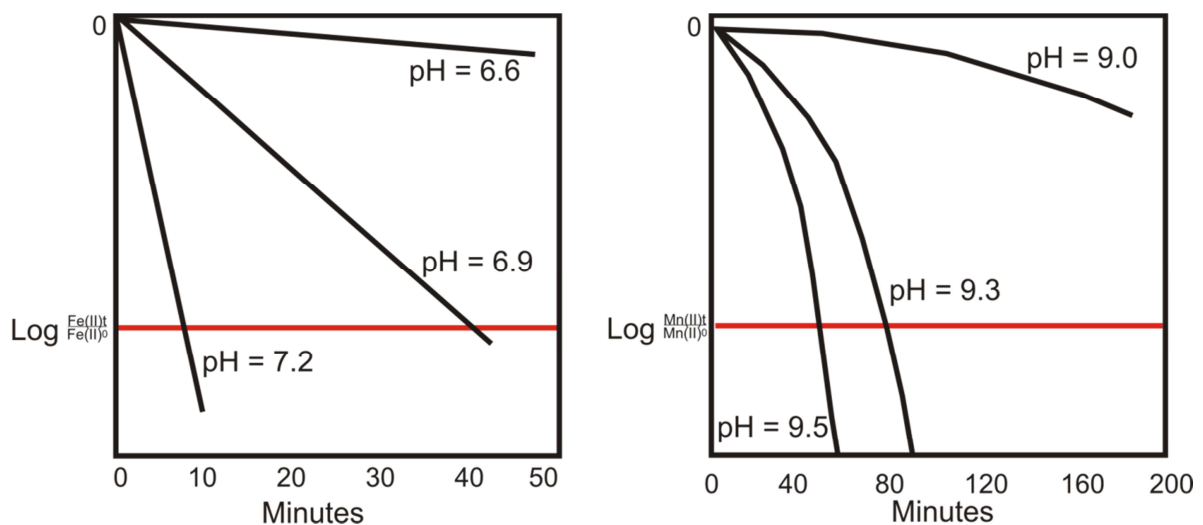
Figure 6: Oxidation rates of Fe^{2+} (left) and Mn^{2+} (right) by oxygen at different pH (modified from Mackintosh and de Villiers, 2002)

Table 2: Oxidant amount required to remove 1 mg of Fe^{2+} or Mn^{2+} (Sommerfeld, 1999; Sharma, 2001; Kgwaila *et al*., 2011)

	Stoichiometric Reaction	Amount	Oxidation time	pH	Other information
O_2	$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+$	0.14 mg	10 minutes	≥ 7.2	Application successful at lower concentrations but pH > 8.5 is necessary for dual oxidation of iron and manganese. If > 5mg/ℓ or complexed, oxygen should be used as a pre-oxidant step to reduce chemical costs.
	$2Mn^{2+} + O_2 + 2H_2O \rightarrow 2MnO_2 + 4H^+$	0.29 mg	1 hour	≥ 9.5	
O_3	$2Fe^{2+} + O_3 + 5H_2O \rightarrow 2Fe(OH)_3 + O_2 + 4H^+$	0.43 mg	< 1 minute	≥ 5.5	Instantaneous oxidation of uncomplexed ions and can oxidise complexes, however higher doses of ozone are required.
	$Mn^{2+} + O_3 + H_2O \rightarrow MnO_2 + O_2 + 2H^+$	0.87 mg		≥ 8	
$KMnO_4$	$3Fe^{2+} + MnO_4^- + 7H_2O \rightarrow 3Fe(OH)_3 + MnO_2 + 5H^+$	0.94 mg	< 5 minutes	≥ 7.5	Efficient for uncomplexed ions at low concentrations but is ineffective when ions are complexed.
	$3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2 + 4H^+$	1.92 mg		5.5-9.0	
ClO_2	$5Fe^{2+} + ClO_2 + 13H_2O \rightarrow 5Fe(OH)_3 + Cl^- + 11H^+$	0.24 mg	< 1 minute	6.8-8.4	Rapid oxidation of uncomplexed ions and effective to some extent with complexed iron or high NH_4^+ concentrations. Reacts faster with uncomplexed manganese than Cl_2 but is more expensive.
	$Mn^{2+} + 2ClO_2 + 2H_2O \rightarrow MnO_2 + 2ClO_2^- + 4H^+$	2.45 mg		5.5-9.0	
HOCl	$2Fe^{2+} + OCl^- + 5H_2O \rightarrow 2Fe(OH)_3 + Cl^- + 4H^+$	0.47 mg	< 1 minute	≥ 8.0	Rapid oxidation of uncomplexed iron but less efficient with manganese in near-neutral conditions and cannot be used for organic-rich water.
	$Mn^{2+} + OCl^- + H_2O \rightarrow MnO_2 + Cl^- + 2H^+$	0.96 mg	2 to 3 hours	≥ 8.5	
H_2O_2	$2Fe^{2+} + H_2O_2 + 4H_2O \rightarrow 2Fe(OH)_3 + 4H^+$	0.30 mg	< 1 minute	5.5-9.0	Rapid oxidation of iron but inefficient for removal of complexed iron and uncomplexed manganese.
	$Mn^{2+} + H_2O_2 \rightarrow MnO_2 + 2H^+$	0.62 mg	> 5 hours	≥ 8.5	

Chlorine gas and $KMnO_4$ are often recommended for small groundwater supply schemes where aeration is not a feasible option because the dosing is easy (requiring simple equipment), which makes it fairly inexpensive to operate (Ahmad, 2012). However, Cl_2 has a poor reaction time with Mn^{2+} and if there is DOC present it may react to form carcinogenic trihalomethanes (THMs) and haloacetic acids (HAAs) (Sharma, 2001; Rajagopaul *et al.*, 2008). Potassium permanganate requires less equipment and capital investment in comparison to Cl_2 but the disadvantages include that the salts are expensive and requires onsite make-up of a noxious solution (Sharma, 2001; Kgwaila *et al.*, 2011). Also dosing is very critical with $KMnO_4$ and over-dosing can result in soluble permanganate ions (MnO_4^-), which turn the water a bright pink or can form mud balls on the sand filters, which is problematic and expensive to resolve (Sharma, 2001; Ahmad, 2012). In comparison to Cl_2, ClO_2 is a stronger oxidant (Table 3) and does not form THMs or HAAs but is more expensive and has potential hazardous chlorite and chlorate by-products (Sharma, 2001; Rajagopaul *et al.*, 2008; Kgwaila *et al.*, 2011).

Hydrogen peroxide is a more powerful oxidant compared to previously discussed options and is cheaper than O_3, as well as can also be used as a bactericide due to the highly oxidising environment created by its by-products, i.e. dissolved oxygen (DO) and the hydroxyl free radical (OH^-) (Sharma, 2001; Cullimore, 2008). However, H_2O_2 is only used as a pre-treatment because it is very slow to react in water and is not a practical oxidant for the removal of Mn^{2+} (Sommerfeld, 1999; Munter *et al.*, 2008). There are also safety concerns when working with H_2O_2, which include protective clothes due to potential chemical burns at high concentrations and the significant temperature increase due to the exothermic reaction and release of carbon dioxide, which requires adequate ventilation (Masten, 2004).

Table 3: Relative oxidation potential of oxides (Vance, 2002; Munter *et al.*, 2008)

	Oxidation power (V)	Relative oxidation potential compared to Cl_2 = 1.0
Fluorine	3.1	2.3
OH^-	2.8	2.1
O_3	2.1	1.5
H_2O_2	1.8	1.3
$KMnO_4$	1.7	1.2
ClO_2	1.5	1.2
Cl_2	1.4	1.0
O_2	1.2	0.9

Ozone was first used in 1893 for drinking water purification treatment in the Netherlands and is the third most powerful oxidant agent (Table 3; EPA, 1999). It is able to oxidise Fe^{2+} and Mn^{2+} in organic-rich groundwater (Cromley and O'Conner, 1976) and has more disinfecting

power than Cl_2 (Driscoll, 1986; Sharma, 2001). Ozone is widely applied for oxidation (e.g. taste, colour and odour control) and disinfection purposes in drinking water and wastewater treatment and over the last two decades, it is increasingly promoted as a replacement for Cl_2 due to its innocuous by-products (e.g. von Gunten, 2003; Plummer *et al.*, 2005; Cullimore, 2008; Rajagopaul *et al.*, 2008). It is also used in a variety of industrial applications from bleaching of paper pulp and textiles, disinfection of pools, air purification and the sterilisation of medical equipment (Rice, 2002). Other advantages of O_3 include simple dosing control, no need for storage of chemicals and fewer safety regulations (Sharma, 2001; Rajagopaul *et al.,* 2008; Kgwaila *et al.,* 2011). Similarly to H_2O_2, O_3 decays to form OH^- and DO, which enhances oxidation reactions. Its disadvantages include the fact that its generation requires electrical power and relatively high initial capital costs of equipment (EPA, 1999). In addition, the chief risk with working with O_3 is the potential inhalation of the toxic gas at high concentrations (Vance, 2002).

Following the oxidation stage, the formed insoluble Fe(III)- and Mn(IV)-oxides need to be removed before distribution either by sedimentation and/or rapid sand filtration (Sharma, 2001; Buamah, 2009). However, in the presence of significant DOC, an aluminium sulphate coagulation agent is added to remove any complexed Fe^{2+} not oxidised (ICRC, 1993). In cases of high iron and manganese concentrations (i.e. > 5 mg/ℓ), sedimentation step or low sand filtration rates (i.e. 0.1-0.3 m/h) prior to rapid sand filtration (i.e. 5-15 m/h) is required due to the formation of floc, which would clog up the filter (Andersson and Johansson, 2002; Buamah, 2009). A disadvantage of the sand filters and sedimentation beds is that they require frequent cleaning, placing a high water and electricity demand on the process and requires disposal of the generated sludge (Andersson and Johansson, 2002).

Sequestration is an alternative treatment of iron and manganese removal, however, it does not remove the ions but rather involves the complexation of the ions such that they remain in solution to resolve aesthetic problems (i.e. colour and turbidity) (ICRC, 1993). This is achieved by adding sodium silicate and Cl_2 or polyphosphate to the water (Sharma, 2001). This treatment is often used in small WTPs with iron and manganese concentrations less than 1 mg/ℓ (ICRC, 1993; Sharma, 2001). However, even though there is no sludge generation, it is more expensive than the use of Cl_2 and $KMnO_4$ and requires skilled operation (Sharma, 2001).

Special water filters using zeolites can also be used as they are an effective removal method at near-neutral pH, where ion exchange reactions takes place with magnesium and calcium cations to remove Fe^{2+} and Mn^{2+} but is only suitable for WTPs where Fe < 5 mg/ℓ and is inefficient in the removal of complexed iron (Sharma, 2001; Buamah, 2009). In addition, this

approach also requires high capital cost, backwashing to maintain effectiveness and skilled personnel to monitor and regenerate (Buamah, 2009). Other commercial filter treatments include special sorption media (e.g. manganese greensand), which are often used in combination with the sand filtration (DWAF, 1996). The manganese greensand process assist in adsorbing any Fe^{2+} and Mn^{2+} (< 10 mg/ℓ) that has not been oxidised in the pre-oxidant step and is oxidised by aeration or a strong oxidant applied intermittently or continuously (Sharma, 2001; Buamah, 2009). The oxidised Fe^{2+} and Mn^{2+} forms coatings on the sand grains (with high adsorption capacity due to surface area and forms new adsorption sites) that grows during prolonged operation (Buamah, 2009). However, the sorption sites become occupied and require regeneration by adequate dosing of $KMnO_4$ (Sharma, 2001). Also adsorption capacity and oxidation of Fe^{2+} and Mn^{2+} is dependent on the pH and require pH > 7 (Buamah, 2009). Iron and manganese can also be removed through the employment of iron-oxidising bacteria through bio-filters (Mettler *et al.*, 2001). However, the bio-filters require specific raw water qualities and it is only economical for groundwater with low or neutral pH (Sharma, 2001; Munter *et al.*, 2008).

The abovementioned methods have a number of requirements for their success and long-term sustainability in providing safe, potable water to the communities, which is often not easily available or economical in small towns or rural areas in developing countries such as South Africa (Sharma, 2001; Andersson and Johansson, 2002; Mackintosh and de Villiers, 2002; Sen Gupta *et al.*, 2009; van Halem *et al.*, 2010). Global and local applications of these *ex-situ* treatments highlighted the following issues (DWAF, 1996; ICRC, 1993; Mettler *et al.*, 2001; Sharma, 2001; Mackintosh and de Villiers, 2002):

- Expert input required for plant development and skilled operation and management;

- High investment costs and space required for equipment such as sedimentation and filter tanks, chemical storage;

- Working and storage of chemicals in cases where these are required for filtration regeneration (typically where groundwater pH is low). Chemicals (e.g. lime or sodium hydroxide) are then required to raise the pH to enhance oxidation, which resulted in increased operation and maintenance costs. In addition, all the oxidation reactions given in Table 2 release hydrogen ions (H^+), which may decrease the pH if there is no carbonate buffer in the groundwater and additional monitoring and base dosing is required to maintain water quality and treatment, thus increasing costs;

- The chemicals used may also need sufficient detention time for the oxidation and precipitation reactions to run to completion, which increases the plant infrastructure costs;

- Potential health risks associated with overdosing or under-dosing;

- Large operational and maintenance costs for running such a plant;

- Water costs involved due to high water demand required for backwashing the filters;

- Proper disposal of large volumes of generated sludge, especially when the sludge may contain toxic elements such as arsenic, which are adsorbed onto the Fe(III)- and Mn(IV)-oxides during filtration.

2.2.2   Treatment options for clogged production boreholes

With years of use all production boreholes with elevated iron and manganese in the groundwater will require periodic maintenance due untenable declines in their yields (Flower and Bishop, 2003; Deed and Preene, 2013). The lowered yield is often the result of clogging of the borehole screen and immediate aquifer, as a result of the abiotic- and biotic-mediated oxidation involving Fe^{2+} and Mn^{2+} in anoxic groundwater (Driscoll, 1986).

The abiotic-mediated oxidation processes (i.e. chemical and physical) are generally initiated by pumping, which shifts the redox environment around the borehole and triggers the immediate precipitation of Fe(III)-oxyhydroxide in near-neural pH conditions (Tredoux *et al.*, 2004). Clogging material is not limited to Fe(III)-oxyhydroxides and can include manganese oxides, Fe(II)-sulphides and Fe(II)-carbonates, depending on the groundwater composition (Walter, 1997). However, Fe(III)-oxyhydroxides are by far the most common clogging material, predominantly as ferrihydrite and goethite, whereas manganese is often found as an accumulate with the Fe(III)-oxide due to its lower abiotic oxidation rate (Walter, 1997; Smith, 2006).

Microbes also exploit the oxidation of Fe^{2+} and Mn^{2+} in their metabolic processes, resulting in the development of a biological residue known as a biofilm (Hallberg and Martinell, 1976; Tredoux *et al.*, 2004). The biofilm is a protective slime residue, which contains the bacteria and grows over time (More Water cc., 2002).

The sources of bacteria include (Deed and Preene, 2013):

- Ubiquitous bacteria that occurred in the soil even before the borehole was drilled;

- Introduced bacteria via contaminated water used during the drilling process;

- Changes in the groundwater chemistry, which provides conditions for the bacteria to flourish.

To minimise the risk of introducing bacteria into the aquifer system, it is recommended that all equipment prior to use is sterilised (Driscoll, 1986).

The lifecycle of a biofilm develops in distinct stages over time, which hampers flow to the borehole and water quality (Cullimore, 2008). In the case of a primary gravel-sand aquifer, the initial phase of growth involves the colonisation of a surface, such as the borehole screen and rapid growth and expansion in the immediate aquifer media by the competitive growth of the bacteria colonies (Cullimore, 2008). This adversely reduces the aquifer transmissivity and borehole yield as well as increases the microbial load in the abstracted water (Cullimore, 2008). This is followed by a stage of stabilisation of the transmissivity and borehole yield, when the bacteria colonies find their eco-niche and reduce in size (Cullimore, 2008). However, another stage of transmissivity and borehole yield fluctuation often follows due to the periodic growth of the bacteria colonies, sloughing off excess biomass and re-stabilisation (Cullimore, 2008). Water quality issues such as increased turbidity, reddish discolouration, presence of slimy biomass and "rotten egg" hydrogen sulphide (H_2S) odour in the abstracted water can also occur during this stage (Cullimore, 2008).

Favourable conditions for iron-oxidising bacterial (e.g. *Gallionella* and *Leptothrix*) growth include (Sharma, 2001; Flower and Bishop, 2003; Smith, 2006; Cullimore, 2008):

- Concentrations of Fe^{2+} (i.e. 0.05-1.50 mg/ℓ) and Mn^{2+} (i.e. 0.05-0.20 mg/ℓ) and availability of nutrients (e.g. DOC and PO_4^{3-});

- Near-neutral pH of 5.5-7.5;

- Temperatures of 10-25°C;

- Low DO conditions;

- High turbidity flow conditions, which enhances nucleation and nutrient uptake;

- A steep redox boundary between aerobic and anaerobic groundwater.

In addition, a mature biofilm hosts a consortium of bacteria species and micro-environments develop within the biofilm with which sulphate-reducing bacteria can also cause clogging by precipitation of Fe(II)-sulphides or MIC of stainless steel borehole equipment (Timmer *et al.*, 2003; Cullimore, 2008). Corrosion could also be initiated by presence of HS^- and sulphide-oxidising bacteria or higher velocities of flow through the non-clogged sections of a borehole screen could cause sand grains to erode and enlarge the screen openings, leading to sand ingress and possible collapse of the borehole (Driscoll, 1986; Engelbrecht, 1998; More Water cc., 2002).

If left unattended, the mature biofilm and precipitated oxides harden, solidifying the aquifer void spaces or borehole screen, which causes the production borehole to effectively "dry up" or the pump to burn out (Flower and Bishop, 2003; Deed and Preene, 2013). In most cases, the clogging problem is identified only once failure occurs (Figure 7; Flower and Bishop, 2003; Deed and Preene, 2013). By that time, the hard deposits are often too difficult to remove by chemical treatments and re-drilling or reconstruction of the borehole or installation of new equipment is the only solution (Engelbrecht, 1998; Riekel and Hinze, 2002; Flower and Bishop, 2003; Deed and Preene, 2013). This is a costly problem, which could also disrupt the WTP capacity at a critical time, with no forewarning if monitoring was not implemented (Flower and Bishop, 2003). Indirect consequences of a lack of maintenance planning and consequential regular equipment failure could result in underlying contamination problems being missed, especially when there is no continual monitoring of the water quality (Deed and Preene, 2013).

Figure 7: Iron-related clogging of a production borehole (left) and pump (right) in Australia (Deed and Preene, 2013)

Biofouling is often blamed for clogging problems but the link between cause and effect has to be carefully researched (Smith, 2006). The rapid oxidation of Fe^{2+} often makes it impossible to distinguish between biotic and abiotic fouling at pH above 7.5 (Figure 8; Sharma, 2001). In general, it can be established that it is biotic-mediated when the bacterial activity becomes significant before there are losses in the production borehole because of the competing bacterial consortia during colonisation, while when abiotic-clogging dominate, bacterial activity does not precede declines in borehole yields (Cullimore, 2008).
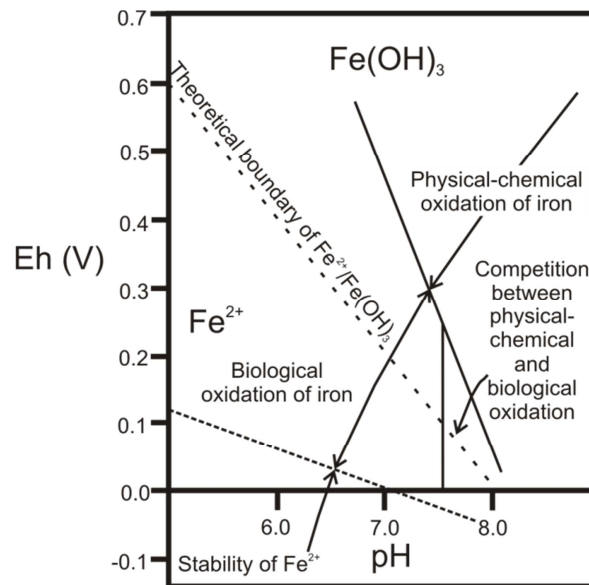
Figure 8: Theoretical boundary conditions between the stability fields of Fe^{2+} and Fe(III)-oxide according to biotic and abiotic oxidation (modified from Sharma, 2001)

Iron-related production borehole clogging is a worldwide, complex water-use problem (e.g. Walter, 1997; Engelbrecht, 1998; More Water cc., 2002; Flower and Bishop, 2003; Timmer *et al.*, 2003; Cullimore, 2008; Anderson *et al.*, 2010; Deed and Preene, 2013). Intermittent, high-rate pumping operations and over-abstraction of a production borehole are the root causes in increasing DO close to the screen or dewatering a fracture, which results in aerated water cascading down within the borehole (Cavé *et al.*, 2004; Flower and Bishop, 2003). The main culprits for the over-use of the water resources are normally increased water demand or incorrectly assigned sustainable yields (Flower and Bishop, 2003).

2.2.2.1   Rehabilitation treatments

According to Driscoll (1986) the rehabilitation treatment aims to restore the production borehole to its most efficient condition, i.e. to restore the yield to its original state and water quality within acceptable limits. However, rehabilitation can only be implemented successfully if there are effective monitoring and maintenance programmes in place (Driscoll, 1986). It is

recommended that in order to limit further increases in maintenance costs, a clogged borehole should be rehabilitated if a 25% decline in specific capacity is observed (Driscoll, 1986). This is because once a borehole has lost greater than 40% of its original specific capacity, it will be difficult to restore to its original performance (Anderson *et al.*, 2010). In reality, clogging is usually identified too late and large-scale costly rehabilitation treatment then have to be implemented to resolve the immediate clogging problems, followed by an on-going monitoring and maintenance programmes (Smith, 2006; Anderson *et al.*, 2010; Deed and Preene, 2013).

There is a wide range of physical and chemical rehabilitation methods currently available to treat clogged production boreholes and reduce the bacterial activity (Flower and Bishop, 2003; Smith, 2006; Anderson *et al.*, 2010; Deed and Preene, 2013):

- Physical methods involve mechanical cleaning and breaking down the precipitates and biofilms by wire brushing and scraping or through hydro-mechanical cleaning by water jetting. There are also surging and purging processes, which use gases such as carbon dioxide. Steam cleaning can also be used by increasing the boreholes water temperatures to 60-70°C but should not be applied in polyvinyl chloride (PVC) constructed boreholes due to potential deformation;

- Chemical rehabilitation methods utilise a combination of chemicals to dissolve the deposits and disinfect the borehole. The chemicals used in dissolving the iron and manganese oxides include sulphamic acid, acetic acid, citric acid and hydrochloric or sulphuric acid. However, acid dissolution requires $pH < 2$, which then requires neutralisation afterwards to prevent corrosion of the borehole. Other chemicals can also be used to oxidise the mineralised organic matter and act as biocides (e.g. H_2O_2, Cl_2, $KMnO_4$ and ClO_2). However, these chemicals also oxidise Fe^{2+} and Mn^{2+} and chlorine-based oxidants could form carcinogenic chlorinated hydrocarbons in the presence of DOC.

There is not a single method that achieves 100% effectiveness in removing the iron-related clogging precipitates and biofilms (Jolly and Engelbrecht, 2002). One extreme example included introducing calcium hydrochloride into a borehole followed by a stick of dynamite (Flower and Bishop, 2003). To date, the most common practise internationally to rehabilitate iron-related clogging is to use a heated chemical treatment in conjunction with physical development (Smith, 2002; Smith, 2006).

The selection and success of any rehabilitation treatment is dependent on the understanding of the clogging problem, i.e. processes involved, production borehole material and construction and the hydrogeology conditions (More Water cc., 2002; Flower and Bishop, 2003; Smith, 2006). Some typical aspects that need to be taken into consideration include:

- The material used and surface characteristics of the casing and screen influences the clogging rate, with uncoated steel readily colonised by bacteria and rougher materials more prone to clogging (Driscoll, 1986; Riekel and Hinze, 2002);

- Borehole construction and materials used also influence the effectiveness of rehabilitation treatment by either limiting the chemical penetration beyond the screen or the materials used preventing it to be treated with chemicals (More Water cc., 2002; Flower and Bishop, 2003);

- The effect of the rehabilitation processes on the water quality, aquifer matrix and its mineralogy must be well understood as to prevent situations where clays or carbonates are dissolved or unacceptable effluents or by-products are formed and/or remain in the aquifer (Flower and Bishop, 2003).

2.2.2.2   Management options

Since iron, manganese and the bacteria are ubiquitous in anoxic groundwater and the ingress of oxygen through pumping cannot be entirely prevented, the long-term success in preventing or limiting rate of clogging will depend upon implementation of an effective monitoring and maintenance programme for each production borehole (More Water cc., 2002; Flower and Bishop, 2003). The protocols applied at the production borehole are site-specific and no "silver bullet" approach can be used (Engelbrecht, 1998), but the common objectives are to keep the costly, full-scale rehabilitation to a minimum, while maintaining the borehole yields, water quality and cost-effective production from the groundwater resource (Flower and Bishop, 2003).

Preventative measures that can be considered for areas prone to iron-related clogging should encompass the following activities (Driscoll, 1986; Jolly and Engelbrecht, 2002; More Water cc., 2002; Flower and Bishop, 2003; Anderson *et al.*, 2010; Deed and Preene, 2013):

- Ensuring the correct physical construction and material of the production borehole, as well as correct placement of the borehole screen to minimising aeration and turbulent flow and to ensure success of rehabilitation work;

- Pumping tests to assign the correct sustainable abstraction rate for the production borehole and to limit the extent of groundwater level drawdown, DO and nutrient supply during production in combination with a continuous, low abstraction rate pumping programme;

- Implement a regular comprehensive monitoring of water quality, bacterial population presence and their activity, as well as groundwater levels in combination with pumping tests to determine the borehole specific capacity and hydraulic parameters of the aquifer. This could potentially identify the onset of clogging and should be performed monthly or at least every six months;

- If iron-clogging is suspected as per the monitoring data, down-hole camera logging is done to get a visual confirmation;

- Once confirmed, physical cleaning of the clogging deposits in the borehole and distribution pipes follows and if necessary chemical treatment to remove the hard biomass and to reduce the bacterial populations.

These preventative measures are known to assist in reducing the frequency and magnitude of production borehole clogging problems, which ensures the sustainability of the groundwater supply scheme by reducing the failures and costly rehabilitation needs (Anderson *et al.*, 2010).

2.2.2.3   Experience in South Africa

In South Africa, such management and rehabilitation recommendations have been adopted and in severe cases the BCHT or EAW method has been applied to recover the losses in borehole yields with some success (More Water cc., 2002; Smith, 2002; Flower and Bishop, 2003; Smith, 2006).

The BCHT method involves three phases, i.e. shock, disrupt and then disperse (Cullimore, 2008). Firstly, the "shock" phase is designed to apply maximum trauma to and within the stratified biofilm, which is achieved through the simultaneous application of a hot alkali (e.g. 8% sodium hydroxide) and surfactant solution with physical brushing and jetting inside the borehole (Smith, 2002; Flower and Bishop, 2003; Smith, 2006). The solution is then left to cool in the borehole for 18 hours (Smith, 2006). The second "disruption" phase involves a pH shift to below 1.5 through the application of another hot strongly chlorinated, sulphamic acid (i.e. 60-95°C, 10% sulphamic acid and calcium hypochlorite) and dispersant solution, also accompanied with high pressure physical cleaning and left to cool for another 18 hours in the

borehole (Smith, 2002; Flower and Bishop, 2003; Smith, 2006). Thirdly, the "dispersal" phase is achieved by surging the chemical blends in the borehole and immediate aquifer and then neutralised the water chemistry (if necessary) before pumping out to waste to remove all loose material and prevent re-colonisation of the bacteria (Smith, 2002). The borehole is pumped to waste until the water quality (i.e. pH and EC) returns to its original levels (Flower and Bishop, 2003; Smith, 2006). In the case study at the KKRWSS production boreholes, this treatment takes approximately three days with approximately 10 m^3 of reagent injected into the boreholes (Smith, 2006).

Before BCHT treatment is initiated down-hole camera logging and a step drawdown pumping test is done to determine the pre-treatment state of the boreholes, which is repeated at the end of the treatment to establish the rehabilitated state of the borehole (More Water cc., 2002). The BCHT has been proven internationally to be a viable rehabilitation option in the treatment of iron-clogging and has been applied in both the AWRMS and KKRWSS wellfields, with good results in returning the borehole yields and removing clogging deposits from the borehole screens obtained at both study sites (Flower and Bishop, 2003; Smith, 2006). However, the following limitations on the success of this treatment have been identified in a South African context:

- Treatment is costly, for example, from February 1999 until May 2002, a total of thirty-seven production boreholes in both AWRMS wellfields were rehabilitated using the BCHT method at a cost of R54 700.00 per borehole (Bishop, *pers. com.* 2010). To date, rehabilitation costs are estimated to be at least R75 000.00 per borehole (Quayle, 2012);

- Due to the BCHT treatment requiring specialised application and equipment by highly skilled operators, as well as the high costs associated, tender regulations are required, which limits the regular and timely application of the treatment and as a result the boreholes are often far too clogged to return to original yields (Flower and Bishop, 2003);

- Some of the chemicals used can be hazardous, which can be problematic to the semi-skilled staff involved at the wellfields as experienced in Botswana and may require regulatory authorisation to proceed, which further delays application (Riekel and Hinze, 2002; Smith, 2006);

- There is the concern of potential contamination of the aquifer due to the long residence time of chemicals (> 36 hours) in the borehole and surrounding aquifer (Smith, 2006).

The lesser known EAW method rehabilitates the clogged production boreholes by introducing a super oxidant solution (Eh = 1 000 mV) known as Anolyte, which acts as a biocide at pH range from 2.0-8.5 (Riekel and Hinze, 2002; Smith, 2006). It is as effective as HOCl but is non-toxic and biodegradable and thus is ideal for use by semi-skilled staff (Riekel and Hinze, 2002). The Anolyte is generated by using water, either from the borehole or drinking water, that is slightly saline (0.2%), which is run through a patented electrolytic cell (Riekel and Hinze, 2002). The water is exposed to a high-density electrical field and produces two streams: the Anolyte and Catholyte solutions (Smith, 2002). The EAW was developed to remove biofilms in distribution pipelines and has been investigated in southern Africa with application in the KKRSWW (Smith, 2002) and throughout Botswana (Riekel and Hinze, 2002). Similarly, to most other borehole rehabilitation treatments, the EAW method involves three phases (Riekel and Hinze, 2002):

- The first phase involves the sterilisation of the biofilm, where large volumes of Anolyte (i.e. 1-2 m^3) are introduced into the borehole, which also softens the clogging particles in the gravel pack and immediate aquifer;

- After approximately an hour, the second phase is initiated with the borehole mechanically bailed using a surge block attached to a cable tool rig, which break ups the biomass. This phase normally takes three to four hours;

- Finally, the third phases involves the removal of biofilm and loosened sediment, which is firstly cleaned out by a mechanical bailer and then the pump is reconnected and water is pumped to waste until clear before the borehole is reconnected to the system.

The EAW method is regarded to have fewer negative consequences compared to the BCHT method, i.e. no handling or storage of toxic chemical or potential aquifer contamination by such chemicals as well as a faster application time but its effectiveness at the KKRWSS is queried by Smith (2006). This is because the iron concentrations in the step drawdown pumping tests after the treatment showed to be hardly above the baseline levels of the clogged borehole (Smith, 2006). In addition, the clogging deposits are known to be predominately Fe(III)-oxides at the study site, which is not soluble at the neutral pH of the Anolyte solution (Smith, 2006). Despite the reservations highlighted by Smith (2006), the borehole yields and visual inspection showed an improvement, leading the author to suggest that the dispersive effect of the reagent along with physical surging is sufficient to dislodge the clogging material. Unfortunately, no further research into the EWA and BCHT has taken place since the mid-2000's.

Other chemical rehabilitation processes also investigated for the AWRMS include the liquid carbon dioxide process and BoreSaver Ultra C (Flower and Bishop, 2003; Bishop, *pers. com.* 2013). The liquid carbon dioxide process entails the injection of carbon dioxide into the borehole under low temperatures and high pressure, which immediately disrupts the biofilm attached to the surface (Cullimore, 2008). The carbon dioxide reacts with the water to form carbonic acid, which reduces bacteria that survived the initial physical and chemical disruption of the biofilm (Cullimore, 2008). The liquid carbon dioxide process was not considered further at the AWRMS because the costs estimated in the early 2000's were double that of the BCHT process and there was concern that the low temperatures could thermally damage the borehole casing (Flower and Bishop, 2003).

The BoreSaver Ultra C treatment involves the introduction of an organic crystalline acid (i.e. oxalic acid) with biocidal copper compounds into the borehole, which dissolves and loosens iron deposits by the mildly acidic conditions (Deed and Preene, 2013). This treatment is favoured due to its biodegradable compounds used and non-toxic by-products (Deed and Preene, 2013). However, oxalic acid should not be applied in calcium-rich waters (i.e. > 125 mg/ℓ) due to the potential clogging (Cullimore, 2008).

Although these treatments are available in South Africa and the BCHT and EWA methods are shown to be successful in returning yields, the long-term success and effectiveness of such management and rehabilitation approaches are limited in South Africa due to the following situations (More Water cc., 2002; Smith; 2002; Flower and Bishop, 2003; Tredoux *et al.*, 2004; Smith and Roychoudhury, 2013):

- Production boreholes were designed and constructed without considering the potential for clogging and/or the need for rehabilitation treatment in mind, so original yields cannot be completely restored;

- Some production boreholes are too severely clogged or damaged by MIC, the pump and/or casing have to be replaced or a new borehole has to be drilled;

- Proposed monitoring and maintenance strategies have not been correctly implemented or followed, e.g. regular over-abstraction occurred when water demands were high, which results in clogging occurring within a short period of time. Presently it is recommended that large-scale rehabilitation treatments should be required every eight months to a year, which is not economically viable for the long-term management of the wellfields;

- Wellfield managers adopt a high rate stop-start abstraction instead of constant lower rate pumping due to the lack of understanding of the system. This type of intermittent production cycle causes large drawdowns and ingress of DO and nutrients during high rate production, followed by non-pumping periods where the bacteria have ample time to settle and anchor on the surfaces of the borehole and aquifer;

- Skilled staff and high costs associated with monitoring equipment and samples collected and subsequently analysed per borehole increases the operation costs of a wellfield with the proposed protocols, which could prevent regular assessment;

- The rehabilitation treatments are costly and can only proceed when funds are available. In addition it requires specialist skills and equipment, which are acquired through time consuming processes like tender applications;

- Regulatory authorisation may be required to proceed with rehabilitation and re-drilling activities, which may lead to potential delays, for example the NWA and the National Environmental Management Act No. 107 of 1998 (NEMA; Republic of South Africa, 1998b).

In addition, further research to complement the monitoring and rehabilitation treatments in South Africa include:

- Laboratory leaching tests to research the source of the iron and mobilisation processes involved in the TMG aquifers of the KKRWSS (i.e. Smith, 2006; Smith and Roychoudhury, 2013);

- *In-situ* iron removal has been proposed and laboratory batch experiments and pilot field trials using nitrate as a nutrient source for the microbial biodegradation of organic matter have shown promise in decreasing DOC concentrations (i.e. Tredoux *et al.*, 2004; Israel *et al.*, 2009).

2.2.3   *In-situ* iron removal

An alternative technique is the *in-situ* treatment of groundwater. The ISIR process involves the oxidation of Fe^{2+} around a production borehole by the periodic injection of a volume of oxygenated water into the anoxic aquifer (Appelo *et al.*, 1999). The precipitated Fe(III)-oxyhydroxides remain in the aquifer and when abstraction is resumed, the pumped groundwater transverses the oxidation zone, which functions as a filter, due to these precipitates being capable of absorbing further Fe^{2+} and other dissolved ions for example Mn^{2+}, arsenic (as As^{3+}), PO_4^{3-} and strontium (Sr) from the groundwater (Mettler, 2002; van

Halem *et al.*, 2010). This delays the movement of Fe^{2+} towards the borehole, which ultimately leads to clogging and water quality problems (Hallberg and Martinell, 1976; Appelo *et al.*, 1999; Mettler *et al.*, 2001; van Halem *et al.*, 2011). This treatment process is also referred to as "source treatment" because it targets the source of the problem rather than comprise rehabilitation treatments, which deals with the problems caused by the presence of Fe^{2+} and Mn^{2+} (ICRC, 1993). With time the filter capacity of the aquifer is exhausted and increasing concentrations of Fe^{2+} and Mn^{2+} are measured in the abstracted water and when the drinking water threshold concentration is reached, a volume of oxygenated water is injected to regenerate the oxidation zone (Mettler, 2002).

The subsurface removal of Fe^{2+} from groundwater for water quality improvement dates back to the early 1900's, where the system consisted of a borehole, which functions alternated between supply and injection borehole (Figure 9; Mettler, 2002; van Halem, 2011). However, little experimental work was done until the 1960's, when the Vyredox design was developed in Finland (Hallberg and Martinell, 1976; Braester and Martinell, 1988). Two decades after the first commercial Vyredox plant was implemented, more than a hundred ISIR plants were built throughout Europe, e.g. Sweden, the Netherlands, Switzerland, Germany, Denmark, Norway and France (Hallberg and Martinell, 1976; Braester and Martinell, 1988; Mettler, 2002; van Halem, 2011). In recent years, it has been applied in rural areas of Egypt for removal of Fe^{2+} and Mn^{2+} (e.g. Olsthoorn, 2000; Karakish, 2005) and in Bangladesh and India for As^{3+} removal (e.g. Sen Gupta *et al.*, 2009; van Halem *et al.*, 2010).
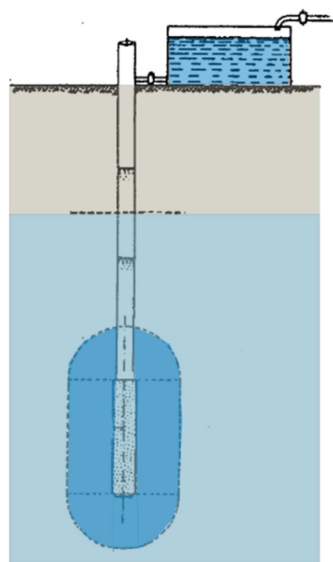
Figure 9: Earliest known ISIR patent applied in Berlin in 1900, where oxygenated water was injection directly into the borehole (modified from van Halem, 2011)

The treatment was developed for semi-consolidated and unconsolidated, gravel-sand aquifers and has been applied successfully in both glacial and alluvial-deposits (e.g. Diliūnas *et al.*, 2006; Mettler *et al.*, 2001) with only one known case study in a fractured aquifer (Maogong, 1988).

There are several different ISIR designs implemented, with the four main approaches being:

- The Vyredox method (Figure 10), which is the most common method applied, consist of multiple injection well-points (e.g. from 3 to 23) surrounding the production borehole in a ring or semi-circle setup to provide an oxidation screen such that iron and manganese-free groundwater is drawn towards the production borehole (Hallberg and Martinell, 1976; Braester and Martinell, 1988);

- The single borehole method, which is typically applied in the Netherlands, where a production borehole is modified to alternately accommodation injection and production (Figure 10; van Halem, 2011);

- The two-production borehole method, involves two modified production boreholes equipped for injection and abstraction, where one produces the recharge water for the one being treated (Sommerfeld, 1999);

- A combination of the Vyredox and the single borehole methods have also been applied (e.g. Maogong, 1988).

Single well for injection-abstraction   Separate wells for injection-abstraction ("Vyredox" method)
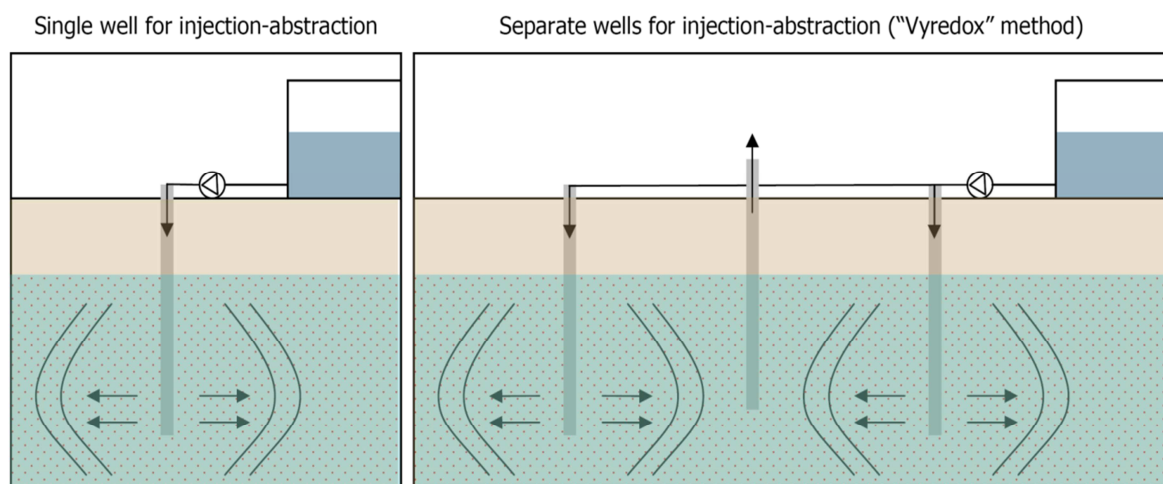
Figure 10: Europe's two most commonly applied ISIR designs (modified from van Halem *et al.,* 2008)

The ISIR design applied (similar to *ex-situ* treatment) is dependent on the raw water quality and hydrogeological conditions of the site, the available financial resources and the philosophy of the water supply company (Sharma, 2001; Ebermann *et al.*, 2013). In some

areas, such as cities, it found that the use of the single borehole approach is not optimal because during the injection phase no groundwater is supplied to the WTP and the oxidation zone is closer to the production borehole (Mettler, 2002). Thus, the Vyredox or two-production borehole system is desirable as the injection take place independently from the production borehole (Braester and Martinell, 1988). In other situations, such as rural areas in Bangladesh and India, it was more economical and easier to apply ISIR by modifying a hand-pump to function as the injection and abstraction well-point (Sen Gupta *et al.*, 2009; van Halem *et al.*, 2010).

2.2.3.1 Operating principles

Treatment is initiated when the monitored concentration of iron and manganese in the production borehole is above the desired threshold. The applied technique includes the following steps:

- The production is stopped in the borehole to be treated and the recharge water source is derived from a nearby production borehole or treated groundwater from a reservoir (Hallberg and Martinell, 1976; Braester and Martinell, 1988; Hinkamp *et al.*, 2004);

- The volume of water to be injected is dependent on the aquifer hydraulic properties and desired treatment zone, which is generally taken as the average amount pumped from the borehole per day (Hallberg and Martinell, 1976) with European case studies ranging between 1 000 m^3 to 3 000 m^3 (Hinkamp *et al.*, 2004; van Essen *et al.*, 2005);

- Before the recharge water is oxygenated, it is degassed by exposure to the atmosphere to remove any undesirable gases (e.g. carbon dioxide, H_2S and methane) and Fe^{2+} and Mn^{2+} ions, which could interfere with DO enrichment (Hallberg and Martinell, 1976);

- The water is oxygenated generally through aeration to achieve DO concentrations of 8-10 mg/ℓ. Aeration is preferable as it reduces ISIR plant costs and is safer to use (Olsthoorn, 2000; Diliūnas *et al.*, 2006). However, aeration can have a limited capacity (especially with organic-rich groundwater) because the saturation levels are difficult to reach and oxidation of iron chelates with organic matter are not generally achievable (Hinkamp *et al.*, 2004). In such cases, oxygen gas is an option as it induces higher DO concentrations of 15-30 mg/ℓ (Hinkamp *et al.*, 2004; Ebermann *et al.*, 2013) or to as much as 60 mg/ℓ (Rott and Meyerhoff, 1994), which increases the removal efficiency by a factor of 2.0-2.5 (Figure 11; van Essen *et al.*, 2005; van Halem, 2011);
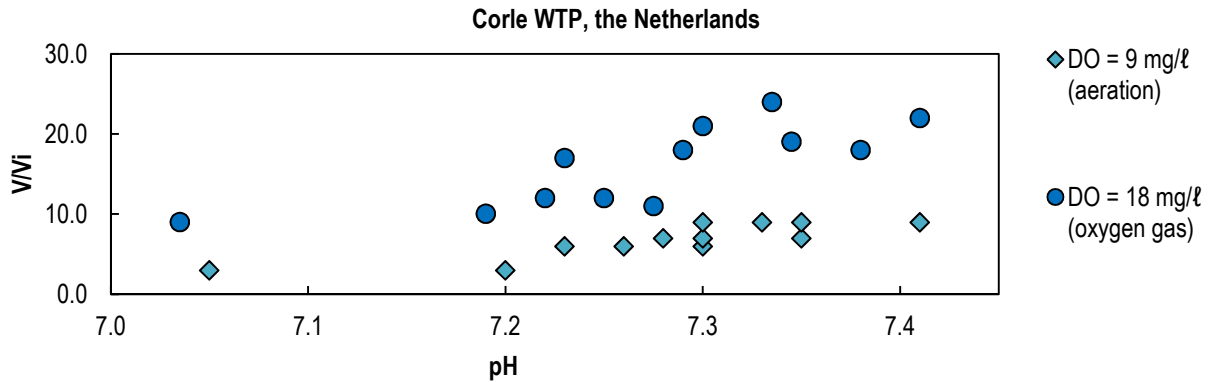
Figure 11: All twelve ISIR boreholes at the Corle WTP, the Netherlands, showed an increase in iron removal efficiency with increased pH and DO conditions (data from van Halem, 2011)

- The oxygenated water is either filtrated or pumped back into the aquifer, which can take 20 to 30 hours to establish an oxidising zone (Hallberg and Martinell, 1976; Braester and Martinell, 1988). Other case studies give longer recharge periods from 51 hours (e.g. Maogong, 1988) up to two weeks (e.g. Hinkamp *et al.*, 2004). The recommended injection rate is between 65% and 100% of the abstraction rate (Maogong, 1988; Hinkamp *et al.*, 2004);

- This oxidation zone depends on the oxidant concentration, injection rate, injection volume and the hydraulic properties of the aquifer and can range between 15-30 m but is often less than 50 m (AWWA, 1984; van Halem *et al.*, 2011). Generally, the size of the oxidation zone is recommended to be designed to be large enough to ensure a lifespan for the treatment plant at least a century (Mettler *et al.*, 2001). This is calculated based on the aquifer porosity, volume injected and density of the expect amount of precipitated Fe(III)- and Mn(IV)-oxides (Hallberg and Martinell, 1976);

- A contact time follows the injection phase for four to ten hours to allow for the suspended Fe(III)-oxyhydroxides and especially Mn(IV)-oxides to settle into the aquifer matrix (Hallberg and Martinell, 1976; Braester and Martinell, 1988).

The borehole can usually be put back into production after a time of one to two weeks or up to a month (depending on study site conditions) after which the concentration of iron and manganese will rise again and once the threshold concentration of either iron or manganese is reached, the treatment is repeated (Hallberg and Martinell, 1976). The duration of each cycle is determined by the volume of water drawn from the production borehole before the threshold concentrations are reached (Sommerfeld, 1999) and those thresholds are dependent on the local water authority standards, which often have to comply with WHO drinking water requirements.

2.2.3.2   Removal efficiency

In-situ removal methodologies have been proven to be an effective technique for the removal of high concentrations of Fe^{2+} and Mn^{2+} accumulating in groundwater even after the complete withdrawal of injected water (Appelo *et al.*, 1999). This is a great advantage over conventional *ex-situ* treatments, with the removal efficiency (V/Vi) of the ISIR process being gauged by the volumetric ratio of the abstracted volume (V) over the injected volume (Vi) (Appelo *et al.*, 1999). The removal efficiency ratios of ISIR plants can vary and ranges from 2 to 50 depending on the given water quality, hydrogeological conditions and set threshold concentrations values (Braester and Martinell, 1988; Maogong, 1988; Rott and Meyerhoff, 1994; Mettler, 2002; Hinkamp *et al.*, 2004; van Halem *et al.*, 2011; Ebermann *et al.*, 2013).

