Preventing Production Borehole Clogging by *In-situ* Iron Removal in South African Aquifer Systems

Report to the
WATER RESEARCH COMMISSION

by

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EXECUTIVE SUMMARY

INTRODUCTION

The development of groundwater supply schemes is on the increase in South Africa. However, the sustainability of many of these schemes is threatened due to the presence of soluble iron (Fe^{2+}) and manganese (Mn^{2+}) ions in the groundwater. This risk manifests from the problems caused in the water quality and supply to consumers. The main water quality problems associated include the aesthetic (e.g. staining of laundry) and potable (e.g. metallic taste), which subsequently limits the use of the water. The World Health Organisation (WHO) recommends the removal of iron (Fe) and manganese (Mn) to concentrations below 0.3 mg/ℓ and 0.1 mg/ℓ, respectively, to circumvent the abovementioned issues. These concentrations levels can easily be achieved by above-ground water treatment after abstraction, but requires high investment costs, needs skilled operators and high operation and management costs to succeed.

However, production borehole clogging is of greatest concern in the operation of groundwater supply schemes as it jeopardises their sustainability, due to the severe cost implications associated with reduced production. The clogging of production boreholes takes place in aquifers where anoxic/anaerobic groundwater with Fe^{2+} and Mn^{2+} in solution is abstracted. By the ingress of oxygen during pumping, oxidation of Fe^{2+} and Mn^{2+} ions into insoluble iron (III) and manganese (IV) oxides at the interface between the borehole screen and immediate surrounding aquifer. The newly-formed oxides accumulate in the aquifer and/or coat the screen and pump, leading to the reduction in flow, which results in losses in the production capacity. The reduced production capacity thus lowers the efficiency of the production borehole to supply water to the groundwater scheme and increases the production costs, due to the higher electricity requirements for pumping and rehabilitation treatments to recover the loss in the borehole yield.

The clogging process is also accompanied by the growth of iron-related bacteria, which further impedes flow to the borehole due to the development of biofilms. The presence of such micro-organisms, together with slime-forming and sulphate-reducing bacteria, also exacerbates the water quality problems by the production of odours and slimy bacterial mats and in severe cases microbial-induced corrosion of the production borehole. Over time, the build-up of iron (III) and manganese (IV) oxides and biofilm can lead to severe clogging of the borehole and can be pumped up in the abstracted water, furthermore clogging the flow meters and distribution mains. This increases maintenance and operation costs and above-ground treatment needs of the water before distribution.

The Fe^{2+} and Mn^{2+} ions can naturally concentrate to elevated levels in anoxic/anaerobic groundwater and the bacterial populations are also naturally present in the subsurface, moreover the ingress of oxygen through pumping cannot be entirely prevented. The approach to controlling the clogging of production boreholes is through management and rehabilitation procedures. In South Africa, management and rehabilitation protocols have been adopted and in severe clogging cases the Blended Chemical Heat Treatment has been applied. However, the effectiveness of these protocols is doubtful and long-term success has been limited. This is generally ascribed to:

- The incorrect design of the production boreholes;
- Management strategies not followed or correctly implemented resulting in clogging to severe to recover loss in yield;
- When water demands are high, wellfield managers adopt a high rate stop-start approach;
- High costs and skilled needs are needed for the continual monitoring and rehabilitation treatments necessary for the prevention.

Since the current knowledge into the controlling of production borehole clogging has not achieved the long-term results in South Africa, more research is required into the prevention of clogging, which is the topic of this Water Research Commission (WRC) project. One such treatment option available to be investigated locally is the *in-situ* iron removal (ISIR) treatment.

IN-SITU **IRON REMOVAL**

The ISIR treatment involves the periodic injection of oxygenated water into the anoxic/anaerobic aquifer to oxidise the soluble Fe^{2+} and Mn^{2+} ions in the subsurface before reaching the production borehole. The treatment process was designed in Europe to reduce the amount of Fe^{2+} and Mn^{2+} carried by the abstracted water to reduce (or obviate) the above-ground water treatment. This treatment has been successfully applied for decade's world-wide and the well-known benefits include:

- Reduction in *ex-situ* iron and manganese removal, including additional side benefits of improved capacity in sand filtration or de-nitrification in *ex-situ* bio-filters;
- The removal efficiency of Fe^{2+} and Mn^{2+} increase with successive treatments;
- Retention of other ions such as phosphate (PO_4) and arsenic (As) in the subsurface;
- Reduction in production borehole clogging resulting in a reduction in rehabilitation treatments;
- The accumulated amorphous iron (III) and manganese (IV) oxides stabilise into thermodynamically stable minerals, which in turn, prevent the mobilisation of Fe^{2+} and Mn^{2+} ions under reducing conditions.

PROJECT AIM AND OBJECTIVES

The aim of the WRC project was to investigate the feasibility of the ISIR technique in preventing clogging of production boreholes in a South Africa context by removing Fe^{2+} and Mn^{2+} from the groundwater. To achieve the abovementioned aim into investigating the feasibility of ISIR, four objectives were outlined:

Objective 1: Preliminary investigation into the feasibility of ISIR application at the suggested study sites.

Objective 2: Design an ISIR prototype and methodology for the selected study site(s).

Objective 3: Assess the immediate effectiveness of Fe and Mn removal by the ISIR treatment at the selected study site(s).

Objective 4: Assess the long-term effectiveness (≤ 1 year) of ISIR by measuring the performance of the production borehole(s) at the study site(s).

Two study sites were selected, which included the primary, intergranular Atlantis Aquifer and the fractured rock aquifers of the Table Mountain Group (TMG). Both aquifers have established groundwater supply schemes (i.e. the Atlantis Water Resource Management Scheme and the Klein Karoo Rural Water Supply Scheme) that have been in operation for at least three decades and are the main contributor to their municipal water supply. In addition, the protection and preservation of the groundwater resource is vital as the areas experience semi-arid conditions and have no nearby surface water supplies. However, the abstracted groundwater from both aquifers contains problematic Fe^{2+} and Mn^{2+} concentrations, which require *ex-situ* treatment and are plagued by production borehole clogging. The severity of production borehole clogging is experienced in nearly every production borehole in both groundwater supply schemes and presently both are operating less than 40% of their original total capacity.

PRELIMINARY INVESTIGATION INTO THE STUDY AREAS

Even though the ISIR treatment has been applied for decades (e.g. Europe and China), there are no established design criteria and its prototype design and application depends on the site characteristics. A preliminary investigation was necessary to evaluate whether such treatment was feasible at the study sites and to understand the sites' characteristics for the ISIR system design and application methodology.

The feasibility of applying the ISIR method in a fractured aquifer was considered because over 80% of South Africa is underlain by fractured aquifers, whereby the aquifers of the TMG are one of the most important aquifers in the Western and Eastern Cape. However, there is a lack of experience aboard and literature on the application of the ISIR treatment in a fractured rock setting is scarce. Furthermore, in view of the complexity associated with groundwater flow in such a setting and the associated logistics and costs expected for such a study to be undertaken, this project could only focused on the testing of the local applicability in a primary aquifer setting.

Based on the literature review of ISIR treatment in aquifers settings similar to that of the Atlantis Aquifer, the probability of success of applying the technique at the primary aquifer study site was high. From the preliminary investigation of the Atlantis Aquifer it was decided that due to the high groundwater table the Vyredox approach would be used in this study. This approach involves the injection of oxygenated water into the subsurface through multiple satellite well-points surrounding the production borehole, providing an oxidation barrier for groundwater approaching the production borehole. Twelve small-diameter well-points were drilled in close proximity to the production borehole for injection and monitoring purposes.

Deviation from the original ISIR methodology had to be made due to the high organic carbon and silica content of the Atlantis groundwater, which forms complexes with the Fe^{2+} and Mn^{2+} ions. The complexed nature of the Fe^{2+} and Mn^{2+} ions in solution prevented the use of aeration and safety and storage concerns eliminated the use of oxygen gas at the study site. It was then decided to use of ozone gas as the oxidant, which amounts to a novel approach for the ISIR treatment. It is, however, widely used in above-ground water treatment for the oxidation and removal of complexed Fe^{2+} and Mn^{2+} in groundwater.

METHODOLOGY

The raw groundwater from the selected production borehole, G30966, had a mean total Fe and Mn concentrations of 0.5 mg/ℓ and 0.2 mg/ℓ, respectively. Ideally to reduce the potential for clogging of production boreholes and obviate the *ex-situ* treatment, the total Fe and Mn concentrations in the abstracted groundwater should both be less than 0.1 mg/ℓ. International ISIR case studies showed that this is achievable through the periodic injection of a volume of oxygenated water directly into the production borehole. For achieving the above thresholds, the DO concentrations ranged between 10 mg/ℓ and 30 mg/ℓ and the injected volumes between 1 000 m^3 to 3 000 m^3.

A mobile ISIR prototype was designed for the study site, whereby groundwater was abstracted from the production borehole to fill a 3 m^3 water tank. The abstracted water was aerated (by spraying and recirculation) to remove any undesirable gases, and then drawn through from the water tank past a venturi to be dosed with the ozone gas. The ozone gas was generated on-site from high purity oxygen gas (also generated on-site by compressed air). The ozonated water was then pumped into the subsurface in a nearby well-point, hydraulically up gradient of the production borehole. Monitoring of various important parameters, including groundwater level changes and important water quality parameters took place in several points (e.g. G30966 and well-points 8 m and 4 m distance from the injection and production points), which included parameters such as electrical conductivity, pH, DO, dissolved ozone, total and dissolved Fe and Mn.

Over the three months of application, a total of four different injection techniques were applied at the study site. The first injection technique saw the direct injection of ozonated water into the subsurface through a well-point 10 m hydraulically up gradient of the production borehole. However, entrained gas bubbles in the ozonated water prevented sufficient injection (i.e. < 1.4 m^3/hr) into the aquifer. This was resolved by the inclusion of a degas column between the venturi and the injection pipe.

The second injection technique also involved a stop-start approach, where abstraction from the production borehole was kept off during the injection phase in the well-point 10 m hydraulically up gradient of the production borehole. Degassing allowed a reasonable injection rate to be maintained (i.e. ~1.8 m^3/hr).

A third injection technique was applied due to the previous techniques not showing the any significant changes in the removal of Fe and Mn concentrations in the abstracted groundwater and the measured Fe and Mn were greater than the baseline concentrations. This modified approach saw the injection in a well-point, 4 m hydraulically up gradient of the production borehole, using the stop-start approach. From the chemical analyses of the previous stop-start injection attempts, it was postulated that this approach contributed to the unanticipated high Fe and Mn concentration in the samples collected.

The fourth methodology was then tested to investigate whether continuous abstraction from the production borehole during injection in the well-point (4 m way from the production borehole) would stabilise the Fe and Mn concentrations at the known baseline concentrations and show the desired removal of Fe and Mn.

RESULTS AND DISCUSSION

This pilot study was operated at a much smaller scale than any of the ISIR studies described in the literature and from the injection tests results it was found that removal of Fe and Mn in the subsurface (although to a lesser extent in Mn compared to Fe) was achievable at much lower injection rates (i.e. $< 2\ m^3$/hr) and injected volumes (i.e. $< 10\ m^3$/day of injection).

In the stop-start injection approaches, a decrease in the Fe and Mn concentrations was observed over the course of treatment. However, unanticipated high concentrations were observed in both the Fe and Mn and these were shown to be associated to the intermittent pumping of the production borehole dislodging deposits (predominately iron-rich) from the aquifer, borehole screen and the pump.

It was found that the fourth injection technique of continuous injection and abstraction achieved the desired Fe removal to below the WHO potable and aesthetic threshold limit (i.e. < 0.3 mg/ℓ). Although, the Mn removal was not as effective it is known that Mn^{2+} oxidation takes longer in comparison to Fe^{2+} and requires higher pH conditions. For various reasons the duration of the injection runs were limited and the effect of longer term treatment on Mn concentrations could not be verified. In addition, no significant changes to the overall water quality were observed.

The use of ozone as the oxidant was found very effective as in the field the dissolved ozone concentrations measured in the injected water (i.e. 0.3-0.5 mg/ℓ) ranged between the typical ozone concentrations found in *ex-situ* treatment for Fe and Mn removal. The DO concentration (i.e. the decay product of ozone together with the surplus oxygen gas not converted to ozone) was greater than that used in ISIR case studies in the literature using aeration. The DO levels were also comparable to DO concentrations found with the use of high purity oxygen gas. These pilot tests showed that the DO can be increased successfully in the subsurface, even at low injection rates and volumes. This is best seen in the third and fourth injection technique results where successive injections over a 4 to 5 day period elevated the DO concentration between 3 to 9 times that of the baseline concentration (i.e. 0.4 mg/ℓ) at a 4 m distance between the injection well-point and production borehole.

CONCLUSIONS

This WRC project arose from the need for more research into the management of production borehole clogging due to the presence of Fe^{2+} and Mn^{2+} in the groundwater. The ISIR approach is an important treatment as it treats the cause of the water quality and clogging problems, rather than managing the symptoms.

Most of the research effort went into creating the necessary infrastructure, i.e. procuring the oxygen and ozone generators, obtaining funding for drilling of the injection and monitoring well-points, obtaining the approval for drilling of the well-points, drilling of the well-points, obtaining approval for the injection of ozonated water into the Atlantis Aquifer, completing the experimental setup, and obtaining the necessary monitoring equipment.

The pilot tests conducted at a production borehole, G30966, within the Witzand Wellfield of the Atlantis Aquifer showed that:

- Iron removal by the ISIR method is feasible, even at small-scale application.
- The ISIR treatment using ozone has the potential to increase the removal efficiency of Fe and Mn in groundwater, particularly in areas with high organic carbon and/or silica concentrations, which complexes with Fe and Mn.
- The use of ozone was found to be very effective in generating the desired high DO concentrations in the subsurface.
- Due to the low injection rate as a result of the high water table, testing could only be done over a 4 m distance between the injection well-point and production borehole. Longer term application over greater distances is needed for resolving the questions, especially into Mn removal.
- Higher injection rate tests will also require the use of larger ozone generation capacity.

RECOMMENDATIONS FOR FUTURE RESEARCH

Considering the benefits associated with the application of ISIR and the success of the small-scale application at the Atlantis Aquifer, continuation of this research is recommended at the investigated study site, making use of the infrastructure created. Future research should aim to understand the long-term effectiveness of this treatment in water quality improvements and the reduction in production borehole clogging. This should be achieved through:

- Investigating the longer term injection of ozonated water into the 4 m distant well-point.
- Injection at the 8 m distance well-point to create a larger oxidation zone to investigate any improvements in Mn removal.
- Injection at higher rate into multiple well-points for ensuring that all the groundwater drawn towards the production borehole will pass the oxidation zone.
- Based on the results of the extended tests, a full scale application should be designed for implementation at a production borehole, where Fe removal has not taken place and the aquifer is still in the original condition.
- Despite the complexity of fractured aquifer, it is still possible to investigate the application in a fractured rock setting and future studies need to be undertaken in suitable study sites.

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As	arsenic
AWRMS	Atlantis Water Resource Management Scheme
BCHT	Blended Chemical Heat Treatment
C/Co	Ratio of final solute concentration divided by initial solute concentration
CCT	City of Cape Town
CGS	Council for Geoscience
Cl_2	chlorine gas
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
EC	electrical conductivity
EPA	Environmental Protection Agency
Fe	iron
Fe^{2+}	ferrous ion
Fe^{3+}	ferric ion
HOCl	hypochlorous acid
H_2S	hydrogen sulphide
ICRC	Inorganic Contaminants Research Committee
ISIR	*In-situ* iron removal
ISRRI	In Situ Remediation Reagents Injection
KKRWSS	Klein Karoo Rural Water Supply Scheme
$KMnO_4$	potassium permanganate
mamsl	meters above mean sea level
mbgl	meters below ground level
meq/ℓ	milli-equivalent per litre
Mn	manganese
Mn^{2+}	divalent manganese ion

Mn^{4+}	quadrivalent manganese ion
NEMA	National Environmental Management Act No. 107 of 1998
NH_4	ammonia
NWA	National Water Act No. 36 of 1998
O_3	ozone
OH^-	hydroxyl free radical
O&M	operation and maintenance
pe	redox potential
pers comm.	personal communication
PO_4	phosphate
PVC	polyvinyl chloride
Q	abstraction rate
SANS	South African National Standards
Sc	specific capacity
SiO_2	silica
Sy	specific yield
T	transmissivity
TMG	Table Mountain Group
V	abstracted volume
Vi	injected volume
V/Vi	abstracted over injected volume ratio known as removal efficiency
WHO	World Health Organisation
WTP	Water Treatment Plant

1 INTRODUCTION

In recent years, groundwater usage and the development of groundwater supply schemes (also known as wellfields) have increased in water scarce countries such as South Africa. This is largely due to the limited capacity for new dam development (given the high evaporative losses) and the relative purity and availability of groundwater in such semi-arid areas (Turton, 2007). In the case of the town of Atlantis, in the Western Cape, where rainfall is approximately 450 mm/annum and there are no readily available surface water resources, groundwater has successfully supplied the water needs for three decades (DWA, 2010). However, the sustainability of many of these groundwater supply schemes, e.g. at Atlantis, is under pressure due to the presence of iron (Fe) and manganese (Mn) in the groundwater. The presence of these elements causes problems in the water quality and supply to consumers.

Production borehole clogging by Fe and Mn in groundwater is a worldwide water-use problem (e.g. Walter, 1997; Timmer *et al.,* 2003; Karakish, 2005; Cullimore, 2008; Anderson *et al.*, 2010; Kazak and Pozdnyakov, 2010; Deed and Preene, 2013). It is rated one of the five major causes of borehole failure (Driscoll, 1986), with clogging having been observed in production boreholes where Fe and Mn concentrations are as low as 0.1 mg/ℓ and 0.2 mg/ℓ, respectively (Walter, 1997; WHO, 2008). This is also experienced in South African wellfields and is currently threatening their sustainability due to the severe cost implications (e.g. Jolly, 2002; Jolly and Engelbrecht, 2002; Flower and Bishop, 2003; Cavé and Smith, 2004; Smith, 2004; Smith and Roychoudhury, 2013).

In addition, the water quality and the subsequent use of the water are negatively affected due to a variety of factors (DWAF, 1996; Alchin, 2008; WHO, 2008):

- The presence of these elements imparts an astringent metallic taste to water at Fe concentrations exceeding 0.3 mg/ℓ and 0.1 mg/ℓ for Mn;
- Aesthetic problems, i.e. reddish-brown or black water discolouration, which results in the staining of laundry and cooked food occurs at levels as low as 0.3 mg/ℓ for Fe and 0.2 mg/ℓ for Mn;
- Staining and clogging of pumping fixtures and other associated pipework at concentrations as low at 0.1 mg/ℓ for both soluble ions; and
- The presence of Fe interferes with water treatment methods, such as water softening since Fe binds irreversibly on the ion exchange resins and is regarded as a common cause of softening plant failure.

To circumvent such problems, the World Health Organisation (WHO) recommends the removal of Fe and Mn to reduce concentrations to below 0.3 mg/ℓ and 0.1 mg/ℓ, respectively (WHO, 2008). Traditionally, to achieve those concentrations, and avoid the abovementioned problems, groundwater is treated after abstraction by a process that involves oxidation followed by coagulation/flocculation, sedimentation and then filtration (Mackintosh and de Villiers, 2002). However, this approach requires relatively high investments costs, expert operator input, skilled operation and high operation and maintenance (O&M) costs (Mettler *et al.*, 2001; Mackintosh and de Villiers, 2002).

However, the main concern of sustainability operating a groundwater supply scheme where there are elevated concentrations of Fe and Mn in the groundwater is the clogging of production boreholes. The clogging of production boreholes is caused by a shift in redox equilibrium between the borehole and the aquifer with the ingress of oxygen during pumping. This results in the oxidation of the available soluble ferrous ion (Fe^{2+}) and bivalent manganese ion (Mn^{2+}), causing precipitation of their respective insoluble iron (III) hydroxides and manganese (IV) oxides, hereafter referred to as “oxides”, which accumulate in the aquifer and/or coat the borehole screen and pump (Tredoux *et al.,* 2004; WHO, 2008). The clogging processes are often accompanied by growth of iron-related bacteria, which causes biofilm development (Sommerfeld, 1999; Tredoux *et al.,* 2004). Over time, the iron (III) and manganese (IV) oxides and biofilm build-up can lead to severe clogging of the production borehole and aquifer in close vicinity of the borehole. In addition, the oxides brought up in the abstracted water can further clog flow meters and distribution pipes (Figure 1; Driscoll, 1986; Sommerfeld, 1999; Tredoux *et al.,* 2004). Furthermore, the microbiological processes often result in slimy bacterial mats and produce odours which deteriorate the water quality further and, in cases of advanced stages of biofilm growth coupled with reducing conditions, can cause microbial-induced corrosion of the borehole screen and pump (Cullimore, 2008).

Figure 1: Clogging of a production borehole pipeline (left) and flow meter (right) as a result of the iron-rich groundwater experienced at the Atlantis Aquifer (More Water, 2001)

Clogging leads to a decrease in production capacity of the borehole by the following process: flow is reduced as a result of decrease of the effective permeability in the aquifer and borehole screen; causing the available drawdown to decrease. This further lowers the borehole efficiency to supply water and negatively affects the water quality and eventually results in increased production costs (Jolly, 2002; Smith, 2004; Tredoux *et al.,* 2004). If left untreated, the production borehole will ultimately fail, further increasing costs due to the need for replacement of pumping equipment (Flower and Bishop, 2003).

Iron and manganese occur commonly in the Earth's crust and occur naturally in elevated concentrations in anoxic/anaerobic groundwater, as do bacterial populations naturally present in the subsurface. Furthermore, the ingress of oxygen through pumping cannot be entirely prevented. Therefore, the approach to control clogging of production boreholes is through management, monitoring and rehabilitation protocols (Flower and Bishop, 2003; DWA, 2010). The protocols applied at wellfields are site-specific and no "silver bullet method" can be used (Jolly and Engelbrecht, 2002), but the common objectives are to keep the costly rehabilitation work to a minimum while maintaining the water quality and the cost-effectiveness of production from the resource (Flower and Bishop, 2003). The recommended protocols for areas prone to clogging of production boreholes include (Jolly and Engelbrecht, 2002; Flower and Bishop, 2003):

- Ensuring the correct physical construction and material of the production borehole, parameters influences the rate of clogging, minimise aeration and turbulent flow at the screen and the success of rehabilitation work.
- Pumping tests to assign the correct sustainable abstraction rates for the borehole, to limit the extent of oxygen and nutrient ingress during pumping and adopt continuous, lower abstraction rates than intermittent, high-rate pumping.
- Regular monitoring of water quality and bacterial activity, groundwater levels and production borehole yields to identify potential clogging.
- Down-hole camera logging to confirm clogging when it is suspected.
- Physical and/or chemical cleaning to reduce the bacterial population and remove the iron (III) and manganese (IV) oxides.

In South Africa, such management and rehabilitation recommendations have been adopted and in severe cases the Blended Chemical Heat Treatment (BCHT) has been applied to recover the losses in production borehole yields (More Water, 2001; Smith, 2004). However, the long-term success and effectiveness of such management and rehabilitation approaches are limited in South Africa due to the following situations (Flower and Bishop, 2003; Tredoux *et al.,* 2004; Less, C., More Water, *pers comm*., 2013):

- Production boreholes were designed 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, and the pump and/or casing have to be replaced or a new borehole drilled.
- Proposed management strategies have not been followed or correctly implemented, e.g. over-abstraction occurred when water demands were high, which resulted in clogging occurring within a short period of time.
- High rate stop-start abstraction instead of constant lower rate pumping adopted by wellfield managers.

- Special skills needed and high costs associated with the monitoring and rehabilitation treatments prevent regular assessment and maintenance.
- Regulatory authorisation is required to proceed with such rehabilitation activities and this may lead to potential delays e.g. the National Water Act (NWA; Act No. 36 of 1998) and the National Environmental Management Act (NEMA; Act No. 107 of 1998).

Despite the current knowledge and implementation of maintenance, rehabilitation and management options, more information is required to deal with the long-term prevention of production borehole clogging in South Africa. Other treatment options should be investigated, such as the *in-situ* iron removal (ISIR) method. The potential of this treatment has been proposed by a number of authors (e.g. Jolly and Engelbrecht, 2002; Cavé and Smith, 2004; Tredoux *et al.,* 2004) as this process has been successfully implemented in groundwater supply schemes overseas for decades (e.g. Europe, China etc.).

The ISIR treatment was designed to reduce the amount of Fe and Mn in abstracted water, in order to decrease or obviate above-ground water treatment. This is achieved through the periodic injection of oxygenated water into the anoxic/anaerobic aquifer, oxidising the Fe^{2+} and Mn^{2+} ions to precipitate out in the subsurface and away from the production borehole. When pumping is resumed, groundwater is then abstracted with lower Fe and Mn concentrations (Appelo and Postma, 2005). However, the other well-known benefit of the ISIR treatment is a reduction in production borehole clogging, which is achieved through (Mettler *et al.,* 2001; van Halem *et al.,* 2011):

- Lower Fe^{2+} and Mn^{2+} concentrations are drawn toward the production borehole with successive ISIR treatment and;
- The iron (III) and manganese (IV) precipitates that accumulate in the aquifer stabilise into minerals, which, in turn, prevents Fe^{2+} and Mn^{2+} mobilisation from the aquifer when reducing conditions prevail again.

1.1 Project Aim and Objectives

The aim of the project was to investigate the feasibility of the ISIR technique in preventing clogging of production boreholes in a South African context by removing Fe^{2+} and Mn^{2+} from the groundwater. The study areas selected were the primary, intergranular Atlantis Aquifer and the fractured rock aquifers of the Table Mountain Group (TMG).

The objectives to achieve the abovementioned aim include:

(1) Preliminary investigation into the feasibility of ISIR application at the suggested study sites.

(2) Design of an ISIR prototype and methodology for the selected study site(s).

(3) Assess the immediate effectiveness of Fe and Mn removal by the ISIR treatment at the selected study site(s).

(4) Assess the long-term (≤ 1 year) effectiveness of ISIR by measuring the performance of production borehole(s) at the study site(s).

2 LITERATURE REVIEW

2.1 Groundwater Development in South Africa

South Africa is a largely semi-arid country, rated among the global top 20 water-stressed countries (Maclear, 1995). Increasing pressure in the future to supplement the already stressed surface water is related to climate change, industrial development and urbanization, as well as government programmes to provide access to adequate water supply and sanitation to millions of previously disadvantaged South Africans (Hassen *et al.,* 2008). South Africa relies primarily on surface water, but in some areas groundwater constitutes the sole supply (Figure 2; Tredoux *et al*., 2004).

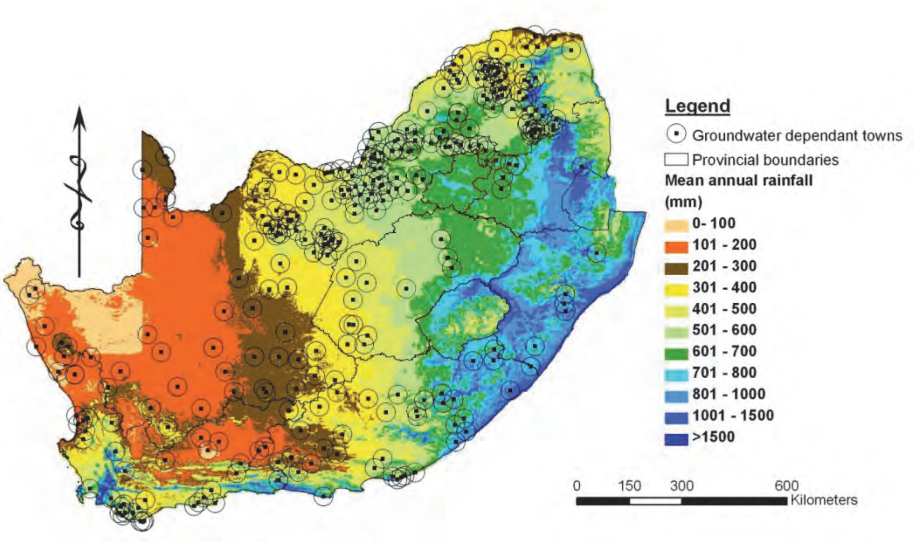


Figure 2: The mean annual rainfall in South Africa and the groundwater dependant towns (data from Middleton and Bailey, 2009; DWA, 2011)

To date, groundwater is underutilised in South Africa, contributing no more than 15% to the overall water consumption in the last two decades (DWA, 1986; Vegter, 1995; DWAF, 2002). This is because groundwater is viewed as a secondary augmentation option due to the general misunderstanding and misuse of this resource, resulting in the assumption that it is unreliable (van Vuuren, 2011). This is despite South Africa's abundance of groundwater and its relative purity in comparison to surface water, and the fact that it is easier to protect groundwater against pollution and climate change (van Vuuren, 2011). Furthermore, groundwater schemes are generally cheaper, faster and more environmentally friendly to implement in comparison with surface water schemes (van Vuuren, 2011).

It has been well established that an unreliable, restricted water supply is a limiting effect on a country's population, development and economic growth (Vegter, 1995). The importance of groundwater development has therefore been identified by the Department of Water Affair's recently published Groundwater Strategy (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 groundwater supply schemes (DWA, 2011). In addition, expenditure on potable water production and treatment costs should be kept to the minimum, to make water accessible to all (Rajagopaul *et al.,* 2008).

2.2 Iron and Manganese in Groundwater

Iron and manganese are relatively abundant elements in the Earth's crust with the geochemical ratio of 50:1 for Fe and Mn, respectively (Figure 3; ICRC, 1993). As a result, they are commonly found in most rock-forming minerals such as silicates (especially micas, pyroxenes and amphiboles), carbonates, oxides and sulphides (Appelo and Postma, 2005).

