DETERMINATION OF THE POSSIBLE REQUIREMENT FOR REMEDIATION OF MANGANESE IMPACTED GROUNDWATER AT AN INDUSTRIAL FACILITY IN NELSPRUIT

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DECLARATION

I, Philip James HUGHES hereby declare that the present dissertation, submitted to the Institute for Groundwater Studies in the Faculty of Natural and Agricultural Sciences at the University of the Free State, in fulfilment of the degree of Magister Scientiae, is my own work. It has not previously been submitted by me to any other institution of higher education. In addition, I declare that all sources cited have been acknowledged by means of a list of references.

I furthermore cede copyright of the dissertation and its contents in favour of the University of the Free State.

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ABSTRACT

A formerly operational manufacturing company, Delta E.M.D (Pty) Ltd (Delta) was, until recently, located in Mbombela (Nelspruit), Mpumalanga and produced electrolytic manganese dioxide (MnO_2:EMD), an inorganic compound used for dry-cell batteries including alkaline and zinc-carbon batteries. The operational site has been subject to various site investigations between 2010 and 2015 which ultimately informed a site-wide rehabilitation and closure plan. The site has since been demolished as part of a site rehabilitation activity undertaken during 2015 and 2016.

During the course of 2014 to 2015, the author developed a site investigation strategy that utilised multiple site investigation technologies to characterise the geological, hydrogeological and contaminated groundwater situation at the site. This allowed for a site specific remediation strategy to be developed.

The site is located within an industrial area of Mbombela (Nelspruit), Mpumalanga within the Mbombela Local Municipality. To the immediate north of the site, a wide single-carriageway road is present which overlooks undeveloped bush land leading towards the Crocodile River located 200 m beyond. The local area is underlain by medium to very coarse grained granite which has been intruded by numerous basic dykes and sills. The granite is fractured and highly weathered in the upper 15 m. North-South trending geological structures are present which represent preferential pathways for groundwater flow and the migration of contaminants.

The site characterisation work undertaken involved several phases of investigation including both non-intrusive and intrusive site investigation and sampling techniques. Specifically, the investigation involved: desktop research; geophysical surveying; borehole drilling and geotechnical drilling; monitoring well construction; soil and groundwater sampling; chemical analysis, and aquifer testing. The work undertaken resulted in identification of several sources of groundwater contamination and ultimately the development of an in-situ groundwater treatment strategy.

Three hot spots of groundwater contamination were identified on site; the majority of the contamination was considered to be present within a phreatic shallow aquifer represented by a weathered horizon. The groundwater flow direction is in a northerly direction towards the Crocodile River, with a constant source of recharge being supplied by a man-made canal located along the western boundary of the site. Groundwater flow and contaminant migration towards the Crocodile River, was shown to be structurally controlled by the presence of faults and dykes.

A source-pathway-receptor (S-P-R) assessment was undertaken which confirmed an active S-P-R model scenario would result in elevated concentrations of manganese and sulphate and low pH groundwater reaching the Crocodile River, which could negatively impact surface water quality.

The information obtained and conceptual model that was developed was used to design the layout of a targeted on-site groundwater remediation system utilising the injection of lime to neutralise low pH water on site and allow for the precipitation of manganese from solution.

The study, explores, how multiple site investigation technologies can be utilised to develop targeted and site-specific remediation strategies for contaminated groundwater within a fractured rock environment.

OPSOMMING

'n Voormalige operasionele maatskappy, Delta EMD (Edms) Bpk (Delta), geleë in Mbombela, Mpumalanga het tot onlangs elektrolitiese mangaandioksied (MnO_2: EMD), 'n anorganiese verbinding wat gebruik word vir droë-sel batterye, insluitende alkaliese en sink-koolstof batterye, vervaardig. Die operasionele area was onderwerp aan verskeie terreinondersoeke tussen 2010 en 2015, wat uiteindelik 'n rehabilitasie- en sluitingplan vir die terrein voorgestel het. Die terrein is sedertdien gesloop as deel van die terreinrehabilitasie-aktiwiteit wat gedurende 2015 en 2016 onderneem is.

Gedurende die periode 2014 tot 2015 het die skrywer 'n terreinondersoekstrategie ontwikkel wat gebruik gemaak het van verskeie tegnologieë om die geologiese, hidrogeologiese en gekontamineerde grondwatersituasie op die terrein te karakteriseer. Dit het toegelaat dat 'n terreinspesifieke remediëringstrategie ontwikkel is.

Die terrein is geleë in 'n industriële gebied van Mbombela Plaaslike Munisipaliteit, in Mpumalanga. Daar is n wye enkelwegpad direk noord van die terrein, wat oor onontwikkelde bosveld terrein uitkyk, en wat na die Krokodilrivier, 200 m verder, lei.

Die onderliggende geologie bestaan uit medium tot baie grofkorrelrige graniet wat deur talle basiese gange en plate ingedring is. Die graniet is genaat en is tot ‘n diepte van 15 meter, hoogs verweerd. Noord-suid strekkende geologiese strukture is teenwoordig wat voorkeurverweringsones vir grondwatervloei en die migrasie van opgelosde kontaminante vorm.

Die terreinkarakteriseringswerk wat onderneem is, het uit verskeie fases bestaan, insluitende nie-indringende− en indringende terreinondersoek− en monsternemingstegnieke. Spesifiek, het die ondersoek die volgende ingesluit: literatuurstudies; geofisiese opnames; boorgat boorwerk en geotegniese boorwerk; monitering van boorgatkonstruksies; grond− en grondwater bemonstering; chemiese analise en akwifer toetsing. Die werk wat onderneem is, het gelei tot die identifisering van verskeie bronne van grondwaterbesoedeling en uiteindelik die ontwikkeling van 'n in-situ grondwaterbehandelingstrategie.

Drie bronne van grondwaterbesoedeling is op die terrein geïdentifiseer. Die meerderheid van die besoedeling is aanwesig in 'n vlak versadigde (phreatic) akwifer in 'n verweringshorison. Die grondwatervloeirigting is in 'n noordelike rigting na die Krokodilrivier toe, met 'n konstante bron van aanvulling vanaf 'n mensgemaakte kanaal langs die westelike grens van die perseel. Grondwatervloei en kontaminante-migrasie na die Krokodilrivier het getoon dat dit struktureel beheer word deur die teenwoordigheid van verskuiwings en gange.

'n Bron-Roete Reseptor (B-R-R) evaluering is uitgevoer wat bevestig het dat 'n aktiewe B-R-R model sal lei tot verhoogde konsentrasies van mangaan, en sulfaat, en ‘n verlaagde Ph van die grondwater wat die Krokodilrivier se kwaliteit as varswaterbron negatief sal beïnvloed.

Die inligting wat verkry is en die konseptuele model wat ontwikkel is, is gebruik om die uitleg van die geteikende terrein grondwater-remediëringsisteem te ontwerp deur gebruik te maak van die toevoeging van kalk om lae pH-water van die terrein te neutraliseer en die presipitasie van mangaan uit oplossing te verseker.

Hierdie studie ondersoek hoe veelvuldige terreinondersoektegnologieë gebruik kan word om geteikende en terrein-spesifieke remediëringstrategieë vir gekontamineerde grondwater binne 'n verbrokkelde, rotsagtige omgewing te ontwikkel.

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LIST OF ABBREVIATIONS AND ACCRONYMS

AEV	Acute Effect Value
AHT	Analytical Hierarchy Technique
ALERT	Automated Time-Lapse Resistivity Tomography
ARP	Automated Resistivity Profiling
CDT	Constant Discharge Test
CEV	Chromic Effect Value
CSM	Conceptual Site Model
D6	Medium sized tracked bulldozer
D7	Medium sized tracked bulldozer
D8	Large sized tracked bulldozer
D11	Large sized tracked bulldozer
DC	Direct Current
Delta	Delta E.M.D. (Pty) Ltd
DO	Dissolved Oxygen
DQRA	Detailed Quantitative Risk Assessment
EC	Electrical Conductivity
EDRS	Environmental Drilling and Remediation Services (Pty) Ltd
Eh	Activity of electrons
EMD	Electrolytic Manganese Dioxide
EOH	End of Hole
ERT	Electrical Resistivity Tomography
FI	Fracture Index
Geosphere	Geosphere (Pty) Ltd
GIS	Geographical Information System
Golder	Golder Associates Africa (Pty) Ltd
IAP	Ion Activity Product
I.D.	Inside diameter
IGS	Institute of Groundwater Studies
IRQC	Interim Resource Quality Objectives
Is	Point load strength index
ISCO	In-Situ Chemical Oxidation
Jones	Jones Environmental Laboratories (UK) Ltd
K	Solubility Product
km	kilometres
KNP	Kruger National Park
l/s	litres per second
m	metres

mamsl	metres above mean sea level
mbgl	metres below ground level
m/d	metres per day
min	minutes
mm	millimetres
mmbgl	millimetres below ground level
MMC	Manganese Metal Company (Pty) Ltd
MPa	Mega Pascals
mS/m	milli siemens per metre
NEM:WA	National Environment Management: Waste Act
NTU	Nephelometric Turbidity Unit
NWD4	Diamond coring bit size 75.7 mm O.D. 51.3 mm I.D.
O.D.	Outside diameter
Ohm.m	Ohm metres
ORP	Oxygen Reduction Potential
pH	Activity of hydrogen ions
PVC	Polyvinyl chloride casing
QRA	Qualitative Risk Assessment
R^2	Coefficient of determination
RQD	Rock Quality Designation
RQO	River Quality Objectives
SANS	South Africa National Standards
SAPPI	South African Paper and Pulp Industries
SAWQG	South African Water Quality Guidance
SCR	Solid Core Recovery
SI	Saturation Index
SP	Self Potential
SPR	Source Pathway Receptor
TCR	Total Core Recovery
TDS	Total Dissolved Solids
TLB	Tractor-Loaded-Backhoe
TWQR	Target Water Quality Range
UCS	Uniaxial compressive strength
UFS	University of Free State
VES	Vertical Electrical Sounding
Waterlab	Waterlab (Pty) Ltd
WRC	Water Research Council
ZVI	Zero Valent Iron

CHAPTER 1:
INTRODUCTION

1.1 PROBLEM STATEMENT

A former operational manufacturing company, Delta E.M.D (Pty) Ltd (Delta) was, until 2016, located in Nelspruit, Mpumalanga where the company produced electrolytic manganese dioxide (MnO_2:EMD), an inorganic compound used for dry-cell batteries including alkaline and zinc-carbon batteries. The site was subject to a small number of site investigations between 2010 and 2015. The economic viability of the manufacturing facility diminished in the years subsequent to the initial 2010 investigation and the site owners made the decision to close the facility. The site investigations undertaken by the author between 2014 and 2015 informed a rehabilitation and closure plan for the site, which was implemented between 2015 and 2016.

Chemical analysis of groundwater samples obtained from monitoring wells constructed on the site by Golder Associates Africa (Pty) Ltd (Golder) during an initial investigation in 2010 (Steyn, 2010) identified groundwater with low pH values and elevated concentrations of manganese and sulphate that exceeded SANS 241:2011 drinking water standards. The source and aerial extent of the contamination across the site was not fully understood at the time, however it was recognised that the contamination had the potential to a) negatively impact upon the underlying groundwater quality and b) negatively impact upon surface water if contaminated groundwater migrated off-site towards the nearby Crocodile River located 200 m to the north of the site.

This dissertation focuses upon the detailed site investigation and site characterisation works that were undertaken by the author between 2014 and 2015 in order to inform and develop a site rehabilitation plan in accordance with the requirements under National Environmental Management Waste Act (NEM:WA) of 2008.

Upon commencement of the site investigation works the nature of the underlying geology and hydrogeology was poorly understood due to the limited availability of site-specific data. Further, the various pathways through which on-site contamination could potentially migrate from site was not well understood, thus limiting the development of an appropriate and detailed conceptual site model. However, based upon his general understanding of the area the author considered it reasonable to predict that a shallow weathered/fractured rock aquifer likely existed on site which represented both a potential receptor and a potential preferential pathway for the migration of contaminants of concern. Further, it was considered that dykes and faults, should they be present, may also act as preferential pathways for the migration of groundwater based contaminants. This simplistic understanding formed the basis from which the detailed site investigation was developed.

The author considered that in order to determine the potential impact of site-based contamination upon the shallow aquifer and the Crocodile River it was first necessary to gain an appropriately detailed understanding of the potentially complex nature of the underlying geology with specific importance being placed upon identifying the possible presence of geological structures and determining the extent and degree of weathering profiles. This would then inform understanding of the quantification and distribution of site based contamination and allow for a detailed assessment to be undertaken and thereafter the development of an effective remediation strategy for the site.

The site investigation reported upon represents a step-by-step guide to how the author considers a contaminated groundwater site investigation within shallow unconfined weathered/fractured rock aquifers should be undertaken in South Africa.

1.2 AIM OF THE STUDY

The aim of the study was to develop a sufficiently detailed conceptual site model which included details on the hydrogeological regime within the site boundary and towards the Crocodile River in order to a) enable the extent and distribution of the source of contamination to be understood; b) determine whether contaminated groundwater was leaving the site, and if so, by which pathway(s); and c) understand if the concentration of contaminants of concern represented a risk to the receiving environment, with emphasis being on the Crocodile River. Further, if unacceptable risk was determined to be present then consideration was to be given to the selection of an appropriate remediation technique or combination of techniques that could be employed to mitigate the risk associated with the contamination.

1.3 STUDY SPECIFIC OBJECTIVES

In order to successfully achieve the aim of the study it was necessary that six site-specific objectives be completed. The six site-specific objectives associated with the study are listed below along with an explanation justifying the requirement for their inclusion:

1. Develop a detailed Conceptual Site Model that details the Source-Pathway-Receptor model.

   South Africa’s legislative requirements with respect to the assessment and management of contaminated land and groundwater necessitates that an appropriately detailed conceptual site model (CSM) be developed to allow the user to assess the impact of contamination upon the receiving environment. Various non-intrusive and intrusive site investigation techniques were utilised during this investigation in order to develop an appropriately detailed understanding of the site. Site-specific information that was required to inform the study included the nature of the source of contamination, the pathways by which the contamination could migrate, and the nature of the receptor subject to the impact of the contamination.

2. Determine the concentration and distribution of the main contaminants of concern across the site and along the site boundary.

   Review of the earlier site investigation report by Steyn (2010) indicated that the main contaminants of concern were likely to be dissolved manganese, sulphate, and low pH value groundwater. The groundwater quality data obtained in 2010 was limited to that obtained from only eight on-site monitoring wells which provided limited spatial distribution and which most certainly straddled multiple weathering profiles within the sub-surface; the data obtained at that time could therefore not be attributed to a specific geological horizon. Further, the wide spacing of monitoring wells across the site limited the user’s ability to effectively map the distribution of contamination and water quality type. The author concluded that further investigation of the site was required to gain a detailed understanding of the site and develop a remedial strategy.

3. Determine if contaminated groundwater is leaving site.

   The site investigation reported upon by Steyn (2010) identified that potential contaminants of concern were present on site. At that time no work had been undertaken off-site as such fell outside of the terms of the terms of reference. However, review of the topography in the near area of the site suggested that any shallow groundwater present in the upper 10 to 15 mbgl was likely to migrate in a northerly direction towards the Crocodile River. It was therefore reasonable to assume that any contaminant of concern within the site groundwater could potentially reach the site boundary and then continue in a northerly direction towards the Crocodile River and ultimately impact upon groundwater and surface water quality off-site. It was considered equally possible that geological structures likely to be present in the subsurface could act as either a barrier or a pathway for the migration of contaminants of concern. If a barrier were found to be present on site then it was possible that any contaminants of concern could remain trapped on site or be diverted to exit site along an unknown fracture set at an unknown location.

4. Determine if contaminated groundwater is leaving the site and if the concentration thereof represents a potential risk to the environment.

   If contaminated groundwater were found to be leaving the site then it would necessary to determine the concentration of the contaminants present and assess the risk to the receiving environment.

5. Assess changes in groundwater quality and provide an estimation of loading to the Crocodile River.

   The loading and associated risk may be shown to be substantial or minor depending upon the load reaching the river. Providing an estimation of load requires consideration of the nature of the on-site contaminants, the nature of the near surface geology through which the contaminants migrate and an estimation of how long the loading will be applied to the river.

6. Evaluate the suitability of potential remediation techniques to be employed on site.

   If contaminated groundwater were found to be leaving the site and the risk were determined to be substantial and/or unacceptable then it would be reasonable to assume that some form of remedial action would be required. Any remedial strategy determined would be dependent upon a number of factors including: the nature of the contamination; accessibility to the contamination for remedial treatment; time-frame requirements for successful completion of remediation; socio-political requirements; cost; and availability of technical resources and ability.

1.4 STRUCTURE OF DISSERTATION

This dissertation has been structured into nine chapters using the chapter headings identified below and for which brief explanation of chapter contents are provided in the accompanying text.

1. Introduction

   This chapter provides a general introduction to the problem under consideration, the aim of the study and the various questions required to be addressed in order to successfully develop an appropriate remedial strategy.

2. Literature Review

   Chapter 2 represents an in-depth review of existing knowledge with respect to the major aspects of this study. This includes review of literature relating to: the impact of manganese, on the environment; the various site investigation techniques utilised during the course of the investigation (i.e.: geophysical surveying; borehole drilling; geotechnical logging; aquifer testing and groundwater chemical analysis); and remediation methods suitable for the treatment of groundwater impacted by elevated concentrations of sulphate and manganese.

3. Site Description

   A full description of the geo-environmental setting is provided in Chapter 3. This includes consideration of site topography, the underlying geology and the hydrogeological and hydrological site setting.

4. Site Investigation

   In Chapter 4, the site investigation undertaken at the site is discussed. The site investigation included non-intrusive geophysical surveying, intrusive borehole drilling, in-situ water measurements, and groundwater sampling for subsequent chemical analysis. This chapter describes the various works undertaken on site, the justification for their inclusion in the overall site investigation design and comment with regard to the appropriateness and effectiveness of their contribution to achieving the aim of the study.

5. Groundwater Quality Assessment

   This chapter reports upon the groundwater quality assessment for the site during which three groundwater sampling events were completed. During these events water level measurements were obtained, field measurements of in-situ water quality were determined, and groundwater samples were obtained for subsequent chemical analysis. The various sources of groundwater data are assessed and used to inform the development of the conceptual site model and the developing remedial strategy.

6. Conceptual Site Model and Risk Assessment

   The initial conceptual site model developed in 2010 (Steyn, 2010) was not sufficient to allow for the development of a remediation strategy because of limited data availability. The site investigation undertaken by the author has substantially increased the availability of data and allowed a detailed conceptual site model to be developed. This chapter presents the latest conceptual site model and provides a detailed understanding of: the geological strata present at site, the depth of weathering, the concentration of contaminants in groundwater, and groundwater flow direction and aquifer parameters.

7. Selection of a Remediation Strategy

   During development of a remediation strategy, consideration was given to various factors that could potentially impact upon any decision-making process. In this chapter, the various factors influencing the main drivers for remediation are derived. This includes a formal hierarchical assessment to determine the main drivers for the remediation and also includes a geochemical modelling section using PHREEQC, a general purpose geochemical model, to prove the effectiveness of various remediation strategies proposed.

8. Discussion

   The site investigation undertaken by the author combined various methods of non-intrusive and intrusive site investigation techniques. In South Africa, this is something that rarely occurs mainly due to site investigations being wrongly perceived as too costly and time consuming. This chapter explains the benefits of undertaking multi-technique site investigations to obtain substantial quantities of data in a relatively quick and cost effective manner allowing for the more expensive components of an investigation (e.g. borehole drilling and monitoring well construction) to be targeted and designed for maximum benefit. Also discussed are the benefits that can be achieved with respect to the design of a site-wide remedial approach, which is able to define areas impacted by contamination and understand the nature of any directional controls that may be present in the sub-surface. The author proposes and describes a twelve step guide to undertaking a multi-phased multi-technique site investigation for contaminated groundwater within shallow weathered/fractured rock aquifers in South Africa.

9. Conclusion

   The study involved the use of various site investigation techniques to produce a detailed conceptual site model for the site and near surrounds and that allowed for a site specific and targeted remedial strategy to be developed. The remedial strategy thereafter developed centred upon massive alkali dosing to increase pH (within a suitable pH range) in groundwater simultaneously resulting in a reduction of manganese concentrations. This in turn will reduce the impact on the Crocodile River located down-gradient of the site with respect to both contaminant loading and duration of impact. This chapter discusses the remedial strategy that was developed, the benefits of the works undertaken for the environment and provides recommendations for future monitoring. The chapter also includes recommendations for further improving ones understanding of the site and the appropriateness of the remedial strategy adopted.

CHAPTER 2:
LITERATURE REVIEW

The subject site under investigation is a former industrial facility that received and processed manganese during in the production of electrolytic manganese dioxide (MnO_2) for battery cells. Wet-processes on site resulted in leakage of low pH process water, manganese and sulphate into the subsurface. If in sufficient concentration these contaminants could represent a risk to the environment. To inform any remediation strategy it is necessary to understand where the contamination is located on site and if any sub-surface pathways exist that allow for the migration of contaminants off-site. The author considered that the utilisation of electrical resistivity tomography (ERT) would help to determine the presence of contamination or geological structures in the sub-surface by detecting the presence of areas containing substantial quantities of dissolved ionic species or otherwise high conductivity zones. Once a detailed conceptual site model was developed the author would then be able to develop an appropriate remediation strategy for the site. The author has therefore conducted a literature review of information available within the public domain in consideration of the following aspects of the study:

1. Manganese and its impact upon the environment;
2. Electrical resistivity tomography for the delineation of contaminated groundwater and geological structures; and
3. Remediation technologies for treatment of groundwater impacted by elevated manganese.

2.1 MANGANESE AND ITS IMPACT UPON THE ENVIRONMENT

Manganese is a naturally occurring element that is found in rock, soil and water (Howe et al., 2004) and represents the 12th most abundant element in the biosphere (Nadaska et al., 2012). It can be found in several oxidation states and has been shown to be very mobile, capable of leaving the solid phase and entering the dissolved phase with ease (Varnavas, 2016) and the most common oxidation states are Mn^{2+} and Mn^{4+}. DWAF (1996a) noted that "commonly occurring manganese containing minerals include: pyrolusite (MnO_3), manganite ($Mn_2O_3.H_2O$), rhodochrosite ($MnCO_3$), and rhodonite ($MnSiO_3$)".

Human activities are responsible for much of the manganese contamination in water (EPA, 2004). DWAF (1996a, and 1996b) listed numerous industrial uses of manganese which may mobilise manganese into the dissolved phase. These include:

1. The manufacture of steel and manganese alloys.
2. The salts of manganese as drying compounds in varnished and oils.
3. Manganese chloride in dry cell batteries.
4. The fertiliser industry (manganese is used as a micro-nutrient fertiliser additive).
5. Manganese carbonate as the pigment “manganese white”.
6. Manganese dioxide in the making of amethyst glass and decorative porcelain.

Elevated concentration of manganese in drinking water are commonly associated with disturbance of sediment within water containment structures e.g. reservoirs. In 2017, following a power outage at the Roodeplaat Water Treatment Centre in Pretoria, Gauteng, South Africa, the subsequent recommencement of pumping activities caused disturbance of sediments in the Montana reservoir. This resulted in water with artificially elevated manganese and iron concentrations being supplied through municipality pipelines to the general public and although not at concentrations that posed a health risk, they were sufficiently elevated to affect the aesthetic appearance of the water. (NEPAD, 2017).

In 1996, the South African Department of Water Affairs and Forestry (DWAF, 1996a), produced a table identifying the effects of elevated concentrations of manganese in drinking water on aesthetics and human health. The table is reproduced as Table 2-1.

Table 2-1: Effects of Manganese of Aesthetics and Human Health (DWAF, 1996a)

Manganese Target Water Quality Range (mg/l)	Effects
0 to 0.05	No health or aesthetic effects; marginal aesthetic problems occasionally found in the 0.02 to 0.05 mg/l range.
0.05 to 0.10	Tolerable range, although slight staining may occur. No health effects.
0.10 to 0.15	Threshold for significant staining and taste problems. No health effects.
0.15 to 1.00	Increasingly severe staining and taste problems. No health effects.
1.00 to 2.00	Very severe staining and taste effects. No health effects.
2.00 to 5.00	Extreme staining, likely to be aesthetically unacceptable to a large proportion of user. No health effects.
5.00 to 14.00	Unacceptable levels of aesthetic effects. Health effects are rare.

14.00 to 20.00	Very severe, aesthetically unacceptable staining. Domestic use unlikely due to adverse aesthetic effects. Some change of manganese toxicity under usual conditions.
>20.00	Domestic use unlikely due to extreme aesthetic effects. Chromic toxicity; at high concentrations, possible acute effects.

The Environmental Protection Agency of the USA (EPA, 2004) proposed a maximum level of 0.05 ppm (0.05 mg/l) for drinking water for human consumption; this value, however, was based upon taste rather than any potential implications for health. South African legalisation is slightly more stringent in this regard and some guidance is provided by SANS 241-1:2015 South African National Standards for Drinking Water wherein the maximum permitted concentrations of manganese in drinking water are set at 0.04 mg/l for health purposes, and 0.01 mg/l for aesthetic consideration (SANS, 2015).

2.1.1 Health Effects of Manganese on Humans

It has been shown though various studies that manganese can impact upon human health in situations of either under exposure or over exposure. Although not the subject of this study, the author considers it important to note that manganese, at appropriate concentrations, is an essential element for human health and deficiency can result in such health effects as (Lentech, 2017):

1. Obesity;
2. Glucose intolerance;
3. Blood clotting;
4. Skin problems;
5. Lowered cholesterol levels;
6. Skelton disorder;
7. Birth Defects;
8. Changes in hair colour; and
9. Neurological symptoms.

Should it be determined that there are humans using groundwater from the site or surface water from the Crocodile River for drinking water then there is the potential for over-accumulation of manganese. The health effects will be dependent upon the route of exposure (EPA, 2004). DWAF (1996a) stated that the “uptake of manganese occurs by ingestion from both food and water, but more so from food”. However, the EPA (2004) stated that there were limited reports of humans experiencing adverse effects from ingestion of manganese via food or water and that the main route was via inhalation. With the primary pathway for the migration of manganese as a contaminant to the human body being inhalation, this would suggest that workers in a manganese industry setting, rather than domestic rural or urban setting, would generally be more prone to the effects of manganese.

Manganese was identified as being neurotoxic over 150 years ago (ASTDR, 2000). Uptake of excess manganese may result in instances of psychiatric changes, depression, agitation and even hallucination (Ascherner et al., 2007). Research has also shown that manganese effects occur mainly in the respiratory tract and brain (Lentech, 2017) and a “causative link between manganese ingestion and Parkinson’s Disease” (DWAF, 1996a) has been suggested.

There are instances where exposure to manganese in drinking water have been shown to have had an adverse impact upon human health. One example is that reported by Kawamura et al. (1941) in which they identified instances of “lethargy, increased muscle tonus, tremor and mental disturbances” in people who has been exposed to elevated concentrations of manganese in drinking water contaminated from buried dry cell batteries (EPA, 2004). More recently, Varnavas (2016) reported an instance where villages and towns of Eleias Prefecture, Greece were supplied with drinking water which contained elevated concentrations of manganese (up to 3.7 mg/l) putting human health at risk for a considerable period of time. The EPA (1995) reported on studies undertaken in the USA that had identified how people exposed to elevated concentrations of manganese in drinking water attained lower test scores compared to people exposed to lower concentrations. Subsequently, research was undertaken in Canada (Bouchard et al., 2011) through which it was identified that a lower intelligence quotient (IQ) was generally associated with people exposed to elevated concentrations of manganese in drinking water. Higher scores attained in tests to determine intelligent quotient (IQ) have typically be achieved by the more highly motivated test taker (Classroom, 2017) rather than the less motivated test takers, which may well be support instances of lethargy being associated with excess uptake of manganese.

2.1.2 Effect of Manganese on the Aquatic Environment

Manganese has been shown to be essential for normal development across the lifespan of all mammals, with some 20 identified functions and enzymes and proteins (Nadaska et al., 2012). However, an increase in manganese concentration can also have an adverse effect on other animals and plants. For example, the accumulation of elevated concentration of manganese within fresh water can affect the respiratory organelles of fishes (Quora, 2017). Work undertaken by Caruso et al. (2011)

stated that concentrations of manganese can accumulate in aquatic biota with uptake being proportional to both temperature and pH but independent of dissolved oxygen content. Niemiec and Wiśniowska-Kielian (2015) reported "poorer immunological activity" in "Norwegian lobsters exposed to excessive amounts of manganese". This was associated with very low levels of dissolved oxygen in the water, which in some way contradicts the suggestion of Caruso et al. (2011) that manganese uptake is independent of dissolved oxygen content.

In aquatic systems, despite manganese being an essential element, a toxic effect could be incurred if the receiving party was subject to excessive accumulation with the toxic effect being expressed though the disturbance "of the activity of the synapses" which in turn leads to "impaired functioning of the central nervous system" (Niemiec and Wiśniowska-Kielian, 2015). Furthermore, research undertaken by Sharma and Langer (2014) on fish exposed to elevated concentrations of manganese concluded that manganese does has a toxic effect on fish, but the effect is both dose and time dependent. It is clear from existing research that elevated concentration of manganese in water can have a negative effect on aquatic life, however the extent of the effect may be reduced due to dilution and decreasing source concentration over time. This may have implications for the development of a remediation strategy should achieving effective remediation within a set period of time be a primary driver for remediation. The South African Department of Water Affairs and Forestry (DWAF, 1996b), produced a table indicating the Target Water Quality Range (TWQR) and criteria for dissolved manganese in the aquatic ecosystems. This is reproduced as Table 2-2. The information used to compile the chronic and acute effect values was based upon the very limited information available for algae, invertebrates and vertebrates (DWAF, 1996b) and the dissolved manganese concentrations.

Table 2-2: TWQR and Criteria for Manganese in aquatic ecosystems (Taken from DWAF, 1996b)

TWQR and Criteria	Manganese Concentration (mg/l)
Chronic Effect Value (CEV)	0.370
Acute Effect Value (AEV)	1.300

DWAF (1996b) recognised that there would be instances where site-specific guidance criteria should be developed. These instances typically related to situations where very sensitive species may be present and where background concentration of manganese are higher than the target water quality range (DWAF, 1996b) and proposed that site-specific guidance values could be developed where sufficient information was available. The information requirements would, however, most likely require a minimum 1-year of site specific data gathered over the various seasons.

2.2 ELECTRICAL RESISTVITY TOMOGRAPHY

The electrical resistivity tomography (ERT) technique method involves the generation of electrical currents that are introduced into the ground, a result of which is the generation of potential differences which can be measured at the surface (Kearey and Brooks, 1993). A line array of electrodes is established along the line of investigation and a Direct Current (DC) electrical current controlled using a terrameter is injected into the ground between one pair of electrode and the voltage measured between another pair (Lewkowicz et al., 2011). The terrameter is also used for measuring deviations in potential from that which would normally be expected for a homogenous mass of a known type, which can be used to infer the presence of variations in the underlying strata e.g. faults and/or conductive solutions.

Most rocks conduct electricity by electrolytic rather than electronic processes with electrical current being carried through a rock mainly by the passage of ions in pore waters (Kearey and Brooks, 1993). Thus, a major control on the movement of electrical currents through a rock is the saturated effective porosity by which rocks with a higher effective porosity will allow for the passage of electrical currents more so than those with a lower effective porosity.

Where the ground is uniform, the resistivity calculated will be uniform and independent of both electrode spacing and surface location. However, the presence of sub-surface variations in homogeneity will result in variations of calculated resistivity (Kearey and Brooks, 1993). This latter referred to resistivity is known as the apparent resistivity. The calculated value of apparent resistivity will therefore depend upon the nature of the inhomogeneity in the subsurface, the nature of the surrounding homogeneous mass, and the orientation of the inhomogeneity. Similarly, where groundwater contaminated with conductive ions are present, zones of impacted groundwater may be delineated from deviations in the apparent resistivity.

2.2.1 Resistivity for Contamination Surveying

Electrical resistivity tomography is commonly used for the detection and delineation of polluted groundwater. Chitea and Ioane (2016) reported upon the successful application of vertical electrical sounding (VES), and ERT to detect a source of pollution and determine the depth of affected soils and groundwater. The work undertaken by Chitea and Ioane (2016) also utilised electromagnetic geophysical methods of investigation to gain an understanding of the very near surface geology (i.e. upper 2 mbgl) during which the recognised that low resistivity measurements obtained from the ERT surveys represented the presence of highly mineralised groundwater. Genelle et al. (2011) reported upon the use of various geophysical methods to characterise the conditions of existing landfill covers in parts of France and compared three geophysical profiling techniques:

1. Automatic Resistivity Profiling (ARP©) a techniques developed by GEOCARTA;
2. Electrical Resistivity Tomography (ERT); and
3. Self-Potential.

The ARP© and ERT methods are similar in that both involve the injection of electrical current into the sub-surface with the measurement of the resulting potential. The methods differ with regard to the method of application of the electrodes. ARP© electrodes are wheel-mounted, can be attached to a quad bike and facilitate rapid data acquisition (Genelle et al., 2011; Costantini et al., 2009), whereas the ERT technique requires the manual inserting of the electrodes into the ground. The Self-Potential (SP) method differs from the ART and ERT methods in that no electrical current is injected into the sub-surface; rather the SP method relies upon potential differences in the sub-surface that result from naturally occurring electro-chemical reactions (Kearey and Brooks, 1993). The authors concluded that interpretation of the site data was easier using the ERT than the ARP© method and suggested that this may be due to the method of interpolation utilised. The authors also found that the SP method was useful in identifying variations in potential, but that careful considering of the sampling step-time was necessary to ensure an appropriate interpretation was achieved.

Ogilvy et al. (2009) described the development of an electrical resistivity tomography imaging system known as ALERT (Automated Time-Lapse Electrical Resistivity Tomography). The system had been developed to provide “real-time” measurements of electrical resistivity thus providing a means to protect sensitive and/or vulnerable water resources that may otherwise be negatively impacted upon by encroaching bodies of contaminated groundwater. The authors provided examples of how seawater intrusion, leachate migration from landfills and mine waste, and groundwater movement through embankment landfills could be monitored. A time–lapse method of ERT was also utilised in Iran (Moghaddam et al., 2015), whereby multiple longitudinal lines were surveyed downstream of the Latian dam, a buttress dam located on the Jajrood River approximately 25 km east of the capital Tehran. There the ERT method was used to determine a) the groundwater velocity through the sub-surface immediately downstream of the dam and b) the direction of groundwater flow.

2.2.2 Benefits and Limitations

The ERT method represents a rapid non-intrusive method of investigation and large sections of a site can be investigated in a single day. Based upon recent practical experience, the author suggests that a motivated 3-person team can complete between 800 and 1,000 m of traverse on a 5 m spacing across an industrial site within a single day. A large amount of data can therefore be obtained for a relatively low cost of between R20,000 and R30,000 per day. This is particularly useful in existing and former industrial sites where many years of industrial activity and potential spillage of contaminants or burial of waste may be hidden beneath layers of concrete and tarmac.

The ERT method is also useful in identifying changes in vertical apparent resistivity to anticipate the type of ground conditions present in the near surface. Such information can be used for engineering purposes to help predict the depth to which building foundations may need to be extended; and for groundwater contamination to predict the depth to which groundwater monitoring wells may need to extend or to which depth they may need to be cased. It is the authors experience that in South Africa it is unusual to undertake geophysical surveys for such purposes and instead consultants and contractors tend to position a minimal number of monitoring wells over parts of the site where surface indications of potential sources of contamination exist or are considered to be probable present e.g. storage tanks, surface stains, and leaking pipes. The author notes that this practice fails to consider that the migration of contaminants in the sub-surface is typically structurally controlled, with surface signs rarely being present to indicate the location of such features in the sub-surface. Furthermore, the typical practice of *drilling-blind* and determining casing and drilling requirements at the time of drilling is without doubt leading to the construction of many monitoring wells which become, through lack of preparation and the failure to form a suitably grouted sanitary seal, conduits for the migration of contaminated near surface waters to deeper aquifers that would otherwise not have been impacted. Such therefore supports the recommended use of ERT before monitoring wells are drilled.

However, interpretations based upon the apparent resistivity can be ambiguous (Kearey and Brooks, 1993) and intrusive methods of drilling are required in order to compare values of apparent resistivity with actual ground conditions. Thus, the ERT method should be considered as a guiding technology used to maximise the potential for drilling success when further investigation is undertaken. One particular limitation associated with the method when undertaken on industrial and otherwise brownfield sites is the phenomenon of near surface resistivity variation masking the effects of deeper variations (Kearey and Brooks, 1993). This can be of particular importance when fill-material has been imported to raise ground levels to construct a relatively flat working platform. To overcome this limitation it is necessary to adjust the electrode spacing to focus on deeper horizons. The method can also be limited in locations where multiple sources of sub-surface heterogeneity are present in close proximity to each other.

2.3 MANGANESE AND REMEDIAL TECHNOLOGIES

Most methods of groundwater treatment for heavy metals rely upon either: a) isolation of the contaminant and subsequent containment, b) mechanical separation of the contaminants from sorbed bodies, or c) incapacitation through precipitation. Hashim et al. (2011) reviewed remediation technologies for the treatment of heavy metals in soils and groundwater. The authors noted that various technologies exist which can be classified dependent upon the end-goal of the proposed remediation, including:

1. Complete or substantial destruction/degradation of the pollutants.
2. Extraction of pollutants for further treatment or disposal.
3. Stabilisation of pollutants in forms less mobile or toxic.
4. Separation of non-contaminated materials and their recycling from polluted materials that require further treatment.
5. Containment of the polluted material to restrict exposure of the wider environment.
6. Dilution and dispersion of pollutants.

The EPA (2000) identified that heavy metals can be removed from solution by a number of technologies including:

1. Geochemical Fixation.
2. Permeable Reactive Barriers.
3. Reactive Zones.
4. Soil Flushing.
5. Electrokinetic.
6. Natural Attenuation.
7. Phytoremediation.

Figure 2-1 is taken from Hashim et al. (2011) and provides a summary of the various types of remediation methods available for the treatment of groundwater impacted by the presence of elevated concentration of heavy metals. The various techniques can be divided into three main treatment technologies: Chemical; Biological/Biochemical/Biosorptive; and Physio-chemical.

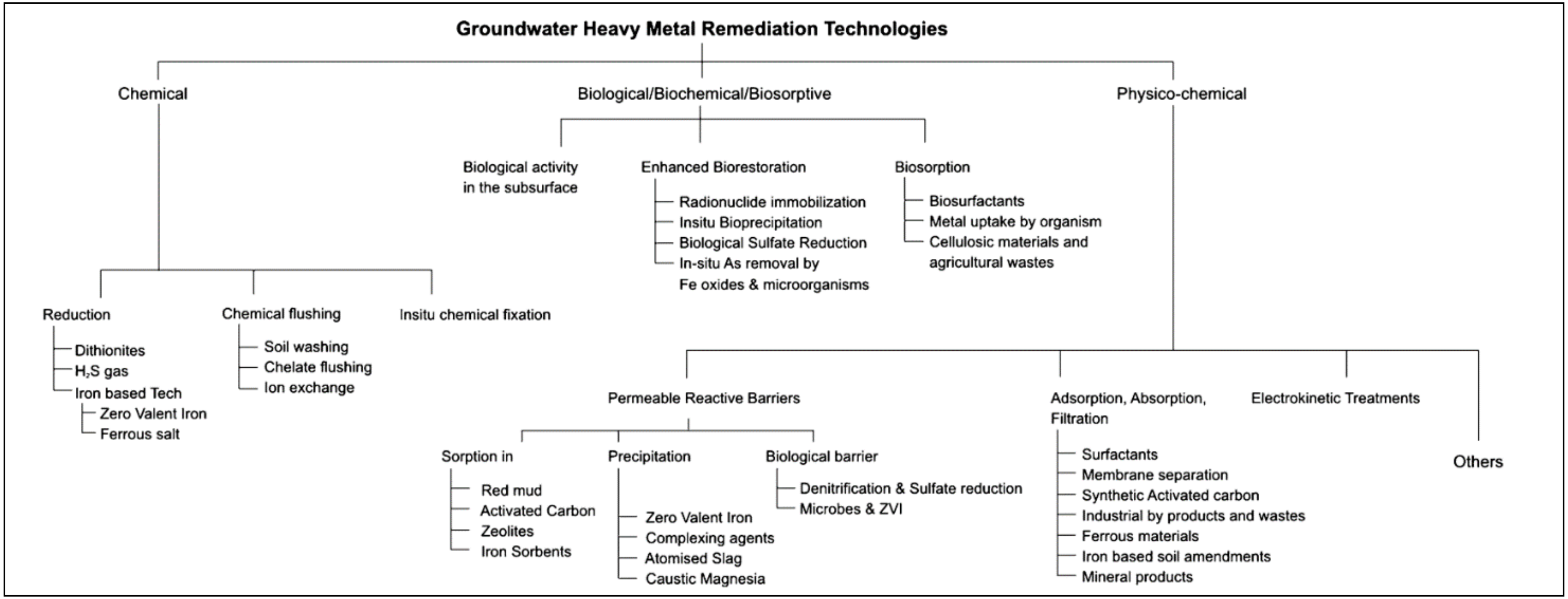


Figure 2-1: Groundwater heavy metal remediation technologies (Taken from Hashim et al., 2011)

The Chemical options are sub-divided into various techniques which include: reduction; chemical flushing; and in-situ chemical fixation. All three techniques are used to convert the metal contaminants to inactive states and thereby decrease the toxicity and/or mobility of the contaminant (Hashim et al., 2011).

Biological, biochemical and biosorptive methods of groundwater treatment are descriptive of those technologies that rely upon naturally occurring biological processes for the transformation and stabilisation of contaminants as either direct or indirect processes. Means and Hinchess (1994) noted that heavy metal remediation of groundwater using biological processes occurs as a result of a variety of mechanisms that include: adsorption; oxidation and reduction reactions; and methylation. These biological processes result in metabolisation of metals and/or changes in redox potential that facilities the oxidation of metals (Silveria, 1988). Ultimately, the biological processes result in changes in the oxidation state that facilitate precipitation of the contaminants, or they are taken up by plants.

Examples of physio-chemical treatment technologies include: a) permeable reaction barriers that are designed for sorption, precipitation or to act as a barrier; b) various techniques for the adsorption, absorption or filtration of contaminants through use of membranes or amendments; and c) electrokinetic treatment which can be used to separate and extract heavy metals from solution (Van Cauwenberghe, 1997).

Innovative in-situ groundwater treatment technologies for the removal of heavy metals from solution have been extensively studied. Vanbroekhoven et al. (2007) undertook some interesting research by which they determined that elevated sulphate and cobalt concentrations in a shallow clayey-sand aquifer in Belgium could be reduced by the addition of a solution consisting of readily available "whey and lactate amended with nitrogen and phosphorous". The process worked by the stimulation of sulphate reducing bacteria facilitating cobalt-sulphide precipitation (Vanbroekhoven et al., 2007). The EPA (2000) discussed various technologies for the removal of hexavalent chromium from solution including in-situ biological processes (i.e. bio-reduction, bio-accumulation, bio-mineralisation and bio-precipitation). Part of the EPA (2000) report discussed trials associated with the addition of molasses, a by-product of sugar processing, to groundwater to promote biological reduction and which were successful in converting Cr^{6+} to Cr^{3+}. Teclu et al. (2009) similarly described the use of molasses to encourage the growth of sulphate reducing bacteria and reduction of As^{5+} in solution. The basis of the treatment technology relied on the reduction of sulphate to sulphide thus removing metals from solution through precipitation.

2.3.1 Ex-Situ Methods of Groundwater Treatment for Manganese

Removal of manganese from groundwater can be undertaken using a wide range of ex-situ technologies. In general these technologies require the construction of above ground treatment facilities with impacted water being abstracted from sumps, wells or boreholes and which allow for the oxidation of manganese present in the Mn^{2+} form. If successfully undertaken this results in the removal of dissolved phase manganese from solution as a precipitate which forms a sludge of manganese in the Mn^{4+} form.

In the Netherlands, amongst other countries, a commonly employed method of groundwater treatment to remove iron and manganese is aeration of water immediately prior to rapid sand filtration. The method facilitates the removal of iron and manganese via: homogenous oxidation, heterogeneous oxidation and biological oxidation (Vries et al., 2016). In the case of manganese, homogenous oxidation results in the conversion of Mn^{2+} to Mn^{4+} ions accompanied by bonding with water molecules and the precipitation of flocculants between sand grains (Vries et al., 2016). Importantly, Vries et al. (2016) stated that homogenous oxidation was dominant "in the zone where an oxidant is present and no adsorbent material, like (coated) sand grains, is present".

Under homogeneous oxidation, both the contaminant and the remediation catalyst are in the same phase. Under heterogeneous oxidation, the contaminant and the catalyst facilitating the water treatment are of differing phase e.g. aqueous contaminant and solid chemical amendment (catalyst).

Biological oxidation involves the addition of iron and manganese oxidising bacteria e.g. *Leptothrix, ochracea, Gallionella ferriginea, Toxothrix trichogenes, Thiobacillus ferrooxidants and Crenothri*x (Vries et al., 2016). The removal of manganese from solution was argued by Vries et al. (2016) to be pH dependent with Mn^{2+} adsorption generally increasing with higher pH and the optimum pH range for removal being between 7 and 7.5. However, Wilopo et al. 2008 stated that manganese is difficult to remove at neutral pH and it is therefore possible that the work undertaken by Vries et al. (2016) has identified a method of treatment that overcomes the difficulty.

Jacobson et al. (1999) presented a paper to the American Society of Mining and Reclamation in which the utilisation of fresh spent mushroom compost for the removal of heavy metals from mine water waste was reported. Jacobson et al. (1999) stated that under oxygen-depleted conditions (anaerobic) the removal of manganese from groundwater by oxidation is minimal with most removal occurring as a result of adsorption "*onto metal precipitates and organic matter*". However, they cautioned that to rely upon adsorption alone for the removal of manganese would be ill-advised as there exist considerable difficulties associated with the '"*low affinity for organic binding site of* Mn^{2+}" (Jacobson et al., 1999).

In 2014, a study was undertaken by Moyosore et al. (2014) in selected areas of Nigeria where 120 samples of groundwater were collected and feasible engineering solutions were proposed for the treatment of groundwater impacted with elevated concentrations of manganese. Moyosore et al. (2014) reviewed water quality data from various wells and identified that elevated manganese was present in wells at concentrations that represented a risk to human health. They thus advised a rather practical solution in that water filters should be supplied to each impacted household to be utilised for the removal of manganese prior to domestic use. Although this approach does not represent the most technically advanced of solutions, it does indicate that the goal of any remediation strategy is to break the connection from a source of contamination to the receptor. In this regard, the use of filters at a household level removed the need for otherwise expensive infrastructure to be developed associated with the possible construction of in-situ and ex-situ remedial solutions and ensured that regardless of where the household obtained its domestic water it could be treated to remove manganese quite easily.