In-situ iron removal plants initially require some time to be established. A number of injection-abstraction cycles are necessary (i.e. often 10) for optimum removal conditions to become established and the removal efficiency to stabilise at a constant value (Braester and Martinell, 1988; Mettler, 2002; Tredoux *et al.*, 2004; van Halem *et al.*, 2011). For example, a Vyredox plant in Sweden had an initial removal efficiency of three after five injection-abstraction cycles but after 15 injection-abstraction cycles, the V/Vi stabilised at nine (Hallberg and Martinell, 1976). During this set-up time, the iron removal efficiency is known to improve with successive injection-abstraction cycles (Hallberg and Martinell, 1976; Appelo *et al.*, 1999). Figure 12 and Figure 13 shows two cases studies in Europe, which both show the delay in arrival of high Fe^{2+} with successive ISIR treatments in the set-up phase and the improved iron removal efficiencies as a result of the better retention of the ion in the aquifer.
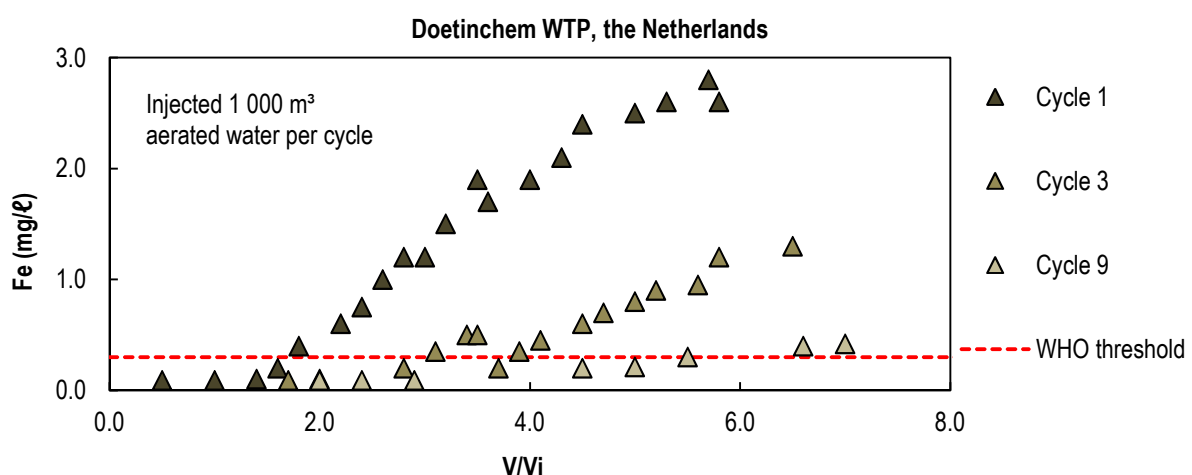
Figure 12: Iron breakthrough curves showing that removal efficiency increases with successive ISIR treatments at the Doetinchem WTP in the Netherlands (data from Appelo *et al*., 1999)
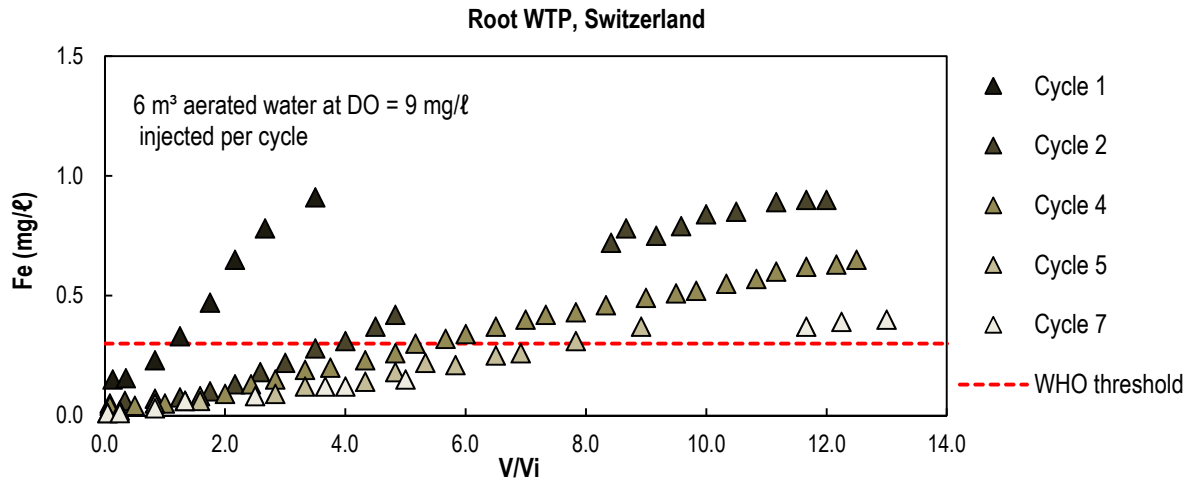
Figure 13: Iron breakthrough curves showing the same behaviour in increasing removal efficiency with successive injections at the Root WTP, Switzerland (data from Mettler, 2002)

Efficiency ratios for manganese are less than that of iron and generally between 3.5 to 12.0 (Figure 14; van Halem, 2011). This is because abiotic oxidation of Mn^{2+} (at pH < 8.5) takes place at appreciably slower rates than that of Fe^{2+} and will start only once Fe^{2+} oxidation is more than less complete (Mettler, 2002). Manganese removal therefore requires a longer start-up phase to become fully efficient (Rott and Meyerhoff, 1994; Olsthoorn, 2000; Mettler, 2002; van Halem, 2011). In addition, the affinity of Mn^{2+} to be adsorbed onto sediments depends mainly on the cation exchange capacity and organic composition of the aquifer (Howe *et al.*, 2004).
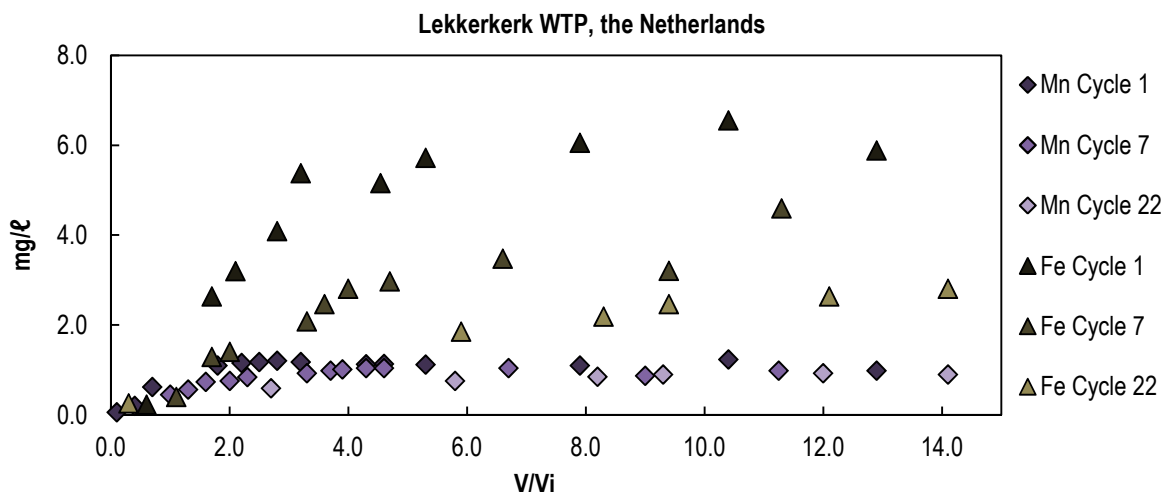
Figure 14: Breakthrough curves of manganese and iron showing that manganese removal efficiency does increase with treatments but to a lesser extent and not as distinctive as for iron at the Lekkerkerk WTP, the Netherlands (data from van Halem, 2011)

2.2.3.3   Mechanism of *in-situ* iron removal

Over the decades of application a number of theories concerning the mechanism of *in-situ* iron and manganese removal have been proposed. The main four theories include:

- *Biotic removal by iron- and manganese-oxidising bacteria* (e.g. Hallberg and Martinell, 1976). This theory suggested that the repeated injection of oxygenated water and withdrawal of reduced groundwater provides the favourable conditions and nutrients for the growth of these bacteria and the increase in efficiency was related to the growth of their colonies with time (Appelo *et al.*, 1999). Studies have found that it takes 50 to 60 days from initiation for biotic oxidation to sufficiently remove iron in sand filters under those optimal conditions (Rott and Meyerhoff, 1994; Sharma, 2001);

- *Mixing at the injection front due to physical dispersion* (e.g. Booch and Barovich, 1981). It has since been excluded as the main mechanism because it could not satisfactorily explain the observed removal efficiencies greater than five without unreasonably large dispersivity and the theory could not explain the efficiency increase with successive cycles (Appelo *et al.*, 1999);

- *Sorption of oxygen on aquifer sediments* (e.g. Rott *et al.*, 1978). During the abstraction phase the oxygen would be released and enable oxidation of Fe^{2+} in the native groundwater; this theory has not been experimentally proven or documented (Appelo *et al.*, 1999);

- *Oxidation-adsorption mechanism* (e.g. Van Beek and Vaessen, 1979), whereby Fe^{2+} is adsorbed on Fe(III)-oxyhydroxides in the aquifer, which are oxidised by the DO in the injected water and the resulting precipitate would coat the existing grain, which would be able to adsorb further Fe^{2+} from the native groundwater when the abstraction phase is initiated, adequately explaining the increase in efficiency (Appelo *et al.*, 1999).

In literature and in this dissertation, the oxidation-adsorption mechanism is considered to be the dominant mechanism controlling ISIR (e.g. Appelo and de Vet, 2003; Tredoux *et al.*, 2004; van der Laan, 2008; van Halem *et al.*, 2010; Ebermann *et al.*, 2013). However, the ISIR treatment initiates a number of different physical, chemical and biological processes in the subsurface, which complement the adsorption-oxidation mechanism (Rott and Meyerhoff, 1994).

In the case of a single borehole approach, a volume of oxygenated water is introduced into an anoxic aquifer, partially displacing the groundwater containing Fe^{2+} some distance from

the injection borehole (Figure 15; Appelo *et al.*, 1999). Both homogeneous and heterogeneous oxidation of Fe^{2+} takes place in the aquifer (van Halem *et al.*, 2011). Homogeneous oxidation of Fe^{2+} takes place in solution, which occurs through physical dispersion at the interface of the two waters (Appelo and de Vet, 2003; van Halem *et al.*, 2011), whereas the heterogeneous oxidation takes place in the oxidation zone created around the injection borehole (Mettler, 2002; van Halem *et al.*, 2011). This is achieved by the oxidation of adsorbed Fe^{2+} directly on the surface of the aquifer grains, predominantly on Fe(III)-oxyhydroxides due to their large surface area or minerals such as magnetite, quartz, calcite or clay (Appelo *et al.*, 1999; Mettler, 2002; van Halem *et al.*, 2011).

In addition to direct oxidation of the adsorbed Fe^{2+}, the oxygenated water promotes exchange of the adsorbed Fe^{2+} on the aquifer grains with other cations, for example calcium and sodium cations in the injected water and subsequent oxidation (Appelo *et al.*, 1999). The Fe(III)-oxyhydroxide forms its own particles or attaches itself to an aquifer grain (van der Laan, 2008). The involvement of cation exchange in ISIR is dependent on (Appelo and de Vet, 2003; van Halem *et al.*, 2011):

- The raw groundwater and injected water quality, for example it increases with higher sodium ions in the injected water but decreases in the presence of other cations in the groundwater;

- The exchangeable Fe^{2+} on the aquifer grains, which depends on sorption capacity of the aquifer, which is in turn dependent on the presence of clay, organic matter and oxides.

Through these processes, the DO front lags behind the injected water (Figure 16; Appelo and de Vet, 2003). The newly-formed precipitate forms a film on the aquifer grains, which increases the ability of the oxidation zone to adsorb more Fe^{2+} (as well as Mn^{2+}, As^{3+}, PO_4^{3-}, SiO_2 and DOC) due to increased surface area and strengthened adsorption capacity (Appelo and Postma, 2005; van Halem *et al.*, 2010). In the case of Fe(II)-silicates and magnetite grains, the coating of the mineral surface by an outer layer of Fe(III)-oxyhydroxide (known as armouring) inhibits any further iron dissolution processes by diffusion control (Appelo and Postma, 2005).
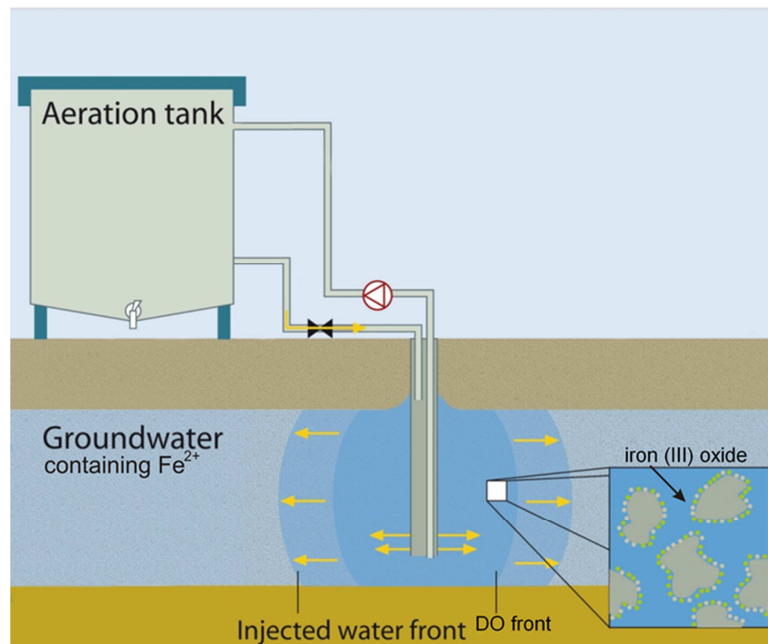
Figure 15: Injection phase of ISIR treatment, where an oxidation zone is created around the injection borehole (modified from van Halem *et al.*, 2008)
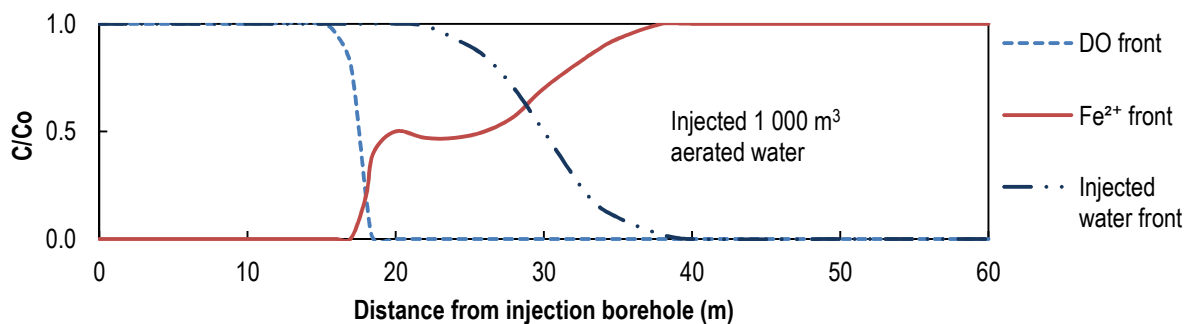
Figure 16: Concentration profiles of Fe^{2+}, DO and injected water during the injection phase, where the DO front lags behind due to Fe^{2+} oxidation (data from Appelo and de Vet, 2003)

When pumping is resumed, the groundwater is naturally filtered through the oxidation zone (Figure 17; Hallberg and Martinell, 1976). At first the injected water is withdrawn with negligible Fe^{2+} concentration, then for some time the groundwater can be pumped with a lower Fe^{2+} concentration compared to the native groundwater (Figure 18; Appelo and de Vet, 2003). This is because the Fe^{2+} is adsorbed on the exchange sites on the newly-formed Fe(III)-oxyhydroxides or depleted exchange sites on the aquifer grains before reaching the production borehole (Appelo and de Vet, 2003).

After some time, the adsorption capacity of the aquifer will be exhausted and higher Fe^{2+} concentrations will break through into the abstracted water (Figure 18; Appelo and de Vet, 2003). When the threshold levels are reached, a new cycle of injection of a volume of oxygenated water is started to "regenerate" the oxidation zone (Sommerfeld, 1999).
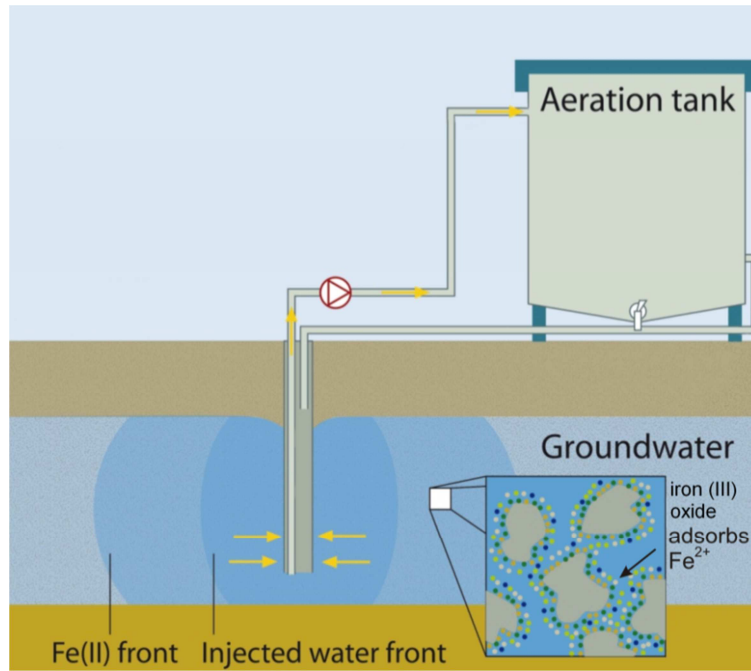
Figure 17: Abstraction phase of ISIR, where Fe^{2+} adsorption allows for reduced iron concentrations in the abstracted water (modified from van Halem *et al.*, 2008)
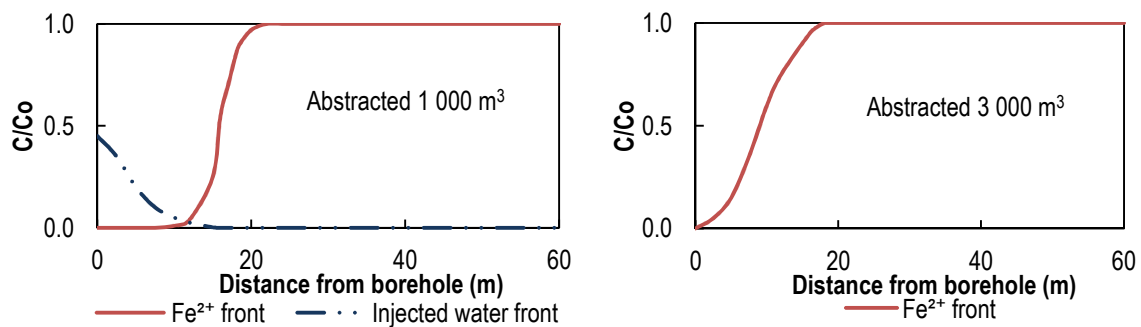
Figure 18: Iron front after abstracting the injected volume (left) and a further 3 000 m^3 (right) until Fe^{2+} breakthrough is seen in the abstracted water (data from Appelo and de Vet, 2003)

Van Halem (2011) suggests that in most cases biotic iron removal is a complementary process to iron removal. But in the case of manganese removal, bacteria accelerate the oxidation rate of Mn^{2+} up to five orders of magnitude compared to abiotic oxidation and therefore is likely to be responsible for much of the Mn^{2+} oxidation in the presence of Fe^{2+} (Rott and Meyerhoff, 1994; Mettler, 2002; Howe *et al.*, 2004; Ebermann *et al.*, 2013). However, with the build-up of Mn(IV)-oxides during successive ISIR treatments, the catalytic oxidation of Mn^{2+} is increased even at pH below 8.5 (Howe *et al.*, 2004).

2.2.3.4   Advantages

The major advantages of the ISIR treatment when compared to conventional above-ground treatment of groundwater (and surface water) include:

- *Lower investment and operational costs*: Investment costs are estimated to be 10 to 20 times less than conventional systems due to lower space requirements. In addition it operates at a lower energy consumption (Hallberg and Martinell, 1976; Radčenko and Hauskrecht, 1982; Rott and Meyerhoff, 1994);

- *Simplicity*: The technique is easy to use and can be automated, reducing the need for extensive supervision. It can also be applied on both small and large scales and in combination with other treatments (Hallberg and Martinell, 1976; Radčenko and Hauskrecht, 1982; Ebermann *et al.*, 2013);

- *No or little application of chemicals*: The sorption sites generated in the aquifer provides a low-cost and robust subsurface filter, which takes longer than conventional sand filtration, resulting in improvements of water quality with little need for *ex-situ* treatment, as well as no need for disposal of generated sludge (Hallberg and Martinell, 1976; Mettler *et al.*, 2001; Appelo and Postma, 2005). In addition, no hazardous by-products are formed in the subsurface by this treatment (van der Laan, 2008).

Side benefits for above-ground water treatment include:

- Improved purification capacity of rapid sand filtration beds, reducing backwashing requirements and decreases sludge production (Hinkamp *et al.*, 2004). For example, a case study in the Netherlands estimated that with ISIR treatment there was a reduction of 75% in rinse water and 50% in sludge production, which more than halved the electricity consumption of the WTP (van Essen *et al.*, 2005);

- Enhanced nitrification processes in subsequent biosand filters due to the removal of Fe^{2+}, Mn^{2+}, NH_4^+ and methane, which interferes with the filtration processes (van Essen *et al.*, 2005; van der Laan, 2008; de Vet *et al.*, 2010).

Apart from Fe^{2+} and Mn^{2+} removal, this treatment also captures problematic components through adsorption onto the newly-formed Fe(III)-oxyhydroxides such as As^{3+} and PO_4^{3-} ions (Appelo and Postma, 2005; van Halem *et al.*, 2010). From studies at the Lekkerkerk WTP, phosphate removal correlated with iron removal, with its removal efficiency also increasing with successive treatment cycles (Figure 19; van Halem, 2011).
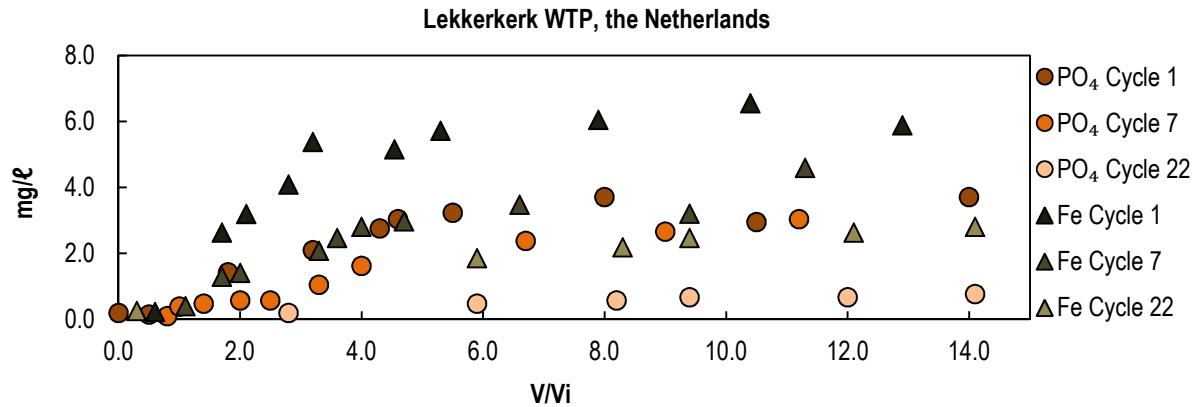
Figure 19: Phosphate and iron breakthrough curves show that PO_4^{3-} removal follows similar trends to Fe^{2+} (data from van Halem, 2011)

While As^{3+} removal at the Lekkerkerk WTP study does not show such a clear improvement compared to iron as a result of ISIR treatment (Figure 20), it still showed a reduction, with As^{3+} adsorption onto Fe(III)-oxyhydroxides seemingly being dependent on pH, the presence of competing anions (especially PO_4^{3-}), contact time with Fe(III)-oxyhydroxides and influenced by high Fe:As ratios (van Halem *et al.*, 2008; van Halem *et al.*, 2010).
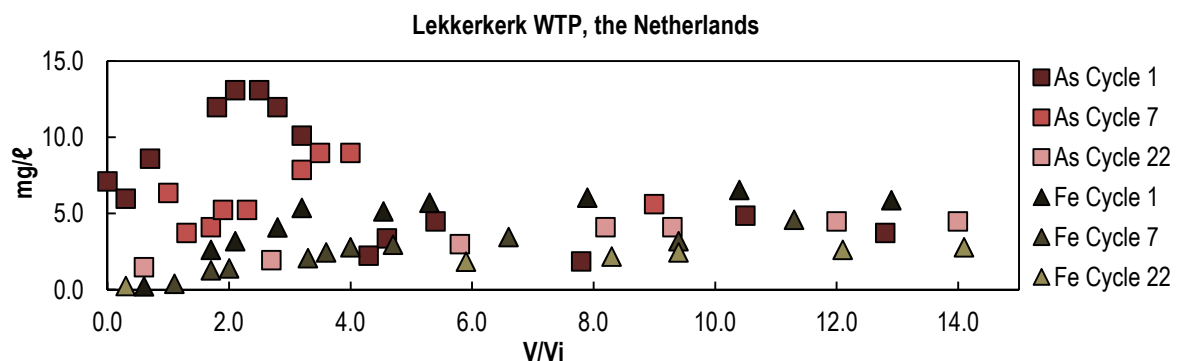
Figure 20: Arsenic and iron breakthrough curves not showing a clear removal trend with treatment when compared to phosphate removal (data from van Halem, 2011)

Regardless of Mn^{2+} and As^{3+} not having the same removal efficiency success as Fe^{2+}, this inexpensive technology holds great promise for both developed and developing countries and is still presently being further investigated for application in the rural areas of Egypt, India and Bangladesh (e.g. Olsthoorn, 2000; Karakish, 2005; Sen Gupta *et al.*, 2009; van Halem *et al.*, 2010; van Halem *et al.*, 2011). In addition, other *in-situ* remediation treatments have since been developed with some modifications of the Vyredox treatment to remove nitrates, known as the Nitredox, or hydrocarbons, i.e. the Hydro-Oxiring or Hydroxiline method (Radčenko and Hauskrecht, 1982; Braester and Martinell, 1988).

2.2.3.5   Potential concerns of *in-situ* iron removal treatment

Although ISIR has been applied over the same time period as conventional *ex-situ* iron removal treatments, it has still not found widespread acceptance due to the following concerns (Sharma, 2001; Mettler *et al.*, 2001; van der Laan, 2008; van Halem, 2011):

- The application itself may clog the production borehole or the aquifer;

- The application may cause the accumulation of heavy metals (e.g. As^{3+}) in the aquifer, which could potentially remobilise later and contaminate the groundwater;

The concern whether ISIR would clog the system is justified since the treatment does indeed increases the Fe(III)- and Mn(IV)-oxides in the subsurface and stimulates microbial growth, however in practise this is not a limitation to the treatment as long as the oxidation zone is properly developed and the plant is run correctly (Hallberg and Martinell, 1976; Driscoll, 1986; Braester and Martinell, 1988; Appelo *et al.*, 1999; Tredoux *et al.*, 2004).

Experience abroad has shown that even after two decades of use there is a lack of clogging experienced in the aquifer or production boreholes, which was proposed to be due to the crystallisation of the amorphous ferrihydrite with time in varying distances from the borehole (Appelo *et al.*, 1999). However, this suggestion had not until recently been researched in depth. The two recent investigations into the iron precipitates from ISIR plants in Switzerland and the Netherlands have been undertaken and in both studies the plants have been in operation for over a decade without any notable clogging problems (Mettler *et al.*, 2001; van Halem *et al.*, 2011).

Both studies found that the iron precipitates to be compact, crystalline Fe(III)-oxyhydroxides chiefly as goethite with trace amounts of ferrihydrite (Figure 21; Mettler *et al.*, 2001; van Halem *et al.*, 2011). The Fe(III)-oxides and other constituents (i.e. Mn, As and Sr) were also found to accumulate at specific depths near the treated boreholes due to preferred flow paths and the mineralogy of the aquifer (Mettler *et al.*, 2001; van Halem *et al.*, 2011). In addition, Mettler *et al.* (2001) found the manganese to not always be found in it oxidised form but as Mn(II) incorporated in calcite or rhodochrosite. This is suggested to be due to Mn^{2+} having a greater affinity for carbonate minerals in very carbonate-rich groundwater, but it was also established that when in presence of high volume of Fe(III)-oxides, manganese was found in its oxidised form, i.e. Mn^{4+} (Mettler *et al.*, 2001). This is assumed to be due to catalytic oxidation by the iron oxide (Mettler *et al.*, 2001).
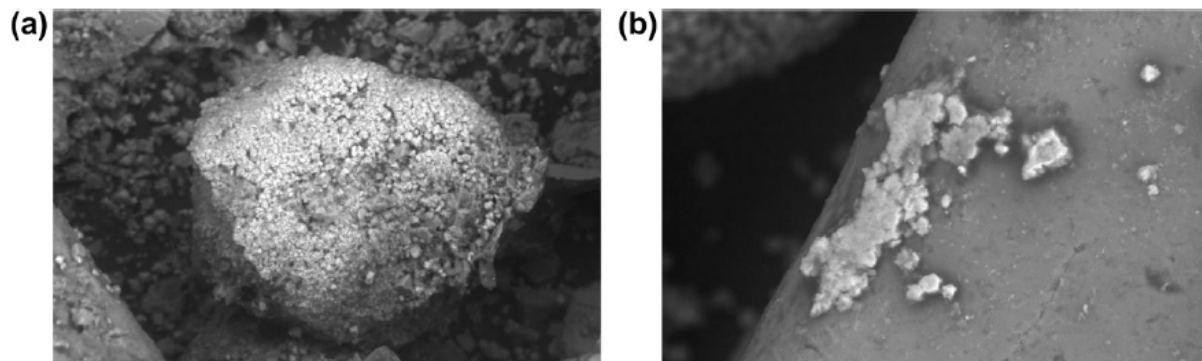
Figure 21: Environmental scanning electron microscope images of Fe(III)-coatings sampled 5 m from an ISIR borehole, (a) an iron-coated sand grain (50 µm) at 19-20 mbgl and (b) local iron precipitate on a sand grain (20 µm) at 21-22 mbgl (van Halem *et al.*, 2011)

The lack of production borehole clogging is ascribed to Fe^{2+} oxidation taking place at various distances away from the production borehole and possibly at varying locations at a time, which results in a spreading of the precipitates throughout the aquifer (Appelo *et al.*, 1999). The oxidation zone is manipulated by changing the configuration of the injection boreholes and/or altering injection-abstraction volumes or rates (Appelo *et al.*, 1999; Mettler, 2002; Tredoux *et al.*, 2004). In comparison to borehole clogging induced by pumping, the oxidation process moves the precipitation of Fe(III)- and Mn(IV)-oxides into a much larger surface area in the aquifer, compared to concentrating at the borehole screen.

Two other studies by Karakish (2005) and van Halem (2011), both mentioned that the microbiological quality of the abstracted groundwater had not been found to be affected (negatively or positively) by the ISIR treatment. However, van Essen *et al.* (2005) did suggest that even though ISIR is not responsible for the introduction of bacteria, the presence of microorganisms in the subsurface can flourish with the injection of oxygenated water, which can enhance Fe^{2+} and Mn^{2+} removal but must be carefully monitored. Even though this study highlighted the concerns it did follow on to mention that no "major" problem was experienced at the 11 ISIR sites in the Netherlands investigated by the van Essen *et al.* (2005).

Moreover, the recent investigation by van Halem *et al.* (2011) has shown that the ISIR treatment has limited the potential for clogging and as a result less rehabilitation is required to maintain the longevity of the production borehole. This is seen in Figure 22 where clogging is evaluated by drawdown (i.e. increasing drawdown is an indication of a reduced borehole yield) whereby the drawdown increase was slower in the treated ISIR borehole than two normal production boreholes (which required rehabilitation) at the Oasen De Put WTP between 2006 and 2008 (van Halem *et al.*, 2011).
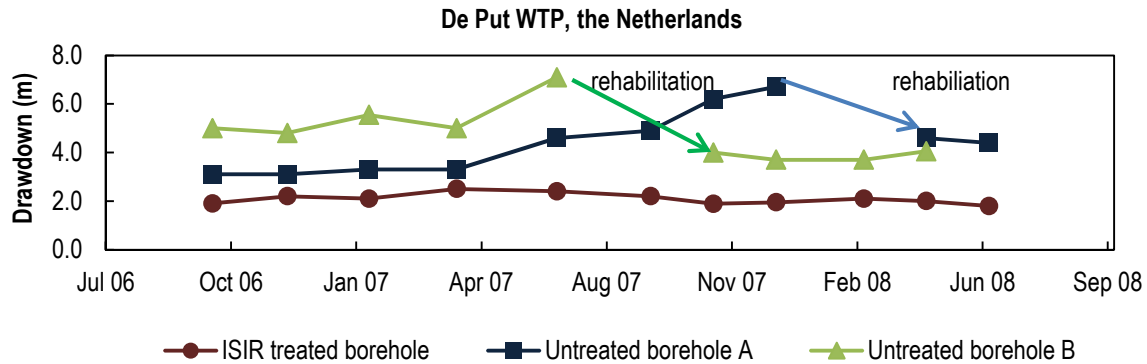
Figure 22: Drawdown in three production boreholes, where the ISIR borehole shows negligible change over time compared to the two untreated boreholes, which required rehabilitation (data from van Halem *et al.*, 2011)

However, clogging problems have occurred in ISIR plants due to incorrect dimensioning and construction of injection well-points (Braester and Martinell, 1988). For example, an ISIR plant in Grimsås, Sweden, drilled six injection well-points around each production borehole, however due to the previous geological logging of the quaternary deposit not showing a thin layer of very fine-grained material, the injection well-points screen slots were too wide and were subsequently blocked by the fine material, requiring the well-points to be reconstructed (Braester and Martinell, 1988). In addition, incorrect running of the ISIR plant could result in the clogging of the production borehole screen (Braester and Martinell, 1988). However, this has only been found when the abstraction phase is regularly run longer than the desired time and the researchers recommend that the production borehole should be cleaned with a weak acid to remove the amorphous Fe(III)-oxyhydroxide and Mn(IV)-oxides (Braester and Martinell, 1988).

The other concern with its application is that when ISIR is stopped and anoxic conditions return, reductive dissolution of the accumulated Fe(III)-oxyhydroxides may promote mobilisation of Fe^{2+}, Mn^{2+} and As^{3+}, especially in areas with high DOC (Appelo and Postma, 2005; van Halem, 2011). Geochemical models by Appelo and de Vet (2003) have proposed that the amount of accumulated heavy metals (e.g. As^{3+}) would not be a risk if reduction dissolution had to occur and other case studies such as at the Lekkerkerk WTP, which abstracts groundwater with a high DOC (i.e. 3 mg/ℓ) and remobilisation of Fe^{2+} and Mn^{2+} has not been observed to exceed its baseline after stopping the ISIR for more than two years (van Halem, 2011). This is because the precipitation of Fe(III)-oxyhydroxides (often as ferrihydrite) in the subsurface is a very important step in the long-term prevention of elevated Fe^{2+} concentrations accumulating in groundwater as the amorphous mineral recrystallise with time to goethite (Mettler *et al.*, 2001; van Halem *et al.*, 2011). Goethite is a thermodynamically more stable mineral, with a smaller surface area (Table 1) and lower

solubility to ferrihydrite (Appelo and de Vet, 2003; Smith, 2006). Thus as the crystallinity of the Fe(III)-oxyhydroxides increase, the microbial and abiotic ability, even in the presence of DOC, limits the potential for iron reduction (Appelo and Postma, 2005). Through the progressive oxidation and stabilisation of Fe(III)-oxyhydroxide in the aquifer, more thermodynamically stable iron oxide minerals are present in the system, which reduces the potential for reductive dissolution of iron when reducing conditions prevail again.

2.2.3.6 Hydrogeological requirements for *in-situ* iron removal

The ISIR treatment needs the following site specific conditions to succeed such as:

- The section of the aquifer injected should be as homogenous as possible and without extremely coarse layers to prevent preferential flow of the injected water or relatively low exchange capacity with the Fe(III)-oxyhydroxides when the treatment is reversed (Appelo *et al.*, 1999);

- The sorption capacity of the aquifer is dependent on the presence of clay, organic matter and iron oxides in the aquifer (Appelo and de Vet, 2003). Also the different Fe(III)-oxyhydroxides present in the aquifer matrix influence the sorption capacity, i.e. ferrihydrite and lepidocrocite has a larger sorption capacity compared to crystalline goethite due to their surface areas. In addition, manganese oxides also have a high capacity for sorption, however the preference of oxide formation is dependent on the water quality parameters (Buamah, 2009).

In addition, other water quality parameters that influence the rate of iron and manganese removal in the subsurface include:

- This method is restricted to situations where the groundwater pH is near-neutral or higher (i.e. pH > 6.5) due to the slow oxidation rate of Fe^{2+} and Mn^{2+} at lower pH (Figure 6; Appelo and de Vet, 2003; van Essen *et al.*, 2005). This also influences the sorption capacity of oxides, for example, a pH increase from 7 to 8 increases the weak sites sorption capacity of Fe^{2+} from 5% to 30% and the rate of crystallisation of ferrihydrite to goethite is preferred at high pH (Appelo *et al.*, 1999).

- Temperature has an inverse relationship with Fe^{2+} oxidation with temperatures below 5°C preventing the oxidation process from proceeding (Sommerfeld, 1999);

- Alkalinity does not have a direct involvement in the Fe^{2+} removal mechanism but is a good proton buffer to counteract the increased proton concentration (and lowered pH) associated with the oxidation reactions and could contribute to higher Ca^{2+} and Mg^{2+}

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concentrations in the water, which improves exchange capacity (Mettler, 2002; Ebermann *et al.*, 2013). However, high alkalinity (i.e. > 300 mg/ℓ as $CaCO_3$) can impact oxidation of Fe^{2+} negativity due to complexes formed (Buamah, 2009);

- The oxidation of Fe^{2+} by oxygen also decreases when complexes are formed with organic and inorganic ions, such as DOC, SiO_2 or PO_4^{3-} (Sharma, 2001);

- ISIR is not recommended in strongly reducing groundwater, which contains large concentrations of methane, HS^-, DOC, nitrite or NH_4^+ because these are high oxygen consuming ions, which would prevent oxidation of desired Fe^{2+} and Mn^{2+} (Mettler, 2002; Tredoux *et al.,* 2004; Ebermann *et al.*, 2013).

2.2.3.7   Disadvantages

The ISIR needs certain conditions to prevent any operational flaws and limitations in treatment from occurring. The following scenarios can be a disadvantage to ISIR:

- The presence of pyrite can be problematic with injection of oxygenated water as pyrite readily oxidises releasing Fe^{2+} and SO_4^{2-} into solution (Equation 2) and this reaction also lower the pH due to the proton release (Appelo *et al.*, 1999);

- Increased risk of bacterial activity if not correctly monitored (van Essen *et al.,* 2005);

- A shortage of injection water often due to the increased water consumption could result in the failure of the ISIR plant if water capacity cannot be increased (Braester and Martinell, 1988);

- Potential corrosion of uncoated steel borehole screens and casing due to high DO in the injected water. Although to what extent this occurs in presently unknown but is recommended that application should be in non-corrosive materials such as PVC or stainless steel (Olsthoorn, 2000; Sharma, 2001);

- A good understanding of the oxidation kinetics may be necessary to optimise the ISIR system, which requires a high level of geochemical understanding and technical know-how, which may be a limitation for rural application (Tredoux *et al.*, 2004). However, successful iron removal at small-scale application ($< 2\,m^3$ injected volume using aeration) in rural areas such as Bangladesh and India (e.g. Sen Gupta *et al.*, 2009; van Halem *et al.*, 2010) has challenged this concern.

2.2.3.8   Case studies

EUROPEAN CASE STUDIES

Throughout Europe, the ISIR treatment is widely applied and in some cases has been in operation for more than three decades (Table 4; Table 5) for the purpose of maintaining iron and manganese concentrations below the European Union standards of Fe < 0.2 mg/ℓ and Mn < 0.05 mg/ℓ (Mettler *et al.*, 2001). The prevalence of ISIR treatment throughout Europe is attributed to groundwater being a major contributor to the populations' drinking water supply, for example almost 100% in Denmark, 72% in Germany, 60% in the Netherlands, 56% in France, 25% in Sweden and 15% in Norway (Hallberg and Martinell, 1976; Sharma, 2001; de Vet *et al.*, 2010; Vestland, 2010).

Table 4: Some of the ISIR plants in operation throughout Europe (Braester and Martinell, 1988; Mettler, 2002; van Essen *et al.,* 2005; van Halem, 2011)

	ISIR since	Production capacity (m³/day)	Initial Fe (mg/ℓ)	Initial Mn (mg/ℓ)
The Netherlands				
Aalten	1977	2 200	> 0.1	> 0.3
Corle	1980	10 300	0.27	0.13
De Put	1981-1988; 1996-	1 250-1 600	2.6	0.6
Switzerland				
Sursee	1984	500	0.2	0.04
Luzern	1991	3 000	3.7-3.9	0.17-0.33
Menznau	1993	1 400	6.0	0.6
Bächau	1996	8 600	0.7	0.17
Germany				
Landringhausen	1973	7 900	2.5	0.25
Isernhagen	1976	2 900	20.0	2.0
Wahlstedt	1982	11 500	0.3	0.19
Oberkirch	1997	430	0.1	1.2
France				
Chalon	1977	4 800	0.08	0.15
Le Baleine	1979	6 000	1.0-10.0	0.5
Denmark				
Orslevkloser	1976	5 400	1.2	0.07
Stoholm	1977	6 480	0.6	0.08
Rødkjaersbro	1980	3 600	1.4	0.06
Sweden				
Grimsås	1971	960	3.9	0.07
Värsås	1974	240	1.2	0.09
Hormantorp	1976	3 360	4.0	1.20
Ljungsarp	1980	480	2.0	0.25

Table 5: European case studies of ISIR plants

Location and reference	Le Neuveville, western Switzerland (Mettler *et al.*, 2001)	Dobra, northern Saxony, Germany (Ebermann *et al.*, 2013)	Grindalsmoen WTP, Elverum, Norway (Vestland, 2010; Ahmad, 2012)
Aquifer type	Alluvial-deltaic aquifer (19 m thick) with water table at 2 mbgl	Aquifer of Pleistocene-age, fine to medium-grained sands (14 m thick) with water table at 1.5 mbgl	Highly permeable glacio-fluvial aquifer
ISIR treatment	Vyredox method at two production boreholes where five well-points at a depth of 15 m and seven metre radius around the production borehole, which are both 18.6 m deep and have an abstraction rate of 40 ℓ/s.	Two-production borehole method using PW2 (5 m deep) as the source of water and PW1 (14 m deep) as the injection borehole.	Vyredox method applied at one of the four production boreholes (i.e. Hovedbrønn 4) within the wellfield. A ring of nine well-points (30-35 m deep) surround the production borehole (30 m deep; 60 ℓ/s). The well-points either supply the recharge water or act as the injection point (Figure 24).
Oxidant	Aerated groundwater (DO = 8.0 mg/ℓ)	Oxygen gas (DO = 15-25 mg/ℓ)	Aerated groundwater (DO = 12 mg/ℓ)
Recharge information	Injection takes place for 24 hours at 8 ℓ/s every five to ten days in the well-points to generate an oxidation zone of 14 m around the production borehole.	A portion of groundwater abstracted from PW2 (300 m^3) is injected into PW1 at 0.33 ℓ/s, which gave an oxidation zone of six metres.	Two well-points (e.g. SB1 and SB3) abstract groundwater at 6 ℓ/s for two hours. The water is degassed and aerated by being kept at the surface for 3 hours. The oxygenated water is then injected at 2.4 ℓ/s into a well-point (i.e. SB2) between the two supply well-points. After a short period of time, groundwater is abstracted from SB2 and SB4 and injected in SB3.
Initial water quality	Fe = 0.3-1.0 mg/ℓ Mn = 0.1-0.2 mg/ℓ pH = 7.0-7.3 DOC = 1.5 mg/ℓ NH_4^+ = 0.8 mg/ℓ	Fe = 9.8 mg/ℓ (PW1) and 4.5 mg/ℓ (PW2) Mn = 0.43 mg/ℓ (PW1) and 0.29 mg/ℓ (PW2) pH = 6.5 NH_4^+ = 0.09 mg/ℓ	Fe = 2.8 mg/ℓ Mn = 0.2 mg/ℓ
Quality after ISIR	Fe and Mn < 0.2 mg/ℓ	Fe^{2+} < 0.2 mg/ℓ within a week	Fe and Mn removal below Norwegian standards,
V/Vi		V/Vi = 2 after four cycles this doubled after a few months at Fe threshold limit given at 0.5 mg/ℓ (Figure 23).	
Additional comments		Small-scale mobile ISIR system developed to improve the drinking water quality for livestock at a dairy farm.	The Grindalsmoen WTP supplies drinking water to a population of approximately 14 500 and is regarded a great success, since it has reduced *ex-situ* treatment to only pH adjustment.

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Location and reference	Beaucaire WTP, south of France (Dumousseau *et al.,* 1990; Ahmad, 2012)	Drösing WTP, Lower Austria (Braester and Martinell, 1988)	Lekkerkerk WTP, the Netherlands (Appelo and de Vet, 2003; van der Laan, 2008)
Aquifer type	Coarse-grained alluvial sand aquifer, which is semi-confined because of a clay-rich loam covering.	Gravel-sand aquifer with high clay content and a water table of 1.35 mbgl.	Coarse-grained sand aquifer (20-30 m thick) recharged by the Rhine River and bank filtration
ISIR treatment	Two-production borehole method applied primarily for Mn removal and this design applied because it was cheaper than drilling well-points.	Three production boreholes (each 30 m deep and abstraction rate of 30 ℓ/s) have six well-points constructed in a ring around them (Figure 24)	Modified production borehole (9.6 m deep) for sourcing recharge water and injection purposes.
Oxidant	Aerated groundwater	Aerated groundwater	Aerated groundwater (DO = 8.8 mg/ℓ)
Recharge information	The plant runs every day where groundwater is pumped from one of the production boreholes and a portion of water is diverted to be used for injection (2 500 m^3 for 18 hours) in the other borehole. After a short interval, approximately six hours, the operation is reversed and injection takes place in the other production borehole.	With three high yielding boreholes it was feasible to use of one for the production for the main supply, while the aerated water from the second borehole is infiltrated into the well-points of the third borehole. Infiltration is for a day, the borehole that was treated is then in production and another borehole is treated.	6% of the abstracted water volume injected at 8.33 ℓ/s for two days and immediately afterwards pumping is resumed at 6.4 ℓ/s for approximately 40 days.
Initial water quality	Fe = 0.18 mg/ℓ Mn > 0.05 mg/ℓ	Fe = 0.27-0.35 mg/ℓ Mn = 0.32-0.48 mg/ℓ	Fe = 6-7 mg/ℓ pH=7.1
Quality after ISIR	Mn < 0.02 mg/ℓ and Fe < 0.05 mg/ℓ (threshold values) after four injection cycles, but pH was lowered as a result of the treatment.	Fe removal immediately below the Austrian threshold concentration (i.e. $\leq$ 0.1 mg/ℓ), while Mn removal to $\leq$ 0.05 mg/ℓ took longer and was only achieved after 20 days of application (Figure 25).	Fe = 3-4 mg/ℓ after 18 injection-abstraction cycles.
V/Vi		Initial V/Vi = 2 but after three months V/Vi had increased to 7	
Additional comments	Manganese concentrations in the groundwater were not problematic historically, but in the late 1960's, Mn levels increased because of the development of the town of Vallabrègues and closing of a dam. This reduced recharge from a river to the aquifer and increased the DOC load. Leading to reducing conditions and mobilisation of Mn(IV)-oxides and Mn(II)-carbonates aided by increased bacterial activity.		The purpose of ISIR treatment was to improve denitrification of the dry bio-filters by reduction of Mn^{2+}, NH_4^+ and methane in the abstracted water. As a result, the iron breakthrough was not a controlling parameter for initiating re-injection but rather volume of abstracted water. After 18 injection-abstraction cycles, the ISIR treatment was stopped for four years, but in mid-2003 it was put back into operation.
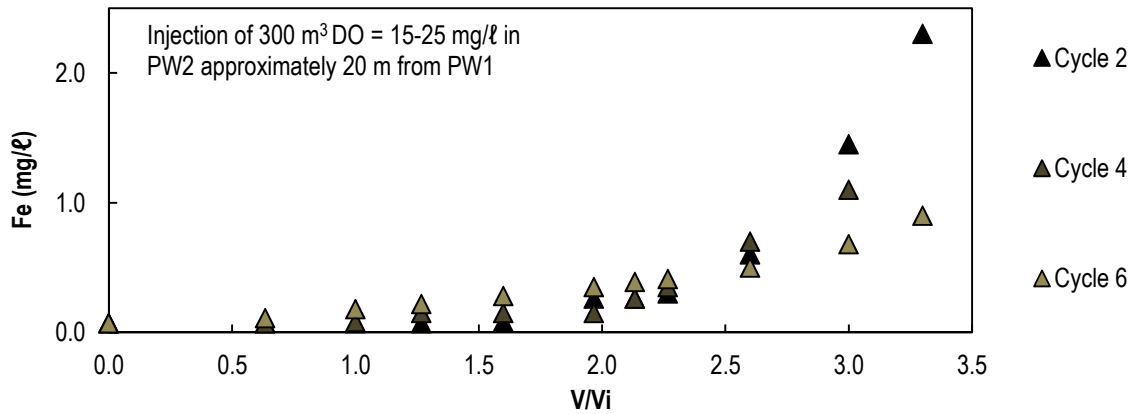
Figure 23: Breakthrough curves of iron during the feasibility study of ISIR in PW1 (data from Ebermann *et al.,* 2013)
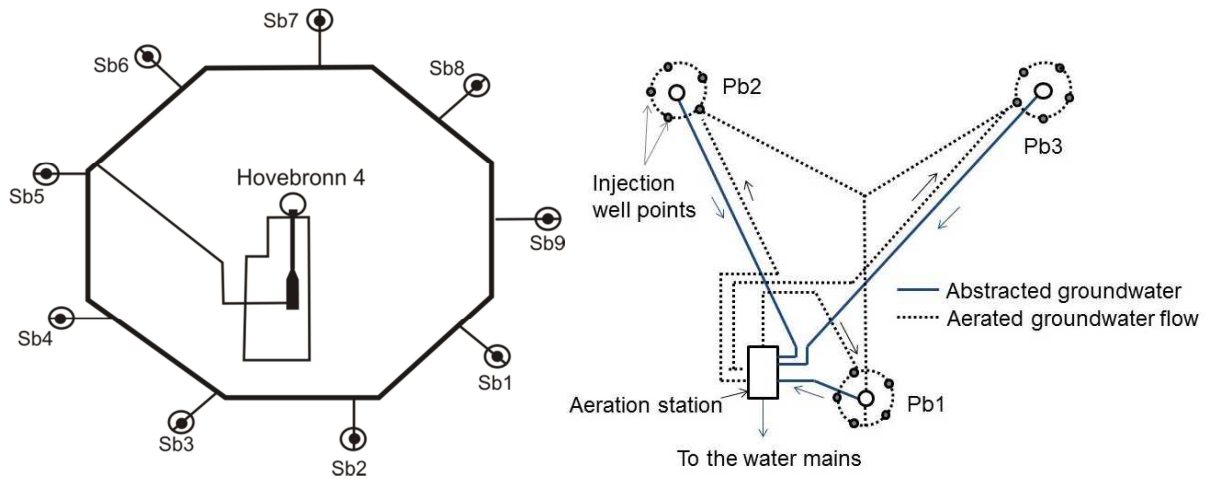
Figure 24: The Vyredox method set-up at the Grindalsmoen WTP (left) (modified from Ahmad, 2012) and at the Drösing WTP (right) (modified from Braester and Martinell, 1988)
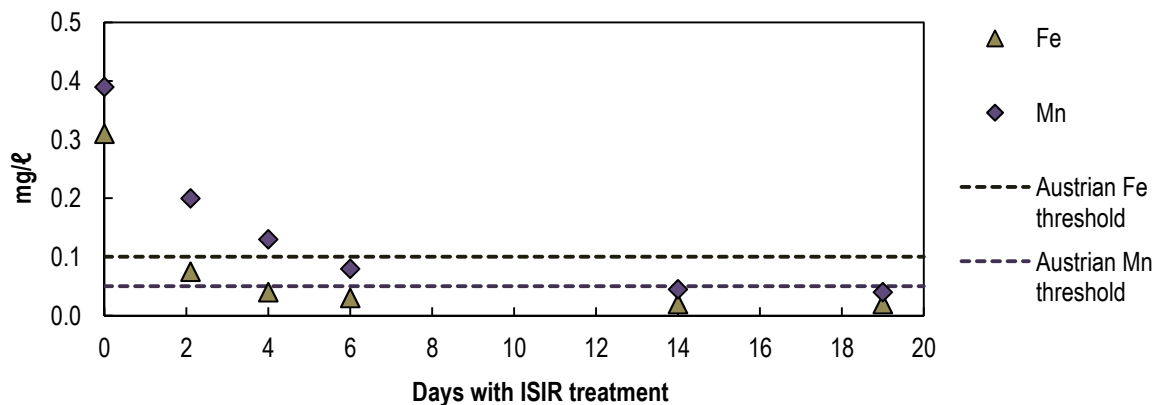
Figure 25: Iron and manganese removal from the groundwater at the Drösing WTP (modified from Braester and Martinell, 1988)

In the United States of America more than a quarter of municipal groundwater supply schemes abstract groundwater with undesirable iron and manganese concentrations (AWWA, 1984). In addition, production capacity losses are well known due to their elevated concentrations with examples of borehole yield reduction up to 75% within three months to a year (Driscoll, 1986). The Vyredox method is not as prevalent in the United States compared to Europe and was marketed only since the late 1970s but there is limited literature on its application in the United States (Rehfeldt *et al.*, 1992; ICRC, 1993). There are currently two ISIR sites in Massachusetts for the town of Pembroke (operation since 1981) and for the town of Seekonk (operation since 1984) and one in Columbus, Ohio (operation since 1982) (AWWA, 1984; Mettler, 2002).

The one well-known example of the Vyredox method is in Seekonk, Massachusetts, at the Newman Avenue wellfield that supplies groundwater for municipal use (AWWA, 1984). The use of the Vyredox method was a means of water quality improvement and other ex-situ treatment options, i.e. sequestration or filtration were considered but sequestration was excluded due to the elevated concentrations of Fe^{2+} and Mn^{2+} and filtration due to its high costs (AWWA, 1984). The details of ISIR treatment at three of their production boreholes is shown in Table 6.

Table 6: Vyredox treatment at the Newman Avenue Wellfield (AWWA, 1984)

Aquifer type	Glacial deposit
ISIR treatment	Two production boreholes surrounded by six injection well-points and the other production borehole is surrounded by four injection well-points
Oxidant information	Aerated treated groundwater from the distribution system
Recharge information	Injection for 24 hours every two to three weeks
Set-up phase	Nineteen cycles for Mn removal to be established
Initial water quality	Fe = 2.6 mg/ℓ ; Mn = 6.2 mg/ℓ
Quality after ISIR	Fe < 0.5 mg/ℓ; Mn < 0.05 mg/ℓ

EGYPT

The most common limit on groundwater use in Egypt is the high iron and manganese concentrations from the Nile Delta Aquifer, often resulting in many production boreholes being abandoned due to clogging and water quality problems (Olsthoorn, 2000; Karakish, 2005). The Nile Delta Aquifer is a 300 m thick aquifer with a semi-confining clay layer above, which resulted in the high manganese concentrations and low DO (Olsthoorn, 2000).