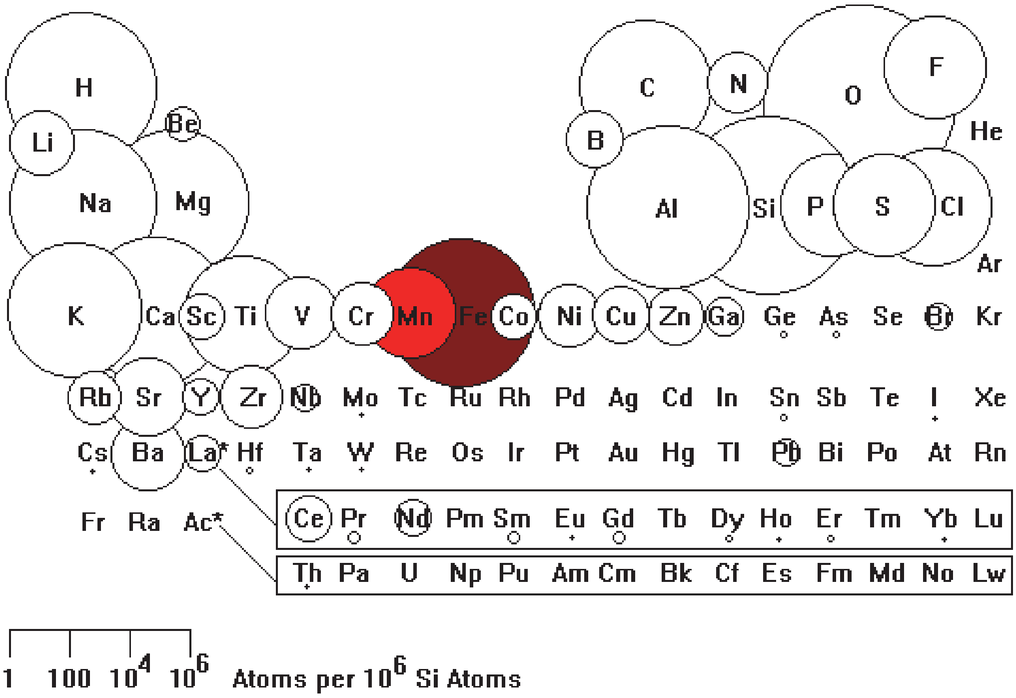


Figure 3: The relative abundances of elements making up the continental crust (Dutch, 2007)

Small amounts of Fe and Mn are incorporated into groundwater through the physical and chemical weathering of minerals at the surface and in the unsaturated zone. In the saturated zone, under reducing conditions, elevated concentrations of Fe and Mn occur in groundwater (Munter *et al*., 2005). These anoxic/anaerobic conditions occur through the removal of dissolved oxygen (DO) from groundwater due to oxidation of organic carbon compounds by abiotic and microbiological processes along the flow path (Smith and Roychoudhury, 2013). Mobilisation of Fe and Mn in groundwater is promoted by reducing conditions and low pH and generally the result of reductive dissolution processes, which can be abiotic or microbiologically mediated (Cavé *et al.,* 2004).

Iron exists in one of two oxidation states, namely the ferrous (Fe^{2+}) and ferric (Fe^{3+}) forms. The form and solubility of Fe in groundwater is strongly dependent on the pH and redox potential (pe) with the presence of sulphur and/or carbonate species also constituting controlling parameters (Figure 4). In natural anoxic/anaerobic groundwater, the Fe^{2+} ion dominates. Conditions where pH ≤ 3, often associated with contamination like acid mine drainage, favour higher Fe^{3+} concentrations (Appelo and Postma, 2005). In some cases, elevated Fe^{2+} concentrations occur within the borehole through the disintegration of steel pipework from corrosive water conditions (Driscoll, 1986; WHO, 2008).

Manganese can exist in many oxidation states ranging from Mn^{3-} to Mn^{7+}, but its occurrence in natural waters is as either the divalent (Mn^{2+}) or quadrivalent (Mn^{4+}) form (ICRC, 1993). Similarly to Fe, the pH, pe, sulphur and carbonate content influences the dominant Mn form in solution, and in anoxic/anaerobic groundwater, the Mn^{2+} ion dominates (Figure 4).

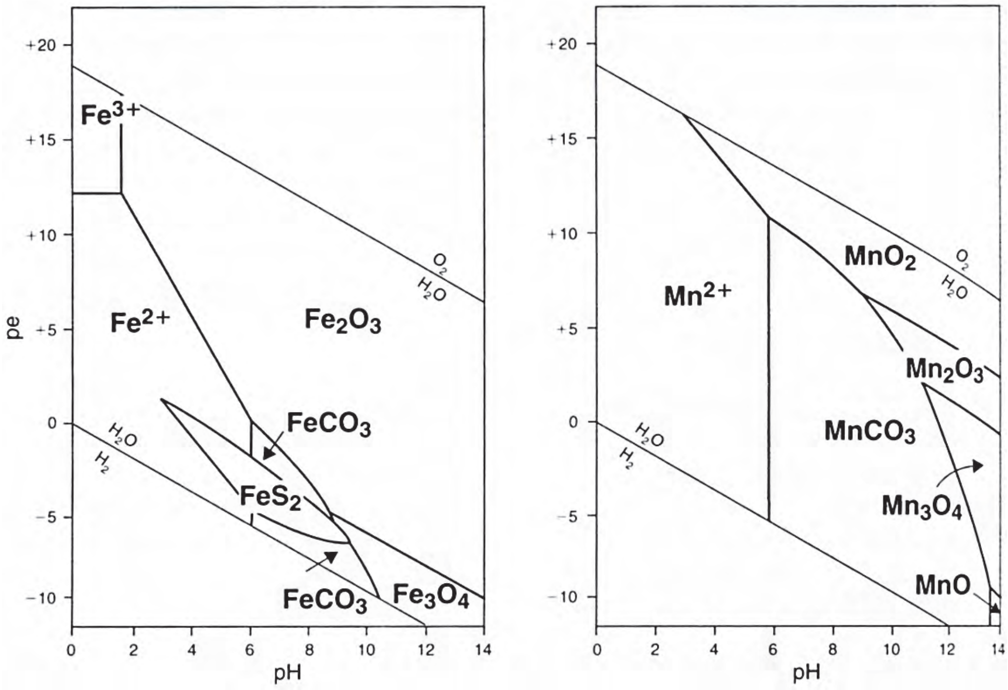


Figure 4: The pe-pH diagrams of Fe (left) and Mn (right) stability fields in natural waters at 25°C, which contains sulphur and carbonates species (Appelo and Postma, 2005)

2.3 Negative Impacts on Groundwater

Jolly (2002) has identified the three main causes that contribute to the failure of groundwater supply schemes: (1) Water quality changes which makes the water unsafe for consumption and unusable; (2) The production boreholes cannot deliver the production amount the scheme was designed for; (3) Water levels drop to such a degree that pumping becomes uneconomical. The presence of Fe^{2+} and Mn^{2+} has the potential to be a limiting factor for the sustainability of groundwater supply schemes as they can contribute to all three of the causes of failure mentioned above.

2.3.1 Water quality

The water quality issues associated with Fe and Mn mainly manifests as aesthetic and potability problems limiting its use. To circumvent these problems WHO (2008) recommends the removal of Fe and Mn to concentrations below 0.3 mg/ℓ and 0.1 mg/ℓ, respectively, before distribution. The standard water treatment approach to remove Fe and Mn from groundwater is well-understood and requires the oxidation of the soluble species by an oxidant into insoluble oxides; the precipitated oxides are then removed from solution by coagulation/flocculation, sedimentation and filtration (Mackintosh and de Villiers, 2002). Generally the oxidation is achieved through aeration, however other chemical oxidants such as chlorine gas (Cl_2) or as hypochlorous acid (HOCl), potassium permanganate ($KMnO_4$) and ozone gas (O_3) can be used, or through the employment of iron-oxidising bacteria through bio-filters (Sommerfeld, 1999; Mettler *et al.,* 2001). Local experience of this *ex-situ* treatment has been successful, but the following requirements are essential for success (Mettler *et al.,* 2001; Mackintosh and de Villiers, 2002):

- Expert input requirements for plant development and skilled operators;
- High investment costs;
- Risks working with and storage of chemicals;
- Potential overdosing or under dosing leading to further water quality problems;
- Large O&M costs for running a plant;
- Water costs involved due to high water demand required to backwash the filters;
- Proper disposal of large volumes of generated sludge.

2.3.2 Health

There are no immediate health risks of Fe in drinking water and toxic symptoms are only observed after massive intake, such as acute poisoning of young children (under the age of 4 years old) or chronic poisoning due to years of excessive intake of Fe on a daily basis of quantities between 40-70 mg/ℓ, but these situation are rare (DWAF, 1996; Mettler, 2002; WHO, 2008).

Manganese toxicity is more controversial due to the potential neurological damage caused (Mettler, 2002; WHO, 2008). Generally, the greatest exposure of Mn is in food, but adverse neurological damage have been found as a result of extended exposure to very high levels of Mn in drinking water sourced from groundwater (WHO, 2008). The health-based guideline recommended for Mn is 0.4 mg/ℓ by the WHO (2008), which can potentially make the groundwater unsuitable as a drinking water resource if not treated before distribution.

The South African drinking water authorities have adhere to the aesthetic risk thresholds Fe ≤ 0.3 mg/ℓ and Mn ≤ 0.1 mg/ℓ and Fe ≤ 2 mg/ℓ and Mn ≤ 0.5 mg/ℓ as chronic health risk limits in potable water (SANS, 2011). Indirect impacts on health can also occur through the *ex-situ* treatment or through the clogged production boreholes which includes:

- Lack of water due to failed borehole could promote the spread of disease in users, particularly in rural areas, which are forced to use inferior or contaminated surface water;
- Chemicals used in water treatment and rehabilitation treatments such as Cl_2 could form carcinogenic trihalomethanes by-products;
- Microbial contamination of the water due to the biofilm development in the subsurface or the use of above-ground filters could contaminate the water and require further disinfectant treatment.

2.3.3 Water supply

Clogging of production boreholes is a worldwide phenomenon that manifests itself in South African groundwater supply schemes, such as the Atlantis Water Resource Management Scheme (AWRMS; More Water, 2001), the Preekstoel WTP (Kgwaila *et al*., 2011) and the Klein Karoo Rural Water Supply Scheme (KKRWSS; Smith, 2004). Other occurrences of problematic iron-rich groundwater are found in the Malmesbury Group rocks in the Western Cape, the Natal Group sandstones in Kwazulu-Natal and alluvium deposits in the Eastern Cape (Tredoux *et al.,* 2004). It is one of the major limiting factors in groundwater supply as it threatens the sustainability of the groundwater supply schemes listed above and is also a concern for proposed wellfield developments such as the aquifers of the TMG and primary Cape Flats Aquifer (Jolly, 2002; Flower and Bishop, 2003; Cavé *et al.,* 2004). Extensive research into clogging of production borehole and monitoring, management and rehabilitation options has been done, because these problems are also prevalent in the mining, agricultural and domestic sectors that are important role-players in the South African economy (Figure 5).

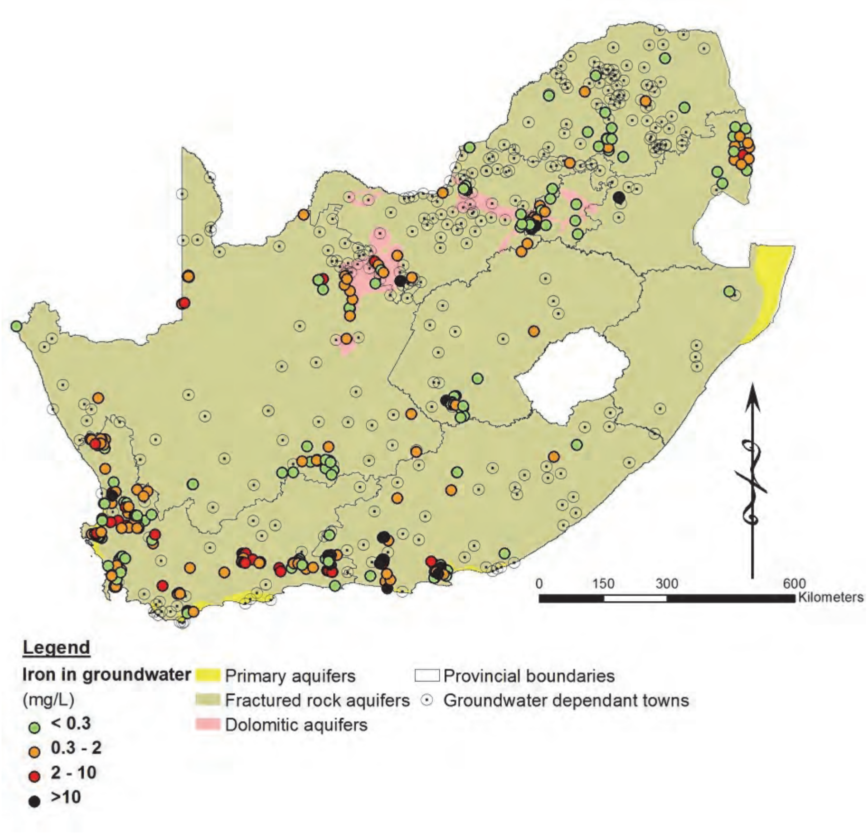


Figure 5: Distribution of South Africa's principal aquifer types and iron concentrations, which can potentially be problematic to water supply in groundwater-reliant towns (data from Middleton and Bailey, 2009; DWA, 2011)

Production borehole clogging occurs through the oxidation of Fe^{2+} and Mn^{2+} at the interface between the borehole and aquifer through physio-chemical and microbiological processes working separately or in combination (Tredoux *et al.,* 2002). Incorrect pumping operations causing high drawdowns are often identified as the main contributor to initiating chemical clogging (Jolly and Engelbrecht, 2002).In addition, the high drawdowns also provide turbulent flow conditions and nutrients promote bacteria growth and iron-related bacteria incorporate the oxidation of Fe as an energy source (Cullimore, 2008). The source of bacteria is not easily constrained; as the bacteria could be already present before the borehole was drilled and then multiply due to the localised continuous food source provided through pumping. Alternatively, it could have been introduced from surface water or drilling mud and/or contamination by drilling operations, even from drilling equipment another site (Driscoll, 1986; Flower and Bishop, 2003).

Over time, the build-up of iron (III) and manganese (IV) oxides and biofilm reduce the production capacity of the borehole and the effective permeability of the aquifer in close proximity (Tredoux *et al.,* 2004). The reduction in permeability and clogging of the borehole screen causes less water to be abstracted and further lowers the water level in the borehole, which increases the cost of production and, in South Africa this is often incorrectly regarded as the borehole drying up (Jolly and Engelbrecht, 2002). In extreme cases, the development of the biofilm has resulted in the corrosion and disintegration of the production borehole which requires replacement (Cullimore, 2008). This has been experienced in Botswana where iron- and sulphate-oxidising bacteria have caused such significant clogging and corrosion that the production boreholes required the replacement of pumping equipment almost annually (Riekel and Hinze, 2002). These high costs and economic losses, which may be incurred as a result of interrupted services, may make the groundwater resource uneconomical and result in general “failure” of the wellfield (Driscoll, 1986; Jolly, 2002; Cavé *et al.,* 2004).

In South Africa the options implemented to deal with clogging of production boreholes include:

- Rehabilitation of production boreholes;
- Improved management of wellfield operation;
- Abandon the production borehole and re-drill at a new or nearby site.

The rehabilitation treatments aim to restore the original yields by removal of the precipitates and biofilms by physical, chemical or electrochemical methods (Smith and Roychoudhury, 2013). In South Africa, chemical treatments such as chemical soaking, whereby citric acid or hydrochloric acid is introduced into the borehole, were attempted initially, but the success of the treatments is short-lived and limited to the production borehole only (DWA, 2010). Rehabilitation with other combination methods such as BCHT has been done at the TMG aquifer wellfield of the KKRWSS (Smith, 2004) and the wellfields of the AWRMS (More Water, 2001) but is a costly exercise and could be an annual operation (Smith and Roychoudhury, 2013). Other rehabilitation treatments such as Electrochemically Activated Water have also been investigated in the KKRWSS (Smith, 2004) but no further investigation followed. The limitations on rehabilitation treatments in South Africa include:

- Monitoring protocol of production borehole performance and water quality is inadequate for early detection of clogging and, once clogging of the production borehole has been identified, it is often too late and extremely difficult to treat and rectify the problem efficiently;

- The borehole construction and materials were often incorrect, due to the lack of knowledge of this problem when the wellfield was developed, resulting in poor recovery of yields;
- Regular cleaning is not implemented due to skills, costs and regulations according to NEMA and NWA.

The monitoring and management protocols to identify borehole production losses include:

- Continuous lower rates of abstraction.
- Regular monitoring of water quality and abstraction rates, with sporadic step drawdown tests to establish specific capacity (Sc) of the boreholes, including down-hole camera logging to confirm clogging.
- Regular cleaning of the production boreholes.

However, this can be unreliable and not properly or rigorously implemented and, in cases such as the KKRWSS, where lower rate abstraction regimes have met with little success in managing the clogging processes as it occurs naturally in the borehole due to mixing of different waters qualities as a result of different aquifers that were intersected (Cavé and Smith, 2004). Smith and Roychoudhury (2013) researched the likelihood of a borehole to have iron-related clogging in the aquifers of the TMG through evaluating the controls aquifer lithology and groundwater conditions (i.e. pe, pH and organic acids) had on the mobilisation of Fe^{2+} and presence in the abstracted groundwater. Their experimental research found that the arenaceous Peninsula and Skurweberg Formations had the potential to release the greatest amount of Fe either under anoxic conditions (independent of pH) or oxic conditions with low pH. It is thus concluded by the authors that the prediction of the likelihood of a borehole in the KKRWSS being affected by iron-related clogging requires knowledge of the redox conditions in the aquifer and the source of lithology of the aquifer. The aforementioned studies allows for the decision makers to consider not drilling into such high risk Fe and Mn formations or casing off those sections of the aquifer to prevent the interaction of different water types to limit the potential for clogging. The abandonment of a production borehole is considered when rehabilitation is unsuccessful or when the cost of rehabilitation with expected low recovery is outweighed by the cost of drilling and infrastructure of a new borehole. However, this does not deal with the problem and with time, if not correctly designed and managed, the problem will recur.

2.4 *In-situ* Iron Removal

The subsurface removal of Fe from groundwater dates back to 1900, however, little experimental work was done until 1971 when the Vyredox design was developed in Finland (van Halem *et al.,* 2011). Two decades after the first commercial Vyredox plant was implemented, more than 100 ISIR plants were built in a number of European countries including Sweden, the Netherlands, Switzerland, Germany, Denmark and France (Braester and Martinell, 1988; van Halem, 2011; Ebermann *et al.,* 2013).

In-situ iron removal involves the oxidation of Fe^{2+} and Mn^{2+} from the groundwater and precipitates of the respective oxides remains in the aquifer (Sommerfeld, 1999). This is achieved by the periodic injection of a volume of oxygenated water via the injection well-points or a modified production borehole into the anoxic/anaerobic aquifer, followed by abstraction of the injected water with groundwater in which the Fe and Mn concentrations are lower than in the native groundwater (Appelo and de Vet, 2003). Although ISIR has been applied over the same time period as conventional processes, it has still not found widespread acceptance due to concerns that the application itself may clog the aquifer and causing the accumulation of heavy metals in the subsurface (van der Laan, 2008; van Halem, 2011).

The treatment was developed for semi-consolidated and unconsolidated, gravel-sand aquifers and has been applied successfully in both glacial (e.g. Hallberg and Martinell, 1976; Hinkamp *et al.*, 2004; Diliūnas *et al.*, 2006) and alluvial-deposits (e.g. Braester and Martinell, 1988; Olsthoorn, 2000; Mettler *et al.*, 2001). Only one case study in a fractured aquifer has been found in China (Maogong, 1988). There are several different ISIR designs and the four main approaches are:

- The Vyredox method, consisting of multiple injection wells (e.g. from 3 to 23) surrounding the production borehole in a "daisy-wheel" setup, providing an oxidation screen for the borehole (Hallberg and Martinell, 1976; Braester and Martinell, 1988);
- The two-production borehole method, involving two production boreholes where one produces the recharge water for the other one that is being treated (Sommerfeld, 1999; Figure 6);
- The single-borehole method, which is applied typically in the Netherlands, where a production borehole is modified for alternative injection and production (van Halem, 2011; Figure 6);
- A combination of the Vyredox method with the modified production borehole approach (Maogong, 1988).

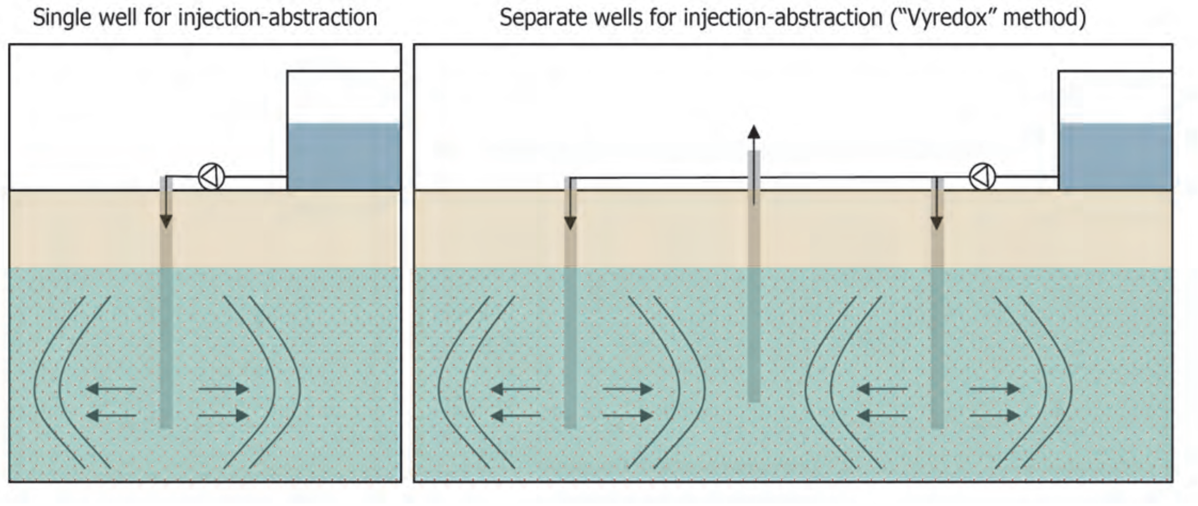


Figure 6: The two most commonly applied ISIR designs in Europe (van Halem *et al.*, 2008)

2.4.1 *In-situ* iron removal principle

The principles of ISIR are based on similar oxidation-adsorption principles as above-ground sand filtration (van Halem, 2011). In the case of a single-borehole approach, a volume of oxygenated water is introduced into an anoxic/anaerobic aquifer, displacing the groundwater containing Fe^{2+} some distance from the injection borehole (Figure 7). Homogenous oxidation of the Fe^{2+} takes place through physical dispersion at the interface of the two waters (Appelo and de Vet, 2003) and the DO in the injected water creates an oxidation zone around the injection borehole. Oxidation of Fe^{2+} in that zone takes place through heterogeneous oxidation of the adsorbed Fe^{2+} on the sorption sites directly on the grains (Mettler, 2002) or through homogenous oxidation where adsorbed Fe^{2+} is displaced from the exchange and sorption sites with cations in the injected water and subsequent oxidation by the DO (Appelo *et al.,* 1999). Through these processes, the DO front lags behind the injected water front (Figure 8; Appelo de Vet, 2003). The newly-formed precipitate forms a film on the sand grains (known as “armouring”) which increases the oxidation zone’s ability to adsorb more Fe^{2+} due to increased surface area and strengthens the adsorption capacity (Appelo and Postma, 2005).

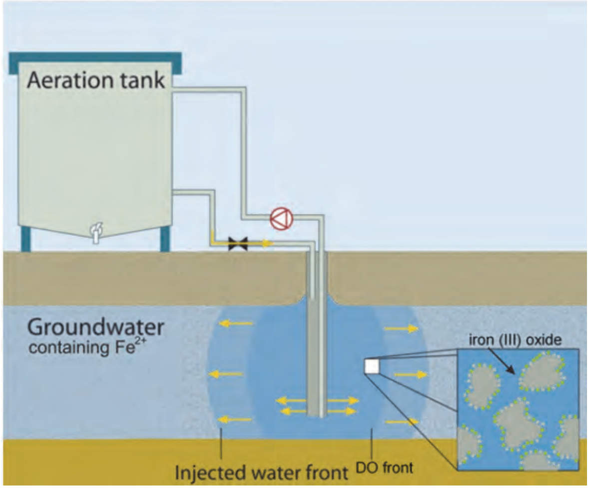


Figure 7: Injection phase of ISIR treatment, where an oxidation zone is created around the injection borehole (van Halem *et al*., 2008)

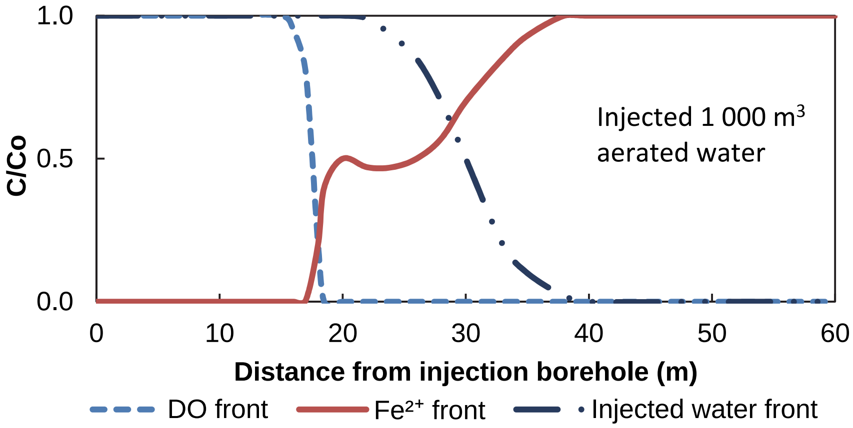


Figure 8: The concentration profiles of Fe^{2+}, DO and injected water fronts during the injection phase, where the DO front lags behind due to Fe^{2+} oxidation (data from Appelo and de Vet, 2003)

When pumping is resumed, the groundwater is naturally filtered through the oxidation zone (Figure 9). At first the injected water is withdrawn with negligible Fe concentration, then for some time the groundwater can be pumped with a lower Fe concentration compared to the raw groundwater (Figure 10; Appelo and de Vet, 2003). This is because the Fe^{2+} is adsorbed on the newly-formed exchange sites on the iron (III) oxides and depleted exchange sites on the sand grains, before reaching the production borehole (Appelo and de Vet, 2003). After some time, the adsorption capacity of the aquifer will be exhausted in the oxidation zone and higher Fe concentrations will break through into the abstracted water (Figure 10; 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). The volume of water to be injected is dependent on the location, but in the European case studies range between 1 000 m^3 to 3 000 m^3 (Hinkamp *et al.,* 2004).

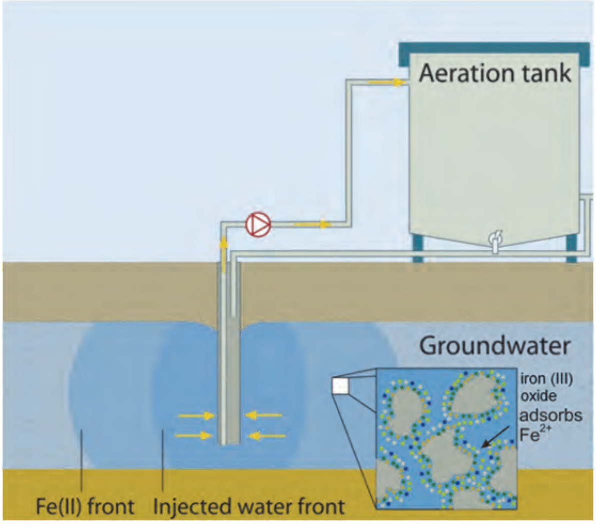


Figure 9: Abstraction phase of ISIR, where Fe^{2+} adsorption allows for lowered Fe concentrations in the abstracted water (van Halem *et al*., 2008)

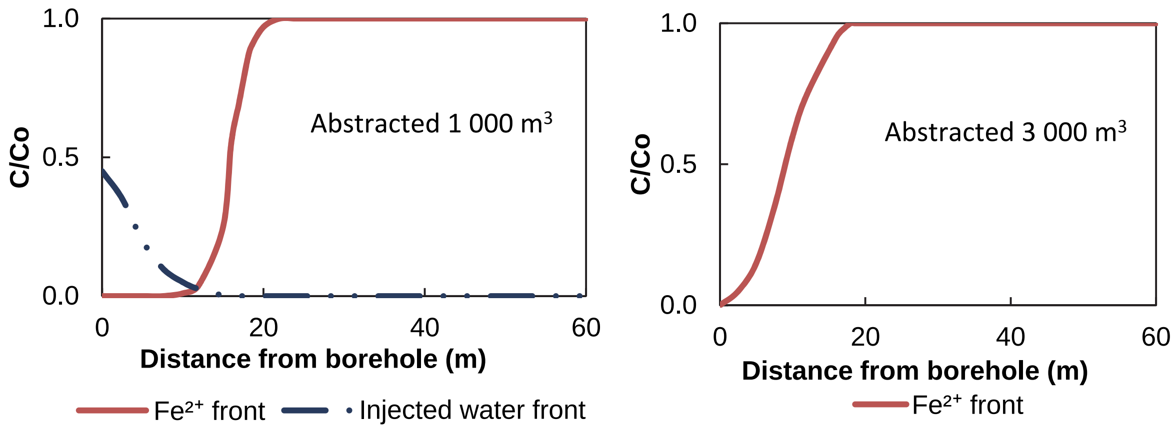


Figure 10: The Fe^{2+} font after abstracting the injected volume (left) and a further 3 000 m^3 (right) until Fe^{2+} breakthrough in the abstracted water (data from Appelo and de Vet, 2003)

2.4.2 Removal efficiency

An advantage of this treatment is that Fe removal continues even after complete abstraction of the injected water, as gauged by the volumetric ratio of the abstracted water (V) over the injected volume (Vi), known as the removal efficiency (V/Vi; Appelo *et al.,* 1999). The removal efficiency of the ISIR plants range from V/Vi = 3-22, depending on the site characteristics (Mettler, 2002; Hinkamp *et al.,* 2004). Another observed benefit is that removal efficiency of Fe increases with successive injection-abstraction cycles (Hallberg and Martinell, 1976; Braester and Martinell, 1988; Appelo *et al*., 1999). Figure 11 and Figure 12 shows two case studies in the Netherlands showing the delay in the arrival of high Fe concentrations with successive treatments and the improved removal efficiencies of Fe as a result. In some cases, the Mn concentration is often much more than that of Fe as seen in clay-rich aquifer in Egypt (e.g. Olsthoorn, 2000; Karakish, 2005) and since Mn is chemically similar to Fe, its co-removal takes place with ISIR treatment. However, the removal efficiency for Mn is less than that of Fe, generally ranges between V/Vi = 4-12 (Figure 13), due to the abiotic oxidation of Mn that takes place a lot slower rate than that of Fe (van Halem, 2011).