Khan et al. (2004) provided an overview and analysis of site remediation technologies. Their discussions included consideration of pump-and-treat systems for the treatment of groundwater impacted by dissolved metals. They noted that although pump-and treat technologies are the most common type of groundwater treatment system they are not necessarily the most efficient. Many systems are installed where hydrogeological conditions are inappropriate for the chosen technology. For instance, the installation of a pump-and-treat groundwater system within a fractured aquifer is likely to be inefficient due to the high probability of abstraction wells only making contact with a relatively small number of interconnected fractures and thus there is a low probability of achieving sufficient groundwater capture.

2.3.2 In-Situ Methods of Groundwater Treatment for Manganese

In-situ treatment for the removal of manganese impacted groundwater can be achieved through a process of oxidation and separation (VACI, 2017) by which part of the aquifer subject to treatment is oxidised through either the introduction of oxygen or chemicals.

In-situ chemical oxidation (ISCO) is a remedial technique that involves the introduction of an oxidant into the sub-surface that acts to “break apart the bonds in a contaminant compound” (IDEM, 2016). The appropriateness of a particular type of chemical oxidant to use will be in part dependent upon the pH of the water under-going treatment and/or the ground conditions present. IDEM (2016) identified seven different types of ISCO:

1. Hydrogen Peroxids or Fenton’s Reaction/Reagent.
2. Modified or non-pH-dependent Fenton’s Reaction.

3. Permanganates.
4. Ozone.
5. Persulphates.
6. RegenOx^{TM}.
7. Zero Valent Iron (ZVI).

Fenton’s reagent is a solution of hydrogen peroxide used to oxidise solutions and which requires acidic conditions with the optimum pH range being between 2.5 and 3.5 (IDEM, 2016). Dekonta (2016) reported upon the use of Fenton’s reagent in Serbia where the technology was successfully used for the treatment of groundwater impacted with 1,2-dichlorethane. There are two types of modified Fenton’s reagent that are non-pH dependent. The first uses hydrogen peroxide with a chelating agent. The second uses calcium or magnesium peroxide for slow-release of hydrogen peroxide (IDEM, 2016). Phatai et al. (2013) reported upon trials in which potassium permanganate was used to remove Mn^{2+} and Fe^{2+} from synthetic groundwater via oxidation. With respect to manganese, the end product of permanganate oxidation is manganese dioxide (MnO_2) as a precipitate. The authors noted that the removal of manganese was assisted by the presence of iron and this was attributed to the “autocatalytic effect of hydrous manganese-iron oxide” (Phataei et al., 2013). Furthermore, the authors identified that the presence of Ca^{2+} and Mg^{2+} and the addition of aluminium potassium sulphate after oxidation reduced the effectiveness of the manganese removal (Phataei, et al., 2013). Upadhyay and Srivastava (2005) undertook a review of ozone in the treatment of industrial and municipal wastewater and noted that ozone has a wide range of potential uses with regard to water treatment due to its high oxidant capability and that ozone “readily decomposes to oxygen” meaning that there is no adverse by-product associated with the use of ozone. Seu et al. (2010) undertook pilot tests in order to evaluate the effectives of ozone in removing heavy metals from mine drainage waters and found that it was possible to use ozone for the treatment of mine water and improve the water to such an extent that it met Korea’s drinking water standards with respect to iron and manganese content. Oxidation of in-situ groundwater through the introduction of persulphate ($S_2O_8^{2-}$) was reported upon by Liu et al. (2014). It was determined that persulphate exhibited a slow rate of decomposition and that it can be advantageous to inject persulphate into groundwater, allowing it to migrate to areas of low hydraulic conductivity (Liu et al., 2014) and thereby ensuring greater site coverage for treatment. RegenOx^{TM} is a permanganate-based chemical oxidant that operates under alkaline conditions (IDEM, 2016) and oxidises contaminants to cause precipitation of metals from solution (Rao, 2016).

Zero valent iron (ZVI) is commonly used in groundwater remediation for the treatment of contamination. ZVI has a capacity to donate electrons and participate in redox reactions with a large range of oxidants and removes contaminants via reduction rather than oxidation (IDEM, 2016). In-situ groundwater treatment for groundwater impacted by elevated concentrations of manganese can be achieved by the use of in-ground permeable reactive barriers. In such a system, a contaminated plume of groundwater will migrate in the direction of flow through the barrier and the concentration of contaminant will reduce as result of biological, physical or chemical reactions dependent upon the nature of the substances used within the barrier. Wilopo et al. (2008) reported upon trials of permeable reactive barriers utilising ZVI and sheep manure and determined that manganese was mostly immobilised through adsorption onto compost and ZVI, and partially as a carbonate precipitate. However, the effectiveness of the treatment diminished with time due to bio-degradation of the compost used, indicating that an essential component in the use of this remediation method would be the replacement of spent compost at established time-periods to be determined based upon the concentration of manganese present in the groundwater. Further, Wilopo et al. (2008) concluded that “microbial activities of heterogeneous bacteria might contribute negatively to immobilisation of manganese in the long term” thus suggesting the possibility of remobilisation of manganese at some time in the future.

Ahmad (2012) reported upon various methods of groundwater treatment for the removal of dissolved manganese from solution. With respect to in-situ removal, Ahmed (2012) reported mostly upon the use of the Vyredox® method, which is designed to remove dissolved manganese from solution prior to groundwater abstraction. The Vyredox® method encourages biological activity in the subsurface by creating an “optimum environment” for bacterial growth at the contact between the reduction and oxidation zone ultimately leading to the oxidation of manganese (Silveria, 1988). This method represents a technique that undertakes groundwater treatment at the abstraction point and only at the time of abstraction. As the treatment undertaken is achieved at the point of use this presumably represents a cost effective method of treatment by avoiding remediation and treatment of water that would otherwise not be utilised and instead limiting the extent of treatment to that which is required by the user.

A diagrammatic representation of the Vyredox® method is provided as Figure 2-2. In explanation of the method, oxygen is injected into the sub-surface for a number of hours before being stopped and allowing for a high potential redox zone to be developed within the aquifer (Ahmed, 2012) which facilitates the precipitation of manganese and iron. The Vyredox® method is simple to develop and manage and can be undertaken under a range pH situations without any requirement for pre-neutralisation of groundwater (Ahmed, 2012). However, precipitation of heavy metals may impact upon yield from a groundwater abstracting well due to precipitation of metals within the pores and fractures in the aquifer. This will reduce the efficiency of the abstraction well and potentially result in ultimate abandonment of the well – a costly undertaking! However, the extent of precipitation will be dependent, in part, upon the concentration of precipitating dissolved metals within the groundwater. For a typical well of low concentration of elevated manganese blockages are unlikely to occur within a human lifetime. However, if such were to occur then there are established chemical amendments and techniques for the rehabilitation of boreholes that could be added to the abstraction well the clear any pores that have become blocked over the passage of time.

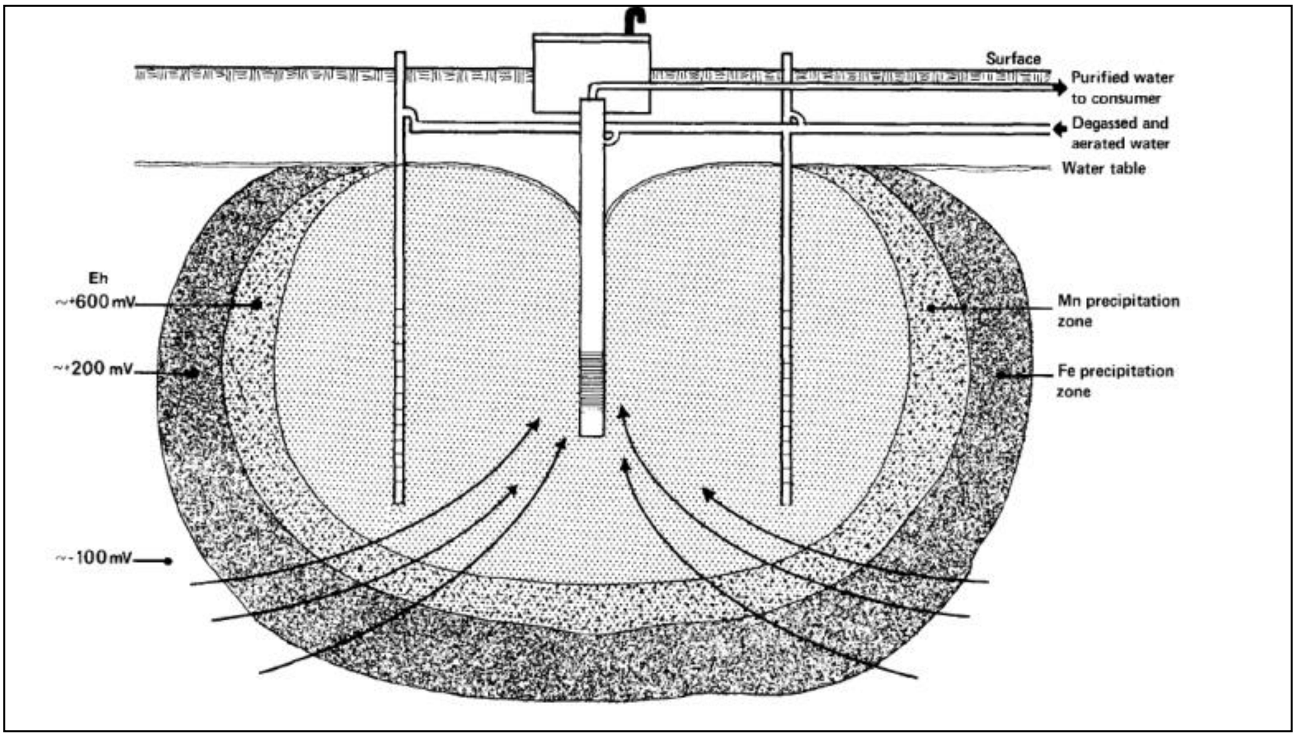


Figure 2-2: Vyredox® Method (Taken from Ahmed, 2012)

CHAPTER 3:
SITE DESCRIPTION

With any contaminated groundwater site investigation that ultimately leads to the development of a remediation strategy it is important characterise the study site through desk top research. The characterisation thus informs the design of the site investigation with respect to probable ground conditions present that may impact upon the choice of technique to use for site investigations and/or identify possible features of the site that may limit the choice of remedial strategy that may be utilised. This section describes the site setting of the study area with respect to the political, geographical and geo-environmental setting. A short history of the industrial development of the study site is also included.

3.1 SITE HISTORY

The study area includes two parcels of adjacent land that was operated by Delta (E.M.D.) (Pty) Ltd, for the manufacture of electrolytic manganese dioxide (MnO_2) for use in the dry battery cell industry. Only 40% of the site was owned by Delta with the remaining 60% being leased from the neighbouring Manganese Metal Company (Pty) Ltd (MMC) (Allen, 2014). Prior to site development in the early 1980’s only informal settlements were present on site. Then in 1981, a pilot plant was constructed on the western part of the site. This proved to be successful and between 1981 and 1988 what became known as the Western Plant was further developed with the construction of cell houses. In 1996, construction began on the Eastern Plant during which additional cell houses were constructed. The site remained operational until production ceased in 2014. During this period however, Delta operated two near identical processing plants, which involved the leaching of reduced manganese ore with sulphuric acid to dissolve the manganese (Steyn, 2010). The leach solution would then be subject to on-site purification and electroplating to form manganese dioxide in the cell houses (Steyn, 2010). Whilst in operation the two plants produced more than 30,000 tonnes of electrolytic manganese dioxide per annum (Allen, 2014).

3.2 SITE LOCATION

3.2.1 General

The study area is located in Nelspruit (now known as Mbombela), a South African city in the province of Mpumalanga located approximately 340 km east-north-east of Johannesburg and close to South Africa’s border with both the Mozambique and the Swaziland. A general site location map is provided as Figure 3-1.

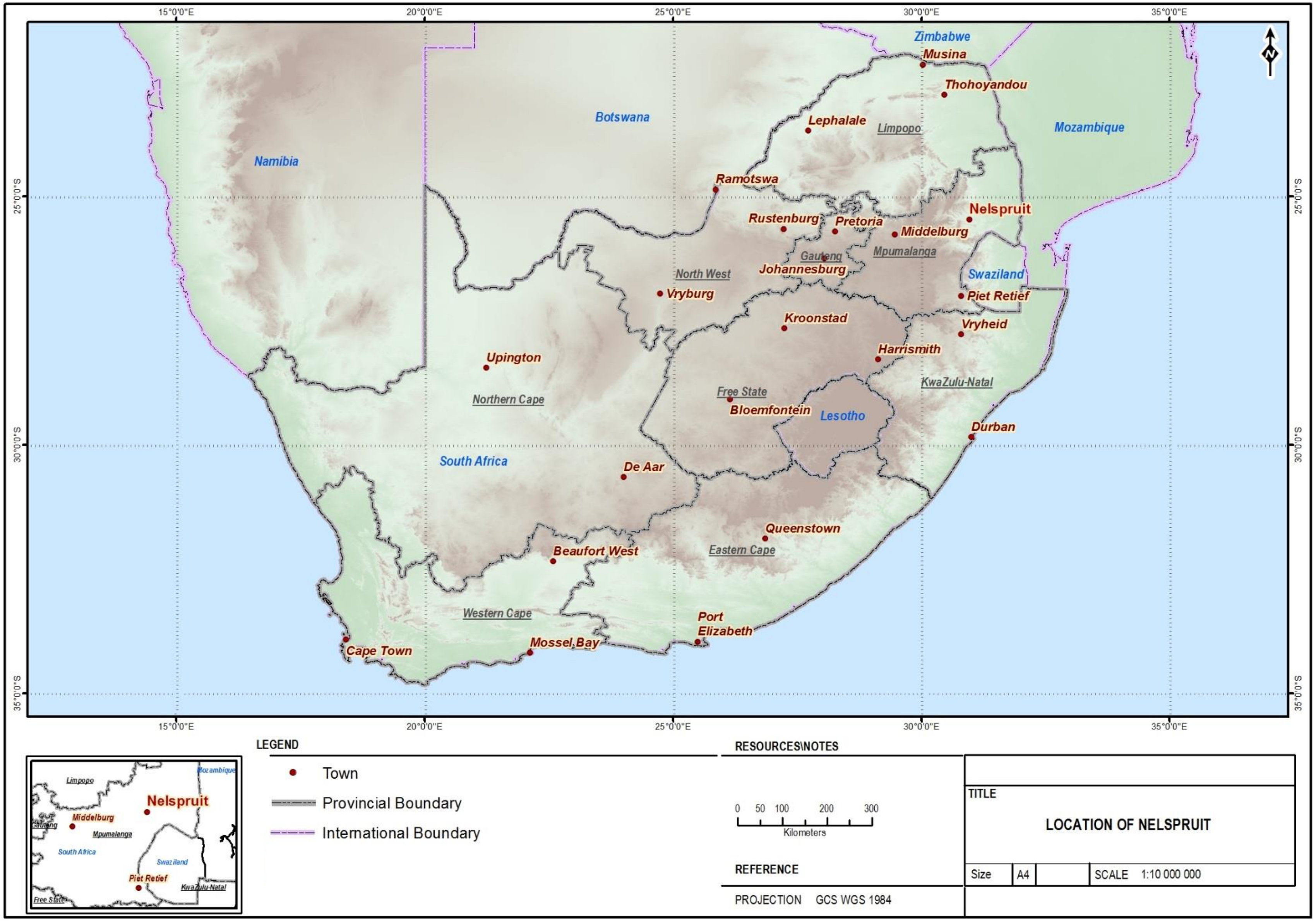


Figure 3-1: Location of Nelspruit within South Africa

Nelspruit (Mbombela) is the provincial capital of Mpumalanga. The economy of the area is focussed upon: a) tourism, whereby Nelspruit represents a major tourist destination due to its close proximity to the southern parts of the Kruger National Park (KNP); b) agriculture, with the fertile soils and subtropical climate providing suitable conditions for citrus fruit farming and sugar production; c) industry, as several industries exist that support manganese processing, fruit canning and agricultural processing; and d) forestry, with the major industry player being the South African Paper and Pulp Industries Ltd (SAPPI).

The site is located within an industrial zone to the north of Nelspruit, within the Mbombela (MP322) Local Municipality, a sub-structure of the Ehlanzeni District Council (DC32). A site location drawing is provided as Figure 3-2. Two images of the site and an image of the facility taken from the south of the site facing north are provided as Figure 3-3 and Figure 3-4, respectively. The Crocodile River is present between the site and the hills shown in the distance in Figure 3-3.

To the immediate north of the site a generally east-west running wide single-carriageway road (R2296) is present which links Nelspruit with residential communities to the north and east (see Figure 3-5). Beyond the road is undeveloped bush land (see Figure 3-6) which slopes moderately steeply down towards the Crocodile River located 200 m north of the site. The eastern boundary of the site is bordered by various light industry typically associated with transportation and vehicular maintenance. Immediately to the south of the site is a railway line, a canal and a fuel depot. At the time of the investigation, the railway line was operational and was used for the transportation of manganese ore to site. The canal is of unknown age, however it is connected to the Crocodile River at its western extremity, and it was constructed to facilitate the movement of water from the Crocodile River to a citrus farming area located to the east of Nelspruit. A picture of the canal looking towards the north-east is provided as Figure 3-7. The fuel depot is operated by BP Southern African (Pty) Ltd and is located approximately 500 m from the site boundary. The site neighbour along the western boundary is the Manganese Metal Company (Pty) Ltd (MMC). There is known to be connectivity between near surface infrastructure on the Delta and the MMC sites.

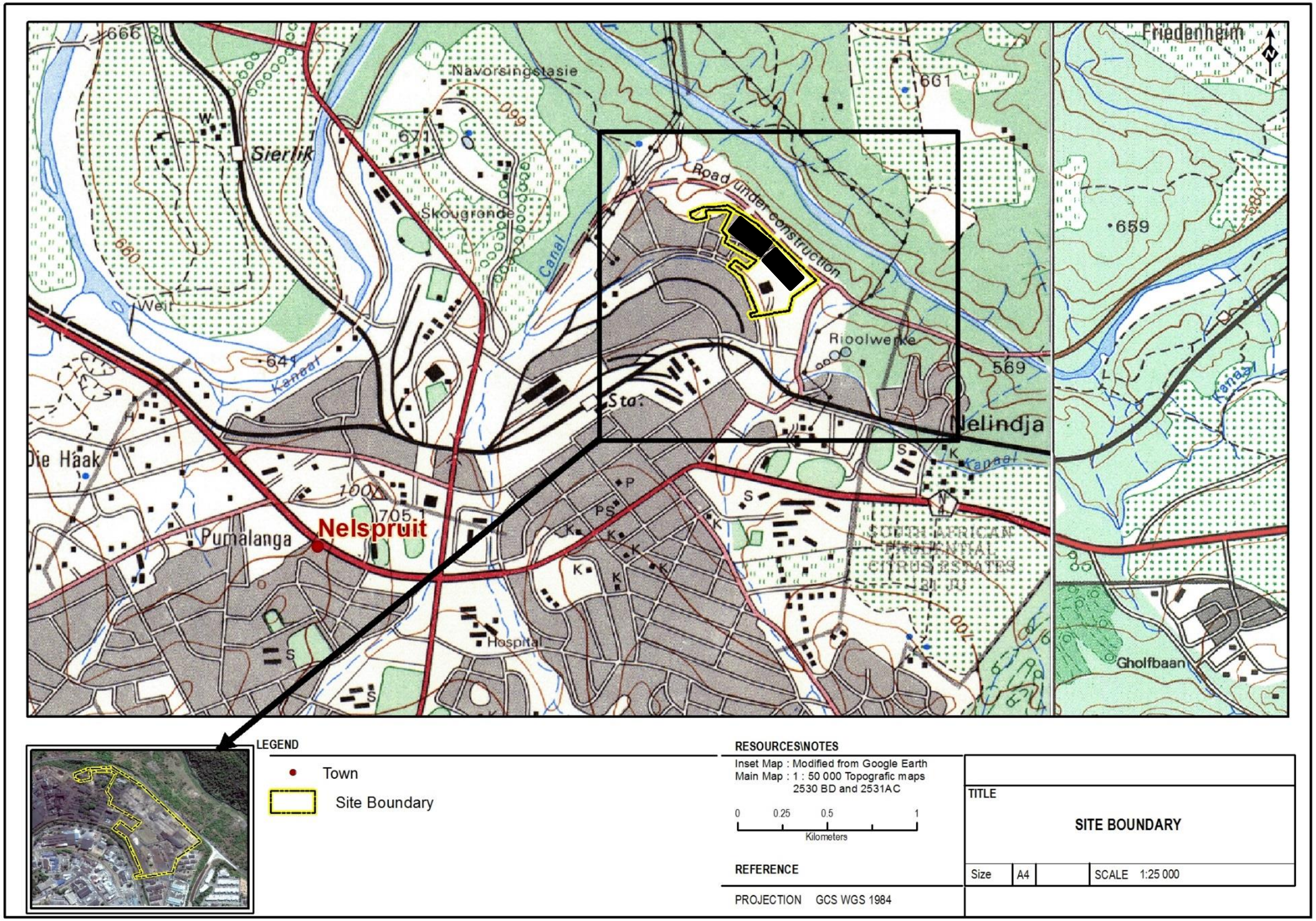


Figure 3-2: Site Boundary

Figure 3-3: Delta E.M.D. facility looking towards the north

Figure 3-4: Delta E.M.D. facility near waste processing area looking towards the north east

Figure 3-5: Northern Boundary Road (R2296) looking to the east

Figure 3-6: Undeveloped Bush Land looking towards to the north-west

Figure 3-7: Canal located immediately south of the site looking north-east

3.3 ENVIRONMENTAL SETTING

3.3.1 Topography

The base of the Makonjwa Mountains are located near Barberton, approximately 45 km south of Nelspruit and range in elevation between 600 and 1,800 metres above mean sea level (mamsl). As one approaches Nelspruit after passing through numerous valleys and ridges the elevation gradually decreases, such that at the study site the topographical elevation is typically between 640 mamsl to the southwest of the site and 620 mamsl to the northeast. The Crocodile River is located 200 m north of the site and is estimated, in the area of the study, to be at an elevation of between 575 and 570 mamsl and gradually reducing in a westerly direction. The topographical elevation for the area is shown on Figure 3-2.

3.3.2 Temperature, Rainfall and Evaporation

Total annual rainfall is estimated at 796 mm per annum with most rainfall occurring between October and February each year. Nelspruit enjoys a sub-tropical climate with average temperatures ranging between 14.6 and 23.6 °Celcius, however, average temperatures have been known to vary by as much a 9 °Celsius year on year (EN, 2017). This data is presented in Table 3-1 and as Figure 3-8.

Table 3-1: Average Rainfall and Evaporation

Month	**Oct**	**Nov**	**Dec**	**Jan**	**Feb**	**Mar**	**Apr**	**May**	**June**	**July**	**Aug**	**Sep**
Rainfall*	74	116	128	130	116	90	51	20	11	11	14	35
Average Potential Evaporation	116	113	130	136	124	117	93	80	66	71	86	106
Average Temperature*	20.5	21.6	22.9	23.6	23.4	22.5	20.4	17.3	14.9	14.6	16.6	18.9

*From EN, (2017)

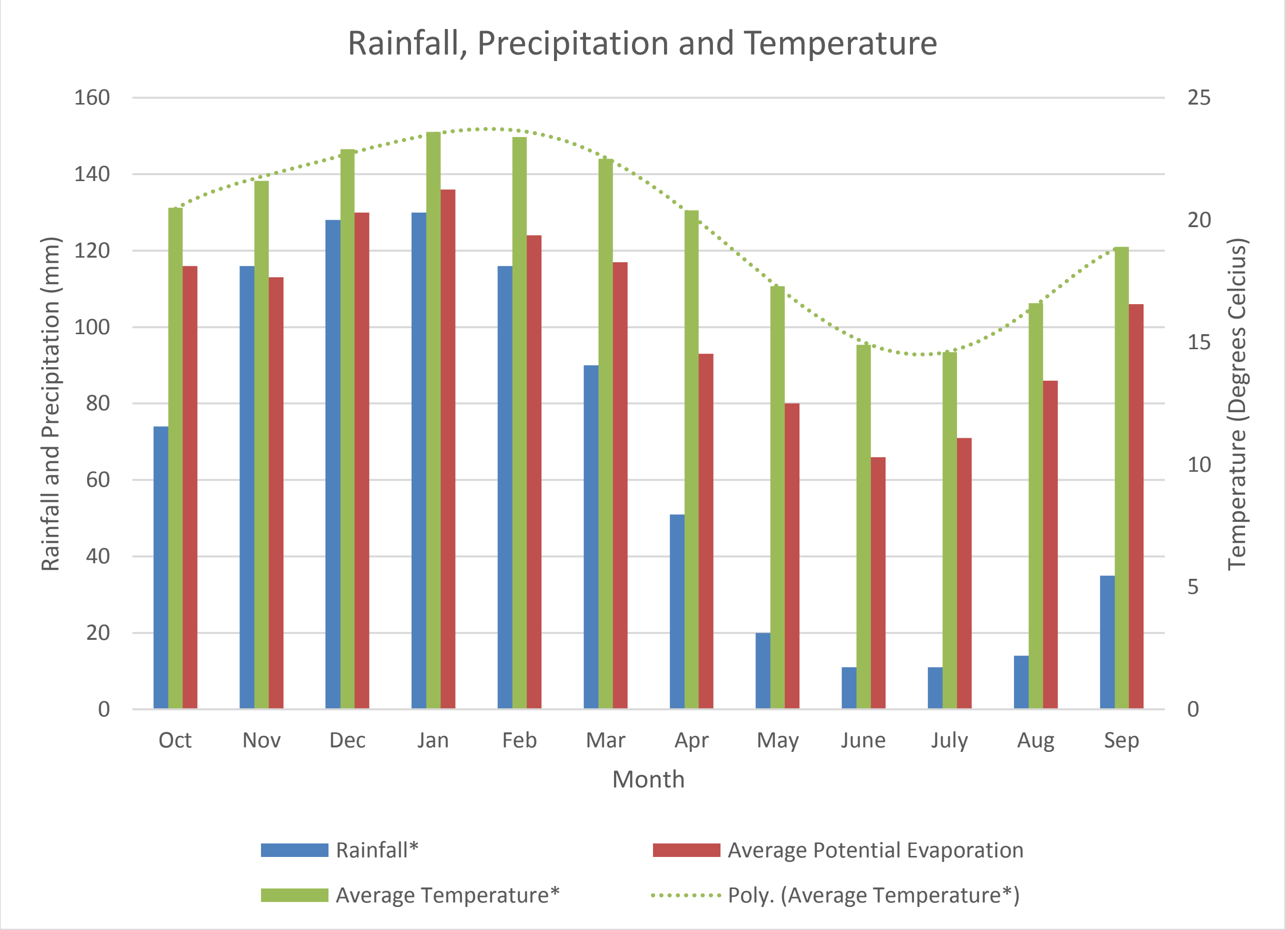


Figure 3-8: Rainfall, Precipitation and Temperature

3.3.3 Geology

Review of the 1:250,000 Geological Series 2530 Barberton Sheet Geological Map (1986) indicates that the southern part of Nelspruit is underlain by grey to white coarse-grained biotite granite, whereas the northern part is underlain by potassic gneiss and migmatite. Both rock types form part of the Nelspruit Suite of Archean granite. Several north-west south-east trending diabase dykes are shown to be located to the north east and west of Nelspruit. An additional east-west trending diabase dyke to shown to be located approximately 1.3 km north of the site which is almost parallel to an even closer linear feature (possible dyke, geological contact, or fault) located 1 km north of the site (see Figure 3-9). It is well-known that the Nelspruit granite suite is characterised by the intrusion of basic sills and dykes and it is considered highly probable that such features are present beneath the study site (Hughes, 2014a). Further, review of historical photography for the area suggests that where present these features are present they are likely to be north-south trending.

3.3.4 Hydrological and Hydrogeological Setting

3.3.4.1 Surface Water

The site lies within the Crocodile River catchment (Catchment Number X22J). A man-made canal is located immediately to the south of the site. The canal is several metres in width and is used to facilitate the diversion of irrigation water from the Crocodile River to nearby citrus farms located to the east of Nelspruit. The age, depth and condition of the canal are not known, however it is considered probable that some leakage from the canal is occurring, and most certainly in the near vicinity of the study site.

Hydrological features close to the site are shown in Figure 3-10. To the north of the site is the Crocodile River. In the area of the study, the river is wide and relatively shallow. A photograph of the Crocodile River in the near vicinity of the site is provided as Figure 3-11. The Crocodile River flows in an easterly direction eventually reaching the Indian Ocean via Mozambique. To the west and east of the site there are two non-perennial streams trending south-west to north-east (see Figure 3-12 and Figure 3-13). These streams are in full flow during time of heavy rainfall whereas at other times of the year they simply capture and divert surface run-off or near surface interflow to the Crocodile River.

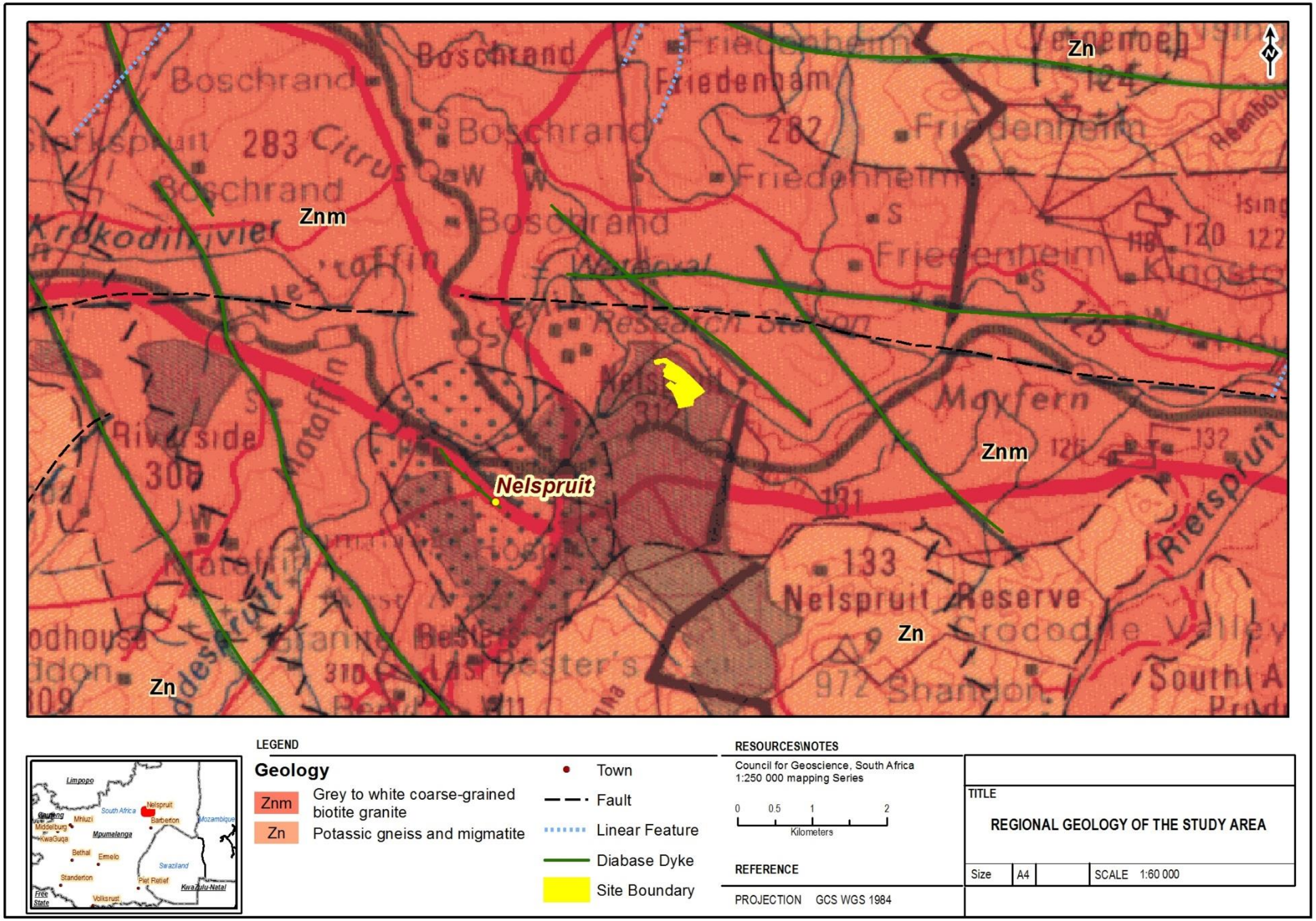
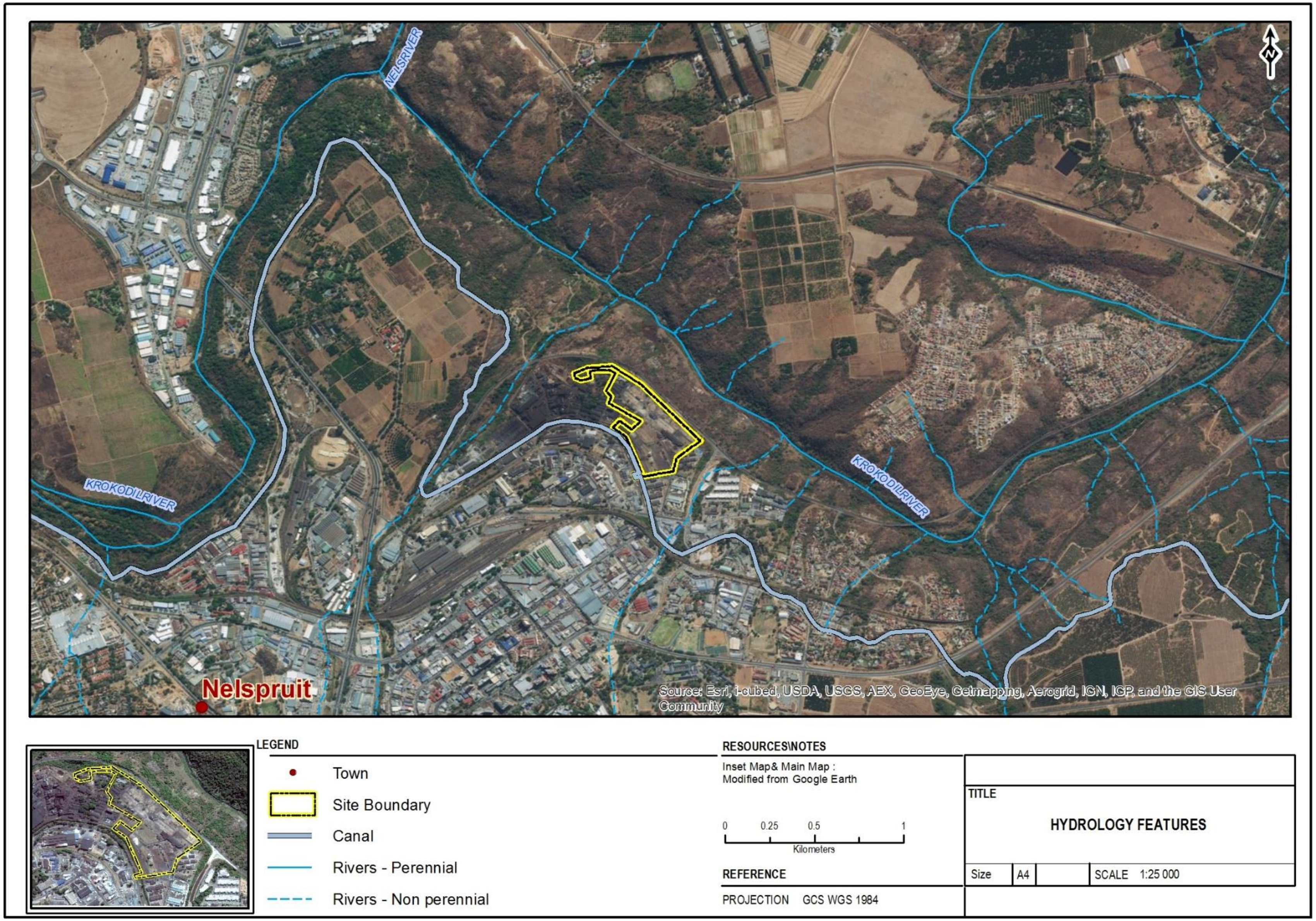


Figure 3-9: Regional Geology of the Study Area



Source: Esri, i-cubed, USDA, USGS, AEX, GeoEye, Getmapping, Aerogrid, IGN, IGP, and the GIS User Community

Figure 3-10: Hydrology Features

Figure 3-11: Crocodile River located to the north of the site looking north

Figure 3-12: Western Stream looking to the north-east

Figure 3-13: Eastern Stream looking to the north

3.3.4.2 Groundwater

The highly weathered granite and granitic gneiss in this part of South Africa is commonly associated with shallow perched phreatic aquifers and the depth to which these are encountered is typically dependent upon the extent (depth) of weathering that the underlying strata has been subject to and the degree of fracturing present within the rock mass. This can result in very shallow aquifers, in some instance the water table may be less than 1 m deep. The presence of a shallow phreatic aquifer at the site is evidenced by seepage through the rock faces that form the site boundary and above which the facility has been constructed. Sustainable basement aquifers are considered to be present in the immediate area of the site.

Figure 3-14 shows the rock face located on the eastern side of the site where there is evidence of groundwater seepage at approximately 1.50 m below surface level. In the area of the site, shallow groundwater flow direction is generally considered to be in a north and north-easterly direction towards the Crocodile River, although some localised variations in flow direction may be anticipated due to the assumed presence of geological structures in the sub-surface creating preferential pathways for the migration of groundwater. It is considered by the author that the shallow groundwater level associated with the shallow aquifer is there because of connectivity with the canal that forms the southern boundary of the site. The canal is considered to be leaking surface water obtained from the Crocodile River from a point approximately 3.25 km west of the site into the sub-surface. The canal has been in place for many tens of years (possibly constructed in the 1940's but not confirmed) and groundwater levels have stabilised to that which they are today. If the canal was not present it is highly probable that groundwater levels would reduce and that fractures that allow for the passage of groundwater would simply facilitate the movement of interflow during times of increased precipitation. A groundwater flow map for the site developed using site specific measurements is provided in Chapter 4.

Figure 3-14: Shallow Water Seepage through Rock face to the west of the site

From practical experience gained in the field the author considers that aquifers identified in this geology type are usually poorly developed and low-yielding. However, the presence of structural features such as intrusions (dykes and sills) and/or faults can improve the potential for obtaining improved groundwater abstraction rates. Further, review of the 1:500,000 Hydrogeological Series Nelspruit Sheet 2530 (1999) indicates that the site is underlain by a Type D3 intergranular and fractured aquifer type for which borehole yields of between 0.5 and 2.0 l/sec may be expected with the cross-section provided on the hydrogeological map indicating that although the weathered strata beneath the site may have large storage potential it is likely to be of low transmissivity. However, boreholes constructed within fractures related to either tensional or compressional stresses can provide relatively high borehole yields. A simplified hydrogeological map is provided as Figure 3-15.

In addition, due to their near surface presence, shallow perched aquifers are often impacted upon by near surface contamination associated with run-off from residential, commercial and industrial areas.

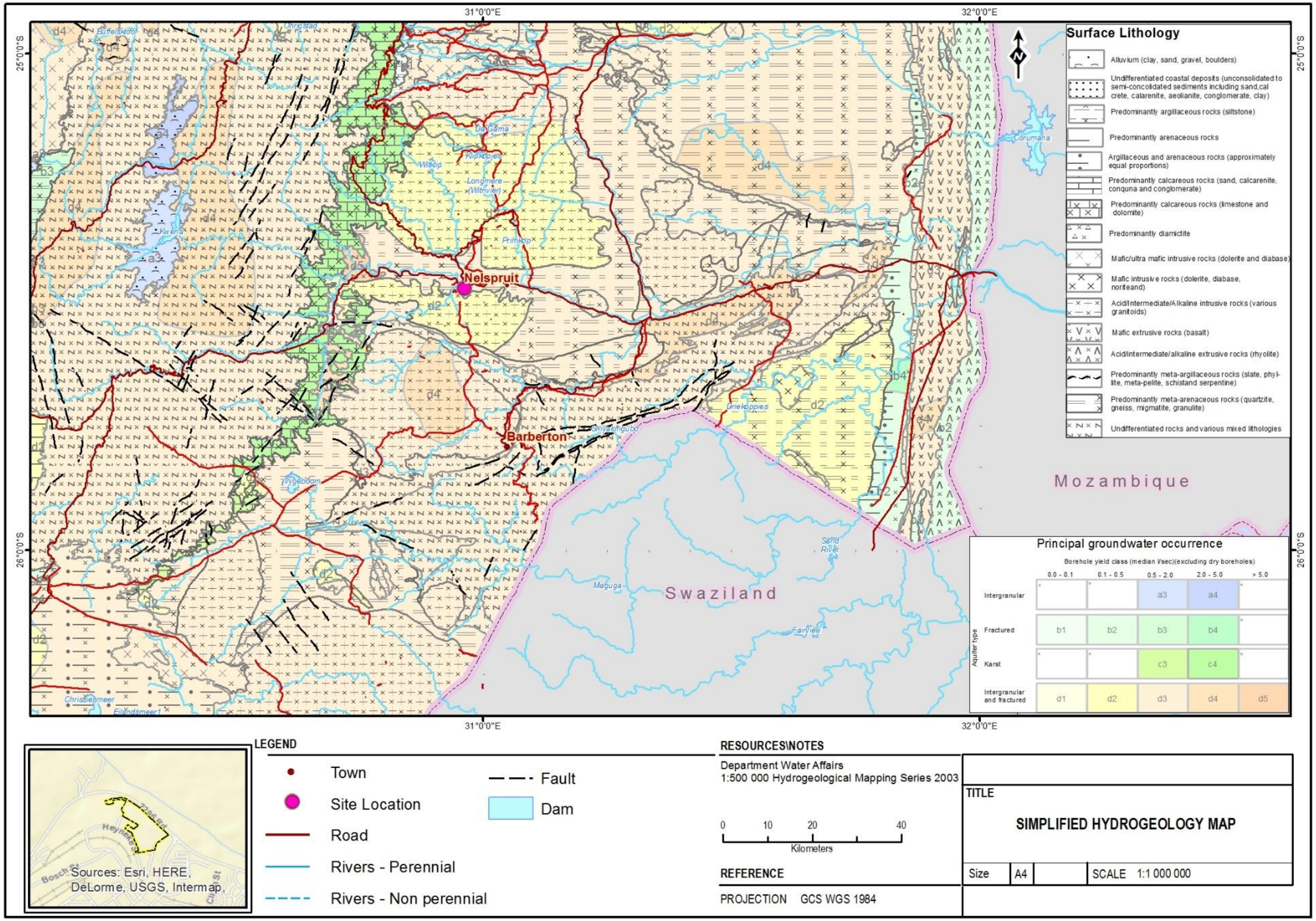


Figure 3-15: Simplified Hydrogeology Map

CHAPTER 4:
SITE INVESTIGATION

4.1 COMPONENTS OF THE SITE INVESTIGATION

At an early stage of the study after review of existing site information, the author determined that there was insufficient information available to allow for a thorough groundwater contamination assessment to be undertaken. Therefore, the author designed and executed a multi-stage and multi-technique site investigation to gain a sufficiently detailed understanding of the distribution of potential contamination within the near surface soils, sub-surface groundwater and the Crocodile River with specific reference being made to manganese, sulphate and pH. The site investigation and assessment was undertaken from early 2014 to early 2015.

This chapter discusses the various site investigations techniques and methodologies that were utilised and followed at the site and which allowed for a detailed understanding of the site to develop. Further, reference is made with regard to how the various site investigation techniques informed the decision making process with regard to placement of monitoring wells and interpretation of the developing conceptual site model.

The site investigation made use of the following methods of investigation and assessment:

1. A geophysical survey.
2. A geotechnical investigation and assessment.
3. A contaminated land assessment.
4. A groundwater assessment.
5. A surface water assessment.

Justification for inclusion of the above noted assessments in development of a remediation strategy is provided in the following sections. The various aspects of groundwater quality assessment are presented and discussed in Chapter 5.

4.1.1 Geophysical Survey

Kearey (1993) noted that crystalline rocks with negligible intergranular porosity are conductive along cracks and fissures. The pre-assessment conceptual site model developed by the author during conceptualisation of the problem presumed the probable presence of geological structures within the sub-surface which may act as preferential pathways for the migration of groundwater and contaminants. This presumption was based upon the various diabase dykes, faults and other linear features shown on the geological map for the area (Figure 3-9) and in close proximity to the site. It was envisaged that geological structures similar to these may be present in the sub-surface beneath the site but may not previously have been geologically mapped. It was therefore proposed to undertake a series of geophysical surveys across the site using Electrical Resistivity Tomography (ERT) in order to determine variations in apparent resistivity of the underlying strata and use the results to guide development of the conceptual site model. It was also considered that the identification of zones of greater relative conductivity may indicate the presence of highly conductive contaminants (e.g. SO_4^{2-} and Mn^{2+}) and or the presence of geological structures (e.g. dykes or faults) the orientation of which could potentially provide a preferential pathway for the migration of contaminants towards the Crocodile River.

Further, the author proposed to compare vertical variations in resistivity with the rock quality designation (RQD) values determined through geotechnical logging of drilling cores undertaken as part of the Geotechnical Investigation (Section 4.1.2 and Section 4.3). In this regard, the author anticipated rock with a lower RQD (being indicated by an increased number of fractures within the underlying rock) would possess a lower apparent resistivity. By combining the geophysical survey with geotechnical drilling and logging the author was able to obtain a substantial amount of information relating to sub-surface variations in rock quality within a relatively short period of time.

4.1.2 Geotechnical Investigation

During early stages of conceptualisation of a potential remedial strategy for the site and before the detailed site investigation work had been undertaken by the author consideration was given by others to the construction of a shallow groundwater interception trench along the northern boundary of the site immediately adjacent to the R2296 road. It was proposed that the trench would be excavated to an appropriate depth (to be determined) in order to intercept migrating contaminated groundwater flowing through the sub-surface in a northerly direction towards the Crocodile River. Then, depending upon the quality of the groundwater intercepted and collected, the water would either be disposed of directly to the municipality sewer or undergo some form of pre-treatment prior to disposal. However, the author identified that such a strategy presumed that the contamination was present only in the near surface and that it would be possible to excavate a suitable interception trench to an appropriate depth along the entire northern boundary the site. The author considered that there were several potential fatal flaws with this strategy including:

1. It may not be possible to excavate a trench through the underlying strata due to a) in-situ strength and b) limited site access due to the trench needing to be constructed in very close proximity to the R2296 road.
2. The interception trench would be constructed off-site and therefore it would be more difficult to maintain serviceability than if it were constructed on the site owners property.
3. Any trench constructed may not be able to be excavated to a suitable depth to intercept deep-seated contamination.
4. Should only localised on-site groundwater contamination be found to be present rather than a presumed extensive lateral distribution then a trench constructed along the full northern boundary could represent a rather costly over-engineered solution.

Therefore, the author proposed that an excavatability assessment be undertaken whereby review of the apparent resistivity from the geophysical surveying used in combination with logging of geotechnical boreholes to determine RQD could be used to determine a realistic depth of excavation for various methods of excavation (e.g. digging, ripping, blasting). Such would then inform the feasibility of the proposed trenching option.