The Egyptian drinking water limits are higher than WHO recommendations with Fe < 1.0 mg/ℓ and Mn < 0.5 mg/ℓ and generally, the groundwater is treated with Cl_2 or $KMnO_4$ because most cases iron is complexed with DOC and aluminium sulphate as the coagulant followed by pressurised sand filters (Olsthoorn, 2000; Karakish, 2005). These WTP require skilled workers and continuous monitoring of the chemical dose to maintain water quality standards (Karakish, 2005).

In partnership with Amsterdam Water Supply and the El-Beheira Water Company, which supplies potable water to the Beheira Governorate in northern Egypt (about 20 Mm³ of groundwater per annum), research was undertaken into other methods for iron and manganese removal (Olsthoorn, 2000; Karakish, 2005). From this partnership the BURMAN (Beheira Underground Removal of Manganese) process was developed (Karakish, 2005). The BURMAN treatment is a two-production borehole method, which works intermittently and has been tested at a number of production boreholes in two wellfields at Itay El-Baroud and Kom Hamada injecting approximately 2 000 m³ aerated groundwater per cycle (Table 7; Olsthoorn, 2000; Karakish, 2005). Initially, entrained air bubbles in the recharge water caused high entry pressures and continuous bubbling in the production borehole at the first test but this was easily solved by connecting the pump to another extraction point in the sedimentation tank after aeration (Olsthoorn, 2000). The applications for all the pilot tests were successful in the removal of manganese with no significant effect on microbiology or production borehole drawdown was reported in the five test boreholes even after 18 months of application (Karakish, 2005).

Table 7: The two ISIR treated wellfields in Egypt (Olsthoorn, 2000; Karakish, 2005)

	Initial quality	Quality after ISIR	Set-up	V/Vi
Kom Hamada	Mn = 0.9 mg/ℓ; Fe = 0.05 mg/ℓ	Mn < 0.1 mg/ℓ; Fe remains low	5	3
Itay El-Baroud	Mn = 1.00 mg/ℓ; Fe = 0.38 mg/ℓ	Mn < 0.4 mg/ℓ; Fe remains low	19	4

In addition, Karakish (2005) did a cost calculation and found that the cost per 1 m³ of groundwater using ISIR was slightly higher than abstraction without ISIR but less than 50% of the production cost of the abovementioned *ex-situ* water treatment (Table 8).

Table 8: Cost breakdown of the four water treatments currently in use in Egypt (Karakish, 2005)

	Groundwater			Surface water
	Biological method	**ISIR**	**Chemical oxidation**	
Capital cost (LE)				
Two boreholes construction	150 000	150 000	150 000	-
Civil work	600 000	-	-	150 000
Electricity supply	50 000	50 000	50 000	50 000
Electro-mechanical work	1 100 000	135 000	700 000	800 000
Total capital cost	1 900 000	335 000	900 000	1 000 000
Water production (m^3)				
Annual production	750 000	750 000	750 000	750 000
Water used in treatment	-	75 000	125 000	-
Net annual production (m^3)	750 000	675 000	625 000	750 000
Expected life span (years)	20	10-20	20	20
Annual depreciation (LE)				
Wells	7 500	7 500-15 000	7 500	-
Civil work	16 250	1 250	1 250	5 000
Electro-mechanical work	82 500	10 125	52 500	60 000
Total annual depreciation	106 250	18 875-26 375	61 250	65 000
Operation and maintenance costs (LE)				
Salaries	11 800	6 250	11 800	11 800
Electricity	54 000	44 000	80 600	60 600
Civil and electromechanical work	26 000	3 700	15 000	17 000
Treatment materials	1 500	1 500	5 500	7 500
Total costs	93 300	55 450	112 900	96 900
Total annual cost	199 550	74 325-81 825	164 650	161 900
Total production cost per 1 m^3	0.27	0.11-0.12	0.28	0.22

Due to elevated iron and manganese concentrations in groundwater, at least five WTPs in China have used ISIR since the 1980's as a pre-treatment for the *ex-situ* treatments to meet the Chinese drinking water standards (Table 9).

Table 9: Four ISIR plants in China (Maogong, 1988)

	Panshi WTP	Yitong WTP	Harbin WTP	Daqing WTP
Aquifer type	Medium to coarse-grained sands with gravel	Medium to coarse-grained sands with gravel	Coarse-grained sands	Sandstone
ISIR treatment	Combined method: three injection well-points in a seven metre radius around the borehole, which is 32 m deep and production rate of 10 ℓ/s.	Vyredox method where four injection well-points are at a seven metre radius surrounding the production borehole, which is 32 m deep and production rate of 11 ℓ/s.	Single borehole approach where the modified production borehole is 65 m deep and production rate of 10 ℓ/s.	Single borehole approach where the modified production borehole is 120 m deep and production rate of 18 ℓ/s.
Oxidant information	Aerated groundwater	Aerated groundwater	Aerated surface water	-
Recharge information	12-13 hours at 8-10 ℓ/s	Three hours at 5 ℓ/s per injection point	Five days	28-51 hours at 11-14 ℓ/s
Set-up cycles	8	7	8	8
V/Vi	4	9	9	8
Initial water quality	Fe^{2+} = 3.2 mg/ℓ Mn^{2+} = 1.2 mg/ℓ pH = 6.7	Fe^{2+} = 20 mg/ℓ Mn^{2+} = 1.0 mg/ℓ pH = 6.0	Fe^{2+} = 6.1 mg/ℓ Mn^{2+} = 1.3 mg/ℓ pH = 7.1	Fe^{2+} = 2.7 mg/ℓ Mn^{2+} = 0.4 mg/ℓ pH = 7.3
Quality after ISIR	Fe^{2+} < 0.3 mg/ℓ Mn^{2+} = 0.4 mg/ℓ	Fe^{2+} = 14 mg/ℓ Mn^{2+} not removed	Fe^{2+} < 0.3 mg/ℓ Mn^{2+} not removed	Fe^{2+} < 0.3 mg/ℓ Mn^{2+} not removed

INDIA

In recent years, research has gone into the co-removal of arsenic during ISIR, especially in rural areas such as India. In 2001, it was estimated that up to 40 million people in India are exposed to arsenic concentrations above the WHO (2008) health guideline of 0.001 mg/ℓ (van Halem, 2011). However, this study by Sen Gupta *et al.* (2009) differed as it was applied at a much smaller scale (i.e. approximately 2 m^3 per cycle at a low rate of 2.7 m^3/h)

compared to the European examples, where injection volumes are greater than 500 m^3 per cycle. The investigated study areas for the application of ISIR were in rural villages in the West Bengal District, where groundwater is abstracted from an anoxic aquifer in the Bengal Delta Aquifer. The six small-scale ISIR plants were implemented at modified hand-pumps (Figure 26) with total arsenic concentrations ranging between 0.09-0.28 mg/ℓ (Sen Gupta *et al.*, 2009; van Halem, 2011). Aeration was achieved by using shower heads and the DO concentrations ranges between 4-6 mg/ℓ (Sen Gupta *et al.*, 2009).

All ISIR sites operated successfully in providing arsenic-free water (i.e. < 0.002 mg/ℓ) with the V/Vi ratios found to be between four to six. The study also emphasised that the ISIR design used was easily constructed from locally available materials obtained from a hardware store and installed by local plumbers and engineers making it accessible and easy to maintain. In addition to the success in arsenic removal the other side benefit of this treatment was that there was no handling of arsenic-rich sludge and required no further water treatment, which made the ISIR treatment very economical for the community costing US\$ 1 per 2 m^3 of drinking water per day (Sen Gupta *et al.*, 2009).
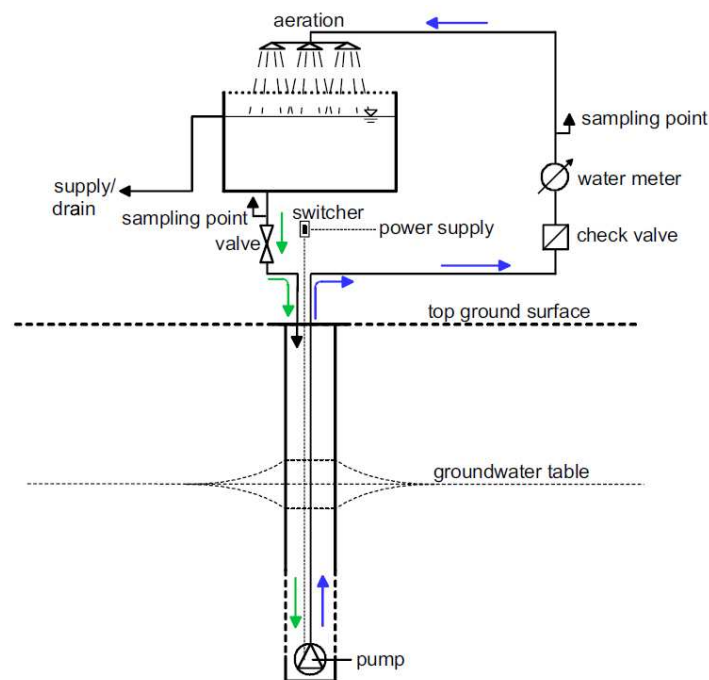
Figure 26: The set-up of the ISIR treatment applied in India (Sen Gupta *et al.,* 2009)

BANGLADESH

Another similar study to the small-scale application in India is the investigation into in-situ removal of Fe^{2+}, Mn^{2+} and As^{3+} in the Manikganj District of Bangladesh by van Halem *et al.* (2010). Similar to the Indian investigation, this research is of great interest as it shows the

diversity of ISIR, whereby it was easily applied in a rural setting at an even smaller scale, i.e. using a modified hand-pump and recharge volumes of less than 1 m^3. Bangladesh requires such innovative treatment options since approximately 65% of the boreholes have total arsenic concentrations above the WHO (2008) threshold, which puts approximately 37 million people at risk (van Halem *et al.,* 2010). As a result many of these boreholes are abandoned, which were initially installed to provide a secure and reliable drinking source to the community, in order to reduce use of unsafe microbial contaminated surface water (van Halem *et al.,* 2010).

Previous research into *ex-situ* arsenic removal options by adsorption media, ion exchange, membrane filtration or coagulation and filtration were found to be too expensive for the poor communities. Other investigations into household filtration systems with non-commercially available adsorption media have also been studied with success but their application is limited by the following disadvantages (van Halem *et al.*, 2010):

- The long-term efficiency of the filters, which clog over time;

- Potential breakthrough of arsenic;

- Regeneration of the filters, which produces an arsenic-rich sludge;

- Microbial contamination of the treated water from growth on filters.

The ISIR treatment was considered since it requires minimal equipment and provided a robust filter, which retained the arsenic in the subsurface (van Halem *et al.*, 2010). The experimental set-up was installed at two study sites (Figure 27) with the baseline water quality given in Table 10.

Table 10: Water quality before ISIR application at the two study sites (van Halem *et al.,* 2010)

Site A	Site B
Fe = 1.0 mg/ℓ	Fe = 15.0 mg/ℓ
Mn = 2.5 mg/ℓ	Mn = 0.3 mg/ℓ
As$_{total}$ = 0.145 mg/ℓ	As$_{total}$ = 0.145 mg/ℓ
As = 0.12 mg/ℓ	As^{3+} = 0.124 mg/ℓ
PO$_4$ = 3.3 mg/ℓ	PO$_4$ = 5.0 mg/ℓ
pH = 6.85	pH = 6.85

Both modified hand-pumps were 0.4 m wide and 31 m deep with the last 3 m screened and abstracted anoxic groundwater from alluvial sands of the Bengal Delta aquifer (van Halem *et al.,* 2010). The abstracted groundwater was "cleaned" before injection (i.e. Fe and

As < 0.01 mg/ℓ) by a SIDKO system, which aerated the water to DO concentrations between 1 to 6 mg/ℓ and filtrated the water through sand and Fe(III)-hydroxide media (van Halem *et al.*, 2010).
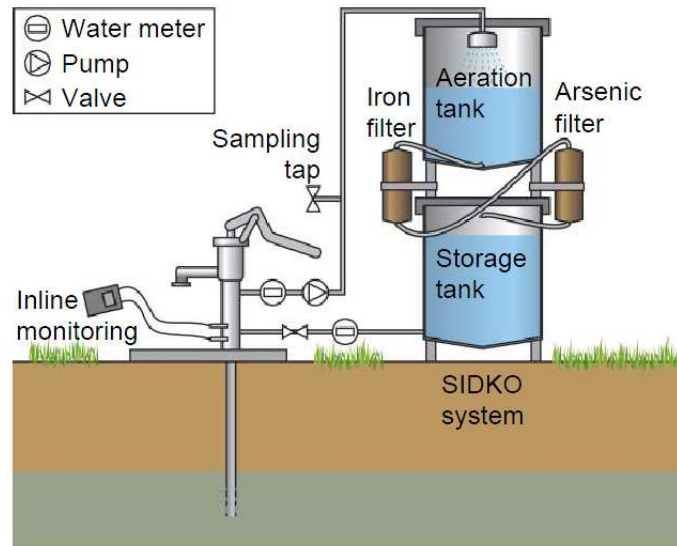
Figure 27: The experimental ISIR set-up at the two study sites (Site A and B) in Bangladesh (van Halem *et al.,* 2010)

The injected volume per cycle were ≤ 1 m^3 at an injection rate of 1.2 m^3/h and after 20 cycles the iron removal showed to be significant even at such a small scale, however the subsurface arsenic removal did not show the same improving trends and was not as efficient for arsenic removal to below WHO (2008) standards for this study (Figure 28; van Halem *et al.*, 2010). The two explanations for the arsenic behaviour are either (van Halem *et al.*, 2010):

- Longer contact time with the iron oxides is required;

- Adsorption competition with other ions (such as PO_4^{3-}) interfered with the adsorption of As^{3+}.
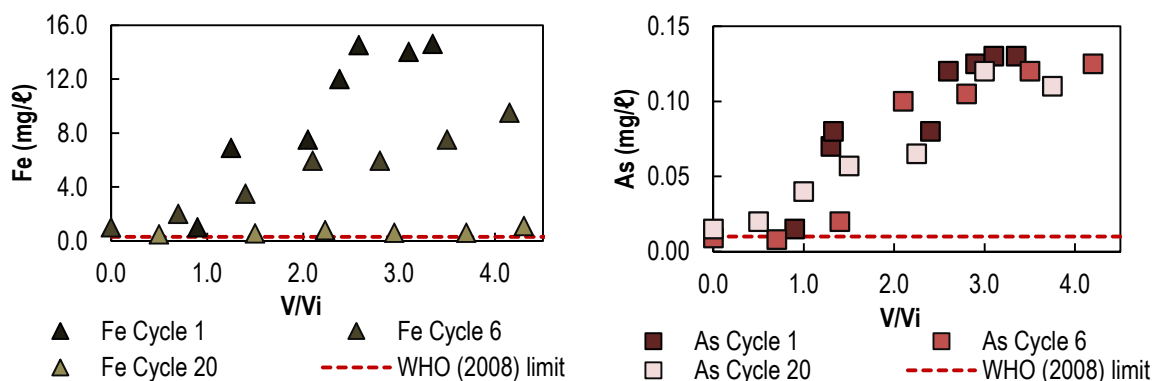
Figure 28: Iron and arsenic breakthrough curves at Site B, Bangladesh (data from van Halem *et al.,* 2010)

CHAPTER 3. STUDY SITE

The literature review of ISIR applications revealed that it has been predominantly applied in sand-gravel aquifer settings, with only one example of a sandstone aquifer (Radčenko and Hauskrecht, 1982; Maogong, 1988). It is assumed that the lack of fractured aquifer application is probably because the majority of European (e.g. Germany, the Netherlands) and African (e.g. Botswana and Egypt) wellfields, which experience clogging problems exploits groundwater from anoxic alluvial aquifers (Radčenko and Hauskrecht, 1982; Riekel and Hinze, 2002; Karakish, 2005; Smith and Roychoudhury, 2013). In South Africa, however, there are only a few potential study areas available to investigate the application of ISIR treatment, since more than 80% of South Africa's exploited aquifers are in fractured rock settings (Woodford *et al.,* 2006). The Cenozoic-aged Atlantis Aquifer is one of the primary, intergranular aquifers in South Africa (Figure 29). It used to be the main contributor to the municipal water supply of the town of Atlantis and the protection of this groundwater resource is vital since the area experiences semi-arid conditions, with no proximal surface water resources to develop (Flower and Bishop, 2003).

Figure 29: Location map of the study area on the West Coast, 33 km from Cape Town

However, the long-term sustainability of the two wellfields, i.e. Witzand and Silwerstroom (Figure 29) has historically been jeopardised by the poor performance of nearly all of their production boreholes as a result of clogging from the persistent iron levels (Tredoux *et al.,* 2002; Flower and Bishop, 2003). For example, from 1976 to 1999 the Atlantis Aquifer reliably supplied the towns water requirements (Tredoux *et al.,* 2002), but as a result of the recurring iron-related clogging of the production boreholes, the wellfields presently supply only 30-40% of the town's needs (DWA, 2011). Between 2.1 Mm^3 to 3.1 Mm^3 of surface water per annum has since been brought in from the Voëlvlei Dam via an 11.6 km pipeline from Melkbosstrand to augment the increasing water needs due to population growth in Atlantis and the lower production capacity of the wellfields (Figure 29; Tredoux and Cavé, 2002; Bugan *et al.,* 2012).

There has been an extensive amount of research available on the Atlantis Aquifer since the inception of the groundwater scheme in the mid-1970's, with recent research focused on remediation of the iron-related operational problems with boreholes that either had to be abandoned or reconstructed. From 1999 to 2002, thirty-seven production boreholes had to be rehabilitated using the BCHT process (Tredoux *et al.,* 2002; Flower and Bishop, 2003). However, the management and rehabilitation protocols have not given the desired long-term results, necessitating a need for investigation of other options such as ISIR treatment (e.g. Tredoux and Cavé, 2002; Tredoux *et al.,* 2004; DWA, 2010), which is the focus of this study. The prevention of production borehole clogging is especially relevant since there are currently plans to rejuvenate the economy of this low-income town of Atlantis, requiring a reliable water supply to support new socio-economic developments (CoCT, 2012; City News, 2013).

3.1 Study Area Location

The Atlantis Aquifer is situated on a low-lying coastal plain on the West Coast, approximately 35 km north of Cape Town and less than 5 km from the coast (Figure 29). Although, production boreholes in both the Silwerstroom and Witzand Wellfields are affected, a production borehole in the Witzand Wellfield was selected because it is the more productive of the two, having contributed 75-96% of the water supply from 2003-2011 (Bugan *et al.,* 2012). The Witzand Wellfield is situated 2.5 km inland from the coastline and covers an area of 3 km^2 (Fleisher, 1990). The production borehole selected (G30966) is located on the eastern side of the R27 West Coast Road, near the Witzand Softening Plant.

3.2 Background on Atlantis and its Water Supply

Atlantis developed in 1976 as an industrial town as a result of the apartheid government's decision to develop it as a de-concentration point under the National Physical Development Plan (Wright, 1991). However, subsequent rapid growth of Atlantis resulted in unplanned pressure on the infrastructure and services (Quayle, 2012). In addition, transport links between Atlantis and Cape Town never materialised and reduction of government subsidies to industry culminated in increasing unemployment and poverty in the area (Quayle, 2012).

Today, the town's population is greater than 100 000 people (DWA, 2011). This is double the total of the 2001 census (DWA, 2010) and triple that of the estimated population in 1990 (Fleisher, 1990). To date, the population consists primarily of working-class people employed in the local industries (Smith, 2006). In the quest to improve the socio-economics of the area, the recently developed "Atlantis Revitalisation Framework" plans to uplift and rejuvenate the town of Atlantis through re-development of industry, for example, establishing it as a Green Hub in the Cape Town Metropolitan (CoCT, 2012). This rejuvenation is also supported and encouraged with the development of the integrated rapid transit system linking Atlantis to Cape Town (City News, 2013).

Water supply to the towns of Atlantis and Mamre is managed through the AWRMS. Initially, groundwater supply to the newly developing town of Atlantis came from the perennial Silwerstroom springs as an interim measure until the surface water scheme from the Berg River some 70 km to the north-west was developed (Tredoux and Cavé, 2002; DWA, 2010). However, this connection did not materialise and forced the AWRMS to focus on developing a scheme that would be fully reliant on groundwater (Flower and Bishop, 2003). The first hydrogeological investigation within the area was completed in 1972 by the Geological Survey, now the Council for Geoscience (CGS). The DWA were charged with the initial development of the scheme, which has since developed to include two wellfields, Silwerstroom (production started in 1978; 15 production boreholes with individual yields between 3-5 ℓ/s) and Witzand (production started in 1982; 43 production boreholes with individual yields between 6-23 ℓ/s with majority ≥ 10 ℓ/s) (Cavé, 1997; Flower and Bishop, 2003; Bugan et al., 2012).

In 1979, as the population grew along with increasing runoff and wastewater, artificial recharge of the aquifer was considered and initiated in 1982 via Basin 7 (Tredoux and Cavé 2002). Artificial recharge was initially used as an alternative to the discharging of wastewater into the ocean and has since been developed as another source of recharge to the aquifer (Wright, 1991). From 1976 to 1999, the water demand was met by groundwater production (Flower and Bishop, 2003; Bugan et al., 2012). Despite the slightly higher operational and

maintenance costs, the groundwater scheme with artificial recharge proved to be an economical option in comparison to capital expenditure on surface water development from the Berg River or desalination (Tredoux and Cavé, 2002; Quayle, 2012). However, since 2000 surface water has been supplied to the AWRMS via the development of a pipeline near Melkbosstrand, which is supplied from the Voëlvlei Dam, initially only to meet peak demands (Tredoux and Cavé, 2002). However, by 2003, groundwater supply had reduced to 2.1 Mm^3/annum, half the historical average production capacity of the wellfields and in 2010, the total groundwater production drastically decreased to 0.67 Mm^3/annum (Bugan *et al.,* 2012).

The AWRMS is currently managed by the CoCT's Bulk Water Department with the CSIR as the appointed hydrological consultants and incorporates the following components (Figure 30; Tredoux and Cavé, 2002; Flower and Bishop, 2003; DWA, 2010):

- Groundwater supply from the Atlantis Aquifer is provided by production boreholes abstracting in two wellfields. The Silwerstroom boreholes are run continuously, whereas the Witzand boreholes are run individually depending on demand and the water softening plant capacity. The wellfield capacity of Silwerstroom is 1.8 Mm^3/annum and 5.0 Mm^3/annum for Witzand.

- After the groundwater is treated at the Witzand WTP, it is pumped for distribution to the Hospital (capacity of 30 000 m^3) and Pella Reservoirs (capacity of 50 000 m^3).

- Natural recharge of the Witzand Wellfield is augmented by up-gradient artificial recharge from two recharge basins (non-perennial Basin 12 to the north and perennial Basin 7 to the west). The basins are currently recharged with water collected from Atlantis urban stormwater and high quality treated domestic effluent after detention in maturation ponds.

- There are also four coastal recharge basins where industrial effluent and stormwater are diverted from the main aquifer in order to raise the water table and prevent seawater intrusion.

- The surface water supply pipeline to Atlantis is an 11.6 km gravity main from reservoirs near Melkbosstrand, which receives water from the Voëlvlei supply line.
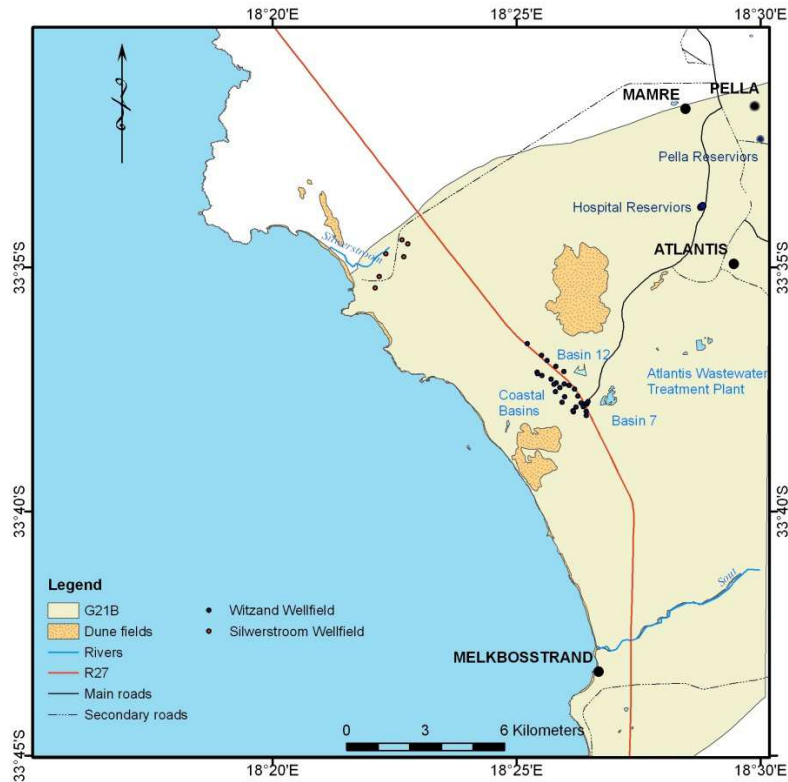
Figure 30: Map showing the various components of the AWRMS

3.3 Climate

The study area experiences a Mediterranean climate of dry, hot summers from October to March, followed by cool, wet winters (Tredoux *et al.,* 2002). The mean monthly maximum and minimum temperatures for the last three decades are given in Table 11. The average annual potential evaporation of the area is 1 613 mm, with the highest evaporation rates during the months of December and January and the lowest during July (Parsons, 2007). The rainfall is mostly associated with winter frontal systems yielding a 33-year mean annual rainfall of 457 mm (Figure 31).

3.4 Topography

The Atlantis Aquifer covers an area of 130 km^2 in a narrow, undulating coastal plain, between the Atlantic Ocean and the town of Atlantis (Tredoux and Cavé, 2002). The surrounding area is characterised by vegetated dune fields with an average height less than 15 m along the coast and granite outcrops in the north, which forms the highest points of the area at 240 meters above mean sea level (mamsl) north of Mamre (Stapelberg, 2005). The topography of the Witzand Wellfield is relatively flat between 50 to 60 mamsl as reflected by ground elevations of the Witzand Wellfield production boreholes (Cavé, 1997).

3.5   Drainage

The AWRMS is located in the hydrological Berg Water Management Area within the Quaternary catchment G21B. The natural drainage of the catchment is either in a south-east direction to the Sout River or in the west towards the Silwerstroom River (Figure 30; Parsons, 2007). However, all rivers in the area are non-perennial and sheet flow manifests during significant rainfall events (Wright, 1991). There are perennial springs in Silwerstroom and Mamre and a minor spring at Groot Springfontyn near the coast just south-east of Silwerstroom (Tredoux and Cavé, 2002).

3.6   Vegetation

The naturally occurring vegetation is classified into three biome types (Stapelberg, 2005):

- *Dune Thicket:* occurs intermittently as dense thicket on sands (mainly the alkaline dunes) along the coastline (< 30 mamsl);

- *West Coast Renosterveld*: this fynbos vegetation is associated with the higher elevations in the area but most of the natural vegetation has been destroyed due to wheat farming in the area;

- *Sand Plain Fynbos*: this vegetation type covers the majority of the area found on the thick, alkaline-poor sands on the coastal plain. However, it has been severely impacted by alien vegetation such as *Acacia saligna* (i.e. Port Jackson) and *Acacia cyclops* (i.e. Rooikans).

Table 11: Mean monthly precipitation, maximum and minimum temperatures from 1980 to 2013 measured at the Atlantis Wastewater Treatment Works (WWTW), 8 km east of the study area (Appendix A)

Mean monthly values	January	February	March	April	May	June	July	August	September	October	November	December
Maximum temperature (°C)	27.5	27.9	26.7	24.1	21.0	18.4	18.0	18.2	19.8	22.6	24.3	26.3
Minimum temperature (°C)	14.4	14.7	13.3	10.9	8.8	6.7	6.0	6.4	8.0	9.8	11.5	13.7
Precipitation (mm)	10.9	12.4	14.5	37.2	56.5	77.9	76.5	68.7	44.1	23.6	20.5	14.0
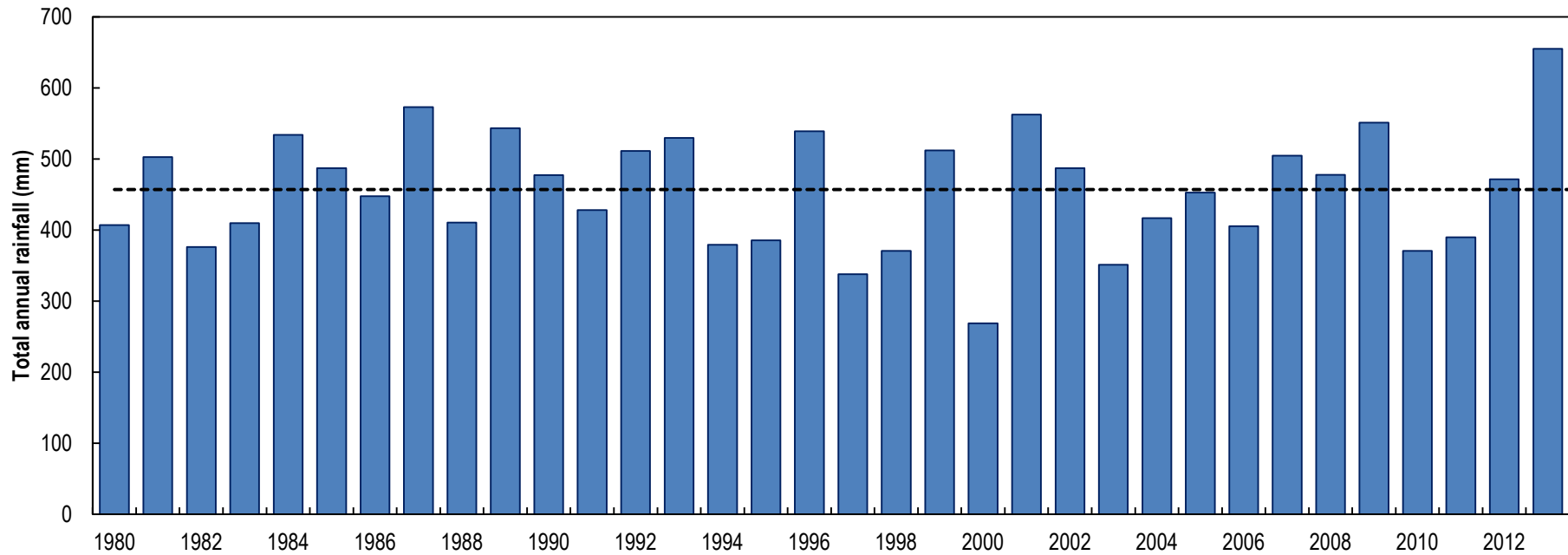
Figure 31: The total annual rainfall measured from 1980 to 2013 with the dashed line showing the long-term average of 457 mm (Appendix A)

3.7   Regional Geology

The Atlantis Aquifer is comprised of Cenozoic sands of the Sandveld Group, a widespread sandy succession extending from False Bay to Elands Bay, which was deposited on the various basement rocks during global sea-level changes (Figure 32; Roberts *et al.,* 2006). The oldest basement rocks are the Malmesbury Group, which is a unit of low-grade, regionally metamorphosed sediments (Stapelberg, 2005). It is represented in this area by the Tygerberg Formation, which is a rhythmic succession of greywacke and phyllitic shale (van der Merwe, 1980). The Malmesbury rocks were intruded by granites of the Cape Granite Suite (c. 550 Ma; Scheepers, 1995). The Malmesbury bedrock underlies the Witzand Wellfield with sporadic shale exposures along the coast, with outcrops of the granites and Malmesbury only found to the north near the town of Mamre (Figure 33; Tredoux and Cavé, 2002). The principal Sandveld Group units present in the Witzand Wellfield are the Varswater, Springfontyn and Witzand Formations (oldest to youngest).

AGE		Formation	Lithology
QUATERNARY	Holocene	Witzand	Aeolian, fine to medium-grained calcareous-rich quartz sands
	Pleistocene	Springfontyn	Marine deposit of fine to medium-grained, calc-poor quartz sands
		Langebaan	Aeolian, fine to medium-grained calcareous semi-consolidated sands with calcrete lenses
		Velddrif	Shallow marine deposit of gravel, shelly and pebble sands
NEOGENE	Pliocene	Varswater	An estuarine/shallow marine deposit consisting of muddy quartz sands, which are shell and phosphate-rich.
	Miocene	Prospect Hill	Aeolian, bioclastic calcareous sands
		Elandsfontyn	Fluvial deposited unit, consisting of gravel-rich, angular quartz sands with peaty clay lenses

Figure 32: The Sandveld Group distribution (left) and stratigraphy (right) (Roberts, 2006; Roberts *et al.,* 2006)

The basal Varswater Formation unconformably overlies the Malmesbury bedrock and consists of a muddy gravel base overlain by well-sorted and rounded, fine-grained quartz sands with peat lenses and phosphatic shell fragments (Fleisher, 1990). It is intersected

within the Witzand Wellfield in various production boreholes at a depth of > 35 meters below ground level (mbgl), displaying a thickness of three to eight metres ($n = 16$; Cavé, 1997).

The Springfontyn Formation is represented by unconsolidated well-sorted quartz sands that are fine to medium-grained (Fleisher, 1990). The base of the unit is muddy and in places the sands are interfingered with much finer peat-rich sand lenses (van der Merwe, 1980). The formation is distinctive due to its absence of calcareous shell fragments, which is thought to have been removed by leaching of shells by naturally acidic rainfall (Tredoux and Cavé, 2002). This unit covers the majority of the study area as vegetated dunes and within the Witzand Wellfield is the targeted water-bearing formation that all the production boreholes extract from due to the coarser grain size compared to the overlying Witzand Formation (van der Merwe, 1980; Fleisher, 1990; Stapelberg, 2005). It is intersected at approximately 15 mbgl and has an average thickness of 22 m within the wellfield and generally screened between 25-35 mbgl ($n = 16$; Fleisher, 1990; Cavé, 1997).

The overlying Witzand Formation is an aeolian deposit consisting of calcareous, fine to medium-grained quartz sands with discontinuous calcrete lenses (Roberts *et al.,* 2006). This unit is characterised as unvegetated, elevated white sand dunes in the central parts of Atlantis and in the Witzand Wellfield, its average thickness is 14 m ($n = 16$; Cavé, 1997; Tredoux and Cavé, 2002).
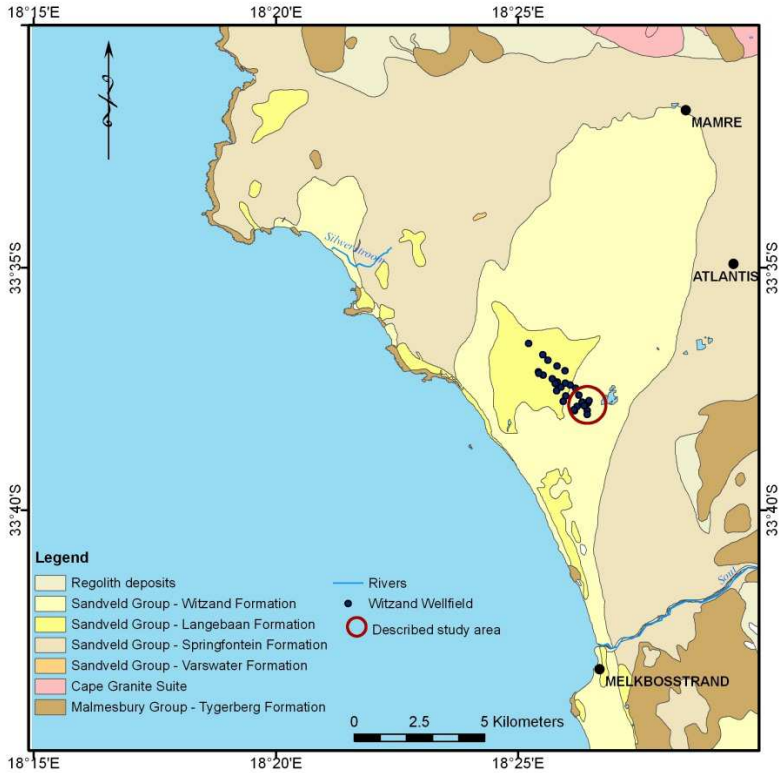
Figure 33: Geological map of the study area (data from Stapelberg, 2005)

3.8   Regional Hydrogeology

3.8.1   Aquifer types

The Atlantis Aquifer is the principal groundwater resource and is defined as the saturated part of the Sandveld Group sediments (Fleisher, 1990). In essence, there are two types of aquifers identified within the Witzand Wellfield, namely the upper primary, intergranular Atlantis Aquifer and the secondary, fractured-rock Malmesbury Group Aquifer (Tredoux and Cavé, 2002). Even though there is groundwater in the underlying bedrock, the upper surface of the bedrock has weathered to form a substantial clay layer, which restricts any flow between the two aquifer systems (Tredoux and Cavé, 2002). The configuration of the Atlantis Aquifer is irregular with the Malmesbury bedrock being the lower limit and the lateral boundaries defined by the coastline in the west, with the pinching out of the saturated Sandveld sands in the north, east and south (Tredoux and Cavé, 2002). The water-bearing sediments can be up to 40 m thick depending on the bedrock elevation, however in the Witzand Wellfield, the maximum saturated thickness does not exceed 35 m (Fleisher, 1990; Tredoux *et al.,* 2002). Although there is no vertical flow between the two aquifers, the bedrock topography plays an important role in compartmentalising the Atlantis Aquifer, dividing it into six hydrogeological sub-units (Figure 34; Tredoux and Cavé, 2002). The Witzand Wellfield is within the Klein Springfontyn-Witzand sub-unit and groundwater flow between adjacent compartments occurs when the water table rises above the palaeoridges (Tredoux and Cavé, 2002).
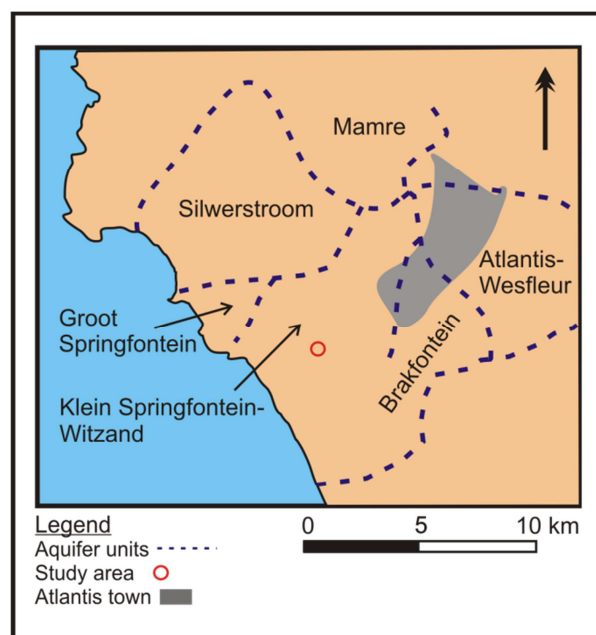
Figure 34: The Atlantis Aquifer is divided into six sub-units due to the bedrock topography (modified from Tredoux and Cavé, 2002)

3.8.2   Groundwater levels and flow direction

The static water level in the Witzand Wellfield is generally shallow, with water table levels varying from 1 to 6 mbgl, which mimics the surface topography (Fleisher, 1990). The static groundwater elevations decrease steeply from 130 mamsl in the interior of the coastal plain to sea level along the coastline (Figure 35; Bugan *et al.,* 2012). The general regional groundwater flow direction within the Witzand Wellfield is in a south-westerly direction, which discharges into the Atlantic Ocean, although local deviations do occur near the recharge basins (Figure 35; Bugan *et al.,* 2012).
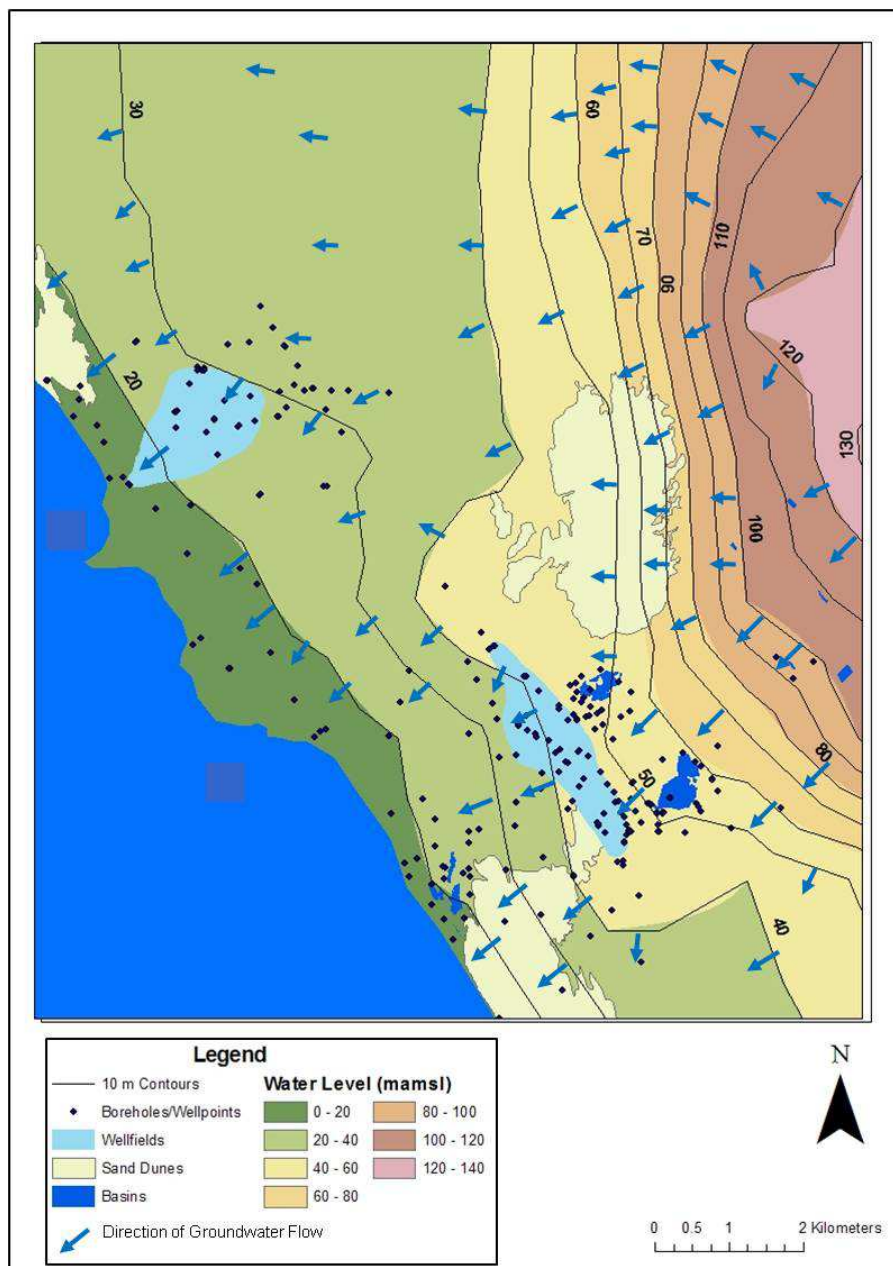
Figure 35: Contour map of the groundwater elevations within the Atlantis Aquifer from water levels taken in December 2010 (Bugan *et al.,* 2012)

3.8.3   Recharge

The natural recharge of the Atlantis Aquifer is limited because of a lack of major surface water drainage and semi-arid climate (Flower and Bishop, 2003). The average recharge in the study area ranges between 15 to 30% of the mean annual precipitation with higher recharge occurring in the mobile unvegetated dune fields (Tredoux *et al.,* 2002). To maximise the groundwater supply, artificial recharge has been incorporated to augment natural recharge (Tredoux and Cavé*,* 2002). However, due to topographic constraints, artificial recharge only takes place up-gradient of the Witzand Wellfield through two infiltration basins. It is estimated that approximately 25-30% of the Atlantis' groundwater supply is supplemented by artificial recharge, which takes between 18 to 24 months to reach the Witzand Wellfield (DWA, 2010).

3.8.4   Hydraulic properties

In general, the Atlantis Aquifer is a phreatic, heterogeneous and anisotropic aquifer (Fleisher, 1990). The facies changes cause lateral and vertical zonation of the aquifer and as a result the hydraulic conductivities (K) vary widely and in some places, the aquifer displays semi-unconfined characteristics (Tredoux and Cavé, 2002). This is often associated with delayed yield behaviour where there are calcrete lenses and/or finer grained sands in the upper units (Tredoux and Cavé, 2002). The calculated average hydraulic conductivity values for the Springfontyn and Witzand Formations are 25 m/day or < 6 m/day when the units contain peat and silt-rich facies changes (Fleisher, 1990). The underlying Varswater Formation has much lower hydraulic conductivity values in the range of 1.0-3.5 m/day due to its high silt content (Fleisher, 1990). The overall hydraulic conductivity value calculated for the Witzand Wellfield is 2.1 m/day (Tredoux and Cavé, 2002).

A wide range of transmissivity (T) values have been found in the Witzand Wellfield as a result of the heterogeneity of the aquifer system, ranging from 100 to 1 400 m^2/day calculated from pumping tests (Fleisher, 1990; Cavé, 1997). Similarly, the calculated specific yield (Sy) within the Witzand Wellfield also varies, with the pumping tests giving values ranging from 0.19-0.27 (Fleisher, 1990) and 0.0004-0.02 (Cavé, 1997). However, the unrealistic low specific yields values reported for some production boreholes in Cavé (1997) have raised questions about the accuracy of the pumping test data and/or its interpretation. Other estimates of the specific yield gave Sy = 0.25 from the water balance (Fleisher, 1990), whereas laboratory analysis of the sediments gave Sy = 0.09-0.18 and model calibrations provided Sy = 0.11-0.17 (Tredoux and Cavé, 2002).

3.8.5 Water quality

The majority of water samples taken over the extent of the entire Atlantis Aquifer have a Na-Cl character due to the marine-origins of the Varswater Formation sands, shale bedrock, wind-blown sea salt aerosols and semi-arid climate (Tredoux *et al.,* 2002). In contrast, the groundwater abstracted from the Witzand Wellfield has a Ca-HCO$_3$ character due to recharge through the calc-rich Witzand Formation as well as a lower salinity due to high recharge from a nearby dune field and it being a thicker sand sequence (Tredoux and Cavé, 2002). In addition, the groundwater pH in the Witzand Wellfield is slightly higher and has a smaller range of values than other parts of the Atlantis Aquifer due to the buffering capacity of the calcareous Witzand Formation (Tredoux and Cavé, 2002). A summary of the groundwater quality from the production boreholes in the Witzand Wellfield from 1976 to 2011 is given in Table 12.

Table 12: Witzand Wellfield groundwater quality from 1976 to 2011 (Tredoux *et al.,* 2012)

Parameter*	Sample size (*n*)	Mean	Range	Q25	Q50	Q75
Electrical conductivity (EC) (mS/m)	5817	80	12-194	69	78	91
pH	5538	7.5	5-10	7.4	7.5	7.7
Total hardness as CaCO$_3$	5435	253	27-1268	226	257	282
Calcium (Ca)	5470	88	12-465	74	92	100
Sodium (Na)	5297	72	2-225	49	70	89
Magnesium (Mg)	5474	8.4	1-82	6	8	10
Potassium (K)	5335	2.2	0.01-36	1.2	1.7	2.5
Total alkalinity as CaCO$_3$	5715	192	28-316	162	208	220
Chloride (Cl)	5671	124	10-416	90	120	152
Sulphate (SO$_4$)	4483	42	10-1904	28	39	51
Nitrate (NO$_3$) as N	4845	0.7	0.1-553	0.1	0.3	0.6
Total Fe	4566	0.7	0.1-637	0.10	0.14	0.40
Total Mn	1598	0.08	< 0.005-2.1	0.005	0.01	0.12
Ammonium (NH$_4$) as N	4483	0.05	< 0.1-6	< 0.1	0.1	0.1
Total organic carbon (TOC)	262	6.6	1-56	4.9	6.7	8.0
*Data in mg/ℓ unless otherwise specified						

The Atlantis groundwater quality is influenced by the aquifer lithology, overlying vegetation and artificial recharge. In particular, the Witzand Wellfield groundwater characterised by high hardness, DOC and iron (Tredoux and Cavé, 2002; Bugan *et al.,* 2012; Tredoux *et al.,* 2012). Due to the different facies changes during the deposition of the Sandveld sands the water quality can vary throughout the aquifer (e.g. the variability of calcrete and peat lenses produces local differences in Ca and SO_4 concentrations). The hardness is due to the calc-rich Witzand Formation and the iron (and sulphate) is often attributed to pyrite in the peat lenses of the Springfontyn Formation (Tredoux and Cavé, 2002). The lack of dense thicket or fynbos on the dunes in the recharge area played a role in the naturally high DOC content of the Witzand groundwater (Bugan *et al.,* 2012). However, the DOC has also been increased by artificial recharge up-gradient of the Witzand Wellfield (Tredoux *et al.,* 2002). Artificial recharge was initiated in the AWRMS to ensure that the Atlantis Aquifer could sustainably supply the town's bulk water demands, even in a semi-arid environment (Tredoux and Cavé, 2002). However, in the first half of the 1980's it increased the trace metals, salinity and DOC load in the groundwater in close vicinity to Basin 7 (Tredoux and Cavé, 2002). This occurred because the industrial wastewater effluent was also recharged with domestic effluent but in November 1986 this was stopped and only urban stormwater was recharged, which saw a water quality improvement (DWA, 2010). From 1992, high quality, treated domestic effluent was recharged improving the salinity levels in the Witzand Wellfield, which has also progressively declined since 1999 due to surface water improving the domestic effluent recharged (Tredoux *et al.,* 2012).

Due to the level of hardness in the Witzand groundwater not meeting the textile industry standards, the blended groundwater is processed through the Witzand Softening Plant (built in 1986) by ion exchange with sulphuric acid (Bugan *et al.,* 2012). During the ion exchange process, hardness is reduced by the removal of Mg and Ca retained in the resin as well as the removal of most of the iron by the ion exchange processes (Tredoux *et al.,* 2012). The H^+ ions released during this treatment forms carbonic acid, which reacts with the bicarbonate ions in the groundwater to form carbon dioxide and water and also reduces the total alkalinity (Tredoux *et al.,* 2012). However, this treatment does not remove the DOC from solution, which is problematic as high DOC causes difficulties in the subsequent chlorination of the groundwater by the formation of THMs compounds (DWA, 2010). The presence of iron in the groundwater is a well-known cause for failure of softening plant operation (e.g. Alchin, 2008), however the current Hazard Assessment and Critical Control Points system for the AWRMS regards the failure of the Witzand Softening Plant as a low risk to the water supply system (Genthe *et al.,* 2012).

3.9 Production Borehole Clogging

The AWRMS faces several challenges with the highest risk to its operation is iron-related clogging of production boreholes (Genthe *et al.,* 2012). Clogging is experienced in all of the boreholes in both wellfields to varying degrees of severity (Flower and Bishop, 2003). The natural occurrence of iron in the groundwater has always been a concern, but only in the early 1990's was the significance of iron-related clogging fully appreciated when a number of the Witzand Wellfield production boreholes went out of commission or were about to fail (Figure 36; Tredoux *et al.,* 2002; Flower and Bishop, 2003). The problems at the AWRMS were only noticed in the late 1980's in the form of declining yields, reddish water, H_2S odour and precipitates lining the distribution pipes (Tredoux *et al.,* 2002; More Water cc., 2002; Flower and Bishop, 2003). In 1991, down-hole camera logging, water samples and slime on the pumps and rising mains were collected from boreholes in both wellfields by DWA. This also identified the extensive clogging of the borehole screens by Fe(III)-oxyhydroxide deposits, which was then ascribed to biofouling (Tredoux and Cavé, 2002; More Water cc., 2002).