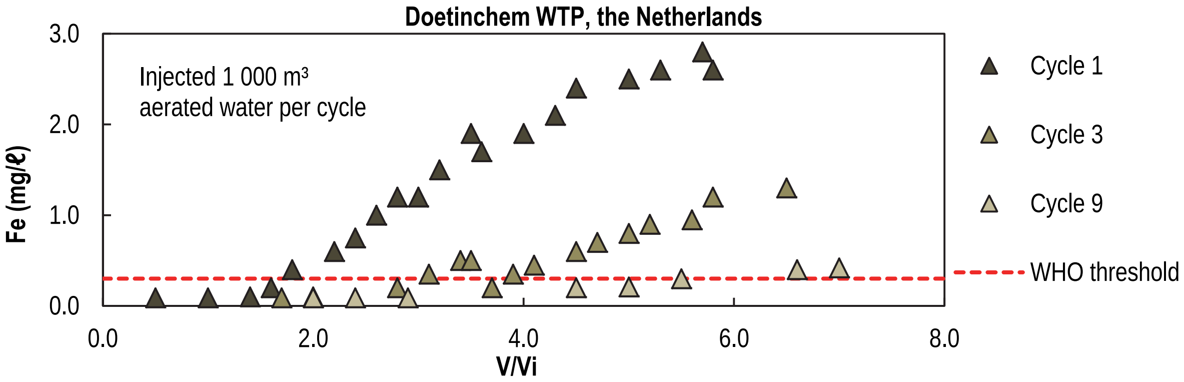


Figure 11: Iron breakthrough curves at the Doetinchem Water Treatment Plant (WTP), in the Netherlands, where 1 000 m^3 aerated water is injected for each cycle and shows that iron removal efficiency increases with successive ISIR treatments (data from Appelo *et al.,* 1999)

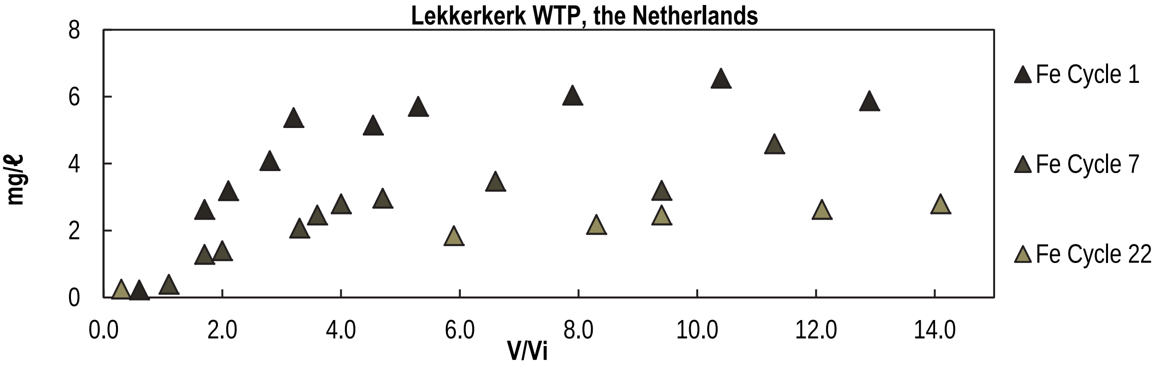


Figure 12: Iron breakthrough curves from the Lekkerkerk WTP, the Netherlands, also showing that with successive ISIR treatments removal efficiency increases (data from van Halem, 2011)

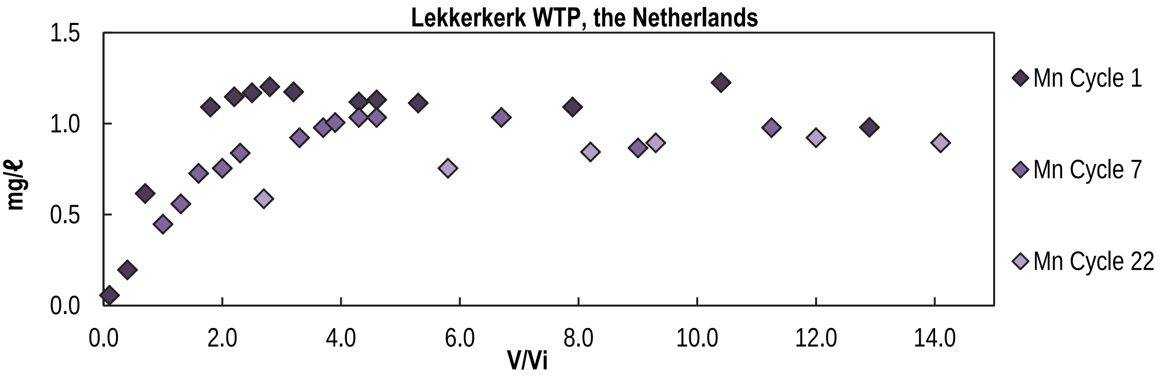


Figure 13: Manganese breakthrough curves from the Lekkerkerk WTP, the Netherlands, the breakthrough curves also show a decline with successive treatments and increased removal efficiency but to a lesser extent and are not as distinctive as for Fe curves, illustrated above (data from van Halem, 2011)

2.4.3 Advantages

In-situ iron removal is a viable treatment for water quality improvements through removal of Fe and Mn from the groundwater and subsequent reduction of the above-ground treatment needs (Appelo *et al.,* 1999). In the Netherlands, case studies have shown that the ISIR enhances the nitrification process in subsequent biosands filters (Tredoux *et al.,* 2004) and purification capacity of the rapid sand filtration beds, thus reducing backwashing required and sludge production (Hinkamp *et al.,* 2004). Modifications of the treatment can also be used for subsurface de-nitrification and hydrocarbon pollution (e.g. Radčenko and Hauskrecht, 1982; Braester and Martinell, 1988).

Apart from Fe and Mn removal, this treatment has a number of beneficial side-effects which include the adsorption of arsenic (As), phosphate (PO_4), selenium and chromium (Vance, 1994; Appelo and de Vet, 2003; van Halem, 2011). From studies in the Lekkerkerk WTP, PO_4 removal is correlated with Fe and Mn removal and removal efficiency of PO_4 increases with ISIR successive cycles, while As does not show such a clear trend, but removal efficiency of As is seen with successive cycles (van Halem, 2011). Regardless of As not having the same removal efficiency success as Fe, ISIR is still presently being investigated in rural areas of Bangladesh for co-removal of As (van Halem, 2011). In addition, the microbiological quality of the abstracted groundwater has not been found to be negatively affected by the treatment (van Halem, 2011).

The main concern of ISIR is the potential clogging of the aquifer and boreholes. However, clogging of the aquifer due to iron (III) oxide build-up has not been reported in literature as a limitation of 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). This is supported with recent investigations into the iron precipitates from plants over a decade of operation that have been characterized as compact, crystalline ferric oxides (often as goethite), suggesting that with time the amorphous precipitates have mineralised to more stable oxides (Mettler *et al.,* 2001; van Halem *et al.,* 2011). The iron (III) oxides and other constituents (e.g. Mn and As ions) were found to accumulate in the aquifer 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, the lack of clogging of the production boreholes is ascribed to the Fe^{2+} oxidation taking place at various distances from the injection well, which results in a spreading of the precipitates throughout the aquifer. The redox gradient is manipulated by changing the configuration of the injection boreholes or altering injection-abstraction volumes or rates (Braester and Martinell, 1988; Appelo *et al.,* 1999; Tredoux *et al.,* 2004). In comparison to borehole clogging during pumping, the oxidation process moves the precipitation of iron (III) oxides into a much larger surface area in the aquifer, rather than concentrating at the borehole screen (Braester and Martinell, 1988). This treatment limits the potential for clogging of production boreholes as it recues the amount of Fe^{2+} and Mn^{2+} drawn towards the production borehole during abstraction and, as a result less borehole rehabilitation is required to maintain the longevity of the production borehole (van Halem *et al.,* 2011).

The precipitation of iron (III) oxides in the subsurface is a very important step in the long-term prevention of high concentrations of Fe^{2+} accumulating in groundwater, even when treatment is stopped and reducing conditions return. This is because the newly formed amorphous hydroxide remains in the aquifer matrix and mineralised with time to predominately mineralised iron (III) oxide, goethite (Mettler *et al*., 2001). Amorphous ferric hydroxides in neutral pH and oxidising conditions have a solubility three orders of magnitude greater than goethite (Vance, 1994). As the crystallinity of ferric oxides increase, the microbiological availability and abiotic ability, even in the presence of highly reactive organic carbon, limits the potential for iron reduction (Vance, 1994; Appelo and Postma, 2005). Through the progressive oxidation and stabilisation of Fe in the aquifer into more thermodynamically stable minerals, there is less potential for reductive dissolution of Fe, and in some cases, As-hosting deposits (van Halem, 2011), which will negatively impact water supply and usage along with the health of communities.

2.4.4 Disadvantages and conditions for *in-situ* iron removal

The application of ISIR is only viable under particular hydrogeological and geochemical conditions (Ward and Less, 1990) and the success and removal efficiency of ISIR is dependent on:

- The oxidant concentrations in the injected water, which results in control on oxidation processes for Fe removal; and
- The local conditions, i.e. pH and the adsorption capacity of the aquifer, which result in control on adsorption processes for Fe removal.

In addition, the chemical composition of the precipitated Fe and Mn (and resultant mineralised oxide) is dependent on the water quality, temperature, and pH within the aquifer (EPA, 1999; Appelo and de Vet, 2003).

The injected water is oxygenated, either by aeration or dosed with pure oxygen gas, and the DO concentrations in the injected water can rise up to 10 mg/ℓ from aeration or 18-30 mg/ℓ to as much as 50 mg/ℓ from pure oxygen gas (Hinkamp *et al.,* 2004; Ebermann *et al.,* 2013). While pure oxygen gas induces high DO concentrations, and increases removal efficiency of Fe (Figure 14; Appelo *et al.,* 1999; Hinkamp *et al.,* 2004; van Halem, 2011), aeration is generally used, as it reduces costs and is safer to use (Diliūnas *et al.,* 2006).

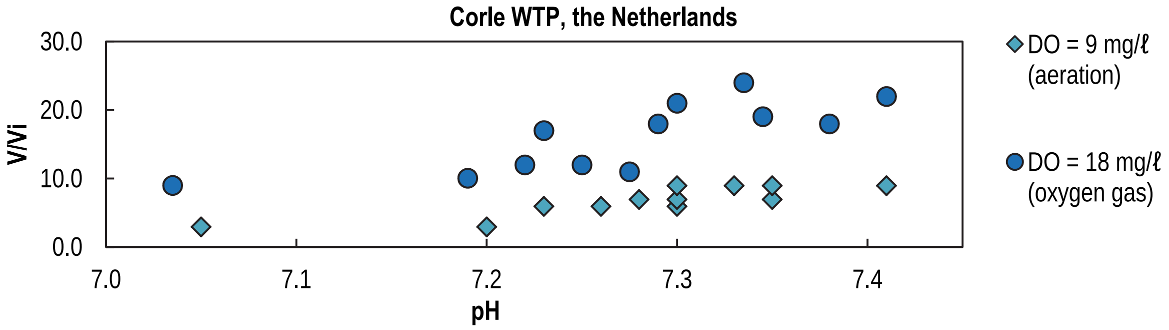


Figure 14: All twelve ISIR-treated boreholes at the Corle WTP, the Netherlands, showed an increase in iron removal efficiency (V/Vi) with increased pH and DO (data from van Halem, 2011)

The groundwater pH is a very important parameter for ISIR, as it influences treatment during both the injection and abstraction phase by controlling both the oxidation and adsorption processes. During the injection phase, the rate of Fe^{2+} oxidation by oxygen is pH dependent (Equation 1), and rapidly decreases at low pH conditions (pH < 5). Consequently, ISIR should only be applied in conditions where pH is above 6 (Appelo *et al.,* 1999) and ideally above 7 for the oxidation process to take place at a reasonably rapid rate (i.e. within 30 minutes) (Figure 15; Cavé *et al.,* 2004). Field observations of these trends are given in Figure 16. A pH < 7 is also optimal for the oxidation of Mn (Mackintosh and de Villiers, 2002). During the abstraction phase, the adsorption ability on the surfaces of newly-formed ferric hydroxides is primarily related to pH conditions, favouring near neutral pH conditions (i.e. pH 5-8), whereby pH = 8 is ideal (Vance, 1994; Appelo *et al.,* 1999).

Equation 1: $-d\,[Fe^{2+}]/dt = k.[Fe^{2+}]\,[OH^{-}]^{2}.pO_2$

Where $k = 8 \times 10^{13}\ min^{-1}atm^{-1}$ at 20°C (Appelo and Postma, 2005)

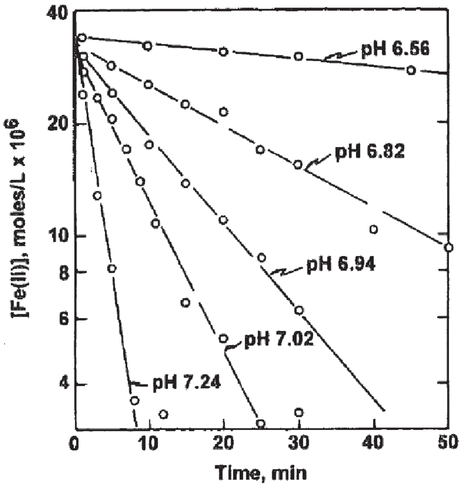


Figure 15: Rates of Fe^{2+} oxidation in contact with atmospheric oxygen is strongly influenced by pH (van der Laan, 2008)

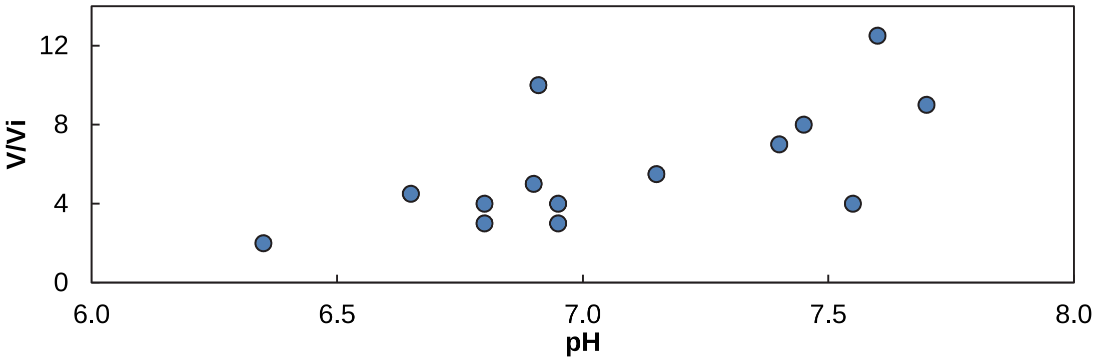


Figure 16: The V/Vi of Fe increased fourfold when the pH increased from pH = 6 to pH = 7.5 (data from van Halem, 2011)

The adsorption capacity of the aquifer sediments is dependent on the type of iron (III) oxides in the subsurface, which in turn increases with the presence of more amorphous ferric hydroxides due to the larger surface area of more mineralized goethite. Thus repeated cycles of injection-abstraction should be performed to build up the amorphous ferric hydroxide content in the aquifer (Appelo *et al.,* 1999). The section of aquifer injected should be as homogenous as possible, and without extremely coarse layers to prevent preferential flow of the injected water through the most permeable parts, which generally has a low exchange capacity (Appelo *et al.,* 1999). The adsorption capacity of the aquifer is dependent on the type of ferric oxide present in the aquifer, where amorphous ferric oxides are larger in size and therefore have more surface area than more crystalline iron(III) oxides like goethite (van Halem, 2011).

Water temperature is also important as saturation of the injected water by oxygen is a function of temperature. It should not be greater than 20°C to achieve ≥ 10 mg/ℓ at 1 bar (Figure 17), but also be > 5°C for the Fe oxidation reactions rate to not be slowed down (Sommerfeld, 1999).

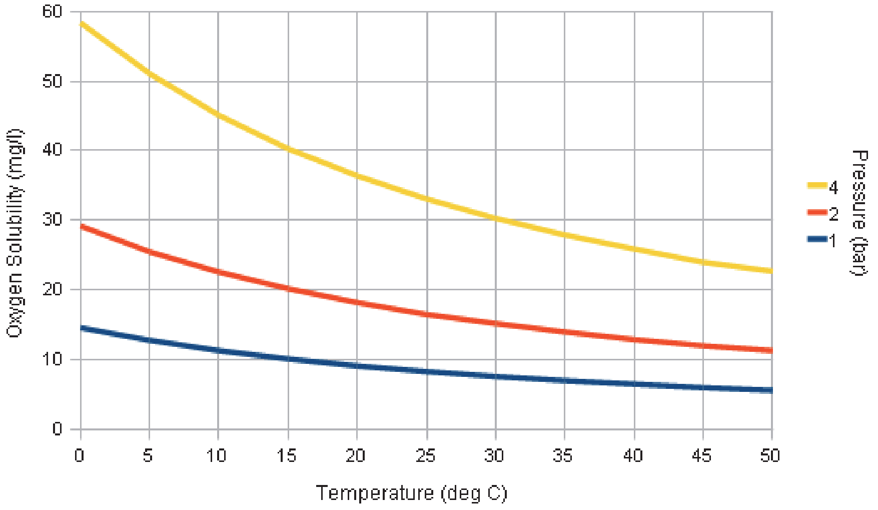


Figure 17: Solubility of oxygen in fresh water as a function temperature and pressure (www.EngineeringToolBox.com/oxygen-solubility-water-d_841.html, Accessed 3 September 2012)

The presence of dissolved organic carbon (DOC) is common in reduced groundwater, which interferes with Fe oxidation, as they form ligands with the Fe^{2+}, and can prevent oxidation, which results in the need to modify the treatment by higher oxygen concentrations or longer contact time or using a stronger oxidant (such as Cl_2, O_3 or $KMnO_4$) (Mettler, 2002). In addition, another major oxygen consumer in the subsurface is ammonia (NH_4) (Ebermann *et al.,* 2013) and ISIR is not recommended in strongly reduced groundwater with high NH_4 (Mettler, 2002).

The aquifer should not contain any sulphides, such as hydrogen sulphide (H_2S) or pyrite, as the oxidation acidifies the system which could significantly reduce the oxidation rate of Fe^{2+} if drops below pH = 6 (Appelo *et al.,* 1999). In addition problems may occur if the pyrite is As-bearing and oxidation could result in increased concentrations of As (van Halem, 2011). Although pyrite and DOC are concerns, Appelo *et al.* (1999) suggested that the known rate equations of those two reductants with oxygen are much slower and oxygen injected in the aquifer would preferentially consume the Fe^{2+}.Other dissolved inorganic compounds in the groundwater which can affect the rate of oxidation of Fe include $PO_{4,}$ silica (SiO_2), and sulphate (SO_4) (van Halem, 2011). However, their effect is believed to be negligible at the natural environmental concentrations (Mettler, 2002). Groundwater with lower total alkalinity also has an effect on the removal efficiency of the ISIR. Alkalinity acts as a pH buffer to maintain the pH during the acidifying Fe^{2+} and Mn^{2+} oxidation during the ISIR, but this may cause increases in calcium (Ca) and magnesium (Mg) in the groundwater (Sommerfeld, 1999; Mettler, 2002; van Halem, 2011).

2.4.5 Case studies

The ISIR treatment has been applied worldwide. It has been applied routinely in a number of European countries, especially in the Netherlands, where its two major water suppliers, Vitens and Oasen, have a number of ISIR plants in operation at their WTPs (Hinkamp *et al.,* 2004; van Halem, 2011). A summary of a number of ISIR plants in various configurations in Europe is given in Table 1. Other international case studies of the application of ISIR is given for China, where the ISIR application is used as pre-treatment of the groundwater before *ex-situ* treatment to meet the Chinese drinking water standards (Table 2; Maogong, 1988).

Table 1: Summary of ISIR case studies in Europe

Location **Reference**	**Saxony, Germany** Ebermann *et al.* (2013)	**Lithuania** Diliūnas *et al.* (2006)	**Oasen's Schuwacht WTP, the Netherlands** van der Laan (2008)	**Vitens' Corle WTP, the Netherlands** Hinkamp *et al.* (2004) and van Halem (2011)
Aquifer type	Fine- to medium-grained sands	Intertill and alluvial sands	Coarse-grained sands	Glacial deposit
ISIR method Oxidant used	Two-production boreholes method using oxygen gas (DO = 15-25 mg/ℓ)	Single-borehole method using aeration and magnetic conditioning (DO = 3-11 mg/ℓ)	Single-borehole method using aeration (DO = 8 mg/ℓ)	Single-borehole method using oxygen gas (DO = 8-30 mg/ℓ)
Injection information	Injection time = 250 hr Injection rate = 1.2 m^3/hr	Injection time = 48-120 hr Injection rate = 2-9 m^3/hr	Injection time = 48 hr Injection rate = 30 m^3/hr	Injection time = 25-36 hr Injection rate = 55-80 m^3/hr
V/Vi	2 (after 3 cycles) 4 (after a month of treatment)	Between 2-7 at Fe < 0.2 mg/ℓ	Not calculated as not used specifically for ISIR	Between 3-8 with DO = 8-9 mg/ℓ Between 5-15 with DO = 18 mg/ℓ Between 7-19 with DO = 30 mg/ℓ
Water quality before	Fe^{2+} = 9.8 mg/ℓ; pH = 6.9	Fe^{2+} = 0.1-1 mg/ℓ; pH = 6.8-7.5	Fe^{2+} = 6.5 mg/ℓ in 1998; pH = 7.1	Viten operates ISIR based on the V/V_i where Fe < 0.1 mg/ℓ. The V/V_i ratio is determined for a borehole and then operated for years before V/Vi is retested, unless the Fe > 0.1 mg/ℓ
Water quality after	Fe^{2+} < 0.5 mg/ℓ	Fe reduced 87% after 10 cycles	Fe^{2+} = 3.5 mg/ℓ in 2000	
Other information		Magnetically conditioning of water improved V/Vi almost double compared to purely aeration	Oasen has 3 *in-situ* plants for nitrification improvement in bio-filters and the retention of Fe, As, PO_4 are side effects	The rapid sand filters efficiency increased more than double through the tripled in DO concentration in the ISIR treatment

Table 2: Summary of three ISIR case studies in China (Maogong, 1988)

	Panshi WTP	**Yitong WTP**	**Daqing Oil Field WTP**
Aquifer type	Gravelly, medium- to coarse-grained sands	Gravelly, medium- to coarse-grained sands	Sandstone
ISIR method	Combination: aerated water introduced through the production borehole and surrounding injection well-points	Vyredox: injection of aerated water through three injection well-points	Single-borehole: aerated water injected through the production borehole
Injection information	Injection time = 12 hr Injection rate = 30-36 m^3/hr	Injection time = 3 hr Injection rate = 73 m^3/hr	Injection time = 28-51 hr Injection rate = 40-50 m^3/hr
V/Vi	4	9	8
Water quality before ISIR	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+} = 2.7 mg/ℓ Mn^{2+} = 0.4 mg/ℓ pH = 7.3
Water 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

2.4.6 Potential in South Africa

To date, ISIR has only been considered in South Africa because of the following reasons:

- Infancy of large-scale groundwater development in South Africa;
- Lack of funding and production borehole clogging is not an immediate threat to the water resource, as opposed to, e.g. research into acid mine drainage;
- Economic effects of iron-related problems were only recognised in the last two decades;
- Other options have been investigated such as wellfield management and rehabilitation treatments.

Since rehabilitation and management programmes have not achieved the long-term results in South Africa, the investigation of other technologies to complement these protocols should be explored with the aim to achieve maximum technical and operational simplicity, along with economic effectiveness (Radčenko and Hauskrecht, 1982). The experience abroad and in Africa (e.g. Egypt) has shown that ISIR is an effective and sustainable Fe and Mn removal technique and has great potential for South African application, as it:

- Is a fast, and simple, cost-effective approach to dealing with iron-related problems in groundwater supply schemes;
- Reduces the above-ground treatment, which are costly, and include the generation of sludge, electricity and water usage and improves production borehole longevity;
- Can be applied on both small- and large-scales, and can be designed to be mobile.

3 INVESTIGATION OF *IN-SITU* IRON REMOVAL IN SOUTH AFRICA

In the aim to investigate the feasibility of ISIR in a South African context, two study sites were suggested: the Witzand Wellfield of the AWRMS, 8 km south-west of Atlantis, and the Calitzdorp Wellfield of the KKRWSS near Calitzdorp. Both groundwater schemes are the main contributors to their respective municipal water supplies, but whereas; the AWRMS exploits groundwater from the Cenozoic-age primary Atlantis Aquifer, the KKRWSS abstracts from the secondary, fractured aquifers of the Palaeozoic TMG. These two wellfields were selected, because both experience semi-arid conditions and have no nearby surface water supplies, and groundwater provides security of water supply to the towns, which are therefore reliant on the sustainability of this resource (Pietersen and Parsons, 2002; DWA, 2010).

The long-term sustainability of the two wellfields is threatened by poor performance of nearly all of their production boreholes as a result of clogging from Fe and Mn in the groundwater (Mackintosh and de Villiers, 2002; Tredoux *et al.,* 2002; Flower and Bishop, 2003; Cavé and Smith, 2004). For example, in 2000, the production at the Calitzdorp Wellfield declined by 77% from its total yield in 1987 and all the production boreholes pumping rates are currently no higher than 20% of their original magnitude (Smith and Roychoudhury, 2013). From 1976 to 1999 the AWRMS reliably supplied the bulk water demand of Atlantis, but due to the recurring clogging of production boreholes, the wellfield presently produce only 30-40% of the town’s needs (DWA, 2011).

Both selected study sites have had extensive research into the production borehole clogging problems and most of their production boreholes were then rehabilitated with the BCHT. However, the management and rehabilitation protocols have not given the long-term desired results, hence the demand for the investigation of other options such as preventative ISIR, which is the topic of this study.

3.1 Preliminary Investigation at the Calitzdorp Wellfield

The feasibility of applying the ISIR method in a fractured aquifer was initially considered in this study. However, there is a lack of literature on its application in such a setting, with only one example given in China (Maogong, 1988), probably because the majority of wellfields developed abroad and in Africa that experience clogging problems are located in anoxic/anaerobic primary aquifers (Mettler *et al.,* 2001; Riekel and Hinze, 2002; Karakish, 2005; Smith and Roychoudhury, 2013). Furthermore, the knowledge and techniques for remediation of fractured systems has only taken off in the last two decades with focus mainly on high health-risk contaminates, such as hydrocarbons (Kinner *et al.,* 2005). Other challenges to overcome with the implementation of an *in-situ* treatment in a fractured aquifer include: the heterogeneous geological setting; complex fracture distribution and orientation; multiple aquifers intersected; depths of targeted fractured zone; challenges in delivering and distribution of the oxidant; different water qualities mixing in the boreholes and logistical and financial issues such as cost of drilling into rock (Tredoux *et al.,* 2004; Kinner *et al*., 2005).

In view of the scarcity of available literature and experience abroad, including the complexity of understanding the hydrodynamics of the aquifers of the TMG to control the oxidation of Fe and Mn in the aquifer, and the associated costs and logistics for such a study, discouraged a field-test in the TMG aquifers. This project, therefore, only tested the applicability of ISIR in a primary aquifer setting. Once the technique has been demonstrated in a primary aquifer and well-understood, future research may then proceed into the fractured aquifer setting, since more than 80% of South Africa's exploited aquifers are in fractured settings (Woodford *et al.,* 2006), with the aquifers of the TMG being one of the most important groundwater resources in the Western and Eastern Cape Provinces (Smith and Roychoudhury, 2013).

3.2 Preliminary Investigation at the Witzand Wellfield

Based on the literature review on ISIR applications in primary aquifers, the potential for success in applying the technique at the Atlantis Aquifer appeared to be high. Once a production borehole was selected, a site characterisation of the area was conducted to establish if it was technically feasible to apply the ISIR treatment at the study site and to understand the current conditions in order to design a prototype for a pilot field test.

3.2.1 Site description

The Atlantis aquifer is situated in a low-lying coastal plain on the West Coast, approximately 40 km north of Cape Town. The study area experiences a Mediterranean climate of dry, hot summers followed by cool, wet winters. From the last three decades, the area's summer months are from October to March. The mean monthly maximum and minimum temperatures are presented in Table 3. The average annual potential evaporation of the study 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 winter months are associated with frontal rainfall systems with a mean annual rainfall of 457 mm (Figure 18).

The area lacks any major surface water resource and groundwater was first exploited through the Silwerstroom spring in 1976 (Flower and Bishop, 2003). The AWRMS has since developed to include two wellfields, called Silwerstroom and Witzand. Since 1979 artificial recharge is practised up gradient of the Witzand Wellfield through Recharge Basins 7 and 12 to augment natural recharge (Tredoux *et al.,* 2002; DWA, 2010). A production borehole within the Witzand Wellfield was selected because it is the more productive of the two wellfields, contributing 75% of the demand (Tredoux *et al.,* 2012).