In addition, the author proposed that same method of analysis be used to interpret changes in vertical rock quality as a means of inferring rock strength such that the depth of weathering could be determined across the site with the more weathered strata more likely representing a preferential flow path for the migration of contaminants and groundwater. Similarly, it was considered that changes in apparent resistivity coupled with geotechnical assessment could be used to indicate any sub-surface changes in elevation between similar units as a result of geological displacement and therefore one may be able to identify the presence of geological structures or other lineaments.

4.1.3 Contaminated Land Assessment

Section 36(5) of the National Environmental Management Act, 1998 (Act 107 or 198) states that: “An owner of land that is significantly contaminated, or a person who undertakes an activity that caused the land to be significantly contaminated, must notify the Minister and MEC of that contamination as soon as the person becomes aware of that contamination”. It was considered probable that elevated contaminants were likely present in the sub-surface soils, however, the distribution of elevated contaminants determined to be present on site during previous investigations (Steyn, 2010) did not necessarily coincide with the location of probable sources of contamination determined by the author through gaining an understanding of site processes. It was therefore conceptualised that potential contaminants of concern may have been distributed across the site under the influence of wind and as such there also existed a potential for off-site contamination to be present in the soils surrounding the site, particularly over the undeveloped land located between the site and the Crocodile River. It was proposed to utilise site specific soil quality data obtained during a previous investigation (Steyn, 2010) and compliment this with additional off-site soils data obtained as part of this assessment (Hughes, 2014c).

4.1.4 Groundwater Assessment

The groundwater assessment was done by reviewing water quality from the eight existing monitoring wells and constructing new monitoring wells to allow for a) representative samples of groundwater to be obtained for subsequent chemical analysis and b) undertaking in-situ aquifer testing to determine groundwater parameters for site assessment and to inform determination of risk to the receiving environment. Data obtained from the geophysical survey and the geotechnical assessment was used to inform the siting of the groundwater quality monitoring boreholes. During the course of the detailed site assessment nineteen new monitoring wells were constructed to depths of between 6 and 40 mbgl. The data obtained from the groundwater assessment was used to provide estimates of contaminant loading into the Crocodile River. The groundwater quality assessment is discussed in detail in Chapter 5.

4.1.5 Surface Water Assessment

During the desktop study phase of the study it was identified that the nearest down-gradient surface water feature to the site was the Crocodile Rover located 200 m to the north of the site. The river meanders in a generally west to east direction beyond the northern boundary of the site. Previous research undertaken by the WRC identified that the Crocodile River is stressed (Palmer et al., 2013) and impact upon by various contaminants including elevated manganese, sulphate and sodium chloride from industrial and agricultural activities. It was therefore proposed to obtain upstream and downstream water quality measurements to determine if any differences in water quality could be identified. In addition, review of historical photographs for the site indicated the possible presence of two geological structures connecting the Crocodile River to the central part of the site. It was considered that such a structure could represent a pathway for the migration of contamination and therefore additional surface water sampling points were established in the location of where these inferred structures or lineaments met with the Crocodile River. Detailed description of the various assessments undertaken with regard to each aspect of the site investigation are provided in the following sections.

4.2 GEOPHYSICAL INVESTIGATION

During July 2014, a geophysical survey using electrical resistivity tomography technique was used to gain an understanding of variations in apparent resistivity across the site, thus allowing the author to determine the possible presence of contaminated groundwater within the sub-surface and geological structures that may act as pathways for the movement of groundwater and/or the migration of groundwater based contaminants.

The survey was conducted using the Wenner survey protocol with a 5 m electrode spacing and a total cable length of 200 m which achieved a depth of investigation of 30 m. In total, five lines of geophysical traverse were undertaken which were mostly orientated north-west to south-east but with one traverse orientated north-south. The survey lines were located along accessible parts of the site and were often limited by the presence of infrastructure, underground services and personal safety associated with road trafficking. The site surface was covered with a layer of concrete hardstanding and in order to achieve good contact between the electrodes and the sub-surface it was necessary, using a hand-held drill to construct small diameter holes to approximately 0.30 to 0.50 mbgl through which the electrodes were hammered into the ground using a heavy rubber hammer. In total 1,700 m of survey lines were completed. Details relating to survey line start and end points and length are provided in Table 4-1 and their locations indicated on Figure 4-1.

Table 4-1: Geophysical Survey Lines (ERT)

Survey Line	Starting Point		Finishing Point		Length of Survey (m)
	Latitude	Longitude	Latitude	Longitude	
DE01	-25.45870	30.98722	-25.45750	30.98598	600
DE02	-25.45610	30.98244	-25.45960	30.98784	200
DE03	-25.46060	30.98529	-25.45880	30.98514	200
DE04	-25.46020	30.98690	-25.45780	30.98413	400
DE05	-25.45990	30.98746	-25.45800	30.98528	300

Detailed descriptions of the position and orientation of the five survey lines are provided in the following text.

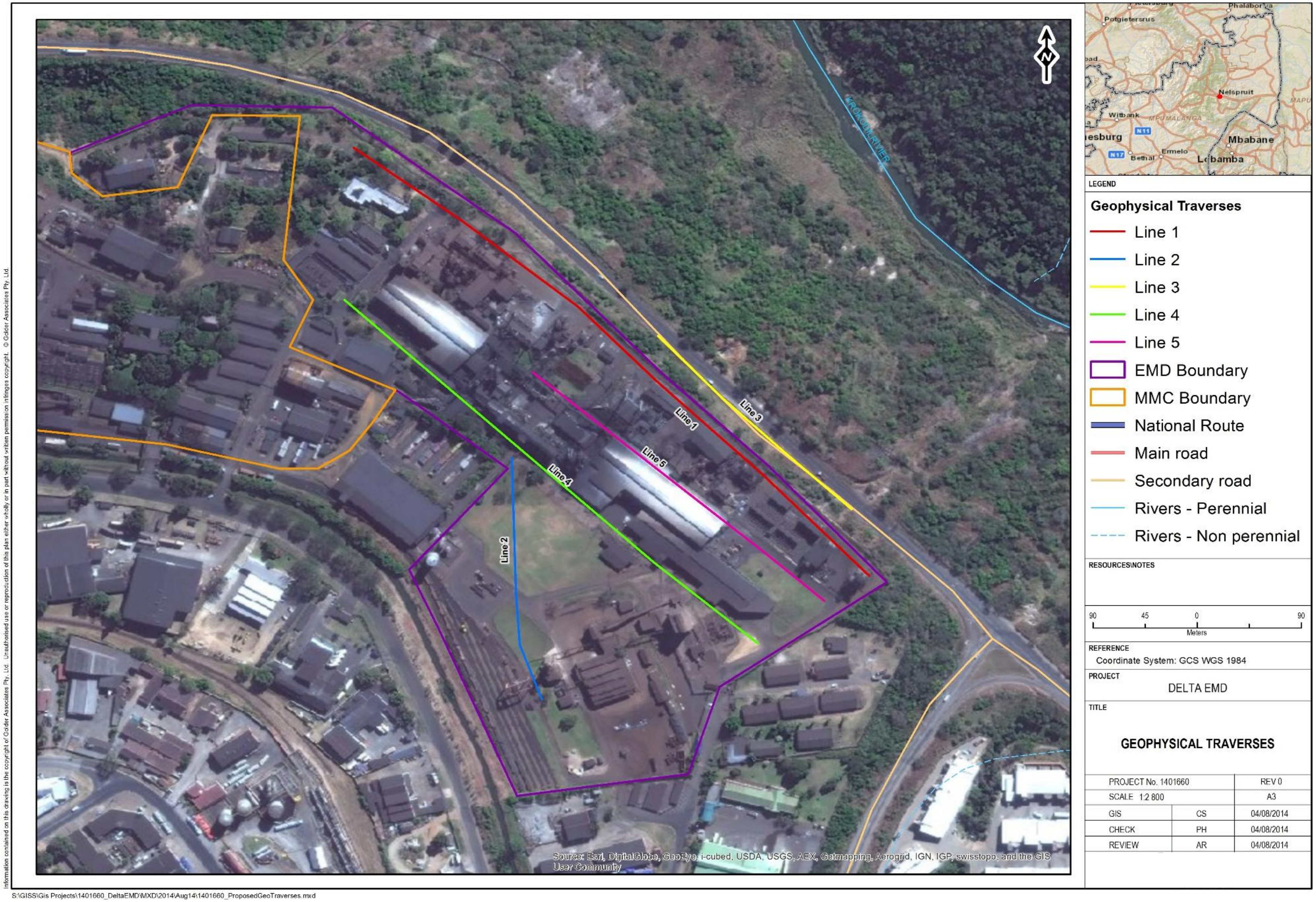


Figure 4-1: Geophysical Survey Lines (Modified from Hughes, 2014b)

ERT Traverse DE01 – Line 1

ERT traverse DE01 was extended over 600 m along an internal road and orientated parallel to the northern site boundary. The survey undertaken along this line identified two zones of very low apparent resistivity (high conductivity) which are indicated by areas of blue colour on Figure 4-2 at the following locations along the length of the survey:

1. 120 m to 230 m.
2. 350 m to 415 m.

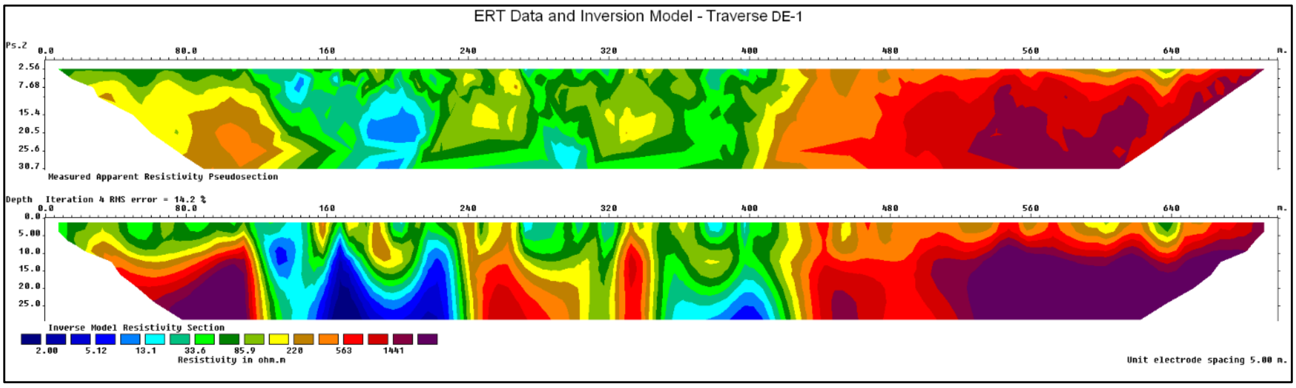


Figure 4-2: DE01 - ERT Data and Inversion Model (Taken from Hughes, 2014b)

The areas of low apparent resistivity were considered to be representative of zones impacted by contamination emanating from wet-process sections of the facility. The zones of low apparent resistivity also correlated with near surface changes in topography and apparent lineaments observed from review of historical photographs for the site. It was therefore considered possible that the low resistivity zones not only represented the presence of conductive contaminants but also represented structural features in the sub-surface along which preferential groundwater and by default contaminant flow was prevalent.

The two areas of low resistivity were separated by areas of high resistivity (230 m to 350 m red/brown colour) and to the eastern end of the line (<120 m) and western end of the line (>350 m) areas of high resistivity were also present. Generally, areas of high resistivity were coincident with outcrops of solid and strong strata indicating that weathering was not as deep in these areas.

ERT Traverse DE02 – Line 2

ERT traverse DE02 was a relatively short survey line of only 200 m in length that was limited in distance due to the presence of buildings and other infrastructure preventing a longer continuous line being surveyed. The traverse was oriented north-south and was taken over a football pitch that had been created on an area backfilled in part with treated sludge “Greenfill”.

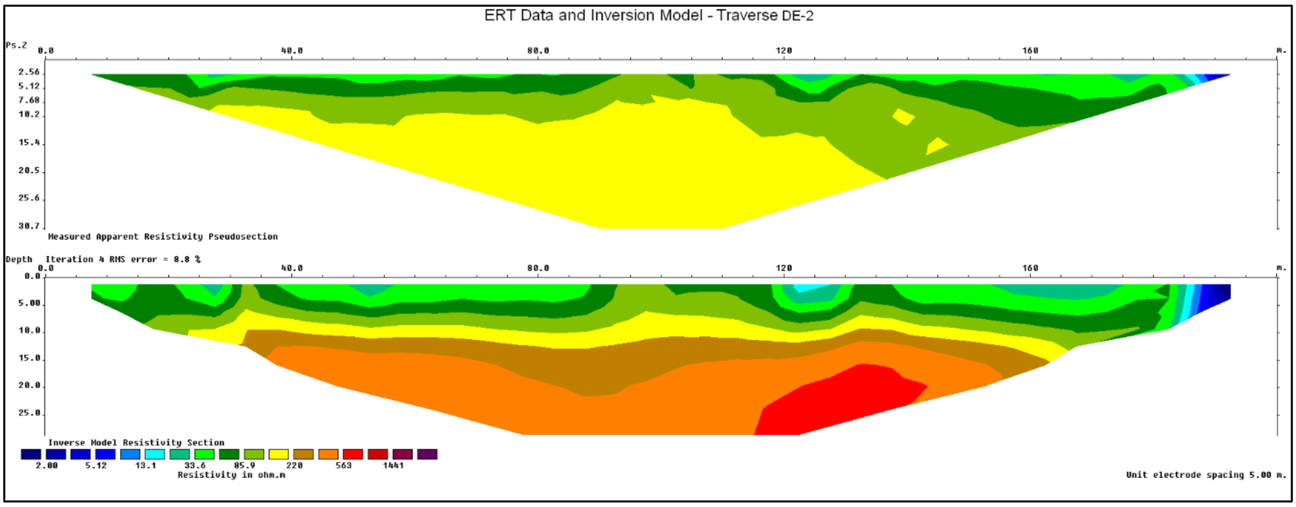


Figure 4-3: DE02 - ERT Data and Inversion Model (Taken from Hughes, 2014b)

The traverse was undertaken up-gradient of the wet-processing parts of the facility and no obvious areas of very low apparent resistivity were identified. Assessment and review of the areas of moderate resistivity value (circa 220 ohm.m) suggest that a highly weathered zone is probably present within the solid strata extending to a depth of between 15 and 18 mbgl (Hughes, 2014b).

ERT Traverse DE03 – Line 3

ERT traverse DE03 was the only traverse undertaken off-site. It was located immediately north of the northern boundary wall and adjacent to the east-west running section of the R2296 road. Safety concerns for site personnel associated with fast-moving traffic immediately adjacent to the line of survey prevented the author undertaking a survey longer that a length of 200 m along a relatively wide-area of layby. A section of low to moderate apparent resistivity was identified from approximately 35 m to 100 m along the traverse (Figure 4-4). This section is considered to represent a zone of moderately weathered and fractured rock to a depth of approximately 8 mbgl (Hughes, 2014b). Observations by the author along the northern external wall of the site suggested that near surface seepage of waters and possible contaminant migration may occur in this area and such may therefore be identified in the ERT cross section.

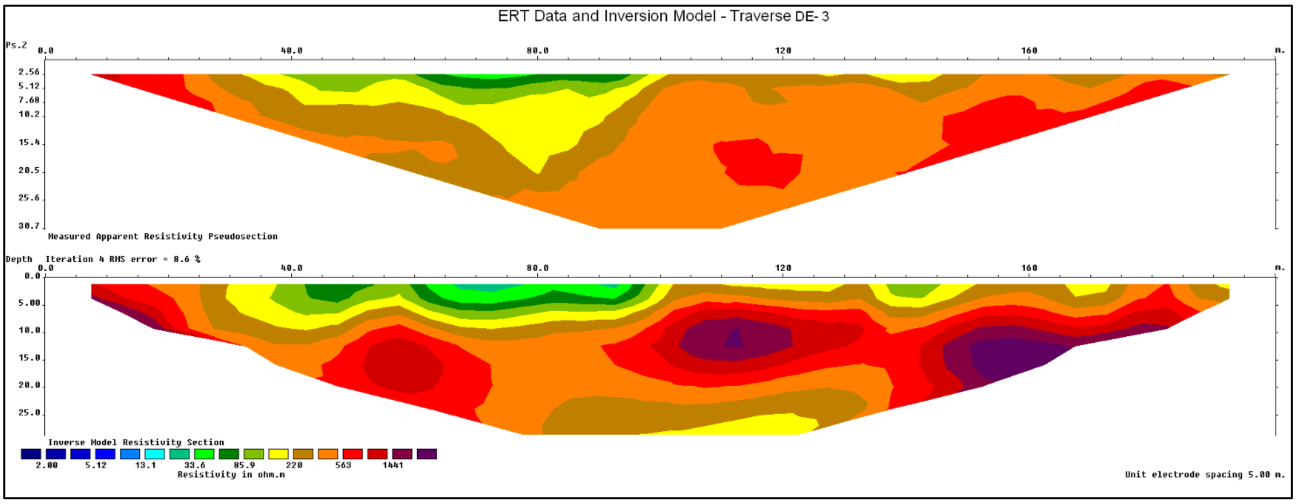


Figure 4-4: DE03 – ERT Data and Inversion Model (Taken from Hughes, 2014b)

ERT Traverse DE04 – Line 4

ERT traverse DE04 was a 400 m long line survey undertaken on an internal site road located between the football pitch and the eastern cell houses (Hughes, 2014b). The survey identified three sections of very low apparent resistivity (high conductivity) indicated by areas of blue colour on Figure 4-5 at the following locations along the length of the survey:

1. 160 m to 195 m.
2. 245 m to 255 m.
3. 315 m to 325 m.

Given the close proximity of this line to the wet-process sections of the facility it is considered that these sections likely indicate areas of in-ground contamination associated with leakage of process water during site operations. The weathering profile is considered to extend to a depth of 15 mbgl (Hughes, 2014b).

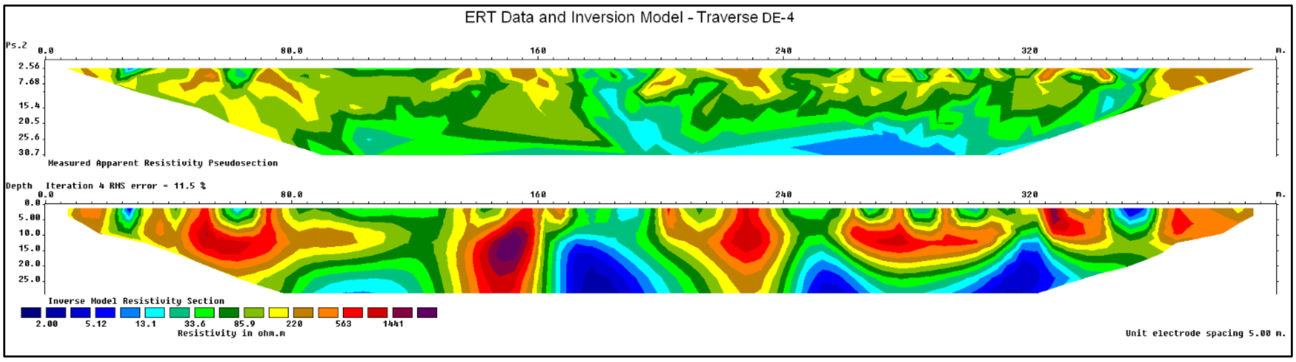


Figure 4-5: DE04 - ERT Data and Inversion Model (Taken from Hughes, 2014b)

ERT Traverse DE05 – Line 5

The fifth survey line DE05 was 300 m in length and was advanced in a south-east to north-west direction along a partially raised internal road adjacent to a retaining wall and in front of Cell House 2 of the Eastern Plant. An area of very low resistivity was identified from 140 m to 220 m and indicated by the blue colour towards the base of Figure 4-6. At this point along the traverse the area under investigation was located immediately down-gradient of Cell House 2 of the Eastern Plant. The depth of weathering was estimated at 12 m to 15 mbgl in this area (Hughes, 2014b) with less weathered strata and more competent rock being present to the east and west of the survey line.

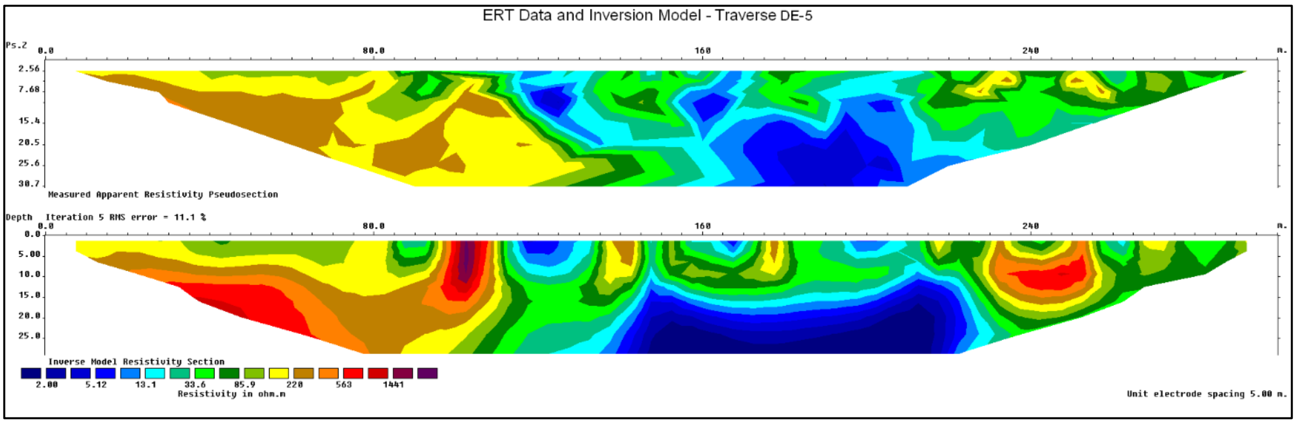


Figure 4-6: DE05 – ERT Data and Inversion Model (Taken from Hughes, 2014b)

Three near surface low resistivity anomalies were identified in the upper 5 m however these are considered to be buried infrastructure (pipes) connecting Cell House 2 with the Leaching Plant.

4.2.1 Discussion

The geophysical survey undertaken at the site consisted of five ERT traverses over a total distance of 1,700 m and to a typical depth of 30 mbgl. Processing of the site data and interpretation of apparent resistivity allowed the author to identify zones of low resistivity that were considered to be indicative of groundwater impacted by contamination and/or the presence of geological structures representing potentially preferential pathway for groundwater flow and the migration of contaminants in a northerly direction towards the Crocodile River.

Historically, the site had been levelled for construction during the 1980's. The geophysical survey was able to identify variations in the resistivity of the underlying strata that were considered to be indicative of the weathering profiles and the pre-construction undulating nature of the near surface prior to construction. Indeed, contrast between high and low resistivity that coincided with lineaments observed in historical photographs were used by the author to infer the presence of geological structures crossing the site in a north-south orientation that potentially connect with the Crocodile River.

The geophysical survey also provided an indication of the potential presence of contamination in the sub-surface through the identification of zones and sections of very low resistivity along the various traverses. Mapping of the low apparent resistivity zones has allowed the author to interpret the presence of two main zones of contamination on site (shown in 3-D in Figure 4-7) with a simplified possible extension of these zones off-site and a smaller area located on site only. The three areas have been labelled: Zone A, Zone B and Area 1 and are shown on Figure 4-8.

The features are described as follows:

- Zone A is an elongated feature extending in a northerly direction from the Western Cell House towards the northern boundary of the site.
- Zone B is more widely dispersed than Zone A and extends from the Eastern Cell House in a northerly direction towards the northern boundary of the site.
- Area 1 indicates the location of a buried culvert that was historically used for diverting storm water from other industries located to the west and south of the site. However, this culvert has since been closed-off and is no longer operational. The date of closure is not known.

The ERT work undertaken on site has proven to be highly successful in the identification and delineation of structural features and areas impacted by contaminated groundwater. The work facilitated the following:

- The selection of on-site monitoring well locations for obtaining groundwater samples within and outside of areas impacted by groundwater contamination.
- The selection of off-site down-gradient soil sampling locations at positions where it was considered that any contamination migrating through or along geological structures would likely day-light as a result of reduced weathering depth close to the Crocodile River. Four locations for off-site soil/precipitate sampling were determined for which chemical analysis was undertaken and details provided within Section 4.4.
- The selection of suitable surface water sampling locations, upstream, downstream and at the point at which the previously mentioned structural; features may connect with the Crocodile River. For this work suitable surface water sampling locations (GACROC01 to GACROC04) were selected and which are discussed further in Section 5.

The location of monitoring wells, proposed soil sampling locations and surface water sampling locations are indicated on Figure 4-8.

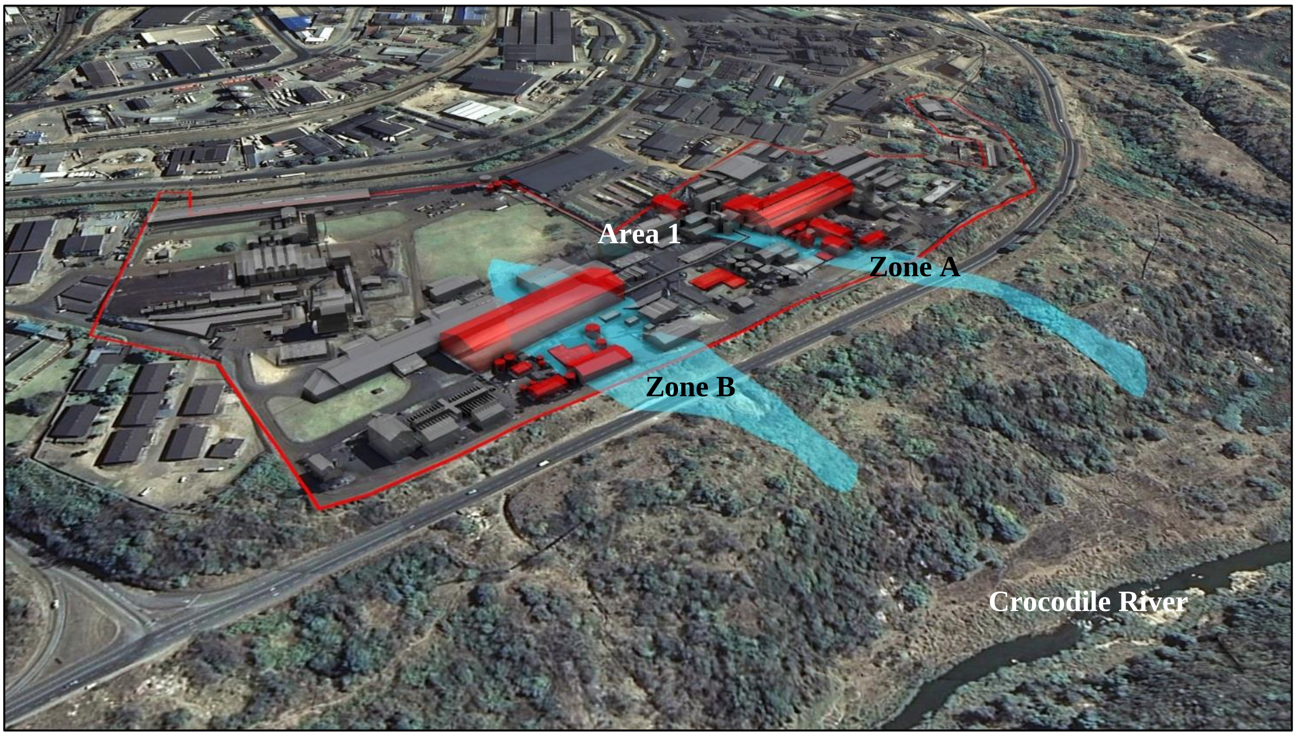


Figure 4-7: 3-D Conceptualisation of Plume Migration Path (Taken from Hughes, 2014c)

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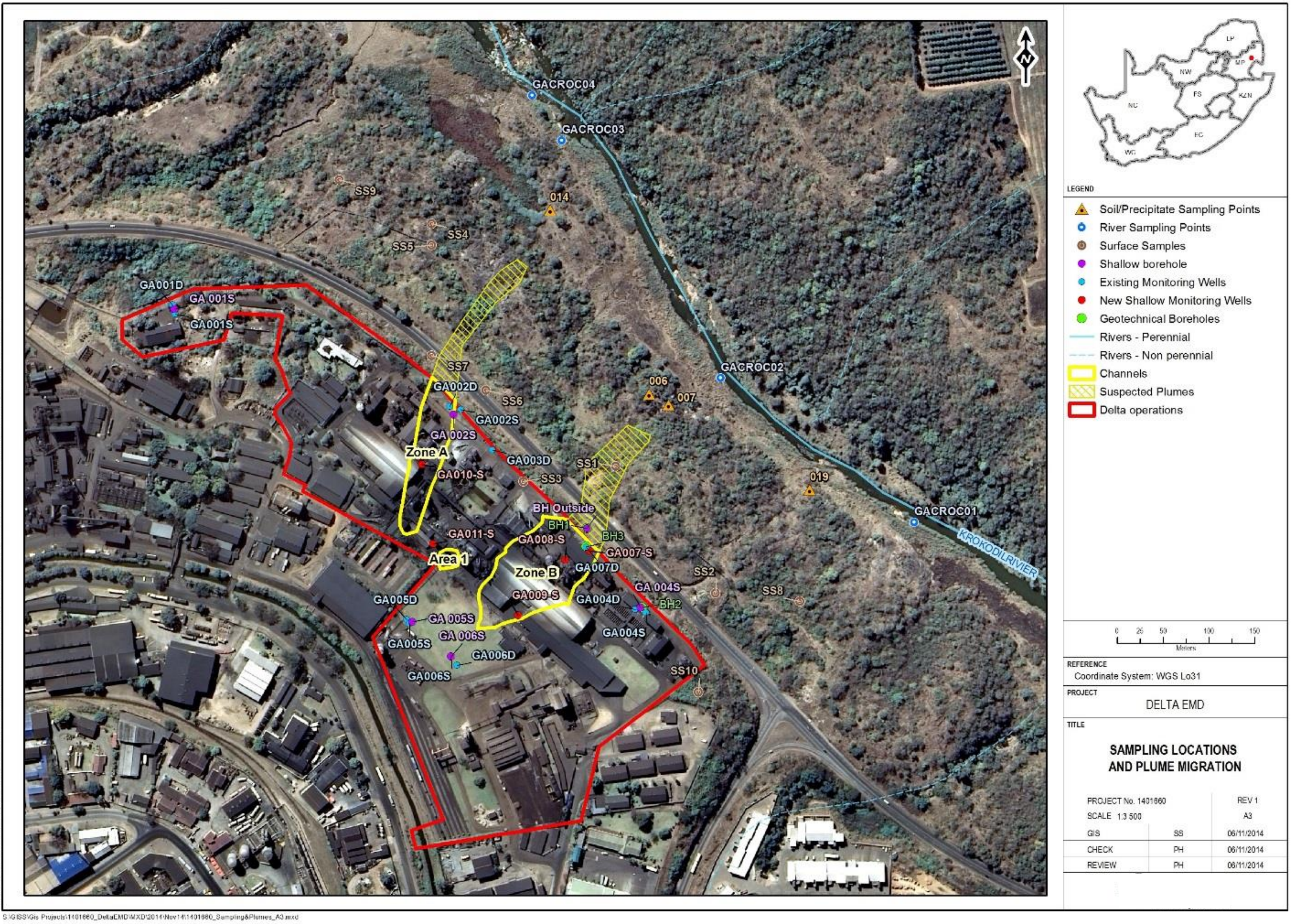

Figure 4-8: Plume Location and Proposed Sampling Points (Taken from Hughes, 2014c).

4.3 GEOTECHNICAL INVESTIGATION

4.3.1 Introduction

The geotechnical assessment forming part of the site investigation involved the drilling of three geotechnical boreholes, geotechnical logging and subsequent construction of piezometers to measure groundwater levels. The purpose of the geotechnical drilling was to obtain a detailed understanding of the strength of the underlying strata and fracture spacing to determine the weathering profile across site.

Three boreholes were drilled at NWD4 core size and extended to depths of between 9.40 and 24.15 mbgl. Two of the boreholes were drilled on site towards the north-eastern side of the site and the third was drilled off-site in a layby located immediately north of the northern site boundary. The boreholes were positioned in areas of high resistivity and low resistivity as interpreted from review of the geophysical surveying.

The three geotechnical boreholes were logged in accordance with the Code of Practice for Site Investigations BS5930:1999 with specific emphasis being placed on determination the: Total Core Recovery (TCR), Solid Core Recovery (SCR), Fracture Index (FI), and RQD. The cores were struck with a geological hammer to obtain in-field estimates of relative rock strength from which various cores were selected by the author for point load testing. Drilling, logging and testing determined that the underlying rocks on site were highly weathered to depths of between 10 and 15 mbgl and possessed an uniaxial compressive strength (UCS) of between 20 and >350 MPa.

After drilling and logging all three boreholes were converted to piezometers to allow groundwater measurements and groundwater quality samples to be obtained at a time in the future. The piezometers were installed with 50 mm diameter plain and slotted PVC casing to the base of the borehole. The annulus between the boreholes and the casing was backfilled with fine quartz sand to a depth of 1 mbgl then finished with a bentonite seal and a lockable borehole cover that was made flush to the ground to avoid representing an obstacle to on-site traffic.

4.3.2 Selection of Drilling Locations

The author reviewed the geophysical survey lines (DE01 and DE03) to select drilling locations for the three geotechnical boreholes. Line DE01 had been surveyed on-site along the northern boundary whereas line DE03 was positioned off-site within the extended layby between the northern site boundary and the R2296 road. Two borehole locations were selected on site and one borehole location was selected off-site. The surface elevation of the off-site borehole (BH1) was approximately 5 to 7 m below that of the on-site boreholes and it was anticipated that the off-site weathering profile would not extend as deeply as the on-site weathering profile and therefore it would be possible to correlate weathering profiles between the two elevations. Borehole drilling location and construction details are shown in Table 4-2 and a borehole drilling location map is provided as Figure 4-9.

Table 4-2: Geotechnical Borehole Location and Piezometer Construction

Borehole	Latitude	Longitude	Elevation (mamsl)	Depth of Drilling (mbgl)	50 mm Diameter Plain PVC casing.		50 mm Diameter Plain PVC casing.	
					From	To	From	To
BH1	-25.45836	30.98669	617	9.41	0	1	1	9.41
BH2	-25.45914	30.98729	622	14.90	0	1	1	14.90
BH3	-25.45854	30.98668	624	22.15	0	1	1	22.15

Borehole BH1 was located off-site and was positioned approximately 80 m from the eastern of line DE03. The two on-site geotechnical boreholes were positioned 80 m (BH2) and 160 m (BH3) from the eastern end of line DE01. The positioning of the three boreholes shown alongside the geophysical survey lines are provided as for borehole BH1 and on for boreholes BH2 and BH3.

Borehole BH1 was positioned to target a zone of low to moderate apparent resistivity which had been identified to be present between 35 and 100 m from the eastern end of line DE03. Review of the apparent resistivity profile for line DE03 suggested that a change in substantial rock strength may occur at a depth of approximately 6 mbgl coincident with an apparent resistivity reading of 85.9 ohm.m.

Borehole BH2 was located to target the high apparent resistivity zone indicated by the red and orange colours on and what was presumed to represent solid strata with a low FI. Borehole BH3 was positioned to target the low resistivity zone extending to considerable depth and indicated by the blue colours similarly on . Areas of low apparent resistivity were presumed to be indicative of a) fractured strata along which groundwater migrates and/or b) where highly conductive contaminants may be present.

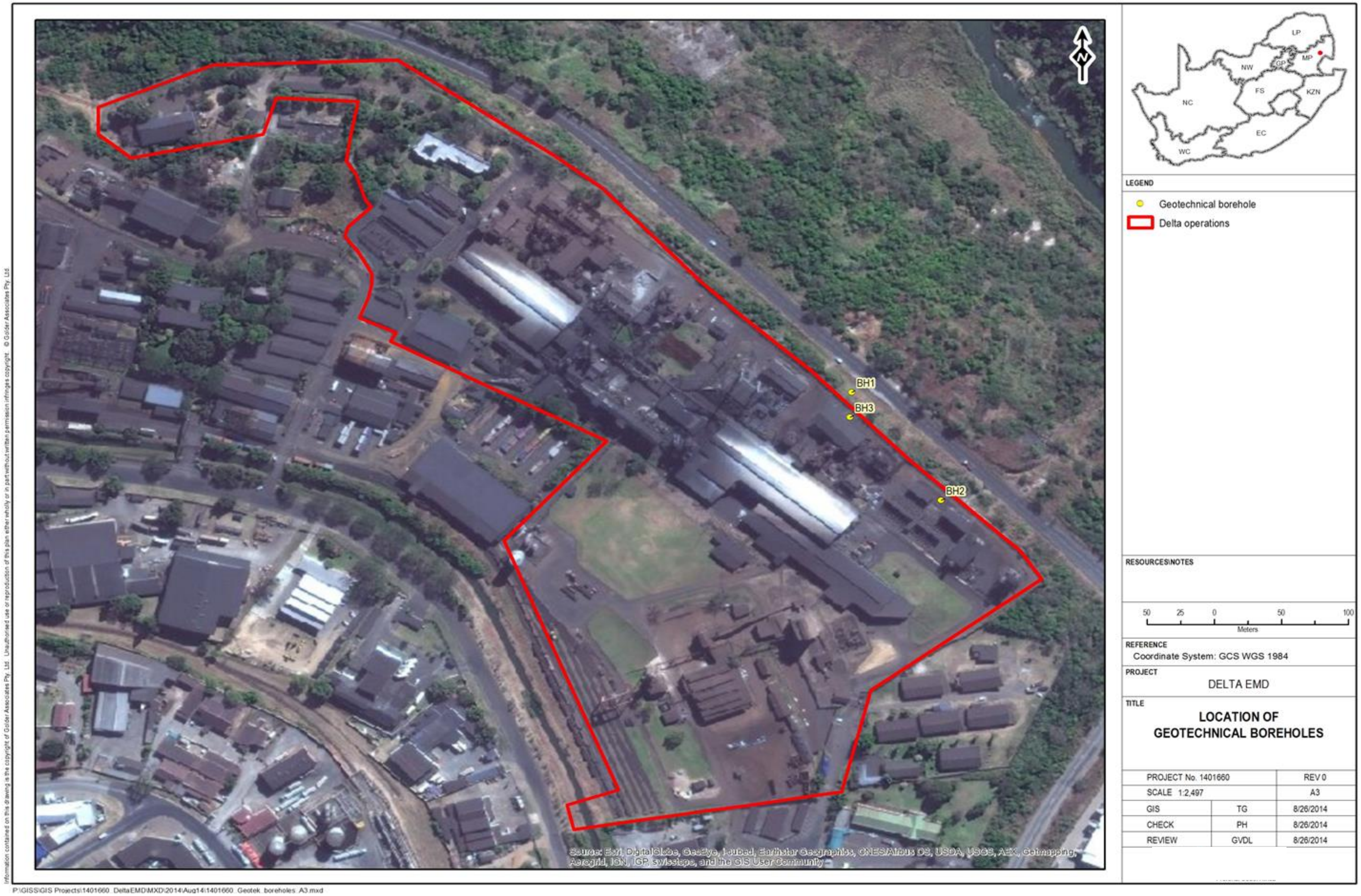

Figure 4-9: Geotechnical Borehole Location Plan (Taken from Hughes, 2014b)

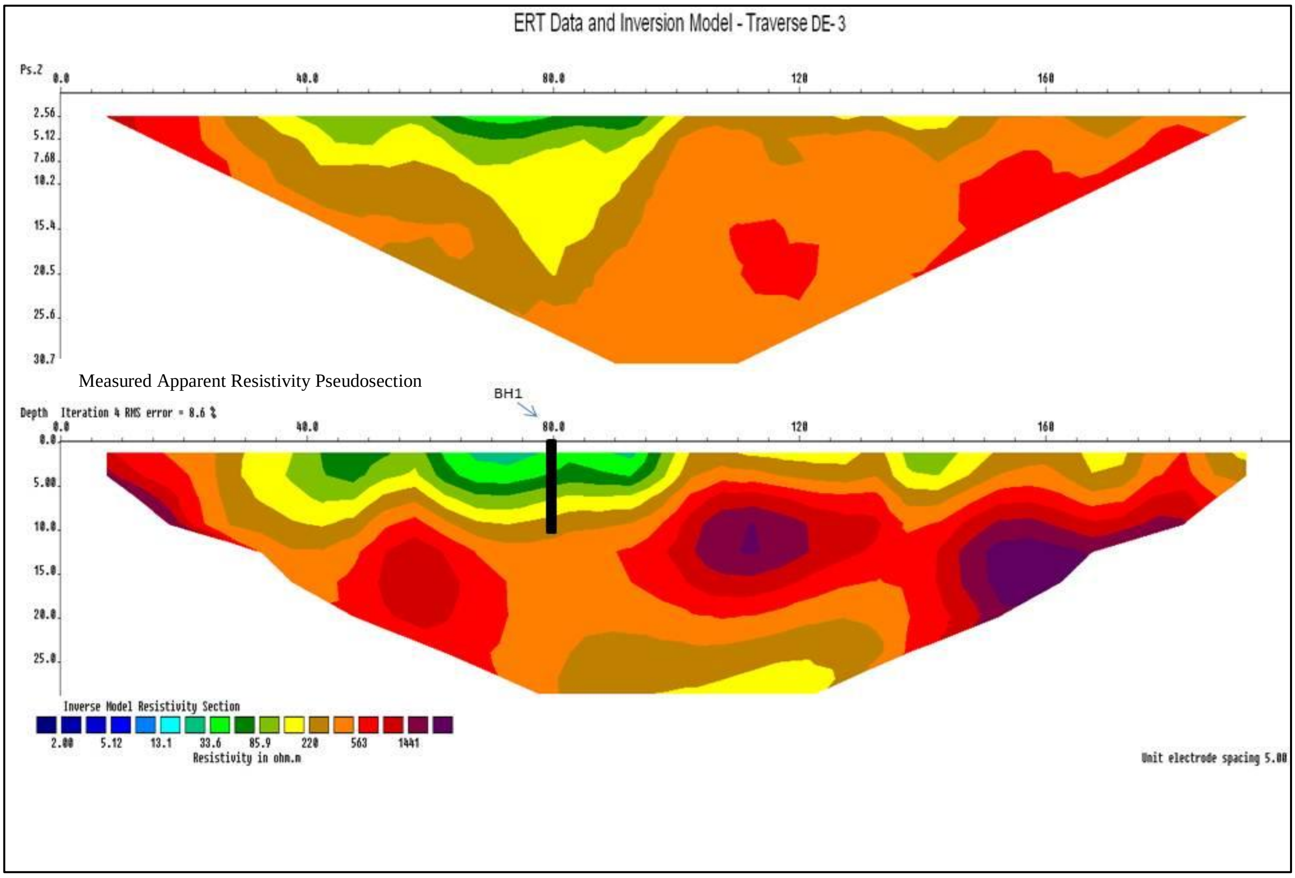

Figure 4-10: Position of borehole BH1 along Line DE03 (Taken from Hughes, 2014b)

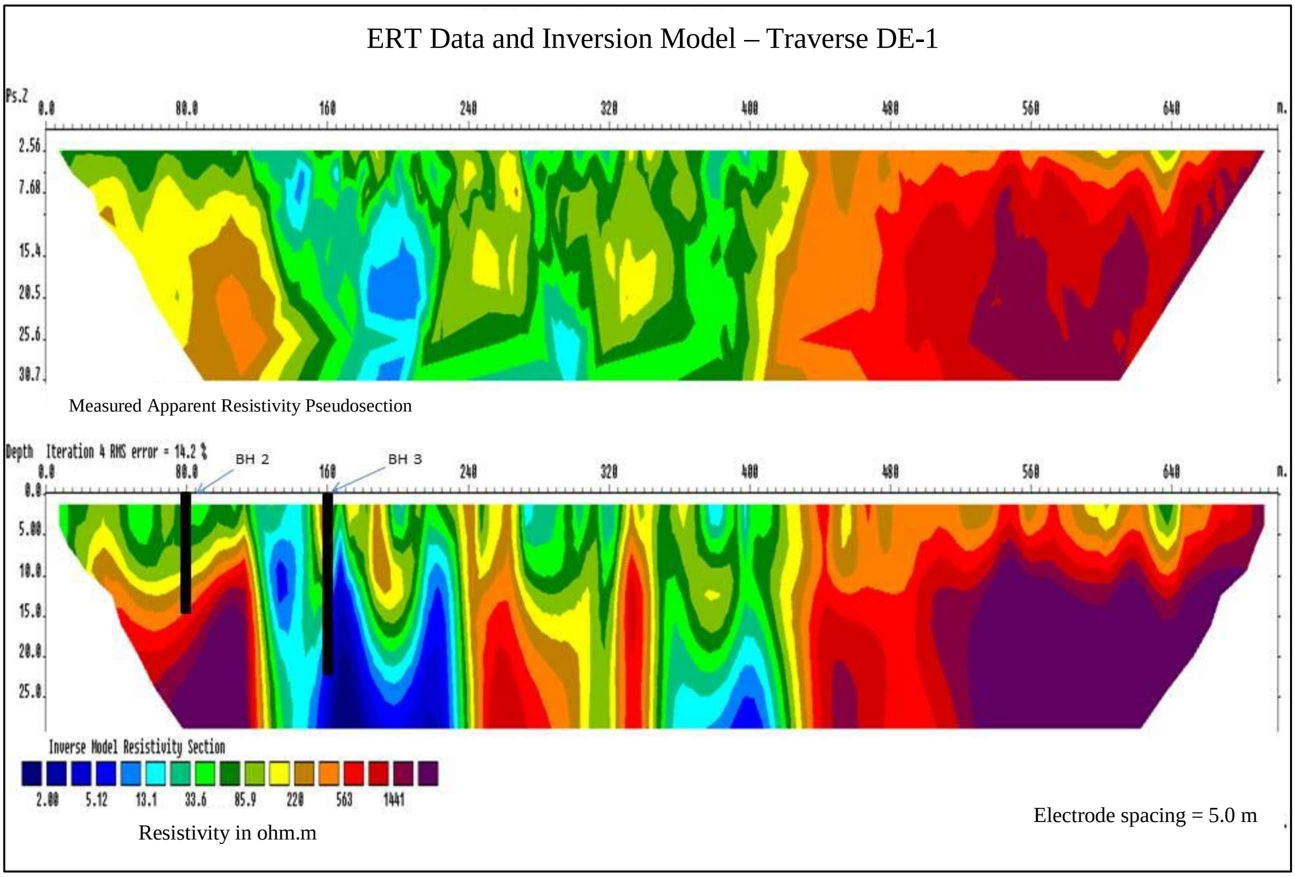

Figure 4-11: Position of borehole BH2 and BH3 along Line DE01 (From Hughes 2014b)

4.3.3 Geotechnical Logging

The Code of Practice for Site Investigations BS5930:1999 provides guidance with respect to: a) the order of descriptive logging terminology to use, b) in-situ field tests to determine estimates of rock strength, and c) requirements for measurements to assess rock quality.