Figure 36: Severe clogging of production borehole G33104 pump intake (left) and MIC by sulphate-reducing bacteria of the non-return valve in production borehole W34001 (right) (More Water cc., 2002)

The presence of iron was attributed to the naturally occurring iron-rich sulphide minerals in the Sandveld Group sediments, aided by the naturally high DOC, which lead to reducing conditions in the aquifer (Tredoux and Cavé, 2002). Furthermore, the start of clogging

processes was primarily attributed to the over-abstraction of the aquifer (Flower and Bishop, 2003).

According to a number of researchers (Tredoux and Cavé, 2002; More Water cc., 2002; Flower and Bishop, 2003; DWA, 2010; Genthe *et al.,* 2012; Quayle, 2012) other factors that also attributed to the severity include:

- *Incorrect borehole construction*: Many different borehole designs were tried and some purely experimental at Atlantis due to the unconsolidated sediments and fine sands as well as costs;

- *Incorrect sustainable yield*: Estimated yields were sometimes too optimistic resulting in over-abstraction and excessive lowering of the water table, which resulted in ingress of oxygen that could have promoted bacterial activity or pyrite oxidation in the peat layers;

- *Lack of a preventative maintenance strategy*: The scheme lacked skilled staff and equipment for monitoring;

- *Artificial recharge:* Increased DOC and nutrients, as well as the microbial risk, from the recharge of stormwater, treated industrial effluent and domestic effluent, which played a role in iron and manganese mobilisation. To mitigate the introduction of an organic load into the aquifer, the recharge of industrial effluent was stopped in 1986 and plans are in place to subdivide Basin 7. However, since the Witzand Wellfield is only artificially recharged and the Silwerstroom Wellfield also experienced clogging problems, artificial recharge is not the main cause of increased DOC and other contributors proposed to have an influence on the iron and manganese movement included the presence of alien vegetation, cemeteries, animal feedlots or unserviced informal settlements in the recharge site.

- *Basin clogging*: over time the clogging of the recharge basins by fine sediments and organics also impacted the Atlantis Aquifer by decreased infiltration rates and coupled with high production, it contributed to the lowered water table. To resolve this Basin 7 was dried out in 1989;

- *Water level decline*: The water level decline was aggravated because the building of the WWTW facilities to separate the domestic and industrial effluent was still in progress and only stormwater runoff could be recharged from 1986 to 1992. In addition, between 1994 and 2000, the area experienced a lower than normal rainfall,

resulting in a declining water table over many years; it is however not clear what influence this might have had on the clogging processes.

In addition, potential risks that could contribute to iron-related clogging problems may be due to the unconfined nature of the Atlantis Aquifer:

- The Atlantis WWTW was initially considered as a source of pollution ingress due to the elevated nitrate, potassium and DOC load down-gradient of the plant due to unlined sludge drying beds, which could cause the reducing conditions and mobilisation. However, subsequently, it has been established that the pollutants are restricted to the Brakkefontein compartment and would not impact the Witzand Wellfield (Figure 34; Tredoux *et al.,* 2002).

- An oil pipeline runs parallel to the R27 West Coast road passing the Witzand Wellfield. Although a spill has not yet occurred, the pipeline presents a threat to the wellfield (Tredoux *et al.,* 2002), as iron and manganese mobilisation is known to be associated with hydrocarbon spills (Appelo and Postma, 2005).

From 1991 to 1995 the initial attempts to treat the clogged boreholes involved treatment with citric acid, which did return some of the borehole yields but this was short-lived as the problem later returned (Flower and Bishop, 2003). By 1997, the reliability of the production boreholes remained very low. The situation became critical in 1998, resulting in extensive and costly rehabilitation over the four years by More Water cc., as well as a need for surface water to be brought in to meet peak demands (Flower and Bishop, 2003).

In total, thirty-seven production boreholes in the Witzand and Silwerstroom Wellfields had to be rehabilitated using the BCHT method in 1999 to 2002, which then restored the yields of many of the boreholes (More Water cc., 2002). The rehabilitation programme also assessed whether it was cost-effective to restore the borehole yields using the BCHT process or whether it would have been better to abandon them altogether due to poor borehole construction or the extent of clogging (More Water cc., 2002). All boreholes investigated were camera logged before and after to have a visual baseline of the severity of clogging and the effects of the treatment in removing the material (More Water cc., 2002). In addition, step drawdown pumping tests and chemical analyses before and after the treatment were done (Flower and Bishop, 2003). All effluents resulting from the treatment of the production boreholes had to be neutralised and safely disposed of. This was achieved by pumping the wastewater into commercially supplied Waste Tech tankers and removing it from site to be disposed of in the industrial waste stream (More Water cc., 2002; Flower and Bishop, 2003).

After the rehabilitation treatment, More Water cc. (2002) also recommended the implementation of a monitoring and maintenance programme for each production borehole with the aim to prevent the production losses from recurring due to iron-related clogging. It was also recommended that nearly all pumping specifications be changed to take into account reassessed borehole yields and new abstraction plans be adopted by decreasing pumping rates and increasing pumping hours, which would limit water level fluctuation (Flower and Bishop, 2003).

However, less than a decade after the intensive rehabilitation treatment and new management protocols were proposed, the wellfields currently contribute only 30-40% of the water demand for Atlantis and Mamre (DWA, 2011). Currently only 28 of the 43 production boreholes are in operation in the Witzand Wellfield and 13 of the 15 production boreholes are in operation in the Silwerstroom Wellfield, due to iron-related clogging (Bugan *et al.,* 2012). According to Tredoux and Cavé (2002), Flower and Bishop (2003) and DWA (2010), the reasons for the lack of long-term success in preventing production borehole clogging are:

- Borehole yields were lowered after the rehabilitation treatment, but it was not always possible to lower the abstraction rates. As more funds become available, more boreholes were drilled to help meet demand and reduce over-abstraction;

- Clogging recurred due to incorrect management or lack of monitoring;

- Rehabilitation treatment programmes are costly and require specialist skills and equipment. They can only proceed when funds are available, usually after a lengthy tendering process.

CHAPTER 4.   SITE CHARACTERISATION

4.1   Preliminary Evaluation

Even though ISIR treatments have been applied for decades, there are no established prototype design criteria and the application methodology is generally dependent on site characteristics (Karakish, 2005; van Essen *et al.*, 2005). A preliminary evaluation is necessary to assess whether such treatment would be feasible at the selected site and to understand the site characteristics upon which the prototype design and methodology could be based. This evaluation involves the compilation of all relevant historical data on the investigated borehole, i.e. borehole construction, local geology, hydrogeological parameters and water quality. Comparison of the known baseline chemistry to the treatment results may then also be used to establish the outcomes and effectiveness of the ISIR treatment.

After discussions with relevant role players in charge of the Witzand Wellfield production borehole G30966 was selected as the most suitable test borehole to undertake the ISIR experiment. The reasons for its selection include:

- It was not used at the time as a production borehole and consequently could be taken off the pumping scheme to carry out the tests without impacting water supply;

- The borehole has been affected by iron-related clogging and was rehabilitated by the BCHT treatment in 2000;

- The site is suitable for construction of an ISIR prototype as it is the closest production borehole to the Witzand WTP, which provides greater security and better logistical support;

- There were already two monitoring points in close vicinity, i.e. G30979 approximately 16 m NE and well-point 63 (WP63) approximately 11 m WNW of G30966 (Figure 37).
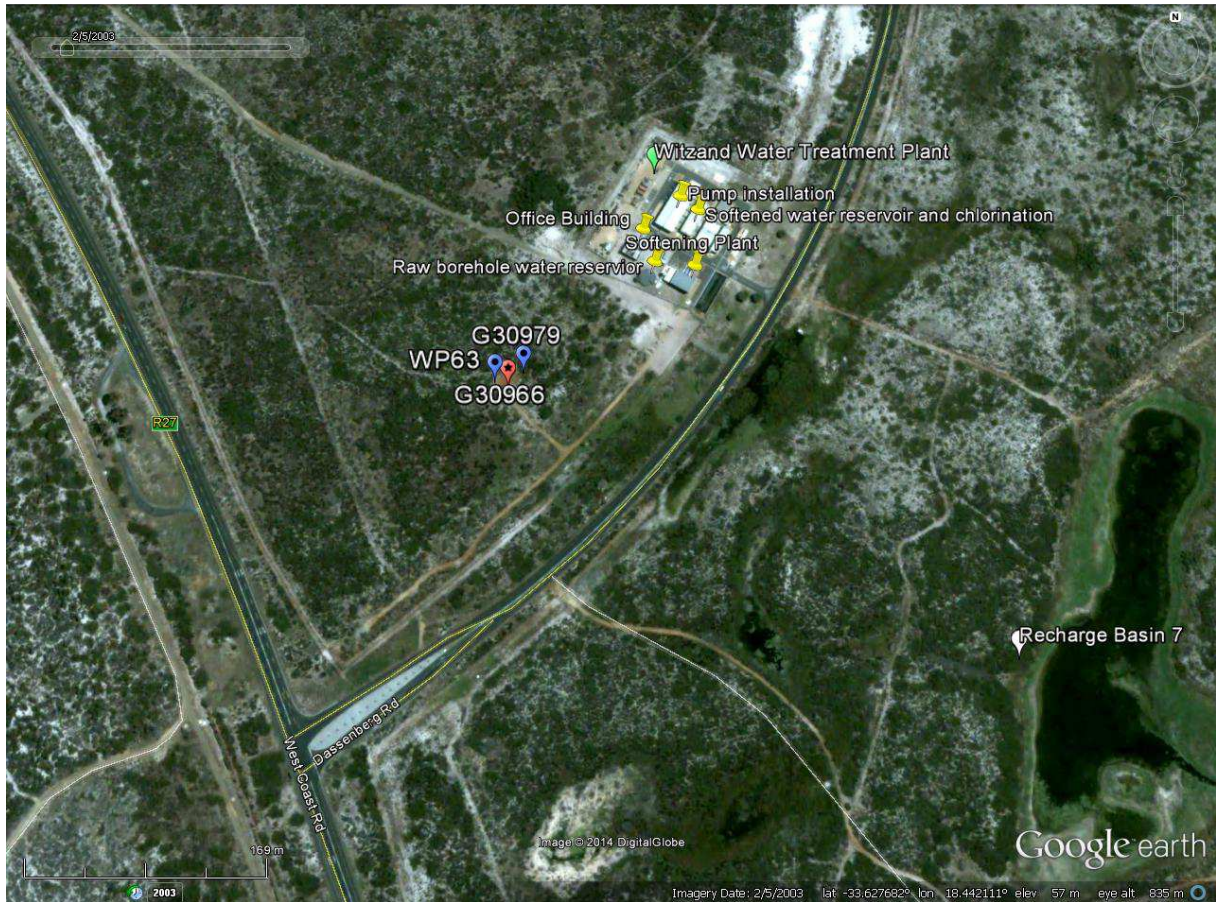
Figure 37: Google Earth image of production borehole G30966 and the two monitoring boreholes (marked blue) in close vicinity to the Witzand WTP (accessed 7 February 2013)

4.2 Borehole Construction

Production borehole G30966 was sited by the CGS and percussion drilled in 1979 to a depth of 42 m using a drilling diameter of 304 mm (van der Merwe, 1980; Cavé, 1997). It was constructed using solid steel casing with a 203 mm internal diameter to a depth of 24 m (van der Merwe, 1980). The borehole was screened from 24 m to 30 m with 150 mm internal diameter Johnson 30 stainless steel wedge pipe (i.e. slot size 0.75 mm) (van der Merwe, 1980). The gravel pack in the annulus between the Johnson screen and Springfontyn Formation is class number 7/16 gravel (i.e. 1.2 mm-2.8 mm) (van der Merwe, 1980).

According to van der Merwe (1980) its collar height is 55.02 mamsl at surface elevation of 54.67 mamsl, however the collar has since been damaged and the current collar elevation is 54.91 mamsl. More Water cc. (2001) mentioned that camera logging G30966 in October 1999 identified the lower nine metres of the borehole to have been lost due to sand infill, reducing the screened length to four metres. Unfortunately there is no further information on this situation that could be used to confirm this loss (i.e. no camera logging record or sand content measurements).

The nearby borehole G30979 was drilled as the observation borehole for G30966 (Nealer, 1979b; Bertram *et al.*, 1984). It was also sited by the CGS and percussion drilled with a drilling diameter of 304 mm in 1979 but only to a depth of 34 m (van der Merwe, 1980). It has a solid steel casing with a 203 mm internal diameter to a depth of 19.5 m and was equipped from 19.5 m to 30.0 m with a steel screen having slot openings of 17 mm x 300 mm and two layers of U-34 bidim wrapped around it (Bertram *et al.,* 1984). Its collar elevation is given as 54.66 mamsl and it has a surface ground elevation of 54.45 mamsl (Bertram *et al.*, 1984). During a field visit on 6 June 2011, it was identified that there is no surface seal on G30979 and the collar has also been reduced to only 0.1 m. The other monitoring point, WP63, was drilled to function as a groundwater level monitoring point for monthly measurements from 1989 (Tredoux and Cavé, 2002). The well-point is constructed of 50 mm PVC pipe but the exact drilling date is unknown. In June 2011 it was measured to a depth of eight metres by the author, a depth which was confirmed in 2012 by Bugan *et al.* (2012).

4.3   Local Geology

The geological logs of G30966 and G30979 are shown in Figure 38. The Witzand Formation is present in the study area to a depth of 13-14 m, with the Springfontyn Formation having been intersected at 13.2 mbgl in G30979 and 14.1 mbgl in G30966 (van der Merwe, 1980; Bertram *et al.*, 1984). The Varswater Formation occurs in both boreholes at a depth of 30.0 mbgl, but is thinner to the NE in G30979 by approximately three metres where the weathered Malmesbury Group was intersect at 33 mbgl, compared to G30966 where the Malmesbury Group was only intersected at a depth of 36.6 mbgl (van der Merwe, 1980; Bertram *et al.*, 1984).

The Springfontyn Formation at 14 to 30 mbgl is the target unit for the injection of oxygenated water because the Witzand Wellfield production borehole screens (including G30966) are all located within this unit. The geological information does not show any structural features (e.g. faults) or lithological complications (e.g. very coarse-grained layers) in the target area that could cause preferential flow-paths of the injected water (e.g. Appelo *et al.,* 1999). According to the sediment logs of G3099, the average grain size in the target zone ranges from fine to medium-grained quartz sand (van der Merwe, 1980). This is ideal as such sand grains normally provide suitable sites for the adsorption of Fe(III)-oxyhydroxides formed when Fe^{2+} is oxidised (e.g. Sharma, 2001). With multiple injection-abstraction cycles, it is expected that a high exchange capacity will develop with increased oxides coating on the clean quartz sands. Since there are only minor amounts of clay and organic matter in the aquifer sediments, it is also expected that the carbonate minerals in the Witzand Formation

will enhance the migration of Fe^{2+}, Mn^{2+} and PO_4^{3-}, as well as provide a sufficient buffering capacity for the acidifying oxidation reactions (Tredoux *et al.*, 2002).
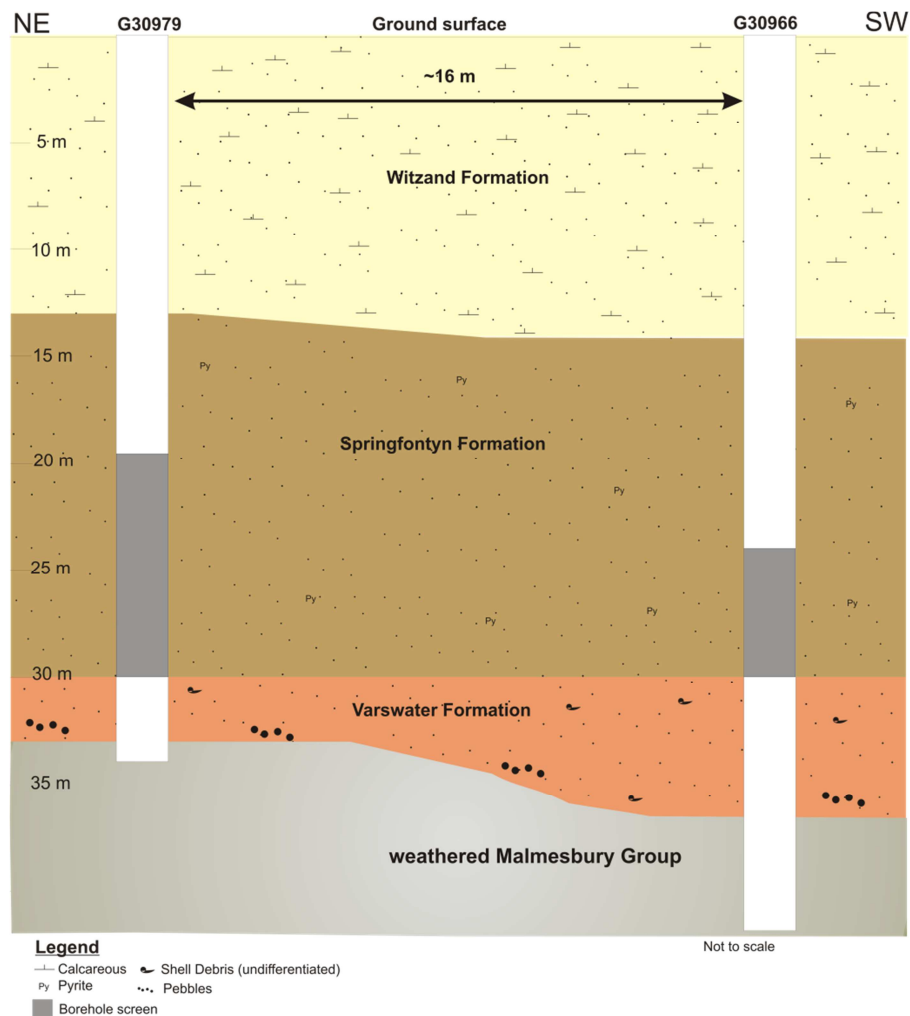
Figure 38: Geological profile between G30966 and G30979

4.4 Long-term Water Levels

The historical groundwater levels measured in G30966 and monitoring boreholes G30979 and WP63 from May 1979 to December 2013 are shown in Figure 39. These water levels were collated from monitoring by the AWRMS, reports (i.e. Nealer, 1979a; 1979b; van der Merwe, 1980; Bertram *et al.*, 1984; Fleisher, 1990; More Water cc., 2001) and additional static water levels collected by the author and AWRMS staff during the current study using a Solinst® dipmeter (Appendix B).

Initial groundwater levels were collected when G30966 and G30979 were constructed and developed in late 1979 (Nealer, 1979a; 1979b). Regular water level monitoring of the wellfield only commenced in 1985 (Tredoux and Cavé, 2002), with only sparse measurements made between 1979 and 1985. The introduction of the production borehole

into the pumping scheme in July 1982 (Bredenkamp and Vandoolaeghe, 1982) is seen from the measured lower pumping levels in G30966 in comparison to the known static level measured in the monitoring borehole G30979 from 1984 to 1993. However, from the reduction of static water and pumping level measurements of G30966 especially from 1993, it can be seen that G30966 was only used intermittently since 1989 for dilution of the brine generated at the Witzand Softening Plant and onsite irrigation (Tredoux and Cavé, 2002). The long-term groundwater level trends collected from G30966 and G30979 and increased drawdowns (i.e. difference between static water level and pumping level) in G30966 show a regional lowering of the water table from 1986 to late 1998. This is ascribed to the high production volumes demanded from the Witzand Wellfield, as well as to below average rainfall between 1994 and 1999 (Figure 31). The water table has progressively recovered since early 1999, rising to its highest recorded levels in 2013, since monitoring began in 1979 (Figure 39). This is the result of recharge (natural and artificial) actually exceeding abstraction from the poorly performing Witzand Wellfield (Bugan *et al.*, 2012).
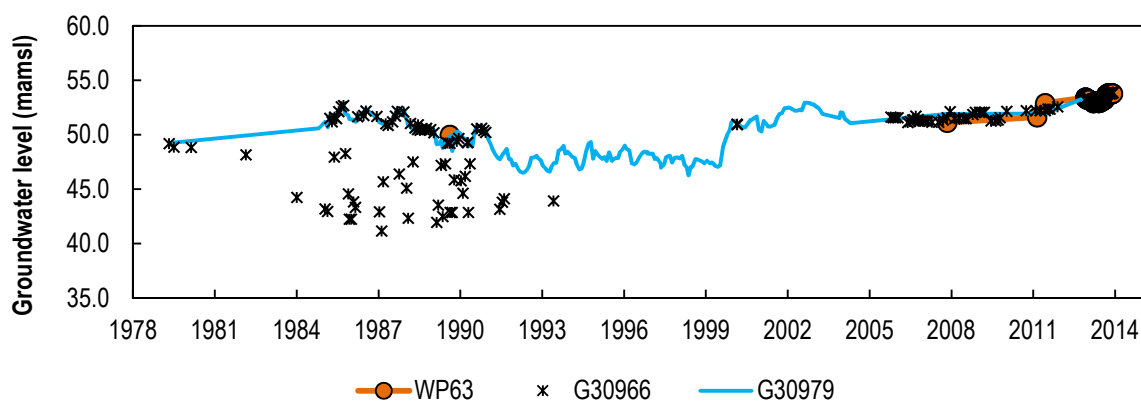
Figure 39: Long-term groundwater levels measured since the inception of the production borehole G30966

The static water table provides information on the ability of the aquifer to "receive" water, which assists in deciding the volume and rate of injection needed when designing the ISIR prototype (ISRRI, 2009). The very shallow water table in the study area (i.e. < 1.5 mbgl at the start of the study in 2012) is not ideal as this restricts the amount and rate of water that can be injected into the aquifer during ISIR because potential backpressure or surfacing of the injected water is more likely (ISRRI, 2009). This is due to there being insufficient space to release the hydrostatic pressure in the aquifer (ISRRI, 2009). In addition, it is known from the static water levels measured in all three boreholes that there are no drawdown responses in the study area by nearby production boreholes during the period G30966 was taken out of the Witzand scheme (since December 2012). This is ideal for the ISIR experiment, since the injected oxygenated water will not be preferentially drawn away from the treated borehole by abstraction at other proximal boreholes.

4.5   Borehole Efficiency

One of the long-term benefits of ISIR treatment is its potential for the prevention of borehole clogging and limiting of reduction in borehole efficiency. This efficiency is gauged by comparing the specific capacity over time with the highest specific capacity obtained immediately after the borehole was drilled and properly developed (Driscoll, 1986; Johnson, 2005). This value can then be used as the 'benchmark' with which to compare future values (Driscoll, 1986; Johnson, 2005). A decline in specific capacity can be indicative of clogging of the borehole screen and/or gravel pack, pump failure or lowering water level (Driscoll, 1986; Johnson, 2005). It has been recommended that a decline of more than 5% should be taken as a "warning" sign of production problems and be followed up by further inspection to confirm whether clogging is the true cause of the decline (Anderson *et al.,* 2010). This baseline performance of a borehole is established by calculating the specific capacity (Sc) from step drawdown pumping test data, which is found by dividing the abstraction rate (Q) over the drawdown (Sw) at the end of each step (Anderson *et al.*, 2010). Although this parameter is commonly regarded as an indicator of only borehole performance, it describes the productivity of both the borehole and aquifer (Kruseman and de Ridder, 2000).

4.5.1   Methodology for step drawdown pumping test

Even though this study is a short-term feasibility investigation into the ISIR application, focusing primarily on the ability of the treatment in reducing the levels of Fe^{2+} and Mn^{2+} in the abstracted groundwater at Atlantis, the specific capacity of G30966 was determined before the injection tests started. This information would be complemented with down-hole camera logging of G30966 after the step drawdown test for a visible inspection of the condition of the borehole screen and construction. All historical step-drawdown pumping test data on G30966 from literature was collected and a step drawdown pumping test was carried out for this study on 9 January 2013. This pumping test consisted of four steps, each an hour long, at successively higher abstraction rates, followed by measurement of water recovery to the original static water level. The author and AWRMS staff used Solinst® dipmeters for measuring the drawdown in the pumped borehole (G30966) and observation boreholes G30979 and WP63 (Appendix C). The pumping test was conducted using the AWRMS 5-stage submersible pump with a 15 kW motor in conjunction with a 15 kW Yaskawa Variable Speed Drive.

The abstraction rate per step, number of steps, step duration and measurement intervals of the water level were decided upon using recommendations from Kruseman and de Ridder (2000) and information from the previous pumping tests performed on G30966 (Appendix C). The abstraction rate was measured using the flow meter on the production borehole setup,

with the average of three measurements taken per step. The pumping tests were carried out with an open-end discharge pipe and the pumped water was discharged at a distance of 26 m down-gradient of the pumped and observation boreholes to prevent any recharge interference. Static water level measurements in all three borehole were taken 48 and 24 hours before the pumping test was started and showed that there was no potential drawdown interference from nearby production boreholes that would affect the pumping data.

4.5.2   Results

At least five step drawdown pumping tests have been performed on G30966 since its construction in 1979 (i.e. Nealer, 1979a; More Water cc., 2001; AWRMS routine test in 2007). This includes the latest pumping test performed on 9 January 2013 (Table 13; Appendix C).

Table 13: The five step drawdown pumping tests performed on G30966 and calculated specific capacity for the related step

Step No.	Q (ℓ/s)	Time (min)	Sw (m)	Sc (m³/day/m)
Step drawdown pumping test No. 1 (08/05/1979)				
1	3.02	60	3.81	68.49
2	6.02	120	8.14	63.90
3	7.75	60	10.41	64.32
Step drawdown pumping test No. 2 (22/02/2000) before rehabilitation				
1	5.00	60	5.14	84.00
2	6.25	60	6.50	83.08
3	10.00	60	8.78	98.41
4	12.50	60	14.55	74.23
Step drawdown pumping test No. 3 (26/02/2000) after rehabilitation				
1	5.20	60	4.91	91.50
2	6.25	60	5.97	90.45
3	10.00	60	8.07	107.06
4	12.50	60	13.55	79.70
Step drawdown pumping test No. 4 (06/11/2007)				
1	0.40	30	0.29	119.17
2	0.90	30	0.77	100.99
3	7.70	30	5.87	113.34
4	14.30	30	11.18	110.51
Step drawdown pumping test No. 5 (09/01/2013)				
1	4.79	60	4.68	88.43
2	6.55	60	6.34	89.26
3	11.92	60	11.18	92.12
4	14.04	60	12.89	94.11

4.5.3   Discussion

To evaluate the accuracy of the specific capacity, values found from the step drawdown pumping tests were validated for agreement with the following conditions (Driscoll, 1986):

- The specific capacity of a borehole is inversely proportional to the increasing abstraction rate with time;

- The specific capacity decreases in proportion to the drawdown for an unconfined aquifer.

This inverse relationship between specific capacity and increasing abstraction rates with time is expected in an unconfined aquifer, as with every metre of drawdown within the cone of depression, that part of the aquifer is dewatered and thus the saturated thickness is decreased, which in turn reduces the rate at which flow to the borehole occurs (Driscoll, 1986). The specific capacity plots for the collected data from G30966 are shown in Figure 40 and Figure 41.
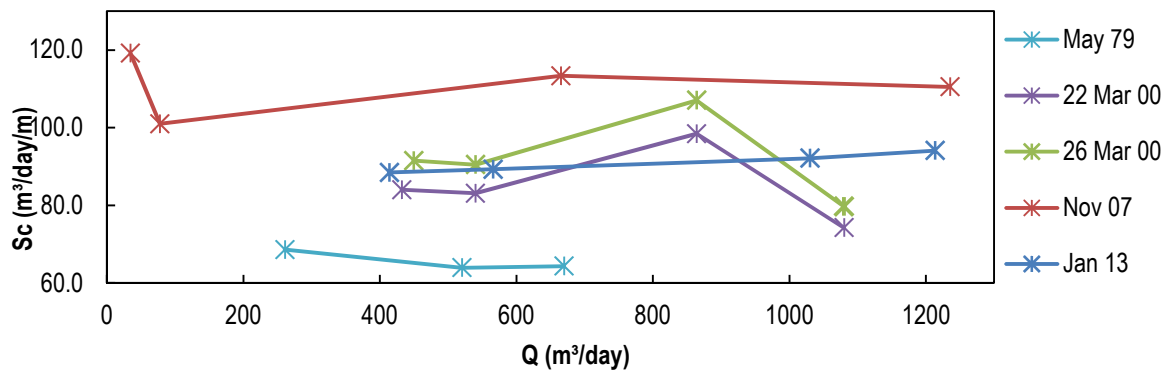
Figure 40: Abstraction rate vs. specific capacity of G30966 from the five step drawdown pumping tests
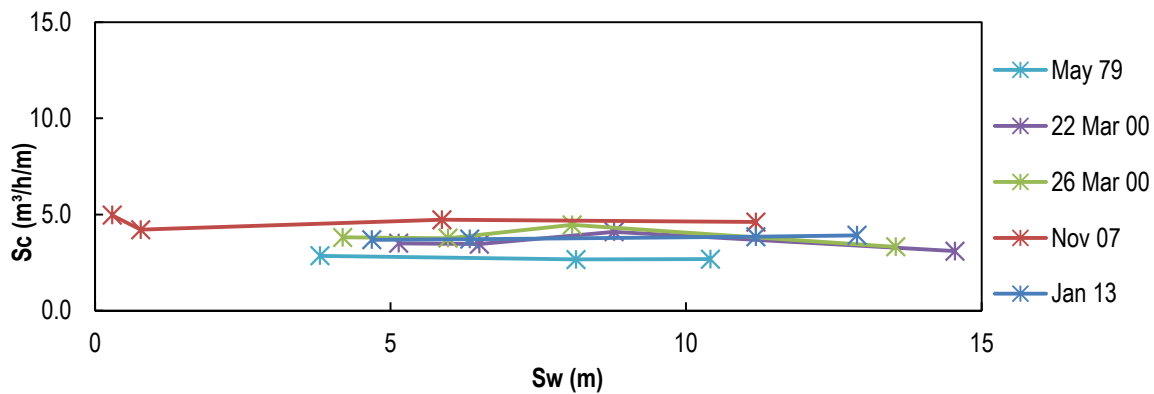
Figure 41: Specific capacity vs. drawdown of G30966 does not show the trends in unconfined aquifers as predicted by Driscoll (1986)

Only the 1979 step drawdown data show a decline with increasing abstraction rates, but there is concern about the accuracy of these results because specific capacity values calculated from the data should be calculated from steps of the equal time duration (Driscoll, 1986). Whereas, in this case the second step is double the other two steps (Table 13). This variability in step duration also causes problems with the comparison of subsequent specific capacity values and the original 'benchmark' specific capacity from 1979 because the subsequent step drawdown pumping tests do not closely match the original step drawdown pumping test (Flower and Bishop, 2003; Johnson, 2005). Contrary to expectations, the 1979 specific capacity values are the lowest of all when compared to subsequent step drawdown pumping test results. Thus, either one or both of the following scenarios could have contributed to the increase in specific capacity since 1979 (Driscoll, 1986; Johnson, 2005; Cullimore, 2008):

- G30966 was not properly developed at the time of the 1979 test and the borehole could have been further developed over time with the additional improvements from the BCHT rehabilitation;

- The increase in the groundwater level increased the specific capacity over time because of an increase of approximately 2 m in the saturated thickness of the aquifer since 1979.

Two step drawdown pumping tests were performed in 2000 to compare the borehole efficiency before (22 March 2000) and after BCHT treatment (26 March 2000). Both plots gave anomalies in the third step, which cannot be easily explained because if it was the result of a change in the system from linear to turbulent flow conditions, the specific capacity is expected to decline dramatically with increasing abstraction rates (Driscoll, 1986) and not to increase.

The November 2007 step drawdown pumping test also showed an anomaly at the second step, which could be attributed to the methodology of the step drawdown pumping test and application of an incorrect abstraction rate, for example it could have been too low in the first step to properly 'stress' the aquifer. In addition, the time intervals might have been too short (i.e. 30 minutes) and should have been at least an hour to allow for the water table to stabilise (Driscoll, 1986). Although there are anomalies in the last three step drawdown pumping tests described, the overall trend shows a decline in specific capacity with increasing drawdown (Figure 40).

The latest step drawdown pumping test in January 2013 showed the converse of what is expected, i.e. an increase in specific capacity with time, which is believed to have resulted from the abstraction rates or pumping levels having not been measured accurately. In addition, the specific capacity vs. drawdown results in all five step drawdown pumping tests do not show the proportional decrease with increasing drawdown (Figure 41), which could be attributed to the borehole screen only covering ≤ 14% of the whole aquifer and/or clogging of the borehole screen.

Down-hole camera logging of G30966 should have formed part of the borehole evaluation after the pumping test were performed but was not done due to constraints imposed by its procurement, which could not be resolved during the project timeframe. The lack of camera logging to investigate the role of clogging of G30966 and the concern over inaccuracies in the data collection from all the step drawdown pumping tests meant that changes in the borehole efficiency over time could not be accurately established, this issue was therefore not further addressed.

4.6   Hydrogeological Characteristics

The hydraulic parameters within the study area are of importance for ISIR application because a setting with high transmissivity is best-suited for any *in-situ* treatment as the mounding effect caused by the injection of a volume of water is smaller (i.e. water dissipates faster into the aquifer) in comparison to a low transmissivity value, which could limit the injection volume or rate of injection by pressure build-up (ISRRI, 2009). The hydraulic conductivity is also valuable as it represents the aquifer's (generally vertical) ability to 'accept' a given volume of water at a given injection rate (ISRRI, 2009). The sustainable yield of the borehole should also be known as it provides an estimate of the rate of injection the ISIR test can be conducted at.

4.6.1   Methodology of the constant discharge pumping test and analysis

Historical hydraulic characteristics of the aquifer within the study area (i.e. T and Sy values sourced from previous CDTs on the investigated borehole reported in van der Merwe, 1980 and Bredenkamp and Vandoolaeghe, 1982) and the sustainable borehole yield assigned to G30966 are given in Table 14. Unfortunately, the pumping test data was not included in both reports, but since van der Merwe (1980) and Bredenkamp and Vandoolaeghe (1982) both provided storativity values, it is assumed that drawdown was measured in an observation borehole and because G30979 is the closest borehole to G30966 (< 30 m) it is assumed to be the observation borehole from which the data was collected. In addition, it is assumed that

Bredenkamp and Vandoolaeghe used the late-time segment of the G30979 time-drawdown curve to find the hydraulic parameters because storativity is given as specific yield.

Table 14: Aquifer parameters of the Atlantis Aquifer at G30966 and its sustainable yield from previous pumping tests

Source	Hydraulic parameter		Method
van der Merwe (1980)	T (m²/d)	556	Cooper-Jacob method
	Storativity (S)	0.004	
	Yield (ℓ/s)	9.72	Maximum pump rate at a pump depth of 23 mbgl
Bredenkamp and Vandoolaeghe (1982)	T (m²/d)	280	Theis method
	Sy	0.14	
Cavé (1997)	Yield (ℓ/s)	5.5	Optimum pumping rate at a pump depth of 23 mbgl
More Water cc. (2001)	Yield (ℓ/s)	5.0	Optimum pumping rate at a pump depth of 23 mbgl
Bugan *et al.* (2012)	Yield (ℓ/s)	7.0	Current yield measured at a pump depth of 26 mbgl

To supplement the historical information on the hydraulic parameters in the study area, a 72 hour constant discharge pumping test (CDT) and 95% water level recovery was performed on G30966 between 10:00 AM on 25 April and 12:30 PM on 28 April 2013. Generally, a CDT comprises constant abstraction for a time period of 24 and 72 hours (depending on the aquifer type), with measurement of the associated drawdown in the pumped borehole and nearby observation borehole(s) (ISRRI, 2009). Based on the recommendations of Kruseman and de Ridder (2000), it was decided for this study that a 72 hour CDT would be run to attain steady-state flow conditions in the unconfined aquifer (i.e. no further drawdown).

This pumping test used the same pump that was used in the step drawdown pumping test. The abstraction rate of this CDT was calculated from the earlier step drawdown test data and is a rate judged as a "rule of thumb", which could be expected to produce a drawdown of between 40 and 50% of the available drawdown in G30966 (Conrad *et al.*, 2010). The maximum available drawdown in G30966 was assumed to be 21.5 m at the time of the study, which was calculated from the difference between the recommended allowable drawdown (i.e. 23 m; Bertram *et al.* 1984) and static water level (i.e. 1.55 mbgl on 24 April 2013). Hence a drawdown between 8.6 and 10.8 m was desired. An abstraction rate of 10-11 ℓ/s was estimated from the measured drawdowns in G30966 from the January 2013 step drawdown data (Table 13).

The time intervals for manual water level measurements during the pumping and recovery periods followed the recommendations of Kruseman and de Ridder (2000) with G30979 (16 m from G30966) used as the observation borehole. The water levels for drawdown were measured manually using two Solinst® dipmeters (Appendix C) and CSIR-sourced Solinst®

Levelogger Edge dataloggers were also installed in both boreholes an hour before the pumping test was initiated. The latter, were set to take water level and temperature (±0.05°C accuracy) measurements at a minute interval. The datalogger water levels are displayed as temperature compensated pressure readings and are barometrically compensated numbers adjusted with the aid of a Solinst® Barologger Edge (±0.05 kPa accuracy), which was installed in a nearby well-point (WP210) approximately 1.5 km NW of G30966.

The static groundwater levels were measured in both boreholes 48 hours and 24 hours before the pumping was initiated to establish if there are known short-term variations expected in the study area, which could affect the pumping test results. Since there was no change in water levels in those measurements, it was established that there was no influence by the nearby production boreholes that could affect the pumping tests. The abstraction rate was measured by the flow meter on the G30966 production borehole setup, with measurements taken at every hour for the first three hours and subsequently checked at least twice per day to assure that the abstraction remained constant (Appendix C). To prevent any interference, the pumped water was discharged from an open-ended lay-flat pipe, which had its outlet more than 60 m down-gradient of the pumped and observation boreholes.

Both mathematical (i.e. Thiem-Dupuit method) and graphic (i.e. Theis, Neuman and Cooper-Jacob) methods were applied to derive the transmissivity, hydraulic conductivity and specific yield values from the observation borehole data (Driscoll, 1986). The curve-fitting methods were computed using the FC-Excel program. In order to use these equations for these methods, the following assumptions and conditions are presumed to be applicable (Kruseman and de Ridder, 2000):

- The aquifer is unconfined and bounded at its base by a confining layer;

- The aquifer has a seemingly infinite areal extent;

- The aquifer is homogeneous, isotropic and of uniform thickness;

- Prior to pumping, the piezometric surface is horizontal over the area;

- The aquifer is pumped at a constant discharge rate;

- All flow is radial towards the well;

- All water pumped from the borehole comes from aquifer storage and borehole losses and storage is negligible;

- The pumping and observation boreholes penetrate the full thickness of the aquifer and thus receive water from the entire saturated thickness of the aquifer.

The Dupuit equation only gives the hydraulic conductivity for the aquifer and transmissivity is calculated by multiplying the estimated K-value by the saturated thickness (i.e. 35.05 m) (Kruseman and de Ridder, 2000). Since there is no drawdown with time under steady-state conditions (and the water is not derived from storage), the Dupuit equation cannot be used for calculating the storativity of the aquifer (Kruseman and de Ridder, 2000).

From the measured drawdown and recovery in G30979, it was decided that the observation borehole data would only be used to calculate the hydraulic characteristics within the study area. Even though it is always preferable to use the observation borehole data, the data from the pumped borehole could also be used to calculate transmissivity, which could then be compared to the G30979 results. However, it was decided that the data from G30966 would not be used because the first minute of drawdown showed a large decline, which could be attributed to borehole losses (that could be either due to clogging or collapse of the screen) as the pump emptied the borehole water column. The large borehole losses results in a significantly larger drawdown in the borehole than in the aquifer and will generally underestimate the transmissivity (Kruseman and de Ridder, 2000).

To ensure that the drawdown was small compared to the original saturated thickness of the aquifer (in order for the requirement of horizontal flow towards the pumped borehole to be approximately satisfied) the maximum drawdown at the end of the CDT must be < 5% of the saturated thickness (Boonstra and Kselik, 2001). If it is greater than 5%, the measured data must be adjusted to compensate for this factor, which is known as the corrected drawdown (Kruseman and de Ridder, 2000). The maximum drawdown in G30979 was only 3% of the saturated thickness (i.e. 31.1 m at the time of the test) and thus the measured drawdown data did not require adjustment prior to being used in the flow equations.

4.6.2 Results

In total, nine flow meter measurements were measured throughout the CDT and resulting in an average abstraction rate of 10.77 ℓ/s (Appendix C). The graphs of the pumped borehole (G30966) and observation borehole (G30979) drawdown and recovery is shown in Figure 42 and Figure 43, with a total drawdown of 10.2 m in G30966 at the end of the pumping test. The water level returned to 95% (i.e. 1.77 mbgl) of its original level within 40 minutes after the cessation of pumping.
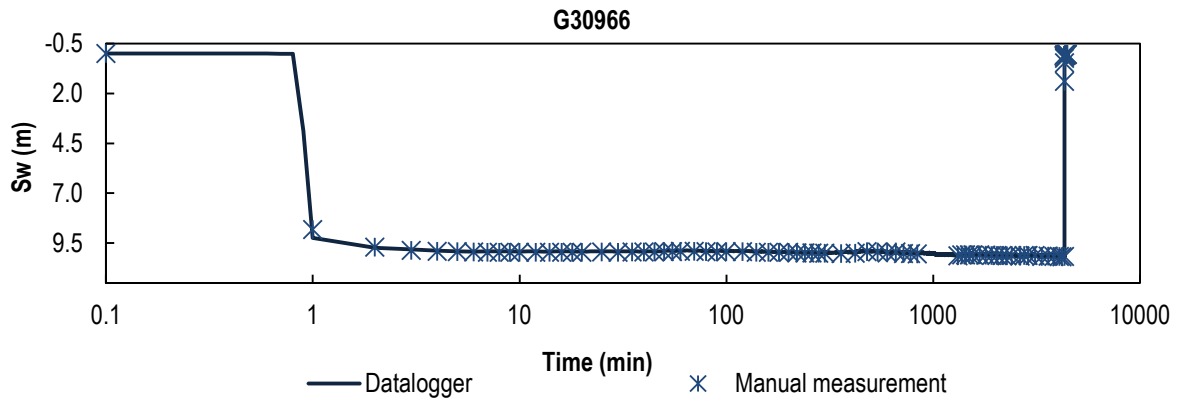
Figure 42: Semi-log drawdown vs. time of the pumped borehole (G30966) and recovery in April 2013
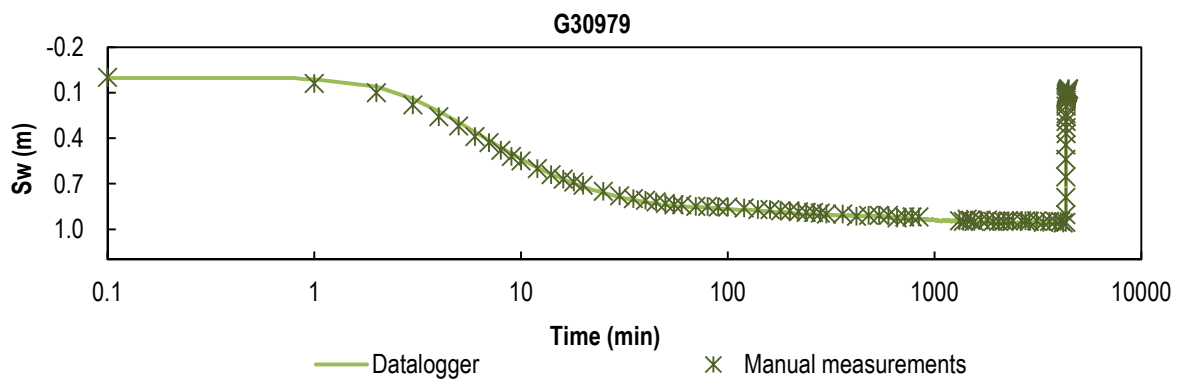
Figure 43: Semi-log drawdown vs. time of the monitoring borehole (G30979) and recovery in April 2013

Since the rate of drawdown in G30966 and G30979 become negligible with time (i.e. 10.16 m and 0.96 m after 2 000 minutes) the Thiem-Dupuit method for steady-state flow in an unconfined aquifer was used to calculate the transmissivity according to Equation 3 (Kruseman and de Ridder, 2000).

Equation 3: $Q = \pi K \frac{h_2^2 - h_1^2}{\ln(\frac{r_2}{r_1})}$

Where:

K = hydraulic conductivity

Q = abstraction rate

h_1 = saturated thickness at pumped borehole and radius (r_1) of the pumped borehole

h_2 = saturated thickness of observation borehole at distance (r_2) from the pumped borehole

For this equation to be used, the following is also assumed to be applicable in addition to the previously discussed assumptions (Kruseman and de Ridder, 2000):

- The gradient between the pumping borehole and monitoring borehole(s) is at steady-state;

- The velocity of flow is proportional to the tangent of the hydraulic gradient (instead of the sine as it is in reality);

- The flow is horizontal and uniform everywhere in a vertical section through the axis of the borehole.

The saturated thickness of the aquifer was 35.05 m at the time of the study and the maximum drawdown in G30966 and G30979 at steady-state conditions was 10.16 m and 0.96 m, respectively. The saturated thickness of G30966 was 24.89 m at $r_1 = 0.10$ m and for G30979, was 34.09 m at a distance of 16 m from the pumped borehole. Using these values, the Dupuit equation method gave a K-value of 2.77 m/day, which translates to a T-value of 97 m^2/day.

Although steady-state flow appeared to have been reached during the tests in the study area, transient flow equations were also used to calculate the storativity values of the aquifer and confirm the steady-state transmissivity value. The Theis (confined aquifer) method and the Neuman (unconfined aquifer) methods were used to calculate both early and late-time transmissivity and storativity values (Figure 44; Figure 45), whereas the Cooper-Jacob method was used for early-time calculations (Figure 46). For the Theis and Neuman solutions, the following additional assumptions were made (Kruseman and de Ridder, 2000):

- The method can be applied for the Theis and Neuman curves, provided the data is from a nearby observation borehole;

- The water initially pumped comes from the instantaneous release of water from elastic storage of the unconfined aquifer matrix (i.e. early-time segment, which give elastic storativity);

- After pumping for some time, water comes from storage due to gravity drainage of the interconnected pores (i.e. late-time segment, which gives specific yield);

- The specific yield is at least ten times greater than the elastic storativity.
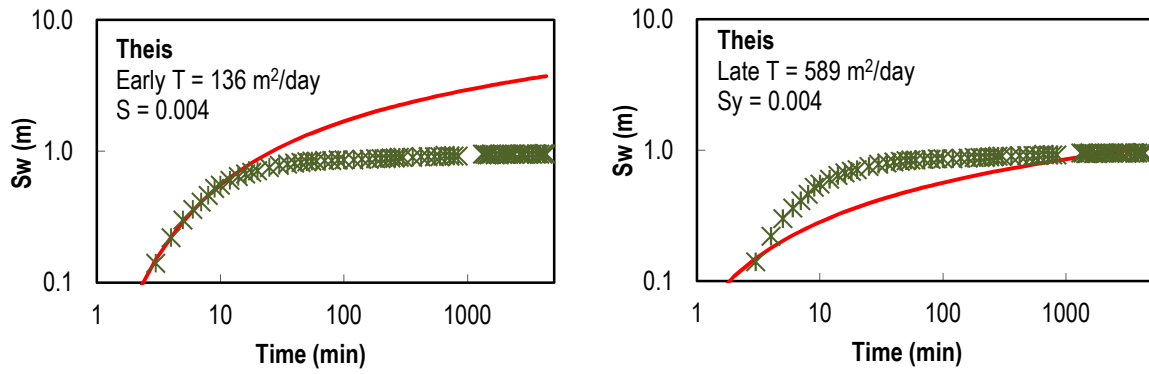
Figure 44: Early (left) and late-time (right) segment of the Theis method with G30979 data
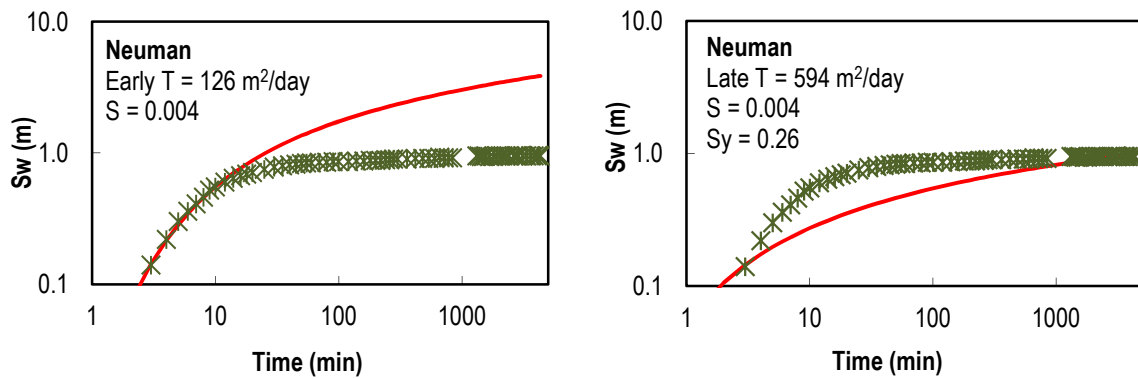
Figure 45: Early (left) and late-time (right) segment of the Neuman method with G30979 data
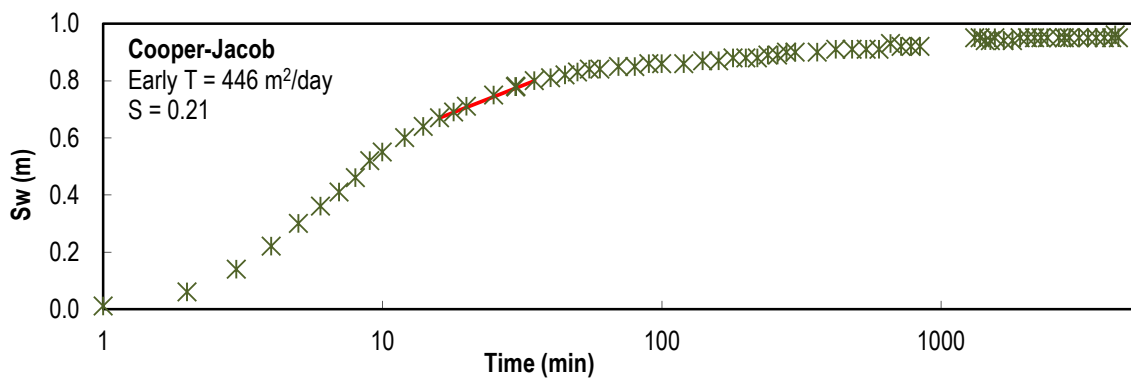
Figure 46: Early-time segment of the Cooper-Jacob method with G30979 data

4.6.3   Discussion

Table 15 provides a summary of the transmissivity, hydraulic conductivity and storativity values collated for the recent CDT data from the different methods. The hydraulic conductivity was calculated by dividing the estimated transmissivity by the saturated thickness.

Table 15: Summary of the hydraulic characteristics of the Atlantis Aquifer at G30966

Method	Transmissivity	Storage
Dupuit equation (steady-state flow)	T = 97 m^2/day K = 2.8 m/day	-
	Early-time data	**Late-time**
Theis method (confined aquifer transient flow)	T = 136 m^2/day K = 3.9 m/day S = 0.004	T = 589 m^2/day K = 16.8 m/day Sy = 0.004
Neuman method (unconfined aquifer transient flow)	T = 126 m^2/day K = 3.6 m/day S = 0.04	T = 594 m^2/day K = 16.9 m/day Sy = 0.26
Cooper-Jacob method (confined aquifers transient flow)	T = 446 m^2/day K = 12.7 m/day S = 0.21	-

A wide range of estimated transmissivity values were calculated from the different methods. The Dupuit steady-state equation resulted in a low transmissivity value in comparison to the known historical values and there is concern that a larger drawdown was measured in the production borehole in comparison to the aquifer, due to the borehole inefficiency. Thus, this resulted in the exclusion of the transmissivity value using the Dupuit equation as it may be an underestimate of the aquifers ability to transmit water (Kruseman and de Ridder, 2000). As a result, the values calculated from the transient flow methods seem to be more appropriate.