Table 3: Mean monthly maximum and minimum temperatures and precipitation from 1980 to 2013, measured at the Atlantis Wastewater Treatment Works, 8 km east of the study site (Appendix A)

Mean monthly values	**January**	**February**	**March**	**April**	**May**	**June**	**July**	**August**	**September**	**October**	**November**	**December**
Maximum temperature (°C)	28	28	27	24	21	18	18	18	20	23	24	26
Minimum temperature (°C)	14	15	13	11	9	7	6	6	8	10	12	14
Precipitation (mm)	11	12	15	37	57	78	77	69	44	24	21	14

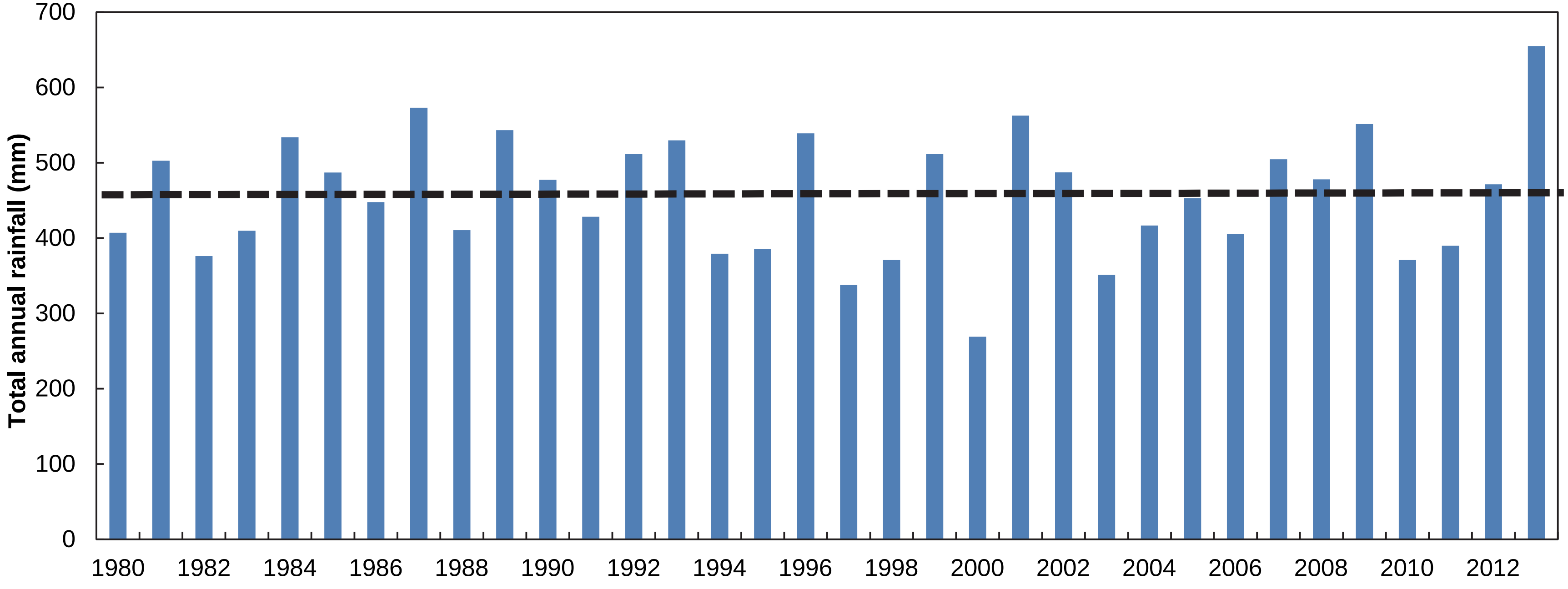
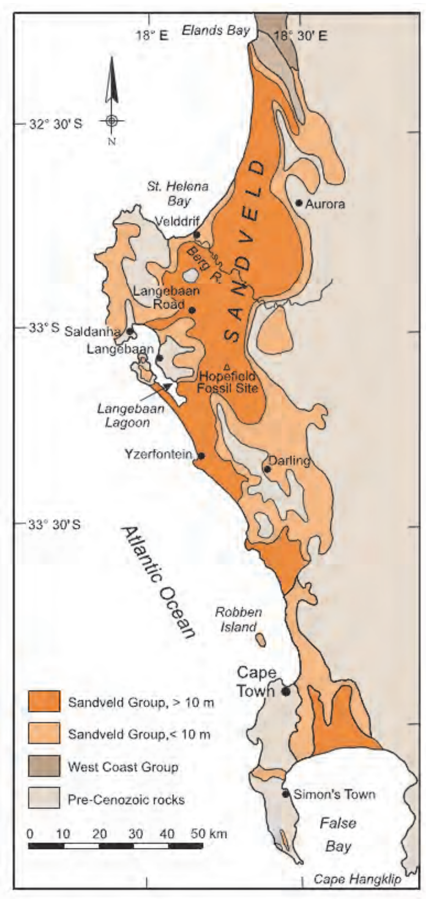


Figure 18: The total annual rainfall measured from 1980 to 2013 with the dashed line showing the long-term average of 457 mm (Appendix A)

3.2.2 Regional geology

The Atlantis Aquifer is located in the Cenozoic-age sediments of the Sandveld Group, which is a widespread sandy succession extending from False Bay to Elands Bay that was deposited on the various basement rocks during global sea-level changes (

Figure 19; Roberts *et al.,* 2006). The principal Sandveld Group units present in the study area are the Varswater, Springfontyn and Witzand Formations (oldest to youngest), which are briefly described below.



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 layers
		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	Fluvially deposited unit, consisting of gravel-rich, angular quartz sands with peaty clay lenses

Figure 19: The Sandveld Group distribution (left) and stratigraphy (right) (Roberts, 2006; Roberts *et al.*, 2006)

The basal Varswater Formation unconformably overlies Malmesbury Group 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 ranging between 3-8 m (*n* = 16; Cavé, 1997).

The Springfontyn Formation is represented as unconsolidated well-sorted quartz sands that are fine- to medium-grained. The base of the unit is muddy and in places the sands are peat-rich (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 formation covers the majority of the study area as vegetated dunes and within the Witzand Wellfield it is the water-target formation with all the production boreholes screened in this unit. It is intersected at approximately 15 mbgl and has an average thickness of 22 m (*n* = 16; Cavé, 1997; Tredoux and Cavé, 2002).

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 meters (*n* = 16; Cavé, 1997; Tredoux and Cavé, 2002).

3.2.3 Regional hydrogeology

Two types of aquifers are identified within the Witzand Wellfield, namely, the upper primary, intergranular Atlantis Aquifer and the secondary, fractured-rock Malmesbury Group Aquifer. Although there is groundwater in the underlying Malmesbury Group, the upper surface of the bedrock has weathered to form a substantial clay zone, which has formed an impervious layer and restricts any flow between the two aquifer systems (Tredoux and Cavé, 2002).

The Atlantis Aquifer is the principal groundwater resource and is defined as the saturated part of the Sandveld Group sediments below the water table (Fleisher, 1990). The static water level in the Witzand Wellfield is generally shallow, with levels varying between 1 to 6 mbgl in the main water-bearing units of the Springfontyn and lower 3-5 m of the overlying Witzand Formation. The general regional groundwater flow direction within the Witzand Wellfield is believed to be in a south-westerly direction with discharge into the Atlantic Ocean, although local deviations do occur particularly near the recharge basins (DWA, 2010; Bugan *et al.,* 2012).

The Atlantis Aquifer is a phreatic (unconfined) heterogeneous, anisotropic aquifer. A wide range of transmissivity (T) values have been found in the Witzand Wellfield as a result of the heterogeneity of the system, and range from 100 to 1 400 m^2/day calculated via pumping tests (Fleisher, 1990; Cavé, 1997). Similarly to the T-values, the calculated specific yield (Sy) within the Witzand Wellfield also varies, with pumping tests giving values ranging from 0.1 to 0.0008, and defining the aquifer as unconfined to semi-unconfined with delayed yield (Fleisher, 1990). This is believed to result from the facies changes in the aquifer where the calcrete layers and/or finer-grained sands in the upper layers give semi-unconfined and delayed yield characteristics (Tredoux and Cavé, 2002).

3.2.4 Production borehole clogging

In the latter half of the 1990s, production borehole clogging emerged as a serious problem in both the AWRMS wellfields (Tredoux and Cavé, 2002). The presence of Fe in the Atlantis groundwater was attributed to the naturally iron- and sulphate-rich minerals in the Sandveld Group and the underlying weathered clay of the Malmesbury Group bedrock, aided by naturally high DOC concentrations (i.e. 5-10 mg/ℓ) in the groundwater of the Atlantis area leading to reducing conditions in the aquifer (Tredoux and Cavé, 2002). However, a number of other factors may have attributed to the severity of the clogging problem experienced (DWA, 2010; Genthe *et al*., 2012; Tredoux *et al*., 2012):

- In 1989 and again in 1993 additional production boreholes were drilled in the Witzand Wellfield and the production boreholes were operated at too high abstraction rates;
- Initially, artificial recharge of a blend of domestic and industrial wastewater increased the nitrogen and DOC load in the aquifer, enhancing reducing conditions and bacterial activity. However only the Witzand Wellfield is artificially recharged, so it is unlikely that this is the main cause for the problems experienced. In November 1986, artificial recharge of the treated wastewater was discontinued and recharge of domestic wastewater was resumed in 1994;
- In 1989, the Recharge Basin 7 was dried out which lowered the water table in the Witzand Wellfield significantly.

3.3 Site Characterisation for *In-situ* Iron Removal

Production borehole G30966 on the eastern side of the R27 (West Coast Road) was selected as the test borehole to undertake the ISIR field study through discussions with the relevant role players in charge of the Witzand Wellfield (Figure 20).

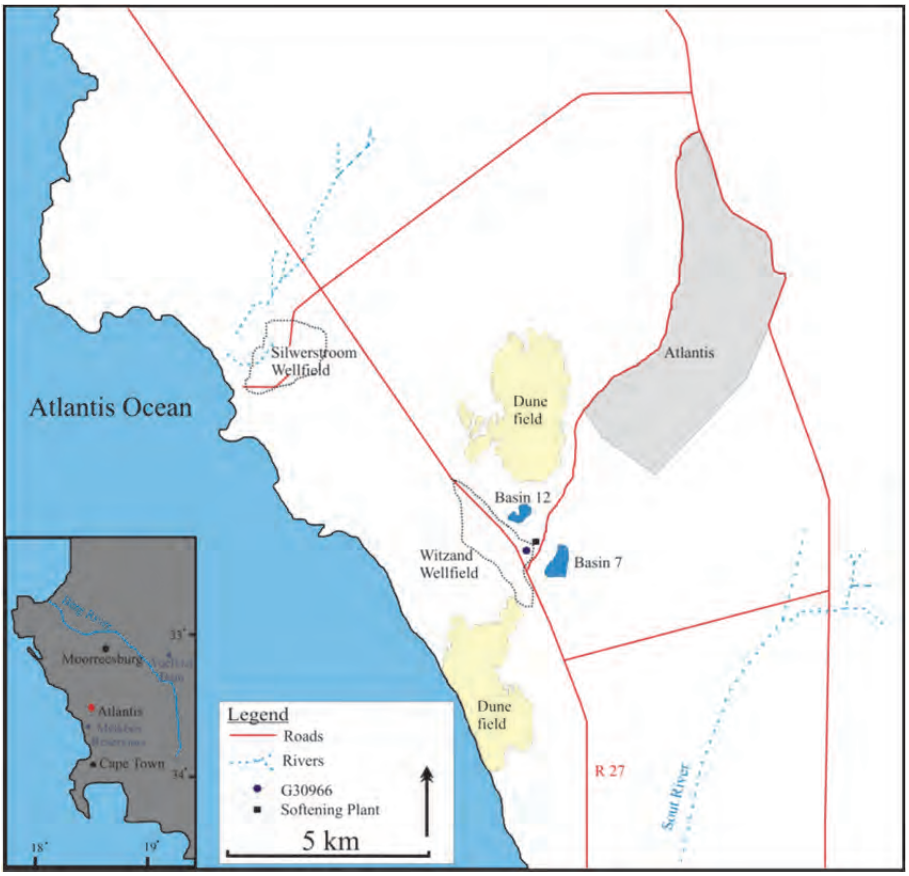


Figure 20: Location map of the study area

The reasons for the selection of this site included:

- It was not used at the time as a production borehole and was only used for dilution of the brine generated at the Witzand Softening Plant and onsite irrigation (DWA, 2010). Consequently, it could be taken off the pumping scheme to carry out the tests;
- It has been affected by iron-related clogging and been rehabilitated by the BCHT method in 2000 (More Water, 2001);
- It was the closest production borehole to the Witzand WTP, which provided for greater security and better logistical support;
- There were already two monitoring points in close vicinity, i.e. G30979 approximately 16 m NE and WP 63 approximately 11 m WNW of G30966, respectively (Figure 21).

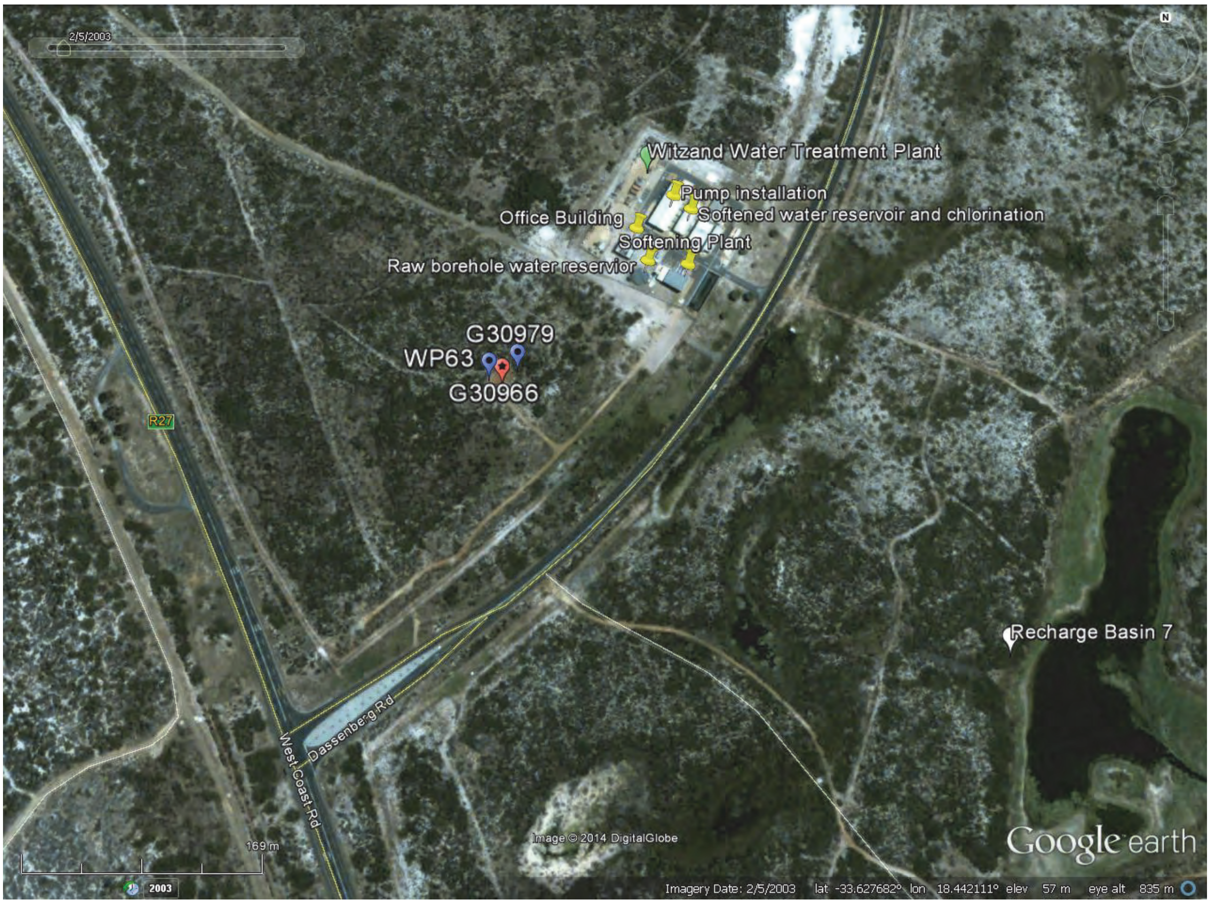


Figure 21: Google Earth image of production borehole G30966 and the two monitoring boreholes (marked blue) in close vicinity of the Witzand WTP (Accessed 7 February 2013)

3.3.1 Borehole construction and local geology

Production borehole G30966 was sited by the Geological Survey (now the Council for Geoscience, CGS) and percussion drilled in 1979 (Cavé, 1997). It was drilled to a depth of 42 m with a drilling diameter of 304 mm (van der Merwe, 1980). The borehole was constructed with a solid steel casing with a 203 mm internal diameter to a depth of 24 m. The borehole screen extends from 24 m to 30 m consisting of Johnson 30 stainless steel wedge wire (i.e. slot size 0.75 mm) with 150 mm internal diameter (i.e. 14% screened) (van der Merwe, 1980). The gravel pack in the annulus between the

Johnson screen and the Springfontyn Formation is class number 7/16 gravel (1.2-2.8 mm) (van der Merwe, 1980).

The geological logs of production borehole, G30966 and the nearby monitoring borehole, G30979 are given in Figure 22. The Springfontyn Formation is found at ~14 mbgl in the study area which is the target unit for the injection of the oxygenated water as it is generally where the Witzand Wellfield production boreholes are screened (including the investigated G30966). From the geological information, there are no structural (e.g. faults or fractures) or lithological complications (e.g. very coarse-grained layers) in the target area that would cause preferential flow-paths of the injected water. According to the G30966 log the average grain size in the targeted zone ranges from fine- to medium-grained (van der Merwe, 1980). This was ideal as the quartz sands provide suitable sites for the iron (III) oxide to attach to when formed and over time with multiple injections it can be expected that a high exchange capacity could be formed in the setting.

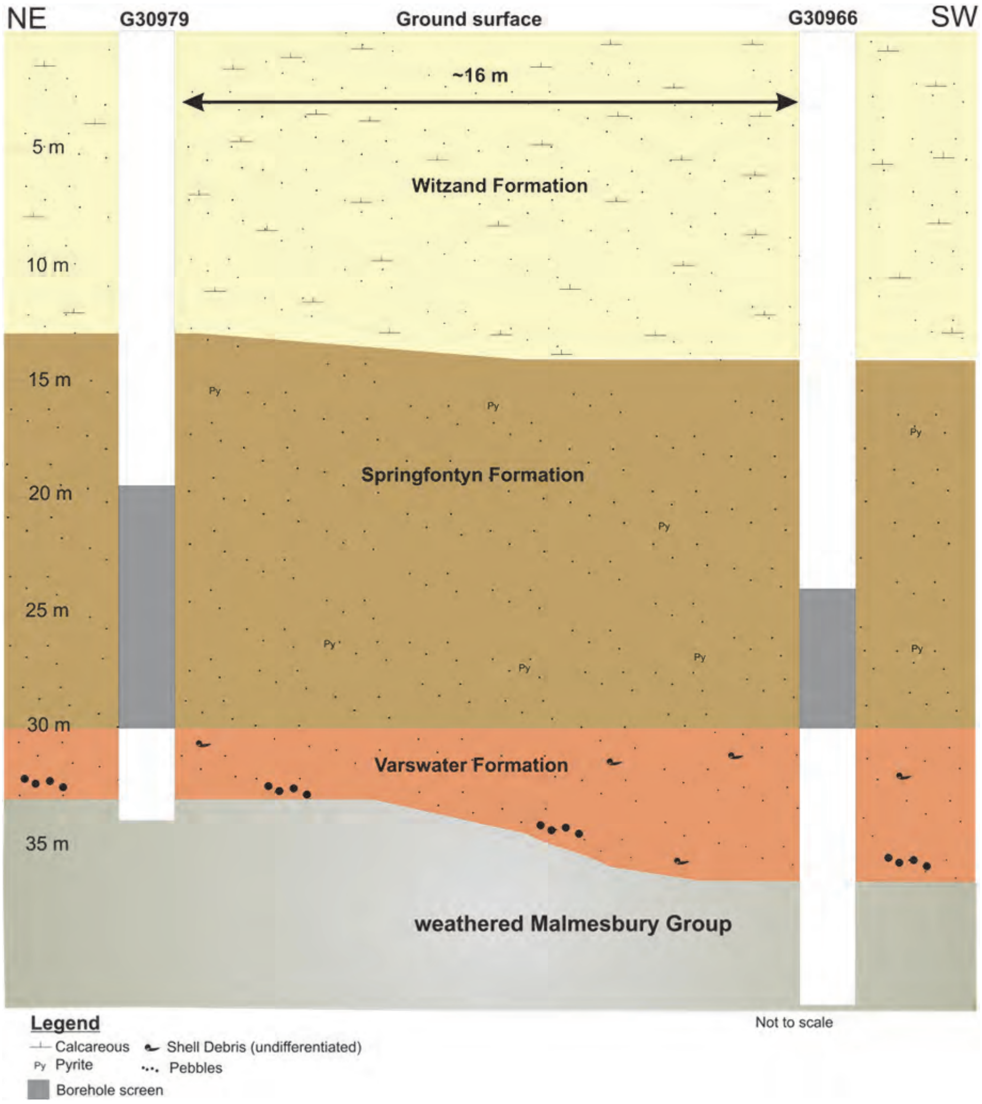


Figure 22: The geological logs of production borehole G30966 and monitoring borehole G30979, the dark grey shows the position of the borehole screens (data from van der Merwe, 1980)

3.3.2 Long-term groundwater level trends

The historical static groundwater levels measured in production borehole, G30966, and monitoring borehole, G30979, from July 1979 to December 2012 are given in Figure 23. The long-term historical groundwater level data collected from G30966 and G30979 showed the lowering of the groundwater table and increased drawdown (in G30966) from 1979 to late-1998. This is ascribed to the high production in the Witzand Wellfield, below average rainfall (which began in 1994) and clogging of the production borehole. However, from early-1999 the groundwater level has progressively recovered and has risen to its highest levels in 2012. This is the result of the natural and artificial recharge greatly exceeding the abstraction from the wellfield (Bugan *et al.,* 2012). The lower abstraction yields from the wellfield are attributed to the poor performance of the production boreholes due to clogging (Bugan *et al.,* 2012).

The static groundwater level provides information on the ability of the aquifer to "take" water which assists in deciding the volume and rate of injection when designing the ISIR prototype. The shallow water table in the study area (< 2 mbgl at the time of the study) is not ideal as this restricts the amount of water injected and the rate of injection into the aquifer during ISIR as potential backpressure or surfacing of the injected water is more likely. This is the result of there being insufficient 'space' to release the hydrostatic pressure in the aquifer (ISRRI, 2009). In addition, due to the high water table it was decided that the G30966 would not be used as the injection point and that the Vyredox approach would rather be applied for this study area.

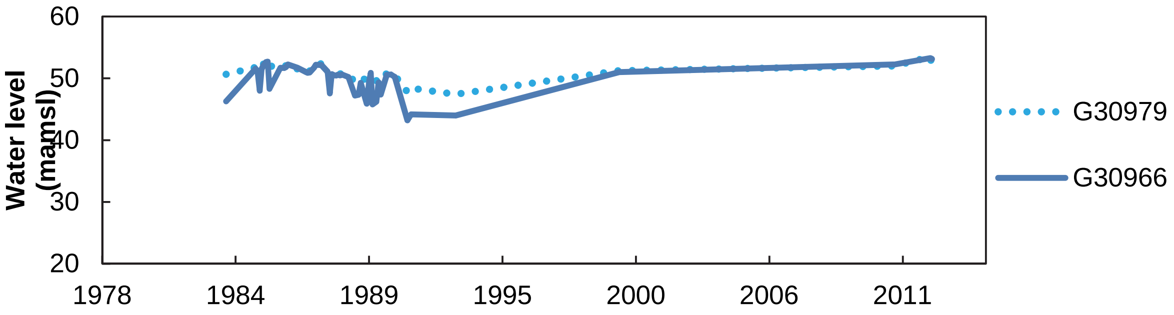


Figure 23: Historical static groundwater levels in G30979 and G30966 over the last three decades

3.3.3 Borehole efficiency

The main aim of this study is to investigate the prevention of iron-related clogging of production boreholes. The baseline performance of the production borehole had to be established by calculating the Sc from step drawdown pumping test data. The Sc of a production borehole is a measure of efficiency of the borehole and nearby aquifer and is calculated by dividing the abstraction rate (Q) by the drawdown at the end of each step. The highest Sc value, which is generally obtained after a borehole is drilled and properly developed, is the 'benchmark' with which to compare future values (Johnson, 2005). A decline in Sc can be indicative of clogging of the borehole screen, pump failure or lower static water levels (Driscoll, 1986; Johnson, 2005). It is recommended that a decline in Sc by more than 5% should be taken as a "warning" sign of production borehole clogging and further inspection through down-hole camera logging is recommended to confirm whether clogging is the cause of the decline (Anderson *et al.*, 2010).

At least five step drawdown pumping tests have been performed on G30966 since its construction in 1979 (i.e. Nealer, 1979; More Water, 2001; AWRMS data collected from routine test in 2007), including the latest performed on 9 January 2013 for this project. The latest step drawdown pumping test consisted of four steps for 1 hour intervals at successively higher abstraction rates, followed by measurement of water level recovery. The abstraction rates, number and duration of the steps and measurement intervals were decided upon using recommendations from Kruseman and de Ridder (2000) and the previous step drawdown pumping tests performed on G30966.

To evaluate the accuracy of the Sc found from the step drawdown pumping tests, the results were checked against the following conditions (Driscoll, 1986):

- The Sc of a borehole is inversely proportional to Q in a primary aquifer;
- The Sc decreases in proportion to the drawdown for an unconfined aquifer.

The Sc plots for the collected data from G30966 are given in Figure 24 and Figure 25.

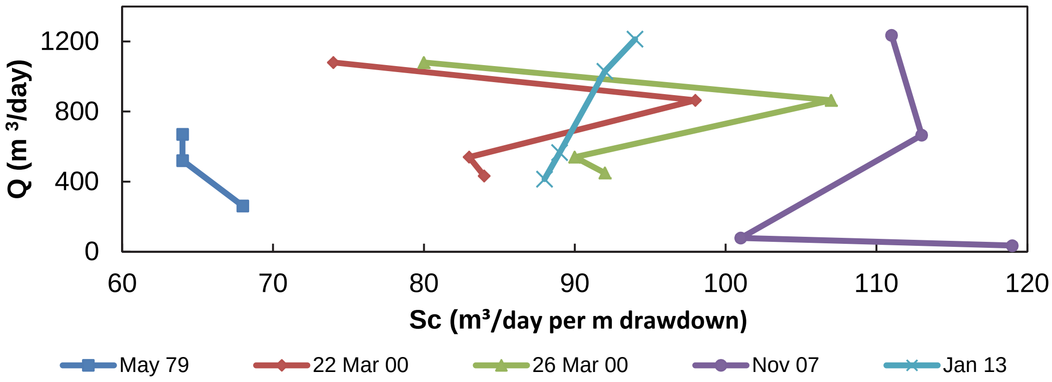


Figure 24: Abstraction rate (Q) vs. Sc of G30966 from the five step drawdown pumping tests performed from 1979 to 2013

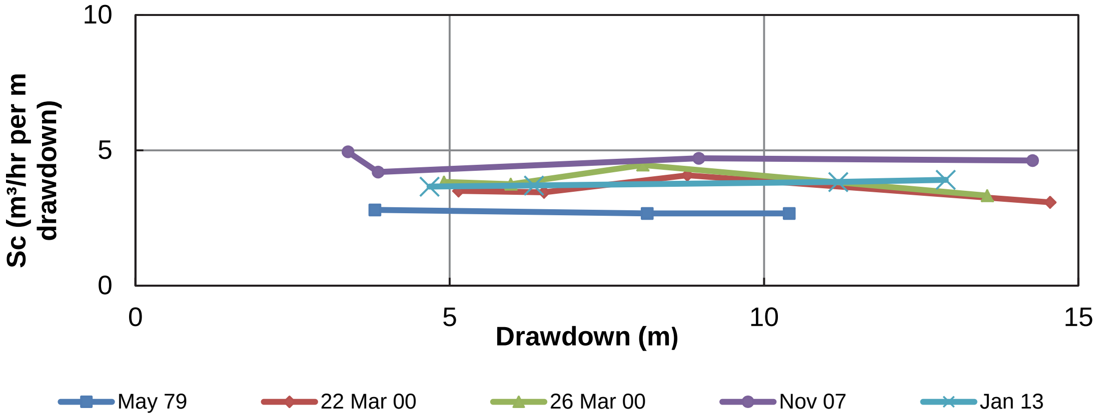


Figure 25: Drawdown vs. Sc of G30966 do not show the trends in unconfined aquifers as predicted by Driscoll (1986)

Only the 1979 step drawdown data shows a decline with increasing discharge, but there is concern about the accuracy of the results. Specific capacity values calculated from step drawdown data should be determined by steps of the same duration (Driscoll, 1986). In this case, the third step was double (i.e. 2 hours) of the other two steps (i.e. 1 hour). This variability in step duration also causes problems with the comparisons between the subsequent Sc values and the original Sc values from 1979 (Johnson, 2005). The two-step drawdown tests in 2000 were performed to compare the borehole efficiency before BCHT (22/03/2000) and after treatment (26/03/2000). Both plots in the graph above give anomalies in the third step that cannot be easily explained. The November 2007 step drawdown test also showed an anomaly at the 2nd step as a result of the incorrect abstraction rates applied. In addition, the time frames were too short and should have been at least an hour long to allow for the water level to stabilise. Although there are anomalies in the last three step drawdown tests, the overall trend shows a decline with increasing drawdown. The latest (2013) test showed an increase over time, which could be due to the abstraction rate not having been measured accurately. Therefore, the Sc of all the step drawdown pumping tests cannot be compared with the previous values to establish the changes in borehole efficiency as a result of inaccuracies in data collection. In addition, the Sc vs. drawdown results in all five step drawdown tests do not show a proportional decrease with increasing drawdown, which could be attributed to the borehole screened only 14% of the whole aquifer and clogging of the borehole screen.

Down-hole camera logging of the production borehole G30966 formed part of the preliminary evaluation to evaluate the condition of the borehole screen after the pumping tests were performed. However, it was not performed due to the constraints imposed by procurement procedure which could not be resolved during the project timeframe.

3.3.4 Hydrogeological characteristics

Historical hydrogeological characteristics of the aquifer (i.e. T and Sy) within the study area and the sustainable yield assigned to production borehole G30966 are given in Table 4. A high T-value setting is best suited for any *in-situ* treatment as the mounding effect caused by the injection of a volume of water would be smaller (i.e. water dissipates faster into the aquifer) in comparison with a low T-value, which could limit the injection volume or injection rate by pressure build-up (ISSRI, 2009).