The site was determined to be underlain by between 1 to 3 m of made-ground of reworked sand, clay and angular cobbles overlying highly weathered very weak to moderately weak granitic gneiss becoming strong to very strong at a depth of 6 to 7 mbgl. The made-ground was likely generated during construction of the site in the 1980's when works were undertaken to level the site. Review of RQD and FI data suggests that the depth to the base of the weathered aquifer is typically between 12 and 15 mbgl on site and 6 mbgl off-site. The rock forming the weathered aquifer is highly fractured and the rock strength varies between weak to extremely strong. Along fractures there are often brown and red deposits of what the author considers to be precipitates of rhodochrosite (manganese carbonate); although it is noted that no chemical analysis was undertaken as part of this investigation to confirm this assumption. The fresh rock underling the weathered shallow aquifer possesses an extremely strong rock strength and has an excellent RQD rating (Hughes, 2014b). Drilling logs for boreholes BH1, BH2 and BH3 are provided as Table 4-3, Table 4-4 and Table 4-5, respectively.

Table 4-3: Drilling Log for Borehole BH1

From (mbgl)	To (mbgl)	Geotechnical Description	TCR	SCR	RQD	FI (mm)
0	0.90	Very soft red-brown becoming yellow very gravelly sandy clay. MADE GROUND.	-	-	-	-
0.90	2.13	Weak completely weathered grey granite recovered as gravel. [RESIDUAL GRANITIC GNEISS].	28	0	0	-
2.13	3.63	Weak to strong moderately weathered grey to pink highly fractured coarse grained GRANITIC GNEISS. Highly fractured with fracture spacing at 60mm; brown staining along discontinuity surfaces.	80	41	23	60
3.63	5.93	Moderately strong to very strong moderately weathered pink to grey highly fractured GRANITIC GNEISS. Highly fractured with fracture spacing at 80 to 100 mm. Fractures orientated at 45 degrees.	85	85	70	100

5.96	9.41 EOH	Very strong pink to grey GRANITIC GNEISS. Note. The base of this section is considered to be the base of the weathered aquifer.	100	100	100	700

Table 4-4: Drilling Log for Borehole BH2

From (mbgl)	To (mbgl)	Geotechnical Description	TCR	SCR	RQD	FI (mm)
0	0.30	Loose very wet dark brown very gravelly clayey sand. MADE GROUND.	-	-	-	-
0.30	1.88	Soft dark grey gravelly very clayey/very sandy clay. MADE GROUND.	-	-	-	-
1.88	5.15	Very weak/weak highly weathered/completely weathered pale grey coarse grained GRANITIC GNEISS.	33	17	13	-
5.15	6.32	Very weak completely weathered pale beige coarse grained granite. Recovered as gravel [RESIDUAL GRANITE GNEISS].	31	7	0	-
6.32	7.12	Very weak highly weathered pale brown GRANITIC GNEISS. Fractures approximately horizontal, spaced at 90 mm and stained brown.	100	5	66	90
7.12	8.62	Strong to very strong slightly weathered pale grey coarse grained GRANITIC GNEISS. Sub-vertical fractures with much red-brown staining. Near horizontal fractures at 180 mm spacing. Note: vertical fractures predominate.	84	15	15	180
8.62	9.80	Strong to very strong moderately weathered pale cream coarse grained GRANITIC GNEISS with occasional coarse phenocrysts of quartz. Highly weathered along fractures displaying surface pitting. Fracture spacing 130 to 200 mm. Fractures orientated at 60	100	67	67	200

		degrees to the horizontal. Significant fracture zone at 8.74 to 8.94 m				
9.80	11.40	Strong to very strong dark grey moderately weathered highly fractured fine grained DIABASE. Much brown and red staining along fractures. Fractures predominantly vertical but where not then 60 degrees. Significant fracture zones: 9.80 to 10.00; 10.22 to 10.50; 10.90 to 11.50 (vertical). Note. Possible diabase intrusion along fracture zone/fault?	73	27	20	-
11.40	14.90 EOH	Very strong fresh coarse grained pink and grey GRANITIC GNEISS. Weathered fractures closely spaced to 11.90 m then spaced at 330 mm. Note drilling induced fractures fresh and horizontal at 400 mm spacing. Note. This represents a transition zone between the weathered aquifer and underlying fresh granite. Majority of groundwater flow in this zone considered to be above the depth of 12.60 mbgl.	100	87	85	330

Table 4-5: Drilling Log for Borehole BH3

From (mbgl)	To (mbgl)	Geotechnical Description	TCR	SCR	RQD	FI (mm)
0	2.70	Loose dark brown gravelly very clayey sand with occasional cobbles of coarse grained granite. MADE GROUND.	-	-	-	-
2.70	5.10	Very weak completely weathered red-brown coarse-grained granite. Recovered as highly fractured core, sand and gravel. [RESIDUAL GRANITIC GNEISS].	29	0.18	0	-

5.10	7.00	Very weak highly weathered pale brown GRANITIC GNEISS. Fracture spacing typically 90 mm; fracture condition rough.	100	16	16	90
7.00	8.18	Very strong fresh pink coarse grained GRANITIC GNEISS. Fracture spacing typically 300 mm. Fractures typically along coarse grained sections within core.	100	100	100	300
8.18	12.75	Very strong to extremely strong pale grey GRANITIC GNEISS. Fractures orientated at 15 to 20 degrees to the horizontal Fractures widely spaced. Fractured zones: 8.38 m to 8.43 m; 11.74 m to 11.84 m; 12.20 to 12.49 m.	100	100	76	700
12.75	17.12	Extremely strong fresh grey GRANITIC GNEISS. Weathered along fractures with brown staining. Fractures orientated at 15 to 20 degrees to the horizontal. Fractures widely spaced. Fracture Zones: 13.60 to 13.90; 15.50 to 15.62; 15.76 to 15.96. Note. Major water bearing zone extending to 15.62 mbgl.	100	100	82	700
17.12	22.15	Extremely strong pink and grey coarse-grained GRANITIC GNEISS. Note. 20.45 m to 20.65 m mica rich horizon.	100	100	98	700

4.3.4 Point Load Testing

Point load testing to determine the rock strength was undertaken on selected sections of core. Results of the point load testing are summarised in , and . UCS was then estimated by multiplying the point load strength by 24. Full point load testing data for all testing undertaken is provided in Appendix 1.

Table 4-6: Summary Point Load Testing for Borehole BH1 (Modified from Hughes, 2014b)

From (mbgl)	To (mbgl)	UCS Range (kN)	Range of Rock Strength Assessment
2.42	6.23	89 to >250	Strong to Extremely Strong

Table 4-7: Summary Point Load Testing for Borehole BH2 (Modified from Hughes, 2014b)

From (mbgl)	To (mbgl)	UCS Range (kN)	Range of Rock Strength Assessment
5.03	6.23	12 to >250	Weak to Extremely Strong

Table 4-8: Summary Point Load Testing for Borehole BH2 (Modified from Hughes, 2014b)

From (mbgl)	To (mbgl)	UCS Range (kN)	Range of Rock Strength Assessment
5.03	6.23	34 to >250	Moderate Strong to Extremely Strong

4.3.4.1 Excavatability Assessment

One of the goals of the geotechnical assessment was to determine the possible methods by which excavation of the ground along the northern boundary of the site adjacent to the road (R2296) could be undertaken. The assessment of the geotechnical data including: Point Load Index, FI, RQD and rock strength was undertaken by the author in accordance with Pettifer and Fookes (1994) which allows for determination of the type of the method of excavation required based upon the various rock properties of the underlying strata. The chart used in the assessment is provided as Figure 4-12.

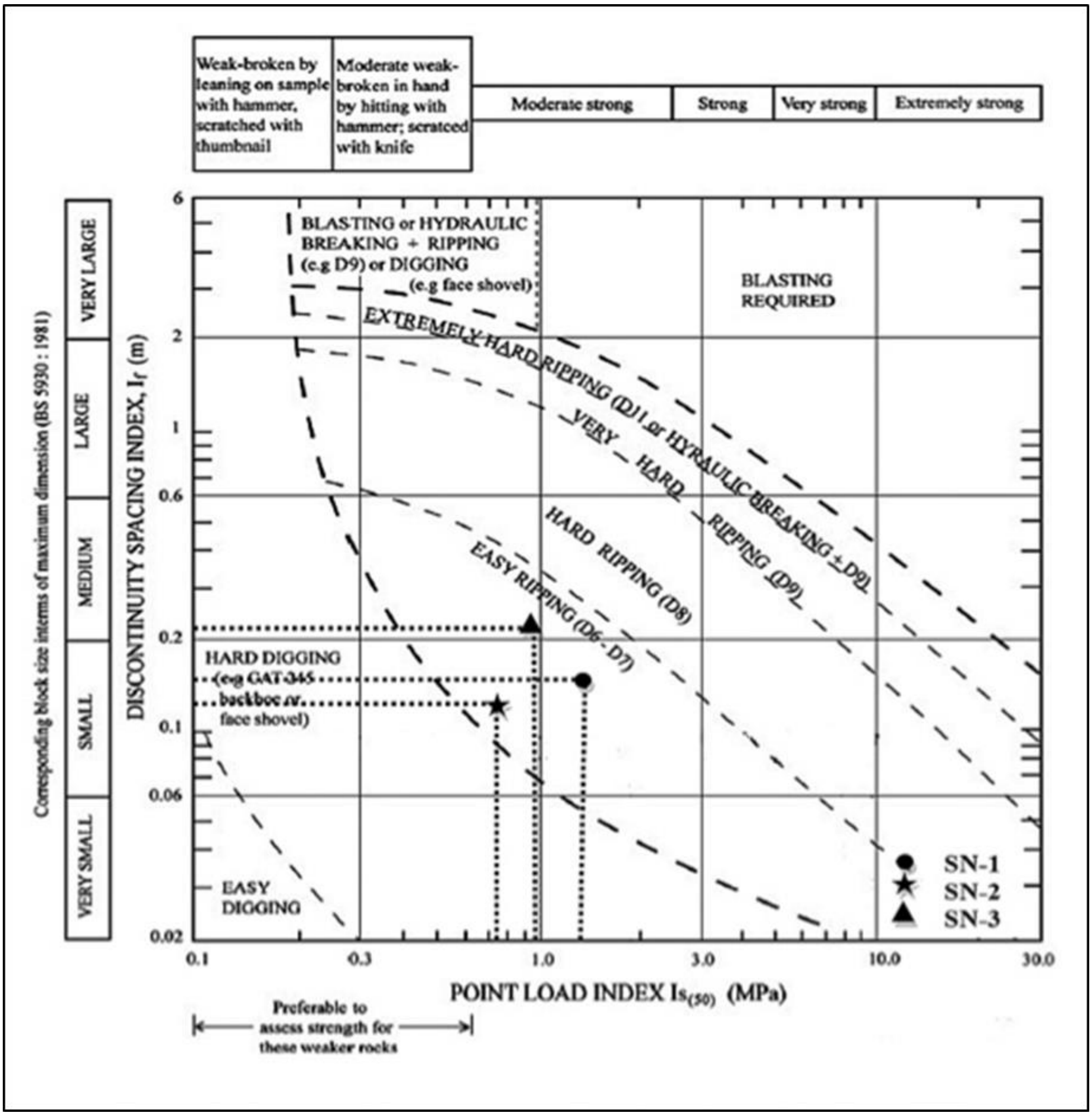

Figure 4-12: Excavatability Assessment (Taken from Pettifer and Fookes, 1994)

The author considered the possible construction of a groundwater interception trench along the northern side of the facility both a) on-site and b) off-site. The author determined that to construct a trench along the northern boundary to depths of up to 7 mbgl on-site or 3 to 4 m off -site would involve a combination of digging ripping and blasting below which extremely hard ripping or hydraulic breaking or blasting would be required (Hughes, 2014b). The author confirmed the methods of excavation that would be required and the equipment that should be used along different sections of a trench and these are provided as Table 4-9 and Table 4-10.

Table 4-9: Excavatability Assessment for an On-Site Trench along the Northern Boundary

Section		Depth	Thickness	Excavatability Assessment
From	**To**	**(mbgl)**	**(m)**	
0	240	0 to 2	2	East Digging (TLB)
		2 to 7	5	East Ripping (D6,D7)
240	270	0 to 2	2	Extremely Hard Ripping (D11 or Hydraulic Breaker)
		2 to 7	5	Blasting
270	325	0 to 2	2	East Digging (TLB)
		2 to 7	5	East Ripping (D6,D7)
325	345	0 to 2	2	Extremely Hard Ripping (D11 or Hydraulic Breaker)
		2 to 7	5	Blasting
345	400	0 to 2	2	East Digging (TLB)
		2 to 7	5	Easy Ripping (D6,D7)
400	600	0 to 7	7	Blasting

Table 4-10: Excavatability Assessment for an Off-site Trench along the Northern Boundary

Section		Depth	Thickness	Excavatability Assessment
From	**To**	**(mbgl)**	**(m)**	
0	35	0 to 4	4	Blasting
35	100	0 to 1	1	Easy Digging to Hard Digging
		1 to 4	3	Easy Ripping (D6,D7) to Hard Ripping (D8)
100	150	0 to 1	1	Extremely Hard Ripping (D11 or Hydraulic Breaker)
		1 to 4	3	Blasting
150	200	0 to 4	4	Blasting

4.3.5 Discussion

The geotechnical logging undertaken by the author determined that the base of the shallow perched fractured and weathered aquifer likely extended to a depth of between 12 and 15 mbgl on site and it is reasonable to presume that any contamination present in the sub-surface has the potential to migrate predominately to this depth rather than to a greater depth and reach any potential deeper aquifer that may potentially exist. Any groundwater capture trench proposed for construction would therefore need to extend to between 12 and 15 mbgl.

The point load testing and RQD assessment informed the excavatability assessment which determined that over most parts of the site it would not be possible to excavate easily to a depth greater than 2 mbgl without the use of hard ripping or blasting; the former being time-consuming and the latter being unlikely to be permitted given the close proximity to surface and buried infrastructure.

Given the limited site access available, the high rock strength of the underlying strata, and the required depth of excavation the author concluded that a groundwater capture trench along the northern boundary of the site did not represent a feasible option for site remediation.

4.4 CONTAMINATED LAND ASSESSMENT

4.4.1 Description of Assessment

The contaminated land assessment undertaken as part of this assessment included: a desktop study; soil sampling; subsequent chemical analysis, screening and assessment. The objective of the contaminated land assessment was to determine if any potential constituents of concern were present in the near surface soils that were associated with processing activities undertaken on-site during the operational lifetime of the facility. Further, if such constituents of concern were identified as being present on-site and off-site, could they negatively impact upon groundwater quality and ultimately, through groundwater migration, be deemed to be detrimental to surface water quality within the Crocodile River.

The initial contaminated land assessment was undertaken by Steyn (2010) and focussed upon site wide soils only. Steyn (2010) provided an initial overview of soil conditions to allow a contaminated land assessment to be undertaken which determined that localised contamination existed in pockets of site soil. This work was supplemented by the collection and assessment of additional soil samples obtained off-site by the author in 2014 (Hughes, 2014c).

4.4.2 Sampling Locations

Off-site soil sampling to the north of the Delta site was undertaken by the author between the 25 and 28 June 2014. A hand held shovel was used to obtain samples of soils to depth of between 0.15 and 0.25 mbgl (Hughes, 2014c). Details of the sampling locations are provided in Table 4-11 and sampling locations are indicated on Figure 4-13. The soil sampling locations were chosen to provide good site coverage of the area between the northern boundary of the site and the Crocodile River. However, access to the soil sampling locations proved difficult due to the presence of thick bush and rocky outcrops.

In addition, during October 2014 additional samples of soils and precipitate close to the Crocodile River were obtained by the author. Details of sampling locations are provided in Table 4-12 and indicated on Figure 4-14.

Table 4-11: Soil Sampling Locations (From Hughes, 2014c)

Sample Number	Latitude	Longitude	Sample Depth (mmbgl)	Description
SS1	-25.45775	30.98727	0 to 200	Brown fine to medium gravelly SAND with fine gravel of granite. (TOPSOIL).
SS2	-25.45877	30.98808	0 to 200	Dark brown very fine to medium gravelly SAND (TOPSOIL).
SS3	-25.45790	30.98625	0 to 200	Reddish brown very fine slightly gravelly LOAM with abundant rootlets and fine to medium gravel of granite.
SS4	-25.45536	30.98469	0 to 200	Light brown fine slightly gravelly SAND (TOPSOIL).
SS5	-25.45557	30.98497	0 to 50	Light brown fine to coarse gravelly SAND (TOPSOIL) with abundant rootlets and fine to coarse gravel of granite and quartz.
SS6	-25.45698	30.98559	0 to 200	Light grey brown very fine to fine slightly gravelly SAND (TOPSOIL) with fine to coarse gravel of granite and quartz.
SS7	-25.45666	30.98517	0 to 50	Light brown fine to medium slightly gravelly SAND (TOPSOIL) with fine to coarse gravel of granite and quartz.
SS8	-25.45908	30.98858	0 to 200	Light brown/beige very sandy medium to coarse GRAVEL. Highly weathered rock head (RESIDUAL GRANITE).
SS9	-25.45493	30.98366	0 to 150	Dark grey brown fine slightly gravelly sandy TOPSOIL with abundant fine to medium gravel of granite and quartz and occasional rootlets.
SS10	-25.45997	30.98791	0 to 150	Dark brown very fine to fine to fine slightly gravelly sandy LOAM with abundant rootlets and fine to medium gravel of quartz.

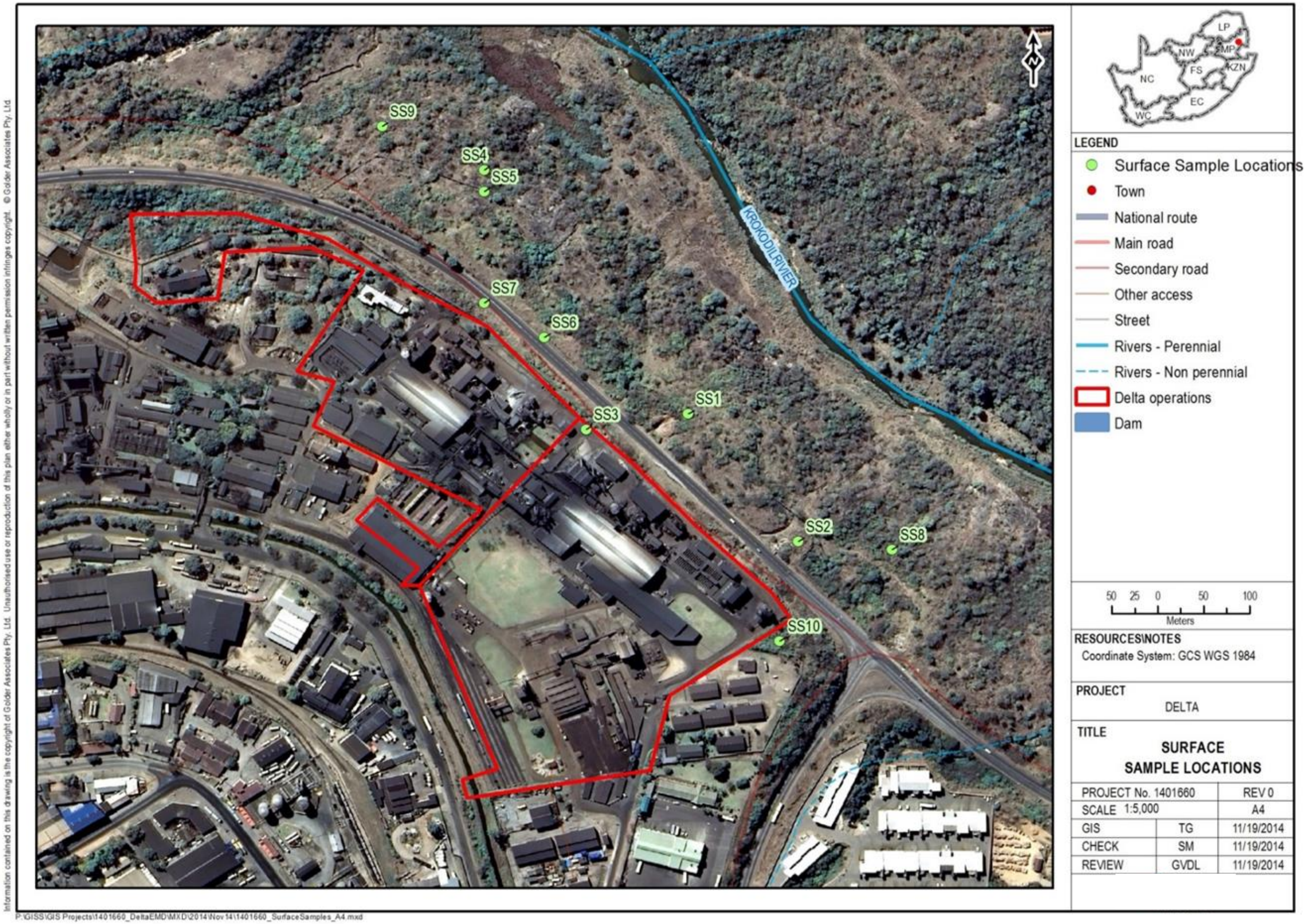

Figure 4-13: Off-site Surface Soil Sampling Locations (Taken from Hughes, 2014c)

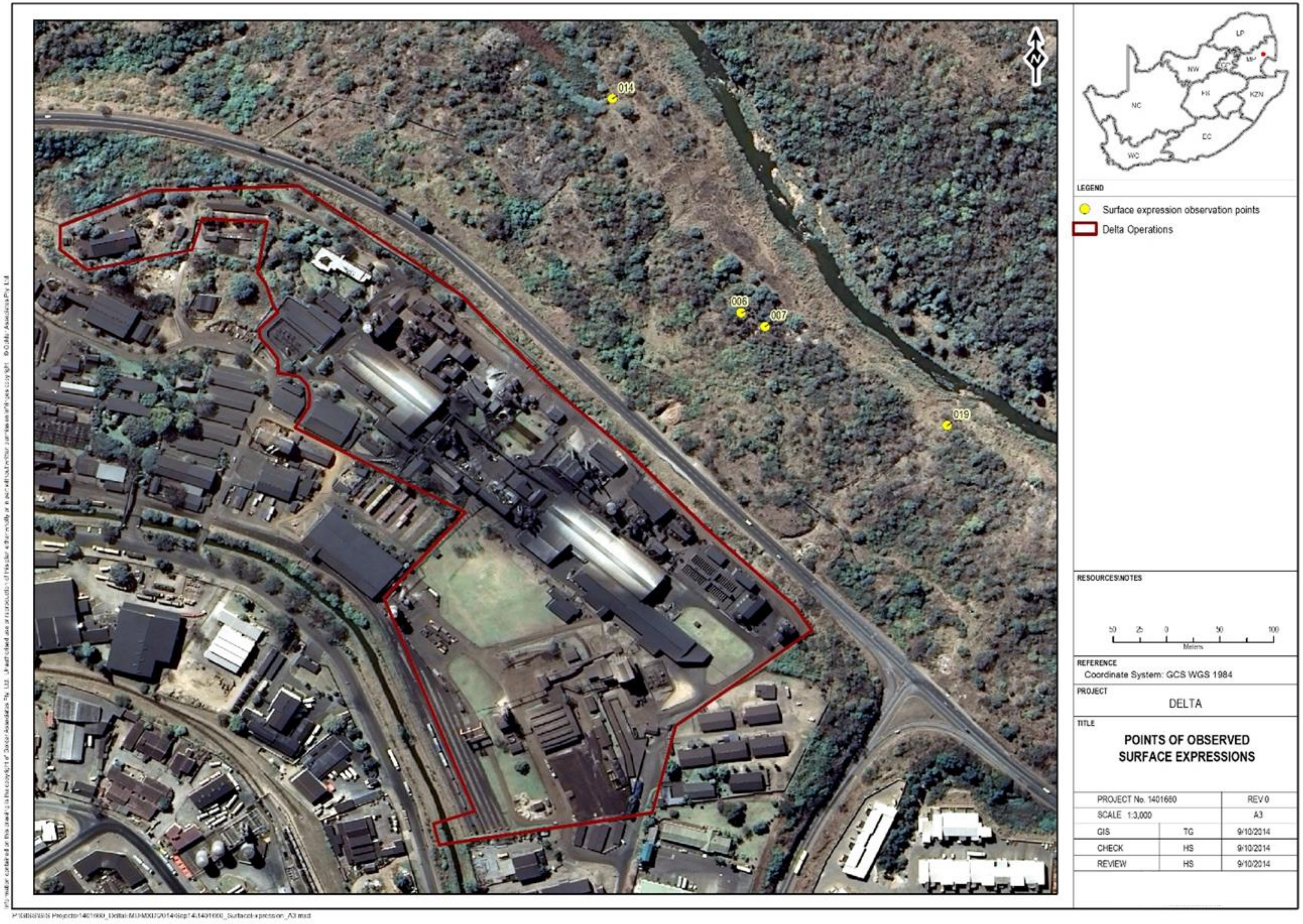

Figure 4-14: Soil Sampling Locations (Hughes, 2014d)

Table 4-12: Soil and Precipitate Samples

Sample Number	Latitude	Longitude	Description
006	-25.4570	30.9874	Dark brown very fine to medium gravelly SAND (TOPSOIL).
007	-25.4571	30.9876	Precipitate
014	-25.4552	30.9863	Yellowish brown very fine to medium gravelly SAND (TOPSOIL).
019	-25.4580	30.9891	Dark brown very fine to medium gravelly SAND (TOPSOIL).

4.4.3 Chemical Analysis

4.4.3.1 Off-site Soils

Ten samples of off-site soils were and sent to Jones Environmental Ltd in the UK for chemical analysis. The chemical analysis included determination of pH and total (aqua regia digestion) and dissolved concentrations (1:2 solid:water ratio) of: As, Cd, Cr(III), Cr(VI), Co, Cu, Pb, Mn, Hg, Ni, V, Zn, and SO_4^{2-} (Hughes, 2014c). The chemical test data is presented in Table 4-13 and Table 4-14. The soil analytical data was evaluated by comparing the total concentrations of potential CoCs to the soil screening values (SSV1) detailed in the South African Norms and Standards (DEA, 2014).

Table 4-13: Total Analysis for Off-Site Soils (Modified from Hughes, 2014c)

Determinand	**Units**	**SS1**	**SS2**	**SS3**	**SS4**	**SS5**	**SS6**	**SS7**	**SS8**	**SS9**	**SS10**		**SSV1**
Depth	mm	**0 to 200**	**0 to 200**	**0 to 200**	**0 to 200**	**0 to 200**	**0 to 200**	**0 to 200**	**0 to 200**	**0 to 200**	**0 to 200**		
As	mg/kg	2.3	3.4	3.4	1.3	2.2	1.1	1.7	2	2.1	2.6		5.8
Cd		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	0.4		7.5
Cr		48.7	56.3	58.8	58.2	63.7	68.8	68.9	57.6	31.8	66.8		46,000
Co		3.5	7.1	9	5.3	8.4	3.4	3.5	4.5	3.9	7.2		300
Cu		10	13	34	21	12	9	17	8	30	23		16
Pb		10	23	29	16	14	9	35	6	37	52		20
Mn		715	7,569	5,525	575	804	1,019	2,067	786	1,060	10,220		740
Hg		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1		0.93
Ni		3.5	4.8	7.5	5.4	8	4.8	8.3	4	10.7	10.4		91
V		11	20	26	21	31	13	12	15	11	19		150
Zn		66	127	88	81	71	32	35	55	296	155		240

Table 4-14: Dissolved Concentrations for Off-Site Soils (Taken from Hughes, 2014c))

Determinand	**Units**	**SS1**	**SS2**	**SS3**	**SS4**	**SS5**	**SS6**	**SS7**	**SS8**	**SS9**	**SS10**		**SSV1**
Depth	**mm**	**0 to 200**	**0 to 200**	**0 to 200**	**0 to 200**	**0 to 200**	**0 to 200**	**0 to 200**	**0 to 200**	**0 to 200**	**0 to 200**		
pH	mg/kg	6.89	5.11	5.01	6.31	7.8	7.18	7.39	7.88	6.64	7.6		5 to 9
As		0.0046	0.0068	0.0068	0.0026	0.0044	0.0022	0.0034	0.004	0.0042	0.0052		0.2
Cd		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.0008	<0.01		0.1
Co		0.007	0.0142	0.018	0.0106	0.0168	0.0068	0.007	0.009	0.0078	0.0144		0.12
Cu		0.02	0.026	0.068	0.042	0.024	0.018	0.034	0.016	0.06	0.046		1.6
Pb		0.02	0.046	0.058	0.032	0.028	0.018	0.07	0.012	0.074	0.104		0.2
Mn		1.43	15.138	11.05	1.15	1.608	2.038	4.134	1.572	2.12	20.44		20
Hg		<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02		0.02
Ni		0.007	0.0096	0.015	0.0108	0.016	0.0096	0.0166	0.008	0.0214	0.0208		1.4
V		0.022	0.04	0.052	0.042	0.062	0.026	0.024	0.03	0.022	0.038		2
Zn		0.132	0.254	0.176	0.162	0.142	0.064	0.07	0.11	0.592	0.31		60
Cr(VI)		<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	0.006	<0.006		1
Cr(III)		<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006		1
Chloride		0.088	0.034	0.056	0.06	0.06	0.046	0.058	0.034	0.048	0.066		12,000
Fluoride		0.0014	0.0008	0.001	0.0012	0.0058	0.002	0.002	0.0024	0.0044	0.004		30
Nitrate as NO_3		<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.0656		120
Nitrite as NO_2		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.00572		120
Sulphate as SO4		305.8	904.2	3,335.2	156.2	341	99	2024	299.2	332.2	602.8		4000

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Review of laboratory test data showed that soil pH varied between 5 and 8. Total copper, lead, manganese, and zinc concentrations exceed the SSV1 for All Sites Protective of a Water Resource. Total zinc values are lower than screening values except for the zinc of SS9 which just exceeded the SSV1. With the exception of manganese the various other heavy metal concentrations are considered to be indicative of background concentrations naturally elevated with heavy metals.

Total manganese concentrations in all of the off-site soil samples were elevated against typical background levels. The soil pH in areas off-site will likely influence manganese solubility. However, it is noted that the sample with the highest soluble concentrations has an above neutral pH (Hughes, 2014c). All the soluble concentrations were below screening values except the manganese concentration in sample SS10.

4.4.3.2 Soils and Precipitate near Crocodile River

Samples of soils and precipitates obtained close to the Crocodile River were analysed by Waterlab in Pretoria. The test results are provided in Table 4-15.

Table 4-15: Soil and Analysis Chemical Analysis (Taken from Hughes, 2014d)

Sample ID	pH	Mn (mg/kg)	Sulphate (mg/kg)
006	9	1.48	<10
007	4	103,340	430,240
014	3.5	8,340	66,960
019	5.5	6,280	72,600

The chemical analysis indicates that at three of the four sampling locations manganese concentrations are in excess of the SSV1 (740 mg/kg) for All Land-Uses Protective of Water Resources. Similarly three of the four sampling locations have sulphate concentrations in excess of the soil screening values for anions (4,000 mg/kg). The soil with the lowest pH value (pH = 3.5) was determined to be sample number 014 which was collected from the northern end of the geological structure that is considered to connect the area of low resistivity (Zone A) identified during the geophysical survey with the Crocodile River. This confirms that low pH acidic waters are leaving the site along preferential pathways and are not increasing in pH (not neutralising) prior to entering the Crocodile River.

The soil sample with the highest pH value (pH = 9) was determined to be sample number 006. This sample was obtained from a location down-gradient of monitoring well GA006-D which as will be shown in Chapter 5 is constructed on the football pitch in backfill “Greenfill” associated with neutralisation of acidic process sludge. This indicates that groundwater leaching through neutralised soils (by the addition of alkaline source) increases the pH of groundwater and is in connectivity with waters reaching the Crocodile River. This observation is important as it will be used to support proposals for in-situ remediation on site and as discussed in Chapter 7.

4.4.4 Discussion

The presence of elevated manganese in site soils located to the north of the site indicates that windblown manganese has the potential to negatively impact upon soil quality. All of the soluble concentrations for manganese are below screening values except for the manganese concentration in sample SS10. The screening values within the Norms and Standards (DEA, 2014) are however considered by the author to be conservative as the values are often higher than naturally occurring background levels in South Africa..

The presence of soils and precipitate close to the Crocodile River with pH similar to up-gradient sources of contaminated groundwater, elevated manganese concentrations and elevated sulphate concentrations indicate that a pathway exists along geological structures/fractured zones within the sub-surface that connect areas of low apparent resistivity (identified during the geophysical survey) and considered to be impacted by contamination with the Crocodile River. There is no evidence to suggest that natural attenuation resulting in lowering of the pH is occurring during the migration of on-site contamination to the Crocodile River. This suggests that monitored natural attenuation would not represent an appropriate remediation strategy for the site.

4.5 GROUNDWATER INVESTIGATION

4.5.1 Introduction

The groundwater assessment undertaken by the author during 2014 and 2015 expanded upon the earlier work undertaken by Steyn (2010) during which an initial groundwater assessment with respect to water quality was undertaken and groundwater flow direction were determined. The author reviewed the existing site information, identified data gaps and proposed a new groundwater assessment strategy that included the positioning of additional monitoring wells that were designed to target specific weathered horizons within the sub-surface and which allowed for representative groundwater samples from different horizons and structural zones to be obtained for subsequent chemical analysis. Positioning of the new monitoring wells was based upon review and assessment of the geophysical site investigation reported upon under Section 4.2. This had allowed the author to develop a sufficiently detailed conceptual site model with regard to the potential for contaminant presence and thereby position monitoring boreholes within and outside of areas of contamination thus proving the correctness of the conceptual site model. In total an additional nineteen monitoring boreholes were constructed at various locations across the site including along the northern perimeter.

Groundwater level monitoring was initially undertaken by Steyn (2010) during April 2010. The author determined groundwater levels on site on eight further occasions between April 2014 and January 2015. The data was used by the author to confirm that groundwater on site was in connectivity with the base of the canal located along the southern boundary of the site and that groundwater flow was in a northerly direction towards the Crocodile River.

Groundwater quality samples were obtained from the monitoring wells using low flow sampling techniques. In-situ physiochemical parameters were measured at the time of sampling to obtain representative measurements of in-situ groundwater conditions

Chemical testing of groundwater samples was undertaken to determine the presence and distribution of potential contaminants of concern. The chemical testing as undertaking by Jones Environmental Ltd (Jones), a laboratory based in the UK.

Due to budget restraints aquifer testing was only undertaken on two boreholes to determine aquifer parameters which were to be used to inform the development of a remediation strategy for the site whereby consideration was being given to options including: monitored natural attenuation, pump and treat, and/or in-situ chemical dosing. The aquifer testing data was used in combination with geological logging data to provide estimates of hydraulic conductivity, storativity and transmissivity. This information was used in combination with the information obtained from geotechnical logging to calculate the likely loading of manganese and sulphate upon the Crocodile River and which is discussed in Chapter 5.

4.5.2 Pre-Study Monitoring Well Construction (2010)

During April 2014, Environmental Drilling and Remediation Services (Pty) Ltd (EDRS) were appointed by Golder to construct eight groundwater monitoring wells to depths of between 18 m and 40 mbgl. The boreholes were drilled at approximately 6.5” diameter using truck mounted rotary percussive drilling methods. All monitoring wells were installed with 215 mm outside diameter plain steel casing and 125 mm outside diameter perforated PVC casing (Steyn, 2010). Monitoring well construction details are provided in Table 4-16. The GAA001-S/D, GAA002-S/D and GAA004-D monitoring wells were positioned along the northern boundary of the site whereas the GAA005-S/D monitoring wells were positioned near the football pitch much closer to the southern boundary of the site. Ground conditions identified during drilling identified made ground overlying weathered granitic gneiss or granite overlying fresh granitic gneiss or granite.

Table 4-16: Existing Monitoring Wells (Taken from Hughes, 2014a)

Monitoring Well Number	Borehole Depth (mbgl)	Latitude	Longitude	Estimated Surface Elevation (mamsl)	UPVC 125mm OD Solid Casing (mbgl)	UPVC 125mm OD Perforated Casing (mbgl)
GAA001-S	18	-25.45625	30.98222	621	0 to 1	1 to 11
GAA001-D	40	-25.45616	30.98219	621	0 to 34	34 to 40
GAA002-S	18	-25.45719	30.98532	625	0 to 1	1 to 10
GAA002-D	40	-25.45716	30.98520	625	0 to 22	22 to 40
GAA003-D	40	-25.45759	30.98566	621	0 to 22	22 to 40
GAA004-D	18	-25.45919	30.98733	621	0 to 6	6 to 9
GAA005-S	40	-25.45916	30.98721	621	0 to 22	22 to 36
GAA005-D	18	-25.45930	30.98476	639	0 to 1	1 to 10

4.5.3 Monitoring Well Construction – Stage 1 (July 2014)

The author had identified that the existing monitoring network (as constructed during April 2010) was limited in number and therefore proposed additional monitoring wells to improve site coverage and target areas of probable contamination (Hughes 2014,b). The initial stage of drilling was undertaken between 10 and 11 July 2014 and involved the construction of three shallow and deep groundwater monitoring wells. The author supervised the construction of the monitoring wells which was undertaken by Geosphere (Pty) Ltd (Geosphere) using air-flush rotary percussion drilling techniques. Construction details for the new monitoring wells are provided in Table 4-17.

Table 4-17: Stage 1 Drilling Locations (From Hughes, 2014d)

Monitoring Well Number	Borehole Depth (mbgl)	Latitude	Longitude	Estimated Surface Elevation (mamsl)	Steel Casing (mbgl)	UPVC 125mm OD Solid Casing (mbgl)	UPVC 125mm OD Perforated Casing (mbgl)
GAA006-D	30	-25.45971	30.98528	633	0 to 18	0 to 18	18 to 30
GAA006-S	18	-25.45962	30.98521	635	0 to 3	n/a	0 to 10
GAA007-D	40	-25.45862	30.98667	629	0 to 18	0 to 18	18 to 40

Monitoring wells GAA006-D and GAA0060-S were drilled to 30 and 18 mbgl, respectively and were positioned towards the south-east of the football field in order to improve upon limited site coverage over the southern part of the site and provide monitoring points up-gradient of the probable sources of contamination i.e. the various cell houses of the Eastern Plant and the Western Plant. The target position for monitoring well GAA007-D was selected as the zone of low apparent resistivity identified at a distance of 160 m along the geophysical survey line DE01. Site wide contamination was postulated to be likely limited to the shallow weathered horizon to a depth of approximately 15 mbgl; however, in order to prove this hypothesis monitoring well GAA007-D was constructed to 40 mbgl and sealed through the weathered horizon to a depth of 18 mbgl. This allowed for sampling of any deeper level groundwater that may be present (Hughes, 2014d).

Drilling identified up to 2 m of fill material consisting of coarse grained reddish-brown loamy soils, overlying 4 m of fine grained brown clay; overlying in excess of 34 m of coarse grained white to grey biotite-rich granitic gneiss which was highly to moderately weathered and substantially fractured from 14 and 18 mbgl. During drilling of GAA006-D (30 m) a water strike was encountered at 14 mbgl which was the approximate base of the weathered horizon and therefore considered indicative of a preferential flow horizon being present at this depth. A blow yield test was undertaken and measured at 0.5 l/s. No water strikes were encountered in GAA006-S (18 m) nor GAA007-D (40 m), however, water levels recovered enabling groundwater levels to be obtained during the subsequent monitoring events (Hughes 2014d).

4.5.4 Monitoring Well Construction – Stage 2 (October 2014)

Between July 2014 and October 2014, the author undertook detailed assessment of the groundwater quality data that had been obtained from the earlier stages investigation and further developed a detailed understanding of the site and confirmed the conceptual site model involving probable contaminant flow through a shallow weathered aquifer in a northerly direction towards the Crocodile River. The then current distribution of monitoring wells remained limited and was focused upon the northern and southern perimeters of the site. The author proposed that additional six shallow monitoring boreholes be constructed to a depth of 15 mbgl in locations closer to probable sources of contamination. The new monitoring well locations are identified in Table 4-18 along with construction details and their relative locations indicated on Figure 4-15.

Table 4-18: Stage 2 Drilling Locations (Taken from Hughes, 2014d)

Monitoring Well Number	Borehole Depth (mbgl)	Latitude	Longitude	Estimated Surface Elevation (mamsl)	UPVC 125mm OD Solid Casing (mbgl)	UPVC 125mm OD Perforated Casing (mbgl)
GAA004-S	15	-25.45919	30.98733	621	0 to 6	6 to 15
GAA007-S	15	-25.45859	30.98673	626	0 to 6	6 to 15
GAA008-S	15	-25.45857	30.984644	626	0 to 6	6 to 15
GAA009-S	15	-25.45923	30.98592	630	0 to 6	6 to 15
GAA010-S	15	-25.45789	30.98501	630	0 to 6	6 to 15
GAA011-S	15	-25.45854	30.08502	635	0 to 6	6 to 15

Borehole drilling identified up to 5 m of fill material consisting of reddish-brown clay fill, overlying 2 m of greyish white granitic gneiss recovered as clay, sand and gravel, overlying greyish white highly fractured biotite-rich granitic gneiss (Hughes. 2014d). The depth of weathering, however, was much deeper in GAA007-S and extended to 7 mbgl.

4.5.5 Monitoring Well Construction – Stage 3 (December 2014)

Following completion of the October drilling works and upon review of the existing site data the author concluded that there was likely sufficient data to develop a remediation strategy for the site where contamination in shallow groundwater had been identified. In order to ensure that there was sufficient defensible information to prove that contamination was not present elsewhere on site particularly along the perimeter and within the shallow weathered aquifer 10 additional perimeter boreholes were constructed. These perimeter wells are identified in Table 4-19 and were constructed to depths of either 6 or 15 mbgl. Monitoring well locations are indicated on Figure 4-15. Perimeter monitoring wells P1 to P4 were positioned along the western and southern boundary of the site to improve general site coverage (Hughes, 2015). Monitoring wells GAA012(6) and GAA012(15) were located on the southern-eastern area of the site similarly to improve site coverage but also to provide future opportunity for obtaining shallow water samples that may be in connectivity with the canal located along the southern boundary.

Table 4-19: Stage 3 Drilling Locations (From Hughes, 2015)

Monitoring Well Number	Borehole Depth (mbgl)	Latitude	Longitude	Estimated Surface Elevation (mamsl)	UPVC 125mm OD Solid Casing (mbgl)	UPVC 125mm OD Perforated Casing (mbgl)
P1 (6)	6	-25.45636	30.98171	618	0 to 0.5	0.5 to 6.0
P1 (15)	15	-25.45645	30.98173	618	0 to 6.0	6.0 to 15.0
P2 (6)	6	-25.45600	30.98301	606	0 to 0.5	0.5 to 6.0
P2 (15)	15	-25.45602	30.98305	607	0 to 6.0	6.0 to 15.0
P3 (6)	6	-25.45831	30.98421	645	0 to 0.5	0.5 to 6.0
P3 (15)	15	-25.45829	30.98421	645	0 to 6.0	6.0 to 15.0
P4 (6)	6	-25.45895	30.98487	637	0 to 0.5	0.5 to 6.0
P4 (15)	15	-25.45893	30.93482	637	0 to 6.0	6.0 to 15.0
GAA012(6)	6	-25.46110	30.98551	629	0 to 0.5	0.5 to 6.0
GAA012-S	15	-25.46106	30.98547	634	0 to 6.0	6.0 to 15.0

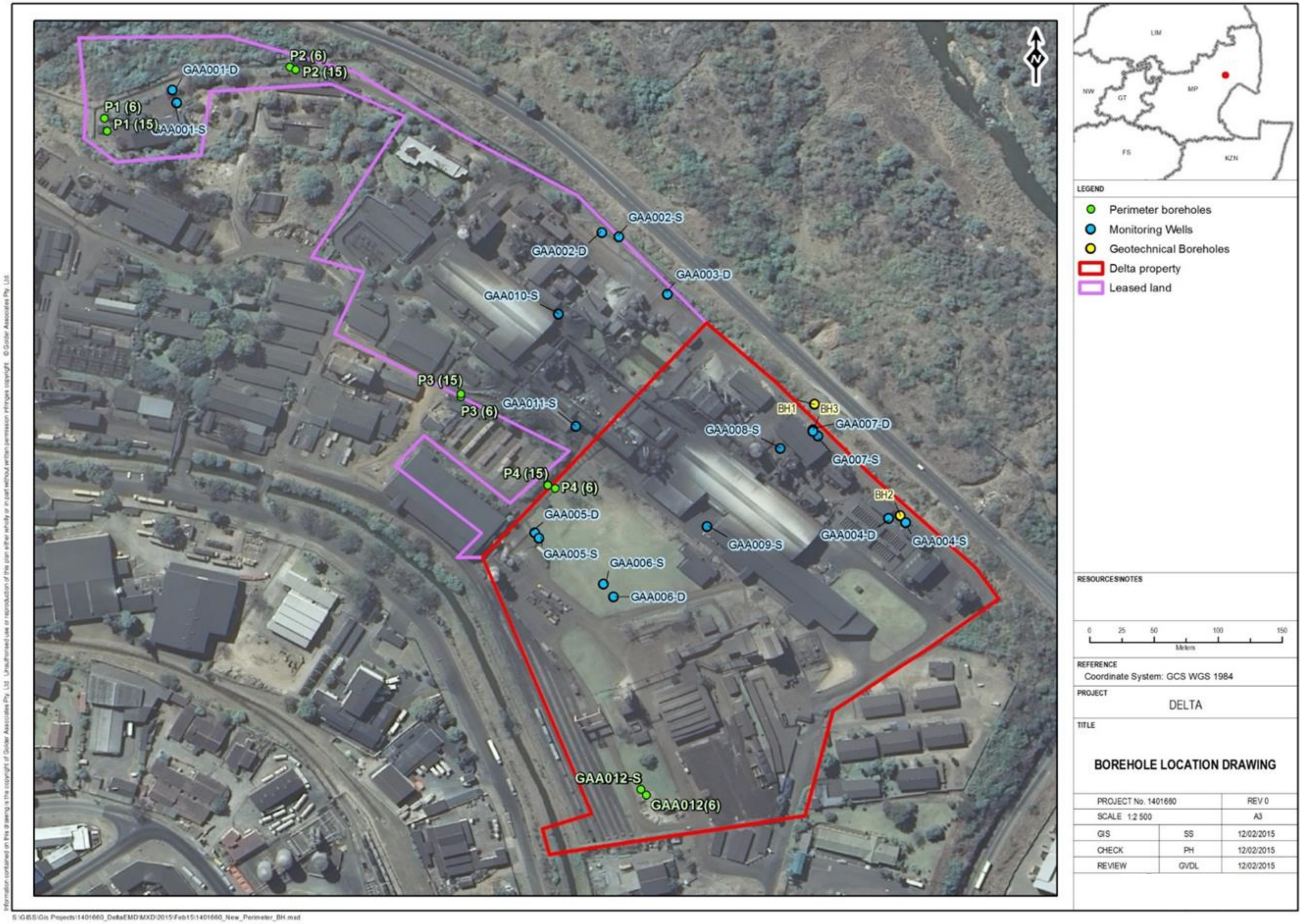

Figure 4-15: Monitoring Well Locations (Taken from Hughes, 2015)

The monitoring wells were constructed by EDRS between 1 and 3 December 2014. Using air flush rotary percussive methods of drilling EDRS drilled at 165 mm diameter to depths of either 6 or 15 mbgl. The 6 m deep monitoring wells were installed with an upper section of 125 mm diameter 0.50 m of plain UPVC connected to 5.50 m of perforated UPVC casing. Formation stabiliser was placed in the annulus between the boreholes and the casing to a depth of 0.50 mbgl before a sanitary seal was put in place and the monitoring well was finished with a lockable flush cover. The 15 m deep monitoring wells were constructed in a similar manner but with the plain casing extending to 6 mbgl and connected to 9 m of perforated casing. Formation stabilisation was placed from the base of the boreholes to 5 mbgl upon which was placed a 5 m section of sanitary seal.