Since G30979 falls within the 10-30 m radius range from the pumped borehole, both the Theis (for confined aquifers) and Neuman (an approximated by the Theis method for unconfined aquifers) methods could be used. The early and late-time transmissivity values calculated using these methods were comparable, although the early-time transmissivity values were found to be more than half that of the Bredenkamp and Vandoolaeghe (1982) value. The late-time transmissivity values from the Theis and Neuman methods, however were comparable to the transmissivity value reported for G30966 from van der Merwe (1980). However, the Neuman method is favoured for this study compared to the Theis method, as it can be applied to unconfined anisotropic aquifers pumped by partially penetrating boreholes (Kruseman and de Ridder, 2000), as is the case in this study.

The storativity calculated in the Theis method early-time segment gave a value of 0.004, which is only representative of the elastic storativity (S) component of the unconfined aquifer during the short time after pumping started, with only the late-time storativity representing the "realistic" specific yield for the aquifer from gravity drainage, where Sy>>S (Kruseman and de Ridder, 2000). However, the calculated specific yield for the late-time segment from the Theis method graph in Figure 44 gave an unrealistically low specific yield, which is not expected for a sandy aquifer. For example, a review of literature gives an expected specific yield range of 0.01-0.1 in an unconfined aquifer (Boonstra and Kselik, 2001), which is generally between 0.2 and 0.3 in fine to coarse-grained sands (Kruseman and de Ridder, 2000), whereas the known Atlantis Aquifer range is between 0.019 and 0.27 (Chapter 3.8.4).

The reasons suggested for the anomalous specific yield value found in this study are either that the steady-state conditions had been reached and water was not derived from storage, or the pumping tests were too short. If the pumping tests were too short, the time-drawdown curve would not have reached the late-time stage (i.e. delayed yield), precluding a meaningful comparison of the data with the Theis curve (Figure 47; Kruseman and de Ridder, 2000; Boonstra and Kselik, 2001). Since no further pump tests were subsequently performed to evaluate this aspect, it was decided that only the Neuman data would be used, as it provided a realistic value of Sy = 0.26. This recent specific yield was almost double that of the Bredenkamp and Vandoolaeghe (1982) value, which could be explained by a rise in the water table (and thus increases the volume drained) by approximately 5 m since the 1982 CDT was done.
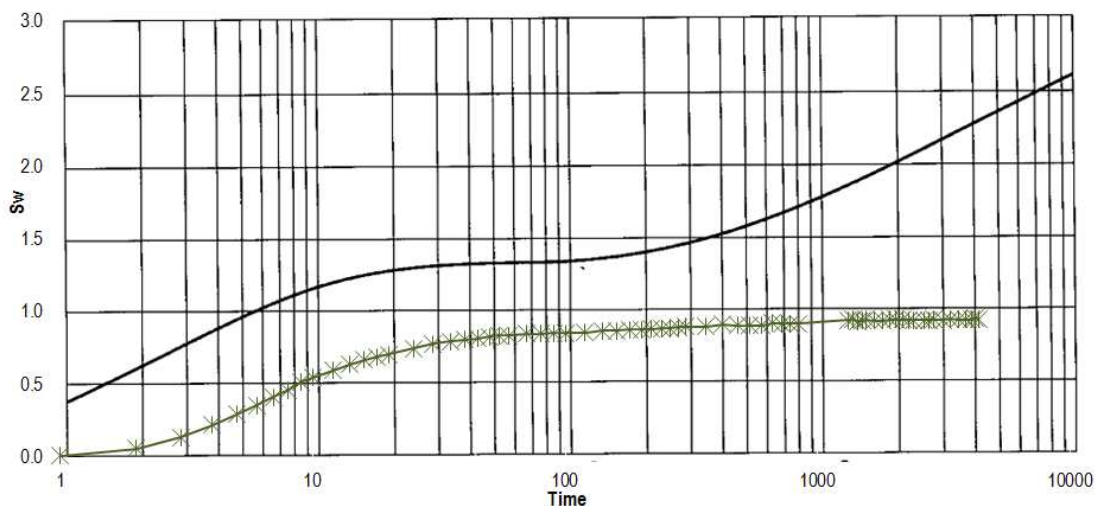
Figure 47: Theoretical time-drawdown plot of an unconfined aquifer (black line) with the delayed yield (late-time segment) compared with G30979, showing that the late time rise was not observed in this test (data from Boonstra and Kselik, 2001)

The Cooper-Jacob method was also applied to compare the values collected from the Theis and Neuman methods but only the early-time segment could be analysed for transmissivity and storativity using this method because no straight-line segment could be plotted after 40 minutes of pumping. Ideally, the straight-line should have been calculated from earlier pumping data (< 20 minutes) but the storativity value (assumed as specific yield) gave an unrealistically high value of Sy = 0.7, especially since even coarse gravels give a specific yield range of 0.13-0.44 (Boonstra and Kselik, 2001). The estimated transmissivity from the data between 20-35 minutes elapsed time gave a high transmissivity, which was within the historical range known for that borehole and a similar specific yield value calculated using the Neuman method.

Thus, the specific yield of the area is assumed to be Sy = 0.2 with an elastic storativity of 0.004. The estimated transmissivity for the study area is high (ranging from 120 m^2/day to 600 m^2/day), which is ideal for ISIR. However, the shallow water table could still be expected to cause problems with injection because it limits available space for a rise in the water level due to injection.

4.7 Water Quality

The suitability for Atlantis groundwater to be treated by ISIR was assessed in terms of water quality in the aquifer using groundwater from G30966. The results also provided a record of water quality conditions prior to the ISIR treatment experiment.

4.7.1.1 Methodology for water sampling and analysis

A compilation was made of historical G30966 water chemistry data from 11 July 1979 to 28 March 2013 (i.e. $n = 200$) using AWRMS monitoring data, a literature review of reports (i.e. DWAF, 1983; Fleisher, 1990; More Water cc., 2001) and water samples collected by the author during this project (Appendix D). The recent water samples from G30966 were collected during the two pumping tests performed in January and April 2013 and comprises four unfiltered samples taken at the sampling tap after sufficient purging of G30966. The samples were collected in 1 ℓ glass bottles that were correctly prepared before sampling and rinsed three times with groundwater from G30966 before collecting the water sample as recommended in Weaver *et al.* (2007). Due to the short period between sample collection and delivery to the laboratory, it was not necessary to add preservatives to the samples. The four samples were analysed by CoCT's Scientific Services, which is a South African National Accreditation System (SANAS) accredited testing laboratory. The water quality parameters analysed for were selected according to the literature review of ISIR case studies (Table 16).

Sample preparation was only necessary for the determination of parameters analysed by ICP-OES, which required that sample was shaken sufficiently to ensure all precipitates are mixed homogeneously before a representative aliquot is collected (M. September, *pers. com.* 2013). Immediately thereafter an aliquot of the sample was then pipetted into a container and acidified with 10M HNO_3. The container is sealed and the sample is digested overnight, the following day the sample is filtered and analysed on the ICP-OES (September, *pers. com.* 2013).

Table 16: Water quality parameters of interest to this preliminary investigation

Parameter*	Reference method of analysis in Scientific Services
EC (mS/m)	TIAMO analyser (i.e. Metrohm automated titrated system)
pH	TIAMO analyser
Ca	Perkin-Elmer 5300 Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES)
Na	ICP-OES
Mg	ICP-OES
K	ICP-OES
Total alkalinity as $CaCO_3$	TIAMO analyser
Cl	Discreet analyser
SO_4	Discreet analyser
Nitrate and nitrite as N	Discreet analyser
Total Fe	ICP-OES
Total Mn	ICP-OES
NH_4 as N	Flow Injection Analyser 8500 series using Phenolate method
Aluminium (Al)	ICP-OES
As	ICP-OES
Fluoride (F)	Discreet analyser
Nickel (Ni)	ICP-OES
PO_4 as P	ICP-OES
Lead (Pb)	ICP-OES
SiO_2 as Si	ICP-OES
Sr	ICP-OES
Vanadium (V)	ICP-OES
Zinc (Zn)	ICP-OES
TOC	TOC analyser (i.e. GE Sievers InnovOx Laboratory TOC Analyser)
*Data given in mg/ℓ unless otherwise specified	

The electro-neutrality (E.N.) plausibility test was used to assess the chemical dataset accuracy. This test evaluates the accuracy of the major ions analysis, since an aqueous solution should always be electrically neutral and therefore, the sums of anions and cations (as milli-equivalent/litre i.e. meq/ℓ) should always balance. This value can be calculated using the following formula (Equation 4; Appelo and Postma, 2005):

Equation 4: E.N. (%) = $100(\frac{\sum \text{cations} + \sum \text{anions}}{\sum \text{cations} - \sum \text{anions}})$

The milli-equivalent of the major ions (i.e. Ca^{2+}, Na^+, Mg^{2+}, K^+, HCO_3^-, Cl^-, SO_4^{2-}, $NO_3^- + NO_2^-$ as N) was calculated in Microsoft Excel 2010 by multiplying the concentration (given as mg/ℓ) by its valence and then dividing it by the atomic or molecular weight of the major cation or anion. The bicarbonate (HCO_3^-) concentrations (as mg/ℓ) were calculated from the total alkalinity concentrations (given as mg $CaCO_3$/ℓ) by multiplying the total alkalinity by 1.22 and then following the same process as for the other major ions to finds its meq/ℓ value (Weaver *et al.*, 2007). All data with values exceeding ±5% were excluded from the dataset following recommendations by Appelo and Postma (2005).

The water type from G30966 was determined from the major ion compositions (as meq/ℓ) plotted in a Piper diagram using the GW-Chart program. The Piper diagram was constructed by plotting the major cations (i.e. Ca^{2+}, Mg^{2+} and the sum of Na^+ and K^+) and the major anions (i.e. Cl^-, SO_4^{2-} and the sum of HCO_3^- and CO_3^{2-}) as points in their respective tri-linear fields and these two points are extended into the main diamond shape field as one point. The carbonate (CO_3^{2-}) concentrations were calculated by the GW-Chart program from the bicarbonate equilibrium constant and the inputted HCO_3^- concentrations per analyses, using a historical mean pH of 7.6 at 20°C.

4.7.1.2 Results

The E.N. calculated for this data set indicated that only 74% of the analyses fall within the ±5% accuracy threshold and within that set 53% fall within the inevitable ±2% E.N. difference (Figure 48). The statistical analysis of the revised data set is given in Table 17.
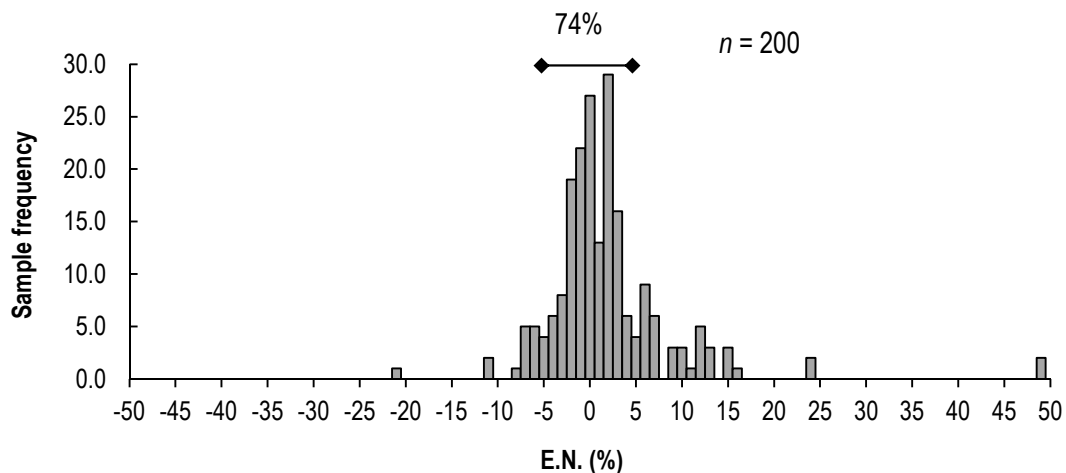
Figure 48: The E.N. calculated for the G30966 dataset indicate that only 74% of the data falls within the ±5% accuracy threshold

The water type was plotted from the revised dataset in a number of Piper diagrams (Figure 49), which resulted in five groupings according to the "life-span" of G30966 and Witzand Wellfield:

- March 1979-June 1982: G30966 was not in use as a production borehole;

- July 1982-1988: Production initiated at the Witzand Wellfield and G30966 was included in the production scheme;

- 1989-1999: G30966 was taken out of the production scheme and used intermittently, while the iron-related clogging problems started to impact the Witzand Wellfield in the latter half of the 1980s;

- 2000-2010: G30966 was in intermittent use but was rehabilitated in 2000 with the rest of the production boreholes within the wellfield, however production remained low;

- 2011-2013: G30966 was in intermittent use and surface water contributed the majority of the water supply to the AWRMS.
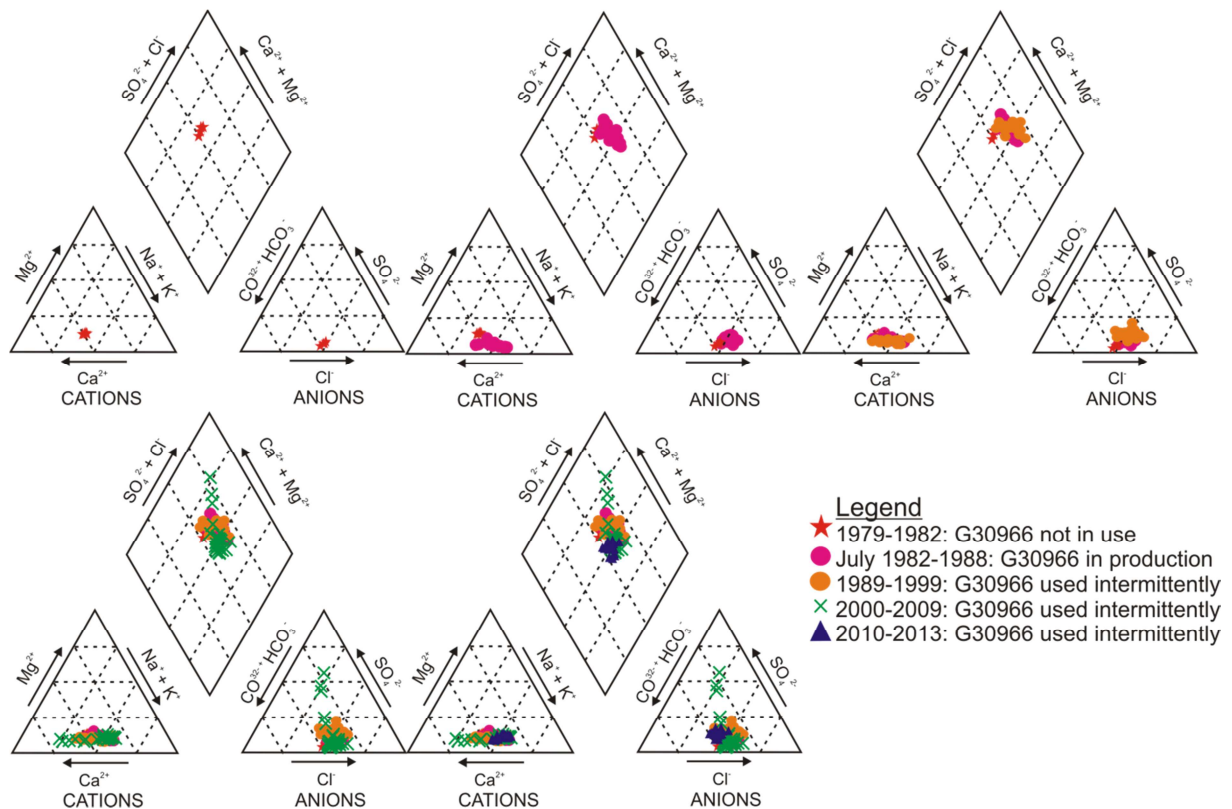
Figure 49: Piper diagrams of the major ion composition of G30966 groundwater from 1979 to 2013

Table 17: The historical groundwater quality abstracted from G30966 from 11 June 1979 through to 28 April 2013

Parameter*	Sample size (*n*)	Mean	Range	Q25	Q50	Q75	SANS 241:2011**
EC (mS/m)	148	86.38	65.30-144.00	72.40	80.00	100.00	≤ 170.00
pH	148	7.57	6.90-9.50	7.41	7.60	7.71	5.00-9.70
Ca	148	77.27	42.20-209.02	60.13	69.15	88.25	-
Na	148	89.47	63.00-129.00	79.30	85.50	97.00	≤ 200.00
Mg	148	10.37	6.67-19.00	8.49	10.00	11.00	-
K	148	4.82	1.4-8.98	2.50	5.20	6.84	-
Total alkalinity as $CaCO_3$	148	172.77	120.00-250.00	151.78	166.00	188.00	-
Cl	148	139.23	93.00-253.00	107.00	125.00	175.00	≤ 300.00
SO_4	148	61.46	15.00-385.80	42.30	49.00	55.00	≤ 250.00
$NO_3 + NO_2$ as N	129	0.19	< 0.001-1.20	0.05	0.10	0.20	NO_2 ≤ 0.90; NO_3 ≤ 11.00
Total Fe	147	0.87	0.01-8.50	0.10	0.34	0.80	≤ 0.30
Total Mn	80	0.25	0.08-0.82	0.13	0.17	0.28	≤ 0.10
NH_4 as N	93	0.17	0.02-0.70	0.10	0.10	0.27	≤ 1.50
Al	80	0.02	< 0.001-0.20	< 0.001	0.01	0.02	≤ 0.30
As	8	All measured values ≤ 0.001	-	-	-	-	≤ 0.01
F	26	0.22	0.11-0.33	0.19	0.22	0.26	≤ 1.50
Ni	11	All measured values ≤ 0.005	-	-	-	-	≤ 0.07
P	7	0.07	0.02-0.20	0.05	0.05	0.10	-
Pb	12	0.04	< 0.001-0.42	< 0.001	0.005	0.005	≤ 0.01
Si	8	4.23	3.49-4.57	3.95	4.34	4.53	-
Sr	7	0.48	0.41-0.53	0.43	0.50	0.51	-
V	12	All measured values < 0.005	-	-	-	-	≤ 0.20
Zn	10	0.03	0.01-0.05	0.02	0.03	0.05	≤ 5.00
TOC	3	7.13	7.10-7.20	7.10	7.10	7.20	≤ 10.00

*Data in mg/ℓ unless otherwise specified; ** If there is multiple standard limit given for the parameter, i.e. operational or aesthetic or heath the lowest value is used

4.7.1.3   Discussion

The historical data showed that the water from G30966 changed from an initial Ca-Na-HCO$_3$ type, with increasing Na and Cl from 1986 to 1992 into predominately a Na-Ca-HCO$_3$ type in the last two decades (Figure 49). This exclude times when the water quality was affected by acid spills and brine leakage from the ponds through damage of the lining at the Witzand Softening Plant from 2003 to 2009 (Tredoux *et al.*, 2012). However, there are at least eight anomalous outliers in the G30966 dataset from 2003 to 2009 that are certainly the result of anthropogenic contamination from the softening plant. These events are easily detected because they resulted in elevated Ca and SO$_4$ concentrations due to dissolution of the aquifer material by the contaminant sulphuric acid. The brine ponds have since 2010 been taken out of operation and the water quality has now returned to its original composition, which has been stable since 2010 (Figure 50).

A decline in the Cl and Mg concentrations is seen from 1987 (Figure 49; Figure 51) due to the improved quality of water used in the artificial recharge basins (only urban stormwater from November 1986) (Tredoux *et al.*, 2012). A gradual decline in Mg (and Ca) in G30966 since 1992 correlates with recharge using domestic effluent that was first treated at the Witzand Softening Plant (Tredoux *et al.*, 2012). Moreover, the salinity (measured by EC) also declined as a result of the artificial recharge. Through progressively introducing lower salinity water into the aquifer, first through the recharge of urban stormwater from 1989, high quality domestic effluent in 1992 and in 1999 by using surface water, the salinity in the effluent recharged in Basin 7 was substantially lowered (Figure 52; Tredoux *et al.*, 2012).
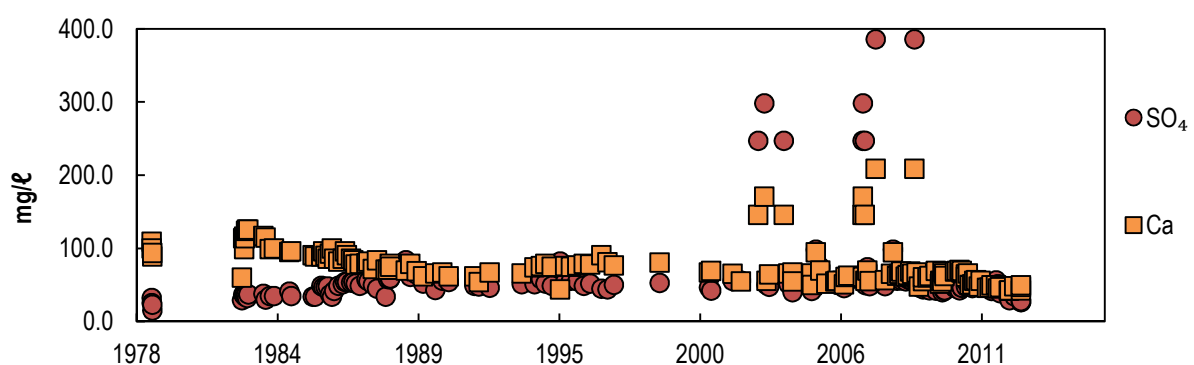
Figure 50: Sulphate and calcium variation in G30966 from 1979-2013, showing outlier elevated concentrations from 2003 to 2009
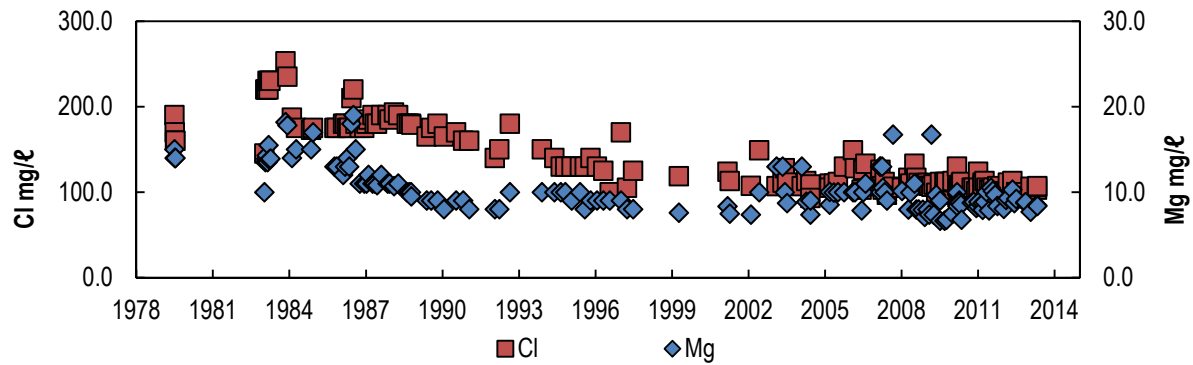
Figure 51: The concentration of magnesium and chloride progressive declined in G30966 from 1979 to 2013 due to the change in artificial recharge water quality
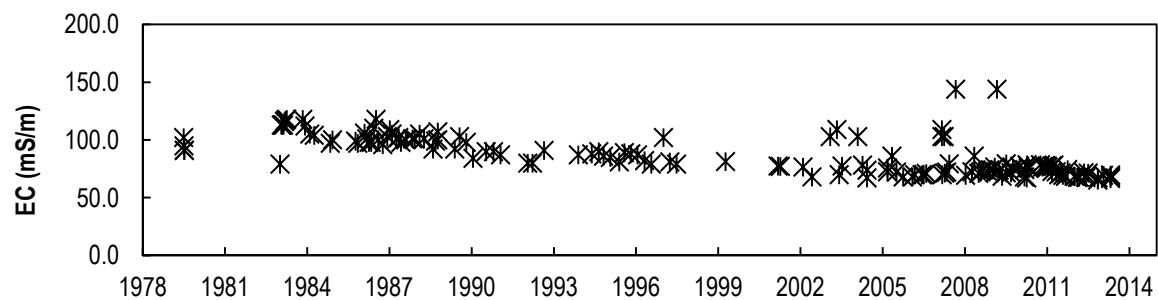
Figure 52: EC has progressively decreases over time with artificial recharge

The total iron concentration in G30966 is given in Figure 53, with a median concentration of 0.34 mg/ℓ, which is just slightly above the WHO (2008) guideline and more than double the median given in Table 12 for the Witzand Wellfield. Prior to 1991, the elevated concentrations in iron (i.e. > 0.8 mg/ℓ, which is the 75% quartile from Table 17) could be associated with incorrect sampling of a clogged borehole (i.e. G30966 was rehabilitated in 2000). These results are indicative of iron accumulating within the borehole and the result of insufficient purging of the borehole before the sample was collected (Weaver *et al.,* 2007). This shows that iron-related clogging was already on the increase from 1983, when regular water quality sampling commenced (Tredoux and Cavé, 2002). However, elevated concentrations are seen to occur in 2007 and 2009, accompanied by the elevated sulphate concentrations because of iron mobilisation during the acid spills (Figure 54). The elevated concentrations prior to 2009 could also be due to incorrect sampling and clogging of the borehole. The iron concentrations found during recent step drawdown and CDT pumping tests ranged between 0.4 and 0.5 mg/ℓ, which is accepted as the iron concentration expected in the groundwater for this study site. This is still above the WHO (2008) guidelines of 0.3 mg/ℓ and therefore necessitates removal before distribution. This is still much greater than the 0.15 mg/ℓ threshold concentration for iron-related clogging processes (Cullimore, 2008).
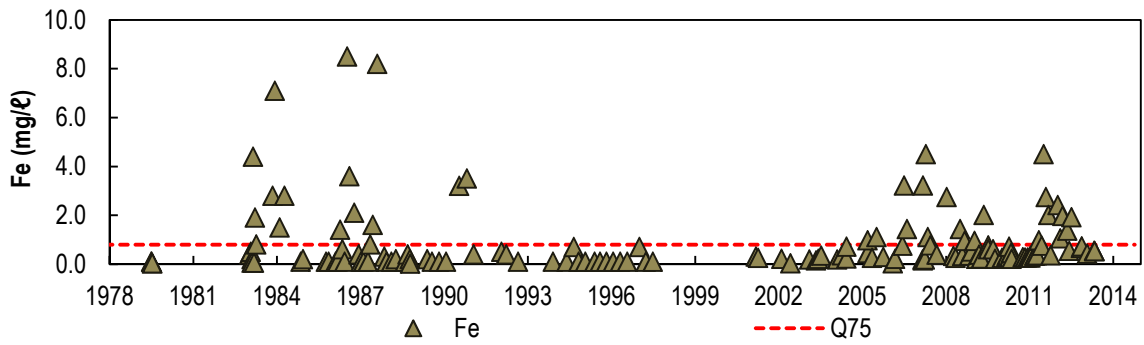
Figure 53: The iron concentration trend over time in G30966 showing sporadic elevated concentrations above the 75% quartile from the dataset
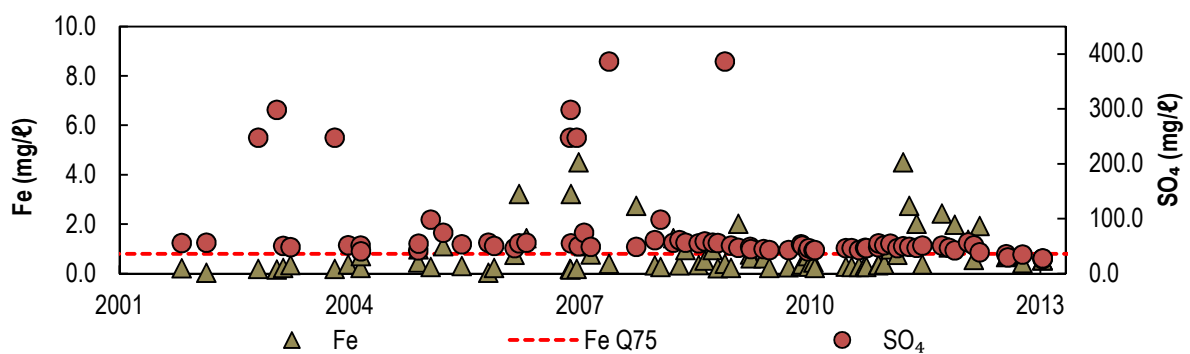
Figure 54: The iron and sulphate concentrations in G30966 shows that the spills could have contributed to iron mobilisation from 2007 to 2009 with pre-2007 and post-2009 highs can be associated to incorrect purging and sampling

Determination of manganese levels was not included in the water analysis programme until 2001 (and included because of the clogging problems in the wellfield) but exhibits a median concentration of 0.17 mg/ℓ (Table 17). The total manganese concentrations are not variable as the iron concentrations but the impact of the acid spill at the Witzand Wellfield is better demonstrated in the elevated manganese concentrations (i.e. > 0.3 mg/ℓ, which is the 75% quartile) than in the iron concentrations. However, the manganese also shows similar peaks after 2009 assumed to be associated with incorrect purging of the clogged borehole (Figure 55). The manganese concentrations are consistently above the WHO (2008) guideline of 0.1 mg/ℓ, requiring the necessity for its removal with iron prior to human consumption. The recent pump test data ensured that G30966 was properly purged before the sample was collected and gave manganese concentrations of between 0.15 and 0.23 mg/ℓ, which falls within the 25-75% quartiles and is accepted as the manganese concentration range in the study area.
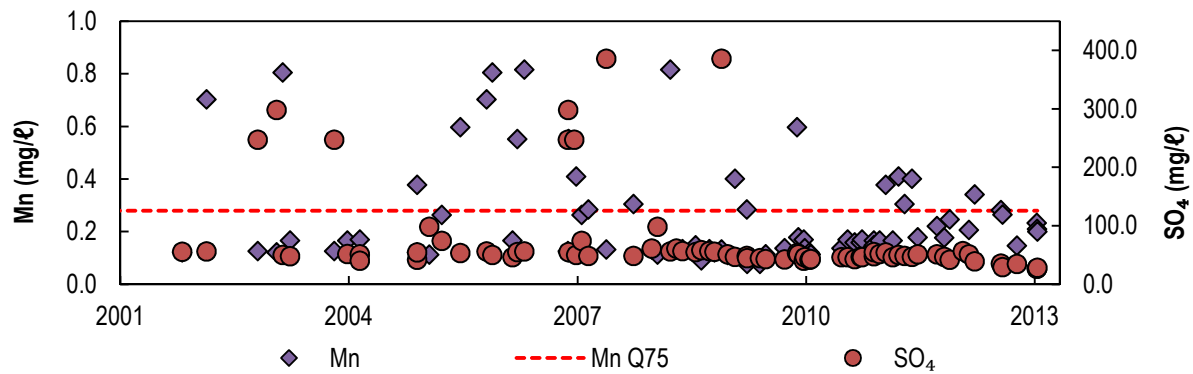
Figure 55: Total manganese and sulphate concentrations in G30966 over time, showing the direct link to increases associated with the acid spills and post-2010, the elevated concentrations associated with incorrect sampling

The review of iron and manganese concentrations in G30966 show that they are not very high in the study area, but over time their presence (even in the observed low concentrations) have caused significant problems in water supply through long-term accumulation and clogging of the borehole.

Other factors to investigate to determine the feasibility of ISIR treatment at the study area include:

- The pH requirements for ISIR must be > 6 and ideally within 7-8 for rapid oxidation of Fe^{2+} and > 8.5 for Mn^{2+}. In addition, a pH between 7 to 8 also increases the sorption capacity on precipitated oxides. The historical pH range is shown in Figure 56 and shows it to vary between 7 and 8 with no significant change over three decades, except for one outlier. The outlier does not correlate with the identified peaks caused by the acid spill and is therefore assumed to be a measurement error.

- Water temperature impacts the kinetics of the oxidation reactions and must be > 5°C. The temperature for the study area was measured by the Solinst® dataloggers during the CDT in April 2013 and gave a range of 17.3-18.3°C, which is within the desired range for ISIR.

- An alkaline environment is ideal for ISIR since it can provide a buffer to any lowering of the pH due to oxidation of DOC, Fe^{2+}, Mn^{2+} or sulphides in the subsurface. In the study area, the Ca-HCO_3 composition of the groundwater due to the calc-rich Witzand Formation is ideal for ISIR (< 200 mg/ℓ as CaCO3) as it would provide a buffer such that the pH will never decrease below 6 (Tredoux, *pers. com.* 2012). In addition, it is also not high (i.e. > 300 mg/ℓ as $CaCO_3$) enough to cause complexes with the Fe^{2+} and Mn^{2+} (Buamah, 2009).

- High DOC concentrations are problematic for the ISIR treatment as it affects the rate of oxidation and sorption processes (e.g. Sharma, 2001; Munter *et al.*, 2005). Although there are limited measurements for TOC (which is always greater than DOC) in G30966, the recent samples show it to be high (i.e. > 5 mg/ℓ), which is close to the known natural TOC levels in the Witzand Wellfield (Table 12).

- Another major oxygen-consuming compound in the subsurface could be NH_4^+ but its concentration in the study area is ≤ 0.7 mg/ℓ. It can be excluded from further investigation in this study because its presence is much lower than the TOC concentration, its concentration is below 1 mg/ℓ, so it will have only a negligible impact on Fe^{2+} adsorption (Sharma, 2001) and is below the recommended SANS 241:2011 guidelines. In addition, the other nitrogen compounds (i.e. NO_3) are also low and not expected to have a significant impact on ISIR.

- The presence of sulphides is not ideal for ISIR treatment. Although the iron is derived from pyrite lenses in the Atlantis Aquifer and there is also a distinct H_2S smell associated with abstracted water from G30966, there is very little sulphide minerals in the aquifer system that would cause significant problems with ISIR application.

- The presence of SiO_2 at concentrations > 10.0 mg/ℓ is known to have a limiting effect on the oxidation process of Fe^{2+} and although is not at the concentrations given by Sharma (2001), it is still relatively high in the G30966 dataset with SiO_2 concentrations ranging between 3.5-4.6 mg/ℓ.

- In addition, Fe^{2+} adsorption is known to decrease on sand grains in *ex-situ* treatment when it has to compete with other ions like Mn^{2+} (> 1.5 mg/ℓ) and Ca^{2+} (> 200 mg/ℓ) for adsorption sites (Sharma, 2001). In the study area, all of these inorganic ions or molecules concentrations are below these levels.
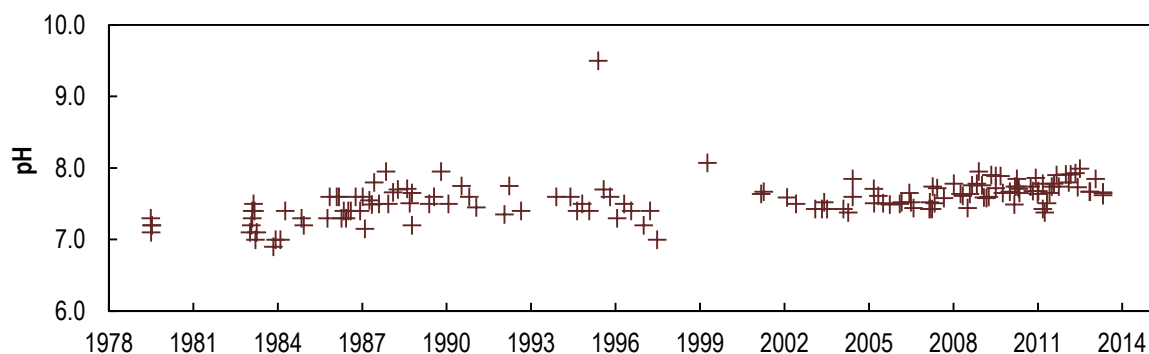
Figure 56: G30966 historical pH varies between 7 to 8 with one outlier at 9.5

Other chemical elements or compounds that were included in the water analysis because of their potential of also being removed by the ISIR process include:

- *Arsenic*: Concentrations of arsenic in G30966 were included due to their health concern and potential removal by ISIR treatment (e.g. Sen Gupta *et al.*, 2009; van Halem *et al.*, 2010). However, the Atlantis Aquifer does not contain any As-minerals such as arsenopyrite and since all measured values are below the detection concentrations, it is excluded from any further discussion.

- *Phosphate*: The phosphate concentration is of interest to this study, due to the potential impacts it has on complexing with iron or competing with adsorption sites. It is also known to be removed by ISIR treatment. However, the historical mean for phosphate was too low (< 1.0 mg/ℓ) to be of significant impact on iron removal forming complexes or for it to act as a competing ion for sorption sites (i.e. PO_4^{3-} > 1.0 mg/ℓ; Sharma, 2001) and this compound was excluded from further investigation.

- *Lead, vanadium, nickel, fluoride, strontium and zinc*: These are minor elements that could be removed from groundwater by ISIR through adsorption onto the newly-formed iron and manganese precipitates (e.g. Tredoux *et al.*, 2004; van Halem *et al.*, 2011). A review of historical concentrations for these elements in G30966 indicates them being only minor constituents. No further investigation into the lead, vanadium, nickel and zinc concentrations will follow because all concentrations measured in G30966 are well below the SAN 241:2011 standard limits. However, the fluoride and strontium concentrations have been included for further investigation in this study.

4.8   Summary

Based on the preliminary findings, the study area was considered appropriate for the ISIR investigation, with the decision taken that groundwater abstracted from G30966 could be used for injection purposes, as it was deemed suitable based on a comparison of historical water quality of G30966 with the requirements of ISIR methodologies based on case studies. The volume of water available would also be adequate since the borehole is excluded from the Witzand production line and injection tests would not affect the water supply demands, which reduced the costs in infrastructure and not use drinking water sourced from the Witzand WTP. However, the oxidant selection for increasing the DO concentration in the recharge water should take into account the high TOC and SiO_2 concentrations in the groundwater.

Ideally, the single production borehole approach would have been favoured for this study as it used the borehole infrastructure optimally and reduced the costs associated with drilling of additional well-points. However, from the preliminary evaluation it was decided that the injection would take place in well-point(s) surrounding G30966, rather than directly into the production borehole. This was because of the high water table and the condition of the borehole being unknown due to the lack of down-hole camera logging.

Although this approach increased the capital cost of the treatment it also allows for new monitoring points in the study area, which would supplement the analysis of the ISIR treatment, especially between the injection well-point(s) and the production borehole. The drilling of additional well-points was also possible at the study area since there was open space available and no underground utilities that would be impacted by the installation of the well-points. The sand samples collected from the drilled boreholes could also improve the conceptualisation of the aquifer within the study area.

CHAPTER 5. DESIGNING AN ISIR PROTOTYPE

5.1   Introduction

Based on the preliminary investigation of the study site and ISIR case studies, a prototype was designed and constructed to be applied at G30966. The following points were considered in the design of the ISIR prototype for this feasibility study:

- The oxidant used for Fe^{2+} and Mn^{2+} removal from groundwater;

- The method of introducing the oxidant into the recharge water and subsurface;

- The prototype must make optimal use of the existing infrastructure with minimal disturbance of the area, i.e. limited permanent above-surface equipment;

- It must be mobile and secure to avoid any potential vandalism;

- It must be simple and easy to operate;

- The treatment application must be user and environmentally safe and not generate any hazardous by-products in the aquifer or groundwater that would require special disposal procedures, i.e. it must require minimal regulatory compliance with the South African NEMA, NWA and health and safety regulations.

5.2   Oxidant Selection

International ISIR treatment methods make use of either simple aeration, or dosing with high purity oxygen gas to increase the DO concentration in the recharge water (Rott and Meyerhoff, 1994). As aeration could optimally be expected to only yield an average DO of 8.0 mg/ℓ at standard temperature (i.e. 25°C) and pressure (i.e. 1 atmosphere) (Vance, 2002), it was believed to be impractical for the oxidation and removal of the Fe^{2+} and Mn^{2+} from the high TOC and SiO_2 groundwater in this study. The use of oxygen gas was considered because it would result in higher DO concentrations of about 40 mg/ℓ at 25°C and 1 atmosphere (Vance, 2002), but this approach was excluded due to the hazards associated with the storage of cylinders of oxygen gas at the site, in addition to concerns of vandalism or theft in this area.

Other stronger oxidants often used in Fe^{2+} and Mn^{2+} *ex-situ* water treatment such as $KMnO_4$, H_2O_2 and O_3 were also considered, as they have recently been investigated for the *in-situ* treatment of hydrocarbon contaminated groundwater (Vance, 2002). The use of H_2O_2 and

$KMnO_4$ has been investigated as alternatives to oxygen for ISIR (Mettler, 2002). It was found that the iron removal efficiency increased slightly and the set-up phase was shortened but this treatment was more expensive and required handling and storage of chemicals (Mettler, 2002). In addition, $KMnO_4$ application also seemed to decrease the hydraulic conductivity of the aquifer (Mettler, 2002). Other studies of *in-situ* treatment using $KMnO_4$ indicated the undesirable potential mobilisation of uranium by permanganate oxidation (Vance, 2002). Similar to oxygen gas, the handling and storage required for the H_2O_2 and $KMnO_4$ was another reason that precluded their use at the study site.

Treatment with O_3 has not been applied in ISIR treatment, but was considered for this study because it is easily generated onsite from air with none of the safety regulations associated with handling or storage of the oxygen gas and chemicals (Rajagopaul *et al.*, 2008). Ozone gas is widely used overseas for the efficient *ex-situ* removal of Fe^{2+} and Mn^{2+} from organic-rich water (e.g. Cromley and O'Conner, 1976; Eriksson, 2005; Munter *et al.*, 2005) and in South Africa (e.g. Rajagopaul *et al.,* 2008) because it does not have the drawbacks associated with the other oxidants listed in Table 2. Another benefit is that ozone decomposes in water to DO, which can enhance the oxidation of DOC, Fe^{2+} and Mn^{2+} (EPA, 1999). In addition, intermediate OH^- ions are formed during the decay process of ozone to oxygen (EPA, 1999; Cullimore, 2008). These free radicals are the strongest oxidants in water and will further enhance the *in-situ* oxidation process (Table 3; EPA, 1999).

Ozone gas is used to reduce microbiological activity in distribution pipes because it creates a pH-independent, extremely oxidising environment (Cullimore, 2008). However, in open systems such as boreholes, it is considered an impractical option for rehabilitation of biofouled production boreholes (Cullimore, 2008). This is because ozone is highly reactive and unstable in water and would be expected to only have a localised effect because its short half-life is expected to limits its penetration into the aquifer and gravel pack, which also affects its effectiveness to reduce the bacteria (Cullimore, 2008). In addition, the lack of residual disinfectant ability of O_3 compared to Cl_2 is a disadvantage in the long-term prevention of re-colonisation of the treated areas (Cullimore, 2008). Cullimore (2008) also suggested that the microorganisms will utilise the organic debris left from the ozonation treatment, resulting in accelerated regrowth.

Whereas, O_3 is not considered a viable disinfectant in the treatment of biofilms, it has recently gained acceptance as an effective oxidant in *in-situ* remediation treatment of hydrocarbon pollution (Nimmer *et al.*, 2000; Masten, 2004; Plummer *et al.*, 2005; Piper and Salvage, 2012).

Compared to other oxidants, *in-situ* ozone treatment has other important advantages because (EPA, 1999; Nimmer *et al.*, 2000; Vance, 2002; Plummer *et al.*, 2005; Ansorge, *pers. com.* 2011; El Araby *et al.*, 2009; Piper and Salvage, 2012):

- Ozone is almost twelve times more soluble than oxygen in water;

- It is non-toxic when dissolved in water and leaves no environmentally harmful residues;

- Oxidation treatment is often accomplished in a shorter period of time with ozone;

- Ozone equipment is compact and can be easily housed in a small wendy house or trailer, thus minimising site disruption;

- No additional chemicals are required and no contaminated wastewater or soil is generated during the treatment, which would require off-site treatment or disposal.

5.3   Introducing the Oxidant into the Recharge Water and Subsurface

Once ozone was selected as the oxidant for the pilot study at Atlantis, the best means of introduction into the subsurface had to be investigated. Traditionally, the ISIR treatment is achieved by the oxygenation of the water before it is injected into the aquifer either by gravity-driven or pump injection (Sommerfeld, 1999). Ozone can be introduced either as a gas (known as *in-situ* ozone sparging) or as a liquid (known as *in-situ* ozonated water). This is advantageous since continuous oxidation can be applied as opposed to the batch applications that are needed for $KMnO_4$ (Figure 57; Plummer *et al.,* 2005; Piper and Salvage, 2012).
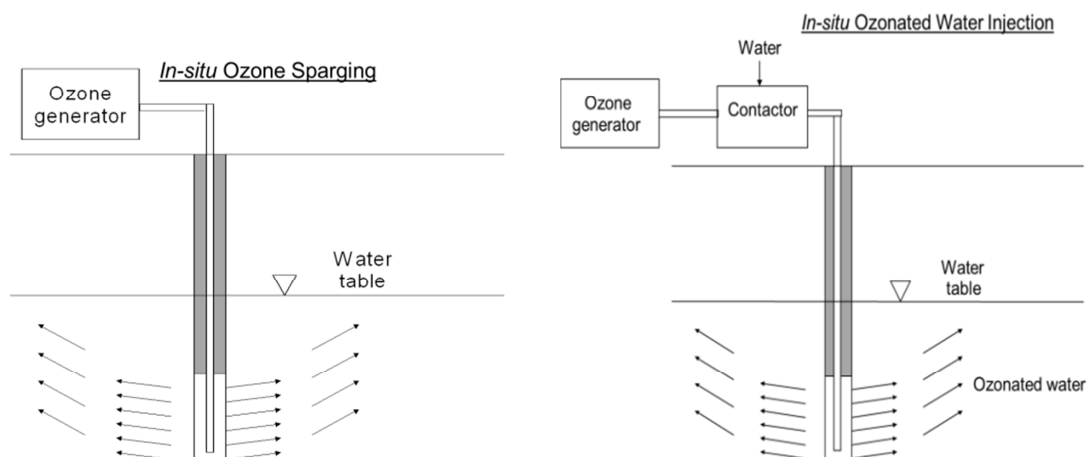
Figure 57: The two approached considered for introducing ozone into the subsurface for ISIR (Masten, 2004)

The direct injection of gaseous ozone into the aquifer is achieved by using an ozone diffuser (e.g. micro-porous ceramic stones, stainless steel holders or gasket seals) at the borehole screen or at the base of an open-ended injection point (Rajagopaul *et al.*, 2008; Ansorge, *pers. com.* 2011). The diffuser works under water pressure and creates a gas bubble column, which efficiently dissolves ozone into the water, with the water column and bubble size influencing the degree of efficiency (Ansorge, *pers. com.* 2011). This approach was not found to be favourable in this study because the radius of influence of such a system is limited to the interior of the borehole and the contact time with the Fe^{2+} and Mn^{2+} in the groundwater of the aquifer with the dissolved ozone would not be adequate and would not achieve the desired effect. It would also require specialised sparging equipment designed specifically for each site, which would increase the capital cost of the prototype. The diffusers are also known to be susceptible to clogging, which requires additional undesirable maintenance (Plummer *et al.*, 2005; Rajagopaul et *al.*, 2008).

The alternative option would be to dose the water with ozone gas before injection, which can be achieved similar to oxygenation by either passive (e.g. bubbling ozone through a column of water) or by forced (e.g. use of a venturi) methods (Sommerfeld, 1999). To keep the capital costs to a minimum while achieving the maximum dissolution of ozone in the water, it was decided that a venturi would be used (Figure 58). The venturi is located immediately downstream of the pump and creates a suction effect when water is pumped through a small orifice and decompresses as it travels through the outlet (Wassertec, 2012). This creates a vacuum on the suction port and draws in the ozone gas from the generator to dose the water (Sommerfeld, 1999).
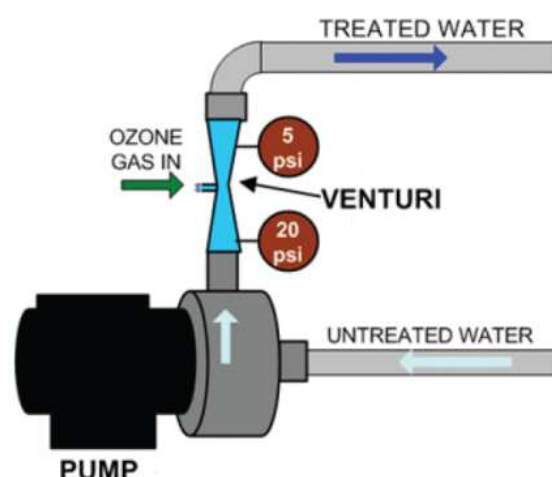
Figure 58: Venturi schematic on how the vacuum is created due to a differential pressure created with water moving from left to right though a conical body (www.ozonesolutions.com/journal/2013/ozone-venturi-injectors-work-dissolve-ozone-water/)

This approach has more than 90% ozone transfer efficiency with water and lower maintenance costs compared to diffusers (Rajagopaul *et al.,* 2008), however Sommerfeld (1999) highlighted the need for regular inspection and cleaning with the treatment of iron-rich groundwater to avoid Fe(III)-oxide build-up in the venturi. This option is preferable with the ISIR treatment in comparison to ozone gas injection, since the ozonated water density would allow for the dispersion of the oxidant-rich water through the borehole screen and into the aquifer, whereas the gas injection option would result in concentrations of the ozone mostly within the borehole (Ansorge, *pers. com.* 2011).

The removal efficiency of the ISIR process is dependent on the concentration of DO in the injected water available to react with the Fe^{2+} and Mn^{2+} ions and the pH of the groundwater in the aquifer, which dictates the rate of oxidation. Since the pH range in the groundwater of the study area is within the optimum level for iron removal, it was only the other parameters that influence the solubility and saturation of dissolved ozone in the injected water that needed to be known. The stability of ozone in solution is directly proportional to the ozone partial pressure introduced into the water and inversely proportional to increasing temperature, pH (Figure 59), EC and alkalinity (Nimmer *et al.,* 2000; von Gunten, 2003). Dissolved organic carbon and sulphides (such as HS^-) are also oxidant-consuming species but it is known that Fe^{2+} reaction rate coefficients with dissolved ozone is much faster than with the two other constituents (Nimmer *et al.,* 2000).
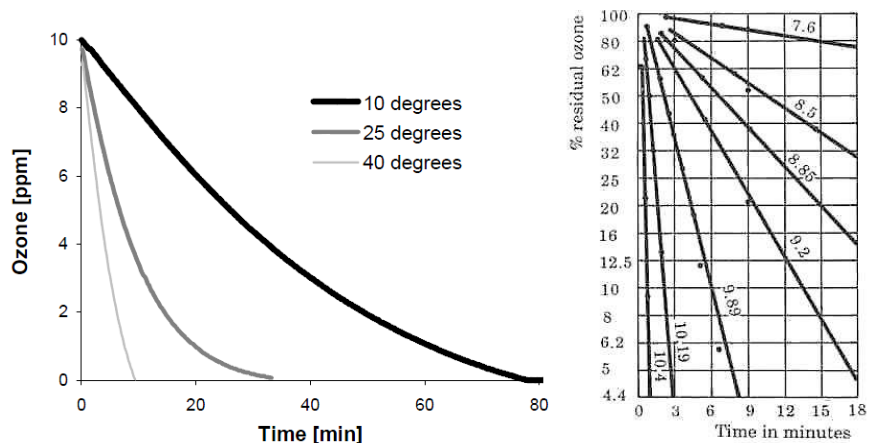
Figure 59: Ozone decomposition rate at increasing temperatures at pH = 7 (left) and increasing pH at 15°C (right) (Eriksson, 2005; www.lenntech.com/library/ozone/decomposition/ozone-decomposition.htm)

There are two mechanisms by which dissolved ozone can react with Fe^{2+} and Mn^{2+} in groundwater, namely by direct oxidation with ozone (i.e. ozone-based) or by the generation of free radical intermediated (i.e. OH^--based) or a combination of the two (Nimmer *et al.,* 2000; von Gunten, 2003). During the injection of ozonated water the dominating oxidation process is considered to be ozone-based (Masten, 2004; Plummer *et al.*, 2005).