Table 4: Aquifer parameters and sustainable yields of G30966 from previous pumping tests

T (m^2/d)	556 (using the Cooper-Jacob method; van der Merwe, 1980) 280 (using the Theis method; Bredenkamp and Vandoolaeghe, 1982)
Sy	0.14 (using the Theis method; Bredenkamp and Vandoolaeghe, 1982)
Sustainable yield (ℓ/s)	9.7 (van der Merwe, 1980) 5.0 (More Water, 2001) 7.0 (Bugan *et al.,* 2012)

In addition, a 72 hour constant discharge test (CDT) and 95% water level recovery was performed on G30966 between 25 and 28 April 2013. The abstraction rate of the recent CDT calculated on the “rule of thumb" rate would produce approximately 40-50% of the available drawdown (Conrad *et al.,* 2010). The maximum available drawdown in G30966 was 21 m, which was calculated from the difference between the pump (23 mbgl) and static water level (1.6 mbgl 25/04/13), hence a drawdown between 8.5 to 10.5 m was desired. An abstraction rate of 10-11 ℓ/s was therefore estimated from the observed drawdowns in G30966 from the January 2013 step drawdown data. The CDT duration and time intervals measurement followed the recommendations of Kruseman and de Ridder (2000) with G30979 used as the observation borehole. Data was collected by manual readings using the AWRMS Solinst dipmeter and Council for Scientific and Industrial Research (CSIR) Solinst dataloggers installed in both boreholes.

The rate measured during the 72 hour CDT was 10.8 ℓ/s, and the graph of the pumped borehole G30966 drawdown and recovery is given in Figure 26, with a total drawdown of 10.2 m at the end of the 72 hour pumping test. From the measured drawdown in G30979 (Figure 27), located 16 m from the pumped borehole, the T and Sy were calculated from graphs (Figure 28) using the Neuman method in the FC-Excel program. 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. 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.

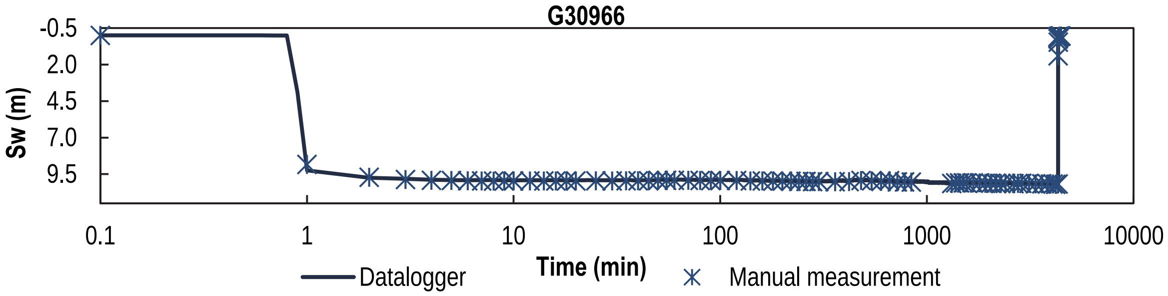


Figure 26: Semi-log of drawdown in pumped borehole, G30966, during the CDT and recovery in April 2013

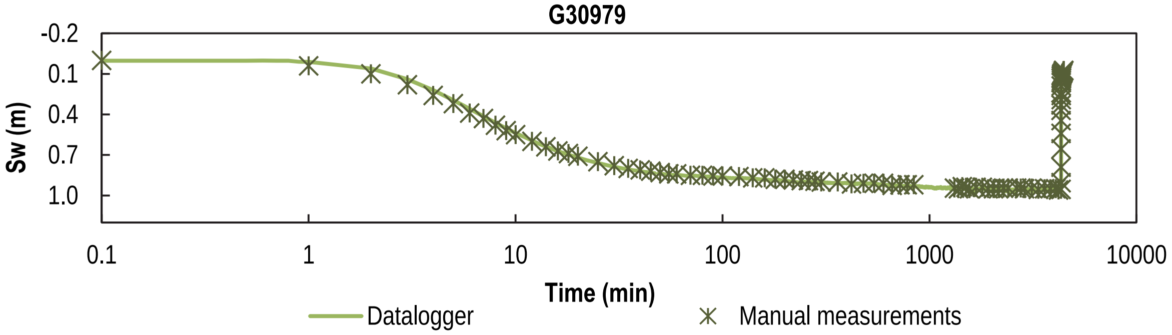


Figure 27: Semi-log of drawdown in monitoring borehole, G30979, during the CDT and recovery in April 2013

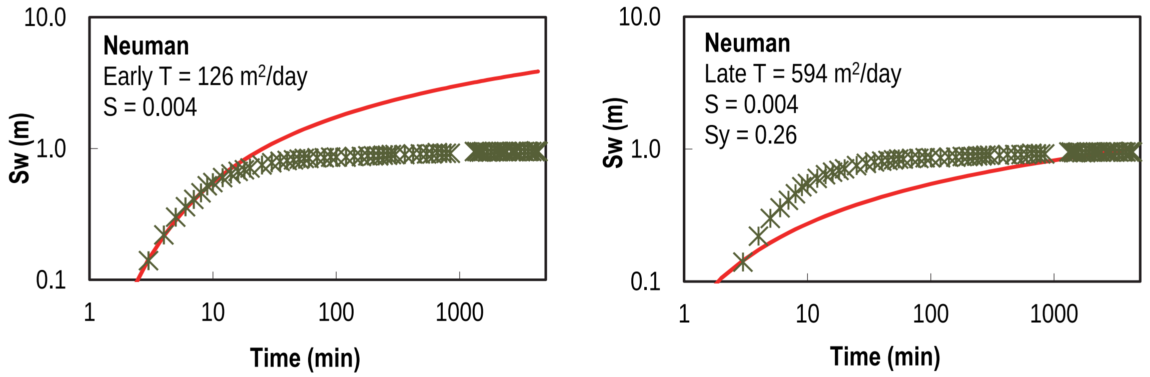


Figure 28: Early (left) and late-time (right) segment of the Neuman method using G30979 data

3.3.5 Water quality

The suitability for the ISIR treatment was assessed according to the water quality in the aquifer as determined from the groundwater abstracted from production borehole G30966. A compilation of the historical G30966 water chemistry data from 11/07/1979 to 28/04/2013 was obtained from AWRMS monitoring data, literature by DWAF (1983), Fleisher (1990), More Water (2001), and water samples collected by the researchers during the project (*n* = 200). The recent water samples were collected during the pumping tests performed in January and April 2013, which consisted of four unfiltered samples taken at the sampling tap after proper purging of the borehole. The samples were collected in 1 ℓ glass sample bottles that were correctly prepared before sampling and rinsed three times before filling. The samples collected were analysed by the City of Cape Town's Scientific Services. The water quality parameters analysed for were selected according to literature review of ISIR case studies.

To assess the data accuracy the electro-neutrality plausibility test was used and data found outside the ± 5% accuracy threshold was excluded (Appelo and Postma, 2005). The electro-neutrality test calculated for the dataset indicated that only 74% of the analyses were within the ± 5% accuracy threshold. The statistical analysis of the revised dataset is given in Table 5.

The water type from G30966 was determined from the major ion composition potted in a Piper diagram. The Piper diagram was plotted using milli-equivalent per litre (meq/ℓ) of the major cations i.e. Ca^{2+}, Mg^{2+}, and sum of Na^{+} + K^{+} and the major anions concentrations i.e. Cl^{-}, SO_4^{2-} and sum of CO_3^{2-} + HCO_3^{-}, which was calculated in Microsoft Excel 2010 by multiplying the concentration (given as mg/ℓ) by its valence and then divided by the atomic or molecular weight of the cation or anion. The HCO_3 and CO_3 concentrations (as mg/ℓ) were calculated from the total alkalinity concentration (given as $CaCO_3$) by multiplying by the total alkalinity by 1.22 or 0.6, respectively, and then followed the same process as the other ions to find its meq/ℓ value.

From the historical data the water type showed an overall change from Ca-Na-HCO_3 to Na-Ca-HCO_3 type in the last decade, except for the times that the water quality was affected by the acid spill and leaking brine pond at the Witzand Softening Plant (Figure 29). The three outliers in the 2001-2009 dataset are certainly the result of elevated SO_4 and Ca concentrations in the groundwater due to dissolution of the aquifer material as a result of this sulphuric spill at the Witzand Softening Plant, but the exact date of the spill is unknown (Tredoux *et al.* 2012). Also the leakage from the brine pond as the liner was damaged at some stage, also the exact date of when the leakage started is unknown (Tredoux, G., *pers comm.,* 2013).

Rises in SO_4 and Ca concentrations are first identified in February 2003 in the dataset, with sporadic highs in 2004, 2007 and 2009. The brine pond has been taken out of use in 2010 and at present the water quality has returned to its original composition, which has been stable since 2010 (Figure 30). The decline in Cl and Mg concentrations, as seen over time in the lower anions and cations triangles of the Piper diagram (Figure 29), can be attributed to change with regard to the composition of the artificial recharge water (Tredoux *et al.,* 2012). The EC (i.e. salinity of the water) has also declined as a result of the lower salinity water used for recharge (Figure 31).

Table 5: Historical groundwater quality of G30966 from 1979-2013

Parameter	***n***	**Mean**	**Range**	**Q25**	**Q50**	**Q75**
Electrical conductivity (EC; mS/m)	148	86	65-144	72	80	100
pH	148	7.6	6.9-9.5	7.4	7.6	7.7
Ca	148	77	42-209	60	69	88
Sodium (Na)	148	89	63-129	79	86	97
Mg	148	10	7-19	8	10	11
Potassium (K)	148	5	1-9	3	5	7
Total alkalinity (as $CaCO_3$)	148	173	120-250	152	166	188
Cl	148	139	93-253	107	125	175
SO_4	148	61	15-386	42	49	55
Nitrate + Nitrite (as N)	129	0.19	<0.001-1.2	0.05	0.1	0.2
Total Fe	147	0.87	0.01-8.5	0.10	0.34	0.80
Total Mn	80	0.25	0.08-0.82	0.13	0.17	0.28
NH_4 (as N)	93	0.17	0.02-0.70	0.1	0.1	0.27
SiO_2	8	4.2	3.5-4.6	3.95	4.34	4.53
PO_4	7	0.07	0.02-0.2	0.05	0.05	0.1
Strontium (Sr)	7	0.48	0.41-0.53	0.43	0.49	0.51
Fluoride (F)	26	0.22	0.11-0.33	0.19	0.22	0.26
Lead (Pb)	12	0.04	0.001-0.42	0.001	0.005	0.005
As	8	≤ 0.001				
DOC	4	8.9	8.6-9.5	8.6	8.7	9.3
Data given as mg/ℓ unless otherwise specified						

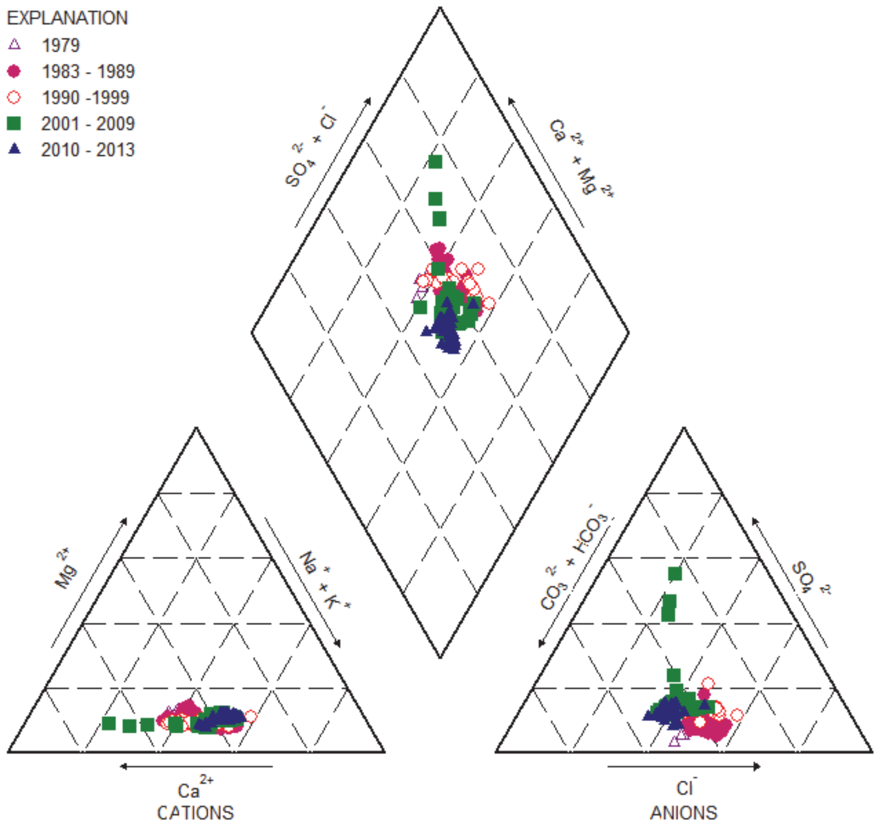


Figure 29: Piper diagram of the major ion composition of G30966 sampled from 1979 to 2013

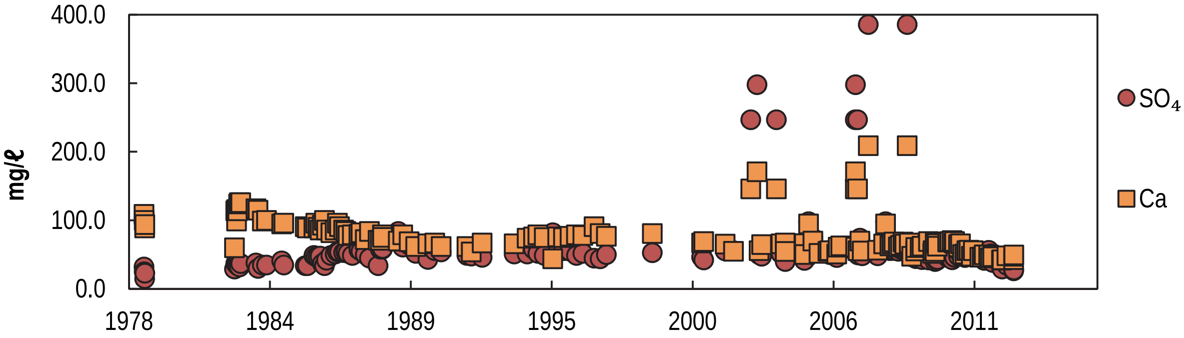


Figure 30: The SO_4 and Ca concentrations in G30966 from 1979 to 2013, showing outlier elevated concentrations in 2003 to 2009

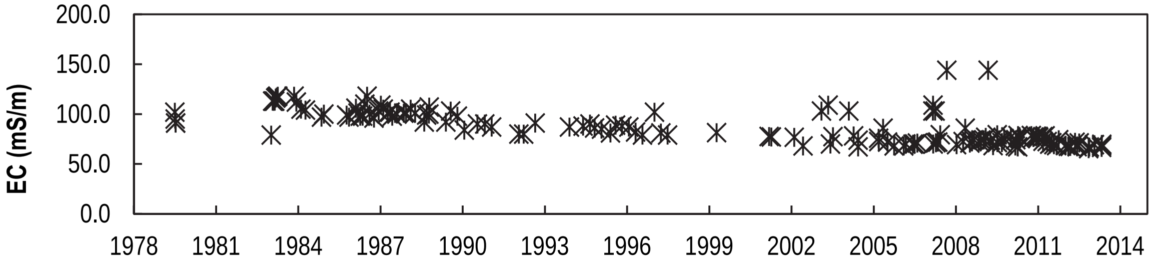


Figure 31: G30966 measured EC has progressively decreases over time with artificial recharge

The Fe concentration in G30966 is given in Figure 32. The median concentration is generally low (0.34 mg/ℓ) in comparison with WHO (2008) guidelines. Prior to 1990, the elevated concentrations of Fe observed (> 2 mg/ℓ) could be associated with incorrect purging and sampling of a clogged borehole (i.e. G30966 was rehabilitated in 2000). This shows that Fe was already on the increase within the production borehole from 1983 onwards when regular water quality sampling commenced. However, elevated concentrations are later seen to occur in 2007 and 2009, accompanied by elevated SO_4 concentrations (Figure 32). The elevated concentrations in 2010 through to 2012 (i.e. 1-2 mg/ℓ) are also partly due to incorrect sampling. The Fe concentrations from the recent step drawdown and CDT in gave ranges between 0.4-0.5 mg/ℓ which will be accepted as the Fe concentrations expected in the groundwater, is slightly above WHO (2008) guidelines but is much greater than the 0.1 mg/ℓ threshold concentration for iron clogging (Walter, 1997).

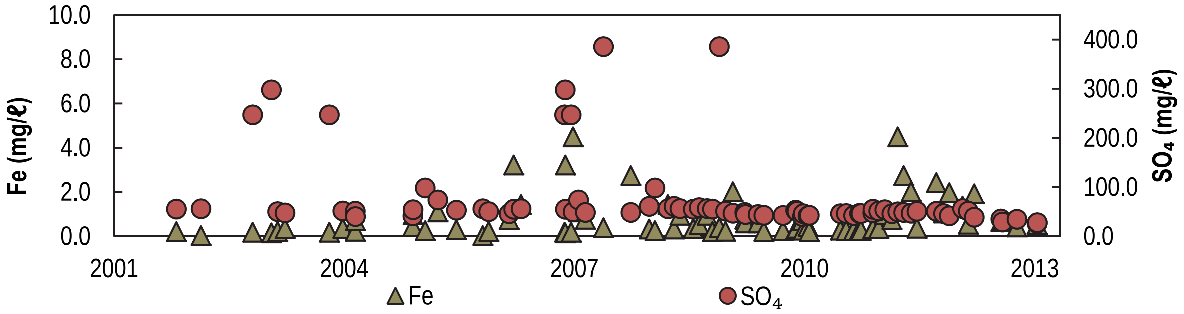


Figure 32: The Fe and SO_4 concentrations in G30966 shows that the spills could have contributed to Fe mobilisation from 2007 to 2009 with pre-2007 and post-2009 highs (> 2 mg/ℓ) can be associated to incorrect purging and sampling and are indicative of Fe accumulating within the borehole.

The impact of the acid spill and brine leakage at the Witzand Softening Plant is better seen in the concentrations of Mn than in Fe, but show a similar peak after 2009 associated with incorrect purging of the borehole before sampling (Figure 33). The Mn concentrations are not as variable as the Fe levels and do not exceed > 1 mg/ℓ. However, the Mn concentrations are always above WHO (2008) and clogging (Walter, 1997) threshold of 0.1 mg/ℓ. The recent pumping tests data which ensured the correct purging of the borehole resulted in a total Mn concentration between 0.15-0.23 mg/ℓ, which is accepted as the total Mn concentration in the native groundwater. The review of the Fe and Mn concentration in G30966 shows that the respective Fe and Mn concentrations are not very high. However, their presence, even at low concentrations, has caused significant problems in water supply through long term accumulation and clogging of the borehole.

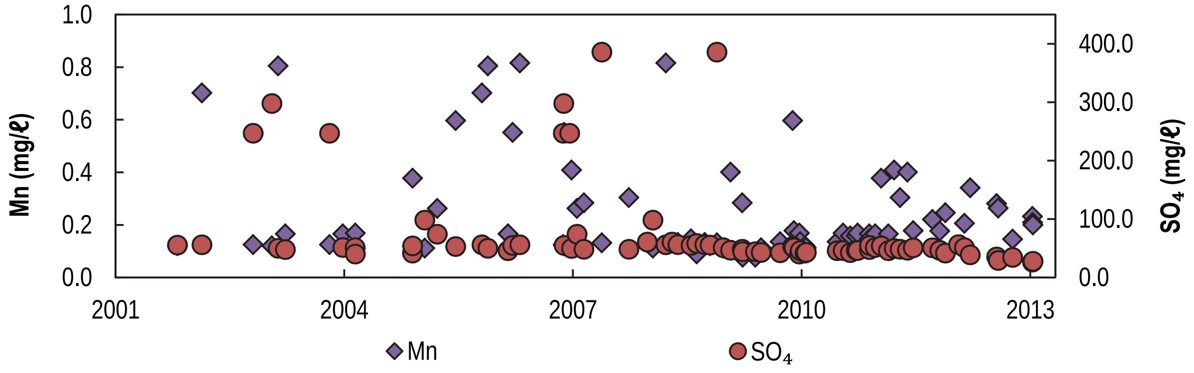


Figure 33: The total Mn and SO_4 concentration over time in G30966 showing a direct link with increases associated to the acid spills and post-2010 elevated concentrations associated with incorrect sampling

The other parameters to investigate the feasibility of the ISIR treatment include pH, temperature, DOC, NH_4 and alkalinity, where recommended conditions for optimal ISIR are:

- A pH between 7 and 8;
- Water temperature between 5 and 20°C;
- No DOC, NH_4, sulphides such as H_2S or pyrite;
- High alkalinity to buffer pH lowering due to oxidation reactions.

The historical groundwater pH measured in the laboratory is given in Figure 34, and indicates that the pH has not changed significantly over the last three decades and varies between 7 and 8. There is one outlier not associated with the identified peaks caused by the acid spill, but this is assumed to be an incorrect measurement. This pH range is ideal for sufficient oxidation of Fe^{2+} and Mn^{2+} for ISIR treatment. The water temperature for the study area was measured by the Solinst dataloggers during the CDT in April 2013 with an average of 17.4°C in G30979, which is within the desired range for ISIR.

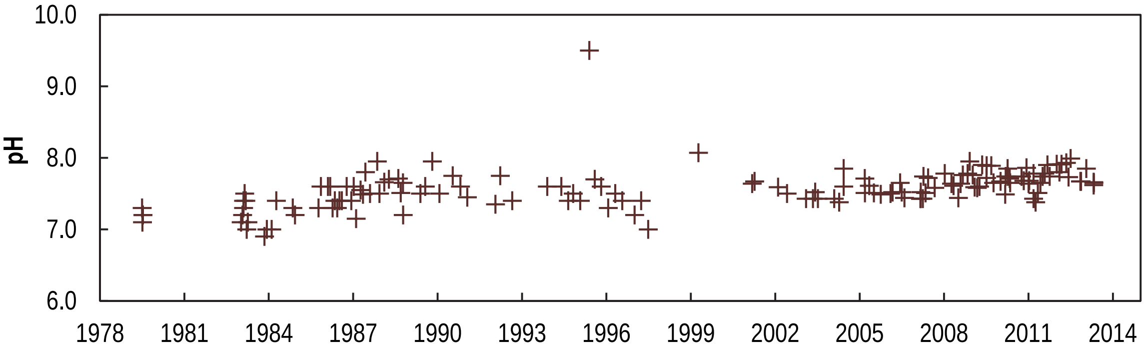


Figure 34: G30966 historical pH ranges between 7 and 8 with an outlier at 9.5

Although there is only limited historical information on the DOC in G30966, the recent samples show it to be high (> 8 mg/ℓ), this is close to the natural DOC levels in the aquifer (10-15 mg/ℓ) (Tredoux *et al.,* 2012). In view of the high natural DOC levels in the Atlantis Aquifer, it is difficult to quantify the additional component introduced by the artificial groundwater recharge especially until 1986 when the industrial wastewater was also recharged in Basin 7. This high DOC is problematic for the project as it affects the rate of oxidation of Fe^{2+} and Mn^{2+}.

The other main oxygen consumer in the subsurface is $NH_{4,}$ but it occurs at a much lower concentration (< 0.3 mg/ℓ) than the measured DOC. There is also a distinct H_2S smell associated with the abstracted water and this H_2S could interfere with the oxidation process. The alkalinity of the water in the study area is also high (> 100 mg/ℓ as $CaCO_3$) which is ideal as this would buffer any lowering of the pH due to the oxidation of sulphides, Fe^{2+} and Mn^{2+} in the subsurface. The SiO_2 is also relatively high in the groundwater and this affects the effectiveness of the proposed ISIR, as SiO_2, similarly to DOC, can have a limiting effect on the oxidation processes of Fe^{2+} and Mn^{2+} by forming complexes with those ions.

The As, PO_4, Pb and V in G30966 were initially included to evaluate their concentrations for the application of ISIR, as other case studies had shown a reduction in concentrations through adsorption on the iron (III) oxides, but they were all found in trace amounts below SANS (2011) threshold limits and were therefore excluded from any further investigation.

Based on these findings, the study site was judged suitable for ISIR, but the oxidant selected should take into account the high DOC and SiO_2 concentrations in the groundwater. In addition, it was decided that groundwater abstracted from G30966 would be suitable to supply the water used for subsequent injection tests.

4 DESIGNING AN *IN-SITU* IRON REMOVAL PROTOTYPE

4.1 Introduction

Although the ISIR approach has been used for decades, there are no established design criteria and its application depends on site characteristics (Karakish, 2005). On the basis of preliminary investigation of the study site and ISIR experience abroad, a prototype was designed and constructed. In designing the ISIR to be applied at production borehole G30966, the following points needed to be decided upon:

- The oxidant used for Fe^{2+} and Mn^{2+} removal;
- The method of introducing the oxidant into the injected water and aquifer;
- Construction of a prototype taking into account volume and rate of injection.

In addition, the design and construction of the prototype took into consideration a number of other factors, which included that it:

- Should make optimal use of the existing infrastructure;
- Must be mobile to avoid any potential vandalism;
- Must be simple and easy to operate;
- Must be environmentally friendly and safe to use;
- Required minimal regulatory compliance with the NEMA and NWA.

4.2 Oxidant Selection

Oxygenation of the injected water for ISIR is commonly achieved through aeration or dosing with pure oxygen gas. In this case study, aeration was impractical because the water quality investigation revealed the study area's groundwater contains high SiO_2 and DOC, which at high concentrations forms chelates with the Fe^{2+} and Mn^{2+} in solution and aeration is unable to oxidise out those complexes (Munter *et al.,* 2005). The use of pure oxygen gas was also considered but excluded because of the storage and safety logistics required with pure oxygen gas at the study site. Other stronger oxidants used for Fe^{2+} and Mn^{2+} *ex-situ* removal were also considered. The use of $KMnO_4$ have been investigated as alternatives to oxygen for ISIR, however the Fe removal efficiencies were lower than those for the use of oxygen, and $KMnO_4$ also decrease the permeability of the aquifer (Mettler, 2002). In addition, Cl_2, HOCl and $KMnO_4$ all require handling and storage of noxious chemicals, which precluded their use in this study.

Ozone was then considered because it is easily generated on-site with no handling or storage of a toxic gas needing special safely regulations (Rajagopaul *et al.,* 2008). It is the most powerful oxidant for Fe and Mn removal in comparison to the oxidants listed above (Table 6), even in the presence of high DOC (Eriksson, 2005). Another benefit is that upon decomposition in water, it forms DO and hydroxyl radicals (OH^-), which further oxidise of Fe^{2+} and Mn^{2+} (EPA, 1999). Ozone is well-known and widely applied for disinfection and oxidation purposes in the treatment of drinking water (e.g. von Gunten, 2003; Rajagopaul *et al.,* 2008) and it has only recently been used in *in-situ* treatment of hydrocarbon pollution (Masten, 2004; Pavlik and Gwinn, 2005).

The fact that this is the first study to test the application of O_3 for ISIR and lack of previous such studies is believed to be due to high initial costs (Rajagopaul *et al.,* 2008), despite the aspects that Fe^{2+} and Mn^{2+} removal is expected to be accomplished in a shorter time, which could be a cost saving in the longer term.

Table 6: Amount of oxidant required to remove 1 mg of Fe and Mn (Sommerfeld, 1999; Appelo and Postma, 2005)

Oxidant	Stoichiometric Reaction	Oxidant (mg)
O_2	$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+$	0.14
	$2Mn^{2+} O_2 + 2H_2O \rightarrow 2MnO_2 + 4H^-$	0.29
O_3	$2Fe^{2+} + O_3 + 5H_2O \rightarrow 2Fe(OH)_3 + O_2 + 4H^+$	0.43
	$Mn^{2+} + O_3 + H_2O \rightarrow MnO_2 + O_2 + 2H^+$	0.87
$KMnO_4$	$3Fe^{2+} + MnO_4^- + 7H_2O \rightarrow 3Fe(OH)_3 + MnO_2 + 5H^+$	0.94
	$3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2 + 4H^+$	1.92
Cl_2 as HOCl	$2Fe^{2+} + HOCl + 5H_2O \rightarrow 2Fe(OH)_3 + Cl^- + 5H^+$	0.47
	$Mn^{2+} + HOCl + H_2O \rightarrow MnO_2 + Cl^- + 3H^+$	0.96

The removal efficiency of ISIR treatment is dependent on the DO concentration available to react with the Fe^{2+} and Mn^{2+}; therefore the parameters which influence the solubility and saturation of dissolved ozone in the water also need to be known. The stability of dissolved ozone in solution is directly proportional to the concentration of the ozone gas introduced into the water and inversely proportional to increasing temperature (Figure 35), pH (Figure 36), alkalinity and organic matter (Masten, 2003; von Gunten, 2003). Ideal conditions for ozone-based oxidation processes include water temperature between 15-20°C and pH > 7 for Fe and pH > 8.5 for Mn (El Araby *et al.,* 2009). At pH (i.e. ≥ 10) and high alkalinity (≥ 300 mg/ℓ as $CaCO_3$) the oxidation reactions are OH^--based as those conditions promotes ozone decomposition, which still advances the oxidation process but the OH^- has a shorter half-live (i.e. in the order of microseconds) compared to dissolved ozone, thus reducing the radius of influence and contact with Fe^{2+} and Mn^{2+} (EPA, 1999; Masten, 2004; Eriksson, 2005).