Ground conditions identified during drilling included 0.50 m of reddish brown clayey soils overlying greyish-white weathered and fractured granitic gneiss with the exception of perimeter monitoring wells P3(15) and P3(6) where up to 9 m of ash and sand associated with historic land raising was identified (Hughes, 2014d).

4.5.6 Groundwater Level Monitoring

Groundwater levels were originally collected for the site during April 2010 (Steyn, 2010). The author collected groundwater levels on eight further occasions between February 2014 and January 2015. Groundwater levels collected on site ranged from 0.50 to 32.83 mbgl. Over the period of monitoring from April 2010 to January 2015, there was a general reduction in water levels of between approximately 0.50 to 3.00 m. This is considered to be a result of the drought that South Africa was experiencing at the time of the study. The calculated relative groundwater levels are presented in Table 4-20.

An assessment of correlation between topographical elevation and water elevation has been undertaken and is presented as Figure 4-16. There is a good correlation (R^2 = 0.87) between topographical elevation and water elevation for the boreholes that were constructed within the relatively shallow perched aquifer. The author considered that this moderately strong correlation indicates that on-site water levels are in connectivity with the canal located along the southern border of the site. However, for the wells that were extended below the weathered aquifer there is poor correlation (R^2 = 0.37). The author considers that this is representative of wells that are in connectivity with waters within fractures under differing piezometric pressures.

Table 4-20: Groundwater Level Monitoring (Modified from Hughes, 2015)

Borehole Designation	Surface Elevation (mamsl)	Static Water Levels (mamsl)								
		April 2010	Feb 2014	July 2014	Aug 2014	Sept 2014	2nd Oct 2014	22nd Oct 2014	Dec 2014	Jan 2015
GAA001-S	621	617.30	616.55	616.10	615.81	615.75	615.88	615.81	615.05	614.93
GAA001-D	621	616.86	616.45	615.74	615.29	615.20	614.65	615.68	613.81	614.05
GAA002-S	625	620.86	622.74	618.95	617.95	-	618.00	617.95	622.64	618.66
GAA002-D	625	621.10	621.96	618.99	617.81	617.65	617.84	617.8	621.11	618.65
GAA003-D	621	614.70	616.90	614.84	614.16	614.00	612.12	611.1	613.68	612.74
GAA004-S	621	n/a	613.46	n/a	612.75	n/a	612.80	612.75	613.59	612.9
GAA004-D	621	n/a	614.68	612.58	612.28	612.40	599.40	612.44	601.45	605.58
GAA005-S	639	637.92	637.89	637.04	636.97	636.70	636.90	636.9	637.32	637.33
GAA005-D	639	621.50	638.28	636.74	636.69	636.70	634.45	635.49	637.35	637.4
GAA006-S	635	-	-	-	634.16	634.50	633.10	633.16	634.31	632.49
GAA006-D	633	-	-	-	609.73	613.30	606.60	611.31	608.66	611.6
GAA007-S	626	-	-	-	-	-	-	618.89	621.84	622.3
GAA007-D	626	-	-	-	593.17	598.00	>586	595.53	594.15	600.26
GAA008-S	626	-	-	-	-	-	-	614.3	619.63	619.71
GAA009-S	630	-	-	-	-	-	-	628.87	628.94	628.86
GAA010-S	630	-	-	-	-	-	-	620.1	623.47	622.89
GAA011-S	635	-	-	-	-	-	-	633.06	633.57	633.44
BH1	618	-	-	-	617.33	-	-	-	-	-
BH2	622	-	-	-	613.76	-	-	-	-	-
BH3	624	-	-	-	610.82	-	-	-	-	-
P1(15)	618	-	-	-	-	-	-	-	611.55	611.83
P1(6)	618	-	-	-	-	-	-	-	612.61	612.79
P2(15)	620	-	-	-	-	-	-	-	608.37	609.11
P2(6)	620	-	-	-	-	-	-	-	616.02	615.87
P3(15)	645	-	-	-	-	-	-	-	638.51	638.53
P3(6)	645	-	-	-	-	-	-	-	-	-

P4(15)	637	-	-	-	-	-	-	-	621.7	624.41
P4(6)	637	-	-	-	-	-	-	-	635.52	635.55
GAA012 (6)	634	-	-	-	-	-	-	-	627.94	632.06
GAA012-S	634	-	-	-	-	-	-	-	619.47	623.81

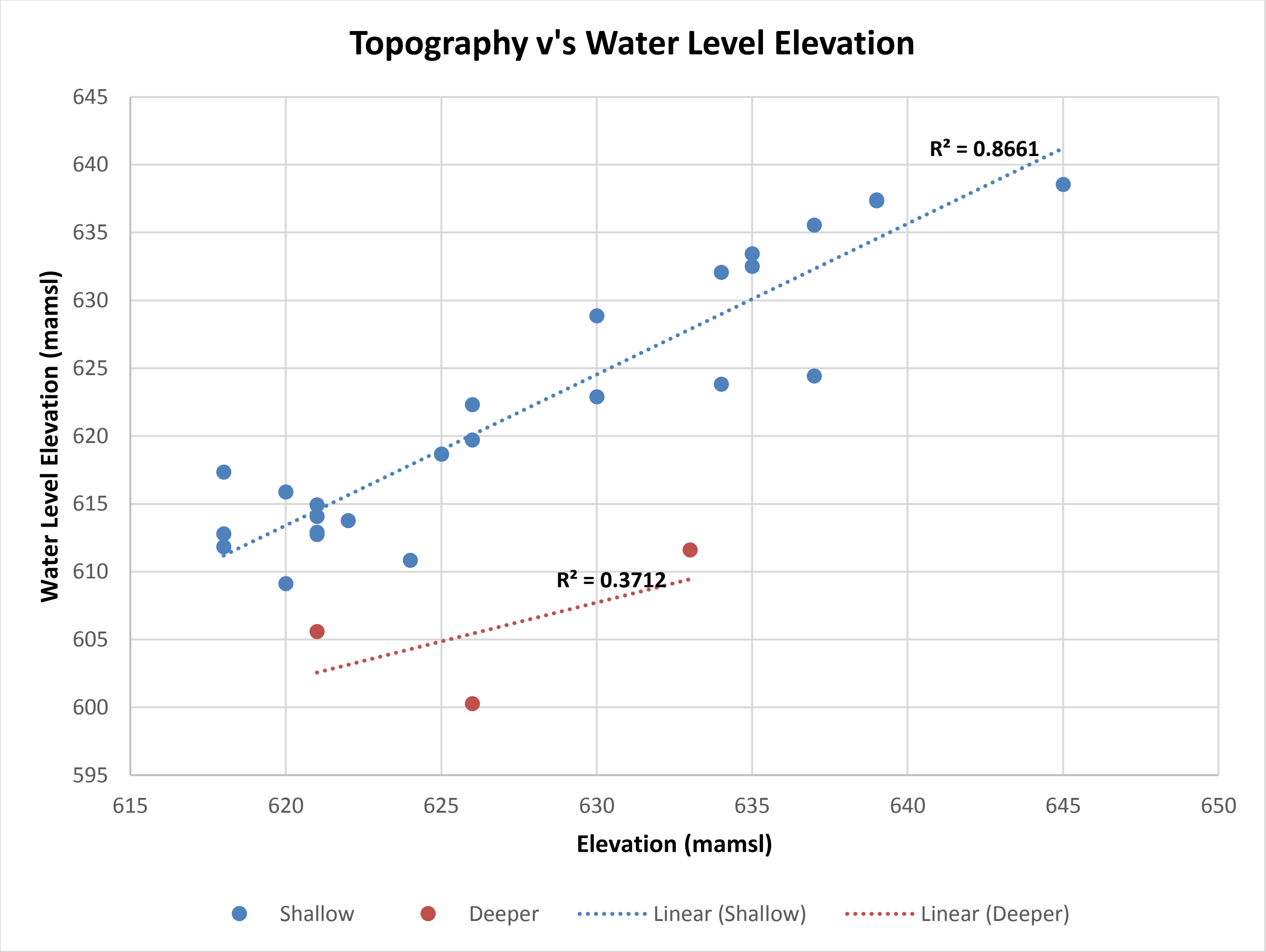

Figure 4-16: Topography and Groundwater Correlation

The groundwater levels have been used to calculated groundwater flow direction for January 2015 which is presented as Figure 4-17. In determining the groundwater contours, the water levels were interpolated using kriging methods to avoid conflict with regard to the close proximity of water levels obtained from groundwater monitoring well pairs. Groundwater flow direction throughout the monitoring period has been confirmed to be in a northerly direction towards the Crocodile River.

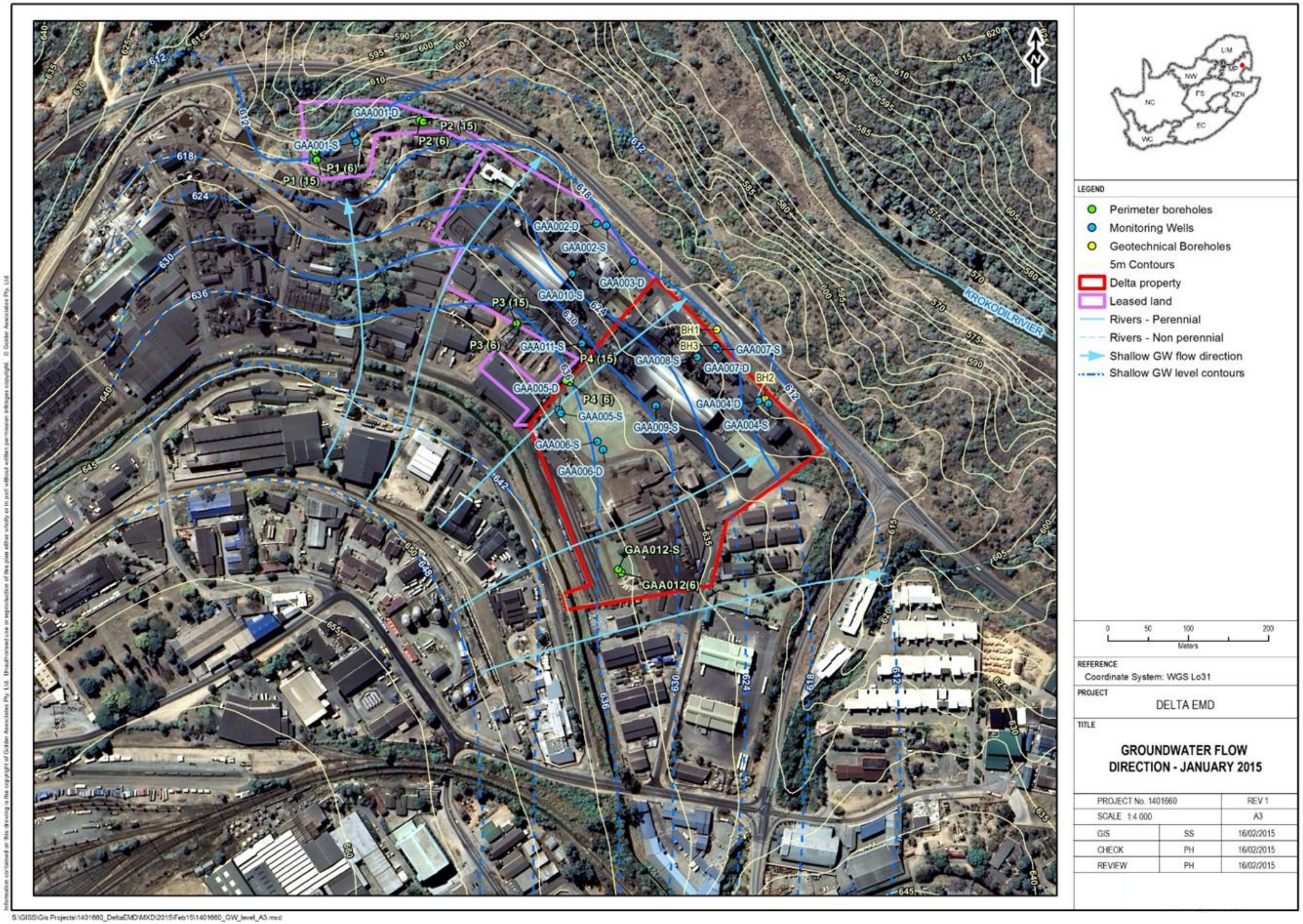

Figure 4-17: Groundwater Flow Direction for January 2015 (Taken from Hughes, 2015)

4.5.7 Aquifer Testing

During October 2014, aquifer testing was undertaken on two monitoring wells in order to obtain an estimation of aquifer parameters across the site. This work was undertaken to complement existing estimates of hydraulic conductivity obtained during earlier site investigation works (Steyn, 2010). During the assessment undertaken by the author, two monitoring wells were chosen for testing: GAA009-S and GAA011-S. Both monitoring wells were located close to the two zones of suspected contamination (Zone A and Zone B).

4.5.7.1 Constant Discharge Test (CDT) Pumping Tests

Prior to testing groundwater levels were measured at 1.13 and 1.94 mbgl for monitoring wells GAA009-S and GAA011-S, respectively and available drawdown was calculated to be 12.87 m and 12.06 m. Calibration testing was not undertaken as both monitoring wells had exhibited very low blow-yields during drilling and the time available to undertake the tests was limited. Rather, the boreholes were pumped at a rate of 0.1 l/s using a Grundfos SQ pump (Model SQ 5-60) lowered to a depth of 14 mbgl. A solonist data logger was placed inside of the monitoring wells and programmed to record changes in pressure (water elevation) every 15 seconds. The test were relatively short running for only 18.75 and 19.00 minutes for GAA009-S and GAA011-S, respectively. No monitoring wells were available to record changes in water elevation within the area of influence when pumping from the testing wells.

4.5.7.2 Recovery Tests

The author did not consider the accuracy of the CDT tests to be highly reliable due to the relatively short duration of testing (<20 minutes) and the lack of monitoring wells and therefore proposed that recovery tests also be undertaken to obtain data for comparative analysis. Furthermore, the Grundfos SQ pump does not possess a non-return valve and the ability to control discharge rates was therefore limited (Hughes, 2014d).

The monitoring wells were pumped and water levels reduced to the level of the pump (14 mbgl). The recovery tests were undertaken for 90.25 minutes for GAA009-S and 160.75 minutes for GAA011-S representing recoveries of 95.80% and 106.60%, respectively. In GAA001-S recovery elevation (1.14 mbgl) was higher than the static water level due to adjustment of the data logger during the latter stages of the test; however, this was only reported upon completion of the test and there was insufficient time available to repeat the test. Recovery test details are provided in Table 4-21.

Table 4-21: Recovery Test

Monitoring Wells Tested	Static Water Level (mbgl)	Borehole pumped dry to (mbgl)	Available Recovery (m)	Recovery Duration (minutes)	Actual Recovery (mbgl)	Percentage Recovery (%)
GAA009-S	1.13	14	12.87	90.25	1.67	95.80
GAA011-S	1.94	14	12.06	160.75	1.14	106.6

4.5.7.3 Data Assessment for CDT

Data obtained during the CDT was analysis using Aquifer Test Version 3 and the FC computer programme developed by the IGS at the University of Free State (Hughes, 2014b and Hughes, 2014c) whereby drawdown in water levels over the duration of the test were assessed to provide an estimate of hydraulic properties.

GAA009-S

Site obtained data was loaded into the Aquifer Test program. The data plot is presented as Figure 4-18. Initial difficulties were experienced during test set-up and establishing a constant abstraction rate of 0.1 l/s. Initially the rate of abstraction was too low which resulted in only limited drawdown then around 200 seconds into the test the abstraction rate was increased which resulted in a rapid drawdown in water levels. The abstraction rate was reduced slightly allowing for a steady drawdown to be maintained and which is shown as a thirty degree declination line in Figure 4-18. Full drawdown to the pump level (14 mbgl) was achieved within 18.75 minutes and the test was stopped. The limited duration of the test due to over abstraction is considered by the author to have negatively impacted upon the quality of the test allowing only a short section of data (from 3 to 7 minutes) being available for analysis.

Semi-logarithmic plot of time-drawdown data was produced with FC and is presented as Figure 4-19. An increase in drawdown is noted from approximately 7 minutes into the test which is coincident with a depth of approximately 4.50 to 5.00 mbgl. Review of the time drawdown plot and the derivative plot (Figure 4-20) indicates that dewatering of an upper fracture (4.50 to 5.00 mbgl) is completed by 7 minutes and a second fracture is encountered at approximately 5.50 and 7.00 mbgl.

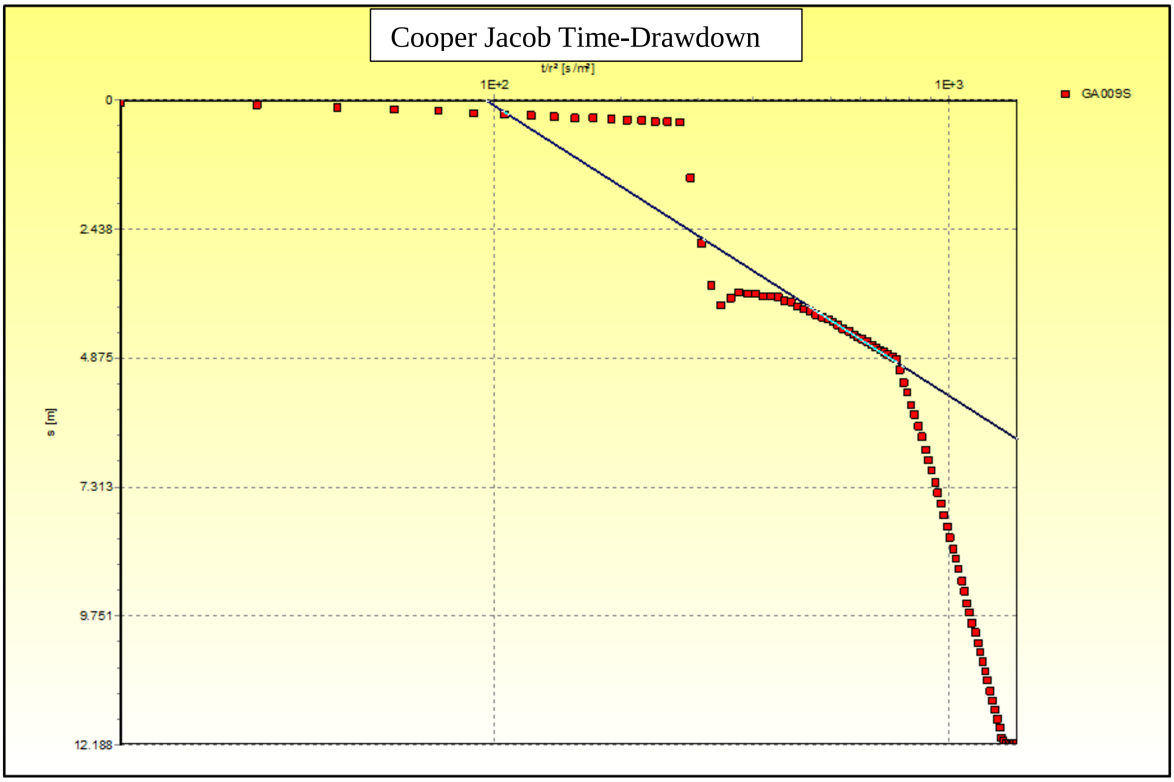

Figure 4-18: Time -Drawdown for GAA009-S (Taken from Hughes, 2014d)

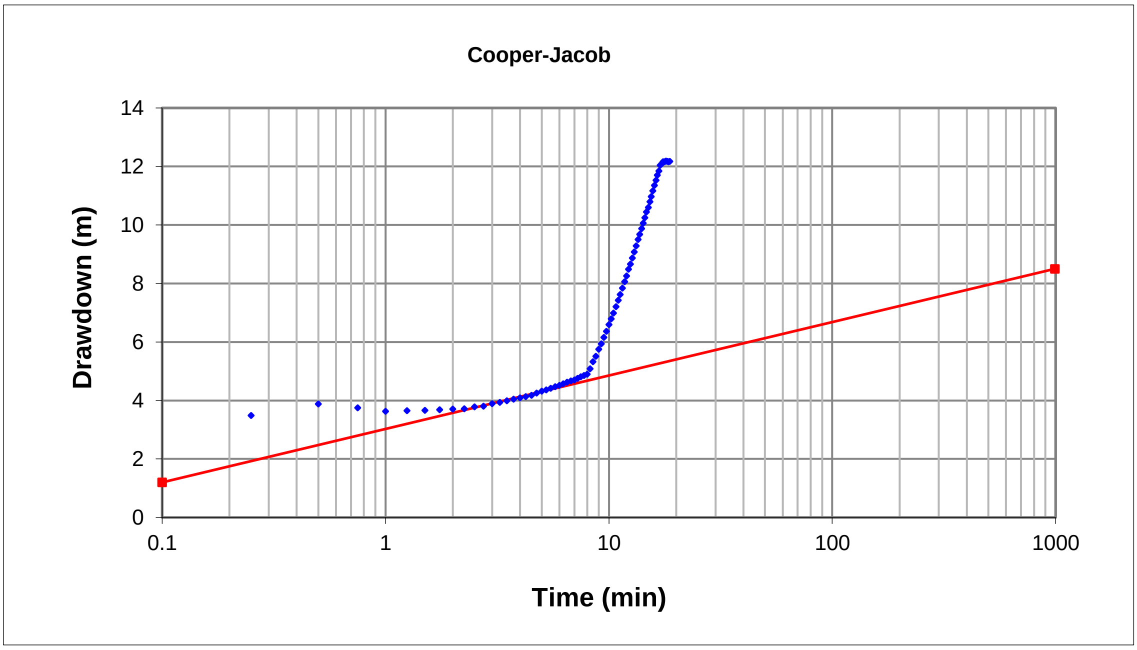

Figure 4-19: Time Drawdowns for GAA009-S (Taken from Hughes, 2014d)

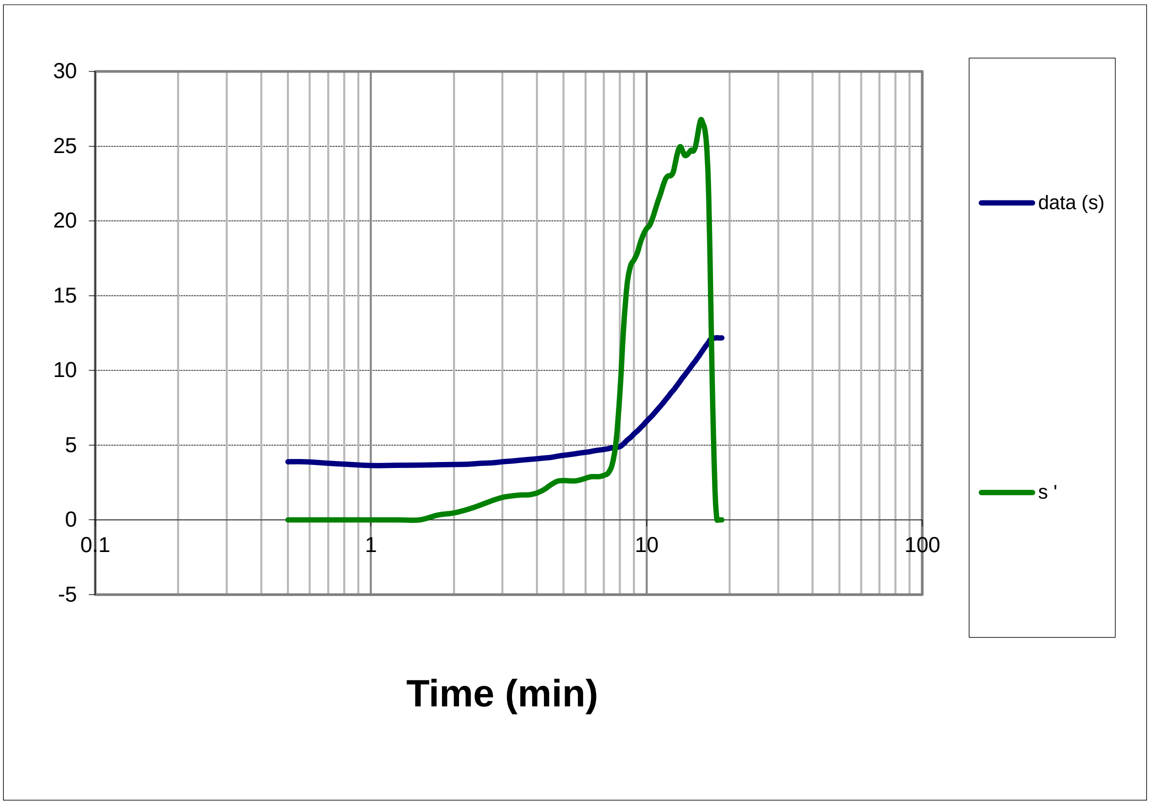

Figure 4-20: Derivative plot for GAA009-S Time Drawdown (Taken from Hughes, 2014d)

GAA011-S

Site obtained data for GAA011-S was similarly loading into the Aquifer Test program. The data plot is presented as Figure 4-21. A constant abstraction rate of 0.1 l/s was established after approximately 120 seconds. A twenty degree slightly undulating declination line for subsequent assessment was obtained and is shown in Full drawdown to the pump level (14 mbgl) was achieved within 19 minutes.

Review of the time drawdown plot (Figure 4-22) and the diagnostic plot (Figure 4-23) shows that the first fractures (or upper weathered zone) were dewatering after approximately 5 minutes at a depth of 5.10 mbgl. The second structure was dewatered at 7 minute at a depth of 5.60 mbgl.

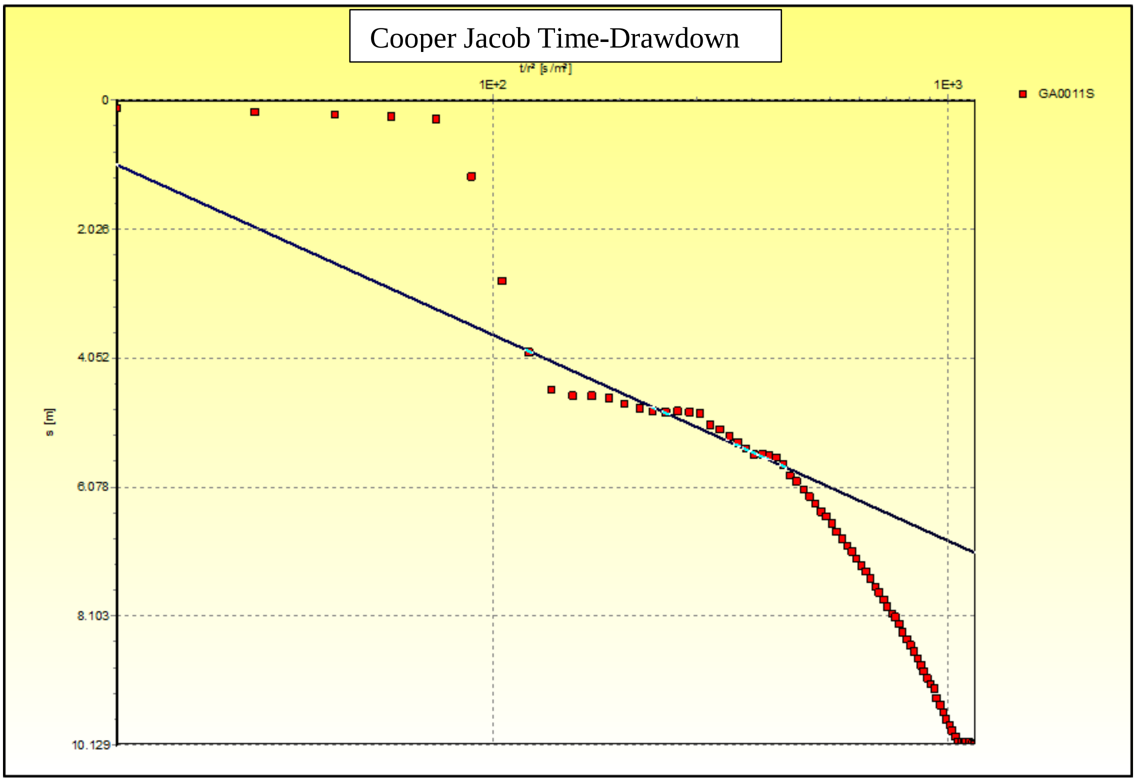

Figure 4-21: Time Drawdown for GAA011-S (Taken from Hughes, 2014d)

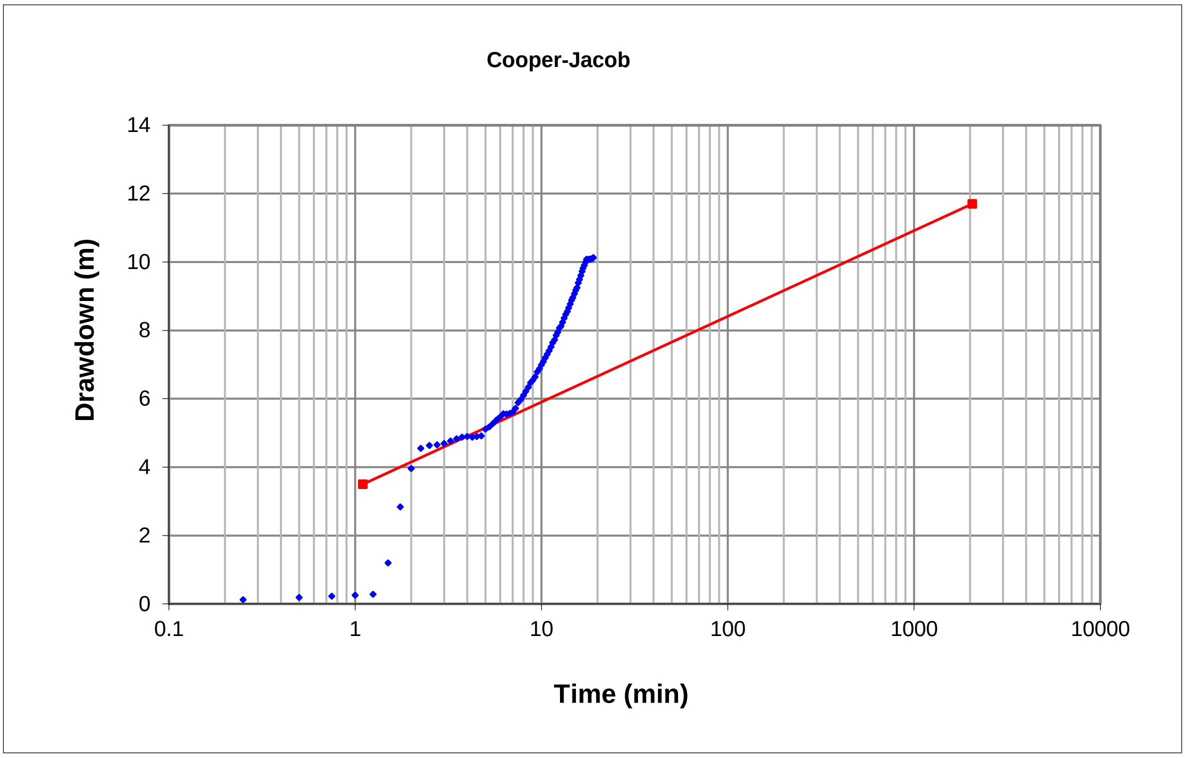

Figure 4-22: Time Drawdown using FC Method for GAA011-S (Taken from Hughes, 2014d)

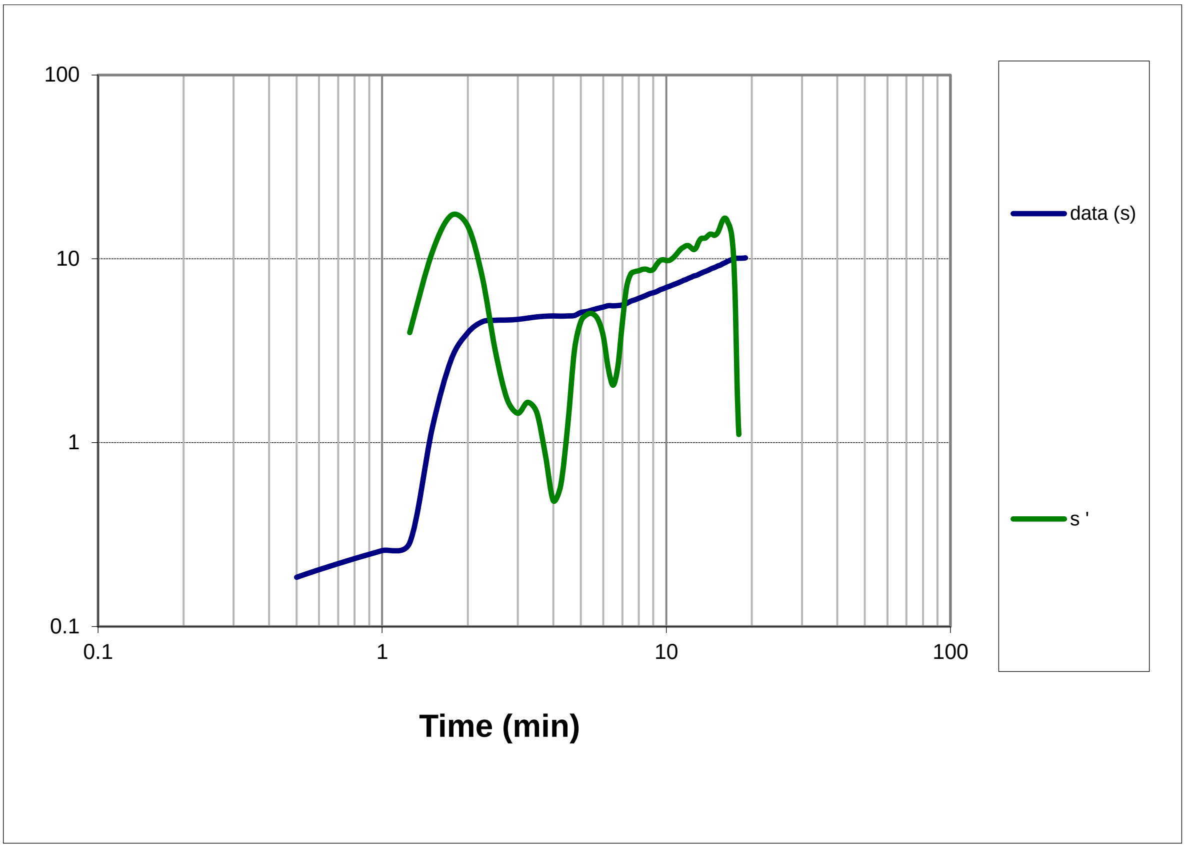

Figure 4-23: Derivative plot for GAA011-S Time Drawdown (Taken from Hughes, 2014d)

4.5.7.4 Interpretation

Estimates of transmissivity from the two methods of assessment are presented in Table 4-22. The calculated transmissivity varied by several order of magnitude between 1.9 and 3.91 x 10^{-2} m^2/day. The large variation in transmissivity calculated is considered to be a result of the short duration of the test and the variability in data quality. Estimates of hydraulic conductivity are provided as averaged values for the two method of analysis for which values of 5 x 10^{-2} and 9 x 10^{-2} m/d have been calculated. These values are considered by the author to be representative of fractured and weathered rock aquifers.

Table 4-22: Estimated Hydraulic Conductivity (Modified from Hughes, 2014c)

Monitoring Well	**Transmissivity (m^2/day)**		**Estimated Hydraulic Conductivity (m/d)**
	Aquifer Test	**FC method**	
GAA009-S	2.88 x 10^{-1}	1	5 x 10^{-2}
GAA011-S	3.91 x 10^{-2}	1.9	9 x 10^{-2}

4.5.7.5 Data Assessment for Recovery Test

GAA009-S and GAA011-S

The recovery test data was collected using a solonist data logger and inputted into the Aquifer Test program. The recovery test data was analysed using the Bouwer and Rice method (Bouwer and Rice, 1976). Data plots for GAA009-S and GAA011-S are presented as Figure 4-24 and Figure 4-25, respectively.

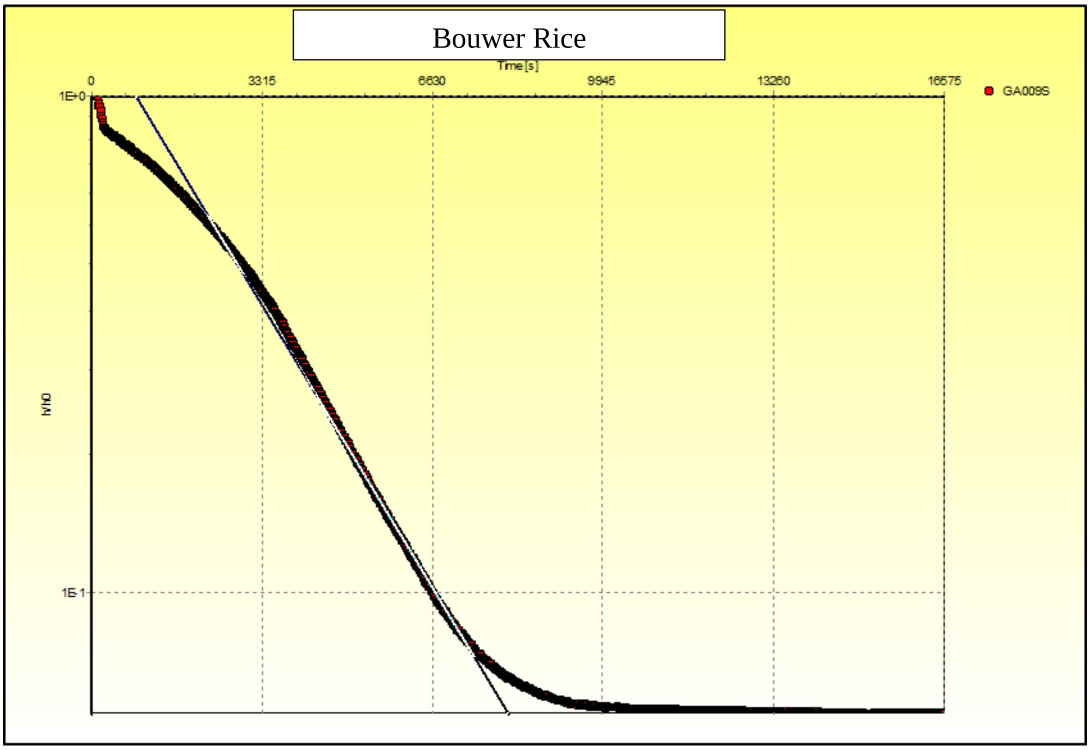

Figure 4-24: Recovery Analysis for GAA009-S (Taken from Hughes, 2014d)

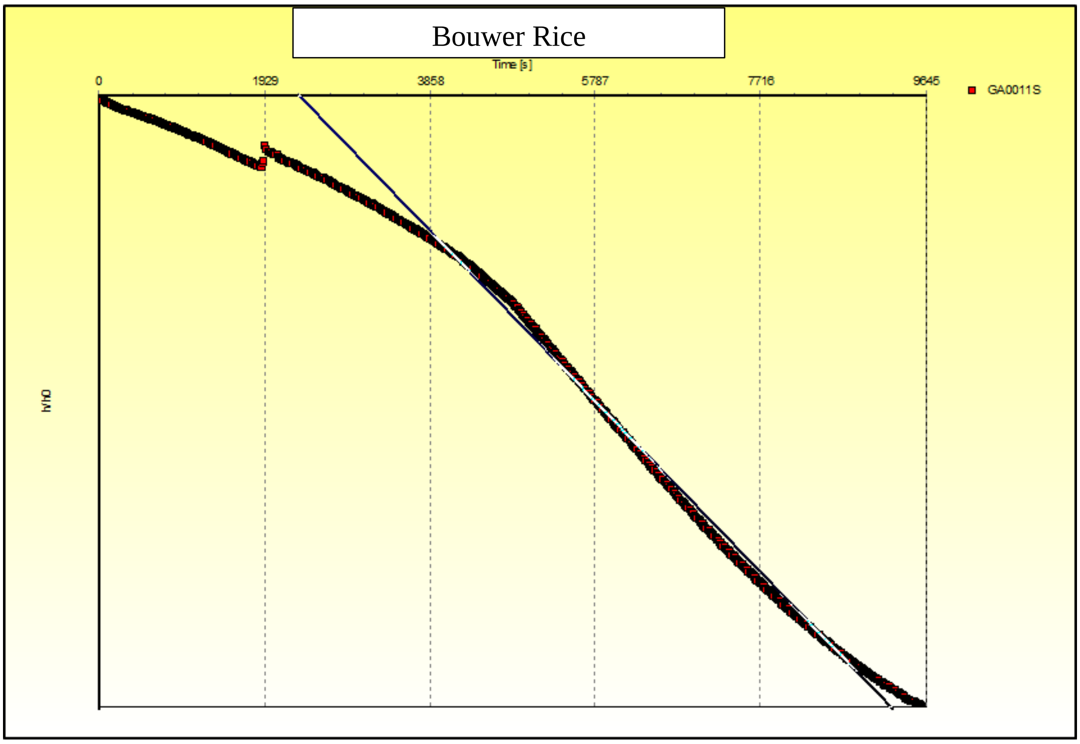

Figure 4-25: Recovery Analysis for GAA011-S (Taken from Hughes, 2014d)

4.5.7.6 Interpretation

Estimates of hydraulic conductivity from the two methods of assessment are presented in Table 4-23. The calculated hydraulic conductivities ranged between 2.1 x 10^{-2} and 3.0 x 10^{-2} m/d which is of the same order of magnitude as that obtained from the CDT analysis and similarly representative of weathered and fractured rock aquifers.

Table 4-23: Estimated Hydraulic Conductivity from Recovery Test (Modified from Hughes, 2014c)

Monitoring Well	Hydraulic Conductivity (m/d)
GAA009-S	2.1 x 10^{-2}
GAA011-S	3.0 x 10^{-2}

4.5.8 Discussion

General drainage across the site is to the north-west and the north towards the Crocodile River (north) and a tributary thereof (northwest). The site is underlain by a weathered rock aquifer that is fractured and weathered to a typical depth of 15 mbgl. The weathered aquifer is underlain by fresh unweathered granitic gneiss. Groundwater flow beneath the site is considered to be predominately within the upper weathered horizon rather than within the underlying (basement) fresh unweathered granitic gneiss the latter of which is considered unlikely to contain groundwater in quantities suitable for sustainable abstraction. Geological structures are thought to be present on site (e.g. dykes, faults) which act to control groundwater flow and contaminant migration by providing preferential pathways for movement. Leakages and spillages of process waters during site operations allowed contaminants to enter the groundwater through permeable made ground and highly weathered/fractured granitic gneiss (Hughes, 2014d).

The transmissivity values calculated for the site (1.9 and 3.91 x 10^{-2} m^2/day) are considered to be representative of "poorly developed secondary aquifers characterised by weathering and slight fracturing" (Hughes, 2014d). However, it is also recognised that the transmissivity values may be too low to allow the geological unit to be classified as an aquifer. Hydraulic conductivity of the site strata is controlled by the degree of weathering and extent of fracturing. Aquifer testing undertaken on site has determined that hydraulic conductivities are very low and therefore groundwater present on site is unlikely to represent a feasible groundwater resource – this means that the groundwater is unlikely to be abstracted for human consumption and thereby the potential source-pathway-receptor linkage for human consumption of site groundwater both on-site and immediately off-site is not present. There is however a source-pathway-receptor linkage associated with migration of contaminated groundwater via baseflow towards the Crocodile River.

Within the two zones of low resistivity (Zone A and Zone B) identified during the geophysical survey and assumed to represent geological structures that allow for the migration of contaminants, the upper 15 m of strata is highly weathered and substantially fractured and for which hydraulic conductivity of in the order of 10^{-2} m/d have been calculated. The underlying fresh rock is not weathered and less fractured and for which hydraulic conductivities of between 10^{-7} to 10^{-9} m/d have been proposed (Hughes, 2014d). The hydraulic conductivity for the upper 15 m of strata outside of the low resistivity zones is estimated at 10^{-4} to 10^{-5} m/d (Hughes, 2014d). No storativity calculations have been undertaken as part of this assessment however storativity was calculated during other works undertake on the site (Steyn, 2010) for which a value of 5 x 10^{-5} was proposed.

Groundwater contamination is present on site but is limited to two low apparent resistivity zones and within these zones the majority is in the upper 15 m. Some contamination may extend to greater depth through interconnection of fracture sets, however this has not been proven by this investigation and the substantially reduced degree of fracturing, as identified during the geotechnical logging, limits capability in this regard.

4.6 SURFACE WATER ASSESSMENT

4.6.1 Introduction

A surface water quality assessment was undertaken by Cassa (2014) which considered water quality in the greater industrial area and at various sections along the Crocodile River including that to the north of the site. The work involved obtaining samples of surface water from thirteen locations including the canal to the south and weirs and other sections along the Crocodile River. Cassa (2014) concluded that the Delta facility did not "significantly impact on the surface water quality of the Crocodile River". This was based upon a single round of sampling and an assessment that the expected loading from sulphate and manganese would be very low and therefore not impact upon existing quality nor change the concentrations of contaminants within the Crocodile River. Upon review of the surface water quality report and with due regard for observations made during the geophysical survey, the author determined that the sampling locations chosen to obtain representative water quality samples under Cassa (2014) had been too widely spaced. Specifically, the samples had not been obtained from sections of the Crocodile River at points where groundwater based contamination migrating from site along sub-surface geological structures would likely meet with the river. The author therefore proposed additional surface water samples at locations informed by an understanding of the developing conceptual site model.

Surface water samples were obtained by the author at locations identified in Table 4-24 and shown on Figure 4-8.

Table 4-24: Surface Water Samples

Sample Designation	Latitude	Longitude	Description
GACROC01	-25.4583	30.9902	Downstream sampling point.
GACROC02	-25.4569	30.9881	In vicinity of presumed connection point of river and geological feature associated with Zone B identified during the geophysical survey.
GACROC03	-25.4545	30.9864	In vicinity of presumed connection point of river and geological feature associated with Zone A identified during the geophysical survey.
GACROC04	-25.4541	30.9861	Upstream sampling point.

The sampling locations were selected in order to:

a) obtain samples of surface water both down-gradient and up-gradient of the likely points in ingress of contaminants into the river (GAGROC01 and GACROC04) thereby being representative of pre- and post- contaminant entry conditions; and

b) obtain samples of surface water in close proximity to the probable locations where contaminants are entering the river (GACROC02 and GACROC03) and therefore provide data to allow a risk assessment to be undertaken with respect to the impact of contaminant upon the local and immediate environment.