Ideal conditions for ozone-based reactions for optimal removal of Fe^{2+} and Mn^{2+} include a water temperature of 15-20°C and a pH range of 7.0-8.5 because a pH greater than 10 or high alkalinity (> 300 mg/ℓ as $CaCO_3$) promotes the decomposition of ozone into OH^- ions (EPA, 1999; Nimmer $et\ al.$, 2000; El Araby $et\ al.$, 2009). The presence of OH^- enhances the oxidation process, but the free radicals have a much shorter half-life (in the order of microseconds) compared to dissolved ozone, which already has a relatively short half-life in the order of approximately 10 to 30 minutes (EPA, 1999; Munter $et\ al.$, 2008). This therefore restricts the radius of influence and contact with Fe^{2+} and Mn^{2+} in the subsurface when the reactions are OH^--based. In addition, even though OH^- formation is favoured under alkaline conditions, the CO_3^{2-} and HCO_3^- ions are radical scavengers, which could prevent oxidation of Fe^{2+}, Mn^{2+} and DOC (EPA, 1999; Vance, 2002; Munter $et\ al.,$ 2008). Other considerations when using ozone for $in\text{-}situ$ treatment include:

- $By\text{-}products$: One aspect that precludes the use of ozone, is if the groundwater has high concentrations of bromide because bromate (BrO_3^-) will form, which is a health concern (Sharma, 2001; Rajagopaul $et\ al.$, 2008). In this case study, there is no bromide that would be of concern. However, groundwater containing high concentrations of complex organic matter is known to form problematic disinfection by-products with carbon dioxide when ozone-based reactions predominate (EPA, 1999). However, this is more of a concern for $ex\text{-}situ$ water treatments rather than $in\text{-}situ$ application because filtration in the subsurface takes place a lot slower than in the filtration sand beds (Hallberg and Martinell, 1976). Although, the release of carbon dioxide during the oxidation could temporarily plug some of the aquifer pore space (Olsthoorn, 2000; Vance, 2002). Another concern is the over-ozonation of water with elevated Mn^{2+} concentrations, which would affect water quality by the mobilisation of soluble MnO_4^- and the resultant bright pink discolouration of the water (Sharma, 2001). However with time, the soluble Mn^{4+} ions are reduced to Mn(IV)-oxide and in this study it is improbable that there would be excess ozone in a natural system rich in DOC;

- $Geological\ setting:$ The fate and reaction mechanisms of ozone in heterogeneous, porous geologic media is not completely understood, but studies suggest increased ozone decomposition through catalytic reactions with natural inorganic and organic material or the converse, whereby the ozone half-life could be prolonged because of lower temperatures in the subsurface (Vance, 2002; Plummer $et\ al.,$ 2005);

- $Health\ and\ safety:$ Ozone is a colourless, toxic gas and ozone production and application should be designed as to limit and protect the plant personnel (EPA,

1999). In this study, which is an outdoor application, no ventilation is required but an ozone destruct unit will have to be included in the design for any off-gas removal. The pungent odour of ozone will also provide adequate warning to the operators of a possible leak (EPA, 1999);

- *Decomposition:* in comparison to ozone gas in a distribution pipe to reduce the microbial populations, *in-situ* treatment must take into consideration that ozone decomposes in water both during the contact stage with the recharge water and within water mixing in the aquifer, which limits the ozone-based oxidation reactions (EPA, 1999; Masten, 2004).

5.4   Prototype Design and Construction

The decision to use ozone as the oxidant was based on the systematic elimination of other commonly used oxidants for the removal of Fe^{2+} and Mn^{2+} in organic- and silica-rich groundwater, using available literature and case studies. Commercial production of ozone gas for water treatment is generally done by passing dried oxygen gas (O_2) through a high-voltage electrical field generated in a corona discharge (CD) cell (Plummer *et al.*, 2005; Rajagopaul *et al.,* 2008). The O_2 molecules pass through two electrodes and when a voltage is applied, electrons flowing across the discharge gap provide sufficient energy to excite and dissociate the O_2 into two singular oxygen atoms (O_1) (Figure 60; EPA, 1999; Vance, 2002). Seeking molecular stability, these atoms recombine with other oxygen molecules in the oxygen stream to form ozone (Plummer *et al.,* 2005). The power requirement for such production is in the range of 8 to 17 kWh per kg of ozone (EPA, 1999).
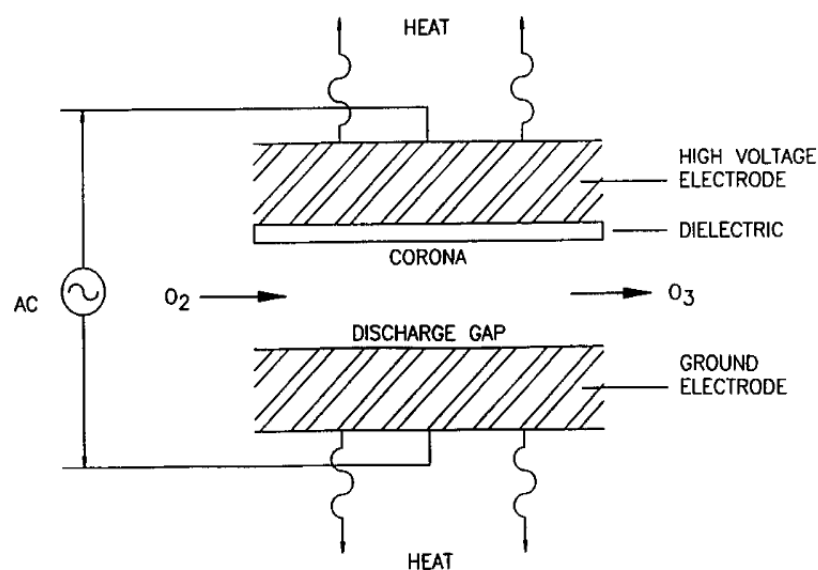
Figure 60: Schematic of ozone generation using a CD generator, which was used in this study (EPA, 1999)

Air or pure oxygen gas is used as the feeder gas, which is passed to the ozone generator at a set flow rate (Rajagopaul *et al.,* 2008). This feed gas must be clean and have a dew point of -60°C (Wassertec, 2012). A CD generator can yield 1-2% O_3 from air compared to the 3-8% attained using oxygen gas (Vance, 2012). The lower concentration and quality of ozone produced from ambient air is because air only contains 23% O_2, as well as impurities and moisture. Generally, raw water treatment requires oxygen gas due to the higher ozone concentrations required (Vance, 2002; Rajagopaul *et al.,* 2008). Additional benefits from the use of oxygen gas to produce ozone are (Vance, 2002; Ansorge, *pers. com.* 2011; Wassertec, 2012):

- Oxygen gas (> 90% purity) almost doubles the O_3 produced, which increases its solubility in water;

- The lower energy required (up to 75%), which decreases initial capital and operation costs because approximately 40% of the cost is for air pre-treatment;

- The gas flow from the generator would consist of a mixture of ozone and oxygen gas, which increases the DO in solution.

The ISIR prototype for this pilot test was designed in partnership with the WRC project team and Cape Town-based ozone engineers from the commercial company Wassertec, well-known for the manufacture of CD ozone generators. It was decided that ozone gas would be produced from oxygen gas sourced from ambient air because oxygen gas almost doubles the ozone gas generation volumes.

The ISIR prototype setup consists of an oil-less compressor, which draws in ambient air and passes it through an oxygen generator. High purity oxygen gas (> 93% O_2 at 5 ℓ/min) is produced by a pressure swing adsorption process, which removes all the nitrogen, carbon dioxide and moisture from the compressed air (EPA, 1999; Wassertec, 2012). The high purity oxygen gas is delivered to the CD generator, which is produces between 7.0 to 8.0 g/h of ozone from 4-5 ℓ/min of input air (Wassertec, 2012). The ozone gas is combined with excess oxygen gas and supplied to the dosage venturi via a Teflon tube (Wassertec, 2012). The complete ozone generation system is very compact because it fits on a 1 m^2 panel of particleboard, which could be semi-permanently fixed to the inside wall of the caravan supplied by the CoCT. The small size and lack of a need for permanent above-surface equipment provided mobility and protected the ozone and oxygen generators from direct sunlight and rainfall, as well as any potential vandalism.

The ISIR prototype was supplied with groundwater production from borehole G30966, which was diverted at the modified air vent on the borehole mains into a lay-flat pipe leading to a 3 m^3 water tank. The water in the tank was degassed and aerated through exposure to the atmosphere, assisted by agitation with a closed-loop, petrol-engine driven mobile pump. Another pump of the type commonly used in domestic swimming pools drew the aerated groundwater from the tank through reinforced PVC tubing (33 mm outside diameter) and pumped it through the venturi pipe section (32 mm diameter x 150 mm length). The suction port of the venturi was connected to the ozone outlet of the CD generator via 8 mm Teflon tubing. When the groundwater flowed through the venturi, it created a vacuum which drew the mixture of O_3 and O_2 into the water. The ozonated water was then pumped into a PVC column (height 1.3 m x 0.1 m diameter), where any excess O_3 and O_2 or by-product carbon dioxide, methane and H_2S gas was released from the ozonated water before injection via a degassing valve at the top of the column. This prevented any remaining entrapped gas from being introduced into the aquifer, which would interfere with the injection process as experienced in Egypt where clogging of the pore space took place due to gas bubbles included into the recharge water (Olsthoorn, 2000). The oxygen and ozone-enriched water (hereafter referred to as ozonated water) was then forced into the subsurface through 20 mm outside diameter thin-walled clear PVC tubing to a depth of greater than 24 mbgl (Figure 61).

The depth of injection between 24 to 27 mbgl was selected according to the screen depth of the G30966 borehole and because the water column would pressurise the ozone to remain in solution and not be lost to the atmosphere, which would be experienced if injections occurred at depths of less than 6 mbgl (Ansorge, *pers. com.* 2011). The diameter of the pipe was selected based upon recommendations by Olsthoorn (2000), i.e. that there should be enough resistance during injection to keep the pipe full of ozonated water, which will prevent the introduction of gas bubbles into the borehole and subsurface.
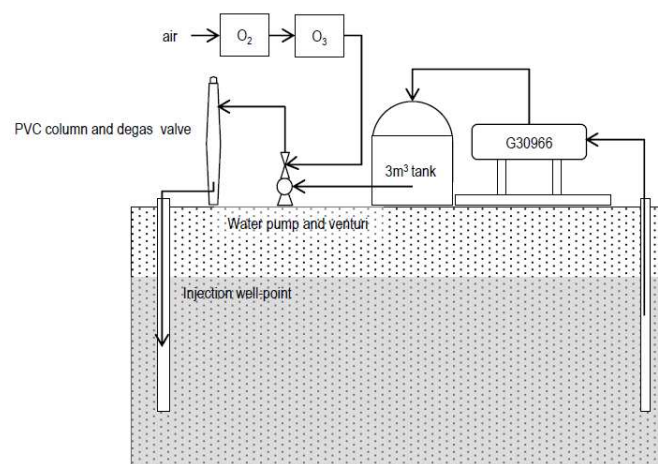
Figure 61: The pilot plant flow diagram at the study site

The ISIR prototype system was designed to run continuously and required little supervision and maintenance, demanding only periodic checking of the suction from the venturi, condition of the water pump, cleaning of the air filters and efficient operation of the cooling fans inside the ozone generator (Ansorge, *pers. com.* 2011; Wassertec, 2012). The components other than the equipment necessary for the ozone system (i.e. oxygen and ozone generators, ozone-rate degas valve, venturi and Teflon tubing for transferring the ozone gas) were easily available from any local hardware store. The tank, engine-driven pump and lay-flat pipe (which are used for firefighting in the summer months) were kindly supplied by the Witzand Wellfield. The caravan and water tank were easy to transport to site and the system was simple to assemble. This made it easy to operate in conjunction with pumping from proximal switchgear from the source borehole (G30966). Other than the drilling of injection and monitoring well-points (explained in the next section) there was minimal disturbance to the study area.

5.5   Installation of Well-points

Since the borehole condition of G30966 and the high water table in the Atlantis Aquifer prevented the direct injection of ozonated water into the aquifer for ISIR treatment, a number of small-diameter well-points had to be drilled within the area to act as injection or monitoring points during the treatment.

The number and positions of the well-points for this pilot test took into consideration the regional flow direction, transmissivity (from the latest CDT test), distance from available water supply (G30966) and the proximity of an electrical power supply needed for the ozone generation, as well as budget constraints. It is generally recommended that the injection well-points should be situated in a ring around the production borehole or semi-ring configuration up-gradient of groundwater flow direction (Hallberg and Martinell, 1976; Hinkamp *et al.,* 2004). The well-point screens should be placed at least at the depth of the production borehole screen (Hallberg and Martinell, 1976). In addition, borehole casing materials used should be ozone-resistant, such as stainless steel or Schedule 40 or 80 PVC (Nimmer *et al.,* 2000; Plummer *et al.,* 2005).

Twelve small-diameter well-points (Figure 62) were mud-rotary drilled within an area of approximately 16 m radius around G30966 by Fairbrother Geotechnical Engineering cc. in January 2013. Ten of the well-points were drilled to a depth of 31 m and two to a depth of 15 m (i.e. 6SNE and 7SSW). The deeper well-points would function as injection or monitoring points for the Springfontyn Formation, whereas the shallower well-points were to be used as

monitoring points for water quality changes and vertical transfer of oxidant (if any) in the upper Witzand section of the aquifer during injection.
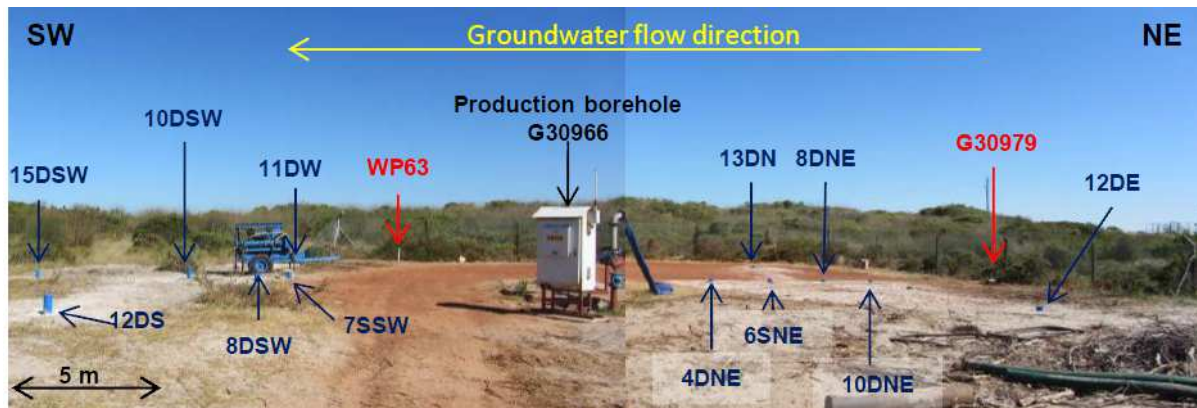
Figure 62: Location of the newly drilled well-points (labelled blue) in close proximately to G30966 (labelled black), G30979 and WP63 (labelled red)

Mud-rotary drilling was used in this study because it is the most commonly used drilling technique for construction of shallow boreholes in semi-consolidated sands (Driscoll, 1986). This technique makes use of a rotating bit attached to the end of a string of the drill rods, which transmits the rotating action from the drill rig to the bit to penetrate the formation. In this study, the drill rods were three metres long and had an outside diameter of 160 mm.

Before a well-point was drilled at each new site, the angle of the drill rig was checked by a leveller to ensure that the drilling would be vertical. The first drill rod is then secured into position within a 0.5 m diameter solid casing for stabilisation of the area during the initial few meters of drilling. To ensure that the hole does not oversize during the drilling operation, drilling is initiated when the 0.5 m solid casing has been hammered into the ground and the casing is then secured to the rig to ensure that it is held in position when the bit and rods continue to drill into the subsurface (Hermelin, *pers. com.* 2012).

During the drilling, a water-based drilling fluid (i.e. drilling mud) is pumped from a temporary sump down the drill rods and out of the bit ports (Driscoll, 1986). In this study, the drill mud was a mixture of polyflip (a natural gum from the guar bean) and groundwater derived directly from G30966 or treated groundwater brought in from the Witzand WTP. This mud is used to lubricate the bit and bond to the sand material to prevent collapsing of the unconsolidated sands before the casing is installed (Driscoll, 1986). The drilled sands are then removed by the continuous circulation of a mud in the annular space between the hole and drill rod (Driscoll, 1986). At surface, the mud fluid is channelled into a temporary pit for the sands to settle out and be collected for subsequent analysis (Driscoll, 1986).

The drilling of each hole had to be continuous to ensure that no back-pressure from the collapse of the hole might clog the bit and bottom rods, preventing drill mud from pushing out into the subsurface (Hermelin, *pers. com.* 2012). Once the desired depth was reached, drilling fluid continues to be pumped down the rods for approximately 5 to 10 minutes to ensure that the drilled hole is filled with drilling fluid before the rods are removed. This condition was confirmed by inspecting the texture of the slurry coming out of the hole simply by feeling it between the fingers. When the slurry was devoid of sand, the rods were slowly raised and removed.

The borehole casing was installed once the last rod was removed. Pressure Class 6 PVC pipe (i.e. working pressure of 600 kPa) was used for both the casing and screen material, with the last six metres of each well-point screened. Since the well-points are for monitoring and injection purposes and not for abstraction, a number of screens slots (i.e. 0.5 mm wide and 69 mm long) were manually cut into the PVC casing, which gave an open area of approximately 5%. The well-points were capped at the base with a 30 mm PVC end cap and the remainder of the drilled hole had solid PVC casing secured to the screen by couplers and stainless steel screws. The solid and screened sections of the well-points are PVC with a 63 mm outside diameter and wall thickness of 1.9 mm. The screened section is surrounded by a 48.5 mm thick gravel pack of 10/30 grade.

The newly equiped well-point was flushed with clean water derived from the G30966 until there was no traces of drilling mud for approximately 30 minutes. All effluent that came to the surface was redirected back into the sump. Once completed a steel standpipe was fitted over the open PVC pipe to ensure that the open pipe is protected.

Unfortunately, due to the length of the drilling rods used, sand samples were only collected at approximately three metre intervals for each well-point, instead of the generally recommended one metre interval for detailed logging of geological formations (Driscoll, 1986). The limitations associated with a choice of drilling technique unfortunately also compromised recording of accurate depths from which the sand samples came because of recirculation of the drilling fluid with slurry also introduced sand from the previously drilled well-points. Nevertheless, the characteristics of the sands (i.e. grain size, sorting and roundness) were described by the author and the depths of the calcrete lenses were noted wherever possible. Samples were then collected in plastic bags and placed in core trays, which is currently stored at the CGS Bellville office. Initially, it was thought that laboratory grain size analyses should be undertaken because it can provide a high resolution analysis of the vertical section of the aquifer in the study area (ISRRI, 2009) but this idea was abandoned because the samples could not be uniquely attached to any stratigraphic depth.

Only sands of the Sandveld Group were expected to be intersected during the drilling process as all indications were that the weathered clay of the Malmesbury bedrock (i.e. the base of the aquifer) would only be intersected at much greater depths, i.e. > 34 mbgl. The sands were found to be fine to medium-grained and grains were devoid of any iron-staining. A number of calcrete lenses were intersected in every hole. These units appeared to be concentrated in the upper 12 m of the drilled section, which would be expected to be the Witzand Formation.

The CGS Marine Division conducted an elevation survey of the study area and recorded the co-ordinates of the newly drilled well-points (Appendix E) using a Carlson Surveyor+ handheld GNSS receiver running SurvCE software (Van Zyl, *pers. com.* 2013). The GNSS receiver utilises GPS L1 and L2 band satellite signals and GLONAS L1 and L2 band satellite signals to increase the accuracy of the survey (Van Zyl, *pers. com.* 2013). The receiver is equipped with a built-in GSM modem utilising a cellular network to receive RTK NTRIP corrections. The RTK positioning allows for very accurate elevation readings up to centimetre accuracy (Van Zyl, *pers. com.* 2013). The ground survey was plotted in Surfer Version 8 and ArcGIS Version 9.3.1, showing that the study area has a relatively flat surface elevation varying between 54.5 and 54.9 mamsl (Figure 63).
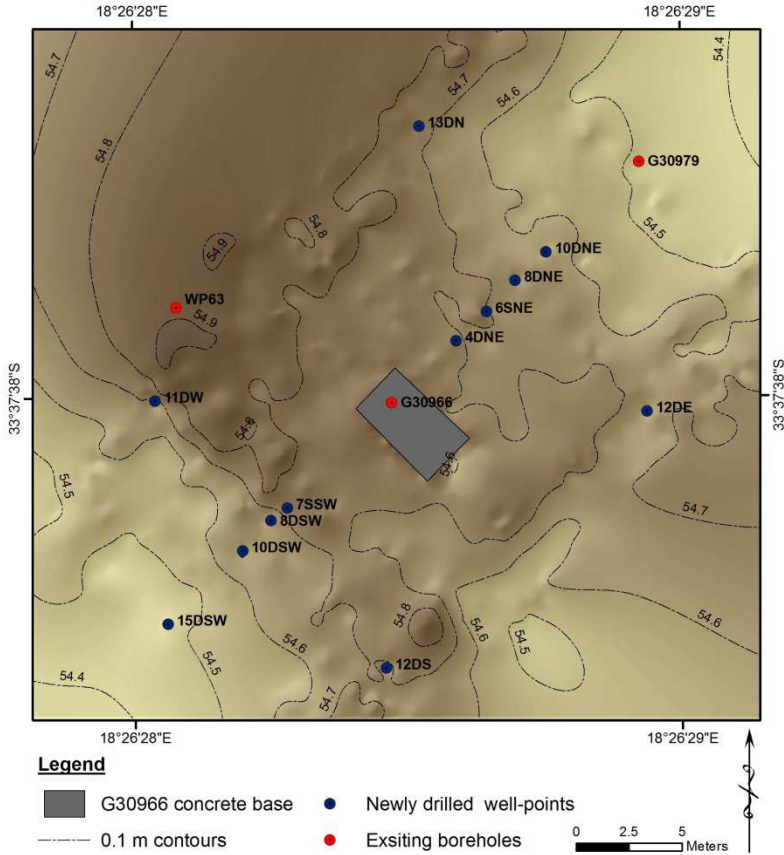
Figure 63: The study area elevation map showing the layout of the twelve well-points in relation to G30966

5.6   Regulatory Requirements

One of the main objectives in designing the ISIR prototype for this study was that the treatment should be user-friendly and environmentally safe to apply, with no generation of hazardous waste that would require subsequent disposal. The aim was also that it should not require any (or minimal) regulatory compliance with NEMA, NWA and health and safety legislation.

There are no regulatory requirements for the use of ozone in drinking water due to its short half-life in water (e.g. 20 minutes at 20°C and pH = 7) and its only residual is DO, which makes it innocuous to drink (EPA, 1999; Wassertec, 2012). However, gaseous ozone is toxic and can be harmful to humans at high levels of exposure (Wassertec, 2012). Currently, no legislation exists in the Occupational Health and Safety Act No. 85 of 1993 (Republic of South Africa, 1993) or the National Environmental Management: Air Quality Act No. 39 of 2004 (Republic of South Africa, 2005) with respect to airborne ozone concentrations. As a result, guidelines by the United States of America Occupational Safety and Health Administration, which requires that workers cannot be exposed to ozone levels in ambient air of more than 0.1 mg/ℓ for eight hours (Wassertec, 2012) were used in this study.

Ozone has a distinct odour at low concentrations and the symptoms for inhalation of ozone include easily identifiable chest pain, coughing, shortness of breath and throat irritation (Wassertec, 2012). If a person shows any of these symptoms in close vicinity to the ozone generator, the system must be turned off and the person should remove himself or herself to a well-ventilated area (Wassertec, 2012). The manufacturer is then contacted to establish if and why there is a leak (Wassertec, 2012). Ozone in gaseous form is also explosive at concentrations ≥ 240 mg/ℓ but generally ozonation systems never exceed concentration greater than 50-200 mg/ℓ, implying that it is generally not regarded as a fire-risk (EPA, 1999). The above issues were taken into consideration with the design of the ISIR prototype because the by-product gases containing any O_3 would be released into the outside atmosphere via a degas valve (situated at the top of the PVC mixing column), which maintained the safety of the personnel working in the area. The by-product gases produced during oxygen generation from air (predominately nitrogen and carbon dioxide) were vented off through a tube leading out through the caravan window.

Although, there are no specified regulatory requirements for *in-situ* treatment methods under the relevant South African environmental (NEMA) and water (NWA) legislation (Tredoux *et al.,* 2004), this project did ultimately include two activities that still required compliance with the legislation. These activities included the drilling of the injection well-points and the injection of ozonated water into the aquifer.

5.6.1 Drilling activities

There were no NEMA listed activities triggered by the mud-rotary drilling of the twelve well-points in the study area, but an Environmental Method Statement was required by the CoCT Environmental Resource Management Department. This statement was prepared according to the requirements outlined in the Standard Environmental Specifications for controlling the impacts on the environment from permanent construction activities (CoCT, 2007) and was approved on 23 October 2012. In addition, the registration of the new well-points on the DWA National Groundwater Archive was required (Appendix E).

5.6.2 *In-situ* iron removal by ozonated water

There were no listed activities triggered in terms of NEMA with regard to this activity, but two water use activities were flagged under Section 21 of the NWA:

- Section 21(a): Taking water from a water resource;

- Section 21(i): Altering the bed, banks, course or characteristics of a watercourse.

A General Authorisation was required for the project to proceed for the injection experiments. A meeting including a presentation took place and a report was submitted to satisfy the terms of the DWA General Authorisation. Permission was granted on 5 June 2013 for initiation of injections tests as the water use activities form part of the existing water use licence of the CoCT (Daniels, e-mail communication 2013).

5.7 Summary

Ozone was chosen as the oxidant for this study because aeration would not be feasible for the organic-rich groundwater present at the study site. Other well-known chemical oxidants (i.e. oxygen gas, H_2O_2 and $KMnO_4$) were also considered because they have historically also been used in ISIR treatment methods, but these were excluded either due to the costs associated with equipment or because of storage and handling risks. Ozone was favoured as it is generally accepted to be non-polluting to an aquifer because it leaves no harmful residuals behind. This requires no disposal or further attention after treatment. The lack of previous studies and the fact that this is the first study to test the application of ozonated water for ISIR is believed to be due to the preconception that ozone generation and injection is a high-cost technology that may have a limited radius of influence (Piper and Salvage, 2012).

However, in comparison to a quote given to the Corle WTP for ISIR at a modified production borehole using oxygen gas (i.e. DO = 18 mg/ℓ per injection cycle) (Bergevoet, email communication 2012), it would suggest that ozone is not such a high-cost treatment when compared to oxygen gas. The quote provided for the use of oxygen gas in the ISIR treatment came to a total cost of R116 762.00 in 2005 (Bergevoet, email communication 2012), which included the construction of a storage system for two oxygen gas cylinders (4.6 m length x 2.0 m width x 2.4 m height), the oxygen dosing system, injection system and the labour for onsite construction. This is more than double the initial capital cost of ozone generation systems designed for the study site in 2012 by three suppliers in South Africa, which ranged between R39 600.00 and R50 000.00. These ozone systems quoted for normally included the compressor, oxygen generator (which produces > 93% oxygen gas), ozone generator, water pump, venturi, mixing column, de-gassing valves and associated tubing and controls, as well as labour and onsite installation at the study site. It was also expected that the DO would be much greater with ozone and Fe^{2+} and Mn^{2+} removal would be accomplished in a shorter time period, hence it would be more cost effective in the long term.

CHAPTER 6.   ASSESSMENT OF ISIR TREATMENT

6.1   Introduction

This chapter discusses the field tests using the ISIR prototype at the investigated production borehole, G30966. The investigation focused on the immediate effectiveness of the ISIR application in reducing the Fe^{2+} and Mn^{2+} concentrations in the abstracted groundwater. For this experiment, the desired concentrations are based on the threshold levels given by WHO (2008), i.e. Fe ≤ 0.3 mg/ℓ and Mn ≤ 0.1 mg/ℓ. At these threshold concentrations, any potential health and aesthetical problems are prevented and iron-related clogging processes are significantly reduced. However, to prevent clogging in production boreholes, a threshold limit for iron of less than 0.1 mg/ℓ (Hinkamp *et al.,* 2004) is more appropriate.

6.2   Methodology

The pilot injection tests started on 3 July 2013, using an ISIR methodology based on the Vyredox procedure described by Hallberg and Martinell (1976):

- Abstraction takes place from G30966 to fill the 3 m^3 tank, with the groundwater initially aerated by allowing it to splash onto the baffle balls as it enters the tank (Figure 64);

- Abstraction is stopped in G30966 once the tank is full and kept switched off during the injection phase;

- The abstracted groundwater was then further aerated by recirculation in the tank for up to 30 minutes using a petrol-powered pump on the water tank. This aimed to further remove any uncomplexed Fe^{2+} and Mn^{2+} ions and undesirable gases, especially H_2S, which could be smelled during abstraction, that would reduce the concentration of ozone and oxygen gas into the recharge water (Figure 64);

- The aerated groundwater was then drawn from the water tank by another pump and pushed through the venturi, which draws in the mixture of ozone and oxygen gas (Figure 65);

- The ozonated water is then pumped through PVC tubing into the aquifer via a well-point up-gradient of the production borehole. Injection is initiated up-gradient so the precipitation of the oxides would create a barrier for attenuation of the Fe^{2+} and Mn^{2+} as the groundwater flows past.

Figure 64: The abstracted groundwater was aerated by increasing the exposure to the atmosphere by splashing the water as it entered the tank (left) and recirculation within the tank(right)

Figure 65: Initial injection technique set-up with injection tests in 10DNE

To evaluate the effectiveness of the ISIR treatment the following information was collected during the injection tests. Groundwater samples from G30966 were collected before the start of the experiment on 1 and 3 July to establish the groundwater baseline quality. Subsequently, G30966 was sampled periodically to evaluate any quality changes as a result of the ISIR treatment.

The water sampling followed the standard protocols outlined in Weaver *et al.* (2007), whereby unfiltered samples were collected in a 1 ℓ glass bottle, which was correctly prepared before sampling by rinsing it three times with abstracted groundwater before collecting the sample from the sampling tap. Additional water samples were collected for analysis of the dissolved iron and manganese concentrations, which is the fraction of iron and manganese ions that passes through a 0.45 µm filter. In this study, these samples were pressure filtered using a luer lock syringe-filter, generally after the unfiltered samples were collected. The filtered samples were collected in correctly prepared 250 mℓ plastic bottles. No preservatives were added to the filtered and unfiltered water samples.

The parameters analysed were selected according to the discussion in Chapter 4.7.1.3. Analyses were performed by the CoCT Scientific Services or the CSIR laboratories (Table 18). Both are SANAS accredited laboratories. The accuracy of the major cation and anion analysis was evaluated using the protocols and water type calculations given in Chapter 4.7.1.1. The accuracy of the total iron and manganese concentrations was also evaluated, where the total concentration values are always greater than the dissolved concentrations and the difference between the two concentrations known as the colloidal concentration (Weaver *et al.,* 2007).

Table 18: Water quality parameters of interest for the ISIR investigation

	Scientific Services reference method	CSIR reference method
EC (mS/m)	TIAMO analyser	Radiometer CDM3
pH	TIAMO analyser	Radiometer TIM860
Ca	ICP-OES	n.m.
Na	ICP-OES	n.m.
Mg	ICP-OES	n.m.
K	ICP-OES	n.m.
Total Alkalinity as $CaCO_3$	TIAMO analyser	n.m.
Cl	Discreet analyser	n.m.
SO_4	Discreet analyser	n.m.
$NO_3 + NO_2$ as N	Discreet analyser	n.m.
Total and Dissolved Fe	ICP-OES	Agilent 7500 ICP Mass Spectrometry (MS)
Total and Dissolved Mn	ICP-OES	ICP-MS
F	Discreet analyser	n.m.
Si	ICP-OES	n.m.
Sr	ICP-OES	n.m.
TOC	TOC analyser	n.m.
DOC	n.m.	Multi N/C® 3100 Analyser
*Date given in mg/ℓ unless otherwise specified		

The sample preparation for ICP-MS analysis follows the same preparation procedure as for ICP-OES analyses (Chapter 4.7.1.1). The DOC analysis by the CSIR laboratory required the sampling of a representative aliquot, which was filtered through a 0.45 µm filter. The aliquot is acidified with 2M HCl to remove any inorganic carbon in the sample and the remaining carbon in the sample is determined in the analyser by thermocatalytic high-temperature oxidation in the presence of a platinum catalyst (Brown, 2014). In the case of the Scientific Services analyses for TOC, no acidification of the sample was necessary for the TOC analyser used, which is based on Supercritical Water Oxidation.

The field measurements of pH, EC and DO were measured during the injection experiment from three points:

- Abstracted groundwater from G30966;

- Ozonated water;

- At monitoring well-points.

The field measurements were done using an Extech Model DO700 meter with the following probes:

- pH using an Extech pH305 glass electrode;

- DO using an Extech DO705 permeable membrane electrode;

- EC using the EC605 polymer conductivity cell.

All three of the probes are equipped with a temperature sensor and were calibrated before each day of testing according to the Extech manual. The field measurements at G30966 were achieved by connecting a flow-through cell to the sampling tap and in the monitoring well-points at the screen depth by lowering a 30 m submersible pump into the well-point and connecting it to the flow-through cell. The field measurements were taken after the reading had stabilised and the water samples collected from G30966 were collected after the field parameter measurements had stabilised. Special care was taken with the DO measurements because the probe required continuously movement (i.e. 5 ℓ/s) for more than three minutes in a flow-through cell to prevent intake of oxygen by the probe, which would give artificially low readings. A Milwaukee Martini pH and EC meter from DWA and a Criston DO meter from CSIR were also used for quality checking by duplicating measurements and while the Extech meter was being repaired. The dissolved ozone concentrations were measured in the injected water to evaluate the oxidant dosage by means of the Hach® ozone test kit, which is a colorimetric method based on the reaction of the ozone with the *N,N-diethyl-p-phenylenediamine* (DPD) Total Chloride reagent.

The water level changes were also measured during the injection tests by placement of Solinst® dataloggers in G30966, the injection well-point and monitoring well-points spaced generally at equidistance from the injection well-point. The water level measurements are given as barometrically compensated numbers, which were adjusted as described in Chapter 4.6.1.

6.3   Results

6.3.1   Baseline water quality

For comparative purposes, the latest baseline quality data was acquired by collection of two water samples from G30966 prior to the injection tests (Appendix F). Both analyses passed the E.N. test and the data was compared to the median (i.e. Q50) calculated from the four samples taken during the 2013 pumping tests (hereafter referred to as the baseline values) and the SANS 24:2011 drinking water standards (Table 19). Field parameters were also measured on 1 July in G30966 and 10DNE, which is ten metres hydraulically up-gradient of G30966, to constrain the DO concentrations in the study area (Table 20).

Table 19: Water quality before injection tests compared to earlier 2013 baseline values and SANS 241:2011

Parameter*	1 July 10:30 AM	3 July 10:30 AM	2013 baseline	SANS 241:2011
EC (mS/m)	67.40	68.40	68.80	≤ 170.00
pH	7.83	7.70	7.66	5.00-9.70
Ca	46.71	47.56	48.03	-
Na	74.70	78.40	80.90	≤ 200
Mg	9.70	8.42	8.39	-
K	6.80	7.56	7.83	-
Total Alkalinity as $CaCO_3$	159.30	162.10	158.40	-
Cl	103.00	106.00	106.10	≤ 300
SO_4	33.10	31.00	27.30	≤ 250
$NO_3 + NO_2$ as N	0.60	0.44	≤ 0.20	$NO_2 ≤ 0.90$; $NO_3 ≤ 11.00$
Total Fe	2.96	2.15	0.53	≤ 0.30
Total Mn	0.49	0.26	0.20	≤ 0.10
F	0.34	0.27	0.22	≤ 1.50
Si	4.10	4.50	4.51	-
Sr	0.46	0.48	0.45	-
TOC	4.90	5.50	7.10	≤ 10.00
*Date given in mg/ℓ unless otherwise specified; n.m. not measured				

Table 20: Field parameters in G30966 and 10DNE during baseline sampling on 1 July 2013 at 10:00 AM

	EC (mS/m)	pH	DO (mg/ℓ)	Temperature (°C)
G30966	65.9	7.86	0.42	17.8
10DNE	68.0	7.47	0.44	18.2

6.3.2   Initial injection test

The first injection test was done using well-point 10DNE because it is hydraulically up-gradient of test borehole G30966 and there are three monitoring well-points between it and G30966 (each spaced two metres apart), which would assist in the monitoring of changes in DO, pH and EC with progressive treatment. However, the first few injection attempts on 3, 4 and 11 July at a depth of 27 mbgl encountered practical difficulties manifesting as continuous bubbling and overflow of water from 10DNE during injection attempts (Figure 66). To prevent overflow, the rate of injection was reduced but this caused a decrease from 0.4 mg/ℓ to 0.1 mg/ℓ in the concentration of dissolved ozone. An injection rate of 1.37 m^3/h was calculated from the average of the time taken to empty the 3 m^3 tank. The water levels on the first day of injection tests are shown in Figure 67 and the measured field parameters in 8DNE (two metres hydraulically down-gradient from injection) during the first two injection tests days are given in Table 21.

Figure 66: The project team struggling to get the ozonated water into the aquifer due to the bubbling and overflow from the injection well-point
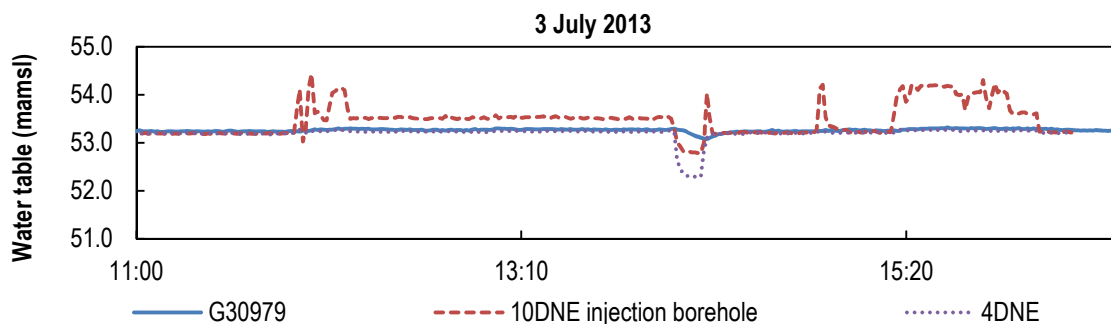
Figure 67: Water level response in the injected well-point and two monitoring well-points. The drawdown observed was due to abstraction in G30966 during the filling up of the water tank for the second injection for that day.

Table 21: Field parameters in monitoring well-point 8DNE before and during the injection tests

	EC (mS/m)	pH	DO (mg/ℓ)	Temperature (°C)
3 July 11:20 AM (before injection)	58.20	7.48	0.47	18.00
3 July 12:10 PM (during first injection test)	58.60	7.64	0.48	18.60
3 July 14:40 PM (during second injection test)	57.50	7.68	0.49	18.90
4 July 10:10 AM (before injection)	57.00	7.63	0.44	18.40
4 July12:10 PM (during first injection)	56.20	7.47	0.40	18.50

6.4 Discussion

6.4.1 Baseline water quality

The July samples were collected to evaluate whether there were any significant changes in the water quality in the last three months since the pumping tests and if so, if there were any parameters of concern (excluding iron and manganese) according to SANS 241:2011. The majority of the parameters measured in July were comparable with the pumping test results, with the major ions defining the same water type (i.e. Na-Ca-HCO_3 type; Figure 68). However, the TOC, $NO_3 + NO_2$, F, Fe and Mn concentrations in both samples differed significantly from the pumping test results (i.e. greater than ±25%). Although there was variation from the 2013 pumping test baseline data, it was established that the water quality abstracted from G30966 is still of a good drinking water standard, with elevated iron and manganese concentrations, which necessitated removal.
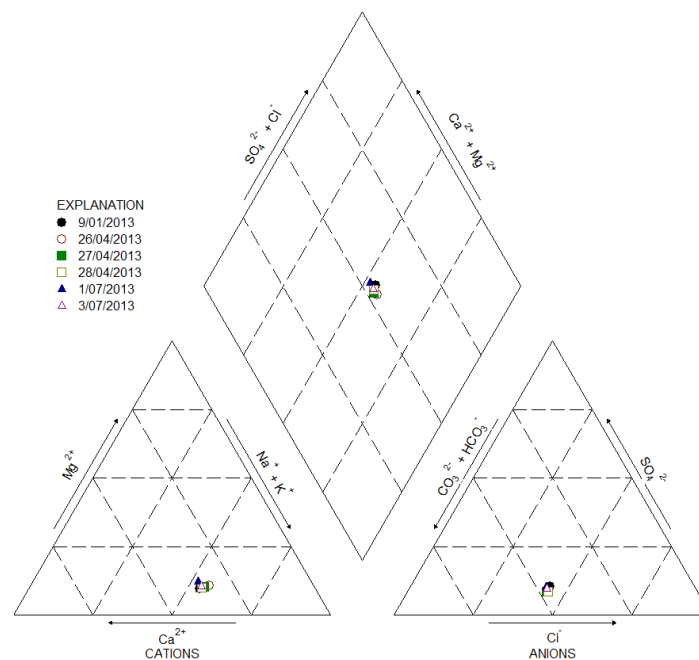
Figure 68: Piper diagram of the major ion composition of G30966 baseline water samples collected in 2013 for this study

The iron and manganese concentrations measured in July showed variability between the two samples and were much higher than the known baseline values. This is related to how well the borehole was purged before the water sample was collected (Figure 69). The longer the pumping of the borehole, the more representative iron and manganese concentrations from the native groundwater would be, while the shorter pumping events show elevated concentrations of both iron and manganese, from their accumulation in the standing water in the borehole (Weaver *et al.,* 2007). The variability was greater in the iron than manganese concentrations, mainly because iron levels are more than double in the groundwater. The iron concentration in the July samples are almost four times the concentration measured after the pumping tests in January and April 2013 (Figure 69). Since G30966 has been taken out of production from December 2012 and has not been used in the months prior to the injection tests, the elevated iron and manganese concentrations are assumed to be due to the standing of iron-rich groundwater and sloughing off of Fe(III)-oxyhydroxides deposits in the borehole and not representative of the native groundwater in the aquifer. The 1 July value is much higher compared to the 3 July sample because a slower abstraction rate was used for sampling on 1 July.
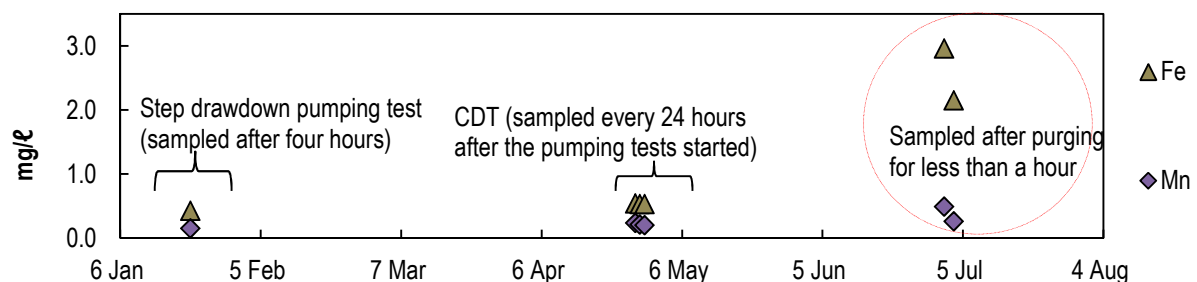
Figure 69: Variations in the iron and manganese concentrations in 2013 according to how well the borehole was purged before a sample was collected

The baseline field measurements in 10DNE and G30966 gave EC levels between 66 and 68 mS/m and a pH from 7.5 to 7.9, which correlated with the laboratory results (Table 19). The DO measurements in both boreholes gave a low value of approximately 0.4 mg/ℓ at 18°C (Table 20). Unfortunately, redox probes were not available at the time of this study to measure the pe conditions, so DO concentrations were used instead as an indicator of the change from anaerobic to aerobic conditions in the groundwater, with an increase in DO indicative of anoxic conditions, which is taken as DO ≤ 0.5 mg/ℓ (http://toxics.usgs.gov/definitions/anoxic.html).

6.4.2   Initial injection methodology

As stated previously, the initial injection methodology applied on 3, 4 and 11 July encountered practical problems due to the prototype set-up as continuous bubbling and overflow in the injected well-point forced a low injection rate (i.e. < 1.4 m^3/h) (Figure 66). The insufficient infiltration of the ozonated water into the aquifer was the result of entrained gas bubbles in the ozonated water, which due to buoyancy forces, resulted in a bubble column flowing upwards along the path of least resistance from the discharge point to the surface in the well-point. The poor penetration of the ozonated water into the aquifer was observed by the negligible change in the monitored water levels, six metres up and down-gradient of injection, with only the injected well-point showing an increase (Figure 67). In addition, the field parameters measured in 8DNE (two metres hydraulically down-gradient from injection) during the first two injection tests showed no noticeable variations (i.e. ±10%) in the EC, pH and DO compared to the known baseline conditions measured before the injection tests (Table 21).

The success of ISIR methodology using the Vyredox approach recommended in Hallberg and Martinell (1976), is known to require the determination of operational parameters through trial testing in the field (Karakish, 2005; ISRRI, 2009). This requires modifying the treatment using multiple injection attempts, each of which would hopefully improve on the performance of the prior injection attempt (Karakish, 2005; ISRRI, 2009). In this study, modifications had to be made to both the ISIR prototype and injection methodology so as to adapt to the site conditions. Three noteworthy changes to the original methodology are described in the following sections.

6.5   Second Injection Technique

6.5.1   Methodology

It was acknowledged that the bubbles entrained in the injected water inhibited injection into the aquifer, necessitating modifications to the first application. This was readily resolved by the inclusion of the degas column between the water pump and injection pipe. The ozonated water was then pumped into the degas column where any excess ozone and by-product gases were released (Figure 70). The initial exclusion of the degas column was done because the researcher wanted to maintain as much dissolved ozone and DO in the injected water. These injection tests followed the same stop-start injection abstraction approach as the previous methodology, where groundwater was abstracted from G30966, directed to the water tank and aerated, drawn by the pump through a venturi where it was ozonated, then pumped through the degas column and injected at depth in 10DNE. It was envisaged that for

this methodology, the abstracted groundwater would be aerated for at least 30 minutes by recirculation before injection and the injection tests should run for at least a week (i.e. five days of injections) at the full injection rate output with at least two to three injections per day.

Figure 70: The modified experimental set-up for the ISIR at the study site after the first injection tests

6.5.2   Results

From 16 July through to 2 August, a total of 18 injection runs (3 m^3 per injection) were carried out at 10DNE at a depth of 26 mbgl. During the days of injection, 6 to 9 m^3 of ozonated water was injected into the subsurface, with an average of 98 minutes needed per 3 m^3. This gave an injection rate of approximately 1.84 m^3/h. Even though there was an increase in injection rate and volume injected per day, a water table rise was only observed in the injected well-point (Figure 71).
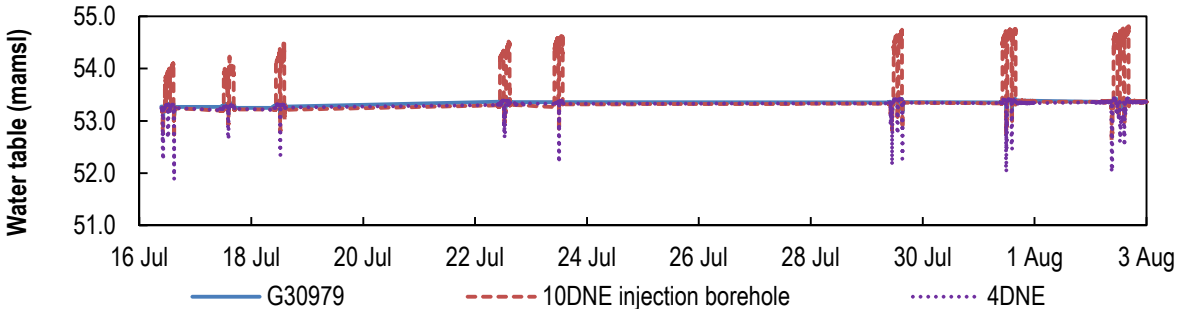
Figure 71: Water table elevation in the injection borehole and two monitoring boreholes again showing that only the injection borehole water table increased with injection

The recharge water was found to be highly oxidising after ozonation, with the dissolved ozone concentration ranging between 0.3 to 0.5 mg/ℓ and an average value of 0.4 mg/ℓ. The DO concentrations were always greater than 10.0 mg/ℓ, with an average concentration of 13.71 mg/ℓ at temperatures between 18.5 to 20°C (Figure 72). To evaluate the effects of the treatment on the water quality parameters, four water samples were collected from G30966, which all passed the E.N. test (Table 22; Appendix F). In addition to those acquired for the full analyses, water samples were collected on 29, 31 and 2 August only for pH, total and dissolved Fe and Mn concentrations (Table 23).
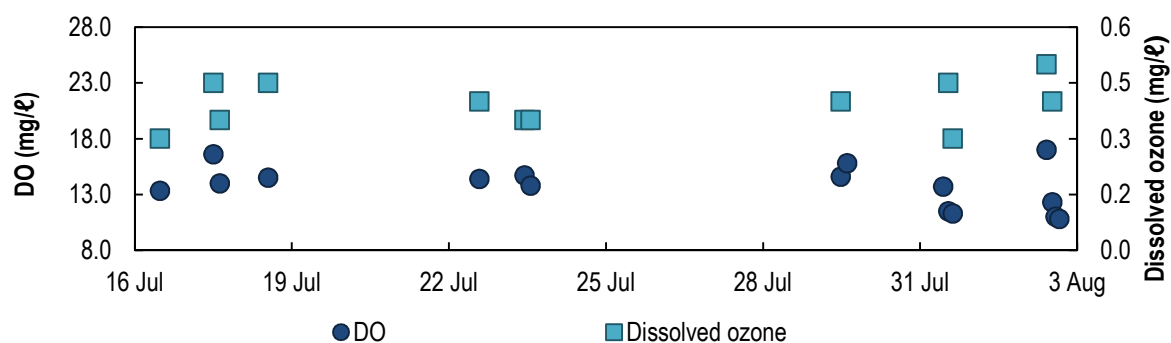
Figure 72: Dissolved ozone and DO variations in the injected water over time

Table 22: Comparison of water quality using the second injection technique with early 2013 baseline values

Parameter*	17 July 9:00 AM	18 July 9:00 AM	22 July 13:00 PM	29 July 10:30 AM	2013 baseline
	18 hours rest period	18 hours rest period	After first injection	Five days since ISIR	
EC (mS/m)	69.70	69.80	69.50	67.30	68.80
pH	7.71	7.64	7.63	7.68	7.66
Ca	47.11	47.65	46.41	48.93	48.03
Na	79.30	83.00	80.40	77.90	80.90
Mg	9.81	9.93	9.69	10.00	8.39
K	7.59	8.17	7.89	7.52	7.83
Total Alkalinity as CaCO$_3$	161.40	160.30	160.50	160.90	158.40
Cl	107.00	107.00	105.00	99.00	106.10
SO$_4$	31.30	28.90	30.70	36.40	27.30
NO$_3$ + NO$_2$ as N	< 0.20	< 0.20	< 0.20	< 0.20	≤ 0.20
Total Fe	3.04	1.83	1.15	1.50	0.53
Total Mn	0.44	0.24	0.23	0.47	0.20
F	0.36	0.36	0.36	0.37	0.22
Si	4.50	3.90	4.70	4.60	4.51
Sr	0.47	0.46	0.46	0.44	0.45
TOC	4.90	5.20	5.10	5.00	7.10
*Date given in mg/ℓ unless otherwise specified; n.m. not measured					

Table 23: Water analyses of G30966 abstracted groundwater for pH, iron and manganese concentrations

Parameter*	29 July 15:00 PM	31 July 14:00 PM	2 August 14:30 PM	2013 baseline
	After two injections	After two injections	After two injections	
pH	7.44	7.40	7.50	7.66
Total Fe	2.98	1.80	1.43	0.53
Dissolved Fe	1.61	1.60	0.72	n.m.
Colloidal Fe	1.37	0.20	0.71	
Total Mn	0.51	0.45	0.37	0.20
Dissolved Mn	0.40	0.37	0.36	n.m.
Colloidal Mn	0.11	0.08	0.01	
*Date given in mg/ℓ unless otherwise specified; n.m. not measured				

The field pH and EC values were also measured with DO in the ozonated water and compared to the values measured in G30966 and the monitoring well-point 8DNE, two metres hydraulically down-gradient from injection (Figure 73; Figure 74). The measured DO in 8DNE and G30966 did not change over the course of the measurements, remaining below 0.5 mg/ℓ.
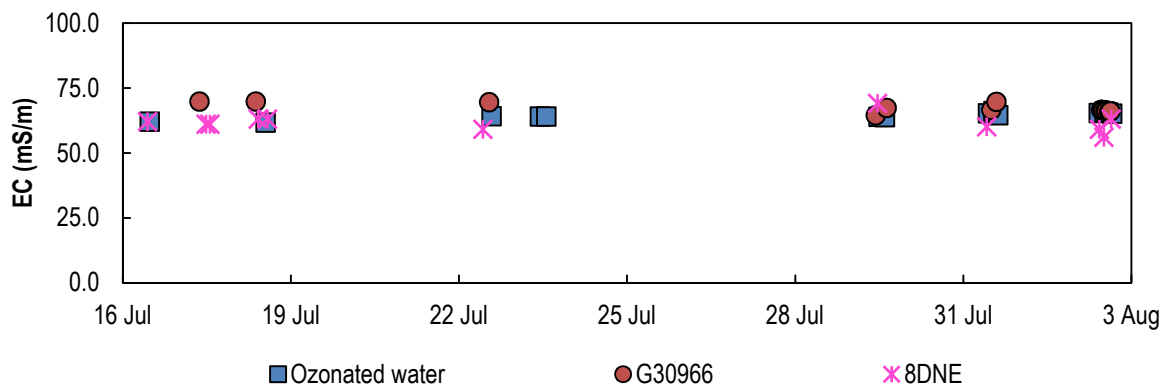
Figure 73: EC levels in the source water from G30966, ozonated water and 8DNE
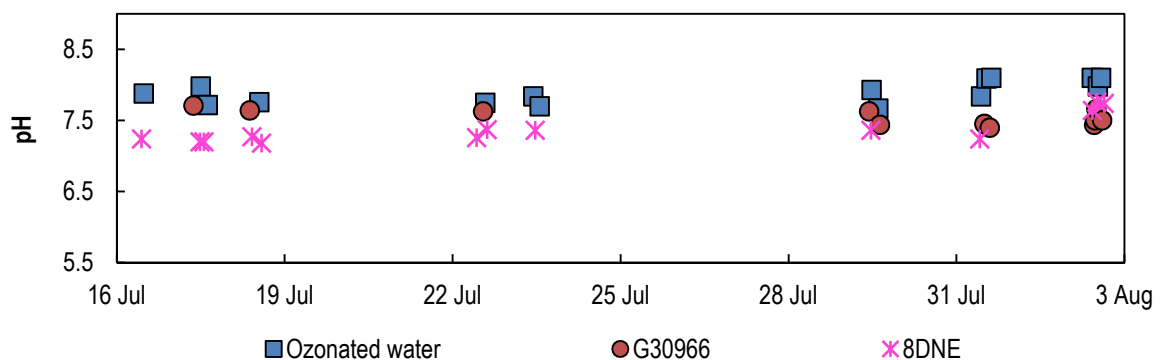
Figure 74: Variation of pH in the ozonated water of G30966 and 8DNE over the course of ISIR treatment

6.5.3   Discussion

With the modifications to the ISIR prototype leading to removal of the entrained gases in the ozonated water, the injection rate increased by 34% from 1.37 m^3/h to 1.84 m^3/h. As a result, this allowed for up to 9 m^3 of ozonated water to be injected per day but even with this increased volume, a rise in the water table was only evident in the injected well-point (Figure 71). The injection rate of the ISIR system also had to be continuously monitored because the high rainfall over July increased the water table by 0.1 m, which limited the available space for injection. As a result, when water overflowed from the injected well-point, the injection rate was lowered. This interfered with the dissolved ozone concentration because of the lowered differential pressure across the venturi. The full week of injections was not possible in this investigation due to electricity cuts at the study site and high rainfall, causing the number of injection days to decline to three consecutive days with a maximum of two injections per day.