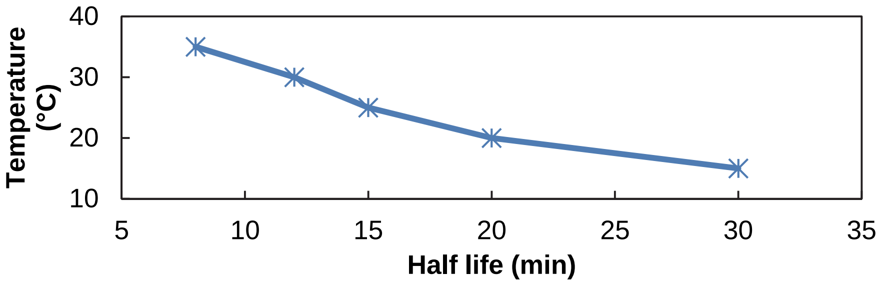


Figure 35: The half-life of dissolved ozone at pH = 7 decreases with increasing temperature (www.lenntech.com/library/ozone/decomposition/ozone-decomposition.htm; accessed 20 February 2013)

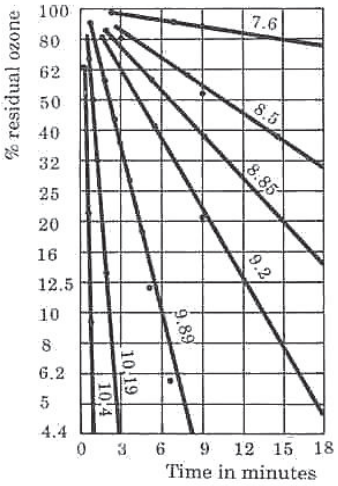


Figure 36: The rate of decay of ozone at 15°C with increasing pH (www.lenntech.com/library/ozone/decomposition/ozone-decomposition.htm; accessed 20 February 2013)

One concern with using ozone is if groundwater is high in bromide, as bromate will form which is a health concern (Rajagopaul *et al.,* 2008). In this study area, there is no bromide which would be of concern. Another concern is that over-ozonation of water with elevated Mn^{2+} could affect water quality by the remobilisation of soluble Mn^{4+}, which turns the water an undesirable pink colour (EPA, 1999). However, with time the soluble Mn^{4+} reduces to manganese (IV) oxide (EPA, 1999) and in this study it is improbable that there would be excess ozone in a natural system rich in organic carbon.

4.3 Options for Introducing the Oxidant into the Subsurface

Once ozone was selected as the oxidant for the pilot study the best means of introduction into the subsurface had to be considered. Traditionally, ISIR is achieved by oxygenation of the water and then the water is gravity-driven or pumped into the subsurface. The use of ozone allows for the injection to be either as a gas (*in-situ* ozone sparging) or as a liquid (*in-situ* ozonated water) (Figure 37).

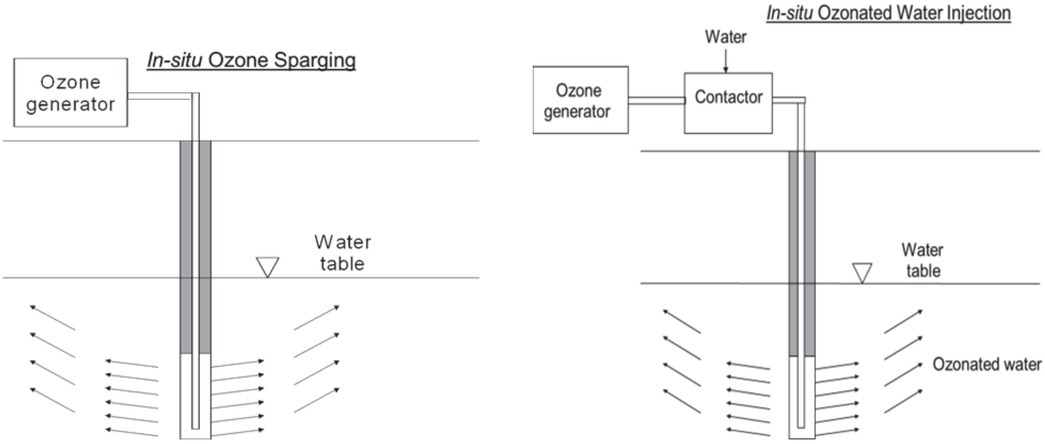


Figure 37: The two approaches considered for introducing ozone into the subsurface for ISIR (Masten, 2004)

The direct injection of gaseous ozone into the aquifer is achieved by using an ozone diffuser (e.g. ceramic porous 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, C., Wassertec, *pers comm.*, 2011). The diffuser works under water pressure and creates a gas bubble column which efficiently dissolves ozone into the water, whereby the water column and bubble size influences the efficiency of dissolved ozone in water (Lenntech, 2014). Sparging of O_3 has been successfully applied in the removal of hydrocarbon pollution in a sandy aquifer (e.g. Pavlik and Gwinn, 2005). However, this option was not found to be favourable in this study as the radius of influence and contact time with the Fe^{2+} and Mn^{2+} in the groundwater with dissolved ozone would be of a limited extent and would not achieve the desired effect needed. This too would require specific equipment that would increase the overall cost of the prototype; moreover the diffuser can easily clog up (Rajagopaul *et al.,* 2008), which would also increase undesirable O&M to the application.

The alternative option would be to dose the water with ozone gas before injection. The well-known process for dissolving ozone in water is through the use of a venturi (Figure 38), located at the pump whereby water is pumped through the high pressure inlet past a small orifice, which creates a vacuum at the suction port and draws in the ozone from the generator to dose the water (Sommerfeld, 1999). This system has greater than 90% ozone transfer efficiency with water and lower maintenance cost to diffusers (Rajagopaul *et al.,* 2008). Sommerfeld (1999) highlighted the need for regular cleaning with the treatment of iron-rich groundwater to avoid iron (III) oxide build up in the venturi.

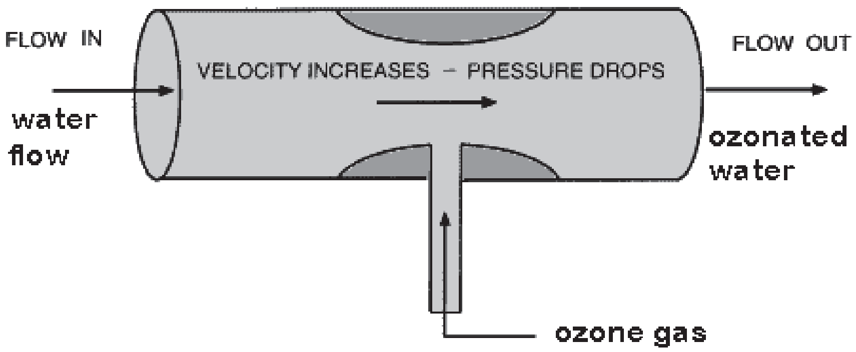


Figure 38: Venturi schematic on how the vacuum is created due to a differential pressure created with water moving from left to right through a conical body (www.lenntech.com/venturi.htm; accessed 3 January 2013)

4.4 Prototype Design and Construction

The use of ozone as the oxidant was based on the systematic elimination of other commonly used oxidants for removal of complexed Fe^{2+} and Mn^{2+} from SiO_2- and organic-rich groundwater. The ISIR prototype for this pilot test was manufactured by Wassertec. The ozone in this case study was produced from high purity oxygen gas generated on site from ambient air. The decision was taken to use high purity oxygen gas instead of air because oxygen gas almost doubles the ozone gas generation, which increases its solubility (EPA, 1999). The constructed system used a compressor to draw in air, which is passed through to the oxygen generator. High purity oxygen (> 93% O_2 at 5 ℓ/min) was then generated through the pressure swing adsorption process which removed nitrogen, carbon dioxide and water vapour from the compressed air (EPA, 1999). The ozone gas was then generated from high purity oxygen gas through a high-voltage electrical current in the corona discharge ozone generator (O_3 = 4 g/hr) (Wassertec, 2012). The oxygen and ozone generators are compact and were easily installed in the City of Cape Town's caravan making the system mobile and protected from direct sunlight or rain.

4.5 *In-situ* Iron Removal Design at the Study Site

The ISIR prototype was designed in such a way that water would be abstracted from G30966 at a depth of 23 mbgl and diverted at the modified air vent on the borehole mains through a lay-flat pipe into a 3 m^3 water tank where the groundwater was aerated through exposure to the atmosphere. A pump would then draw water from the tank through Polyvinyl Chloride (PVC) tubing and pump it through a venturi. The suction port of the venturi was connected to the ozone outlet of the ozone generator via 8 mm Teflon tube and when the water flowed through the venturi, the created vacuum that draws the ozone gas into the water. The ozonated water was then pumped into a PVC column where any excess or by-product gas was removed by a degasing valve fitted at the top of the column. The ozonated water was then pumped into the subsurface through PVC tubing to a depth of > 24 mbgl.

The depth of injection between 24 to 27 mbgl was selected according to the screen depth in borehole G30966 and because the water column would pressurise the ozone to remain in solution and not be lost to the atmosphere if injection were at depths < 6 m (Ansorge, C., Wassertec, *pers comm*., 2011). The ISIR prototype system was designed such that it could run continuously and required little maintenance, with periodic checking of the suction of the venturi, condition of the water pump, cleaning the air filter and operation of the cooling fans inside the ozone generator (Wassertec, 2012).

Ideally, the single production borehole approach would have been favoured for this study as it used the infrastructure optimally and reduced costs associated with drilling of injection 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 borehole, because of the high water table (1.5 mbgl July 2013) and because the borehole condition was unknown (due to lack of down-hole camera logging). This approach also allowed for new monitoring points which supplemented the analysis of the ISIR treatment, especially between the injection well-point(s) and the production borehole.

Twelve small-diameter boreholes, hereafter referred to as well-points, (Figure 39), were mud-rotary drilled and installed within an area of approximately 16 m radius around production borehole G30966, by Fairbrother Geotechnical Engineering cc. in January 2013. The positions of the well-points took into consideration the groundwater flow direction, T-value, available water supply from G30966 and nearby electricity supply for ozone generation. 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 shallower boreholes were drilled to be used as monitoring points of the water quality and aquifer conditions in the upper part of the aquifer.

Polyvinyl chloride pipe (pressure Class 6) was used for both the casing and screen material. The last 6 m of each well-point was screened, with 0.5 mm wide slots cut at an arc length of 69 mm into solid PVC casing by Fairbrother, giving an open area of approximately 5%. The screens is 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 slotted screen by couplers and stainless steel screws. The solid and screened sections of the borehole are 63 mm outside diameter surrounded by approximately 48.5 mm thick gravel pack of 10/30 grade. No pumping tests were performed on the well-points due to their small diameters.

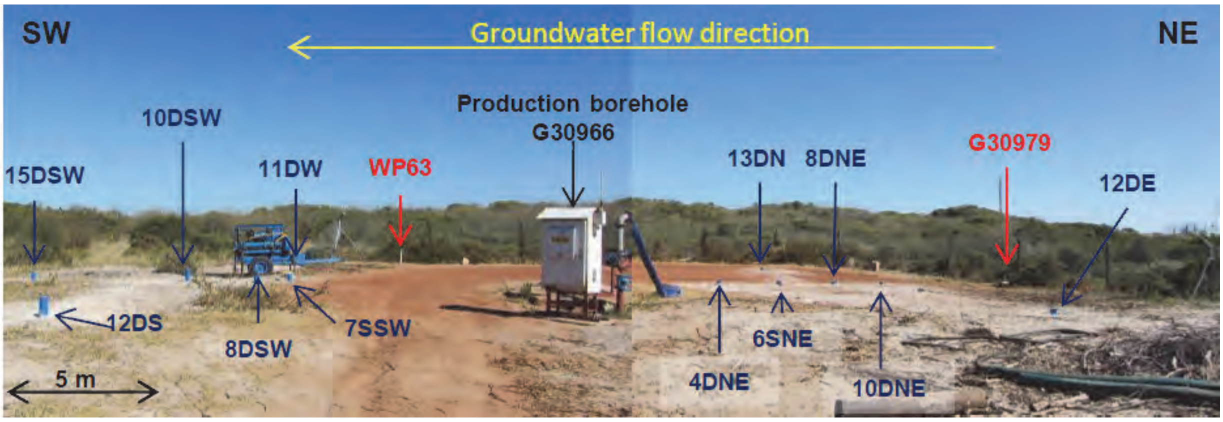


Figure 39: Location of the newly drilled well-points (labelled blue) in close proximately to G30966 (labelled black), G30979 and WP 63 (labelled red)

The use of ozone-resistant material such as stainless steel casing and Teflon tubing is preferable when working in direct contact with ozone gas (Pavlik and Gwinn, 2005). However, with this short-term project the use of PVC would be acceptable as it reduces the costs significantly (e.g. 1 m of 8 mm Teflon tubing cost R75.00 in 2012).

Unfortunately, due to the drilling rod used in the mud rotary drilling process, only 3 m interval samples could be collected. The recording of the depth from which the sand samples were collected was also compromised due to the recirculation of the drilling fluid with slurry, which contains sands from previously drilled well-points. However, where possible the sand was described and depths of calcrete lenses noted. The Sandveld Group sands were only intersected as all indications were that the weathered Malmesbury bedrock would only be interested much deeper, as its depth at the site is > 34 mbgl. The sands were found to be fine to medium-grained and iron-staining on the sand grains was absent. A number of calcrete lenses were intersected in every drilled well-point. They were concentrated in the upper 12 m of the drilled sands, which would be representative of the Witzand Formation. The Marine Division of the CGS conducted the elevation survey of the study area and recorded the co-ordinates of the newly drilled well-points. The ground survey was plotted and showed that surface elevations at the study site are relatively flat (54-55 mamsl; Figure 40).

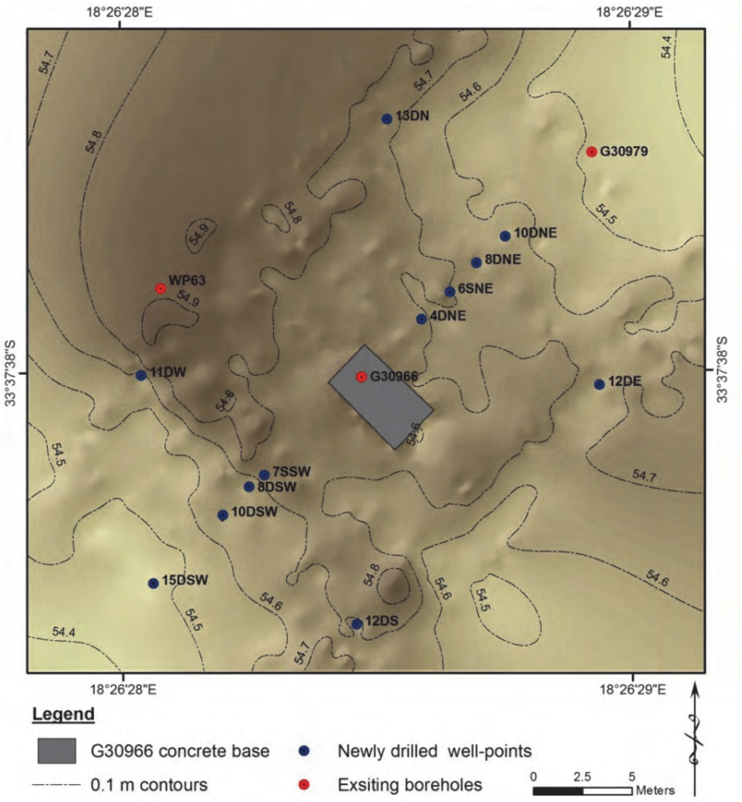


Figure 40: The study site elevation map showing the location of the newly drilled 12 well-points in relation to G30966

4.6 South African Legislation and Regulatory Requirements

This pilot test study planned at the Atlantis Aquifer included two activities that required consultation with South African legislation for authorisation.

4.6.1 Drilling of injection well-points

No listed activities under NEMA were triggered by the drilling of well-points in close vicinity of the production borehole G30966. However, an environmental method statement document was requested by the Environmental Resource Management Department of the CCT concerning the drilling and installation of the well-points. A method statement was prepared according to the requirements outlined in the Standard Environmental Specifications for controlling the impacts on the environment from permanent construction activities (CCT, 2007) and was approved on 23 October 2012. In addition, registration on Department of Water Affairs' (DWA) National Groundwater Archive of the twelve well-points used for this study was required. The registration of all the well-points on the National Groundwater Archive was completed on 29 November 2013 (Lambani, A., DWA, *e-mail communication,* November 2013).

4.6.2 *In-situ* iron removal by ozonated water

Regulatory requirements for *in-situ* treatment methods are not specifically covered under South African law but such treatments are subject to stipulations in the NWA and the NEMA (Tredoux *et al.,* 2004). Prior to the injection test, the relevant environmental and water legislation was considered for the application of ISIR by ozonated water. The outcome was that no listed activities were triggered in terms of NEMA, however in terms of the NWA two water use activities were flagged under Section 21, which included:

- 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 and to satisfy the terms of the general authorisation a presentation/meeting and report was submitted to DWA. Permission was granted on 5 June 2013 to initiate with injections tests as the water use activities form part of the existing water use licence of the CCT (Derril, D., DWA, *e-mail communication,* 2013). 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 (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 South Africa's Occupational Health and Safety Act (Act No. 85 of 1993) or the National Environmental Management: Air Quality Act (Act No. 39 of 2004) with respect to airborne ozone concentrations. The project team therefore used the guidelines by the USA 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). The project team has taken this into consideration and the by-product gases containing ozone were released into the atmosphere outside, which maintains the safety of the personnel working in the area.

5 ASSESSMENT OF *IN-SITU* IRON REMOVAL EFFECTIVENESS

5.1 Introduction

This chapter discusses the pilot test studies using the ISIR prototype at the investigated production borehole G30966 with focus on the immediate effectiveness in reducing the Fe and Mn in the abstracted groundwater. The concentrations desired in the abstracted groundwater after ISIR treatment is based according to threshold concentrations by Walter (1997) and WHO (2008) i.e. Fe and Mn ≤ 0.1 mg/ℓ. At such threshold concentrations potential health, aesthetical, and production borehole clogging problems are significantly reduced and is implemented by the Netherlands water company Vitens for their ISIR threshold standard (e.g. Hinkamp *et al.,* 2004; van Halem, 2011).

The project initially proposed to also evaluate the "long-term" effect (≤ 1 year) of the ISIR treatment on the study production borehole and surrounding aquifer. This would have been achieved by camera logging of the borehole G30966 before and after ISIR treatment to provide a visual insight of the borehole condition and evaluate if any change on the interior of the borehole was identified. In addition, a step drawdown and CDT pumping test, following the same procedure as in the preliminary evaluation, would have been conducted at the end of a year of treatment to compare the aquifer response (i.e. T-value) and borehole efficiency. However, the long-term effectiveness of the ISIR treatment could not be determined during the project timeframe.

5.2 Methodology

The injection tests were initiated from the 3 July 2013 and completed in 18 October 2013. The first injection methodology applied followed that of Hallberg and Martinell (1976) protocol. However, when put into application, modifications to the ISIR prototype and injection methodology had to be made to adapt to site conditions. In addition, due to adverse weather conditions, malfunction of monitoring equipment, logistical issues (e.g. time consuming water chemistry analyses) and electricity cuts at the site, the pilot tests were conducted irregularly over the three month period. The longer continuous injection runs that were envisaged for attaining a low steady-state Fe and Mn concentration in the abstracted water could not be realised. In total twenty-six days of injections were conducted, with three noteworthy changes to the original methodology. To evaluate the effectiveness of the treatment the following data was collected during the injection tests.

Groundwater samples from G30966 were collected before the start of the injection tests on the 1 July and 3 July 2013 to establish the baselines groundwater quality. Subsequently G30966 was sampled periodically to evaluate the effect of the treatment on the groundwater chemistry. The sampling followed the standard protocols outlined in Weaver *et al.* (2007), whereby the unfiltered samples were collected in 1 ℓ glass sample bottles that were correctly prepared before sampling and rinsed three times before filling from the sampling tap. The parameters analysed for were selected according to ISIR case studies and a review of G30966 historical water chemistry, which included: pH, EC, total alkalinity, Ca, Mg, K, Na, Cl, SO_4, total and dissolved Fe and Mn, F, Si, Sr, NO_3 + NO_2 , total organic carbon (TOC) and DOC. The dissolved Fe and Mn concentrations were determined on 0.45 µm syringe-filtered (i.e. pressure filtered) samples collected at the same times as the unfiltered sample. No preservatives were added to the water samples. The water analyses were completed by either Scientific Services or CSIR laboratory; both are accredited testing laboratories according to the South African National Accreditation System.

The pH, DO and EC parameters were measured in the field during the injection tests on water from G30966, injected water, and at monitoring well-points. The measurements were done using an Extech Model DO700 meter and the respective probes. The pH was measured using an Extech pH305 glass pH electrode, the DO by the Extech's DO705 permeable membrane electrode and the EC605 polymer conductivity cell. All three of the probes are equipped with a temperature sensor and calibrated before each day of testing. Measurements were taken at G30966 by connecting a flow-through cell to its sampling tap and in the monitoring well-points at the screen depth by lowering a submersible pump connected to the flow-through cell. Readings were taken after the measurement had stabilised. The Milwaukee Martini pH and EC meters from DWA and a Criston DO meter from the CSIR were used when the project team's Extech meter was in for repairs. The dissolved ozone concentration was also measured in the injected water by means of the Hach® ozone test kit, which is a colorimetric method using DPD Total Chloride reagent. The water level and temperature were also measured at depth by the CSIR's Solinst dataloggers installed in G30966, the injection borehole, and monitoring boreholes during the injection runs.

5.3 Results

5.3.1 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. Both analyses passed the electro-neutrality test and is given in Table 7, which is compared to the mean value calculated from the 2013 pumping tests results and SANS (2011) drinking water standards. Comparison with the pumping test results is to evaluate whether there were any significant changes in water quality in the last three months from July onwards and to see if there is any parameter of concern according to SANS (2011) drinking water standards. The baseline data collected in July 2013 shows the same water type to the pumping test average which is a Na-Ca-HCO_3 water type (Figure 41). The water quality abstracted from G30966 is of a good standard according to SANS (2011).

Table 7: Baseline groundwater quality collected before injection tests compared to 2013 pumping test mean values and SANS (2011)

Parameter	**1 July**	**3 July**	**2013 pumping test mean (*n* = 4)**	**SANS (2011)**
EC (mS/m)	67.4	68.4	68.5	≤ 170
pH	7.8	7.7	7.7	5 ≤ x ≤ 9.7
Ca	46.7	47.6	47.1	
Na	74.7	78.4	80.7	≤ 200
Mg	9.7	8.4	8.2	
K	6.8	7.6	7.7	
Total alkalinity (as $CaCO_3$)	159.3	162.1	159	
Cl	103.0	106.0	106	≤ 300
SO_4	33.1	31.0	29	≤ 250
Nitrate + Nitrite (as N)	0.60	0.44	0.1	≤ 0.9
Total Fe	2.96	2.15	0.5	≤ 2.0
Dissolved Fe	2.24	n.m.	n.m.	
Total Mn	0.49	0.26	0.2	≤ 0.5
Dissolved Mn	0.41	n.m.	n.m.	
SiO_2	4.1	4.5	4.5	
Sr	0.46	0.48	0.5	
F	0.34	0.27	0.2	≤ 1.5
DOC	5.0	5.5	8.7	< 10*
Data given as mg/ℓ unless otherwise specified; n.m. not measured * for total organic carbon (TOC) but can be used for DOC limit as TOC ≥ DOC				

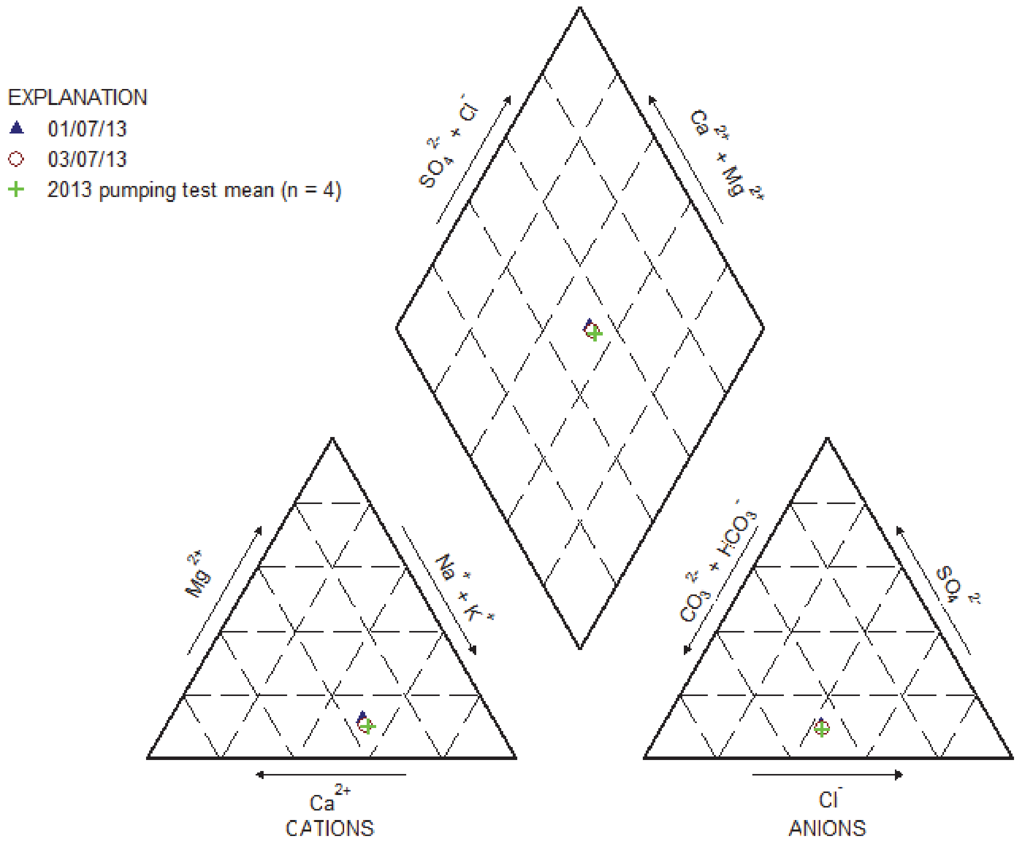


Figure 41: Piper diagram of the major ion composition of G30966 baseline water samples collected in July 2013 and mean values of the earlier 2013 pumping tests results

The Fe and Mn concentrations in groundwater abstracted from borehole G30966 vary significantly according to how well the borehole was purged before the sample was taken. The longer pumping of the borehole provided accurate Fe and Mn concentrations from the aquifer, while the shorter pumping rates show elevated concentrations of Fe which are associated with the accumulation in the borehole. The concentration variations are of greater significance in Fe, mainly because Fe concentrations are higher in this study area. This is evident in G30966 samples with the total Fe value from 1st July 2013 and 3rd July 2013 being almost four times greater than amounts found after the pumping tests (Figure 42). Since G30966 has been taken out of operation since December 2012 and had not been used in the months before the injection tests, the higher Fe and Mn concentrations in the sample are due to iron-rich water and sloughed off iron (III) oxide deposits in the borehole rather than representative of the native groundwater in the aquifer. The 1st July value is higher than the 3rd July due to the slower pumping rate the sample was taken at.

The baseline EC, pH, temperature and DO were also measured in the field in 10DNE (at screened depth) and G30966 on the 3 July 2013 and gave EC between 66-68 mS/m and pH from 7.5 to 7.9, which correlate with the laboratory measurements. The DO measurements in both boreholes gave 0.4 mg/ℓ at 18°C.

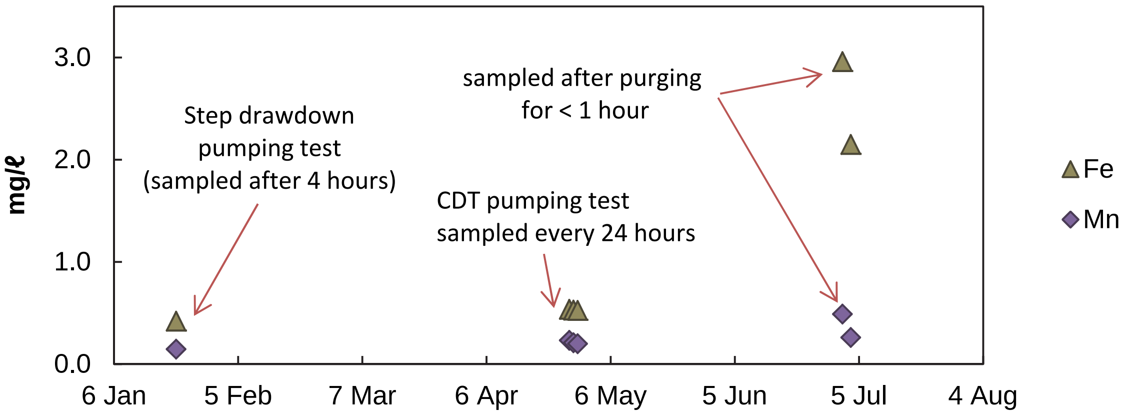


Figure 42: Variation in measured Fe and Mn concentrations in G30966 according to how well the borehole was purged before a sample was collected in 2013

5.3.2 First injection technique

The first methodology applied at the study site followed the procedure outlined by Hallberg and Martinell (1976) for the Vyredox method which included the following steps:

- Abstraction of groundwater from G30966 to fill the 3 m^3 storage tank while allowing the water to splash on the baffle balls for aeration (Figure 43).
- Abstraction from G30966 was stopped once the tank was full and kept switched off during the injection phase.
- The groundwater to be injected was then further aerated by recirculation in the water tank (up to 30 minutes) to remove further uncomplexed Fe^{2+} and Mn^{2+} and any undesirable gases (e.g. H_2S, which could be smelt during abstraction) that would interfere with the enrichment of ozone (Figure 44).
- The aerated water was then drawn from the storage tank past the venturi to be dosed with ozone (Figure 45).
- The ozonated water was pumped into the aquifer by in a nearby well-point to create an oxidation barrier near the production borehole.

Figure 43: Aeration of the abstracted water from G30966 was achieved by splashing the water onto the baffle balls as it entered the water tank

Figure 44: The water in the tank was further aerated by running the motor-driven pump where water was drawn from the base outlet through the yellow pipe (left) to the top outlet, which increased the exposure to the atmosphere (right)

Figure 45: The initial injection technique set-up

The injections were initiated in 10DNE as it was hydraulically up gradient of G30966 and there were three monitoring points between itself and the production borehole (each distanced 2 m apart), which would assist in identifying any changes in the DO, pH and EC. However, the first three injection attempts encountered operational difficulties due to the prototype set-up. This was identified by the continuous bubbling and overflow of water from the injection well-point (Figure 46), including poor penetration into the aquifer (injection rate < 1.4 m^3/hr), which was noted by little change in the monitored groundwater levels (Figure 47). In the aim to prevent surfacing of the injected water, the rate of injection was reduced but this decreased the amount of ozone dosed into the injected water due to the decrease in differential pressure in the venturi (i.e. dissolved ozone = 0.1 mg/ℓ).