4.6.2 Surface Water Quality Data

Screening and data interpretation during the groundwater quality assessment had determined that groundwater with low pH, elevated sulphate and elevated manganese was leaving the site along sub-surface geological structures. For this reason and that of cost the suite laboratory analysis was limited to those three determinands. The chemical test results are presented in Table 4-25.

The chemical test results for pH, manganese and sulphate were initially screened against water quality guidance provided by DWAF (1996) with respect to domestic, livestock and irrigation use. The screening criteria is provided in Table 4-26. The pH of the surface water was found to be within the acceptable limits for both domestic and irrigation use. However, manganese concentrations were in excess of appropriate guidance for use for irrigation in all four samples and for domestic use in three of the downstream samples. Similarly, sulphate concentrations exceeded guidance for domestic and livestock use in all four samples.

Table 4-25: Surface Water Quality Chemical Analysis

Sample Designation	Determinand			Relative Location
	pH	Mn mg/l	Sulphate mg/l	
GACROC01	7.6	0.17	6	Most down-stream sampling point
GACROC02	7.6	0.27	9	Second feature (Zone B) intercept
GACROC03	7.5	0.93	18	First feature (Zone A) intercept
GACROC04	7.5	0.05	7	Most up-stream sampling point

Table 4-26: SA WQG (DWAF, 1996)

Determinand	Units	Domestic	Livestock	Irrigation
pH	pH	6 to 9	ng*	6.5 to 8.4
SO4	mg/l	0.2	1	ng*
Manganese	mg/l	0.05	10	0.02

*ng=no guidance

The chemical test results were also screened against the Interim Resource Quality Objectives (IRQC) for the Crocodile River (as received by the Inkomati-Usuthu Catchment Management Agency (Table 4-27). The pH of the surface water was found to fall within the acceptable designation. Sulphate concentration all fell below the ideal criteria. Manganese concentrations however, exceeded the tolerable limit.

Table 4-27: Crocodile River Interim Resource Quality Objectives

Determinand	Units	Ideal	Acceptable	Tolerable
pH	pH Units	-	6.5 to 8.4	-
SO4	mg/l	20	40	60
Manganese	mg/l	0.02	0.10	0.30

4.6.3 Location of Contaminant Entry

Analysis of the relative manganese and sulphate concentrations was undertaken by dividing point concentration by the total concentrations. The percentages are provided in Table 4-28. The analysis indicates that the main location that manganese and sulphate enter the Crocodile River is at GACROC03 near the end of the geological structure connecting to the zone of contamination identified on site as Zone A. Down-stream of this point, concentrations of manganese and sulphate reduce and although the concentration of manganese and sulphate associated with outlet from Zone B (GACROC02) are more elevated than the most upstream sample (GACROC04). It is not possible to determine if this concentration is simply the result of dilution within the Crocodile River or if additional contribution is being received at this location (see Figure 4-8).

Table 4-28: Relative Percentage Contribution

Sample Designation	Relative Location	Relative Manganese Contribution	Relative Sulphate Contribution
GACROC01	Most down-stream sampling point	11.97%	15.00%
GACROC02	Second feature (Zone B) intercept	19.01%	22.50%
GACROC03	First feature (Zone A) intercept	65.49%	45.00%
GACROC04	Most up-stream sampling point	3.52%	17.50%

4.6.4 Conclusions

Work undertaken by Schneider (2014) in development of a rehabilitation action plan for the site argued that although groundwater with elevated concentrations of manganese and sulphate in the shallow aquifer was entering the Crocodile River it was doing so at such low concentrations that groundwater quality with respect to the two contaminants remained either within ideal or acceptable ranges. The author agreed with Schneider (2014) in that the sulphate levels would likely remain below the IRQC guidelines for sulphate as they were much less stringent than the SAWQG proposed by DWAF (1996a). However, the author disagreed with the inference that there was minimal change in manganese concentrations and argued that the manganese levels had been shown to be in excess of both tolerable limits proposed by IQRC and SAWQG limits proposed by DWAF (1996a). The author also argued that regardless of any reduced impact associated with dilution of manganese within the Crocodile River that may occur, it remained evident that at the point where contaminants entered the Crocodile River and for a section of river of at least 500 m, manganese concentrations had an unacceptable detrimental impact of water quality and represented a risk to the environment.

By using an understanding of the conceptual site model, the author was able to determine appropriate sampling locations to: a) prove the correctness of the conceptual site model by determining the locations where contamination enters the Crocodile River; b) inform and improve upon the surface water assessment by obtaining representative samples of surface water in the area or probable impact; c) confirm that site activities were having a negative impact upon surface water quality; and d) ultimately guide the remediation strategy towards one of pro-active in-situ remediation rather than monitored natural attenuation which had been suggested by others.

CHAPTER 5:
GROUNDWATER QUALITY ASSESSMENT

Between 2014 and 2015, the author undertook three groundwater sampling events. This chapter discusses the sampling protocol adopted, the in-situ physiochemical measurements determined and provides an assessment of the chemical test results from laboratory testing undertaken in both South Africa and the UK. The sampling was undertaken during: a) July 2014, b) October 2014, and c) December 2014 and January 2015 with each new sampling event including the sampling of additional site-wide monitoring wells and perimeter monitoring wells. In the most part, the field measurements and chemical test results were compared to South African drinking water standards (SANS 241:2011) as this is considered by the author to represent the minimal assurance necessary assuming lifetime consumption of water. Some chemical analysis was also compared to South African surface water guidelines and those specific to the Crocodile River Catchment area.

The chemical tests results were reviewed to determine water-type distribution across the site and physiochemical measurements were used to determine where groundwater ORP and pH conditions were suitable to enable manganese to remain in solution as dissolved phase Mn^{2+}. In addition, concentrations of dissolve phase manganese and sulphate were compared to determine water type variations across the site.

Upon review of the initial chemical test results from the July 2014 sampling event it became evident that the majority of the eight initial monitoring wells constructed in 2010 had been formed outside of areas impacted by substantial groundwater contamination i.e. those areas of low apparent resistivity identified during the geophysical survey. Distribution of water-types across the site correlated in-part with changes in apparent resistivity identified during the geophysical survey and therefore the geophysical survey helped inform the positioning of additional monitoring wells drilled during October and November 2014 and reported upon in Chapter 4.

Importantly, the groundwater sampling identified that alkalinity associated with pre-treated process sludge (“Greenfill”) used as backfill was leaching through soils in the area of the football pitch was having a positive impact upon groundwater quality elsewhere on site by neutralising acidic waters down-gradient of the eastern cell house and facilitating the precipitation of manganese as rhodochrosite ($MnCO_3$). This observation subsequently informed the remediation strategy and encouraged the author to explore opportunities for alkali dosing to reduce pH in acidic areas and precipitate manganese from solution.

Prior to undertaking sampling, each borehole was dipped to determine groundwater levels and base of boreholes. Low-flow sampling was undertaken using a 12Volt Waterra sampling pump powered by a portable 12 V car battery. The pump was lowered by hand into each borehole to a depth of 1 m above the base of the borehole and then pumped at the minimum flow rate to ensure minimal disturbance of any sediments within the monitoring wells. During pumping prior to sampling both EC and pH were recorded and only when stabilisation had occurred (i.e. consecutive readings of EC and pH were to within 10%) were samples collected.

Both unfiltered and filtered samples were collected with the latter involving the use of a 0.25 micron filter in the field at the time of sampling. The unfiltered samples were to be used to determine total concentration of metals whereas the filtered samples were to be used to determined dissolved concentrations.

Sample bottles were provided by the contracted analytical laboratory with preservatives pre-added. Samples were stored in a cooler box with ice packs and were maintained in a cool state until delivery to the laboratory within the required holding times.

An Aqua Read Multi-Parameter probe was used to obtain physiochemical water quality measurements for: pH, EC, Dissolved Oxygen, TDS and ORP and in some instances Turbidity and Temperature.

5.1 JULY 2014 SAMPLING EVENT

During July 2014, the author undertook groundwater sampling of the then eight monitoring wells on-site that had been constructed during the earlier site investigation undertaken in 2010.

5.1.1 Physiochemical Measurements

The physiochemical measurements obtained at the time are presented in Table 5-1. The physiochemical measurements were screened against guidance provided by SANS 241:2011 and where the measurements were in excess of guidance they have been highlighted in Table 5-2. After consideration of the physiochemical properties, the author determined that the water quality across site was poor, with high turbidity and EC values obtained for the majority of the samples (Hughes, 2014a). Importantly, the author determined that pH values down-gradient were generally lower than those up-gradient indicating that a source of acidic water must be present on-site at some point between the up-gradient and down-gradient monitoring wells and most likely in close proximity to the cell houses where wet-processes were undertaken during operation of the site facility.

Table 5-1: Physiochemical measurements from July 2014 (Taken from Hughes, 2014a)

Monitoring Well	Turbidity (NTU)	pH	EC (mS/m)	TDS (mg/l)	ORP (mV)	DO (% sat)
GA001-D	3.2	6.22	28.53	219	267.0	30.9
GA001-S	54.6	6.26	56.12	277	280.0	25.0
GA002-D	27.1	3.96	479.60	3,117	431.0	35.1
GA002-S	469.0	4.51	427.00	3,647	367.0	39.5
GA003-D	23.7	6.84	338.00	1,854	265.0	47.8
GA004-D	5.6	7.71	219.00	860	266.0	73.3
GA005-D	not recorded	7.42	164.10	1,066	161.2	47.2
GA005-S	7.4	6.91	285.30	1,423	206.0	46.9

Table 5-2: Screening Guidance to SANS 241:2011

Screening Guidance	Turbidity (NTU)	pH	EC (mS/m)	TDS (mg/l)	ORP (mV)	DO (% sat)
SANS 241 (2011)	≤ 5	≥5 to 9.7≤	≤170	≤1200	not provided	not provided

5.1.2 Laboratory Chemical Analysis

Groundwater samples obtained from the eight monitoring wells were dispatched to UIS laboratories in South Africa for chemical analysis. The chemical test results are presented in Table 5-3 where they have been screened against SANS 241:2011 and where in exceedance they are highlighted.

Table 5-3: Chemical Analysis July 2014 Sampling Event (Modified from Hughes, 2014a)

Determinand	SANS241 (2011)	GAA001-D	GAA001-S	GAA002-D	GAA002-S	GAA003-D	GAA004-D	GAA005-D	GAA005-S
pH	≥5 to 9.7≤	6.62	6.6	3.64	4.17	5.36	7.95	8.21	8.28
EC (mS/m)	≤170	34.9	37.8	433	540	303	163	158	217
TDS (mg/l)	≤1200	280	286	5580	6770	2430	1350	1120	1540
Ca Hardness as $CaCO_3$ (mg/l)	-	92.4	101	747	479	227	424	70.9	49.7
Mg Hardness as $CaCO_3$ (mg/l)	-	64.7	68.4	795	725	221	441	88.1	42.8
Total Hardness (mg/l)	-	157	169	1540	1200	448	865	159	92.5
Turbidity (NTU)	≤ 5	3.28	229	6.5	84.6	12.2	9.02	1.42	341
P.Alkalinity as $CaCO_3$ (mg/l)	-	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
M.Alkalinity as $CaCO_3$ (mg/l)	-	29.8	25	<3.5	<3.5	8.5	345	335	391
Ca (mg/l)	-	27	30.3	194	192	91	170	28.4	19.9
Fe (mg/l)	≤2	<0.05	<0.05	0.43	0.16	<0.05	<0.05	<0.05	<0.05
K (mg/l)	-	1.98	2.71	12.5	10.5	5.44	16.5	6.85	1.35
Mg (mg/l)	-	11.7	13.6	163	176	53.7	107	21.4	10.4
Mn (mg/l)	≤0.5	2.18	1.22	682	682	53.8	0.44	<0.05	<0.05
Na (mg/l)	≤0.2	20.2	23.7	210	618	546	70.5	350	536
Si (mg/l)	-	14.8	16.7	62.9	50.7	41.5	18	21.6	34.6
F (mg/l)	≤1.5	0.18	0.151	2.97	3.47	1.61	1.42	7.73	10.1
Cl (mg/l)	≤300	11.7	12.6	33.4	49.5	277	43.5	27.9	96.8
NO_2 (mg/l)	≤0.9	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
NO_3 (mg/l)	≤11	29.4	32.1	18.5	18.4	17.7	9.06	5.64	62.1
PO_4 (mg/l)		<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8
SO_4 (mg/l)	≤500	86.8	108	3590	4400	1250	599	440	557
Ion Balance %	-	-8.24	-9.5	-8.75	-7.7	-3.48	-0.37	2.8	0.73

NH_4 (ppm)	≤1.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
Cd (mg/l)	≤0.003	0.0001	0.0005	0.0333	0.0033	0.0017	0.0002	0.0001	0.0003
Cu (mg/l)	≤2	0.002	0.003	0.162	0.125	0.03	0.006	0.003	0.005
Hg (mg/l)	≤0.006	0.002	0.0001	<0.0001	<0.0001	<0.0001	0.0001	<0.0001	<0.0001
Pb (mg/l)	≤0.01	0.006	0.27	0.198	0.0058	0.072	0.03	0.024	0.077
U (mg/l)	≤0.015	<0.0001	<0.0001	0.0225	0.0105	0.0032	0.0175	0.0243	0.0154
Cr (mg/l)	≤0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

5.1.2.1 Site Groundwater Characterisation

The groundwater quality data for the July 2014 sampling event was reviewed and the various cation and anions were converted to milliequivalent per litre and then plotted on as a Piper Diagram using the computer programme WISH, developed by the Institute for Groundwater Studies (IGS) at the University of Free State (UFS). A Piper Diagram is used to define and characterise groundwater types based upon the various concentrations of sulphate, chloride, nitrate, total alkalinity, sodium, potassium, calcium and magnesium. The Piper Diagram for the July 2014 sampling event is provided as Figure 5-1.

The data was also assessed to determine the most prevalent ionic species present at each monitoring location by plotting Stiff diagrams. The Stiff diagrams display the major ion compositions to define a water type and are presented as Figure 5-2. Descriptions of the water types found across the site based upon review of the piper diagrams and the stiff diagrams are provided in the following sections.

Southern up-gradient Monitoring Wells

Boreholes GAA005-D and GAA005-S are located up-gradient of the processing plant and towards the western side of the football pitch which has been constructed on an area underlain by treated process sludge known as “Greenfill”. The monitoring wells are also located down-gradient of two large sulphuric acid tanks. The predominant water type in this area is Na-SO_4 type (see Figure 5-1). This water type is most likely associated with the nature of the backfill leaching into the groundwater rather than the natural geological surroundings and/or potential spillages from the sulphuric acid tanks, which are not known to have occurred.

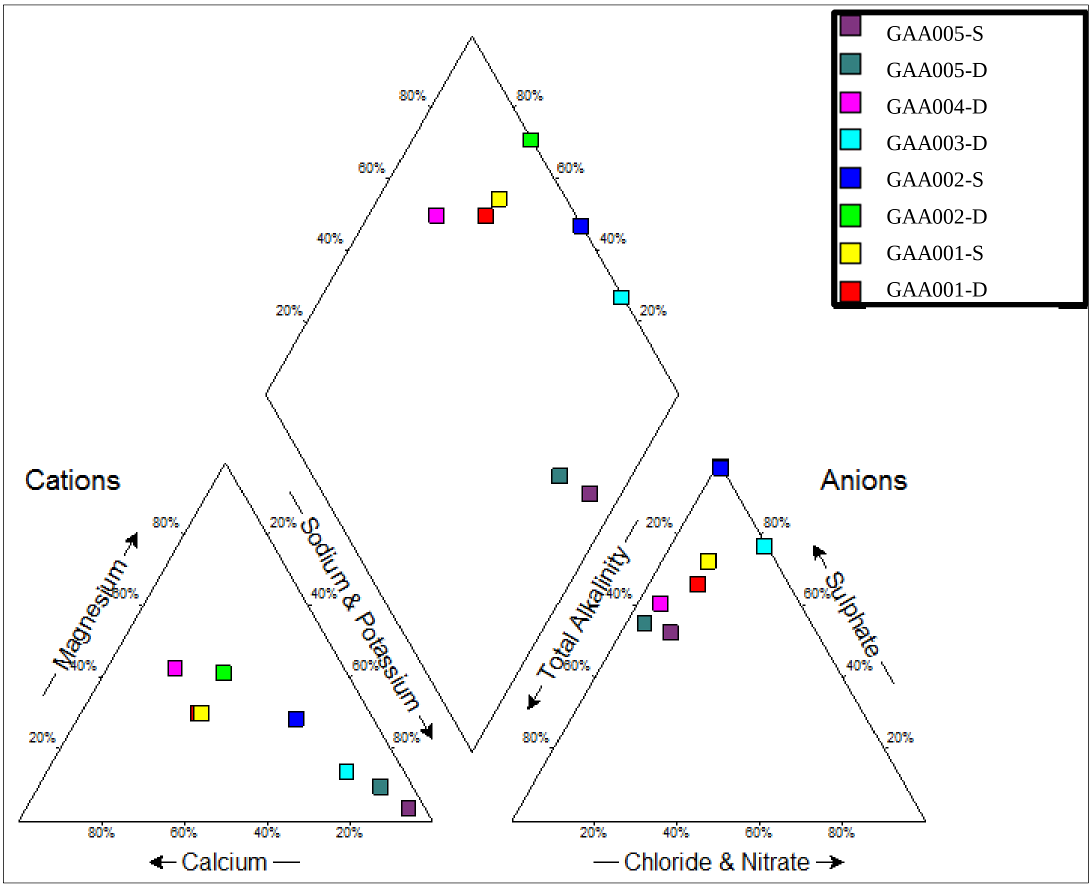

Figure 5-1: Piper Diagram for July 2014 Monitoring Event (Modified from Hughes, 2014a)

Northern down-gradient Monitoring Wells

Monitoring wells GAA002-D and GAA002-S are located down-gradient of the western cell house and within the area of low resistivity known as Zone A identified during the geophysical survey. The water type in this area is predominately (Ca,Na)-SO_4 type (see Figure 5-1). This water type is considered to be representative of areas where leaking process water has entered the sub-surface and has been treated with a neutralising agent (sodium hydroxide (NaOH)) to increase pH and through which, because of groundwater flow, naturally occurring Ca-HCO_3 waters tend to migrate from the southern boundary towards the northern boundary.

Monitoring wells GAA003-D is located down-gradient of eastern cell house but between the two areas of low resistivity identified as Zone A and Zone B. Groundwater obtained from this monitoring well is classified as Na-SO_4 type (Figure 5-1). It is considered by the author that this area is likely impacted by the neutralising agent (NaOH) placed in this area to raise low pH values in the process water and groundwater. Monitoring well GAA004-D is located to the south-east of Zone B and some distance from the eastern cell house. The water type here is (Ca,Mg)-SO_4 type (see Figure 5-1). This represents an area where sulphate is migrating from the eastern cell house but where neutralising agent (NaOH) has not been added to the process water or groundwater.

North-western Monitoring Wells

Monitoring wells GAA001-D and GAA001-S are located towards the north-west of the site far from the wet-process areas but down-gradient of the adjacent processing facility belonging to Manganese Metal Company (MMC). Groundwater obtained from these monitoring wells is classified as either Ca-SO_4 or (Ca,Mg)-SO_4 type (see Figure 5-1). As this area is located far from the site wet-process areas and is not down-gradient of groundwater flow from the same wet-process areas it is probable that the source of sulphate in the groundwater in this area is from an off-site location not yet determined.

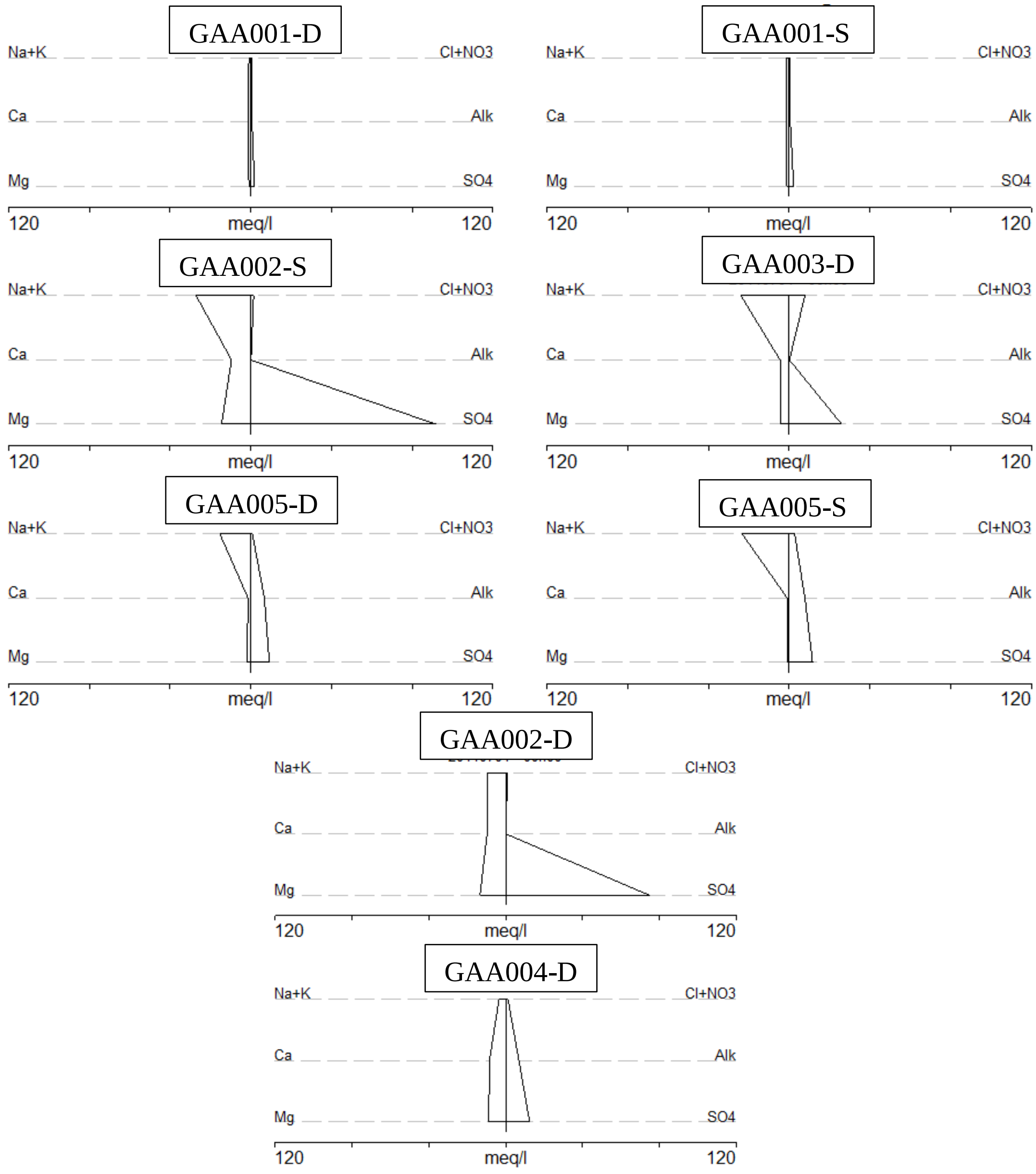

Figure 5-2: Stiff Diagrams for July 2014 (Taken from Hughes, 2014a)

5.1.2.2 Site Groundwater Quality Assessment

A groundwater quality assessment has been undertaken by the author based upon the chemical test data presented in Table 5-3.

Across the majority of the site pH values ranged between 6.60 and 8.28. However, very low pH values were detected (3.64 and 4.17) in monitoring wells GAA002-D and GAA002-S located along the northern boundary at the edge of the area of low apparent resistivity known as Zone A. No pH data was available for Zone B, at that time however it was suspected that pH values similar to that found in Zone A would be present. The low pH values determined for the monitoring wells within Zone B are considered to be directly associated with leakage of process water from the wet-processes undertaken on site.

All of the groundwater samples obtained during the July 2014 monitoring event are shown to have been impacted upon by some form of contamination which has resulted in additional sulphate being added to the groundwater mix. The author does not consider that any of the groundwater samples obtained are representative of natural groundwater conditions or groundwater up-gradient of the southern site boundary. All groundwater samples obtained towards the north of the site i.e. down-gradient of processing areas contained detectable concentrations of manganese. Further, with the exception of the groundwater samples obtained from monitoring well GAA004-D all of the manganese concentrations are in excess of the 0.50 mg/l water quality guidance provided by SANS 241:2011. However, manganese concentration below the laboratory detection limit of 0.05 mg/l is reported for monitoring wells GAA005-D, GAA005-S located up-gradient of the processing plant and in an area thought to be impacted by leaching following the placement of backfill of treated sludge (“Greenfill”). It is noted that for these two monitoring wells the pH of the groundwater was higher than elsewhere on the site (8.21 and 8.28). The author postulates that the higher pH ensures that any residual manganese that may be present in the backfill “Greenfill” prevent manganese dissolving into solution.

The highest manganese concentrations were detected along the northern boundary of the site down-gradient of the western and eastern cell houses. The elevated concentrations of manganese were associated with very low pH values. A very poor correlation between pH and manganese concentration was determined due in part of the small data set and the large spatial distribution of the monitoring wells. This, the author considers, represents an indication that the presence of manganese in groundwater is localised to certain geographical areas rather than representing natural groundwater quality across the entire site. As such it is reasonable to conclude that manganese is not naturally occurring and is instead a localised contaminant.

A very good correlation ($R^2 = 0.9542$) can be shown between manganese and sulphate concentrations although there is a substantial data gap in the data available for manganese concentrations between 100 and 600 mg/l (Figure 5-3). A much stronger correlation ($R^2 = 0.9928$) can be shown between TDS and sulphate concentrations (Figure 5-4). This indicates that a) sulphate is the primary dissolved phase constituent in groundwater at the site and b) sulphate is associated with the presence of manganese in groundwater. Further, as manganese sulphate is used in the industrial process it is reasonable to assume that both of these contaminants of concern are anthropogenic contaminants rather than representative of naturally occurring groundwater conditions.

Sodium was detected in all groundwater monitoring wells at concentrations that exceed the SANS 241:2011 groundwater quality guidance for sodium (0.2 mg/l). The most highly elevated concentrations (210 to 618 mg/l) were detected in groundwater monitoring wells GAA002-D, GAA002-S and GAA003-D. It is understood that historically NaOH was added to the process waters and wash-out as a means of neutralising the acidity. Once the site stops processing manganese then it would be expected that the sodium concentration in the groundwater will deplete as less sodium rich groundwater migrate northerly diluting the zones of impacted groundwater.

Slightly elevated lead was detected in most monitoring wells including those where no manganese was present suggesting that lead is potentially naturally elevated in groundwater in this area. Two monitoring wells contained slightly elevated uranium, however there was insufficient data to determine any correlation with these metals and pH conditions.

Nitrate was detected in all of the monitoring wells and elevated above guidance provided in SANS 241:2011 in six of the eight monitoring wells.

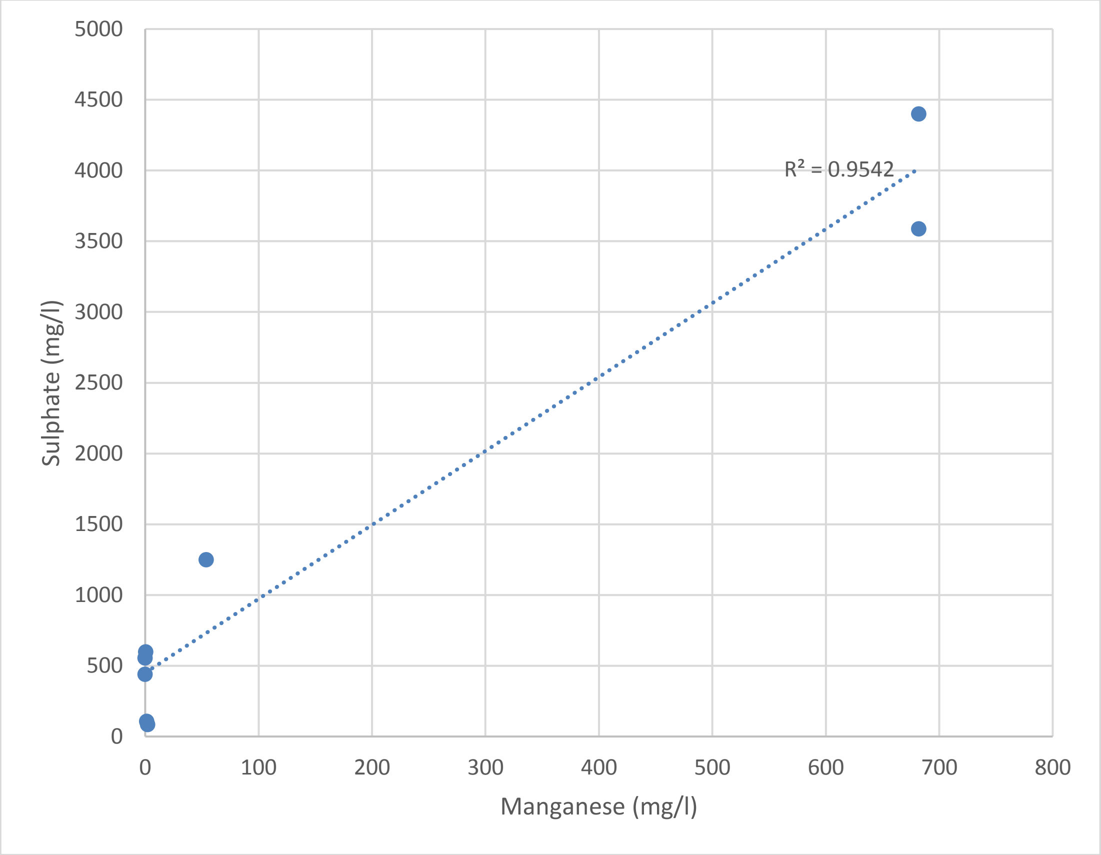

Figure 5-3: Correlation between Manganese and Sulphate

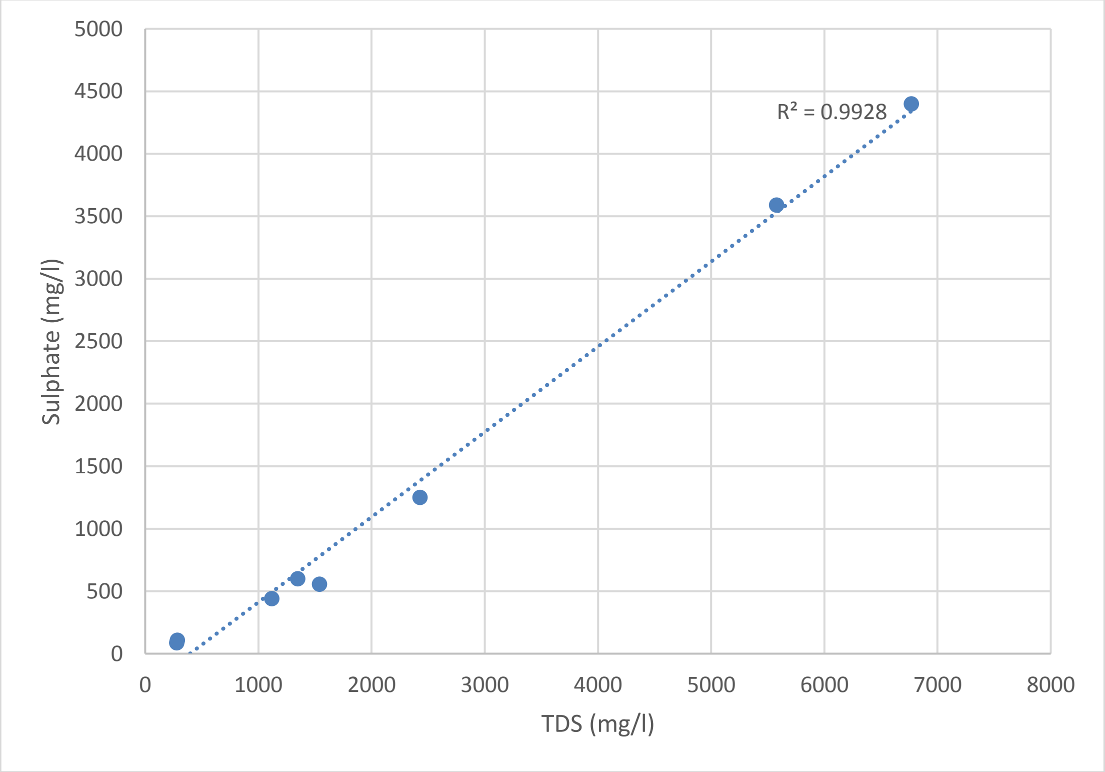

Figure 5-4: Correlation between TDS and Sulphate

5.1.3 Comparison of Field and Laboratory Analysis

The author undertook a review and comparison of field measurements and laboratory test data to determine the accuracy of field measurements as a future guide for assessment during the additional monitoring events planned for October and December 2014. The comparison is presented in Table 5-4 and discussed in the bullets that follow.

Table 5-4: Comparison of Field and Laboratory Measurements

Determinand	Laboratory or Field Measurement	GA001-D	GA001-S	GA002-D	GA002-S	GA003-D	GA004-D	GA005-D	GA005-S
pH	Lab	6.62	6.60	3.64	4.17	5.36	7.95	8.21	8.28
	Field	6.22	6.26	3.96	4.51	6.84	7.71	7.42	6.91
	Difference %	**6.43**	**5.43**	**8.08**	**7.54**	**21.64**	**3.11**	**10.65**	**19.83**
EC	Lab	34.9	37.8	433	540	303	163	158	217
	Field	28.53	56.12	479	427	338	219	164	285.3
	Difference %	**22.33**	**32.64**	**9.72**	**26.46**	**10.36**	**25.57**	**3.72**	**23.94**
TDS	Lab	280	286	5580	6770	2430	1350	1120	1540
	Field	219	277	3117	3647	1854	860	1066	1423
	Difference %	**27.85**	**3.25**	**79.02**	**85.63**	**31.07**	**56.98**	**5.07**	**8.22**
Turbidity (NTU)	Lab	3.28	229	6.5	84.6	12.2	9.02	1.42	341
	Field	3.2	54.6	27.1	469.0	23.7	5.6	n/a	7.4
	Difference %	**2.50**	**319**	**76.01**	**81.96**	**48.52**	**61.07**	**n/a**	**4508**

There was generally a strong correlation ($R^2 = 0.80$) between laboratory and field measurement for pH, although percentage differences ranged between 3.11% and 19.83% (Figure 5-5).

There was strong correlation between laboratory and field measurements for EC ($R^2 = 0.90$). The percentage difference between the two measurements ranged between 3.72% and 32.64% with field measurements generally being higher than laboratory measurements (Figure 5-6).

The highest correlation (R^2 = 0.967) was recorded between field measurements of TDS and measurements of TDS obtained in the laboratory (Figure 5-7). The percentage difference between ranged between 3.25% and 85.64%. The highest percentage differences were noted for very high TDS concentration suggesting that where TDS concentration is greater than 2,000 mg/l the accuracy of the field measurement decreases, probably because the field equipment was calibrated against a water type with lower TDS concentration.

There was very poor correlation (R^2 = 0.0004) between field measurements and laboratory measurements for turbidity with errors ranging between 2.50% and 4508% (see Table 5-4). The least error difference was identified where laboratory measurements for turbidity were <5 NTU.

The assessment indicated that the field equipment could be utilised in further assessment of the site and could relied upon to provide accurate measurements of pH, EC and TDS. However, a degree of caution was required to accommodate percentage errors particularly associated with very high TDS concentrations.

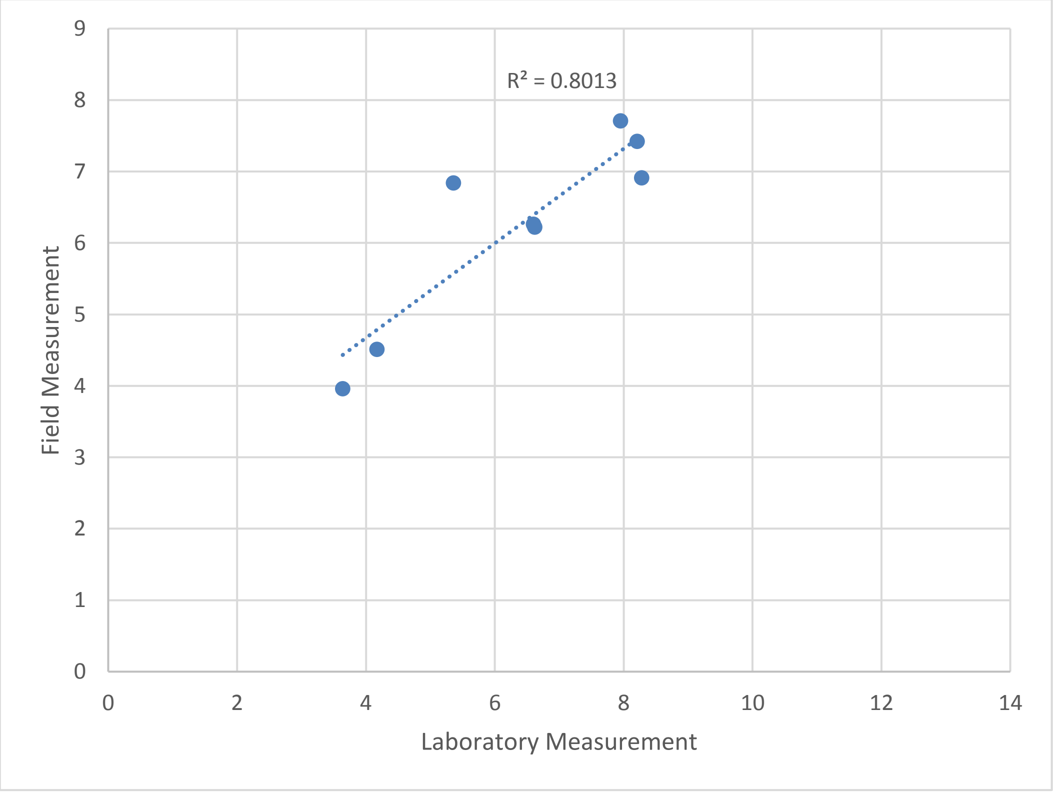

Figure 5-5: pH Correlation

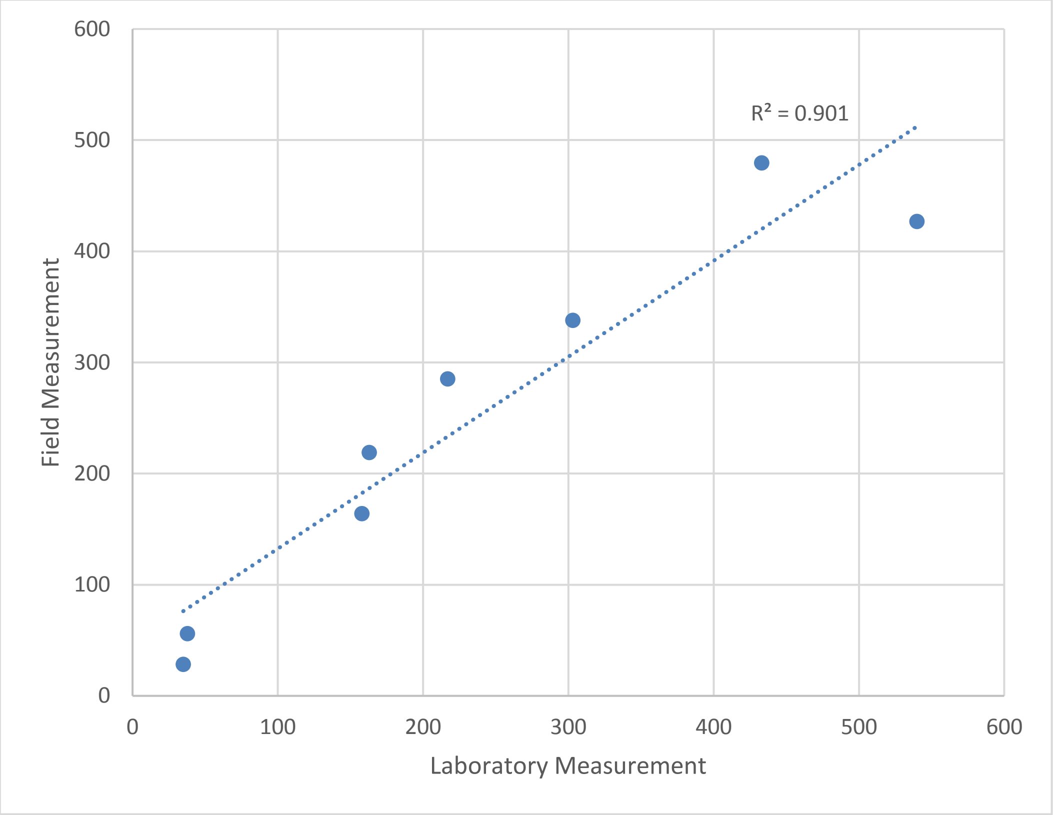

Figure 5-6: EC Correlation

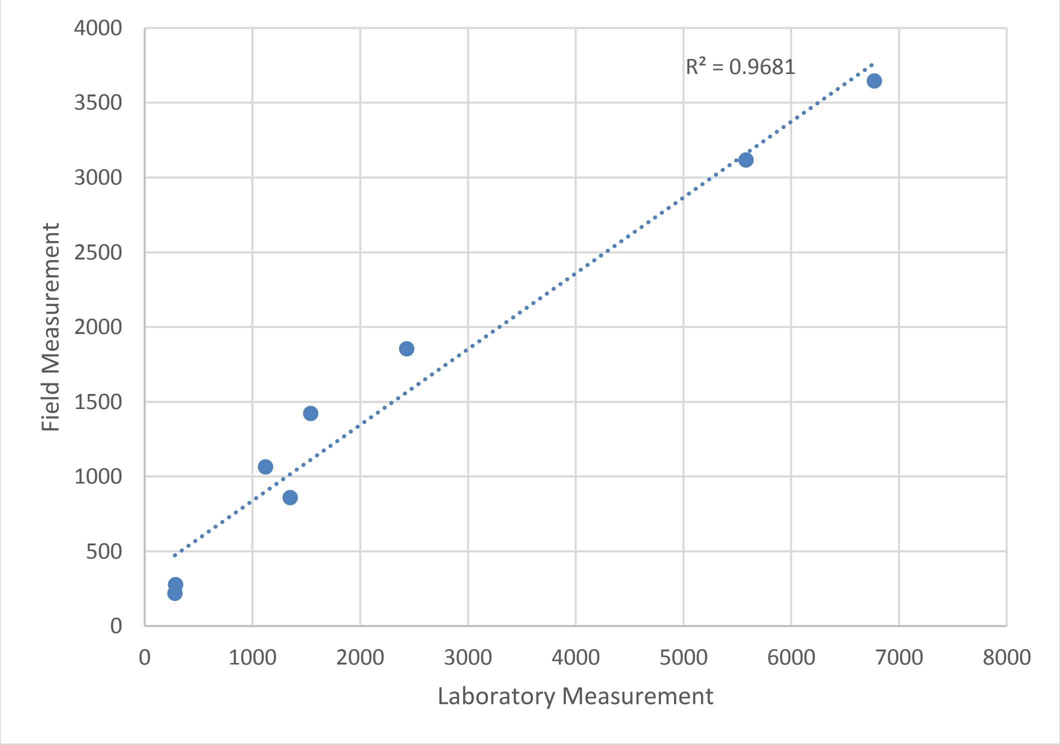

Figure 5-7: TDS Correlation

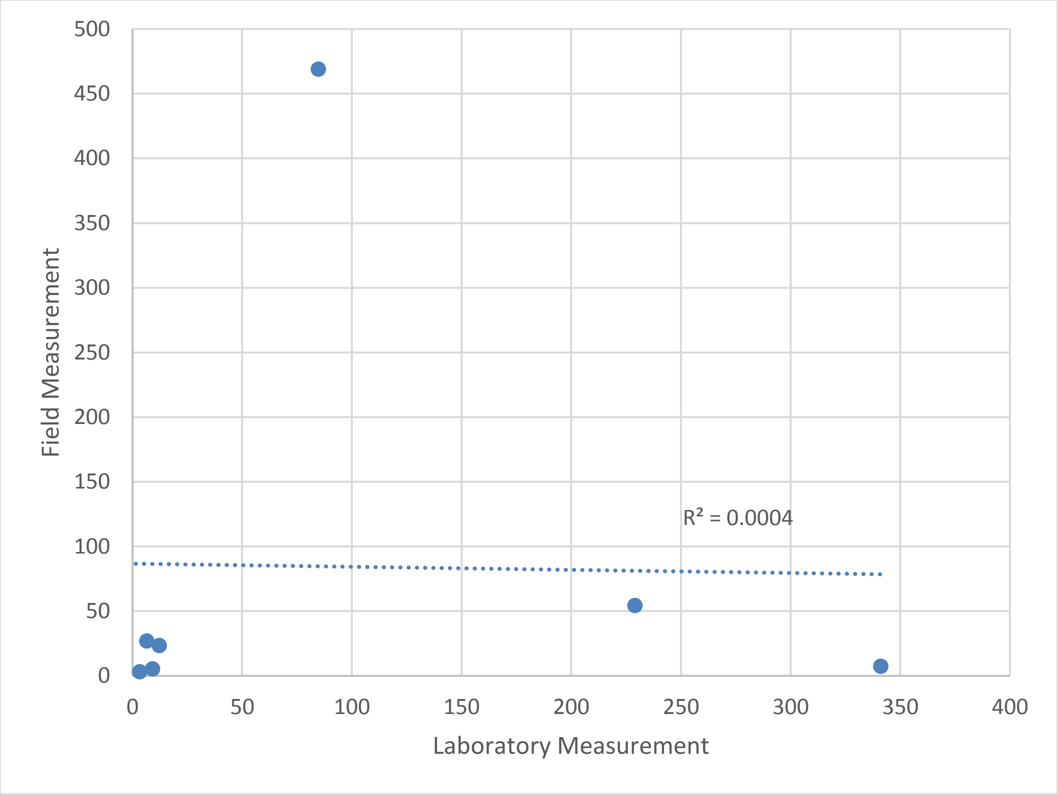

Figure 5-8: Turbidity Correlation

5.2 OCTOBER 2014 SAMPLING EVENT

During the July 2014 sampling event and following-on from the geophysical assessment it had been identified that the existing borehole network was insufficient and did not include for monitoring wells in areas likely to be representative of natural groundwater quality nor in areas likely to be impacted by contaminated groundwater. Therefore, nine new additional monitoring wells were constructed as discussed in Chapter 4. The borehole construction commenced during early October (02/10/14) and at that time groundwater monitoring and sampling was undertaken by the author. As some of the monitoring wells had not been completed at that time an additional round of sampling was undertaken later in October (22/10/14) to collect samples from the remaining monitoring wells. In total seventeen groundwater samples were collected during October 2014. Due to a requirement for quick turnaround of chemical testing the samples were sent to Jones Environmental Laboratory in the UK.