The dissolved ozone concentrations measured in the recharge water were found to be promising with a range between 0.3 and 0.5 mg/ℓ, which were within the typical concentrations of ozone found during *ex-situ* water treatment (i.e. < 0.1 to 1.0 mg/ℓ; EPA, 1999). However, the most impressive findings is the high levels of DO in the recharge water, which increased significantly from the baseline, i.e. 0.4 mg/ℓ to greater than 10.0 mg/ℓ (Figure 72). These DO concentrations in the recharge water are even above the known levels achieved by aeration, i.e. 8 mg/ℓ at standard temperature and pressure.

Even through there was a volume of highly oxidising water introduced into the aquifer, the total and dissolved Fe and Mn concentrations remained above the G30966 baseline and WHO threshold (Figure 75; Figure 76). However, both total and dissolved iron and manganese concentrations do show an overall decline with successive days of treatment, except for the two measurements on 29 July before and after ISIR treatment, which showed an increase. The increase in both total iron and manganese could be attributed to precipitated oxides drawn along with the abstracted water and collected in the sample because the oxidation process did not have sufficient time to run to completion with the precipitates remaining in the subsurface. This assumption was supported by the high concentration of the colloidal iron and manganese measured in the 29 July 15:00 PM sample (Table 23). Due to the elevated concentration in both total and dissolved analyses there was the concern that the clogged borehole could be contributing to the unexpectedly high values.
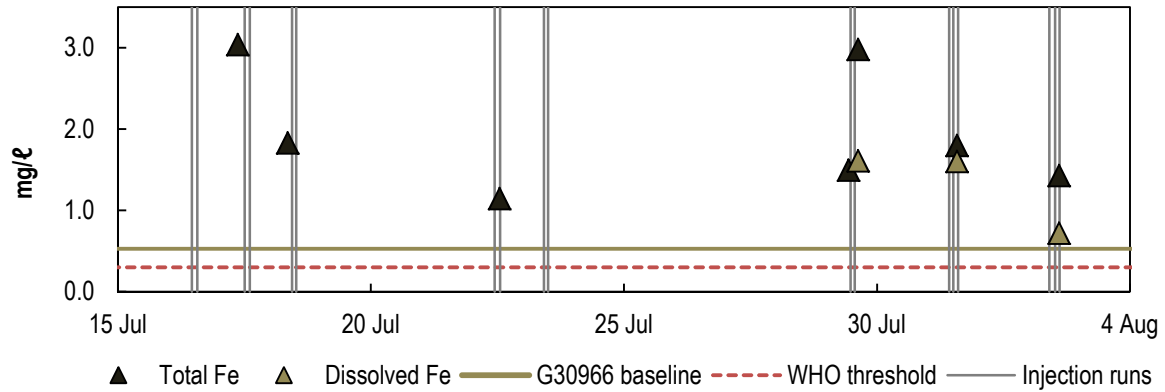
Figure 75: Total iron concentrations showing a decrease with successive injection runs but still remains above the baseline and threshold concentrations (vertical lines indicate the start of each injection)
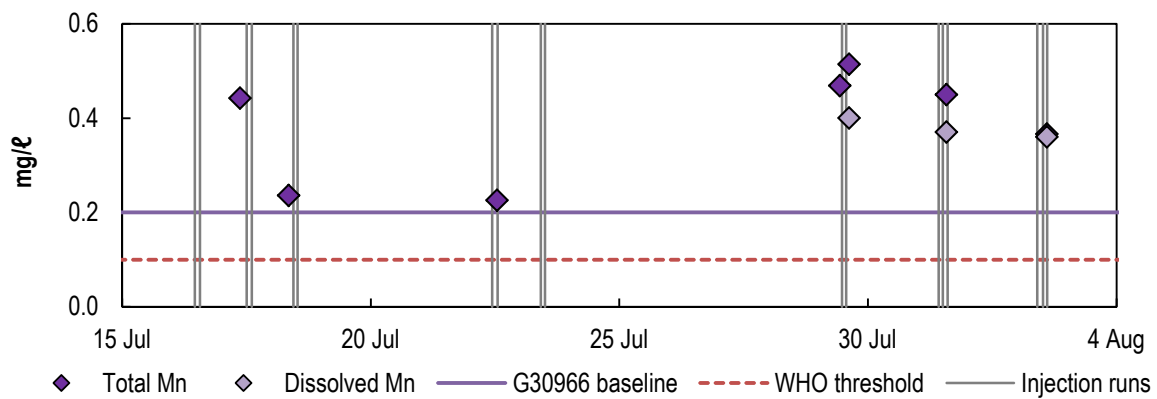
Figure 76: Manganese concentrations showed a similar trend to iron but also had concentrations above the baseline and threshold concentrations

Although the iron and manganese removal was not successful in lowering the concentrations below the desired threshold, another objective of this investigation was to establish that the ISIR does not adversely change the water quality, which would require additional *ex-situ* water treatment to remediate. This does not appear to be a concern from the results in the full water analyses because most of the parameters measured (i.e. EC, pH, Ca, Na, K, Cl, total alkalinity, $NO_3 + NO_2$, Si, Sr) did not deviate from the baseline chemistry by more than ±10% (Table 22).

The measured TOC in the sampled water remained approximately 5.0 mg/ℓ, which is comparable to the concentrations found in the earlier (July) samples but is 30% lower than that of the 2013 pumping test baseline. The decrease in TOC could be attributed to the dynamic behaviour of a shallow primary aquifer, where water quality can change depending on recharge history. In the study area, the preceding months also experienced high rainfall,

which could have lowered the organic load in the aquifer, with high recharge in the unvegetated dune field.

The fluoride concentrations were found to be more than double the 2013 baseline, which could suggest that mobilisation had taken place with ISIR treatment. This is opposite to what is reported in ISIR case studies (e.g. van Halem, 2011) and can be a concern as elevated concentrations of fluoride are a health risk, causing mottling of teeth at concentrations between 0.9 to 1.2 mg/ℓ and in severe cases, crippling skeletal fluorosis at concentrations greater than 10.0 mg/ℓ (WHO, 2008). There is little information on the fluoride concentrations in the Witzand Wellfield to compare with, but the values reported in More Water cc (2001) and Tredoux and Cavé (2002) gave concentrations of 0.10 to 0.40 mg/ℓ, which is within the range measured in this study. Since there is no significant changes in calcium concentration with ISIR treatment, it is not assumed that mobilisation from fluorite (CaF_2) or fluorapatite ($Ca_5F(PO_4)_3$) took place with ISIR treatment as calcium is a limiting factor for fluoride mobilisation (Appelo and Postma, 2005). In addition, at such low concentration (i.e. < 1.0 mg/ℓ) it is possibly related to experimental errors in the laboratory analyses and since the concentrations are still well below the threshold concentration for SANS 241:2011 (i.e. ≤ 1.5 mg/ℓ), it could be viewed as positive, since the presence of fluoride below threshold concentrations increases the prevention of tooth decay (WHO, 2008).

An increase in sulphate concentrations with injection runs can be attributed to ISIR treatment, which could be the result of oxidation of sulphides in the aquifer, such as pyrite, or possibly the prevention of sulphate reduction due to the increased pe as a result of increased DO (Appelo and Postma, 2005) but the increase is still below the SANS 241:2011 threshold.

The increase in magnesium is less than 20% from the baseline median and it could have been released by dissolution of aquifer material due to the acidifying oxidation reactions of Fe^{2+}, Mn^{2+} and sulphides (pyrite) in the subsurface as a result of ISIR treatment. However, the lack of a calcium increase suggests that the magnesium increase is more the result of natural water quality changes, rather than ISIR treatment.

Comparison of pH and EC in G30966 and 8DNE over the injection period did not show any variation from their baseline measurements and the EC in the ozonated water is comparable with the EC from G30966 (Figure 73). However, a slightly high pH is observed in the ozonated water, which could be the result of the buffering effect of the acidifying reactions (Figure 74). Another observation during the injection tests was that the clear PVC tubing used to transfer the ozonated water into the injection well-point became discoloured after a few injection runs. By the end of the 18 injections, the tubing was opaque, due to the extremely fine-grained, dark-brown Fe(III)-oxyhydroxides coating the interior of the pipe.

6.6 Third Injection Technique

6.6.1 Methodology

Following the results of the second injection methodology, the technique had to be modified again as the Fe and Mn concentrations measured were still above the desired threshold and moreover the DO did not increase noticeably above the baseline in close vicinity to the production borehole. This methodology included the injection into well-point 4DNE, four metres hydraulically up-gradient of G30966, where it was hoped that a DO change would be observed. This injection attempt was planned to run for a full week from 5 August to 9 August, but electricity cuts at the Witzand Softening Plant on 8 August prevented a week long study. However, a full week (five days of injection) took place from 26 to 30 August. This methodology followed the same stop-start process of injection as described before.

6.6.2 Results

Nineteen injections were completed in this injection run in 4DNE at an injection depth of 25 mbgl. The average time taken per injection was 99 minutes, which gave an injection rate of 1.81 m^3/h. The water levels were monitored throughout the injection run, but will not be discussed further in this section because the change in water level is only observed in the injected well-point, which increased by less than 0.5 m.

The dissolved ozone concentration in the injected water gave the same average as the previous methodology, i.e. 0.4 mg/ℓ and the DO levels remained above the required 10.0 mg/ℓ, averaging 15.8 mg/ℓ at 18-19°C (Figure 77). The concentration of DO in the aerated water after 30 minutes of recirculation was compared to the known levels in the ozonated water, G30966 and 8DNE (both four metres hydraulically down and up-gradient of injection, respectively) and a DO measurement was taken one metre below the water table in the injected well-point (Figure 78).

Comparison was made of the EC and pH from the native groundwater monitoring points (i.e. 8DNE and G30966) with levels in the aerated groundwater and levels in the ozonated water before injected into the aquifer (Figure 79). Unfortunately, the Extech pH probe malfunctioned on the 29 July 2013 at 9:00 AM, which accounts for the absence of data for that increment in Figure 80. Four water samples for pH and total and dissolved concentrations for iron and manganese were also collected during the first injection run to monitor the change in levels with treatment (Table 24). Three water samples for full water analyses were also collected (Table 25). It was originally planned that more samples be

taken throughout that week but the high rainfall made sampling problematic. All the analyses passed the E.N. test (Appendix F).

Table 24: Water analyses for only pH, iron and manganese levels from G30966

Parameter*	5 August 9:45 AM	5 August 15:15 PM	6 August 15:20 PM	7 August 12:30 PM	2013 baseline
	Before injections	After two injections	After two injections	After two injections	
pH	7.43	7.40	7.50	7.41	7.66
Total Fe	1.92	2.10	1.10	0.85	0.53
Dissolved Fe	0.14	0.50	1.10	0.74	n.m.
Colloidal Fe	1.78	1.60	0.00	0.11	
Total Mn	0.36	0.39	0.47	0.41	0.20
Dissolved Mn	0.30	0.32	0.39	0.22	n.m.
Colloidal Mn	0.06	0.07	0.08	0.19	
*Date given in mg/ℓ unless otherwise specified; n.m. not measured					

Table 25: Groundwater quality during the injection tests from 26 to 30 August compared to earlier 2013 baseline values

Parameter*	26 August 10:00 AM	26 August 15:00 PM	30 August 12:00 PM	2013 baseline
	Before injections	After two injections	After first injection	
EC (mS/m)	67.70	68.50	68.40	68.80
pH	7.65	7.63	7.62	7.66
Ca	48.33	48.82	48.36	48.03
Na	79.40	80.60	80.00	80.90
Mg	9.87	9.90	9.78	8.39
K	7.27	7.39	8.07	7.83
Total Alkalinity as $CaCO_3$	159.00	158.30	160.70	158.40
Cl	98.00	99.00	108.00	106.10
SO_4	40.30	38.00	33.40	27.30
$NO_3 + NO_2$ as N	0.26	0.50	0.47	≤ 0.20
Total Fe	1.59	1.48	0.85	0.53
Dissolved Fe	1.27	1.30	0.67	n.m.
Total Mn	0.48	0.46	0.251	0.20
Dissolved Mn	0.38	0.32	0.247	n.m.
F	0.35	0.35	0.30	0.22
Si	4.60	4.50	4.30	4.51
Sr	0.44	0.43	0.43	0.45
TOC	4.80	4.90	5.10	7.10
*Date given in mg/ℓ unless otherwise specified; n.m. not measured				
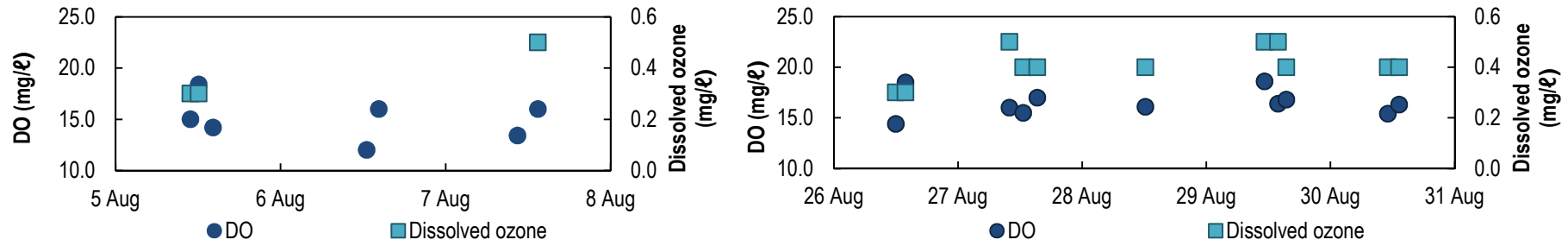
Figure 77: Overall higher dissolved ozone and DO concentrations measured in the injected water using the third injection methodology
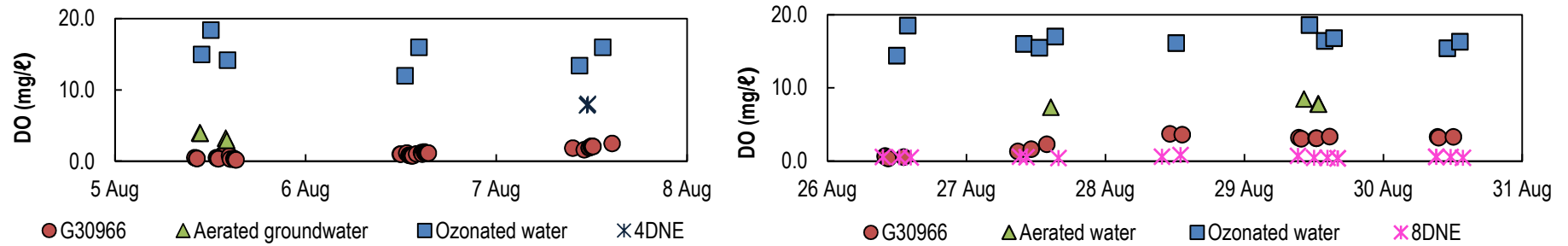
Figure 78: Comparison of the measured DO concentration in the different waters during the injection tests
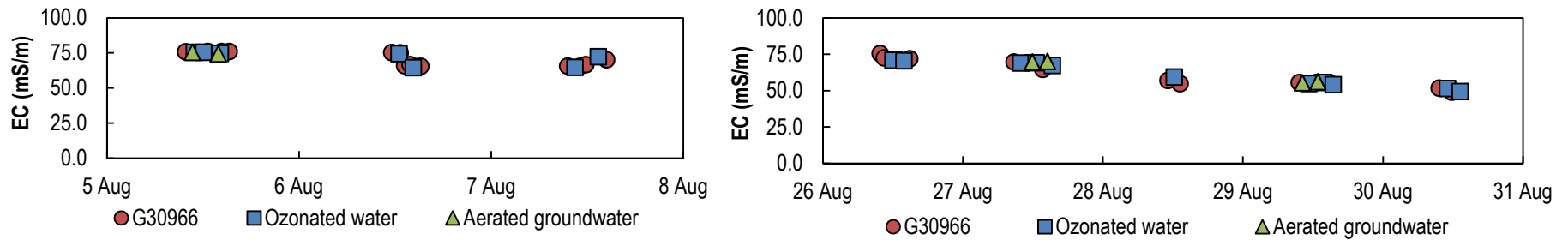
Figure 79: Comparison of the EC from source groundwater (G30966) to aerated groundwater and then ozonated water
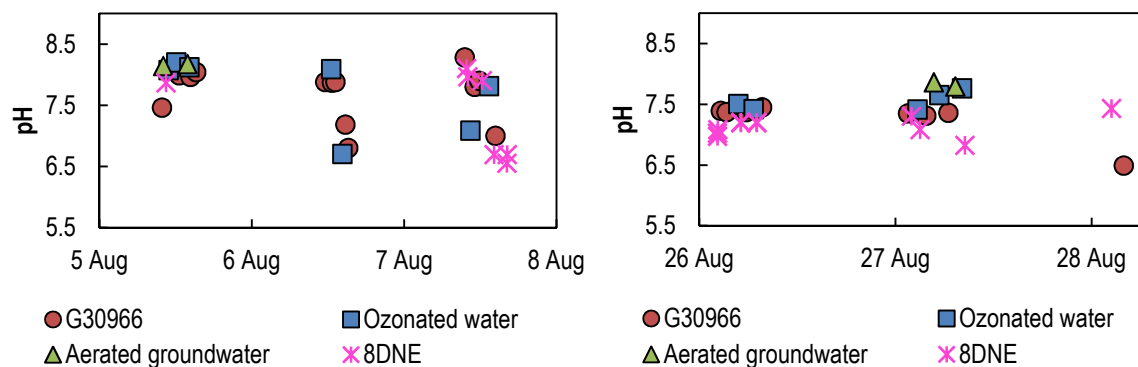
Figure 80: The comparison of the pH levels in the four different waters sampled during injections showing little variation

6.6.3   Discussion

The injection rate and the dissolved ozone concentrations measured in the injected water into 4DNE were comparable to the previous two injection rates for 10DNE. However, the average DO concentration was 15% higher when compared to the previous methodology (Figure 77) and comparable to the DO concentrations using oxygen gas found by the Hinkamp *et al.* (2004) and Ebermann *et al.* (2013) investigations. This is attributed to the recirculation of the water for at least 30 minutes before injection, whilst the previous methodology had some injection runs without recirculation, due to logistical issues with starting the motor or running out of petrol.

The comparison of the different levels of DO in the source water (G30966) before aeration and after ozonation, showed that recirculation increased the DO concentration to between 4 to 8 mg/ℓ (Figure 78), which is slightly below the ranges found in the case studies in Chapter 2.2.3.8. This is acceptable as the groundwater is organic-rich and contain some H_2S, implying that aeration would not be as effective.

Higher DO concentrations were found in the aerated water with successive injection runs in the week-long test because there was an increase in DO in the abstracted water. The DO in the abstracted water also increased with each successive injection to a maximum of 2.5 mg/ℓ after the third day of injection (7 August), which was after approximately 21 m^3 of ozonated water was introduced into the subsurface and a maximum of 3.5 mg/ℓ at the end of the five days of injection (30 August) after an injected volume of 36 m^3. This is an impressive increase when compared to the baseline DO levels in 8DNE. One measurement was taken in the injection well-point at the first few meters below the water table to see what the levels of DO were in that injected well-point and showed a relatively high concentration of 7.5 mg/ℓ.

The EC measured in the source water from G30966, aerated water and ozonated water showed no variation with treatment in the 5 to 7 August study, while a progressive decrease

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is seen in the week-long study later that month (Figure 79). When comparing those field measurements of G30966 to the laboratory EC measured (Table 25), there is concern that the EC probe may have been giving lower reading than the true range of 67-69 mS/m. This was due to the high rainfall events during this injection test, which did cause problems with sampling and taking measurements. The pH in the different water types showed little variation, with aerated and ozonated water generally higher due to the buffering capacity of the water (Figure 80). Unfortunately, the Extech pH probe malfunctioned on 28 August, resulting in limited measurements during subsequent injection runs.

Although there was a notable increase in DO within close proximity of the production borehole, the total iron in the 5 to 7 August study show an initial rise at the end of the first day of ISIR treatment and then a continuous decline. This could be the result of clogged material or newly formed precipitates being included in the sample because the dissolved iron concentration is very low. However, a decrease is then seen in both dissolved and total Fe with successive treatments for that week (Figure 81). The opposite is seen in the manganese samples, where the colloidal Mn concentration is low in the first three samples (Table 24) and the dissolved and total concentration increase in the successive cycles between the 5 to 6 August. There is a decrease in total manganese but the colloidal concentration is high (Figure 82). The week-long test shows the expected progressive decrease in both total and dissolves iron and manganese concentrations with successive injections. However, the iron and manganese concentrations remained above the baseline, raising a concern that clogged particles in the boreholes are interfering with the results.
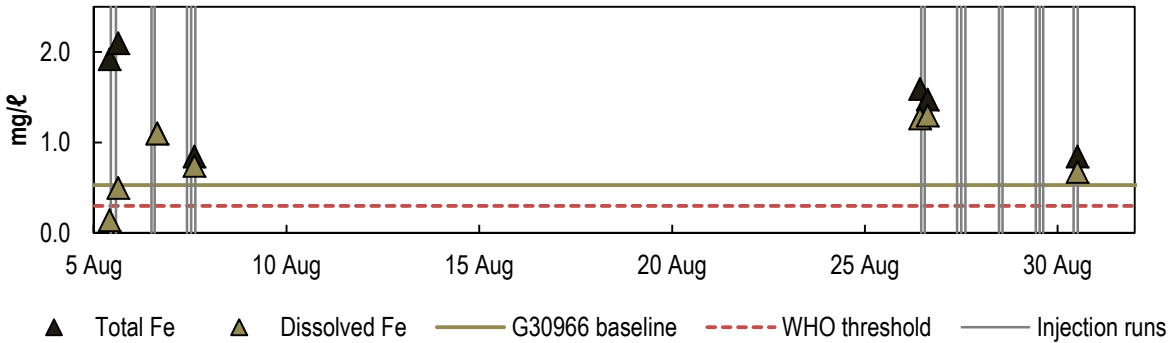
Figure 81: Iron concentrations in G30966 showed a decrease with successive injections but concentrations still remained above the baseline concentration
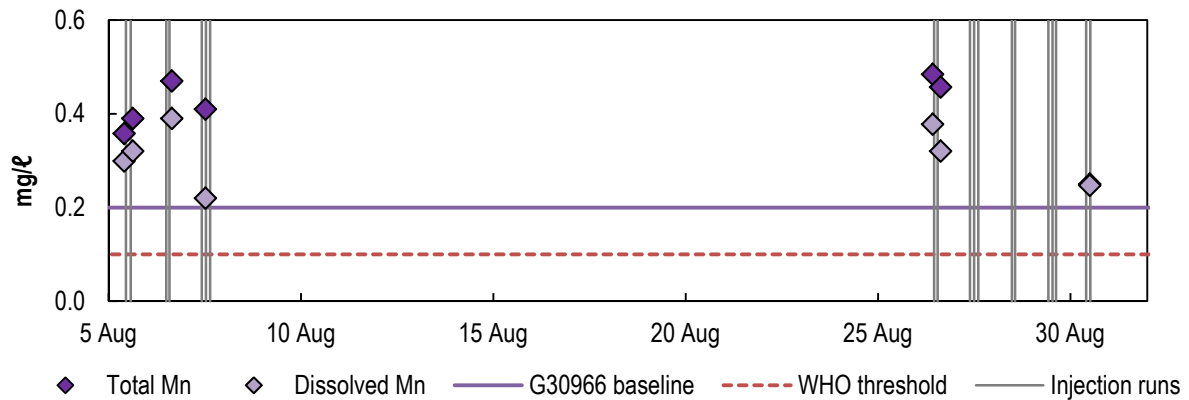
Figure 82: Manganese concentrations in G30966 showed an increase in the injection runs between 5 and 6 August, while the later injection phase showed a decrease with successive injections but the concentrations are still above the baseline concentration

After the injection of approximately 33 m^3 consecutively for five days, the full chemical water analyses (Table 25) from this injection run showed no noteworthy change that would be of concern to the South African drinking water standards (i.e. SANS 241:2011). Similar trends are observed for EC, pH, Ca, Na, K, Cl, Si, Sr and total alkalinity with deviations no more than ±10% after ISIR treatment in comparison to 2013 baseline concentrations. The TOC concentrations remain at approximately 5 mg/ℓ and the same is seen in the magnesium and fluoride levels, which were within the ranges found in the previous injection tests.

A parameter that may have been affected by ISIR treatment was the NO_3 concentrations, where NO_3 is assumed to be the dominant form making up the $NO_3 + NO_2$ concentration in the Atlantis Aquifer as described in previous investigations (e.g. DWA, 2010; Tredoux *et al.,* 2012). In this study an increase to approximately 0.5 mg/ℓ after injections from the baseline concentration (i.e. ≤ 0.2 mg/ℓ) was observed. This could be attributed to the oxidation of organic nitrogen or trace amounts of NH_4^+ in the groundwater (e.g. Tredoux *et al.,* 2012). However, this increase is negligible and is still well below the SANS 241:2011 drinking water limit of 11 mg/ℓ. The SO_4 concentration remained higher than the 2013 baseline when the sample was collected before injection, which could indicate a natural variation in the aquifer over time since there had not been any ISIR treatment for a month. In addition, during ISIR treatment, the SO_4 concentrations were within baseline concentrations, suggesting that no sulphides were oxidised with this treatment.

6.7 Fourth Injection Technique

6.7.1 Methodology

The chemical analyses of water from the previous two methodologies suggested that the stop-start operation of the clogged production borehole could be contributing to the unanticipated high iron and manganese concentrations measured in the water samples. Disturbance of the borehole equilibrium through stop-start pumping action could have resulted in the sloughing off of iron-rich deposits from the production borehole, resulting in the false highs. Continuous pumping of G30966 while injecting in 4DNE was proposed to test this hypothesis.

This revised methodology was attempted from 15 to 18 October, with a lay-flat pipe connected to the overflow at the water tank, which directed any excess groundwater a distance of more than 60 m down-gradient of the study site. Due to the new set-up, no recirculation of the abstracted groundwater could take place, which limited the aeration to splashing of the abstracted groundwater on the baffle balls as it entered the tank.

The injection tests were planned for five days of injection, but the water tank was not delivered to the site in time on the first day, resulting in the injection run taking place over four days. Like the previous injection runs, water level and field parameters were monitored and water samples collected. However, from the previous injection runs, the number of samples collected proved to be too small and provided limited information to make adequate assumptions on the effects of ISIR treatment. To improve on this, field EC and pH measurements and water samples for EC, pH and total and dissolved Fe and Mn laboratory analyses were collected in the morning before injection after G30966 was sufficiently purged at a high rate for more than 30 minutes and then every hour during the injection. In addition, a 1 ℓ water sample for full analyses was collected on 14 October before injection commenced and on 18 October after the treatment was completed, to compare water quality changes as a result of ISIR treatment.

6.7.2 Results

The continuous injection in 4DNE at an injection depth of 26 mbgl took an average of 5 hours and 32 minutes per day. Based on the previous injection runs, it was assumed that the injection rate was 1.8 m^3/h, which estimated that just short of 10 m^3 of ozonated water was injected per day and the water table elevations are given in Figure 83.
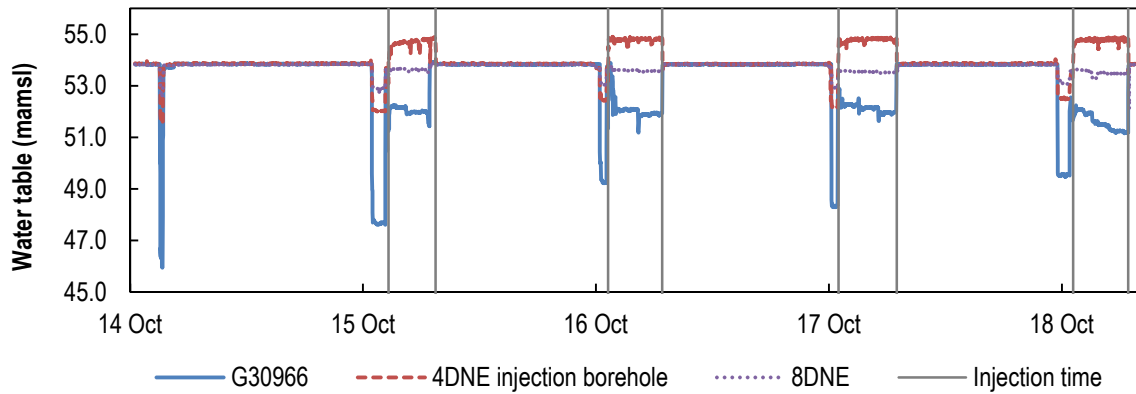
Figure 83: Water level response in the injected well-point (4DNE) and monitoring well-point (8DNE) and abstraction borehole (G30966) showing that there was only a rise in water level in 4DNE (the vertical lines indicate the starting and end times of the injection)

The DO in the ozonated water increased from 12.0 to 14.0 mg/ℓ and the dissolved ozone was generally measured at 0.3 mg/ℓ, with higher dissolved ozone concentrations at 0.4 mg/ℓ occurring when the DO concentration was greater than 13.0 mg/ℓ (Figure 84). Measurements of the DO concentration in 4DNE were also taken occasionally in the first metre under the water table of the injected well-point (Figure 84), to see if the water column had elevated DO as suggested by the measurements in Figure 78. The DO in G30966 also showed an increase from the baseline concentrations with successive injections over the four days of ISIR application (Figure 85).
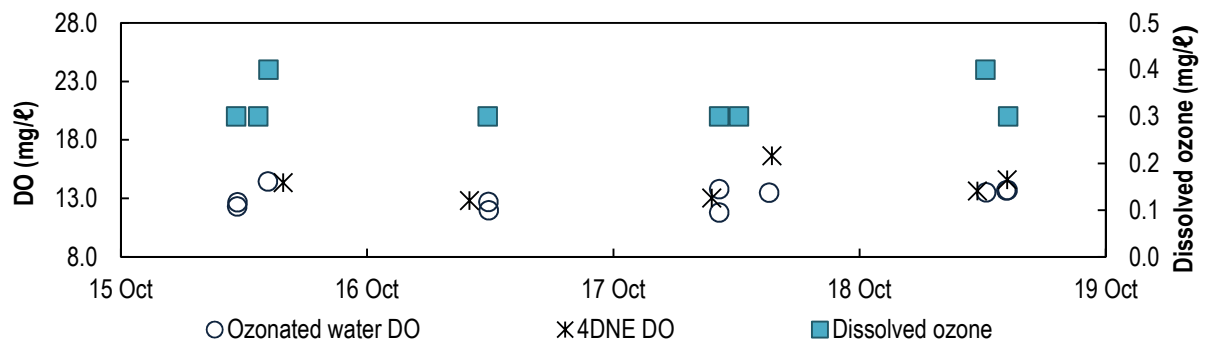
Figure 84: Dissolved ozone and DO in the injected water before being introduced into the aquifer and DO measured in 4DNE
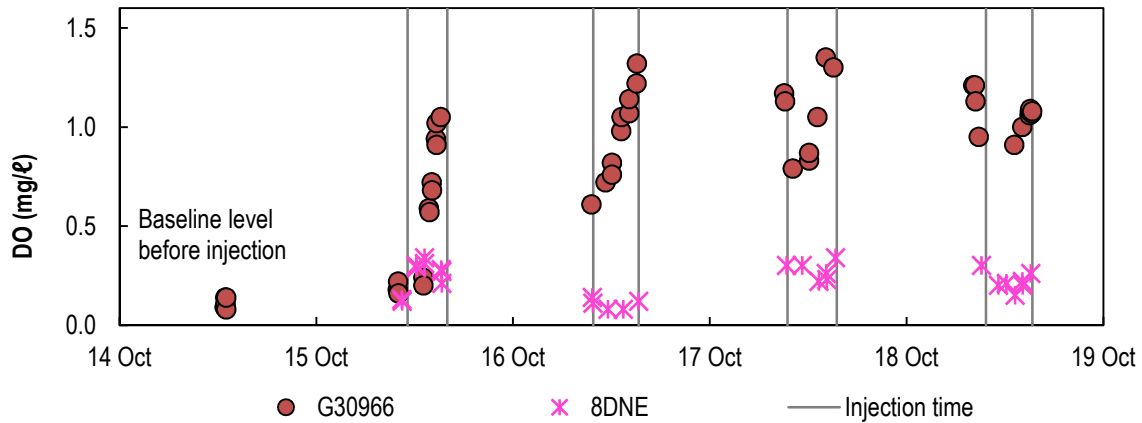
Figure 85: G30966 DO increased significantly from the baseline concentration with the continuous injection-abstraction technique, while 8DNE remained within the natural DO levels

In total, 44 samples were collected during this injection run, of which 40 were to be analysed for pH, EC, DOC, Fe and Mn changes by CSIR (Figure 86; Figure 87; Appendix F) and two samples for full chemical analyses by Scientific Services (Table 26). Both water analysis samples passed the E.N. test.

Table 26: Groundwater analyses from the fourth injection technique compared to the earlier 2013 baseline values and SANS 241:2011

Parameter*	14 October 12:30 PM	18/10/13 3:00 PM	2013 baseline	SANS 241:2011
	Before injections	After injection treatment was completed		
EC (mS/m)	69.60	69.50	68.80	≤ 170.00
pH	7.61	7.60	7.66	5.00-9.70
Ca	50.71	48.52	48.03	-
Na	73.60	77.10	80.90	≤ 200
Mg	9.62	9.16	8.39	-
K	6.33	7.63	7.83	-
Total Alkalinity as CaCO$_3$	158.30	163.90	158.40	-
Cl	109.00	114.00	106.10	≤ 300
SO$_4$	36.80	23.20	27.30	≤ 250
NO$_3$ + NO$_2$ as N	0.59	1.26	≤ 0.20	NO$_2$ ≤ 0.90; NO$_3$ ≤ 11.00
Total Fe	1.49	0.60	0.53	≤ 0.30
Dissolved Fe	1.22	0.52	n.m.	-
Total Mn	0.48	0.269	0.20	≤ 0.10
Dissolved Mn	0.48	0.265	n.m.	-
F	0.29	0.25	0.22	≤ 1.50
Si	4.60	4.20	4.51	-
Sr	0.46	0.43	0.45	-
TOC	4.80	5.40	7.10	≤ 10.0
*Date given in mg/ℓ unless otherwise specified; n.m. not measured				
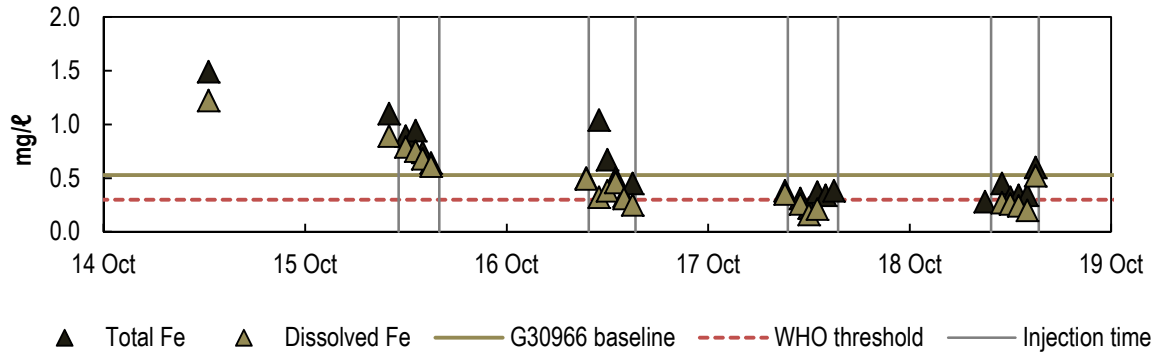
Figure 86: Both total and dissolved iron concentrations in the abstracted water showed a decline with successive injections
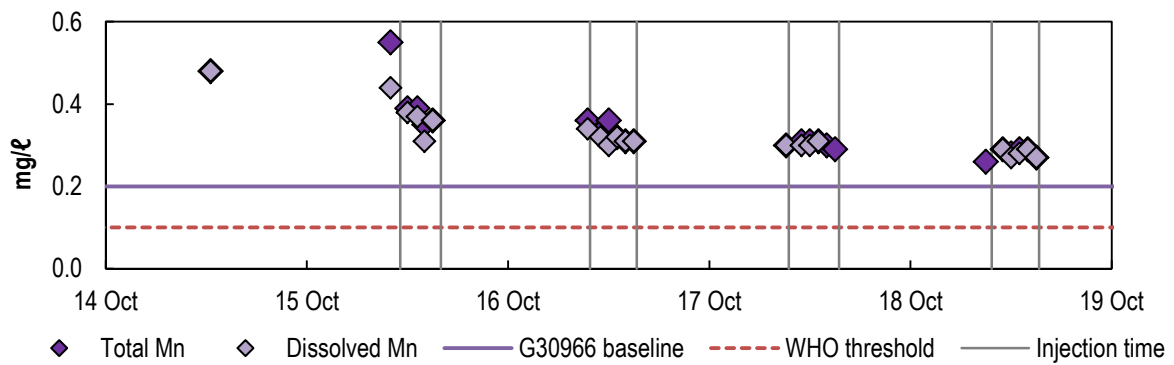
Figure 87: Both total and dissolved manganese concentrations from G30966 showed a decline but not as distinctive as iron and remained above the known baseline and desired threshold concentrations

The EC and pH in G30966 from both the field measurements and laboratory analyses are given with ozonated water field measurements in Figure 88 and Figure 89.
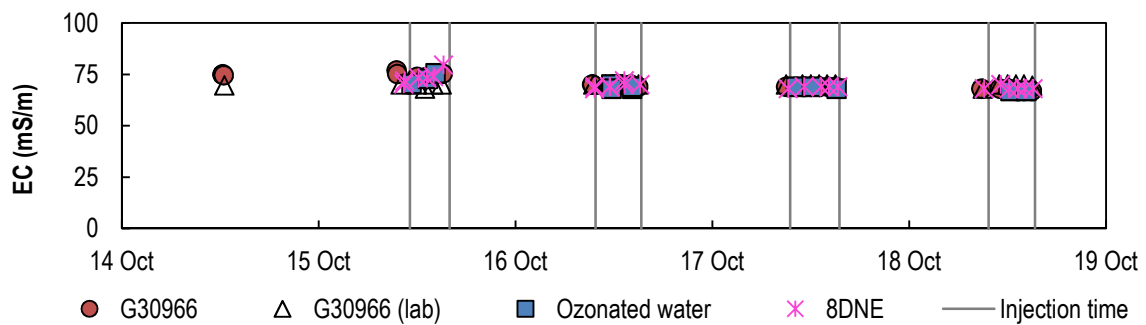
Figure 88: Field and laboratory measurements of EC in G30966 and the ozonated water correlate and remain within known baselines values
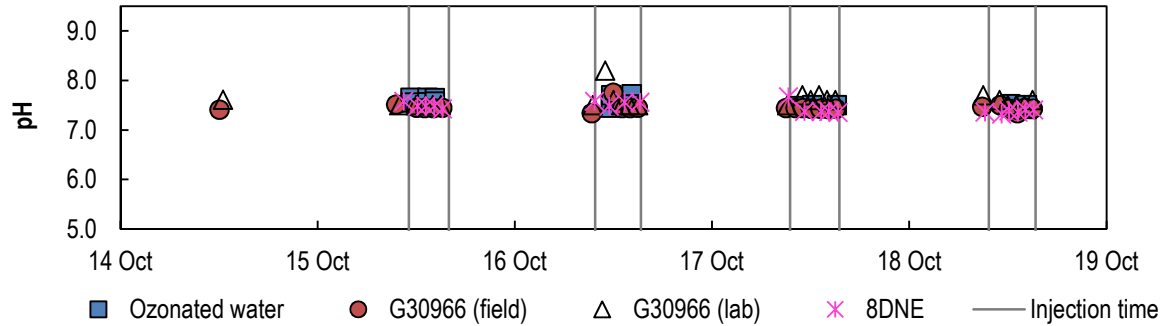
Figure 89: Water pH in the ozonated water remains slightly higher than the measured G30966 values in field measurements and laboratory analyses, both remain within the known baseline values

6.7.3   Discussion

This revised methodology, with injection in 4DNE, was attempted from 15 to 18 October. The water table elevations did not show much variation from that observed in the previous injection tests, except for a decline in G30966 due to the pumping with injection (Figure 83). It was found to be easier to apply the ISIR treatment with continuous abstraction by rather increasing abstraction to prevent overflow in the injected well-point rather than lowering the injection rate. This allowed for the full injection output to be applied during the injection phase. However, even at the full injection output, the DO and dissolved concentrations were generally found to be lower in the ozonated water than for the previous two injection methodologies. This is due to the abstracted groundwater not having been sufficiently aerated and degassed before ozonation occurred by the current set-up. Even though the DO levels were lower, the concentrations measured in 4DNE showed elevated DO levels ranging between 13 and 17 mg/ℓ (Figure 84).

Similar to the August injection runs, an increase in DO resulting in aerobic conditions in G30966 was identified with successive injection over the four days, while the monitoring well-point 8DNE, showed the baseline concentration to remain at anoxic conditions, i.e. < 0.5 mg/ℓ (Figure 85). This was also expected due to the injected water being drawn towards G30966. However, the DO did not reach the same high concentrations (i.e. 2-3 mg/ℓ) as during the previous technique in G30966 (Figure 78), attaining a maximum of 1.35 mg/ℓ, however this is still significantly higher than the baseline level. The possible reasons for the lower DO with successive injections are:

- The lowered DO concentration in the injected water due to less aeration;

- The abstraction from G30966 with injection causes a cone of depression around the borehole, which draws in water from all sides and thus dilutes the DO concentration measured in the abstracted water.

Although lower DO concentrations were found, the results did show that there was residual DO measured in the abstracted groundwater after the injection was completed and a rest period of approximately 18 hours followed before the next injection run commenced. The lower DO concentration on the last day (18 October) was due to the higher abstraction rate in G30966, compared to the previous injection days (Figure 83).

Both the total and dissolved Fe and Mn concentrations showed a decline with successive ISIR treatment (Figure 86; Figure 87). After the third day of injection, the Fe concentrations were below the baseline concentration and by the fourth day, the Fe was dominantly in the dissolved form and within the desired levels of the WHO (2008) threshold. As the dissolved Fe concentration becomes the dominant form of iron measured in the abstracted water with time, this could indicate that natural iron concentrations in the native groundwater were being sampled through the continuous abstraction, rather than the spurious high colloidal iron measured in the previous injection runs. However, two measurements did not conform to the trend, the high total Fe on 16 October, which was sampled an hour after injection started and had a high colloidal Fe concentration, indicating that oxides could have been included in the analysis. In addition, the final sample measured at the end of treatment on the 18 October at 3:30 PM did not conform to the trend in declining Fe concentrations, but was still within the known baseline concentration. This could be due to analytical detection limits of the equipment used (since those concentrations were measured by the Scientific Services ICP-OES), while the other samples were measured using the ICP-MS, which has a more sensitive detection method compared to ICP-OES (Brown, *pers. com.* 2013).

By the end of the week of treatment, removal of iron was higher than for manganese. The manganese concentrations also initially decreased with iron, but remained at 0.3 mg/ℓ after the second day of treatment, which is still greater than the desired WHO (2008) limit. The dissolved Mn was always found to dominate the total Mn concentration count. This indicates its lesser role than iron in clogging of the production borehole, generally also because it is found at lower concentrations than iron. In addition, the lower removal efficiency of manganese compared to that of iron in this study where the groundwater pH ranges between 7 to 8 is to be expected because its oxidation is much faster in the presence of Fe^{2+} than Mn^{2+} at those pH conditions and manganese removal is only effective at pH greater than 8.5 and in the absence of Fe^{2+} as described in the literature review in Chapter 2.2.

Measurements and water analyses before and after the treatment on 14 and 18 October showed that the EC, pH, Ca, Na, Cl, Si, Sr and total alkalinity remained relatively stable as observed in the previous investigations. The TOC measurements continue to plot within the 4.8 to 5.5 mg/ℓ range as seen in the previous studies and no strong relationship between ISIR treatment and removal of TOC by oxidation could be established. The DOC concentrations were also measured by the CSIR laboratory (Appendix F), but were always higher than the TOC measured by the CoCT Scientific Services laboratory. This is attributed to the different methods of analyses used by these laboratories to calculate TOC and DOC, i.e. supercritical water oxidation (CoCT) and thermocatalytic oxidation (CSIR), respectively. Since TOC should be expected to be greater than DOC, no further discussion on the DOC results is deemed necessary.

The magnesium and fluoride concentrations remained slightly higher than the 2013 baseline but were also not affected by ISIR treatment. The nitrate concentration measurements before injection initiated (14 October) remained elevated at the concentrations found in the previous injection (approximately 0.5 mg/ℓ), but the concentration after treatment was significantly higher than expected at 1.26 mg/ℓ. The sulphate concentration was also found to be much lower in the 18 October sample than the 14 October values and unfortunately, the sample was discarded before it could be reanalysed to confirm the sulphate and nitrate concentrations. The EC and pH of the abstracted water measured in the field and laboratory remained constant throughout the treatment, with the ozonated water plotting similar values (Figure 88 and Figure 89), except for one pH value of 8.2 in the CSIR analysis, which is assumed to constitute an analytical error.

6.8   Summary

The pilot tests were designed to evaluate the technical feasibility of ISIR method as a means of removing elevated concentrations of Fe^{2+} and Mn^{2+} in abstracted groundwater from the test borehole, G30966. This was achieved by the injection of oxidant-rich water into the subsurface and after multiple injections the Fe^{2+} and Mn^{2+} concentrations were expected to be reduced below a set threshold concentrations by the adsorption-oxidation processes in the aquifer. The WHO (2008) drinking water minimum standards were used as the aesthetical and potable threshold concentrations in this study because at those levels it reduces the amount of above-ground water treatment and also assist in limiting production borehole clogging. It is recommended for preventing of clogging problems that the threshold concentrations should be less than 0.1 mg/ℓ for both iron and manganese (e.g. Hinkamp *et al.,* 2004).

Over the course of four months, a total of twenty-six days of injection testing were conducted, with three noteworthy changes to the original methodology. It was found that ISIR was successfully operated at a small-scale (i.e. injection rate less than 2 m^3/h and injected volume less than 10 m^3) for the removal of Fe^{2+} and Mn^{2+} from abstracted groundwater in a short period of time. In addition, there were no immediate changes to the water quality as a result of this treatment that would pose a health risk to the consumer.

It was found that the continuous injection and abstraction approach, with injection of ozonated water at a four metre distance from the production borehole achieved the desired iron removal results and kept iron concentrations below the WHO (2008) threshold. The ISIR treatment was not as successful in manganese removal because the Mn^{2+} oxidation takes longer in comparison to Fe^{2+}, requiring higher pH conditions and/or contact time and generally will not be as efficient in the presence of elevated Fe^{2+} concentrations. The capability of this treatment in removing other inorganic species such as Sr, F and Si by co-accumulation with the Fe(III)-oxyhydroxides was also investigated but no measurable changes were observed in this study. This probably resulted from the short testing period at a small-scale application and quantity of oxidant injected into the aquifer for this study, which would be expected to only affect the other reactive species that compete with Fe^{2+} and Mn^{2+} oxidation in the reducing conditions, i.e. organic matter, sulphides and reduced nitrogen molecules (Appelo and Postma, 2005). The study area was found to be suitable for ISIR treatment as the pH of injected water remained relatively constant between 7.7 and 8.0, as a result of the buffering capacity of the water, which is optimal for Fe^{2+} oxidation. The pH of the abstracted groundwater remained constant throughout the study, which eliminated the need for adjustment.