Figure 46: The project team struggling to get the injected ozonated water into the aquifer due to the bubbling and overflow from the injection well-point

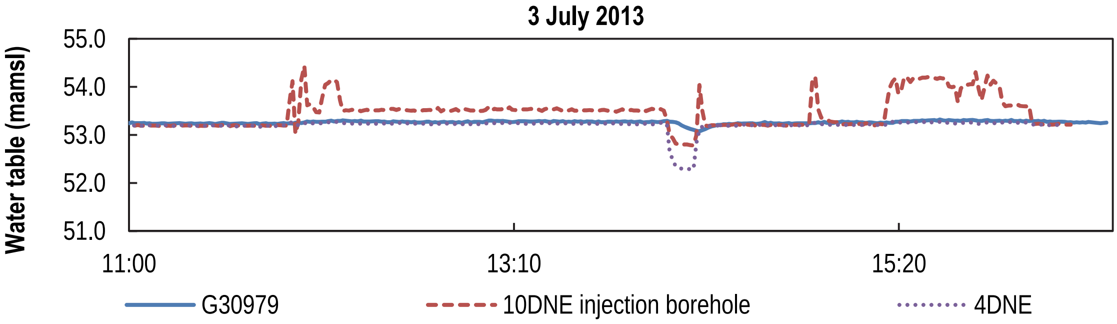


Figure 47: Groundwater level response in the injection well-point and two monitoring boreholes shows that a rise in groundwater occurred only in 10DNE. The drawdown observed was due to pumping at G30966 to fill up the water tank for a second injection run for that day.

In addition, the field parameters measured in 8DNE (2 m down gradient from injection) during the first two injection tests showed no significant variation in the measured EC, pH and DO as a result of injection compared to the baseline data (Table 8).

Table 8: Field parameters in 8DNE during the injection tests sampled at screened depth

	EC (mS/m)	**pH**	**DO (mg/ℓ)**	**Temperature (°C)**
3 July 2013	58	7.7	0.48	19
4 July 2013	57	7.5	0.44	19

5.3.3 Second injection technique

It was acknowledged that the entrained gas bubbles in the injected water prevented that a sufficient injection rate into the well-point and aquifer could be attained and modification to the first prototype design was required. This was readily resolved by the inclusion of the degas column between the pump and the injection pipe. The ozonated water was pushed into the degas column where any ozone and by-product gases in the water are released at the top of the column by an ozone-rated de-gas valve (Figure 48). The exclusion of the degas column was initially done to maintain as much dissolved ozone and oxygen in the injected water when introduced to the aquifer.

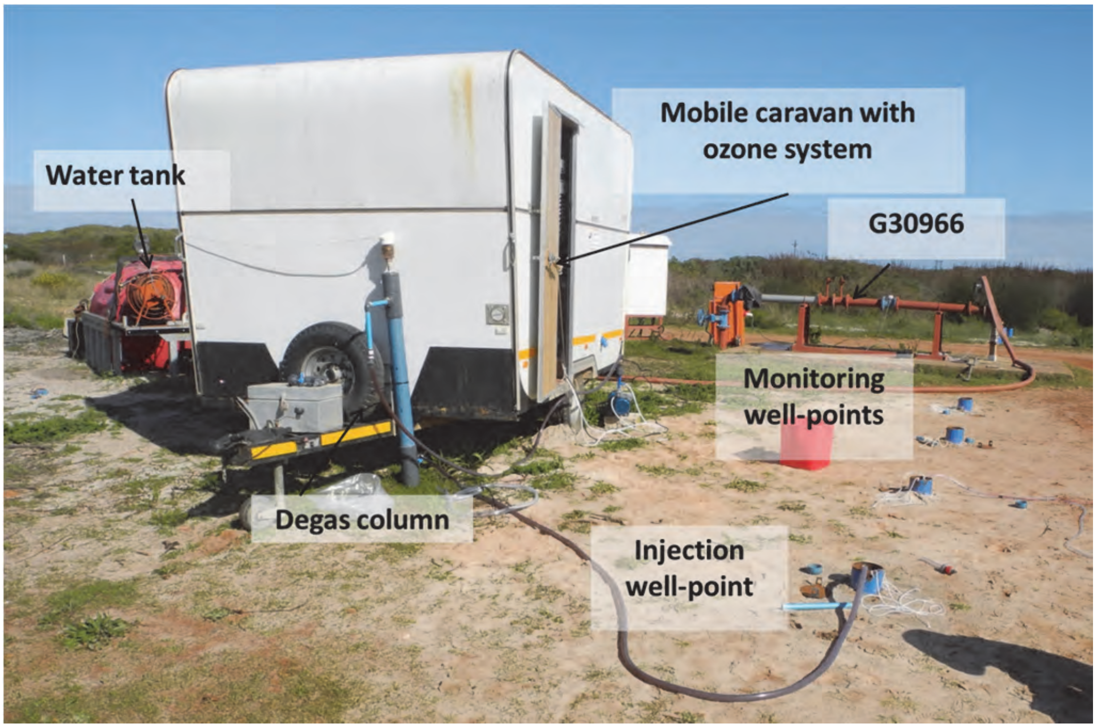


Figure 48: The modified experimental set-up of the ISIR at the study site after the first attempt

From 16 July through to 2 August, a total of 18 injection runs (where 3 m^3 is the volume per injection run) were carried out at well-point 10DNE at the screened depth of ~27 mbgl. This followed the stop-start approach, where groundwater was abstracted from G30966, directed to the water tank and aerated, drawn by a pump through a venturi where it was ozonated, passed through the degas column and then injected into the injection borehole at depth. From the injections the following information was determined:

- The injection runs were performed at an average rate of 1.8 m^3/hr which was calculated from the average time taken to empty the 3 m^3 water tank and between 6-9 m^3 was injected per day.
- A rise in water level was only seen in the injection borehole and over the course of July the high rainfall raised the groundwater table, which caused lowering of the injection rate when surfacing of the injected water occurred (Figure 49).

- The clear PVC injection pipe discoloured and became opaque over time due to the iron (III) and manganese (IV) oxide precipitation with the subsequent injection runs.

- The dissolved ozone in the injected water ranged between 0.3 to 0.5 mg/ℓ (average 0.4 mg/ℓ) and the DO in the injected water was always greater than 10 mg/ℓ with an average concentration of 14 mg/ℓ and the pH and EC in the injected water did not change considerably from the baseline values after ozonation (Figure 50).

- The total Fe and Mn concentrations in G30966 remained above the baseline and threshold concentration (Figure 51 and Figure 52). However, an overall decline was seen in both the Fe and Mn concentrations with successive treatments. Two measurements taken on 29 July before and after treatment showed an increase in both Fe and Mn during treatment, which is attributed to the oxidation of the Fe and Mn not having sufficient time to run to completion and precipitation of the oxides to remain in the subsurface but were drawn along with the abstracted water.

- Four full water samples were collected during this period and the results showed that the majority of the parameters did not deviate from the baseline chemistry (Table 9). The DOC was the only parameter found to decrease while F doubled and Mg and SO4 were found slightly higher than the known mean. The decrease in DOC could be attributed to the oxidation by the dissolved ozone and DO, while the increase in Mg could be due to the mobilisation of Mg due to the pH buffering caused by the acidifying oxidation of the Fe, Mn, DOC and sulphides in the subsurface. The SO_4 increase could be due to oxidation of sulphides in the subsurface or possibly the prevention of sulphate reduction due to the increase in redox potential due to the increased DO. It is unknown why the F values would be doubled as it is expected from case studies that F would decline with successive treatments (e.g. van Halem, 2011) and could have been an analytical error in the laboratory analysis.

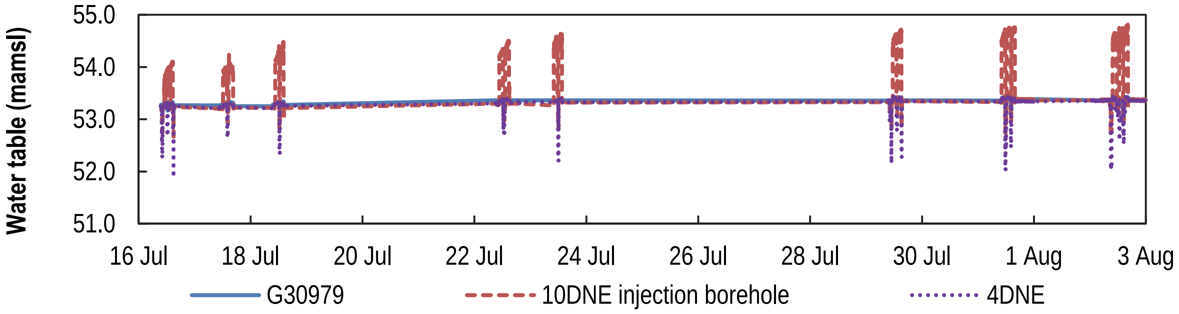


Figure 49: The water table elevation in the injection borehole and two monitoring boreholes again showing that only the injection borehole water table increased with injection

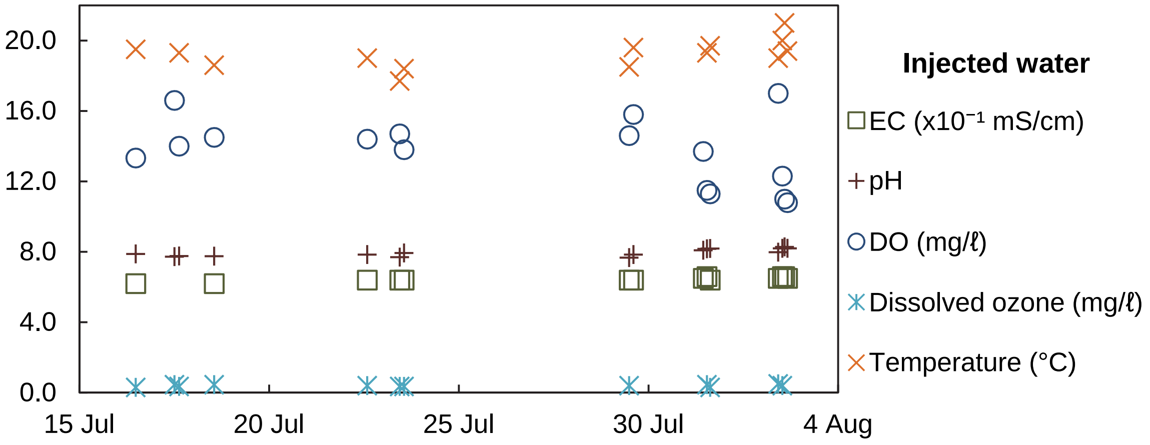


Figure 50: The EC, pH, DO, dissolved ozone and temperature measurements in the injected ozonated water

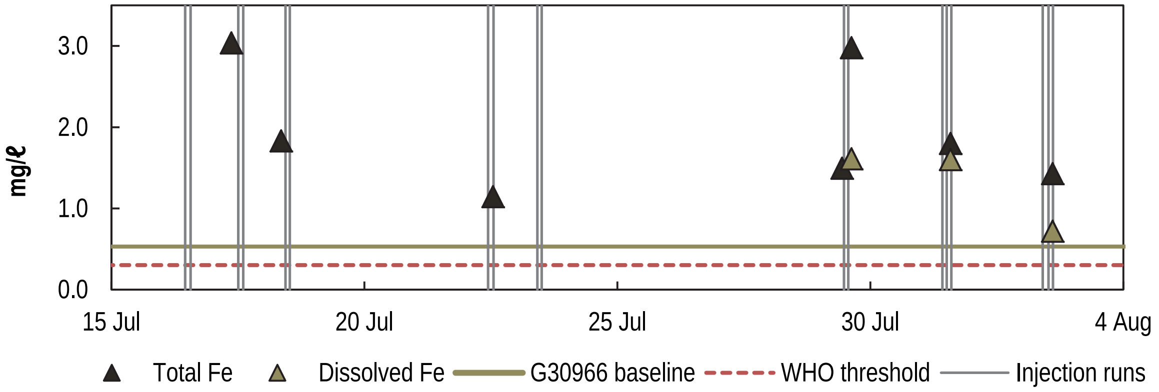


Figure 51: Iron concentrations in G30966 during the injection tests showed a decrease with successive injection runs but remained above the baseline and threshold concentrations

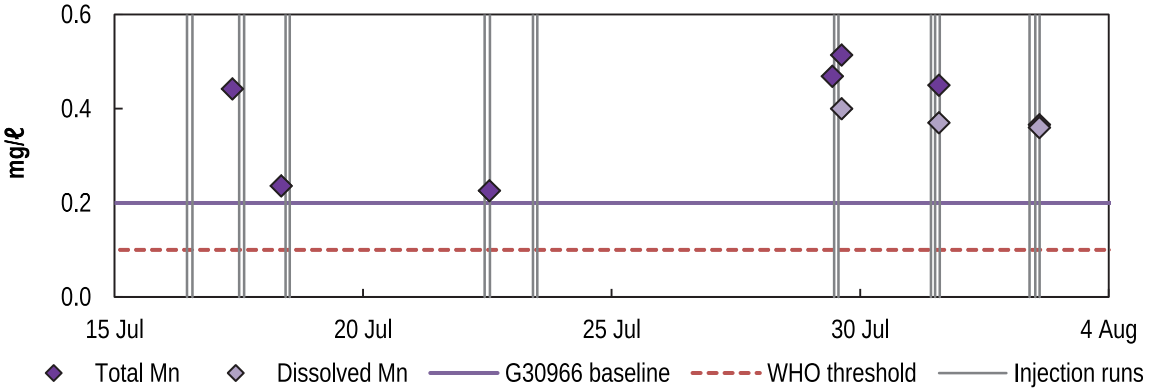


Figure 52: Manganese concentrations in G30966, showed a similar trend to Fe, but also had concentrations above the baseline and threshold concentrations

Table 9: Groundwater quality during the injection tests compared to 2013 pumping test mean and SANS (2011) values

Parameter	**17 July**	**18 July**	**22 July**	**29 July**	**2013 pumping test mean (*n* = 4)**	**SANS (2011)**
EC (mS/m)	70	70	70	67	69	≤ 170
pH	7.7	7.6	7.7	7.7	7.7	5 ≤ x ≤ 9.7
Ca	47	48	46	49	47	
Na	79	83	80	78	81	≤ 200
Mg	10	10	10	10	8	
K	8	8	8	8	8	
Total alkalinity (as $CaCO_3$)	161	160	161	161	159	
Cl	107	107	105	99	106	≤ 300
SO_4	31	29	31	36	29	≤ 250
Nitrate + Nitrite (as N)	0.1	0.1	0.1	0.1	0.1	≤ 0.9
SiO_2	4.5	3.9	4.7	4.6	4.5	
Sr	0.5	0.5	0.5	0.4	0.5	
F	0.4	0.4	0.4	0.4	0.2	≤ 1.5
DOC	4.9	5.2	5.5	5.0	8.7	< 10
Data given as mg/ℓ unless otherwise specified.						

5.3.4 Third injection technique

Following the findings of previous attempt, the technique was modified as no significant changes in Fe and Mn in G30966 were observed and it was recommended to inject into 4DNE, 4 m up gradient of G30966. The injection attempts were planned to run for a full week from 5 August however, electricity cuts prevented this but from 26 to 30 August a full week (5 days of injections) took place. From the 19 injection runs (3 m^3 per injection) the following conditions were found:

- The average injection time to empty the water tank while injecting in 4DNE was 99 minutes, similar to the rate in the previous injection attempts. Similar to the previous injection test in 10DNE, no significant water table changes were observed in the monitoring boreholes but the groundwater table rose in the injection borehole (< 0.5 m).
- The dissolved ozone in the injected water gave the same concentration range (i.e. 0.3-0.5 mg/ℓ) and average (i.e. 0.4 mg/ℓ) as previously found and the DO continued to be above 10 mg/ℓ with a higher average of 18 mg/ℓ found than the previous methodology (Figure 53). This was ascribed to the injected water being recirculated for 30 minutes before each injection while the previous methodology had some injections with no recirculation due to logistical issues. The EC, pH and temperature measured in the injected water remained similar to the previous results. The Extech pH probe broke on 28 August resulting in the limited measurements during that injection phase.

- In comparison to the previous tests the DO in G30966 abstracted water increased with successive injections to 2.5 mg/ℓ after third day of injection and 3.5 mg/ℓ at the end of five days of injecting between 6 and 9 m^3 of ozonated water per day, which is significantly greater than the baseline concentration. In addition, with no significant changes in the water pH and EC in abstracted water from G30966 (Figure 54).

- In both successive injection runs the Fe concentrations steadily decreased (Figure 55) but the Mn concentration increased in the 5 and 6 August samples (Figure 56). The total and dissolved Fe and Mn concentrations remained above the baseline and desired threshold concentration of ≤ 0.1 mg/ℓ. This could be attributed to the 4 m distance between the injection well-point and the production borehole, which was too short a distance for sufficient contact time for sufficient oxidation and precipitation of the oxides in the subsurface.

- Full chemistry analyses for the last injection run showed that no significant changes in the water quality occurred as a result of injection of 36 m^3 over 5 days (Table 10). The same trends in decline in DOC, Mg, SO_4, F and a marginal increase in nitrate and nitrite measurements was also observed, which could be attributed to the oxidation of a possible nitrogen-containing compound in the DOC.

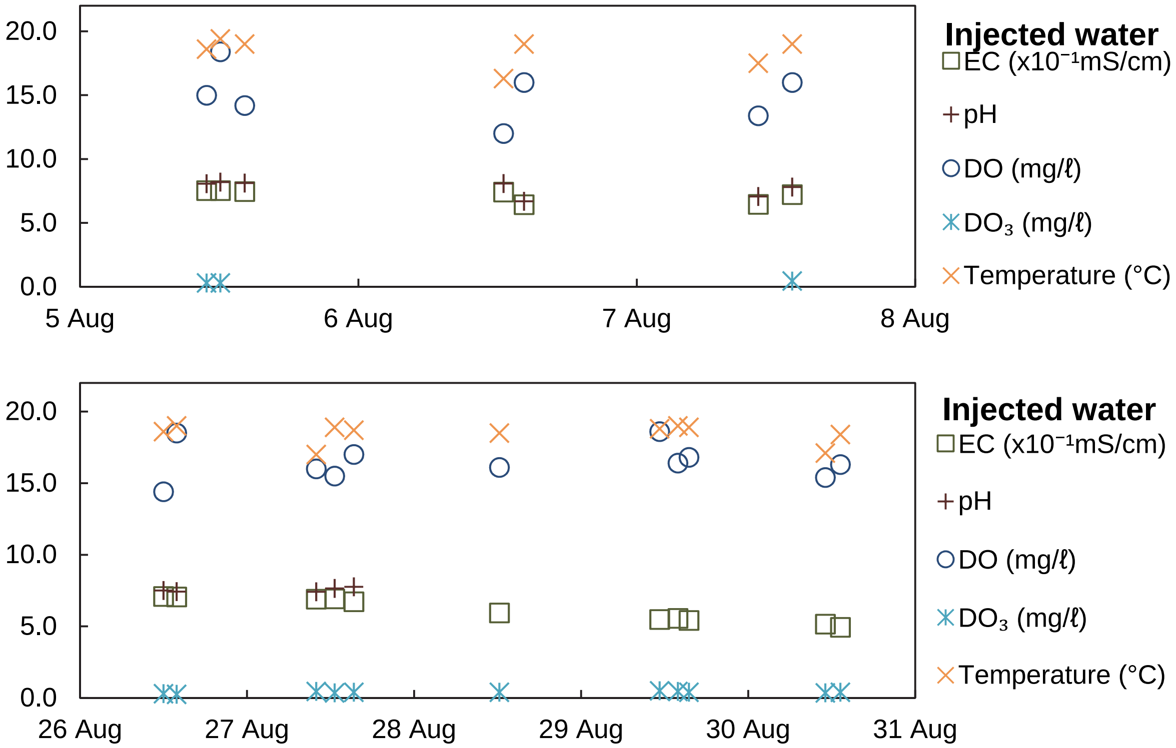


Figure 53: The field parameters measured in the injected ozonated water over the two attempts applying the third injection methodology

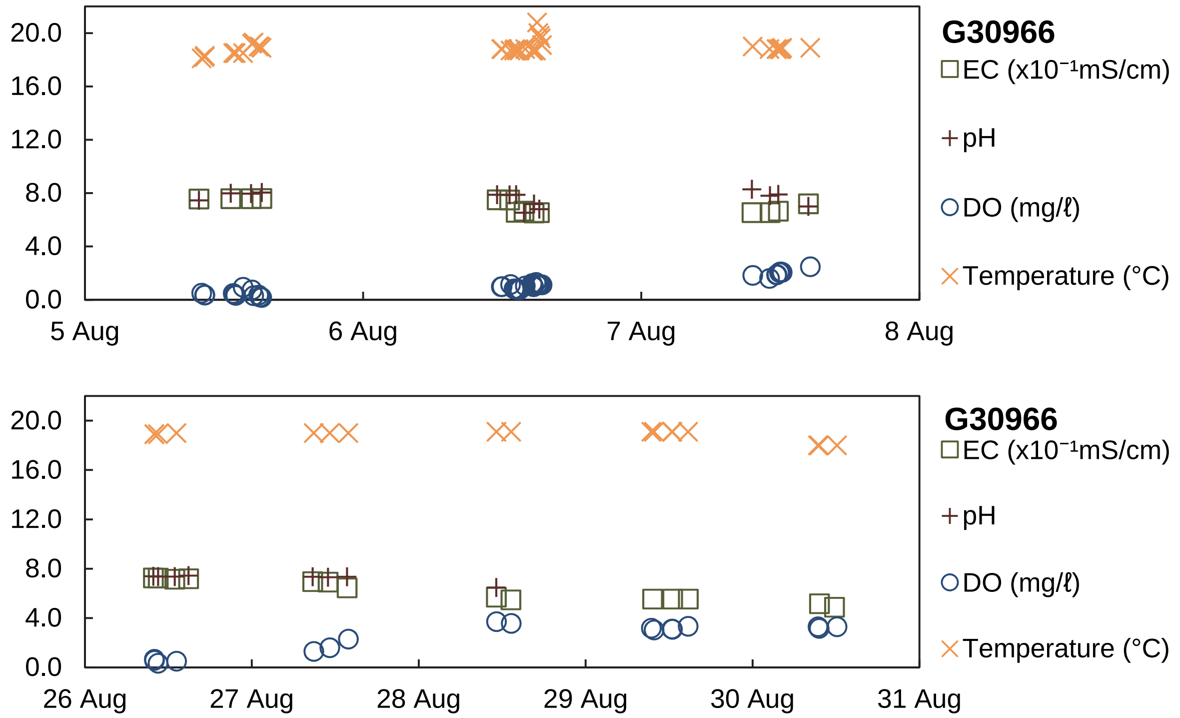


Figure 54: The EC and pH values remained the same in G30966 with injections but in both cases DO steadily increased from the baseline concentration with successive injection days

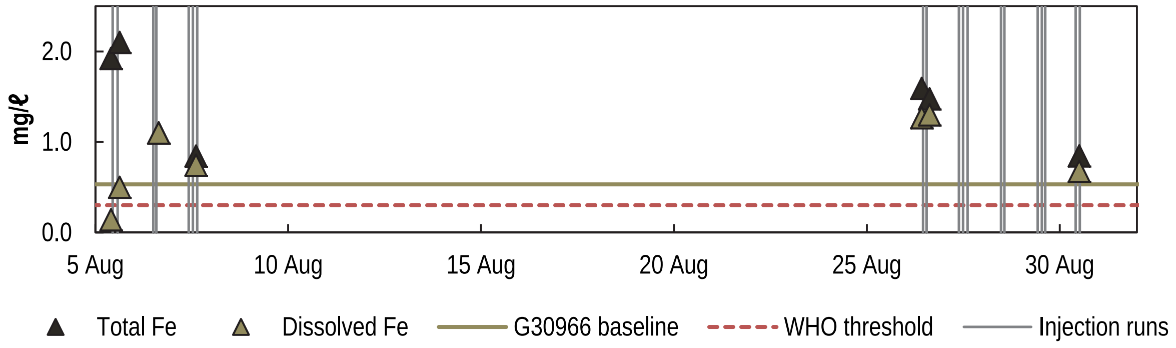


Figure 55: Iron concentrations in G30966 showed a decrease with successive injections, however concentrations still above the baseline concentration

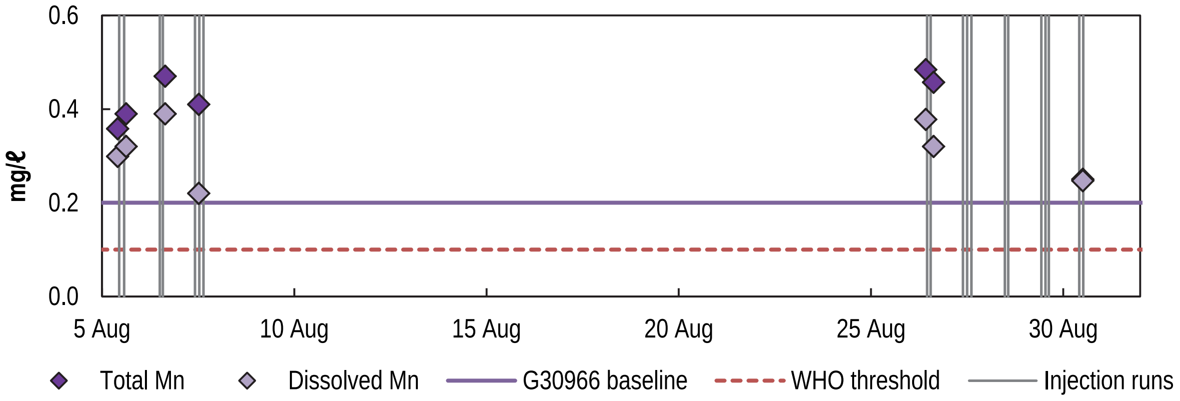


Figure 56: Manganese concentrations in G30966 showed an increase in the injection runs between 5 and 6 August, while the later injection phase showed a decrease with successive injections, although the concentrations are still above the baseline concentration

Table 10: Groundwater quality during the injection tests from 26 to 30 August 2013 compared to 2013 pumping test mean and SANS (2011)

Parameter	26 August 10:00	26 August 15:00	30 August	2013 pumping test mean	SANS (2011)
EC (mS/m)	68	69	68	69	≤ 170
pH	7.7	7.6	7.6	7.7	5 ≤ x ≤ 9.7
Ca	48	49	48	47	
Na	79	81	80	81	≤ 200
Mg	10	10	10	8	
K	7	7	8	8	
Total alkalinity (as $CaCO_3$)	159	158	161	159	
Cl	98	99	108	106	≤ 300
SO_4	40	38	33	29	≤ 250
Nitrate + Nitrite (as N)	0.3	0.5	0.5	0.1	≤ 0.9
SiO_2	4.6	4.5	4.3	4.5	
Sr	0.4	0.4	0.4	0.5	
F	0.4	0.4	0.3	0.2	≤ 1.5
DOC	6.0	n.m	5.1	8.7	< 10
Data given as mg/ℓ unless otherwise specified. n.m. not measured					

5.3.5 Fourth injection technique

From the chemical analyses from the previous two methodologies, it was suggested that the stop-start operation of G30966 could be attributing to the unanticipated high Fe and Mn concentrations. Therefore the continuous pumping of G30966 while injecting in 4DNE was proposed to test the hypothesis. This revised methodology was attempted from 15 to 18 October where injection continued in 4DNE for an average of 332 min/day. It was assumed that the injection rate was 1.82 m^3/hr so it can be estimated that at least 10 m^3 of water was injected per day. A lay-flat pipe was connected to the overflow at the water tank which directed any excess abstracted water a distance of more than 60 m from the study site so that no local artificial recharge of the water occurred. There was no recirculation of the abstracted water possible due to the new set-up so aeration was limited to the splashing of the abstracted water onto the baffle balls as it entered the water tank.

From the water chemistry and field parameters the following was found:

- The DO concentration in the injected water ranged within 12 to 14 mg/ℓ the average dissolved ozone concentration was 0.3 mg/ℓ, which could be due to the abstracted water not degassed as sufficiently before ozonated.

- Similar to the 26 to 30 August injection run, the DO in G30966 steadily increased with successive injections over the four days (Figure 57). However, the DO in G30966 did not reach the same high concentrations as during the previous technique attaining a maximum of 1.35 mg/ℓ, which is significantly higher than the natural level of 0.4 mg/ℓ. The two possible reasons for lower DO with successive runs is (1) lower DO in the injected water and (2) the abstraction causes a cone of depression around the borehole therefore drawing water in water from all sides and thus ‘diluting’ the DO from the injected water. Although lower DO concentrations were found, the results still show that there is residual DO measured in the abstracted water from G30966 after the injection test was completed and a rest period of approximately 18 hours followed before the next injection run commenced. The lower concentrations found for the last day of injection (18/10/2013) was due to the shorter injection run.
- In addition to the field EC and pH measurements, water sample for EC, pH and total and dissolved Fe and Mn laboratory analyses taken in the morning after sufficient purging of the borehole and then every hour during the injection run. The EC and pH of the abstracted water remained constant throughout the treatment (Figure 58). Both the dissolved and total Fe and Mn showed a declined with the successive ISIR treatment (given in Figure 59 and Figure 60). The dissolved Fe concentration also become the dominate form of Fe measured in the injected water with time, which could be indicative of the natural dissolved Fe levels in the aquifer being samples, through the continuous abstraction, rather than the spurious high colloidal Fe (i.e. the difference between total Fe and dissolved Fe) measured in the initial injection runs. The removal efficiency is better seen in the Fe concentrations, which were found lower than the baseline concentration and WHO (2008) threshold (i.e. < 0.3 mg//ℓ) by the end of the week of treatment but still not at the clogging threshold of < 0.1 mg/ℓ. While the Mn concentrations also initially decreased with Fe but remained at ~0.3 mg/ℓ after the second day of treatment, which is still greater than the desired WHO (2008) ad Walter (1997) threshold concentrations of 0.2 mg/ℓ and 0.1 mg/ℓ, respectively. The dissolved Mn concentration was always found to be the dominate form making up the total abstracted concentration, which indicate that its process in clogging of the borehole is not as significant as the Fe, generally because it is found at a lower concentration to Fe. The lower removal efficiency in Mn compared to the Fe in groundwater with a pH = 7-8 is expected as Fe^{2+} oxidation is faster than Mn^{2+} at near-neutral pH and the Mn removal is only effective at pH greater than 8.5 as described in case studies in the literature (e.g. El Araby *et al*., 2009). Since Mn requires a longer contact time with an oxidant in comparison to Fe, the 4 m path between injection well-point and abstraction borehole also contributed to the lower removal efficiency.
- Two 1 ℓ samples were collected on 15 October before injection and 18 October 2013 after treatment was complete to compare the water quality changes as a result of the treatment, but the 18 October sample showed inaccuracies in a number of the major ion parameters analysed

for and could not be reanalysed so no further discussion into the water quality could be achieved.