5.2.1 Physiochemical Measurements

The physiochemical measurements determined at the time are presented in Table 5-5. The physiochemical measurements were screened against guidance provided by SANS 241:2011 and where the water quality was in excess of the guidance they have been highlighted as indicated in Table 5-5.

The field physiochemical properties indicate that the water quality on site is of generally poor quality. This is confirmed by high turbidity and high EC values measured in all samples with all samples having electrical conductivity values exceeding SANS 241:2011 drinking water standards (170mS/m) (Hughes, 2014d).

The author utilised pH as a defining parameter to describe various groundwater conditions across the site. In-situ physiochemical measurements determined that pH was found to range between 3.69 and 11.03 which was generally in line with expectations given the various locations of the monitoring wells in relation to the developing understanding of the conceptual site model and where contamination was present. In this regard, pH values down-gradient of the processing facilities (i.e. to the north of the site) were generally lower than pH values obtained up-gradient of the processing facilities (i.e. to the south of the site). The one surprising pH value that was determined was the very high pH for GAA006-D (pH = 11.03). Although monitoring well GAA006-D was located within the area of backfill (“Greenfill”) now occupied by the football pitch and made-up of treated process sludge the author remained surprised at the very high pH value present and had thought that natural attenuation through the infiltration of rainwater over time would have reduced the pH value much further.

Monitoring wells GAA001-S and GAA001-D are located towards the north-western boundary of the site and as previously mentioned down-gradient of other industrial facilities located to the west of the site. The pH values determined at this location were slightly lower than circum-neutral and it is therefore difficult to determine if they are impacted upon by acidic water or not. However, should the groundwater in this area be impacted by acidic water then as the location of the monitoring wells are far away from the processing facilities and not immediately down-gradient thereof it is unlikely to be associated with on-site process waters.

Table 5-5: Physiochemical measurements from July 2014 (Taken from Hughes, 2014d)

Monitoring Well	Turbidity (NTU)	pH	EC (mS/m)	TDS (mg/l)	ORP (mV)	DO (% sat)	Temperature
GAA001-D	0	5.52	43.8	284	257.50	57.50	24.00
GAA001-S	247	5.38	44.7	290	272.20	17.80	23.5
GAA002-D	0.90	3.69	506.8	3294	439.90	50.80	27.20
GAA002-S	933	4.21	741.9	4822	345.50	16.00	27.10
GAA003-D	0	5	209.2	1359	300.90	103.70	26.50
GAA004-D	83.40	7.28	166.3	1080	63.00	0	25.40
GAA004-S	53.40	7.10	Not recorded	Not recorded	144.90	4.60	23.90
GAA005-D	0	7.03	182.3	1184	140.40	49.20	25.20
GAA005-S	87.80	6.84	229.6	1492	150.20	45.50	23.90
GAA006-D	0	11.03	154.3	1002	-45.70	0	22.90
GAA006-S	0.50	7.88	61.4	399	99.60	40.40	23.30
GAA007-D	238	6.82	315.2	2048	-13.90	15.90	1.57
GAA007-S	12.8	6.76	127.0	732.5	-124	9.50	5.63
GAA008-S	88.50	6.46	365.4	2375	50	11.30	1.82
GAA009-S	8.40	6.67	217.3	1412	28.10	9.30	1.08
GAA010-S	27.40	6.65	176.6	1147	-38.30	6.90	0.88

GAA011-S	399	6.93	55.4	360	-80.50	13.90	0.27

Table 5-6: Screening Guidance to SANS 241 (2011)

Screening Guidance	Turbidity (NTU)	pH	EC (mS/m)	TDS (mg/l)	ORP (mV)	DO (% sat)	Temperature
SANS 241 (2011)	≤ 5	≥5 to 9.7≤	≤170	≤1200	not provided	not provided	not provided

Monitoring wells GAA002-S, GAA002-D and GAA003-D are located along the northern boundary of the site down-gradient of the various sources of contamination. Low pH values (3.69 to 5) were detected in these monitoring wells along with: a) relatively high ORP (300.90 to 439.90 mV) values; b) relatively high EC values (209.20 to 741.90 mS/m); and c) TDS (1,359 to 4,822 mg/l). A very strong correlation between EC and TDS was determined with $R^2 = 0.9981$ (Figure 5-9).

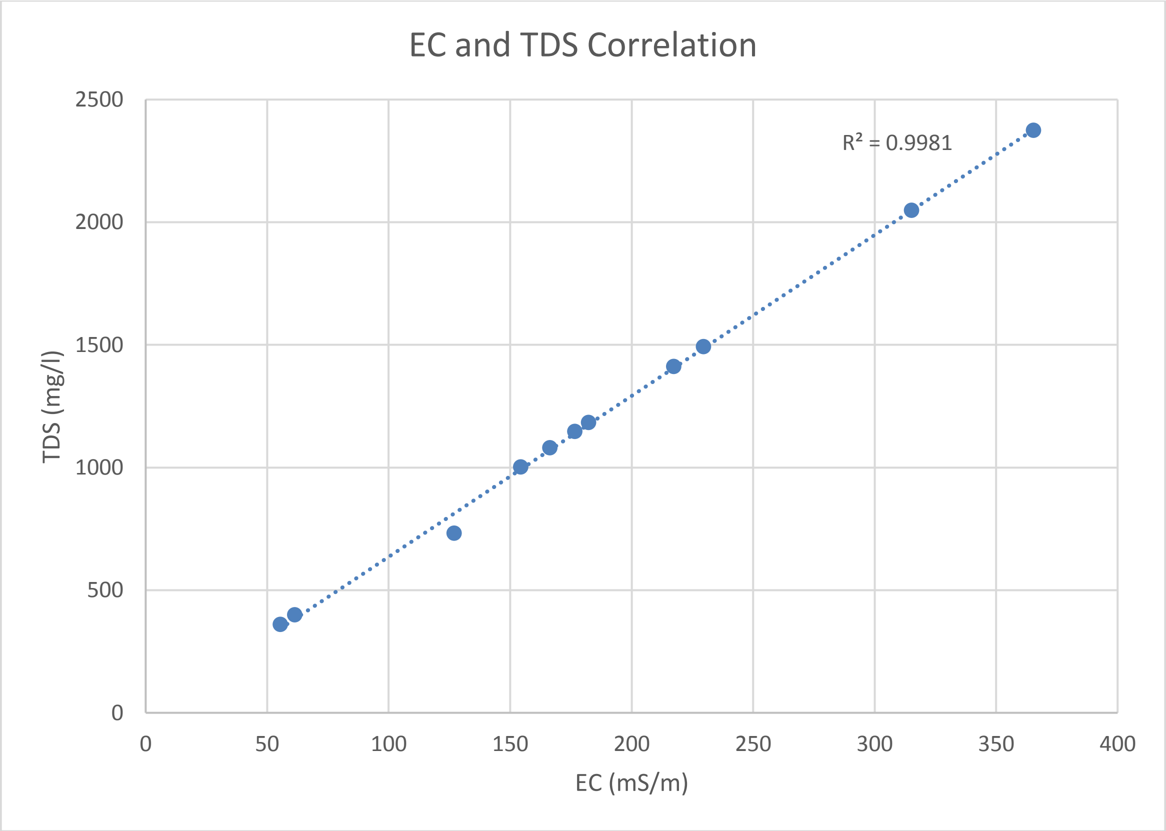

Figure 5-9: EC and TDS Correlation

The TDS and EC correlation has been back calculated and is defined by the Equation 5-1.

$$TDS = (6.5612 \times EC) - 20.378 \qquad \text{Equation 5-1}$$

It is considered that the water quality indictors confirm that groundwater impacted by contamination from wet-process sections of the facility has reached the northern boundary of the site and most probably migrates off-site in a northerly direction towards the Crocodile River.

Monitoring wells GAA007-S, GAA007-D, GAA008-S, GAA009-S, GAA010-S and GAA011-S were all constructed within or in close proximity to the two contaminated zones identified as Zone A and Zone B during the geophysical survey. Of these monitoring wells GAA007-D, GAA008-S, GAA009-S and GAA010-S all exhibited elevated EC and TDS values above the SANS 241:2011 guidance values which has previously been used as a guide for determining the presence of contamination. As such the author had expected the pH values in these monitoring wells to be more acidic rather than the circum-neutral values that were determined. The author noted that groundwater flow across the site was from the south to the north and considered that naturally occurring circum-neutral pH groundwater or induced high pH groundwater from the area underlying the backfill ("Greenfill") beneath the football pitch was migrating through the acidic groundwater in the contaminated zones effectively neutralising the acidity. As groundwater continues to migrate in a northerly direction further neutralisation is anticipated (Hughes, 2014d).

Monitoring wells GAA005-S, GAA005-D and GAA006-D are located towards the south of the site in close proximity to the area of backfill ("Greenfill"). The pH values measured in the groundwater samples from these wells is circum-neutral (6.84 to 7.88) and they are considered to be only slightly more alkaline than natural groundwater pH levels due to the presence of backfill ("Greenfill") leaching into the subsurface.

ORP values range between -124 and 439.90 mV with the highest ORP being associated with areas of lowest pH (GAA001-S, GAA001-D, GAA002-S, GAA002-D and GAA003-D) all located along the northern boundary of the site. In these locations the combinations of pH and ORP are unlikely to allow for the precipitation of manganese from solution (Hughes, 2014d). Further discussion in this regard is provided in Section 5.2.2.3.

5.2.2 Laboratory Chemical Analysis

During October 2014 the author, recognising that the likelihood of natural attenuation occurring on site was negligible and impacted groundwater was reaching the Crocodile River, undertook to screening against not only SANS 241:2011, but also the SAWQG for domestic, livestock and irrigation use (DWAF, 1996) and the Crocodile Interim Resource Quality Objectives (IRQO's) for the Crocodile River as provide by the Inkomati-Usuthu Catchment Management Agency (Table 5-7, Table 5-8, Table 5-9) (Hughes, 2014d).

Screening against SAWQG and IRQC supported the screening against the SANS 241:2011 guidelines and identified that there were in exceedance with respect to EC, pH, aluminium, antimony, cadmium, calcium, chromium, cobalt, iron, lead, magnesium, manganese, potassium, selenium, sodium, fluoride, sulphate, chloride, nitrate, TDS and turbidity. Much of these exceedances were, however, possibly associated with naturally elevated concentrations of the determinands in the surrounding soils and groundwater.

Table 5-7: Screening Against SAWQG (Taken from Hughes, 2014d)

CoCs	SA WQG DWAF 1996			Units	GAA001-D	GAA001-S	GAA002-D	GAA002-S	GAA003-D	GAA004-D	GAA004-S	GAA005-D	GAA005-S	GAA006-D	GAA006-S	GAA007-S	GAA007-D	GAA008-S	GAA009-S	GAA010-S	GAA011-S
	Domestic Use	Livestock	Irrigation																		
Electrical Conductivity	ng	ng	40	mS/m	41.4	42.2	469.5	757.5	205.9	175.1	379.8	166.2	222.1	108.8	57.9	1187	344.6	340.5	217.6	171.2	52.9
pH	6-9	ng	6.5-8.4	pH units	6.2	6.0	3.87	4.5	3.61	7.1	6.9	7.8	7.9	11.54	8.6	7.26	7.08	6.75	6.98	6.91	7.03
Aluminium	150	5000	5000	ug/l	brl	brl	14120	15210	1111	brl	brl	brl	brl	1131	35	brl	brl	brl	brl	brl	brl
Antimony	ng	ng	ng	ug/l	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl
Arsenic	10	1000	100	ug/l	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	6.6	brl	brl	brl
Cadmium	5	10	10	ug/l	brl	brl	3.3	5.1	brl	brl	brl	brl	brl	brl	brl	brl	brl	0.6	brl	brl	brl
Calcium	32	1000	ng	mg/l	37	27.1	201	404	60.3	177	558	31.9	14.2	26.4	11.2	370	526	398	315	296	58.1
Chromium	ng	ng	ng	ug/l	brl	brl	285	223	22.8	brl	brl	brl	brl	4.1	brl	6.7	3.7	24	brl	brl	brl
Cobalt	ng	1000	50	ug/l	brl	brl	332	335	22	brl	brl	brl	brl	brl	brl	5	brl	14	3	3	3
Copper	1000	500	200	ug/l	brl	brl	150	140	20	brl	brl	brl	brl	brl	brl	brl	brl	9	brl	brl	brl
Iron	100	10000	5000	ug/l	brl	brl	178	146	brl	brl	brl	brl	brl	brl	brl	1268	2110	brl	120	586	62
Lead	10	100	200	ug/l	brl	5	166	146	15	brl	brl	brl	8	brl	brl	7	6	17	brl	brl	brl
Magnesium	30	500	ng	mg/l	12.8	14.8	244	373	24.9	93.3	451	19.7	5.4	0.40	1.4	686	132	169	64.5	52.4	12.0
Manganese	50	10000	20	ug/l	2459	2928	1262000	2406000	35550	1292	4160	33	77	5	11	58730	28660	181300	2002	1389	1481
Mercury	0.001	1	ng	ug/l	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl
Nickel	ng	1000	200	ug/l	brl	brl	180	184	45	brl	brl	brl	brl	brl	brl	6	7	14	3	6	3
Potassium	50	ng	ng	mg/l	1.7	1.9	8.9	12.9	3	14.2	3.0	4.1	0.4	15.2	1.5	29.3	20.8	68.8	16.2	19.9	10.9

CoCs	SA WQG DWAF 1996			Units	GAA001-D	GAA001-S	GAA002-D	GAA002-S	GAA003-D	GAA004-D	GAA004-S	GAA005-D	GAA005-S	GAA006-D	GAA006-S	GAA007-S	GAA007-D	GAA008-S	GAA009-S	GAA010-S	GAA011-S
	Domestic Use	Livestock	Irrigation																		
Selenium	20	50000	20	ug/l	brl	brl	693	415	21.0	brl	brl	brl	brl	brl	brl	brl	brl	69.0	brl	brl	brl
Sodium	100	2000	70	mg/l	17.6	19.1	92.6	134	340	52.7	87.5	270	453	114	106	2369	297	242	203	93	36.9
Uranium	70	ng	ng	ug/l	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl
Vanadium	100	1000	100	ug/l	brl	brl	43	72	2.0	brl	brl	brl	3.0	9.8	brl	2.1	2.4	4.9	2.3	2.9	1.9
Calcium Hardness dissolved (as CaCO3)	ng	ng	ng	mg/l	92.5	67.8	502.5	1011	150.8	442.8	1396	79.8	35.5	66.0	28.0	924.0	1314	994.5	787.8	740.3	145.3
Magnesium Hardness dissolved (as CaCO3)	ng	ng	ng	mg/l	53.8	62.2	1023	1565	105	392	1893	82.7	22.7	1.7	5.9	2882	552	709	271	220	50.4
Total Hardness dissolved (as CaCO3)	ng	ng	ng	mg/l	146	130	-	-	255	835	-	162	58	68	34	3806	1866	1704	1059	960	196
Fluoride	1	2	2	mg/l	brl	brl	2.7	5.7	0.9	0.7	4.3	7.1	10.1	8.4	10	0.4	1.4	1.0	1.0	0.6	0.5
Sulphate	200	1000	ng	mg/l	91.75	95.07	3889	4768	784.3	545.3	2184	458.6	485.7	36.14	20.83	8116	1917	2024	1050	760.0	96.01
Chloride	100	1500		mg/l	14.6	14.5	20.4	31.6	121	47.8	28.7	32.8	97.2	39.7	40.1	188	117	101	56.2	62.3	27.2
Ortho Phosphate as PO4	ng	ng	ng	mg/l	brl	brl	brl	0.23	brl	brl	0.11	brl	brl	brl	0.08	brl	brl	brl	brl	brl	brl
Nitrate as N	ng	100	ng	mg/l	4.9	3.2	brl	0.35	0.34	0.43	44.3	0.58	6.8	0.12	0.12	brl	0.090	4.9	2.8	0.75	0.13
Nitrite as N	ng	10	ng	mg/l	0.093	0.032	0.007	brl	brl	brl	0.13	brl	brl	0.019	brl	0.007	brl	0.13	0.77	0.027	0.006

CoCs	**SA WQG DWAF 1996**			**Units**	**GAA001-D**	**GAA001-S**	**GAA002-D**	**GAA002-S**	**GAA003-D**	**GAA004-D**	**GAA004-S**	**GAA005-D**	**GAA005-S**	**GAA006-D**	**GAA006-S**	**GAA007-S**	**GAA007-D**	**GAA008-S**	**GAA009-S**	**GAA010-S**	**GAA011-S**
	Domestic Use	**Livestock**	**Irrigation**																		
Total Alkalinity as CaCO3	ng	ng	ng	mg/l	66	48	NDP	10	NDP	373	392	371	409	308	217	430	284	136	196	214	174
P Alkalinity as CaCO3	ng	ng	ng	mg/l	brl	brl	NDP	brl	NDP	brl	brl	brl	brl	224	27	brl	brl	brl	brl	brl	brl
Silica	ng	ng	ng	mg/l	21.5	15.2	43.3	43.8	28.2	27.3	19.7	25.5	54.2	14.7	23.4	25.8	29.7	24.5	25.3	26.5	20.6
Total Dissolved Solids	450	1000	ng	mg/l	267	300	5775	10739	932	1103	24125	1100	1455	533	438	1741	3461	3482	1512	1325	404
Turbidity	1	ng	ng	NTU	0.5	0.4	0.5	1.0	0.4	0.3	0.9	0.3	1.6	3.4	0.9	4.3	2.8	1.4	9.3	13.7	25.9

Exceed only domestic

Exceed only livestock

Exceed only Irrigation

Exceed all available SA WQG criteria

Exceed Domestic and livestock

brl: below reporting limit

NDP: No determination possible - Sample pH is acidic and not suitable for this test

Table 5-8: Screening against SANS 241:2011 (Taken from Hughes 2014d)

Dissolved CoCs	Units	SANS 241: 2011	GAA001-D	GAA001-S	GAA002-D	GAA002-S	GAA003-D	GAA004-D	GAA004-S	GAA005-D	GAA005-S	GAA006-D	GAA006-S	GAA007-S	GAA007-D	GAA008-S	GAA009-S	GAA010-S	GAA011-S
Electrical Conductivity	mS/m	170	41.4	42.2	469.5	757.5	205.9	175.1	379.8	166.2	222.1	108.8	57.9	1187.3	3446	3405	2176	1712	529
pH	pH units	5-9.7	6.2	6.03	3.87	4.5	3.61	7.12	6.93	7.84	7.91	11.54	8.56	7.26	7.08	6.75	6.98	6.91	7.03
Aluminium	ug/l	300	brl	brl	14120	15210	1111	brl	brl	brl	brl	1131	35	brl	brl	brl	brl	brl	brl
Antimony	ug/l	20	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl
Arsenic	ug/l	10	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	6.6	brl	brl	brl
Cadmium	ug/l	3	brl	brl	3.3	5.1	brl	brl	brl	brl	brl	brl	brl	brl	brl	0.6	brl	brl	brl
Calcium	mg/l	ng	37	27.1	201	404.3	60.3	177.1	558.2	31.9	14.2	26.4	11.2	369.6	525.6	397.8	315.1	296.1	58.1
Total Chromium	ug/l	50	brl	brl	285.4	222.8	22.8	brl	brl	brl	brl	4.1	brl	6.7	3.7	24.4	brl	brl	brl
Cobalt	ug/l	500	brl	brl	332	335	22	brl	brl	brl	brl	brl	brl	5	brl	14	3	3	3
Copper	ug/l	2000	brl	brl	150	140	20	brl	brl	brl	brl	brl	brl	brl	brl	9	brl	brl	brl
Total Iron	ug/l	2000	brl	brl	178	146	brl	brl	brl	brl	brl	brl	brl	1268	2110	brl	120	586	62
Lead	ug/l	10	brl	5	166	146	15	brl	brl	brl	8	brl	brl	7	6	17	brl	brl	brl
Magnesium	mg/l	ng	12.8	14.8	243.5	372.7	24.9	93.3	450.7	19.7	5.4	0.4	1.4	686.1	131.5	168.9	64.5	52.4	12
Manganese	ug/l	500	2459	2928	1262000	2406000	35550	1292	4160	33	77	5	11	58730	28660	181300	2002	1389	1481
Mercury	ug/l	6	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl
Nickel	ug/l	70	brl	brl	180	184	45	brl	brl	brl	brl	brl	brl	6	7	14	3	6	3
Potassium	mg/l	ng	1.7	1.9	8.9	12.9	3	14.2	3	4.1	0.4	15.2	1.5	29.3	20.8	68.8	16.2	19.9	10.9

Dissolved CoCs	Units	SANS 241: 2011	GAA001-D	GAA001-S	GAA002-D	GAA002-S	GAA003-D	GAA004-D	GAA004-S	GAA005-D	GAA005-S	GAA006-D	GAA006-S	GAA007-S	GAA007-D	GAA008-S	GAA009-S	GAA010-S	GAA011-S
Selenium	ug/l	10	brl	brl	693	415	21	brl	brl	brl	brl	brl	brl	brl	brl	69	brl	brl	brl
Sodium	mg/l	200	17.6	19.1	92.6	134.4	340.3	52.7	87.5	269.5	452.9	113.7	105.8	2369	296.5	241.9	202.5	93	36.9
Uranium	ug/l	15	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl
Vanadium	ug/l	200	brl	brl	43.3	71.6	2	brl	brl	brl	3	9.8	brl	2.1	2.4	4.9	2.3	2.9	1.9
Calcium Hardness dissolved (as CaCO3)	mg/l	ng	92.5	67.8	502.5	1010.8	150.8	442.8	1395.5	79.8	35.5	66	28	924	1314	994.5	787.8	740.3	145.3
Magnesium Hardness dissolved (as CaCO3)	mg/l	ng	53.8	62.2	1022.7	1565.3	104.6	391.9	1892.9	82.7	22.7	1.7	5.9	2881.6	552.3	709.4	270.9	220.1	50.4
Total Hardness dissolved (as CaCO3)	mg/l	ng	146	130	-	-	255	835	-	162	58	68	34	3806	1866	1704	1059	960	196
Fluoride	mg/l	1.5	brl	brl	2.7	5.7	0.9	0.7	4.3	7.1	10.1	8.4	10	0.4	1.4	1	1	0.6	0.5
Sulphate	mg/l	500	91.75	95.07	3889	4768	784	545	2184	458.6	485.7	36.14	20.83	8116	1917	2024	1050	760.0	96.01
Chloride	mg/l	300	14.6	14.5	20.4	31.6	121	47.8	28.7	32.8	97.2	39.7	40.1	188	117	101	56.2	62.3	27.2
Ortho Phosphate as PO4	mg/l	ng	brl	brl	brl	0.23	brl	brl	0.11	brl	brl	brl	0.08	brl	brl	brl	brl	brl	brl
Nitrate as N	mg/l	11	4.9	3.2	brl	0.35	0.34	0.43	44.3	0.58	6.8	0.12	0.12	brl	0.09	4.9	2.8	0.75	0.13
Nitrite as N	mg/l	0.9	0.093	0.032	0.007	brl	brl	brl	0.13	brl	brl	0.019	brl	0.007	brl	0.13	0.77	0.027	0.006
Total Alkalinity as CaCO3	mg/l	ng	66	48	NDP	10	NDP	373	392	371	409	308	217	430	284	136	196	214	174

Dissolved CoCs	**Units**	**SANS 241: 2011**	**GAA001-D**	**GAA001-S**	**GAA002-D**	**GAA002-S**	**GAA003-D**	**GAA004-D**	**GAA004-S**	**GAA005-D**	**GAA005-S**	**GAA006-D**	**GAA006-S**	**GAA007-S**	**GAA007-D**	**GAA008-S**	**GAA009-S**	**GAA010-S**	**GAA011-S**
P Alkalinity as CaCO3	mg/l	ng	brl	brl	NDP	brl	NDP	brl	brl	brl	brl	224	27	brl	brl	brl	brl	brl	brl
Silica	mg/l	ng	21.5	15.2	43.3	43.8	28.2	27.3	19.7	25.5	54.2	14.7	23.4	25.8	29.7	24.5	25.3	26.5	20.6
Total Dissolved Solids	mg/l	1200	267	300	5775	10739	932	1103	24125	1100	1455	533	438	1741	3461	3482	1512	1325	404
Turbidity	NTU	5	0.5	0.4	0.5	1	0.4	0.3	0.9	0.3	1.6	3.4	0.9	4.3	2.8	1.4	9.3	14	26
Risk Type	brl: below reporting limit NDP: No determination possible - Sample pH is acidic and not suitable for this test																		

Table 5-9: Screening against RQO and TWQR (Taken from Hughes 2014d)

Dissolved	Units	Crocodile Interim Resource Quality Objectives			GA001-D	GAA002-D	GAA003-D	GAA004-D	GAA005-D	GAA006-D	GAA001-S	GAA002-S	GAA004-S	GAA005-S	GAA006-S	GAA007-S	GAA007-D	GAA008-S	GAA009-S	GAA010-S	GAA011-S
		Ideal	Acceptable	Tolerable																	
Electrical Conductivity @25C	mS/m	30	50	60	41.4	469.5	205.9	175.1	166.2	108.8	42.2	757.5	379.8	222.1	57.9	1187.3	3446	3405	2176	1712	529
pH	pH units		6.5 - 8.4		6.2	3.87	3.61	7.12	7.84	11.54	6.03	4.5	6.93	7.91	8.56	7.26	7.08	6.75	6.98	6.91	7.03
Aluminium	ug/l	30	70	90	brl	14120	1111	brl	brl	1131	brl	15210	brl	brl	35	brl	brl	brl	brl	brl	brl
Antimony	ug/l	ng	ng	ng	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl
Arsenic	ug/l	10	50	80	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	6.6	brl	brl	brl
Cadmium	ug/l	ng	ng	ng	brl	3.3	brl	brl	brl	brl	brl	5.1	brl	brl	brl	brl	brl	0.6	brl	brl	brl
Calcium	mg/l	ng	ng	ng	37	201	60.3	177.1	31.9	26.4	27.1	404.3	558.2	14.2	11.2	369.6	525.6	397.8	315.1	296.1	58.1
Chromium	ug/l	ng	ng	ng	brl	285.4	22.8	brl	brl	4.1	brl	222.8	brl	brl	brl	6.7	3.7	24.4	brl	brl	brl
Cobalt	ug/l	ng	ng	ng	brl	332	22	brl	brl	brl	brl	335	brl	brl	brl	5	brl	14	3	3	3
Copper	ug/l	ng	ng	ng	brl	150	20	brl	brl	brl	brl	140	brl	brl	brl	brl	brl	9	brl	brl	brl
Iron	ug/l	10	550	750	brl	178	brl	brl	brl	brl	brl	146	brl	brl	brl	1268	2110	brl	120	586	62
Lead	ug/l	ng	ng	ng	brl	166	15	brl	brl	brl	5	146	brl	8	brl	7	6	17	brl	brl	brl
Magnesium	mg/l	ng	ng	ng	12.8	243.5	24.9	93.3	19.7	0.4	14.8	372.7	450.7	5.4	1.4	686.1	131.5	168.9	64.5	52.4	12
Manganese	ug/l	20	100	300	2459	1262000	35550	1292	33	5	2928	2406000	4160	77	11	58730	28660	181300	2002	1389	1481
Mercury	ug/l	ng	ng	ng	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl
Nickel	ug/l	ng	ng	ng	brl	180	45	brl	brl	brl	brl	184	brl	brl	brl	6	7	14	3	6	3
Potassium	mg/l	ng	ng	ng	1.7	8.9	3	14.2	4.1	15.2	1.9	12.9	3	0.4	1.5	29.3	20.8	68.8	16.2	19.9	10.9

Dissolved	Units	Crocodile Interim Resource Quality Objectives			GA001-D	GAA002-D	GAA003-D	GAA004-D	GAA005-D	GAA006-D	GAA001-S	GAA002-S	GAA004-S	GAA005-S	GAA006-S	GAA007-S	GAA007-D	GAA008-S	GAA009-S	GAA010-S	GAA011-S
		Ideal	Acceptable	Tolerable																	
Selenium	ug/l	ng	ng	ng	brl	693	21	brl	brl	brl	brl	415	brl	brl	brl	brl	brl	69	brl	brl	brl
Sodium	mg/l	ng	ng	ng	17.6	92.6	340.3	52.7	269.5	113.7	19.1	134.4	87.5	452.9	105.8	2369	296.5	241.9	202.5	93	36.9
Uranium	ug/l	ng	ng	ng	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl	brl
Vanadium	ug/l	ng	ng	ng	brl	43.3	2	brl	brl	9.8	brl	71.6	brl	3	brl	2.1	2.4	4.9	2.3	2.9	1.9
Calcium Hardness dissolved (as CaCO3)	mg/l	ng	ng	ng	92.5	503	151	443	79.8	66	67.8	1011	1396	35.5	28	924	1314	995	788	740	145
Magnesium Hardness dissolved (as CaCO3)	mg/l	ng	ng	ng	53.8	1023	105	392	82.7	1.7	62.2	1565	1893	22.7	5.9	2882	552	709	271	220	50.4
Total Hardness dissolved (as CaCO3)	mg/l	ng	ng	ng	146	-	255	835	162	68	130	-	-	58	34	3806	1866	1704	1059	960	196
Fluoride	mg/l	200	500	750	brl	2.7	0.9	0.7	7.1	8.4	brl	5.7	4.3	10.1	10	0.4	1.4	1	1	0.6	0.5
Sulphate	mg/l	20	40	60	91.75	3889	784.3	545.3	458.6	36.14	95.07	4768	2184	485.7	20.83	8116	1917	2024	1050	760.0	96.01
Chloride	mg/l	25	40	50	14.6	20.4	120.9	47.8	32.8	39.7	14.5	31.6	28.7	97.2	40.1	188.1	117.3	101.1	56.2	62.3	27.2
Ortho Phosphate as PO4	mg/l	0.03	0.05	0.01	brl	brl	brl	brl	brl	brl	brl	0.23	0.11	brl	0.08	brl	brl	brl	brl	brl	brl
Nitrate as N	mg/l	0.015	0.058	0.1	4.91	brl	0.34	0.43	0.58	0.12	3.2	0.35	44.3	6.84	0.12	brl	0.09	4.91	2.79	0.75	0.13
Nitrite as N	mg/l	ng	ng	ng	0.093	0.007	brl	brl	brl	0.019	0.032	brl	0.134	brl	brl	0.007	brl	0.133	0.767	0.027	0.006
Total Alkalinity as CaCO3	mg/l	ng	ng	ng	66	NDP	NDP	373	371	308	48	10	392	409	217	430	284	136	196	214	174
P Alkalinity as CaCO3	mg/l	ng	ng	ng	brl	NDP	NDP	brl	brl	224	brl	brl	brl	brl	27	brl	brl	brl	brl	brl	brl

Dissolved	Units	Crocodile Interim Resource Quality Objectives			GA001-D	GAA002-D	GAA003-D	GAA004-D	GAA005-D	GAA006-D	GAA001-S	GAA002-S	GAA004-S	GAA005-S	GAA006-S	GAA007-S	GAA007-D	GAA008-S	GAA009-S	GAA010-S	GAA011-S
		Ideal	Acceptable	Tolerable																	
Silica	mg/l	ng	ng	ng	21.5	43.3	28.2	27.3	25.5	14.7	15.2	43.8	19.7	54.2	23.4	25.8	29.7	24.5	25.3	26.5	20.6
Total Dissolved Solids	mg/l	ng	ng	ng	267	5775	932	1103	1100	533	300	10739	24125	1455	438	1741	3461	3482	1512	1325	404
Turbidity	NTU	ng	ng	ng	0.5	0.5	0.4	0.3	0.3	3.4	0.4	1	0.9	1.6	0.9	4.3	2.8	1.4	9.3	13.7	25.9
🟩 Ideal	brl: below reporting limit NDP: No determination possible - Sample pH is acidic and not suitable for this test																				
🟨 Acceptable																					
🟥 Tolerable																					

5.2.2.1 Site wide Groundwater Characterisation

The appropriate chemical test data from the October 2014 monitoring event has been plotted as a Piper Diagram using the WISH computer programme and is presented as Figure 5-10.

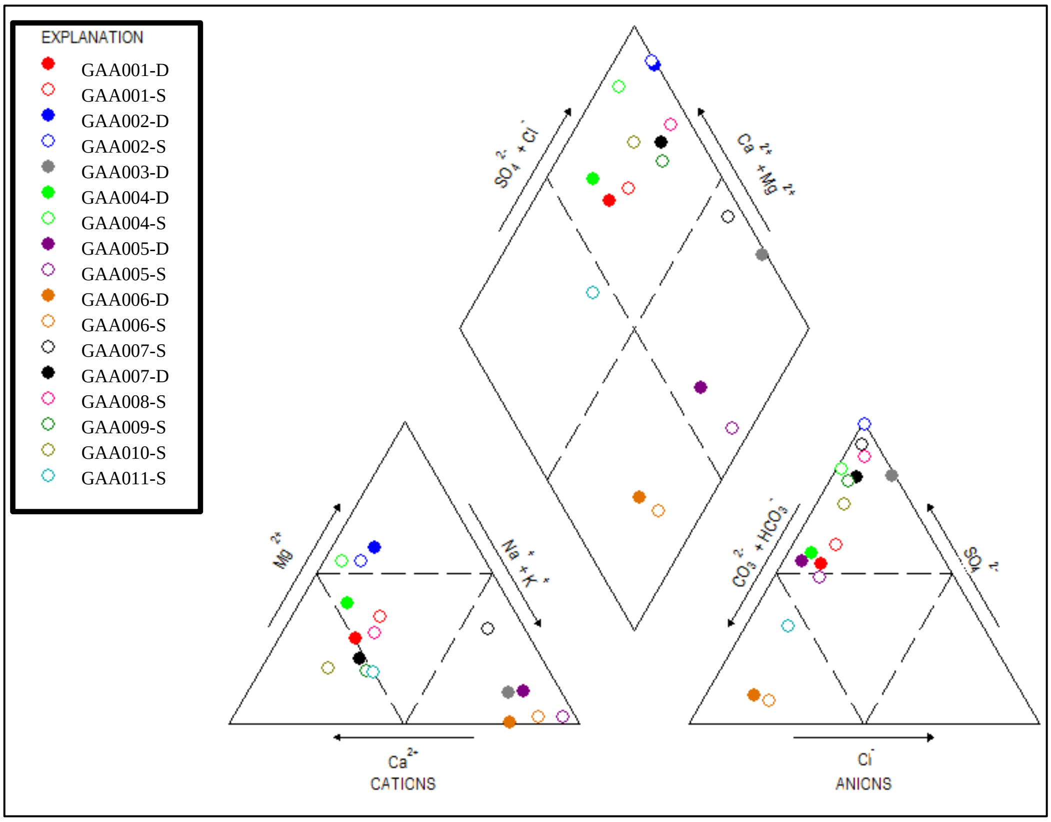

Figure 5-10: Piper Diagram for October 2014 Monitoring Events (Taken from Hughes, 2014d)

Southern-up gradient Monitoring Wells

Monitoring wells GAA005-D and GAA005-S are located up-gradient of the wet-process sections of the facility and the water collected from that area is classified as Na-SO$_4$ type (Figure 5-10). Monitoring wells GAA006-D and GAA006-S are also located up-gradient of the processing facilities but are to the south east of GAA005-D and GAA005-S. The water from there is classified as Na-HCO$_3$ type (Figure 5-10). The water type obtained from GAA006-D and GAA006-S (Na-HCO$_3$) (Figure 5-10) is considered to be representative of groundwater not necessarily directly impacted by site processes but rather by ionic changes associated with fresh water ingress from the canal interacting with waters impacted by placement of high pH backfill (“Greenfill”). Given the close proximity of the monitoring wells one would have expected GAA005-D and GAA005-S to have a similar water type. The author considered that possible leakage from the sulphuric acid tanks located immediately adjacent to GAA005-D and GAA005-S may have resulted in changes to water type in this location or it may be associated with the placement of backfill (“Greenfill”). Without an increased sulphate contribution the predominant facies of the upstream groundwater at boreholes locations GAA005-D and GAA005-S would probably be Na-HCO_3 type (Hughes, 2014d).

Northern down-gradient Monitoring Wells

Monitoring wells GAA002-D, GAA002-S, GAA003-D, GAA004-D, GAA004-S GAA007-D, GAA007-S, GAA008S, and GAA010-S are located down-gradient of the eastern and western cell houses whereas GAA009-S is located immediately up-gradient of the eastern cell house. The groundwater in these area is classified as (Ca,Na)-SO_4 type (Figure 5-10) (Hughes, 2014d).

Monitoring Well GA011-S

Monitoring well GAA011-S is located up-gradient of the western cell house and the water is classified as (Ca,Na)-HCO_3 type. The author considers that groundwater obtained from GAA011-S is probably representative of an area of mixing of two water types: (Ca,Na)-SO_4 type and Na-HCO_3 (Figure 5-10) (Hughes, 2014d).

5.2.2.2 Groundwater Quality Assessment

The author has undertaken a groundwater quality assessment using data obtained from the October 2014 monitoring event. The assessment is presented in the following bullets.

1. The pH of groundwater along the northern boundary ranged between 3.87 and 7.26 with the lowest pH detected (3.69 to 4.5) being identified within the two contaminated areas designated Zone A and Zone B. Up-gradient pH values range between 7.84 and 11.54.
2. Manganese at concentrations ranging between 0.005 and 2,406 mg/l was detected across the site. All down-gradient boreholes have manganese levels exceeding the SANS 241:2011 drinking water limits of 0.5 mg/l (Hughes, 2014d). Substantially elevated manganese was found in close proximity to the processing plant with the highest concentrations being found down-gradient of the eastern and western cell houses.
3. Elevated sulphate in excess of the SANS 241:2011 drinking water limits of 500mg/l has been identified in all of the boreholes (except GAA001-S) down-gradient or in immediate proximity of Cell House 1 and Cell House 2 (Hughes, 2014d). Sulphate is most highly elevated along the northern boundary with concentrations ranging between 20.83 and 8,116 mg/l. The elevated sulphate concentrations are considered to originate from spillages and leakages of H_2SO_4 acid during site processes. High sulphate concentrations are also associated with the electrolyte $MnSO_4$, H_2SO_4 and Na_2SO_4 as part of the neutralisation process (Hughes, 2014d).
4. Lead was found in groundwater across the site at concentrations ranging between 0.006 and 0.166 mg/l and in excess of SANS 241:2011 drinking water limits of 0.01 mg/l in boreholes

GAA002-D, GAA002-S, GAA003-D and GAA008-S. Lead was not used in the site processes and therefore elevated lead may either be representative of naturally occurring background levels or may have been mobilised into solution as a result of low pH groundwater.

5. Groundwater with an elevated concentration of sodium ranging between 17.6 and 2,369 mg/l has been identified across the site. The most elevated concentration was found close to the western cell house (Cell House 2) and the concentrations exceeded the SANS 241:2011 drinking water limits of 200 mg/l.
6. Nitrate was found in the groundwater across the site ranging in concentrations of between 0.12 and 44.30 mg/l. Elevated nitrate in excess of the SANS 241:2011 drinking water standards of 11mg/l has been identified in GAA004-S (Hughes, 2014d). Nitrate was not used on site and the source of NO_3 has not been confirmed.
7. Elevated concentrations of aluminium, cadmium, chromium, nickel and selenium were detected along the northern boundary of the site (GAA002-D, GAA002-S, and GAA003-D) as a result of low pH water. Aluminium has also been mobilised into solution in borehole GAA006-D – however, this is considered to be as a result of the high pH groundwater present in that location (Hughes, 2014d).

5.2.2.3 Oxidation Reduction Potential (ORP) and pH effect on Mn Solubility

The solubility of manganese is dependent upon ORP conditions and the master variable pH. Where circum-neutral to acidic waters are present (i.e. pH <6) then manganese is likely to be found in solution as Mn^{2+}. At higher pH manganese has the potential to precipitate from solution as $MnCO_3$, MnO_2, Mn_2O_3, Mn_3O_4 or rarely as MnO (Hughes, 2014d).

ORP across the site ranged between -124.00 and 439.90 mV and pH between 3.69 and 11.03. The assessment of pH and ORP conditions for the site indicates that across the majority of the site groundwater conditions exist that allow for the potential precipitation of manganese as rhodochrosite ($MnCO_3$). The areas with a pH <6 do not represent areas where precipitation of manganese is probable. Areas where ORP and pH conditions are not suitable for the precipitation of manganese from solution are identified in Table 5-10 as GAA001-S/D, GAA002-S/D and GAA003-S/D.

Boreholes advanced into the suspected plumes (i.e. GAA007-S, GAA008-S, GAA009-S and GAA010-S) identified much lower concentrations of dissolved manganese (1.39 to 181 mg/l) and higher pH values (6.75 to 7.28) than had been anticipated, indicating that groundwater migrating in a northerly direction is neutralising the acidic water and allowing for precipitation of manganese; most probably as rhodochrosite.

Table 5-10: pH and ORP Conditions (Taken from Hughes, 2014d)

Borehole	Description of Borehole Area	pH	ORP (mV)	Potential for Mn to precipitate under existing ORP and pH conditions
GAA001-S	North of site. Within horseshoe area.	5.38	272.20	No
GAA001-D		5.52	257.50	No
GAA002-S	Northern boundary in front of Cell House 1.	4.21	345.50	No
GAA002-D		3.69	439.90	No
GAA003-D	Northern boundary between Cell House 1 and Cell House 2.	5	300.90	No
GAA004-S	Northern boundary east of Cell House 2.	7.10	144.90	Yes.
GAA004-D		7.28	63.00	Yes
GAA005-S	Football pitch in front of acid tank.	6.84	150.20	Yes
GAA005-D		7.03	140.40	Yes
GAA006-S	Football pitch near backfill (“Greenfill”) processing area.	7.88	99.60	Yes
GAA006-D		11.03	-45.70	Yes
GAA007-S	Northern boundary in front of Cell House 2.	6.76	-124.00	Yes
GAA007-D		6.82	-13.90	Yes
GAA008-S	Within plume (Area B) north of Cell House 2.	6.46	50.00	Yes
GAA009-S	Within plume (Area B) south of Cell House 2.	6.67	28.10	Yes
GAA010-S	Within plume (Area A) north of Cell House 1.	6.65	-38.30	Yes
GAA011-S	South east of Cell House 1.	6.93	-80.50	Yes

5.2.2.4 Manganese and Sulphate Correlation

An assessment of manganese and sulphate concentration has been undertaken and is presented via a log manganese and log sulphate plot as Figure 5-11. The plot has allowed the author to divide the site into different areas based upon water quality.

Descriptions for different parts of the site are provided in the following sections:

Area 1

This area is indicative of naturally occurring background concentrations of manganese and sulphate.

Area 2

This area is indicative of background concentration of manganese. However, sulphate concentrations are higher than background levels as the sampling boreholes (GAA005-D and GAA005-S) from which the samples were obtained are located immediately down-gradient of a tank containing sulphuric acid (Hughes, 2014d).

Area 3

This area is indicative of groundwater located within contaminant plumes that previously had low pH but have subsequently undergone an increase on pH due to recharge with high pH waters leading to subsequent precipitation of manganese.

Area 4

This area is indicative of impacted groundwater i.e. that either located within or in close proximity to the two zones of contamination (Zone A and Zone B). This type of water has low pH ensuring that manganese remains in the dissolved phase.

Area 5

This area is indicative of groundwater that is subject to lower sulphate concentration than other contaminated areas on site whilst maintaining a relatively high manganese concentration. It is possible that the sources of contamination on this area are due to an off-site source (Hughes, 2014d).

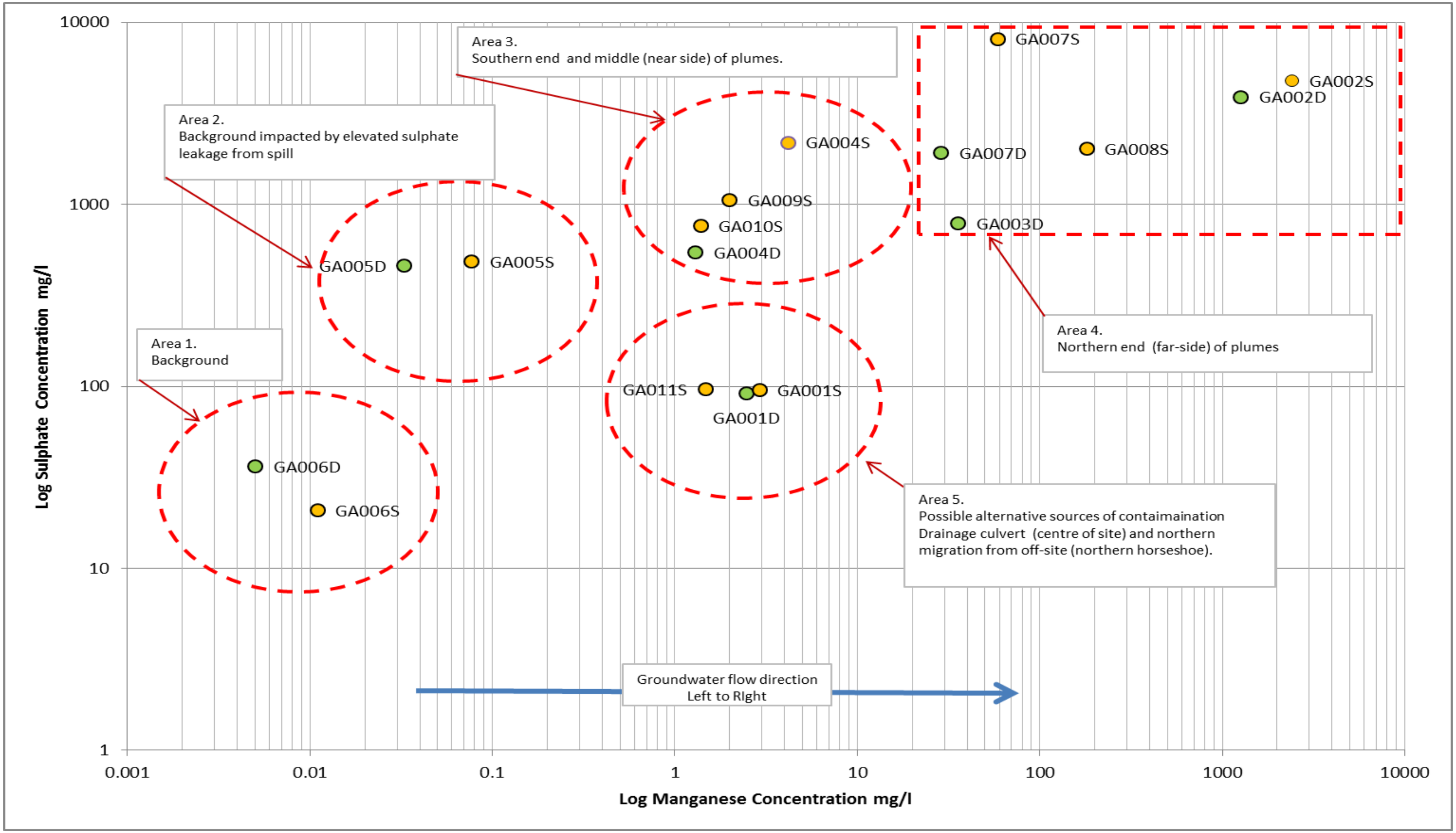

Figure 5-11: Log Manganese vs Log Sulphate (Taken from Hughes, 2014d)

5.3 DECEMBER SAMPLING EVENT

During early November and December 2014 additional perimeter monitoring wells were constructed on site. Some of the monitoring wells were dry at the time of drilling and therefore groundwater sampling was undertaken by the author on both the 11 December 2014 and 15 January 2015. In total twenty three monitoring wells were measured and sampled. Low-flow sampling techniques were employed on all monitoring wells with the exception of monitoring well GAA006-D for which a bailer was used to obtain a water sample as the depth to water level was too deep, for the single pump which was available to the author, to overcome the head. All samples were subsequently issued to Jones Environmental Laboratory in the UK for chemical analysis.