The use of ozone gas as the oxidant for ISIR treatment is a novel approach to removal of Fe^{2+} and Mn^{2+} in organic-rich groundwater. The dissolved ozone concentrations in the recharge water were found to attain the typical range of dissolved ozone during above-ground water treatments (e.g. EPA, 1999). The DO was elevated by either the decay product of dissolved ozone, or the high purity oxygen gas used to form ozone. It was greater than DO concentrations achieved in ISIR case studies where water was saturated with atmospheric oxygen and comparable with the range found in studies that made use of high purity oxygen gas. The ability of ozone gas to provide the required strongly oxidising conditions, as well as generate high DO concentrations makes it a very suitable oxidant for ISIR. The ease of onsite ozone generation in comparison with the complex storage and handling requirements for oxygen gas, as well as its lower than expected cost, make it an ideal oxidant for ISIR.

The field tests took place during above average rainfall (the highest rainfall recorded in more than three decades) and the lowest production in the Witzand Wellfield, causing the water table to rise to the highest known levels (Figure 90). Over the four months of injection tests, the water table rose from 1.5 mbgl in the beginning of July 2013 to 0.8 mbgl in October 2013, this increase halved the available space for injection, which necessitated the reduction in injection rates due to overflow in the injection well-point. As a result the injection rate was restricted to less than 2 m^3/h, which is considerably lower than the case studies given in Europe and China (Table 5; Table 9). The restricted injection rate also resulted in less dissolved ozone and DO introduced into the aquifer for Fe^{2+} and Mn^{2+} removal. It can be assumed that higher oxidation concentrations would have been achieved if the system was operating at its optimal rate and the high transmissivity of the area would allow for higher injection rates if the water table was lower than 1.5 mbgl.
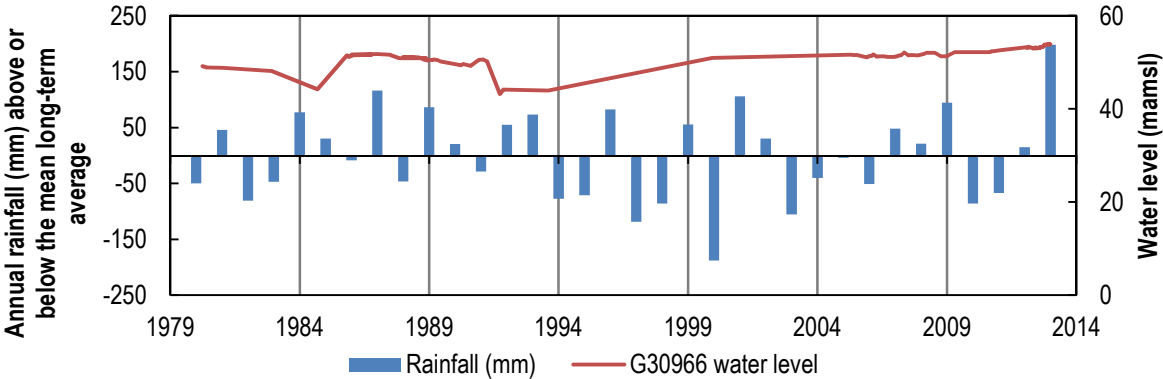
Figure 90: Rainfall variations from the mean annual rainfall compared to the long-term average and G30966 static water level, showing that the pilot tests took place during the highest recorded rainfall and water table for the last 34 years (Appendix A)

CHAPTER 7.   CONCLUSION AND RECOMMENDATIONS

7.1   Conclusion

A reliable, sustainable water supply is a necessity for the socio-economic development of any country. In the case of a water-scarce country, such as South Africa, groundwater can provide a readily available water resource, which is often cheaper to develop and fewer environmental impacts in comparison with surface water supply schemes or desalination plants. However, protection of water quality and proactive management of this resource is essential to sustain these groundwater supply schemes and ensure water security.

A threat to the long-term sustainability of many wellfields worldwide is the presence of naturally-occurring Fe^{2+} and Mn^{2+} in elevated concentrations in anoxic aquifers, which cause problems with regard to both water quality and its sustainable supply to consumers. The AWRMS is an example in South Africa of this situation, where the Atlantis Aquifer has proven itself to be a viable resource that can provide the bulk water supply to Atlantis. This ability has been compromised by the presence of iron (and to a lesser extent manganese), which by lowering of the borehole yields through iron-related clogging is jeopardising the production capacity of the wellfields to supply water.

The rate of clogging can be managed by correct construction of the production borehole and operating the abstraction at lower, continuous pumping regimes. However, these approaches are dealing with the symptoms and not treating the source of the problem, i.e. mobilisation and concentration of Fe^{2+} and Mn^{2+} in the groundwater. Furthermore, once the borehole yields have been reduced by more than 25% rehabilitation is necessary.

This research arose from the need for an investigation of preventative measures to complement the currently applied techniques for dealing with the water quality problems (i.e. *ex-situ* treatment) and production borehole clogging (i.e. monitoring, management and rehabilitation methods). Thus, the aim of this research was to evaluate the feasibility of the ISIR method in reducing Fe^{2+} and Mn^{2+} in the abstracted groundwater in a South African context, with the primary aquifer at Atlantis having been selected to test its applicability.

The investigation into the feasibility of the ISIR method in a South African context came about because it has been proven with case studies in Europe, North America, Asia and Africa (Chapter 2.2.3.8) to be a simple and robust approach in reducing the Fe^{2+} and Mn^{2+} concentrations in primary aquifers. This technique has also been applied since conventional *ex-situ* iron and manganese removal treatments were first applied, but did not attain widespread acceptance. This is due to the misconception that its application may clog the

aquifer around production boreholes. However, ISIR plants that have been in operation for more than three decades have proven the opposite, with successive treatments lowering the potential for production borehole clogging. This is due to less Fe^{2+} and Mn^{2+} being drawn towards the borehole screen and the negligible effect on hydraulic parameters. This is due to the oxidation reactions taking place on a much larger surface area in the aquifer, rather than at the borehole screen. In addition, its long-term application limits potential reductive dissolution and mobilisation of Fe^{2+} when reducing conditions prevail, as the amorphous precipitates stabilise with time to the thermodynamically stable mineral goethite (e.g. Mettler *et al.,* 2001; van Halem *et al.*, 2011).

This project had three objectives based upon key questions that had to be answered:

- Was the proposed study area suitable for ISIR?

- From the preliminary evaluation of the test site, how should the ISIR system be designed and applied in the study area?

- How effective was the ISIR treatment in reducing the amount of Fe^{2+} and Mn^{2+} in the abstracted groundwater?

The potential for the ISIR treatment to succeed in the study area appeared high because of the high transmissivity of the aquifer, which allowed for easy injection of oxygenated water into the subsurface to create the oxidation zone. The ISIR treatment also seemed appropriate because of the mineralogical composition of the Atlantis Aquifer, i.e. primarily consisted of relatively clean quartz sands, with surfaces that would provide suitable sites for the newly-formed Fe(III)-oxyhydroxides to attach to. Successive injections would also increase the extent of the oxide coating on the grains matrix, thereby assisting in the continued removal of Fe^{2+} and Mn^{2+} from the groundwater through adsorption and oxidation processes. The high bicarbonate concentration in the groundwater would also provide a sufficient buffering capacity to reduce acidifying oxidation reactions, which would keep the pH within the optimal (slightly alkaline) levels for efficient iron removal.

Once it was determined that the study site was suitable for treatment, the design of the ISIR application had to take into account the high concentration of organic compounds and silica-rich groundwater quality characteristics of the area. This saw the novel use of ozone gas as the oxidant to remove complexed Fe^{2+} and Mn^{2+}. In addition, the high water table in the study area required that the injection of oxygenated water be applied in a satellite well-point rather than directly into the production borehole.

Four different ISIR techniques were applied during the pilot tests to assess the effectiveness of Fe^{2+} and Mn^{2+} removal in the abstracted groundwater. The initial trials showed that the injection of ozonated water without the degassing column was near-impossible, due to the incessant bubbling in the injected well-point caused by entrained gases. Once this was resolved, it was found that continuous abstraction during injection was essential for ISIR application, since the stop-start approach did not provide the satisfactory results in iron and manganese removal, most likely due to the clogged condition of the production borehole, which resulted in spurious high concentrations when precipitates in the borehole were dislodged.

Both the iron and manganese concentrations showed a decline in the abstracted groundwater from the continuous injection-abstraction results, due to the increase in DO in the aquifer, caused by successive injections. The effectiveness of the treatment was more evident in the iron concentrations, which was reduced to within the WHO (2008) drinking water minimum standards in a short test period and confirmed the suitability of the ISIR treatment in the study area. The subdued results for manganese removal is expected as ISIR case studies have found removal efficiency of Mn^{2+} to have a longer start-up phase when compared to Fe^{2+} (e.g. Rott and Meyerhoff, 1994; Olsthoorn, 2000; Mettler, 2002; van Halem, 2011), especially when the pH is below 8.5.

Even though these pilot tests were completed under adverse weather conditions with above average groundwater levels, the elevated DO in the recharge water and the increase in DO in the subsurface established that ozone is an appropriate oxidant to use for ISIR and a feasible alternative to oxygen gas, especially in organic-rich groundwater.

There is clearly a need for new and innovative groundwater treatments that aim to achieve maximum efficiency with operational simplicity. These innovative treatments should also take into account user safety and environmentally safe protocols. These treatments must be a cost-effective option relative to any other currently applied methods. However, the success of any groundwater treatment for a wellfield, such as ISIR, ultimately depends upon effective monitoring and maintenance programmes. Only proactive management of the wellfield can achieve the desired long-term results and sustainability of the groundwater resource.

7.2   Recommendations

Considering the benefits associated with the ISIR treatment abroad and the success of this small-scale field investigation in the Atlantis Aquifer, it is recommended that research into ISIR at the investigated study site should continue, making use of the infrastructure created. Future research should investigate the long-term effectiveness of ISIR treatment using ozone

gas on the mitigation of water quality and production borehole clogging problems experienced at the AWRMS wellfields.

Before the longer term injection tests are started, camera logging of G30966, step drawdown pumping tests and vertical logs for every metre depth of the important hydrochemical parameters (i.e. pH, ORP, EC, temperature and DO) in the production borehole should be determined. This would be useful in understanding the conditions within the borehole and surrounding aquifer similar to the investigation by Cavé and Smith (2004) in the KKRWSS. This should be repeated immediately after the ISIR treatment is completed to identify any changes as a result of the treatment in the production borehole performance.

Due to the clogged borehole and high water table, the stop-start approach often applied abroad is not recommended for this study area. Chemical rehabilitation is initially required to return the borehole to its original yield and prevent any contamination as a result of the existing borehole clogging before ISIR is initiated. However, future injection studies should continue concurrently with abstraction from G30966, with slight modifications to the production borehole set-up that a portion of the abstracted water should be diverted from the distribution mains and into a water tank. Aeration of the abstracted water can be improved from the pilot test procedures to rather use a sparging device, which does not have to be expensive (e.g. a shower head as in the Sen Gupta *et al.* (2009) study). The treatment could follow the same process used in this study, namely utilising a pump to ozonate and inject treated water into the subsurface. This could be continuously applied with minimal supervision. The high water table should also cause the injection to be operated under pressure to improve the extent of injection into the aquifer and also in multiple well-points hydraulically up-gradient to increase the volume of oxidant into the aquifer. A distance greater than 4 m between the injection well-point and production borehole is also recommended to provide longer contact flow paths for the newly formed precipitates and could aid in manganese removal.

Future studies should see the installation of multimeter probes for continuous measurement of pH, EC, DO and pe in the injected water, production borehole and monitoring well-points at screen depth, which would be valuable in understanding the zone of influence and assist in optimising the system design. Injection and abstraction volumes should also be monitored using flow meters. It is recommended that field measurements of iron speciation, utilising for example the ferrozine method as used in Smith (2006) or colorimetric field test kits used by van Halem *et al.* (2010), should be employed to complement the water laboratory analyses and to give an immediate indication of the success of treatment. In addition, future investigations should make provision for water samples to be taken at regular intervals for

water analyses by the same laboratory to avoid problems experienced with comparison of iron and manganese concentration results using both ICP-MS or ICP-OES instrumentation, as well as for the TOC and DOC analyses. Duplicate samples (and in some cases triplicate samples) should also be collected to check the analysis results and determine the best method of sampling.

Future studies can also be enhanced by incorporating geochemical modeling to improve the ISIR treatment at the Atlantis Aquifer to determine the operational conditions for study site, e.g. the saturation indices of Fe(III)-hydroxides at a specific oxygen concentration.

In addition, the role of microorganisms was not investigated in this study and the involvement of a microbiologist to assist in the collection and comparison of microbial activity and in evaluating the effects of the treatment on the population size, type and activity of organisms in the subsurface, may prove to be essential.

Other complementary research that should be undertaken to assist with the long-term ISIR field studies at the Atlantis Aquifer and other South African aquifers should include:

- Batch dissolution tests from representative samples of the Atlantis Aquifer's sediments of the main lithologies. These could be used to identify conditions and processes of importance involved in the iron and manganese mobilisation, similar to the TMG fractured-rock aquifers study undertaken in Smith (2006).

- Column tests using the Atlantis groundwater and sands could be done to evaluate the removal efficiency of iron and manganese using ozone gas, oxygen gas or aeration as the oxidant and assess the biogeochemical processes involved similar to the studies undertaken by Israel *et al.* (2009) for denitrification of nitrate-rich groundwater.

- Evaluations of the cost, environmental and user friendliness of the ISIR application compared to the currently applied methods.

- Evaluate the potential for ISIR application in a fracture aquifer because South Africa's groundwater resources are principally found in fractured aquifers.

- Investigate the potential removal of arsenic from groundwater by ISIR is also recommended, especially in certain parts of the Northern Cape and Limpopo Provinces.

CHAPTER 8.   REFERENCES

Ahmad, M. (2012). *Iron and Manganese Removal from Groundwater. Geochemical Modeling of the Vyredox Method.* Published MSc. Department of Geosciences, University of Oslo, Olso. Published by Digitale Utgivelser ved Uio.

Alchin, D. (2008). *Ion Exchange Resins.* [Online] Available at: http://nzic.org.nz/ChemProcesses/water/13D.pdf [Accessed 20 Febuary 2014].

American Water Works Association (AWWA) (1984). Removing Iron and Manganese From Groundwater. *Journal of American Water Works Association*, **76**(11), 67-68.

Anderson, T., Cauchi, T., Ibrahimi, F., Llewellyn, B., Mozina, M. and Ray, E. (2010). *Groundwater Bore Deterioration: Schemes to Alleviate Rehabilitation Costs.* [Online] Available at: http://archive.nwc.gov.au/__data/assets/pdf_file/0018/10962/32_Groundwater.pdf [Accessed 6 January 2014].

Andersson, H. and Johansson, J. (2002). *Iron Removal from Groundwater in Rakai District, Uganda. A Minor Field Study.* Unpublished MSc. Department of Environmental Engineering, Division of Sanitary Engineering, Luleå University of Technology, Luleå.

Appelo, C.A.J., Drijver, B., Hekkenberg, R. and de Jonge, M. (1999). Modeling In Situ Iron Removal from Ground Water. *Ground Water*, **37**(6), 811-817.

Appelo, C.A.J. and de Vet, W.W.J.M. (2003). Modeling in situ iron removal from groundwater with trace elements such as As. *In:* A.H. Welch and K.G. Stollenwerk (eds.) *Arsenic in Groundwater.* Kluwer Academic, Boston, pp. 381-404.

Appelo, C.A.J. and Postma, D. (2005). *Geochemistry, Groundwater and Pollution, 2nd ed.* A.A. Balkema Publishers, Leiden.

Bertram, W.E., Havenga, P.L., Timmerman, K.M.G. and Vandoolaeghe, M.A.C. (1984). *Atlantis: Witzand Wellfield Extension 1983.* Technical Report No. Gh 3317, Division Geohydrology, DWA, Cape Town.

Booch, P.W. and Barovich, G. (1981). Numerical model describing ground-water treatment by recharge of oxygenated water. *Water Resource Research*, **17**, 49-56 [cited in Appelo *et al.,* 1999].

Boonstra, J. and Kselik, R.A.L. (2001). Chapter 5: Theory of step-drawdown test analysis. *In: SATEM 2002: Software for Aquifer Test Evaluation*. International Institute for Land Reclamation and Improvement, Publication 57, Wageningen.

Bouchard, M.F., Sauvé, S., Barbeau, B., Legrand, M., Brodeur, E., Bouffard, T., Limoges, E., Bellinger, D.C. and Mergler, D. (2011). Intellectual Impairment in School-Age Children Exposed to Manganese from Drinking Water. *Environmental Health Perspectives*, **119**(1), 138-143.

Braester, C. and Martinell, R. (1988). The Vyredox and Nitredox Methods of In Situ Treatment of Groundwater. *Water Science Technology*, **20**(3), 149-163.

Bredenkamp, D.B. and Vandoolaeghe, M.A.C. (1982). *Die Ontginbare Grondwater Potensiaal van die Atlantisgebied.* Afdeling Geohidrologie, DWA, Kaapstad.

Brown, S. (2014). *Determination of TOC and DOC in water samples by thermo-catalytic digestion and NDIR detection.* CSIR Report, CSIR Analytical Laboratory, Stellenbosch.

Buamah, R. (2009). *Adsorptive Removal of Manganese, Arsenic and Iron from Groundwater.* Published PhD Thesis. Wageningen University, Wageningen. Published by CRC Press.

Bugan , R.D.H., Jovanovic, N.Z., Tredoux, G., Clarke, S. and Petersen, C. (2012) *Atlantis Water Supply Scheme Support: Hydrogeological Resource Assessment.* CSIR Report No. SCMB 45/01/11/1.2. CSIR, Stellenbosch.

Cavé, L.C. (1997). *Inventory of Atlantis Production Boreholes.* CSIR Report No. ENV/S-C97134 B, CSIR, Stellenbosch.

Cavé, L.C., Clarke, S. and Engelbrecht, J.F.P. (2004). *Review of iron bioclogging and strategies for management.* Unpublished CSIR report, CSIR, Stellenbosch.

Cavé, L.C. and Smith, M.E. (2004). In-borehole measurements of chemical parameters in a wellfield affected by iron fouling. Paper from the *11th Water-Rock Interaction Conference,* Saratoga Springs, 27 June – 2 July 2004.

Christensen, T.H., Bjerg, P.L., Banwart, S.A., Jakobsen, R., Heron, G. and Albrechtsen, H. (2000). Characterization of redox conditions in groundwater contaminant plumes. *Journal of Contaminant Hydrology*, **45**, 165-241.

City of Cape Town (CoCT) (2007). *Standard Environmental Specification.* [Online] Available at:

www.capetown.gov.za/en/EnvironmentalResourceManagement/functions/Documents/CCT_EMP_01_ STANDARD_Env_Specification_Revised2007.pdf [Accessed 2 September 2012].

City of Cape Town (CoCT) (2012). *City's new framework set to redevelop Atlantis as an industrial node.* [Online] Availiable at: www.capetown.gov.za/en/achievementsandawards/Pages/CitynewframewsettoredevAtlantisasanindu strialnode.aspx [Accessed 4 January 2014].

City News (2013). *MyCiti services expand.* [Online] Available at: www.capetown.gov.za/en/CityNewsPrint/Documents/CityNews_43_web.pdf [Accessed 4 January 2014].

Conrad, J., Rose, R. and Lasher, C. (2010). *Drilling and Pumping Tests of Additional Boreholes for the Klein Karoo Rural Water Supply Scheme.* GEOSS Report No. G2009/12-13, GEOSS, Stellenbosch.

Cromley, J.T. and O'Conner, J.T. (1976). Effect of Ozone on the Removal of Iron from a Ground Water. *Journal of American Water Works Association*, **68**(6), 315-319.

Cullimore, D.R. (2008). *Practical Manual of Groundwater Microbiology, 2nd ed.* CRC Press, Taylor and Francis Group, Boca Raton.

de Vet, W.W.J.M., van Genuchten, C.C.A., van Loosdrecht, M.C.M. and van Dijk, J.C. (2010). Water quality and treatment of river bank filtrate. *Drinking Water Engineering and Science*, **3**, 79-90.

Deed, M. and Preene, M. (2013). *Groundwater Asset Management in the Mining Industry.* [Online] Available at: http://gwd.org.za/sites/gwd.org.za/files/02%20M%20Deed_GW%20Asset%20Management%20in%20 Mining%20Final.pdf#page=1&zoom=150,0,808 [Accessed 5 December 2013].

Department of Water Affairs (DWA) (2010). Strategy and Guideline Development for National Groundwater Planning Requirements. *The Atlantis Water Resource Management Scheme: 30 years of Artificial Groundwater Recharge.* PRSA 000/00/11609/10-Activity 17 (AR5.1), dated August 2010.

Department of Water Affairs (DWA) (2011). *Groundwater Strategy 2010.* [Online] Available at: www.dwa.gov.za/Groundwater/gs.aspx [Accessed 2 February 2012].

Department of Water Affairs and Forestry (DWAF) (1983). *Atlantis Grontwaterbestuurprogram: Boorgatgegewens.* Bosbou en Omgewingsbewaring, Kaapstad.

Department of Water Affairs and Forestry (DWAF) (1986). *Management of the Water Resources of the Republic of South Africa.* DWAF, Pretoria.

Department of Water Affairs and Forestry (DWAF) (1996). *South African Water Quality Guidelines Volume 1: Domestic Water Use, 2nd ed.* Directorate of Water Quality Management, DWAF, Pretoria.

Diliūnas, J., Jonaitis, K., Jurevičius, A. and Rinkevičienė, E. (2006). Intensified elimination of iron and other thindispersed compounds from groundwater *in situ* by magnetic activation. *GEOLOGIJA*, **56**, 60-66.

Driscoll, F.G. (1986). *Groundwater and Wells, 2nd ed.* Johnson Screen, Minnesota.

Dumousseau, B., Jaudon, P., Massiani, C., Vacelet, E. and Claire, Y. (1990). Origin of manganese in the water table of Beaucaire (Gard, France): An attempt of demanganization *in situ* (Vyredox process). *Revue Des Sciences De L'Eau,* **3**(1), 21-36.

Ebermann, J.P., Eichhorn, D., Macheleidt, W., Ahrns, J.J. and Grischek, T. (2013). Field tests for subsurface iron removal at a diary farm in Saxony, Germany. *In:* P. Maloszewski, S. Witczak and G. Malina (eds.) *Groundwater Quality Sustainability.* Taylor and Francis Group, London, pp. 29-40.

El Araby, R., Hawash, S. and El Diwani, G. (2009). Treatment of iron and manganese in simulated groundwater via ozone technology. *Desalination,* **249**(3), 1345-1349.

Engelbrecht, J.F.P. (1998). Borehole Clogging, A Threat to Drinking Water Supply. Paper from the *1998 Biennial Conference and Exhibition of the Water Institute of Southern Africa (WISA),* Cape Town, 4-7 May.

Environmental Protection Agency (EPA) (1999). Chapter 3: Ozone. *In*: *Alternative Disinfectants and Oxidant Guidance Manual.* [Online] Available at: www.epa.gov/ogwdw000/mdbp/pdf/alter/chapt_3.pdf [Accessed 11 February 2013].

Eriksson, M. (2005). *Ozone chemistry in aqueous solution – Ozone decomposition and stabilisation.* Licentiate thesis, Royal Institute of Technology, Sweden.

Fleisher, J.N.E (1990). *Atlantis Groundwater Management Programme: The Geohydrology of the Witzand Field.* CSIR Report, CSIR, Bellville.

Flower, P.R. and Bishop, R.C. (2003). *Atlantis Water Scheme: A Case Study on Borehole Clogging and Bioclogging Management Initiatives.* Bulk Water, Water Department of City of Cape Town, Cape Town.

Genthe, B., Petersen, C., Bugan, R.D.H., Jovanovic, N.Z., Tredoux, G. and Clarke, S. (2012). *Atlantis Water Supply Scheme Support: Risk Assessment, Management and Communication.* CSIR Report No. SCMB 45/01/11/1.7. CSIR, Stellenbosch.

Hallberg, R.O. and Martinell, R. (1976). Vyredox-In Situ Purification of Ground Water. *Groundwater*, **14**(2), 88-93.

Hassan, R., Thurlow, J., Roe, T., Diao, X., Chumi, S., Tsur, Y. (2008). *Macro-Micro Feedback Links of Water Management in South Africa: CGE Analyses of Selected Policy Regimes.* Policy Research Working Paper 4768, The World Bank. [Online] Available at: http://elibrary.worldbank.org/doi/book/10.1596/1813-9450-4768 [Accessed 7 January 2012].

Hinkamp, J., Bergevoet, H., Skoonenberg, F. and Könning, G. (2004). *Ondergrondse ontijzering met behulp van technisch zuiver zuurstof.* Unpulbished report 2003/01/Corle, Vitens Gelderland, Corle.

Howe, P.D., Malcolm, H.M. and Dobson, S. (2004). *Manganese and Its Compounds: Environmental Aspects.* United Nations Environment Programme, the International Labour Organisation and the WHO, Geneva.

Inorganic Contaminants Research Committee (ICRC) (1993). Research Needs for Inorganic Contaminants. *Journal of American Water Works Association*, **85**(5), 106-113.

In Situ Remediation Reagents Injection (ISRRI) Working Group (2009). *Technical Report: Subsurface Injection of In Situ Remedial Reagents within Los Angeles.* [Online] Available at: www.waterboards.ca.gov/rwqcb4/water_issues/programs/ust/guidelines/Subsurface_injection_of_ISRR.pdf [Accessed 22 September 2012].

Israel, S., Engelbrecht, J.F.P, Tredoux, G. and Fey, M.V. (2009). In Situ Batch Denitification of Nitrate-Rich Groundwater Using Sawdust as a Carbon Source-Marydale, South Africa. *Water, Air and Soil Pollution*, **204**, 117-194.

Johnson, T. (2005). *Specific Capacity – A Measure of Well Performance, Well Problems and Aquifer Transmissivity: Part 1 of 2.* WRC Technical Bulletin Volume 2. [Online] Available at: www.wrd.org/engineering/specific-capacity-well-1.php [Accessed 9 February 2013].

Jolly, J.L. (2002). Sustainable Use of Table Mountain Group Aquifers and Problems Related to Scheme Failure. *In*: K. Pietersen and R. Parsons (eds.) *A Synthesis of the Hydrogeology of the Table Mountain Group – Formation of a Research Strategy.* WRC Report No. TT 158/01, WRC, Pretoria, pp. 108-111.

Jolly, J.L. and Engelbrecht, J.F.P. (2002). Occurance and Management of Iron Related Borehole Clogging in Table Mountain Group Aquifers. *In*: K. Pietersen and R. Parsons (eds.) *A Synthesis of the Hydrogeology of the Table Mountain Group – Formation of a Research Strategy.* WRC Report No. TT 158/01, WRC, Pretoria, pp. 131-140.

Karakish, A.A.K. (2005). Subsurface Removal of Iron and Manganese from Groundwater – Case Study. Paper from the *9th International Water Technology Conference,* Sharma, El-Sheikh, 17-20 March.

Kgwaila, D., de Carvalho, S., Visagie, C., Honey, H. and Theunissen, B.R. (2011). *Planning Report for the Upgrading of the Preekstoel Water Treatment Works.* Aurecon Report No. 5096/105625, Aurecon, Cape Town.

Kruseman, G.P. and de Ridder, N.A. (2000). *Analysis and Evaluation of Pumping Test Data, 2nd ed.* International Institute for Land Reclamation and Improvement, Publication 47, Wageningen.

Mackintosh, G.S. and de Villiers, H.A. (2002). Treatment of Soft, Acidic and Ferruginous Groundwaters. *In:* K. Pietersen and R. Parsons (eds.) *A Synthesis of the Hydrogeology of the Table Mountain Group – Formation of a Research Strategy.* WRC Report No. TT 158/01, WRC, Pretoria, pp. 124-130.

Maclear, L.G.A. (1995). *CAPE TOWN NEEDS GROUNDWATER: A Note on the Potential of the Cape Flats Aquifer Unit to Supply Groundwater for Domestic Use in the Cape Town Metropolitan Area.* Technical Report No. Gh3868, Geohydrology Directorate, DWAF, Cape Town.

Maogong, F. (1988). The Application of Vyredox Method Regarding Iron Removal From Ground Water in China. *Ground Water*, **26**(5), 647-648.

Masten, S.J. (2004). *Chemical Oxidation Technologies.* [Online] Available at: www.egr.msu.edu/tosc/gelman/gelmanmeetings.shtml [Accessed 15 April 2013].

Mettler, S., Abdelmoula, M., Hoehn, E., Schoenenberger, R., Weidler, P. and von Guten, U. (2001). Characterization of Iron and Manganese Precipitates from an In Situ Ground Water Treatment Plant. *Grounwater*, **39**(6), 921-930.

Mettler, S. (2002). *In Situ Removal of Iron from Ground Water: Fe(II) Oxygenation and Precipitation Products in a Calcareous Aquifer.* Unpublished PhD Thesis. Swiss Federal Institute of Technology, Zürich.

Middleton, B.J. and Bailey, A.K. (2009). *Water Resources of South Africa, 2005 study (WR 2005).* WRC Report No. TT 381/08, WRC, Pretoria.

More Water cc. (2001). *Atlantis Wellfield Rehabilitation – Consolidation Report of Phases 1 to 4.* June 2001. More Water cc., Cape Town.

More Water cc. (2002). *Atlantis Wellfield Rehabilitation – Consolidation Report of Phase 1 to 5.* June 2002. More Water cc., Cape Town.

Munter, R., Ojaste, H. and Sutt, J. (2005). Complexed Iron Removal from Groundwater. *Journal of Environmental Engineering*, **131**(7), 1014-1020.

Munter, R., Overbeck, P. and Sutt, J. (2008). Which is the Best Oxidant for Complexed Iron Removal from Groundwater: The Kogalym Case. *Ozone: Science and Engineering*, **30**(1), 73-80.

Nealer, E. (1979a). *Trapaftrektoets by G30966 – Waarneming Atlantisprojeck.* Bosbou en Omgewingsbewaring, Department of Waterwese, Kaapstad.

Nealer, E. (1979b). *Trapaftrektoets by G30979 – Waarneming Atlantisprojeck.* Bosbou en Omgewingsbewaring, Department of Waterwese, Kaapstad.

Nimmer, M.A., Wayner, B.D. and Morr, A.A. (2000). *In-Situ* Ozonation of Contaminated Groundwater. *Environmental Progress*, **19**(3), 183-196.

Olsthoorn, T.N. (2000). *Background of Subsurface Iron and Manganese Removal.* Unpublished report, Amsterdam Water Supply Research and Development Department, Amsterdam.

Parsons, P.R. (2007). *Extension and Upgrading of the Wastewater Treatment Works and Associated Infrastructure Serving the Blaauwberg Area: Specialist Groundwater Assessment.* Report 214/CCA-F1 prepared for CCA Environmental (Pty) Ltd. By Parons and Associates, Somerset West.

Pérez-Guzán, L., Bogner, K. R. and Lower, B. H. (2010). *Earth's Ferrous Wheel.* [Online] Available at: www.nature.com/scitable/knowledge/library/earth-s-ferrous-wheel-15180940 [Accessed 29 March 2014].

Piper, J. and Salvage, J. (2012). Successful Ozone Application for Petroleum Hydrocarbons. Presentation from the *19th International Petroleum Environmental Conference,* Denver, 30 October to 1 November 2012.

Plummer, C., Luckett, M., Porter, S. and Moncrief, R. (2005). Ozone Sparge Technology for Groundwater Remediation. [Online] Available at: www.westshoreconsulting.com/download/ozone/Plummer2005.pdf [Accessed 2 June 2012].

Quayle, T. (2012) *Recycling wastewater to bolster ground water supply: Atlantis Story.* [Online] Available at: www.awasla.org/programmes.php?id=casestudies [Accessed 2 January 2014].

Radčenko, I. and Hauskrecht, J. (1982). New possibilities and methods of *in situ* groundwater treatment in gravel-sand aquifers*. In:* P.J. Jones (ed.) *Improvement of Methods of Long Term Prediction of Variations in Groundwater Resources and Regimes due to Human Activity.* Proceedings of the 1st IAHS Symposium, Exeter. IAHS Publication No. 136, pp. 121-126.

Rajagopaul, R., Mbongwa, N.W. and Nadan, C. (2008). *Guidelines for the Selection and Effective Use of Ozone in Water Treatment.* WRC Report No. 1596/01/08, WRC, Pretoria.

Rehfeldt, K.R., Raman, R.K., Dar Lin, S. and Broms, R.E. (1992). *Assessment of the Proposed Discharge of Ground Water to Surface Waters of the American Bottoms Area of Southwestern Illinois.* [Online] Available at: www.isws.illinois.edu/pubdoc/CR/ISWSCR-539.pdf [Accessed 1 May 2014].

Republic of South Africa (1993). *Act No. 85 of 1993: Occupational Health and Safety Act*, Government Gazette No. 14918, Cape Town.

Republic of South Africa (1998a). *Act No. 36 of 1998: National Water Act.* Government Gazette Vol. 398 No. 19182, Cape Town.

Republic of South Africa (1998b). *Act No. 107 of 1998: National Environmental Management Act.* Government Gazette Vol. 401 No. 19519, Cape Town.

Republic of South Africa (2005). *Act No. 39 of 2004: National Environmental Management: Air Quality Act.* Government Gazette Vol. 476 No. 163, Cape Town.

Rice, R.P. (2002). Century 21-Pregnant with Ozone. *Ozone: Science and Engineering*, **24**(1), 1-15.

Riekel, T. and Hinze, G. (2002). *Rehabilitation of Wells Using the "Electrochemically Activated Water" (EAW) Technology.* [Online] Available at: www.aquaox.net/uploads/EAW_Rehab.pdf [Accessed 24 April 2012].

Roberts, D.L. (2006). SANDVELD GROUP. *In*: M. Johnson (ed.) *CATALOGUE OF SOUTH AFRICAN LITHOSTRATIGRAPHIC UNITS.* South African Committee of Stratigraphy, Pretoria, **9**, pp. 25-26.

Roberts, D.L., Botha, G., Maud, R. and Pether, J. (2006). Coastal Cenozoic Deposits. *In:* A. Johnson, C.R. Anhaeusser and R. Thomas (eds.) *The Geology of South Africa.* Geological Society of South Africa, Johannesburg/CGS, Pretoria, pp. 605-628.

Rott, U., Boochs, P.W. and Baroich, G. (1978). In situ groundwater treatmeny by injection of oxygenated water. *Wasser Boden*, **30**, 206-210 [cited in Appelo *et al.,* 1999]

Rott, U. and Meyerhoff, R. (1994). Physical, chemical and biological processes in consequence of *in-situ* treatment of groundwater. *In:* K. Kovar and J. Soveri (eds.) *Groundwater Quality Management (GQM).* Proceedings of the 1993 GQM Conference, Tallinn. IAHS Publication No. 220, pp. 439-447.

Scheepers, R. (1995). Geology, geochemistry and petrogenesis of the Lat Precambrian S-, I- and A-type granitoids in the Saldania belt, Western Cape Province. *Journal of African Earth Science*, **21**(1), 35-58.

Sen Gupta, B., Chatterjee, S., Rott, U., Kauffman, H., Bandopadhyay, A., DeGroot, W., Nag, N.K., Carbonell-Barrachina, A.A. and Makherjee, S. (2009). A simple chemical free arsenic removal method for community water supply - A case study for West Bengal, India. *Environmental Pollution*, **157**, 3351-3353.

Sharma, S.K. (2001). *Adsorptive Iron Removal from Groundwater.* Published PhD Thesis. Institute for Water Education, Delft University of Technology, Delft. Published by Swets and Zeitlinger B.V., Lisse.

Smart, M.C. and Tredoux, G. (2002). Groundwater Quality and Fitness for Use. *In*: K. Pietersen and R. Parsons (eds.) *A Synthesis of the Hydrogeology of the Table Mountain Group – Formation of a Research Strategy.* WRC Report No. TT 158/01, WRC, Pretoria, pp. 118-123.

Smith, L.A. (2002). *Iron related bacterial clogging of boreholes in Oudtshoorn, South Africa, and the remediation thereof.* Directorate of Geohydrology, DWAF, Cape Town.

Smith, M.E. (2006). *Prediction, control and rehabilitation of iron encrustation in water supply boreholes, Western Cape, South Africa: A geochemical approach.* Unpublished PhD Thesis. Department of Geological Sciences, University of Cape Town, Cape Town.

Smith, M.E. and Roychoudhury, A.N. (2013). Mobilisation of iron from rocks in a fractured aquifer: Lithological and geochemical controls. *Applied Geochemistry,* **31**, 171-186.

Sommerfeld, E.O. (1999). *Iron and Manganese Removal Handbook.* American Water Works Association, Denver.

South African National Standards (SANS) (2011). *South African National Standards for water for domestic supplies (SANS 241:2011).* The Council for the South African Bureau of Standards, Pretoria.

Stapelberg, F.D.J. (2005). *The Engineering Geology of the Melkbosstrand Area. Explanation of the 1:50 000-scale Map Sheet 3318 CB Melkbosstrand, Western Cape.* CGS, Pretoria.

Timmer, H., Verdel, J. and Jongmans, A.G. (2003). Well Clogging by Particles in Dutch Well Fields. *Journal of American Water Works Association,* **95**(8), 112-118.

Tredoux, G. and Cavé, L.C. (2002). *Atlantis Aquifer. A status report on 20 years of groundwater management at Atlantis.* CSIR Report No. ENV-S-C 2002-069, CSIR, Stellenbosch.

Tredoux, G., Cavé, L.C. and Bishop, R.C. (2002). Long-term chemical monitoring of wastewater infiltration in a sandy aquifer, South Africa. *In*: P.J. Dillon (ed) *Management of Aquifer Recharge for Sustainability.* Proceedings of the 4th International Symposium on Artifical Recharge of Groundwater, Balkema Publishers, pp. 35-40.

Tredoux, G., Israel, S. and Cavé, L.C. (2004). *The Feasibility of In Situ Groundwater Remediation as a Robust Low-Cost Water Treatment Option.* WRC Report No. 1325/1/04, WRC, Pretoria.

Tredoux, G., Israel, S., Jovanovic, N.Z., Bugan, R.D.H and Petersen, P. (2012). *Atlantis Water Supply Scheme Support: Database Compilation Process and Chemical Data Assessment.* CSIR Report No. SCMB 45/01/11/1.1, CSIR, Stellenbosch.

Turton, A. (2007). *Overview of the Water Situation in South Africa.* [Online] Available at: www.enviropaedia.com/topic/default.php?topic_id=352 [Accessed 19 April 2014].

Vance, D.B. (2002). *A Review of Chemical Oxidation Technology.* [Online] Available at: http://2the4.net/html/chemoxwp.htm [Accessed 5 December 2012].

Van Beek, C.G.E.M and Vaessen, H. (1979). In situ iron removal from groundwater. *H2O,* **12**, 15-19 [cited in Appelo *et al.,* 1999].

van der Laan, H. (2008). *MODELING SUBSURFACE IRON REMOVAL. Application of a Geochemical Model to Describe Subsurface Aeration at Pumping Station Schwacht.* Unpublished MSc. Faculty of Civil Engineering and Geosciences, Department of Water Management, Delft University of Technology, Delft.

van der Merwe, A. (1980). *Eksplorasie, Ontginning en Evaluering van grondwater van die Sandafsetting in die Atlantisgebied vir watervoorsiening aan die Antlantis-Ontwikkelingsgebied.* Tegniese Verslag No. Gh3187, Bosbou en Omgewingsbewaring, Department of Waterwese, Kaapstad.

van Essen, J., Young, M., Dijkstra, I. and Schoonenberg, F. (2005). *Underground Deferrization.* Vitens Report, Vitens, the Netherlands.

van Halem, D., de Vet, W., Amy, G. and van Dijk, H. (2008). *Subsurface iron removal for drinking water production: understanding the process and exploiting benefitial side effects.* [Online] Available at:
http://citg.tudelft.nl/fileadmin/Faculteit/CiTG/Over_de_faculteit/Afdelingen/Afdeling_watermanagement/Secties/gezondheidstechniek/leerstoelen/Drinkwater/News_and_Events/Colloquium_Series/doc/WQTC_vanHalemdeVet_finalversion.ppt [Accessed 10 June 2010].

van Halem, D., Heijman, S.G.J., Johnson, R., Huq, I.M., Ghosh, S.K., Verberk, J.Q.J.C, Amy, G.L. and van Dijk, J.C. (2010). Subsurface iron and arsenic removal: low-cost technology for community-based water supply in Bangladesh. *Water Science and Technology*, **62**(11), 2702-2709.

van Halem, D. (2011). *Subsurface Iron and Arsenic Removal for Drinking Water Treatment in Bangladesh.* Published PhD thesis. Delft University of Technology, Delft. Published by Water Management Academic Press.

van Halem, D., de Vet, W., Verberk, J., Amy, G. and van Dijk, H. (2011). Characterization of accumulated precipitates during subsurface iron removal. *Applied Geochemistry*, **26**, 116-124.

van Vuuren, L. (2011). Groundwater – from 'inferior' to 'superior'. *The Water Wheel*, *November/December 2011,* **10**(6), 12-15.

Vegter, J.R. (1995). *An Explanation of a Set of National Groundwater Maps.* WRC Report No. TT 74/95, WRC, Pretoria.

Vestland, M. (2010). *Sunndalsøra Groundwater Works – Water quality assessment.* Unpublished MSc. Faculty of Engineering Science and Technology, Norwegian University of Science and Technology, Trondheim.

von Gunten, U. (2003). Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Research*, **37**(7), 1443-1467.

Walter, D.A. (1997). *Geochemistry and Microbiology of Iron-Related Well-Screen Encrustation and Aquifer Biofouling in Suffolk Country, Long Island, New York.* United States Geological Survey Water-Resources Investigation Report. [Online] Available at: http://ny.water.usgs.gov/pubs/wri/wri974032/WRIR97-4032.pdf [Accessed 24 January 2014].

Wassertec (2012). *CD Aqua Manual.* Wassertec Ozone Systems, Cape Town.

Weaver, J.M.C., Cavé, L.C. and Talma, A.S. (2007). *Groundwater Sampling: A Comprehensive Guide for Sampling Methods, 2nd ed.* WRC Report No. TT 303/07, WRC, Pretoria.

Woodford, A., Rosewarne, P. and Girman, J. (2006). *How much groundwater does South Africa have?* [Online] Available at: www.srk.co.za/files/File/newsletters/groundwater/PDFs/1_A_Woodford.pdf [Accessed 3 January 2011].

World Health Organisation (WHO) (2008). *Guidelines for Drinking-Water Quality: Incorporating 1st and 2nd Addenda, Vol. 1, Recommendations, 3rd ed.* [Online] Available at: www.who.int/water_sanitation_health/dwq/gdwq3rev/en/ [Accessed 5 June 2012].

Wright, A. (1991). *The Artificial Recharge of Urban Stormwater Runoff in the Atlantis Coastal Aquifer.* Unpublished MSc. Rhodes University, Grahamstown.

APPENDICES

Appendix A: Historical Climatic Data

Appendix B: Historical Water Levels

Appendix C: Historical Pumping Test Data

Appendix D: Historical Groundwater Quality

Appendix E: Study Site Borehole Information

Appendix F: Injection Test Groundwater Quality

Appendices A to F are on the accompanying CD.

ABSTRACT

The sustainability of many wellfields is threatened due to elevated iron (Fe^{2+}) and manganese (Mn^{2+}) concentrations in groundwater. Their presence causes aesthetic and potability problems but the greatest concern is production borehole clogging. Physico-chemical processes and biological activities cause clogging by oxidation of these ions at the borehole and aquifer interface resulting in lowered borehole yields, increases operation and maintenance costs. South African research has focused on the remediation of clogging problems, but knowledge is needed for preventative measures in controlling the source of the problems (i.e. Fe^{2+} and Mn^{2+}). The *in-situ* iron removal (ISIR) method is a technique involving periodic injection of oxygenated water into the aquifer. It has successfully been applied overseas for decades and more recently in Egypt in reducing the need for *ex-situ* removal of Fe^{2+} and Mn^{2+}. Long-term applications maintain borehole yields by reducing Fe^{2+} and Mn^{2+} movement towards the borehole and spreading the oxidation processes over a larger surface area in the aquifer. The precipitates stabilise into crystalline oxides, inhibiting reductive dissolution and Fe^{2+} and Mn^{2+} mobilisation.

The study site was the Atlantis Aquifer, where clogging has reduced the wellfield capacity by 60%, necessitating surface water augmentation. The aims of investigating ISIR applicability in a South African context were:

- Feasibility investigation at the Atlantis Aquifer;

- Design a site-specific ISIR prototype and methodology;

- Assess Fe^{2+} and Mn^{2+} removal effectiveness of the prototype.

In-situ iron removal literature suggested there was a high probability of success for applying the technique at this locality. The high water table necessitated injection into surrounding well-points, rather than directly into the test borehole (G30966). The presence of organic compounds and silica-rich groundwater also required the novel use of ozone. The World Health Organisation (WHO) drinking water standards guided the desired thresholds, i.e. Fe < 0.3 mg/ℓ and Mn < 0.1 mg/ℓ. The study area showed native Fe and Mn concentrations of 0.5 mg/ℓ and 0.2 mg/ℓ, respectively.

A mobile ISIR prototype using aerated water from G30966 supplied ozonated groundwater with a high dissolved oxygen content. Initial tests saw injection in a well-point 10 m from G30966 with abstraction being shut down. Entrained gases in the ozonated water prevented sufficiently high injection rates being reaches. These gases were subsequently removed using a degas column, resulting in a reasonable injection rate. Due to the previous test not

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showing removal, a third technique was applied with injection into a well-point 4 m from G30966. The iron and manganese concentrations at G30966 showed a decline but concentrations remained higher than the known baselines, suggesting that intermittent pumping dislodged deposits from G30966 contributing to spurious high iron and manganese levels. A fourth methodology was tested with abstraction during injection. This resulted in iron and manganese concentrations within the baseline concentrations and desired removal of iron removal below the WHO standard. Manganese removal was not as effective because the Mn^{2+} oxidation takes longer compared to Fe^{2+} and requires a higher pH.

This study operated at a smaller scale than international case studies but showed that iron and manganese removal is achievable at much lower injection parameters (i.e. < 2 m^3/h and < 10 m^3/day). The use of ozone was very effective in increasing DO concentrations, better than aeration investigations and comparable to using oxygen gas. The test also showed that DO can be increased in the subsurface with successive injections over 4 to 5 days, elevating the DO between 3 to 9 times above the baseline of 0.4 mg/ℓ in the aquifer.

Keywords: *In-situ* groundwater treatment; Groundwater; Iron; Manganese; Wellfield development and management; Borehole clogging; Water quality improvement; Ozone; Atlantis Aquifer; Pilot study

OPSOMMING

Die volhoubare benutting van menige produksieveld word bedreig deur die aanwesigheid van verhoogde yster (Fe^{2+}) en mangaan (Mn^{2+}) konsentrasies in die grondwater. Hul teenwoordigheid bring estetiese probleme mee en belemmer drinkbaarheid, maar die grootste bron van kommer is die verstopping van produksieboorgate. Fisies-chemiese prosesse en biologiese aktiwiteit veroorsaak verstopping vanweë oksidasie van hierdie ione by die boorgat-waterdraer tussenvlak wat tot verlaagde boorgat-lewering, verhoogde bedryf- en instandhoudingskoste, en bevordering van ooronttrekking lei. Suid-Afrikaanse navorsing het tot duser op die remediëring van verstoppingsprobleme gefokus, maar kennis is nodig vir voorkomende maatreëls by die bron, d.w.s. Fe^{2+} en Mn^{2+} mobilisasie. Die *in-situ* ysterverwyderingsmetode (*In-situ* iron removal, ISIR) is 'n tegniek gebaseer op gereelde toediening van suurstofryke water in die waterdraer. Dit word reeds dekades lank suksesvol in die buiteland toegepas en meer onlangs in Egipte vir *ex-situ* behandeling en vermindering van Fe^{2+} en Mn^{2+}. Gewoonlik handhaaf langtermyn toepassings boorgat lewerings deur die vermindering van die migrasie van Fe^{2+} en Mn^{2+} uit die akwifeer na die boorgat en die verspreiding van die oksidasieproses oor 'n groter oppervlakte in die waterdraer. Die neerslae stabiliseer in kristallyne oksiede, wat die reduktiewe ontbinding van die neerslag en gevolglike Fe^{2+} en Mn^{2+} mobilisasie verminder.

Die studieterrein is die Atlantis-waterdraer, waar verstopping die produksieveld se kapasiteit met 60% verminder het en die toevoeging van oppervlakwater genoodsaak het. Die doel van die ondersoek na die toepaslikheid van ISIR in die Suid-Afrikaanse konteks was:

- Ondersoek die haalbaarheid van ISIR in die Atlantis-waterdraer;

- Ontwerp 'n terrein-spesifieke ISIR prototipe en metode;

- Bepaal die doeltreffendheid van Fe^{2+} en Mn^{2+} verwydering.

Die literatuurstudie oor *in-situ* ysterverwydering het op 'n hoë waarskynlikheid van sukses vir die toepassing van die tegniek in hierdie omgewing gedui. Die hoë watervlak het die toediening van die suurstofryke water in omliggende boorgate genoodsaak, eerder as toediening direk in die toetsboorgat (G30966). Verder het die voorkoms van organiese verbindings en silika-ryke grondwater ook die innoverende gebruik van osoon genoodsaak. Die Wêreld Gesondheidorganisasie (WHO) se drinkwaterstandaarde van Fe < 0,3 mg/ℓ en Mn < 0,1 mg/ℓ is as gewenste drempel-waardes gebruik van. Die grondwater in die studiegebied het Fe en Mn konsentrasies van onderskeidelik 0,5 mg/ℓ en 0,2 mg/ℓ.

Grondwater uit produksieboorgat G30966 is eers belug en daarna met 'n mobiele ISIR prototipe eenheid geösoneer. Tydens die eerste toetse is die geösoneerde water op die regte diepte in 'n boorgat 10 m van G30966 toegedien met gelyktdige staking van wateronttrekking uit G30966. Ingeslote gasse in die geösoneerde water het stoedieningstempo's belemmer, maar die gasse is later met 'n ontgassingskolom verwyder, wat tot 'n redelike stempo gelei het. Gegewe die feit dat die tweede toetslopie nie ysterverwydering getoon het nie, is 'n derde tegniek toegepas, wat toediening in 'n boorgat 4 m van G30966 behels het. Hoewel die Fe en Mn konsentrasies by G30966 begin afneem het, was die konsentrasies hoër as die bekende basislyne, wat daarop gedui het dat die onderbroke onttrekking uit boorgat G30966 yster en mangaan aanpaksels in boorgat G30966 laat loskom het wat bygedra het tot anomale hoë Fe en Mn vlakke. 'n Vierde metode met wateronttrekking uit die produksieboorgat tydens toediening van die geösoneerde water het Fe en Mn konsentrasies laer as die basislyn opgelewer en die gewenste verwydering van Fe tot onder die WHO standaard bereik. Mangaan-verwydering was nie so effektief nie omdat die Mn^{2+} oksidasie 'n hoër pH vereis en langer neem as met Fe^{2+}.

Hierdie studie is op 'n kleiner skaal as die internasionale gevallestudies uitgevoer, maar het getoon dat Fe en Mn verwydering haalbaar is teen baie laer toedieningstempo's (bv. $< 2 \, m^3/h$ en $< 10 \, m^3/dag$). Die gebruik van osoon het opgeloste suurstofkonsentrasies effektief verhoog tot waar dit vergelykbaar was met die gebruik van skoon suurstof gas en het beter gevaar as studies waar atmosferiese lug gebruik is. Die toets het ook getoon dat die opgeloste suurstof in die waterdraer 3 tot 9 keer bo die basislyn van 0,4 mg/ℓ verhoog kan word met opeenvolgende toedienings oor 'n tydperk van 4 tot 5 dae.