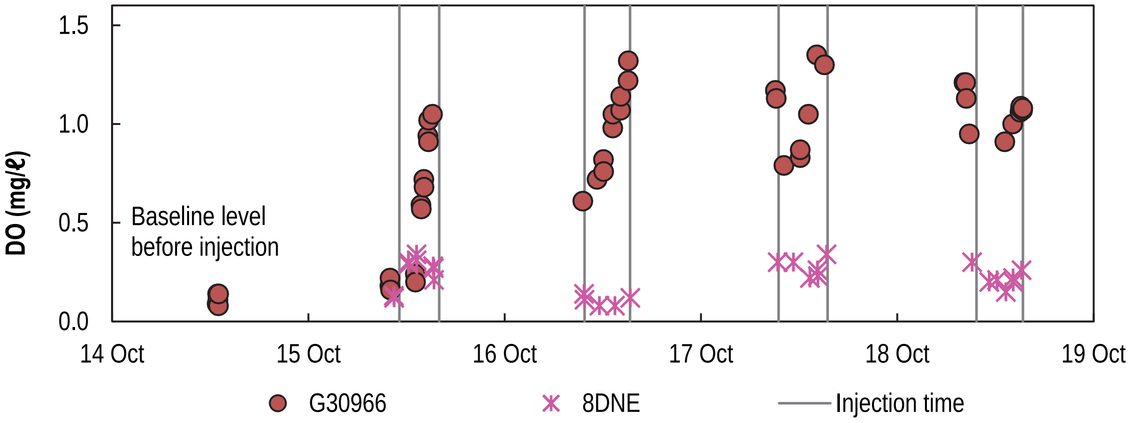


Figure 57: The DO in G30966 increased significantly from the baseline concentration during the continuous injection-abstraction technique, while 8DNE remained below the natural DO (the vertical lines indicate the starting and end times of the injection runs)

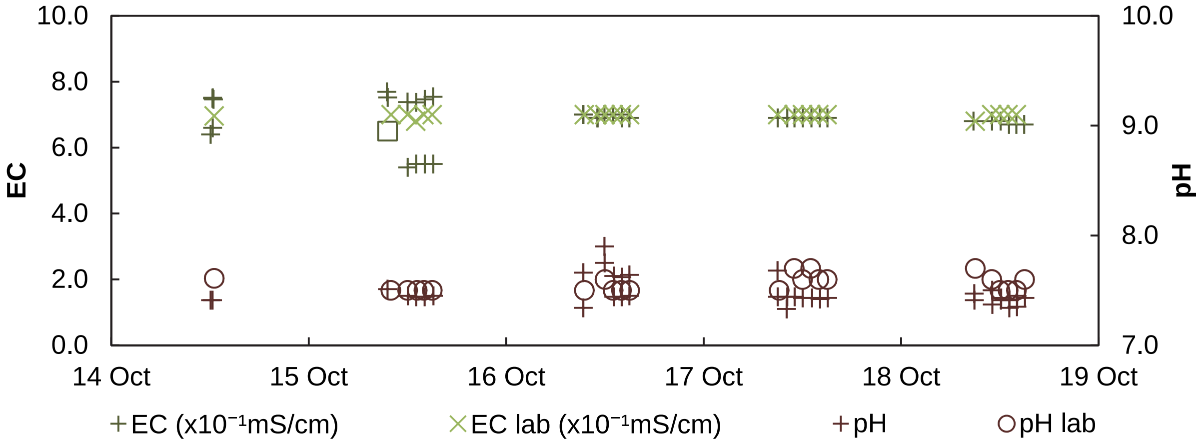


Figure 58: Field and laboratory measurement of pH and EC at G30966 correlate and remain within the known baseline values

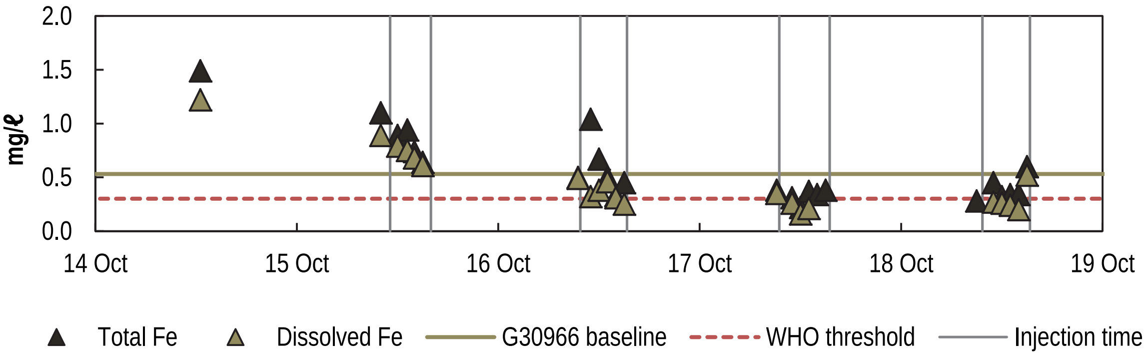


Figure 59: Both total and dissolved Fe concentrations from G30966 showed a decline with successive injection. After the second day they were below the known baseline concentrations and by the third run the Fe was dominantly in the dissolved form and closer to the desired threshold.

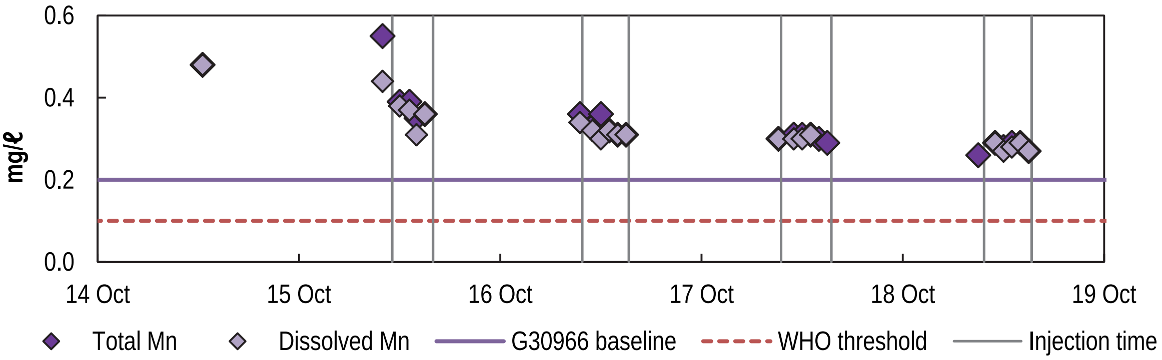


Figure 60: Both total and dissolved Mn concentrations from G30966 showed a decline but not as distinctive as Fe and remained above the known baseline and desired threshold concentrations

5.4 Discussion

The main objective of this research project was to evaluate whether the ISIR treatment would reduce the Fe^{2+} and Mn^{2+} concentrations in the abstracted groundwater from production borehole G30966 below the potable and clogging threshold levels given in WHO (2008) and Walter (1997).

Over the course of three months, four different injection techniques were applied at the study site. From the injection tests it was found that ISIR was successfully operated at a small-scale (injection rate < 2 m^3/hr and injected volume < 10 m^3) for the removal of Fe^{2+} and Mn^{2+} from groundwater with no significant changes in the water quality. It was found that the continuous injection and abstraction approach, with injection of ozonated water at a 4 m distance from the production borehole, achieved the desired Fe removal according to WHO (2008) potable threshold. Although, ISIR treatment was not as successful in Mn^{2+} removal, the Mn^{2+} oxidation is known to take longer in comparison to Fe^{2+} and requires higher pH conditions or longer contact time.

The use of ozone as the oxidant for ISIR was a novel approach to treatment of Fe^{2+} and Mn^{2+} oxidation in SiO_2- and DOC-rich groundwater. The dissolved ozone concentration in the injected water (i.e. 0.3-0.5 mg/ℓ) found with the field studies were within the typical dissolved ozone concentrations ranges during above-ground water treatments (i.e. 0.1 to 1 mg/ℓ; EPA, 1999).

The DO, which is a decay product of ozonation, was greater than DO concentrations achieved in ISIR case studies where water was saturated with atmospheric oxygen, and comparable to the ranges found in studies, which used high purity oxygen gas. This makes ozone an appropriate oxidant to use for ISIR as it is effective in also generating high DO concentrations (including the stronger oxidising dissolved ozone concentrations) while eliminating the storage and handling requirements for oxygen gas.

5.4.1 Limitations of research

The pilot field study was only initiated in the last ten months of the three year research project and after the first month of overcoming operational challenges, intensive rainfall during the months of July to September 2013 interrupted the injection tests runs and data collection. The field tests took place during an above average rainfall (i.e. the highest rainfall on record for more than 30 years) and the lowest production in the Atlantis wellfields causing the water table to rise to the highest known levels in the last three decades (Figure 61). The water table in G30966 rose from 1.5 mbgl in the beginning of July 2013 to 0.8 mbgl in October 2013 that rise in water level which halved the available space for injection which necessitated reduction in injection rates due to the overflowing in the injection well-point, which in turn resulted in less dissolved ozone and DO introduced into the aquifer for Fe^{2+} and Mn^{2+} removal. It can be assumed that higher oxidant concentrations would have been achieved if the system was operating at its optimal rate.

In addition, due to the limited time left for the pilot project, injection tests were run during the rain but this also resulted in difficulty in collecting water samples and taking the field measurements. The pH and DO equipment malfunctioned as a result of working in the poor conditions which caused further delays in injection tests and data collection. Although it should be noted that no problems were experienced with the oxygen and ozone generators due to the high rainfall and the operation was sufficiently throughout the pilot tests.

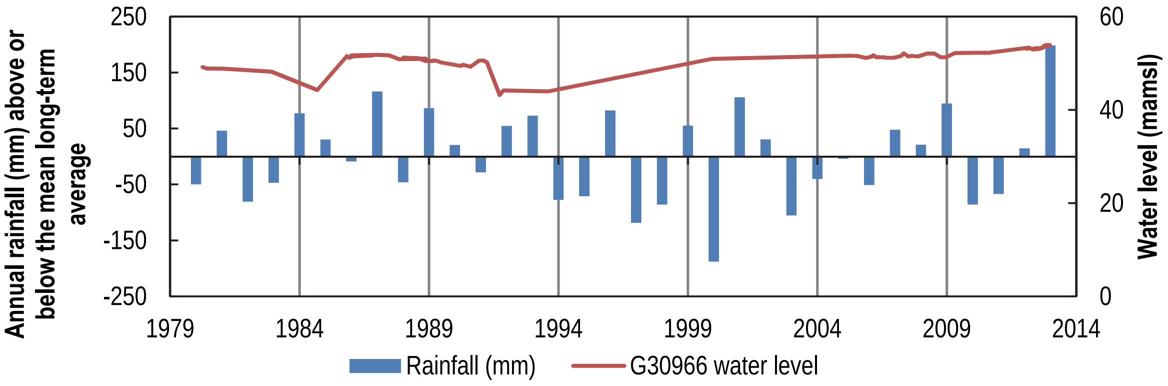


Figure 61: Rainfall variations from the mean annual rainfall compared to the long-term average and G30966 static water level, showing that the pilot tests took place during the highest recorded rainfall and water table for the last 34 years

6 CONCLUSIONS

The main aim was to investigate the feasibility of the ISIR application by removing Fe and Mn from the abstracted groundwater in a South African setting. This research project arose from the need for the investigation of preventative options to complement the management and rehabilitation protocols in dealing with production borehole clogging caused by soluble Fe^{2+} and Mn^{2+} ions in the groundwater. This project tested the applicability of ISIR in the primary Atlantis Aquifer. A lack of funding ruled out the possibility of investigating the application of the ISIR technique to a fracture rock system. In addition, the available literature on such application was extremely limited.

The potential for success in applying the technique at the Atlantis Aquifer appeared high due to:

- The high T-value of the aquifer, which allows for easy injection of an oxygenated water into the subsurface to create an oxidation zone;
- The mineralogical composition of the quartz sands, which would provide suitable sites for the iron (III) oxide to attach to when formed and over time assist in the removal of Fe^{2+} and Mn^{2+} from the groundwater through adsorption.

Modifications had to be made to the proposed ISIR application due to the groundwater quality (i.e. DOC and SiO_2-rich), which saw the novel use of ozone as the oxidant for complexed Fe^{2+} and Mn^{2+} removal, and the high groundwater level, which required the "daisy-wheel" option of injection of oxygenated water to be applied.

From the four different ISIR techniques applied at the study site, it was found that continuous pumping was essential during injection, as it remove the spurious high total Fe concentrations experienced with the stop-start abstraction approach. From those results, even though the tests were completed in adverse weather conditions and above average groundwater levels, both the Fe and Mn showed a decline in the abstracted groundwater from production borehole G30966 due to the increased DO in the aquifer, with successive injections. From the DO concentrations achieved in the subsurface it was established that ozone is an appropriate oxidant to use for ISIR and the feasibility of this treatment was confirmed in the study area. Considering the benefits associated with this application, continuation of research is recommended to understand the long-term effectiveness of this treatment on reducing production borehole clogging and water quality improvement should be investigated at the study site.

The pilot *in-situ* iron removal facilities created at production borehole G30966 successfully served their purpose and are available for continuation of the studies with different configurations of injection and monitoring.

7 RECOMMENDATIONS FOR FUTURE RESEARCH

7.1 Longer Term Injection into Well-point 4DNE

The four day intermittent injection run in October 2013 proved that the DO concentration can be increased successfully in the subsurface, even at the low injection rates. At the same time the Fe concentration reduced significantly confirming the feasibility of Fe removal. In order to ensure a successful continuation of the research the injection in well-point 4DNE should be repeated for a longer period while taking regular readings as before. Abstraction from borehole G30966 should continue but it should also be investigated whether it would be possible to reduce the pumping rate from borehole G30966 in order to reduce the water level gradient between the injection borehole and the production borehole and reduce the flow rate to allow a longer contact time in the subsurface. Better degassing of the abstracted water should also be attempted, e.g. spraying the water as it enters the storage tank. In this way the same higher DO and dissolved ozone concentrations should be attained that were possible with better degassing by recirculation of the abstracted water before ozonation.

7.2 Injection into Well-point 8DNE

Following the longer term injection into well-point 4DNE and the establishment of the injection and abstraction parameters the injection should be moved to well-point 8DNE. This will extend the flow path and ensure that Mn was more completely removed as the reaction and contact time would be longer. Abstraction from production borehole G30966 should continue as this is the scenario foreseen for the full scale development of the ISIR systems at the production boreholes.

7.3 Injection in Multiple Well-points

The next step would be injection of ozonated water into multiple well-points as was envisaged with the design of the well-points at the study site. For this purpose at least two additional ozone generators of similar size will be procured to allow injection into at least three boreholes, e.g. 8DNE, 11DW, and 12DE. Alternatively a larger unit that can provide enough ozone for injection into more than one borehole could be considered to simplify logistics. All possible preparations should be made to camera log the production borehole before and after these extended Fe and Mn removal runs. For these runs the abstraction rate from the production borehole should be gradually increased to eventually reach the design rate for the borehole.

7.4 Develop Prototype for Application at Production Boreholes

Based on the results of the extended tests described above a full scale application should be designed for testing at another borehole where ISIR has not taken place and the aquifer is still in the original condition. Testing should again be preceded by camera logging of the borehole and brushing or cleaning in the best possible way.

7.5 Re-evaluate the Possibilities of Application to a Fractured Aquifer

Despite the complexities of groundwater flow in fractured aquifers it may still be possible to carry out ISIR and provided a suitable test site can be found, e.g. Brooklands near Simon’s Town, or somewhere in the KKRWSS where suitable setup can be found. The tests could be carried out on a single borehole in a batch mode as was often done abroad. Alternatively the test site could have two boreholes spaced closely together, e.g. within 20 m distance where one of these could be used for injection while abstracting from the other. It is, however, important that pumping tests should confirm good hydraulic linking between the boreholes.

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APPENDIX A: South African Weather Services Climate Data

Mean Monthly Maximum Temperature (°C) recorded at the Atlantis Wastewater Treatment Plant Weather Station 0020/846												
	Jan	**Feb**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**	**Sept**	**Oct**	**Nov**	**Dec**
1980	27.3	26.7	26.5	22.6	19.3	18.8	20.7	19.3	19.8	22.3	22.6	24.4
1981	25.6	28.3	24.5	23.9	22.0	17.9	16.5	16.5	19.1	23.2	23.2	27.0
1982	25.1	26.0	26.3	22.3	20.8	17.3	17.6	17.5	22.1	23.9	23.1	23.0
1983	25.9	25.5	26.0	25.7	19.4	17.1	17.8	18.8	17.8	22.8	24.1	25.7
1984	27.3	28.2	28.3	24.9	19.8	19.4	18.5	18.1	19.2	21.0	26.7	23.8
1985	27.2	27.6	24.3	23.0	21.7	18.6	17.5	19.6	N.M.	N.M	N.M	N.M.
1986	N.M.	27.9	24.7	23.5	21.1	18.4	17.4	18.6	20.3	22.4	24.3	27.2
1987	24.8	26.1	25.8	22.7	22.2	18.7	17.7	18.4	19.3	22.8	22.7	23.9
1988	25.5	29.6	25.2	22.7	21.8	18.0	16.4	18.7	19.3	20.3	25.3	27.6
1989	28.5	28.5	25.4	24.4	20.3	17.7	17.0	17.9	19.2	20.6	25.3	25.5
1990	27.5	28.6	26.7	22.4	20.6	16.6	16.2	17.8	21.6	22.5	23.0	25.6
1991	26.4	25.6	27.9	24.8	22.0	18.1	17.1	16.6	19.2	21.4	23.0	25.4
1992	27.0	26.2	26.8	22.1	18.9	17.4	16.8	18.0	18.2	21.4	23.9	24.3
1993	27.6	26.4	27.6	22.1	18.6	17.8	18.5	19.0	20.6	23.2	25.4	26.5
1994	28.1	29.4	26.4	25.3	19.4	17.4	17.7	18.4	20.3	23.3	23.2	26.7
1995	27.0	28.9	27.5	24.0	22.3	18.5	15.5	17.6	19.6	20.6	24.1	27.4
1996	27.9	28.0	24.9	25.8	22.1	18.4	16.5	17.2	17.3	20.9	21.0	24.7
1997	27.2	26.6	25.1	22.5	21.8	16.4	18.9	17.9	22.7	25.2	23.7	26.6
1998	26.3	29.0	26.0	24.7	20.0	18.4	17.5	19.0	19.7	23.3	23.9	26.8
1999	28.4	28.8	28.5	25.1	21.4	20.5	18.3	19.3	18.8	24.5	24.6	28.9
2000	28.7	28.1	26.9	24.6	21.5	20.5	19.1	19.4	18.8	23.1	25.0	25.4
2001	26.8	29.2	25.7	23.9	21.4	18.5	17.9	17.3	19.3	22.8	25.1	26.0
2002	25.3	29.6	27.0	23.7	19.7	16.5	16.6	18.5	22.0	21.4	23.2	27.8
2003	26.7	27.2	25.7	24.8	22.0	20.4	19.4	16.8	19.5	23.6	24.6	24.8
2004	28.4	28.1	24.9	23.8	22.6	19.3	18.8	18.2	21.4	22.7	25.5	27.4
2005	28.5	29.1	27.6	24.1	19.7	17.1	20.5	16.1	19.6	21.6	24.8	26.2
2006	28.4	29.8	27.1	24.6	21.1	20.3	17.1	18.0	20.6	23.3	26.3	25.6
2007	29.1	27.1	27.7	24.7	21.6	18.4	18.3	18.2	20.1	24.6	23.7	27.9
2008	29.9	25.3	28.0	24.9	21.7	18.8	17.3	18.6	17.9	22.6	24.8	27.8
2009	27.1	30.1	28.8	25.7	21.2	18.8	19.7	18.7	19.3	24.4	25.3	26.0
2010	27.8	25.2	29.1	24.6	21.5	19.9	19.9	21.0	22.0	23.3	25.0	29.0
2011	30.5	31.0	28.8	25.6	21.7	18.7	21.1	20.3	21.2	23.2	24.1	25.9
2012	30.4	28.0	28.0	25.6	21.0	18.8	18.1	17.1	18.8	21.8	24.4	28.9
2013	29.2	28.0	27.4	24.3	22.1	17.8	18.4	17.1	17.6	22.3	25.7	28.6
Mean	**27.5**	**27.9**	**26.7**	**24.1**	**21.0**	**18.4**	**18.0**	**18.2**	**19.8**	**22.6**	**24.3**	**26.3**
N.M. indicated that data is missing												

Mean Monthly Minimum Temperature (°C) recorded at the Atlantis Wastewater Treatment Plant Weather Station 0020/846

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
1980	13.1	11.5	11.6	10.2	6.5	6.6	5.6	6.8	8.2	8.4	11.2	13.0
1981	12.7	14.9	10.9	10.0	9.4	4.7	4.9	6.3	7.5	9.7	11.4	13.6
1982	12.9	13.4	12.3	10.2	7.6	5.6	4.8	5.3	8.0	10.1	10.2	10.4
1983	12.6	12.0	11.6	11.6	8.0	5.6	5.0	4.2	6.6	9.3	10.7	N.M.
1984	13.6	14.7	14.4	10.0	8.7	6.9	7.2	5.5	8.6	9.3	N.M.	12.5
1985	14.4	14.6	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.
1986	N.M.	14.6	12.4	11.9	9.8	8.5	7.3	9.3	N.M.	N.M.	11.8	14.4
1987	N.M.	N.M.	N.M.	10.5	N.M.	N.M.	6.7	6.6	8.7	10.2	N.M.	N.M.
1988	12.9	15.1	13.0	9.9	8.1	5.2	4.7	7.1	6.0	7.3	12.0	14.4
1989	15.1	14.9	13.1	10.6	7.5	N.M.	4.8	6.0	7.3	6.9	11.6	12.4
1990	13.7	14.9	12.4	10.7	7.2	4.4	5.1	5.2	7.5	7.9	10.2	13.1
1991	13.3	13.2	13.8	9.8	9.0	4.7	6.3	3.2	7.2	10.0	10.8	11.8
1992	14.1	14.0	13.0	9.9	7.9	6.9		5.8	7.5	10.6	11.3	12.7
1993	14.4	12.6	14.2	10.4	8.5	6.3	7.2	5.7	7.7	9.8	11.7	13.8
1994	14.4	15.1	14.3	11.7	7.3	7.3	4.7	5.7	8.0	10.1	11.7	13.1
1995	14.6	15.3	14.3	9.2	9.6	6.9	4.5	6.8	8.1	9.1	12.1	15.7
1996	15.4	14.3	11.8	11.3	8.0	6.5	4.8	5.4	7.8	10.2	10.8	13.3
1997	14.4	14.2	12.6	9.8	8.8	6.0	6.4	7.7	9.6	11.0	12.2	14.0
1998	14.2	17.2	13.4	11.5	9.0	6.5	5.8	5.4	6.1	9.4	11.0	14.0
1999	15.1	16.2	15.1	12.3	10.6	8.4	7.2	8.7	7.9	12.6	12.6	16.9
2000	16.2	16.1	14.6	12.0	9.7	8.8	7.3	9.1	8.3	10.3	12.8	13.7
2001	14.0	14.9	12.9	12.1	9.9	7.3	7.6	7.8	9.1	11.3	13.2	13.8
2002	13.6	14.8	13.5	10.8	8.4	4.9	5.7	6.0	9.6	9.5	9.0	14.5
2003	13.9	14.5	13.5	11.7	8.2	4.2	4.7	4.6	7.8	10.6	11.1	12.9
2004	15.2	14.7	11.2	11.1	9.7	7.4	5.1	7.6	7.8	10.0	12.8	14.4
2005	13.7	12.9	13.5	10.8	9.8	6.5	7.0	6.0	8.3	8.6	12.2	12.1
2006	15.2	15.7	12.2	11.3	9.0	7.3	7.2	6.9	9.3	10.0	11.8	12.7
2007	15.2	14.6	12.8	10.6	7.8	7.3	5.6	6.5	9.9	10.4	10.9	14.5
2008	15.8	16.6	14.5	11.3	11.6	9.4	5.5	6.2	6.5	9.3	11.5	15.3
2009	14.9	15.5	14.6	12.5	10.6	9.0	7.3	7.4	11.0	12.4	13.2	12.6
2010	15.5	14.7	14.5	10.3	9.5	7.4	5.5	6.9	8.1	9.9	11.9	14.9
2011	15.5	16.8	14.4	11.4	10.0	7.6	6.2	6.4	7.7	9.3	10.6	13.2
2012	16.3	15.1	14.6	11.7	7.5	7.3	6.1	6.0	5.8	8.2	9.8	15.3
2013	14.6	15.5	14.1	9.9	9.0	7.8	8.0	7.4	7.2	10.7	12.6	14.8
Mean	**14.4**	**14.7**	**13.3**	**10.9**	**8.8**	**6.7**	**6.0**	**6.4**	**8.0**	**9.8**	**11.5**	**13.7**

N.M. indicated that data is missing

Total monthly rainfall data (mm) recorded at the Atlantis Wastewater Treatment Plant Weather Station 0020/846 (only rainfall ≥ 0.1 mm is recorded)

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Total
1980	15.7	8.4	1.5	37.0	62.4	60.1	26.0	47.0	16.2	18.3	86.8	27.6	407.0
1981	64.8	0.1	37.8	38.0	14.3	44.2	121.6	83.2	51.9	15.8	13.8	17.3	502.8
1982	21.7	6.9	7.7	35.9	36.3	69.3	48.7	59.8	15.5	20.3	12.2	41.8	376.1
1983	6.2	31.6	18.6	8.0	90.7	94.2	62.5	26.1	38.5	12.2	8.0	13.2	409.8
1984	3.2	2.2	47.5	41.4	131.3	32.9	52.9	24.4	82.8	73.6	0.0	41.7	533.9
1985	18.6	16.3	50.4	51.3	27.3	60.9	106.3	64.7	62.5	24.1	2.5	2.1	487.0
1986	9.5	2.6	34.0	17.7	22.4	126.3	90.7	80.8	34.2	13.3	9.8	6.6	447.9
1987	17.0	12.0	14.4	28.2	121.2	67.8	100.0	127.2	43.8	17.7	6.4	17.3	573.0
1988	2.8	0.0	34.5	58.8	36.2	35.9	58.9	97.2	42.2	27.0	8.2	8.9	410.6
1989	6.3	19.6	49.8	39.4	44.9	52.7	101.2	68.7	87.0	37.6	33.0	3.1	543.3
1990	12.5	18.8	0.0	100.8	66.8	102.8	82.0	37.3	22.1	2.3	7.5	24.5	477.4
1991	7.3	4.1	13.1	11.1	56.6	81.1	129.4	23.5	50.3	33.4	10.6	7.8	428.3
1992	1.3	16.5	10.0	33.0	64.8	170.9	91.9	45.6	31.9	37.7	3.8	4.1	511.5
1993	3.9	23.8	9.2	119.2	103.4	61.7	128.6	41.0	5.3	0.9	3.6	29.2	529.8
1994	5.0	0.0	4.7	20.0	39.6	189.2	43.8	19.7	37.8	7.8	6.0	5.6	379.2
1995	7.0	4.4	2.5	5.3	36.1	74.3	97.8	57.2	16.8	49.5	4.4	30.3	385.6
1996	4.6	45.3	15.9	23.6	41.0	96.2	60.0	61.4	81.9	46.6	43.8	18.8	539.1
1997	12.7	1.5	3.5	31.1	55.2	98.9	41.7	54.8	4.7	4.8	23.8	5.4	338.1
1998	2.9	0.2	8.4	22.8	88.4	52.7	70.1	39.8	17.5	9.2	38.7	20.1	370.8
1999	0.1	0.2	0.0	53.9	35.7	87.4	59.6	145.7	87.2	0.7	20.5	21.0	512.0
2000	20.5	0.0	0.0	3.0	32.4	39.3	48.4	44.0	60.8	2.5	14.0	4.1	269.0
2001	9.1	6.0	0.0	24.2	89.7	50.0	185.2	93.6	50.5	35.7	9.9	8.8	562.7
2002	61.0	21.4	6.5	33.3	68.7	53.5	74.3	67.2	38.7	29.7	12.6	20.3	487.2
2003	5.8	4.1	23.5	18.0	27.1	10.8	27.7	141.5	51.1	18.8	0.5	22.5	351.4
2004	11.4	1.7	18.0	58.9	5.2	77.4	75.3	45.6	23.5	90.9	6.5	2.3	416.7
2005	21.0	3.2	3.0	77.5	75.9	91.3	27.5	87.7	42.0	9.2	13.0	1.5	452.8
2006	1.7	7.2	5.3	41.5	101.7	40.9	64.7	56.5	14.9	25.6	27.5	18.2	405.7
2007	0.5	20.6	20.3	56.8	46.2	89.8	80.2	82.6	33.4	18.9	28.1	27.2	504.6
2008	4.1	14.1	3.7	7.7	38.0	60.6	116.0	82.1	91.8	18.0	40.4	1.5	478.0
2009	2.0	3.6	1.2	43.7	73.8	103.3	104.1	61.4	52.7	14.7	86.7	4.2	551.4
2010	0.3	11.8	10.7	22.4	79.2	73.4	38.8	42.6	21.4	28.4	35.0	6.8	370.8
2011	3.6	42.2	7.4	27.0	44.4	110.4	22.4	49.0	33.8	14.6	25.2	9.8	389.8
2012	0.8	0.8	21.0	29.8	34.6	72.4	94.2	101.0	83.2	23.2	10.0	0.4	471.4
2013	7.2	70.4	9.8	45.0	28.2	115.2	66.8	174.6	70.0	19.2	45.2	3.4	655.0
Mean	**10.9**	**12.4**	**14.5**	**37.2**	**56.5**	**77.9**	**76.5**	**68.7**	**44.1**	**23.6**	**20.5**	**14.0**	**456.8**