5.3.1 Physiochemical Parameters

Measurements obtained for the perimeter wells and the site wide monitoring wells are presented in Table 5-11 and Table 5-12. For initial screening purposes both the field physiochemical measurements and analytical water quality results were compared to the South African drinking water standards (SANS 241:2011) as indicated in Table 5-11.

No exceedance were noted for the perimeter wells tested in the field. However, it was not possible to obtained measurements for monitoring wells: P3(6); P4(15); GAA012-S; and GAA012(6) due to problems with the measuring equipment at the time of testing.

Table 5-11: Perimeter Wells Field Measurements (Modified from Hughes 2015)

Monitoring Well	pH	ORP (mV)	DO (%Sat)	EC (mS/m@25C)	TDS (mg/l)	SAL (ppt)
P1(15)	6	209.6	0	48.5	315	0.24
P1(6)	n/a	n/a	n/a	n/a	n/a	n/a
P2(15)	6.81	-73	0	83.5	542	0.41
P2(6)	6.49	144.7	0	41.5	269	0.2
P3(15)	6.35	80.1	0	46.6	367	0.28
P3(6)	n/a	n/a	n/a	n/a	n/a	n/a
P4(15)	n/a	n/a	n/a	n/a	n/a	n/a
P4(6)	5.61	240.5	0	6.9	44	0.03
GAA012-S	n/a	n/a	n/a	n/a	n/a	n/a
GAA012-(6)	n/a	n/a	n/a	n/a	n/a	n/a

Similarly, due to problems with the monitoring equipment at the time of sampling it was not possible to obtain measurements for monitoring wells: GAA006-D; GAA009-S; GAA010-S; and GAA011-S. For the site wide monitoring wells, exceedances were noted along the northern boundary monitoring wells GAA001-D, GAA002-D and GAA002-D for pH, EC and TDS. Similarly, exceedances of EC and TDS were noted for monitoring wells GAA003-D; GAA004-S; GAA004-D; GAA005-S; GAA007-S; GAA007-D; and GAA008-S. The physiochemical measurements obtained from the monitoring wells indicate that groundwater present to the south of the site may be considered to be of fair quality however as it migrates through the site its quality deteriorates to a poor quality (see Table 5-12 where exceedances of SANS 241:2011 are highlighted). Water quality screening criteria is provided as Table 5 13.

Table 5-12: On-Site Monitoring Wells Field Measurements (Modified from Hughes, 2015)

Monitoring Well	pH	ORP (mV)	DO (%Sat)	EC (mS/m@25C)	TDS (mg/l_	SAL (ppt)
GAA001-S	5.41	256.7	0	51.5	334	0.25
GAA001-D	3.72	438.7	0	505.5	3,285	2.52
GAA002-S	3.97	413.9	0	248.4	1,614	1.24
GAA002-D	4.63	355.3	0	220.3	2,203	1.1
GAA003-D	6.16	-3.7	0	18.2	118	0.09
GAA004-S	6.41	156.7	0	398.5	2,590	1.99
GAA004-D	6.12	199.3	0	421.9	2,740	2.1
GAA005-S	7.06	160	0	197.6	1,284	0.98
GAA005-D	7.71	-130.3	0	56.3	365	0.28
GAA006-S	9.21	-14.6	0	39.8	258	0.19
GAA006-D	n/a	n/a	n/a	n/a	n/a	n/a
GAA007-S	6.44	-20.9	0	1,322.4	8,602	6.61
GAA007-D	6.63	120.4	0	202.7	1,217	1.01
GAA008-S	6.97	163.9	0	250.9	1630	1.25
GAA009-S	n/a	n/a	n/a	n/a	n/a	n/a
GAA010-S	n/a	n/a	n/a	n/a	n/a	n/a
GAA0011-S	n/a	n/a	n/a	n/a	n/a	n/a

Table 5-13: Screening Guidance to SANS 241:2011

Screening Guidance	Turbidity (NTU)	pH	EC (mS/m)	TDS (mg/l)	ORP (mV)	DO (% sat)
SANS 241 (2011)	≤ 5	≥5 to 9.7≤	≤170	≤1200	not provided	not provided

pH values of groundwater entering the site along the southern perimeter ranged between 5.61 and 6.82, whereas pH values determined for the site-wide monitoring wells range between 3.72 and 9.21. This suggests that there is both a) an acidic source and b) an alkaline source on site impacting upon pH values at different parts of the site (Hughes, 2015). The source of acidity is considered to be the wet-process sections of the plant around the eastern and western cell houses whereas the source of alkalinity is considered to be waste treatment site and backfill (“Greenfill”) located in the area of the football pitch.

5.3.2 Groundwater Classification

The computer programme WISH developed by the Institute for Groundwater Studies (University of Free State) was utilised to characterise groundwater types present on site using a piper diagram. A piper diagram for groundwater samples obtained from the site is provided as Figure 5-12.

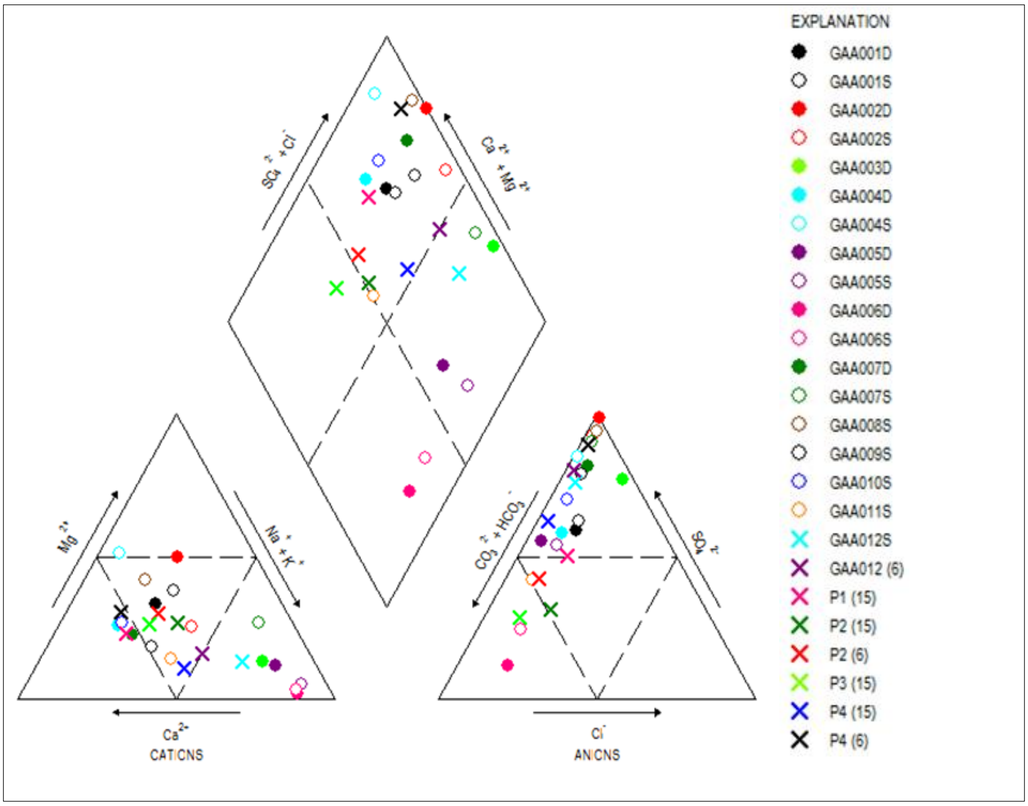

Figure 5-12: Piper Plot for December 2014 sampling event (Taken from Hughes 2015)

5.3.2.1 Perimeter Monitoring Wells

The site wide monitoring wells have been classified under Section 5.2 and 5.3 and therefore only perimeter monitoring wells are discussed in this section.

Northwestern part of Site

Groundwater obtained from monitoring well P1 (15) is classified as $CaSO_4.(HCO_3)$ type (see Figure 5-12). This water type is the same as that identified in on-site monitoring wells GAA001-S and GAA001-D. The water quality type is considered to be indicative of mixing of potentially contaminated water with recently re-charged groundwater (Hughes, 2015). The source of the contamination may potentially be from off-site.

Northern part of Site

Groundwater obtained from monitoring wells P2 (15) and P2 (6) is classified as $Ca\text{-}SO_4.(HCO_3)$ type (see Figure 5-12). This water type is the same as identified in on-site monitoring wells GAA001-S and GAA001-D. This water type is considered to be representative of the resultant mixing of potentially contaminated waters with recently re-charged water (Hughes, 2015).

Southern part of Site

Groundwater obtained from monitoring wells P3(15) is classified as $Ca\text{-}HCO_3$ type (see Figure 5-12). This is considered to be representative of local groundwater not impacted by groundwater contamination.

Groundwater obtained from monitoring wells P4 (15) and P4 (6) is classified as $(Ca,Na)\text{-}SO_4$ type (see Figure 5-12). Perimeter monitoring well P4 (6) which was constructed to 6 mbgl had a greater proportion of sulphate than the deeper well P4 (15) taken to 15 mbgl. This suggest that sulphate is being introduced to the groundwater via seepage through the soils and after which dilution through mixing with recharge waters is occurring (Hughes, 2015). The sodium component is most probably associated with leaching of placed backfill (“Greenfill”) in the area of the football pitch.

Eastern part of Site

Groundwater obtained from monitoring wells GAA012-S and GAA012-D is classified as $Na\text{-}SO_4$ type (see Figure 5-12). This water type is extremely rare in nature and is considered unlikely to be naturally present within the subject site’s geological setting. It is considered that groundwater in this area has been impacted by groundwater contamination that may be associated with waste neutralisation processes historically undertaken in the southeastern part of the site (Hughes, 2015).

5.3.3 Laboratory Chemical Analysis

During December 2014 and January 2015, laboratory test data was compared to SANS 241:2011 only. The laboratory test data is presented in Table 5-14, Table 5-15 and Table 5-16 with exceedances of the guidance highlighted in the various tables.

5.3.3.1 Perimeter Wells Groundwater Quality Assessment

Review of the chemical test data indicates that groundwater quality at the perimeter of the site is locally elevated with respect to manganese, fluoride, nitrate and nitrite. Further, the quality of groundwater leaving site is of a poorer quality that that entering the site. The concentration of manganese at the site perimeter is much lower than that determined to be present in on-site monitoring wells. This confirms that the source of manganese in groundwater is within the site boundary.

Although elevated manganese was identified in the perimeter wells located to the north-west of the site (P1 and P2) and the centre of the site (P4) it is considered possible that the source is off-site and migrates to site either by surface water run-off or groundwater seepage.

Perimeter fluoride concentrations range in concentration between <0.3 and 1.5 mg/l. One of the perimeter monitoring wells (P4-(6)) has fluoride concentration at the maximum SANS 241:2011 drinking water limits of 1.5 mg/l. Na-HCO_3 type waters are present in the southern part and it is postulated that this allows for the dissolution of fluoride thought to be naturally present in the granitic rock below the site thus allowing for increased fluoride ion and sodium ions in the groundwater (Hughes, 2015). GAA012-S/D monitoring wells have identified elevated sulphate in the groundwater. These monitoring wells are located approximately 50 m from the southern perimeter and it is therefore considered that these boreholes are more representative of existing on-site groundwater quality rather than groundwater entering the site from the south-east of the site (Hughes, 2015).

During the December sampling event various potential constituents of concern (COC) were identified along the perimeter of the site which included manganese, fluoride, nitrate and nitrite. These are identified in Table 5-17 and compared with those COC's identified elsewhere on site from the on-site monitoring wells.

Table 5-14: Perimeter Monitoring Wells Chemical Test data for December 2014 sampling event (Taken from Hughes, 2015)

Dissolved CoCs	Units	SANS 241:2011	P1(15)	P1(6)	P2(15)	P2(6)	P3(15)	P3(6)	P4(15)	P4(6)
Electrical Conductivity	mS/m	170	52.7	-	82.4	46.5	54.9	-	107.0	67.7
pH	pH units	5-9.7	6.65	-	7.3	6.72	7.08	-	7.29	5.89
Cadmium	μ g/l	3	<0.5	-	<0.5	<0.5	0.5	-	<0.5	<0.5
Calcium	mg/l	ng	57.6	-	65.8	37	57.7	-	83.5	55.6
Total Chromium	μ g/l	50	<1.5	-	<1.5	<1.5	<1.5	-	<1.5	<1.5
Copper	μ g/l	2000	<7	-	<7	<7	<7	-	<7	<7
Total Iron	μ g/l	2000	<20	-	767	<20	82	-	<20	35
Lead	μ g/l	10	<5	-	<5	5	6	-	<5	11
Magnesium	mg/l	ng	14.9	-	29.4	16.8	20.2	-	12.9	19.6
Manganese	μ g/l	500	1462	-	1515	43	480	-	1105	3214
Mercury	μ g/l	6	<1	-	<1	<1	<1	-	<1	<1
Potassium	mg/l	ng	4.3	-	19.4	2.4	9.8	-	11	6.6
Sodium	mg/l	200	24.8	-	65.9	29.5	35.2	-	102	16.9
Uranium	μ g/l	15	<5	-	<5	<5	<5	-	6	<5
Calcium Hardness dissolved (as CaCO3)	mg/l	ng	144	-	164.5	92.5	144.3	-	208.8	139
Magnesium Hardness dissolved (as CaCO3)	mg/l	ng	62.6	-	123.5	70.6	84.8	-	54.2	82.3
Total Hardness dissolved (as CaCO3)	mg/l	ng	207	-	288	163	229	-	263	221
Fluoride	mg/l	1.5	<0.3	-	0.9	<0.3	0.6	-	1.1	1.5
Sulphate	mg/l	500	116.48	-	139.15	94.57	87.61	-	361.27	277.33
Chloride	mg/l	300	27	-	62.2	17.3	24.8	-	14.6	5.4
Ortho Phosphate as PO4	mg/l	ng	<0.06	-	<0.06	<0.06	<0.06	-	<0.06	<0.06
Nitrate as N	mg/l	11	47.5	-	<0.2	36.7	8.4	-	1.1	45.3
Nitrite as N	mg/l	0.9	0.51	-	<0.02	<0.02	0.31	-	0.04	1.04
Ammoniacal Nitrogen as N	mg/l	1.5	-	-	-	-	-	-	0.92	-
Total Alkalinity as CaCO3	mg/l	ng	82	-	225	109	190	-	205	27
P Alkalinity as CaCO3	mg/l	ng	<1	-	<1	<1	<1	-	<1	<1
Silica	mg/l	ng	21.8	-	23.2	16	23.1	-	20.2	45.10

Dissolved CoCs	Units	SANS 241:2011	P1(15)	P1(6)	P2(15)	P2(6)	P3(15)	P3(6)	P4(15)	P4(6)
Total Dissolved Solids	mg/l	1200	385	-	571	339	370	-	851	668
Turbidity	NTU	5	1.1	-	2.8	0.5	0.6	-	0.7	0.8
Risk Type					brl: below reporting limit NDP: No determination possible - Sample pH is acidic and not suitable for this test					
Operational										
Chronic Health										
Aesthetic										
Acute Health – 1										

Table 5-15: Site Wide Chemical Test Data for December 2014 sampling event (Modified from Hughes, 2015)

Dissolved CoCs	Units	SANS 241:2011	GAA001-D	GAA001-S	GAA002-D	GAA002-S	GAA003-D	GAA004-D	GAA004-D	GAA005-D	GAA005-S	GAA006-D	GAA006-S
Electrical Conductivity	mS/m	170	45.8	49.8	450	1321	200	184	372	182	234	48.6	57.2
pH	pH units	5-9.7	6.1	6.1	3.9	7.1	5.4	7.5	7.0	7.9	7.7	10.2	8.2
Cadmium	μ g/l	3	<0.5	<0.5	2.4	1.3	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Calcium	mg/l	ng	29.6	23.2	178	112	69.6	255	544	56.5	41.9	13.5	11.7
Total Chromium	μ g/l	50	<1.5	<1.5	37	12	8.9	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5
Copper	μ g/l	2000	<7	<7	162	60	52	12	<7	12	13	<7	<7
Total Iron	μ g/l	2000	<20	<20	155	142	<20	<20	<20	<20	<20	<20	<20
Lead	μ g/l	10	6	6	130	41	17	6	7	18	12	<5	<5
Magnesium	mg/l	ng	15.1	16.8	219	52.6	34.4	72.4	404	32	16.5	1.5	2.1
Manganese	μ g/l	500	2848	1486	1320000	269800	40050	130	16190	105	91	38	49
Mercury	μ g/l	6	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Potassium	mg/l	ng	2	2.1	10	3.4	5.2	9	4.6	6.6	0.5	13.4	1.4
Sodium	mg/l	200	21.4	24.3	205	163	348	91.9	95.9	385	519	117	111
Uranium	μ g/l	15	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Calcium Hardness dissolved (as CaCO3)	mg/l	ng	74	58	445	280	174	637	1361	141	105	33.8	29.3
Magnesium Hardness dissolved (as CaCO3)	mg/l	ng	63.4	70.6	918	221	145	304	1696	134	69.3	6.3	8.8
Total Hardness dissolved (as CaCO3)	mg/l	ng	137	129	1362	501	318	941	3056	276	174	40	38
Fluoride	mg/l	1.5	<0.3	<0.3	2.3	2.9	0.8	0.7	3.6	7.6	9.4	7.2	10
Sulphate	mg/l	500	96.03	110	2668	9203	787	640	2503	526	642	31.5	84.4
Chloride	mg/l	300	16.8	17.5	25.2	176	150	80.9	31	34.7	90.6	32.6	35.2
Ortho Phosphate as PO4	mg/l	ng	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	0.11	<0.06	<0.06	<0.06	0.090
Nitrate as N	mg/l	11	69.8	68.7	19.2	<0.2	10.2	29.1	19.3	5.9	57.1	<0.2	<0.2
Nitrite as N	mg/l	0.9	1.7	0.11	<0.02	<0.02	<0.02	<0.02	0.070	0.030	<0.02	<0.02	<0.02
Ammoniacal Nitrogen as N	mg/l	1.5	-	-	-	-	-	-	-	-	-	-	-

Dissolved CoCs	Units	SANS 241:2011	GAA001-D	GAA001-S	GAA002-D	GAA002-S	GAA003-D	GAA004-D	GAA004-D	GAA005-D	GAA005-S	GAA006-D	GAA006-S
Total Alkalinity as CaCO3	mg/l	ng	46	45	<1	518	32	364	419	394	446	206	221
P Alkalinity as CaCO3	mg/l	ng	<1	<1	<1	<1	<1	<1	<1	<1	<1	102	<1
Silica	mg/l	ng	29.0	28.9	80.6	26.3	52.6	30.2	28.7	45.6	50.5	21.3	28.8
Total Dissolved Solids	mg/l	1200	379	420	5600	13832	1485	1408	4226	1256	1643	319	331
Turbidity	NTU	5	0.6	0.4	0.8	2.6	1.1	0.9	0.7	0.7	0.4	0.4	0.8

Risk Type	
Operational	brl: below reporting limit NDP: No determination possible - Sample pH is acidic and not suitable for this test
Chronic Health	
Aesthetic	
Acute Health – 1	

Table 5-16: Site Wide Monitoring Wells Chemical Test Data for December 2014 sampling event (Taken from Hughes, 2015)

Dissolved CoCs	Units	SANS 241:2011	GAA007-D	GAA007-S	GAA008-S	GAA009-S	GAA010-S	GAA011-S	GAA012-S	GA0012-(6)
Electrical Conductivity	mS/m	170	334.1	806	362.5	152.9	62.4	33.6	282	271.6
pH	pH units	5-9.7	7.3	6.8	6.7	7.4	6.5	6.8	7.37	7.19
Cadmium	µ g/l	3	<0.5	<0.5	1.5	<0.5	<0.5	<0.5	<0.5	<0.5
Calcium	mg/l	ng	579	224	359	173	67.7	28.6	128.7	226.1
Total Chromium	µ g/l	50	<1.5	<1.5	8.3	2.8	<1.5	<1.5	<1.5	<1.5
Copper	µ g/l	2000	<7	<7	20	<7	<7	<7	<7	<7
Total Iron	µ g/l	2000	2288	<20	45	<20	<20	<20	136	<20
Lead	µ g/l	10	8	5	46	8	7	<5	5	<5
Magnesium	mg/l	ng	150	345	234	39.1	20.6	5.5	45.3	63.4
Manganese	µ g/l	500	21760	11990	467900	30	8852	63	1140	240
Mercury	µ g/l	6	<1	<1	<1	<1	<1	<1	<1	<1
Potassium	mg/l	ng	15	2.2	22	10	5.7	4.3	15.6	5.5
Sodium	mg/l	200	305	1516	193	129	24.5	28	412.7	376.5
Uranium	µ g/l	15	<5	<5	<5	<5	<5	<5	<5	10
Calcium Hardness dissolved (as CaCO3)	mg/l	ng	1447	811	897	432	169	71.5	321.8	690.3
Magnesium Hardness dissolved (as CaCO3)	mg/l	ng	630	1659	983	164	86.5	23.1	190.3	266.3
Total Hardness dissolved (as CaCO3)	mg/l	ng	2077	2470	1880	596	256	95	512	957
Fluoride	mg/l	1.5	1.0	5.4	1.1	1.4	0.5	0.6	5.8	4
Sulphate	mg/l	500	1905	488	2733	689	215	81.9	1247.47	1346.71
Chloride	mg/l	300	107	134	63.3	37.3	13.4	12.4	57.5	30
Ortho Phosphate as PO4	mg/l	ng	<0.06	<0.06	<0.06	0.12	<0.06	<0.06	<0.06	<0.06
Nitrate as N	mg/l	11	<0.2	43.5	22.3	33	19.3	0.4	0.7	5.7
Nitrite as N	mg/l	0.9	0.070	0.20	0.16	0.040	<0.02	0.21	<0.02	0.24
Ammoniacal Nitrogen as N	mg/l	1.5	-	-	-	-	-	-	0.2	0.41
Total Alkalinity as CaCO3	mg/l	ng	290	nd	99	140	78	101	324	302

Dissolved CoCs	Units	SANS 241:2011	GAA007-D	GAA007-S	GAA008-S	GAA009-S	GAA010-S	GAA011-S	GAA012-S	GA0012-(6)
P Alkalinity as CaCO3	mg/l	ng	<1	<1	<1	<1	<1	<1	<1	<1
Silica	mg/l	ng	24.1	38.8	44.0	31.7	20.6	11.5	32	35.3
Total Dissolved Solids	mg/l	1200	3274	7341	4041	920	461	213	2296	1827
Turbidity	NTU	5	0.9	0.6	0.4	0.4	0.4	0.5	1.2	0.5

Risk Type
Operational
Chronic Health
Aesthetic
Acute Health – 1

brl: below reporting limit
NDP: No determination possible - Sample pH is acidic and not suitable for this test

Table 5-17: COC for the December 2014 sampling event (Taken from Hughes, 2015)

COC	Units	SANS 241:2011	Perimeter Monitoring Wells P1, P2, P3, P4	On-Site Monitoring Wells + GAA012 Monitoring Wells
EC	mS/m	170	46.5 to 107	45.8 to 2,820
pH	pH Units	5-9.7	5.89 to 7.3	3.9 to 10.2
Fe	µ g/l	2000	<20 to 767	<20 to 2,288
Pb	µ g/l	10	<5 to 6	<5 to 130
Mn	µ g/l	500	43 to 3,214	30 to 1,320,000
Na	mg/l	200	16.9 to 102	21.4 to 1,516
F	mg/l	1.5	<0.3 to 1.5	<0.3 to 10
SO_4	mg/l	500	87.61 to 361.27	31.5 to 9,203
Nitrate	mg/l	11	<0.2 to 47.5	<0.2 to 69.8
Nitrite	mg/l	0.9	<0.02 to 1.04	<0.02 to 1.7
TDS	mg/l	1200	339 to 851	213 to 13,832

EC and TDS measurements of groundwater of perimeter groundwater monitoring wells along the western and southern perimeter are within acceptable limits. EC and TDS measurements for GAA0012-D/S monitoring wells exceed the SANS241:2011 drinking water limits.

The concentration of manganese in groundwater obtained from the perimeter monitoring wells ranges between 0.04 and 3.2 mg/l. Four of the perimeter monitoring wells (P1-(15), P2-(15), P4-(15) and P4-(6)) have manganese concentrations exceeding the SANS drinking water limits of 0.5 mg/l (Hughes, 2015). This indicates that groundwater in some parts of the site is already elevated with manganese prior to entering the site.

Elevated concentrations of nitrate was found to be present in groundwater obtained from the site perimeter at concentration ranging between <0.2 and 47.5 mg/l and with concentrations in excess of SANS 241:2011 being identified in a) the northwest perimeter monitoring wells (P1-(15) and P2-(6)) and b) the southern central perimeter monitoring well (P4-(6)). Perimeter Nitrite concentrations range in concentration between <0.02 and 104 mg/l. It is postulated by the author that groundwater with elevated concentrations of nitrate and nitrite may be entering the site from an off-site source or may represent a decay product from a different off-site source of contamination e.g. Ammoniancal Nitrogen (Hughes, 2015). In this regard, testing for Ammoniacal Nitrogen was undertaken on groundwater obtained from GAA012-S, GAA012-D and P4-(15) and was found to be present at concentrations ranging between 0.2 and 0.92 mg/l which are below the SANS 241:2011 guideline value of 1.5 mg/l.

5.3.4 Estimate of Loading to the Crocodile River

The main contaminants associated with site activities are dissolved phase manganese and sulphate. It has been shown that the concentration of these contaminants represent a risk to the environment. The concentrations of manganese and sulphate on site are considered to be representative of that which would reach the Crocodile River as no natural attenuation is considered to be occurring as the contaminants migrate in a northerly direction towards the river. The author has therefore undertaken to estimate the contaminant load that would reach the Crocodile River using: the average concentration in Zone A and Zone B, the size of the zones identified using geophysics, and the estimated effective porosity of the fractured and weathered horizon which was determined from the geotechnical logging.

The initial step to estimating the load to the Crocodile River was to calculate the flow rate across the site towards the northern boundary which represented a drop in hydraulic head of 12 m. The calculated flow rate varied between 1.87 and 18.75 m^3/day depending upon which area was under consideration i.e. Zone A, Zone B or the remainder of the northern boundary, as presented in Table 5-18.

Table 5-18: Calculation of Flow from Source Area to Northern Boundary

Channel	Thickness of Water Column (m)	Average Hydraulic Conductivity (m/day)	Width of Plume (m)	Area (m2)	Length (m)	Head Reduction (m)	Flow, Q. (m^3/day)
Zone A	6.580	5.62×10^{-2}	65	427.70	154	12	1.87
Zone B	8.310	5.62×10^{-2}	110	914.10	154	12	4.00
Remainder of Northern Boundary	7.445	5.62×10^{-2}	575	4280.88	154	12	18.75
Total							20 to 30

A similar calculation was then undertaken for the same area from the northern site boundary to the Crocodile River which this time represented head reduction of 45 m. The calculated flow rate was determined to be between 5.41 and 54.13 m^3/day as presented in Table 5-19.

Table 5-19: Calculation of Flow from Northern Boundary to Crocodile River

Channel	Thickness of Water Column (m)	Average Hydraulic Conductivity (m/day)	Width of Plume (m)	Area (m^2)	Length (m)	Head Reduction (m)	Flow, Q. (m^3/day)
Zone A	6.580	5.62×10^{-2}	65	427.70	200	45	5.41
Zone B	8.310	5.62×10^{-2}	110	914.10	200	45	11.56
Remainder of Northern Boundary	7.445	5.62×10^{-2}	575	4280.88	200	45	54.13
Total							60 to 80

The load of manganese and sulphate reaching the northern site boundary was then determined by multiplying the flow rate by the contaminant concentration. This determined a total manganese load of ±5 kg/day and a total sulphate load of ±55 kg/day. The results for manganese and sulphate are presented in Table 5-20 and Table 5-21, respectively.

Table 5-20: Calculating Manganese Loading to the Northern Boundary

Channel	Flow Q (m^3/day)	Concentration of manganese in groundwater (mg/l)	Manganese Load reaching Site Boundary (kg/day)
Zone A	1.87	2406	4.51
Zone B	4.00	181.30	0.73
Remainder of Northern Boundary	18.75	9.28	0.17
Total			±5

Table 5-21: Calculating Sulphate Loading to the Northern Boundary

Channel	Flow Q (m^3/day)	Concentration of sulphate in groundwater (mg/l)	Sulphate Load reaching Site Boundary (kg/day)
Zone A	1.87	4768	8.93
Zone B	4.00	8115	32.48
Remainder of Northern Boundary	18.75	740	13.87
Total			±55

It has been assumed that all load reaching the northern site boundary will, without intervention, reach the Crocodile River and that no natural attenuation will occur.

To estimate the time duration required for contaminants to a) leave the source area and reach the northern boundary and b) leave the northern boundary and reach the Crocodile River it was first necessary to estimate the effective porosity. Upon review of the geotechnical logs the author estimated that the effective porosity ranged somewhere between 0.05 and 0.2.

The effective velocity was then estimated by dividing the calculated flow rate by both the area of the plane through which groundwater is moving and the estimate of effective porosity, where:

$$\text{Duration} = \frac{Q}{A.n}$$

and,

Q = Flow rate in m^3 per day

A = Area in m^2

n = Effective porosity.

The estimated duration for contaminants to migrate from a) the source to the northern boundary perimeter and b) the northern boundary perimeter to the Crocodile River are presented in Table 5-22 Table 5-23.

Table 5-22: Time taken from Source to Northern Site Boundary

Channel	Flow Q (m^3/day)	Area (m^2)	Estimate of Effective Porosity, n		
			0.05	0.1	0.2
			Years to reach the Site Boundary		
Zone A	1.87	427.7	4.82	9.63	19.27
Zone B	4.00	914			
Remainder of Northern Boundary	18.75	4281			

Table 5-23: Time Taken from Northern Site Boundary to Crocodile River

Channel	Flow Q (m^3/day)	Area (m^2)	Estimate of Effective Porosity, n		
			0.05	0.10	0.20
			Years to reach the Crocodile River		
Zone A	5.41	427.7	3.12	6.24	12.48
Zone B	11.56	914			
Remainder of Northern Boundary	54.13	4281			

It is estimated that the total duration of time that on-site contamination will impact upon the Crocodile River will be between 8 and 32 years depending upon the estimate of effective porosity considered appropriate for the site (see Table 5-24). During this period it is estimated that up to ±5 kg of manganese and ±55 kg of sulphate could reach the Crocodile River each day.

However, this calculation assumes that a constant source of contaminants is applied to the source area. In this instance the primary source of the contamination (leakage from cell houses) will be removed during rehabilitation of the site therefore meaning that there is a finite amount of contaminant in the groundwater and this will decrease with time as will loading to the river. It is considered by the author that the estimate of loading of ±5 kg per day of manganese and ±55 kg per of sulphate is appropriate for the lower end of the estimation of duration i.e. 8 years. The calculation also neglects possible dispersion within the fracture network as it is assumed that all contaminant will reach the Crocodile River.

Table 5-24: Total Years from Source to Crocodile River

Effective Porosity	To reach Site Boundary (Years)	To reach Crocodile River (Years)	Total Duration (Years)
0.05	4.82	3.12	±8
0.10	9.63	6.24	±16
0.20	19.27	12.48	±32

5.4 DISCUSSION

The groundwater quality monitoring and laboratory chemical test analysis has confirmed that site water quality becomes progressively worse as groundwater migrates through the site. This indicates that sources of on-site contamination are present and they have a negative impact on groundwater quality. In particular, elevated concentrations of manganese and sulphate are present and correlation of the two can be used as a means to describe the distribution of contamination across the site. The main source of contamination appears to be located within the areas of low apparent resistivity identified during the geophysical survey and known as Zone A and Zone B and located immediately below and down-gradient of the eastern and western cell houses. Elevated concentration of manganese and sulphate are present within these zones and have been proven to extend to the northern site boundary. It can be assumed that any contamination reaching the northern boundary continues to migrate in a northerly direction towards the Crocodile River.

There is no evidence of natural attenuation occurring as a result of contaminants migrating through the sub-surface in a northerly direction. There is however, an indication that natural groundwater migrating from the south of the site may have a neutralising effect on acidic waters located to the north of the site with the potential to raise pH and result in the precipitation of manganese from solution. Further, the football pitch located on the southern part of the site is underlain by backfill of neutralised sludge known as “Greenfill”. The material possesses a high pH which as a result of leaching through soils is causing groundwater to become more alkaline. As the more alkaline waters migrate through the acidic water and mixing occurs the pH raises to circum-neutral facilitating the precipitation of manganese from solution.

Several other heavy metals are present in solution. These metals are not associated with the process undertaken on site but are most probably associated with the very low or very high pH groundwater conditions taking the metals into solution. pH can therefore be considered to be a master variable controlling the distribution and species or various dissolved metals in solution.

Some parts of the site e.g. the north-western side, contain areas where elevated concentrations of manganese are in solution but are not considered to be associated with site processes. For these area it is possible that off-site sources of manganese are migrating onto site. This would similarly explain the distribution of nitrate and nitrite across site which may be a decay product associated with Ammoniancal Nitrogen used in other areas of the industrial zone.

The estimate of effective porosity is critical to understanding of the duration of impact. The estimated effective porosity chosen to estimate the loading upon the river and the duration of impact has been made based upon review of the fractures identified in the drilling cores during the geotechnical logging. The estimate of effective porosity used in the calculation are considered by the author to be appropriate. Further, the author’s preference tends towards the lower range of effective porosity for the large part of the site (i.e. 0.05 to 0.10) and for the fracture zones a higher estimate of 0.10 to 0.20. The author undertook additional assessment using a simple analytical model developed in accordance with Ogata and Banks (1961) to consider the possible effects of dispersion upon contaminant concentration and predict concentrations 200 m down-gradient of the site. The author determined that the head gradient associated with the steep topography between the northern site boundary and the Crocodile River was the major controlling factor that limited the potential for substantial dispersion to occur and only a 10% reduction in manganese concentration was predicted at the point of impact to the Crocodile River.

Due to the reduced hydraulic gradient across the site as compared to the area between the northern site boundary and the Crocodile River it takes over twice as long for contaminants to reach the northern site boundary than to reach the Crocodile River.

Should only on-site remediation be undertaken then this would reduce the period of time that the Crocodile River is impacted to between 3 and 12 years. In conceptualisation, such in-situ remediation may involve the use of drilling to allow for direct injection of a chemical amendment to neutralise the pH of the on-site groundwater and facilitate the precipitation of manganese.

CHAPTER 6:
CONCEPTUAL SITE MODEL AND RISK ASSESSMENT

6.1 INTRODUCTION

Chapter 6 describes and discusses the conceptual site model (CSM) that was developed for the site following completion of the site investigation and the qualitative risk assessment that was undertaken to determine the risk posed to potential by the contamination present in both the soils and the groundwater.

A CSM is a simplified representation of real-life (Younger, 2007) that requires various statements describing the assumptions made in developing the model and which ultimately becomes a tool that provides a visualisation of a theorised situation describing all of the essential components of a system. In the case of contaminated groundwater related issues, a CSM is typically produced to define various sources of contamination and how they may migrate from a source, at a particular concentration, via various pathways to reach and potential impact upon a receptor or multiple receptors.

The degree to which a contaminant may have an impact upon a receptor can then be assessed either qualitatively or quantitatively via a qualitative/quantitative risk assessment (QRA). Should a QRA determine that an unacceptable risk exists then mitigation measures may be proposed to reduce the risk to an appropriate rating.

6.2 SITE SPECIFIC CONCEPTUAL SITE MODEL

The author used the information obtained during the various stages of investigation to update the conceptual site model for the site, which is presented in Table 6-1. The conceptual site model is described further as an illustration in Figure 6-1. The main benefit of the updated CSM is that it has allowed the author to focus attention upon developing an appropriate remedial strategy for the site.

Table 6-1: Updated Conceptual Site Model

Model Element	Description
Site Strata	On-site the surface covering is represented either by a) a layer of sandy soils or b) concrete hardstanding and backfill of sand, clay and gravel to depth of typically 1 to 3 m; overlying, highly to moderately weathered and highly fractured granitic gneiss to a typical depth of 15 mbgl; overlying fresh slightly fractured extremely strong granitic gneiss to depths of at least 40 mbgl.

	Off-site to the north is a thin veneer of sandy soil often less than 0.25 m in thickness; overlying moderately weathered granitic gneiss to depth of between 1 and 8 mbgl; overlying fresh slightly fractured extremely strong granitic gneiss to unknown depth. The presence of precipitate with elevated concentrations of manganese and sulphate down-gradient of the site and close to the river indicates that the depth of weathering is likely reduced to less than a one metre as the slope of the land reduces in gradient and reaches the Crocodile River. Using historical aerial photography and site observations, geological structural features on site are conceptualised to act as both a barrier and pathway for the migration of contaminants.
Groundwater and Aquifer Parameters	Groundwater flow is down-gradient from the south to the north. There is a moderately strong correlation between topography and groundwater level for the shallow weathered aquifer. Groundwater flow direction is not influenced by changes in groundwater salinity. Rather the controlling features with regard to groundwater flow are the depth of weathering and the presence of fracture zone. Precipitation of metals along fractures will reduce available effective pore space and lower hydraulic conductivity. The majority of the groundwater is conceptualised to be present within the weathered and fractured strata within the upper 15 m. Groundwater is in connectivity with the canal that forms the southern boundary of the site. All groundwater flow is assumed to be laminar and follows Darcy’s Law. The weathered and highly fractured rock in the upper 15 m within a fracture zone flow has a hydraulic conductivity of between 10^{-2} m/d and 10^{-3} m/d. For near surface strata in the upper 15 m but located between and outside of the fracture zones a hydraulic conductivity of between 10^{-4} and 10^{-5} m/d is proposed. For the underlying fresh rock a hydraulic conductivity of between 10^{-7} to 10^{-9} m/d is estimated. Low to very low storativity may be expected.

Potential Sources of Contamination	Elevated manganese is present in groundwater on site at concentrations of up to 2,000 mg/l. Elevated sulphate is present in groundwater on site at concentrations of up to 4,000 mg/l. Low pH groundwater is present is groundwater on site at values as low as 3 to 4. Small areas of the site also have high pH of between 9 and 10. The extent of contaminant migration off-site is unknown at this time but is assumed to remain primarily within the fracture zones and not be subject to substantial dispersal. Contaminant flow is along fractures zones which do not contain organic material and therefore no natural attenuation of contaminants of concern occurs. Redox and precipitation represent the most important geochemical processes.
Pathways	Two low resistivity zones have been identified on site and they represent preferential pathways for the migration of contamination off-site and providing connectivity with the Crocodile River. The zones are elongate in a south-north direction.
Receptor	The weathered rock aquifer represents a minor aquifer that and generally extends to approximately 15 mbgl expect where fresh rock gently grades towards the surface. Exploitation of the groundwater resource is not feasible and therefore the source-pathway-receptor model is not considered to be complete with respect to groundwater contamination. However, the site lies within the Crocodile catchment and general drainage in the area is towards a tributary of the Crocodile River to the northwest and directly to the Crocodile Rover to the north. The Crocodile River is considered to the main receptor. Thus the source-pathway-receptor model is considered to be complete with respect to surface water contamination. The Crocodile River along the section in close proximity to the site has formed along a preferential structural lineament probably associated with faulting. Interaction between surface water and deeper groundwater along the line of the river is therefore probable.

Model Boundaries	The southern canal represents a head dependent boundary. The Crocodile River located to the north and the two streams located to the east and west of the site also represent head dependent boundaries. The base of the shallow weathered aquifer/top of the unweathered granitic gneiss (i.e. 15 mbgl on site and between 1 and 8 mbgl offsite) represents a zero-flux boundary Within the body of the main body two fracture zones exist that represent zones of higher hydraulic conductivity and provide a pathway for the migration of on-site contamination to the Crocodile River.

6.2.1 Qualitative Risk Assessment

The author has undertaken a qualitative risk assessment (QRA) to determine if and where intervention is required to reduce any risk scenarios to acceptable levels of risk. For each scenario and likelihood of occurrence (LOI) and a potential impact (PI) have been proposed to calculate an initial risk rating. Where required a mitigation measure or series of measures are proposed to reduce the risk rating to a lower risk rating. The risk assessments are presented in Table 6-2, Table 6-3 and Table 6-4.

The QRA has determined that low pH and elevated concentrations of manganese represent a high risk to the Crocodile River and that in order to reduce the risk to an acceptable level pro-active intervention is required to improve groundwater quality prior to the groundwater reaching the river.

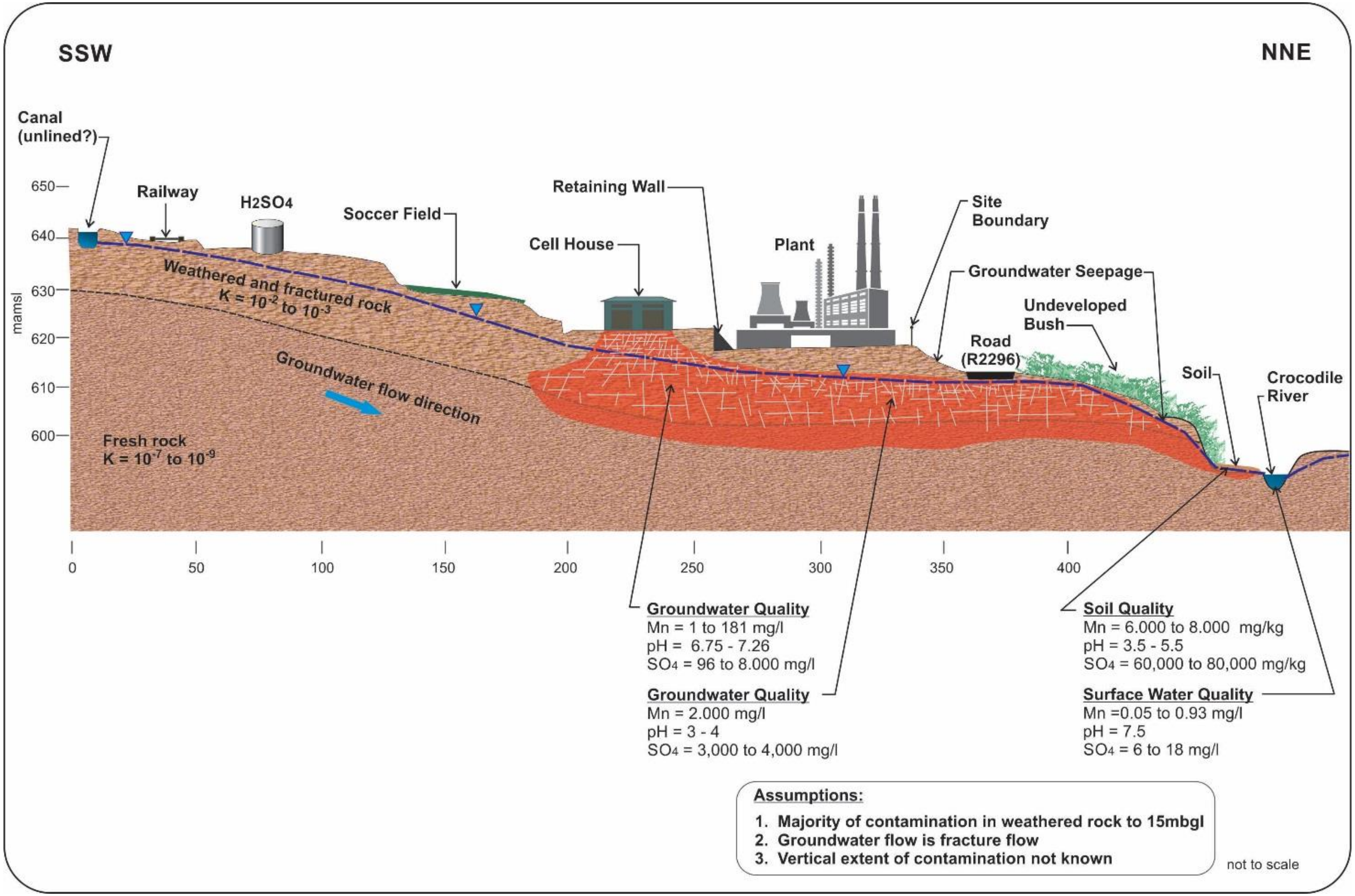

Figure 6-1: Updated Conceptual Site Model (Modified from Hughes, 2014d)

Table 6-2: Qualitative Risk Assessment for Manganese

Source	Pathway	Receptor	LOI	PI	Initial Risk Rating	Mitigation Measure	Revised Risk Rating
Elevated Manganese in Soil	Leaching through Soils	Shallow groundwater	Low	Low	Low	Not required	Not applicable
Elevated Manganese in Process Water	Leaking into Sub-Surface	Shallow groundwater quality	High	High	High. During operation of the facility leakage of contaminants has been occurring in the area for the Cell Houses.	The facility is to be closed thereby all primary sources of contamination will be removed. No other action required.	Low
Elevated Manganese in Groundwater	Migration of Contamination through Groundwater	Crocodile River, downstream water users, ecological health.	High	High	High. Elevated levels of manganese in excess of guidance levels have been found to be present in groundwater that is migrating in a northerly direction towards the Crocodile River.	Reduce manganese concentration of on- site groundwater prior to groundwater reaching the Crocodile River.	Low Any intervention undertaken is likely to take time to become effective. During the initial stages of any remedial activity the risk is likely to be remain high but as the remedial activity advances the risk will reduce.

Table 6-3: Qualitative Risk Assessment for Sulphate

Source	Pathway	Receptor	LOI	PI	Initial Risk Rating	Mitigation Measure	Revised Risk Rating
Elevated Sulphate in Soil	Leaching through Soils	Shallow groundwater	Low	Low	Low	Not required	Not applicable
Elevated Sulphate in Process Water	Leaking into Sub-Surface	Shallow groundwater quality	High	High	High During operation of the facility leakage of contaminants has been occurring in the area for the Cell Houses.	The facility is to be closed thereby all primary sources of contamination will be removed. No other action required.	Low
Elevated Sulphate in Groundwater	Migration of Contamination through Groundwater	Crocodile River, downstream water users, ecological health.	Mod	Low	Moderate Elevated levels of sulphate on site are far in excess of guidance values however off-site at the point of connection with the river they are marginal.	The facility is to be closed thereby all primary sources of contamination will be removed. No other action required.	Low

Table 6-4: Qualitative Risk Assessment for pH

Source	Pathway	Receptor	LOI	PI	Initial Risk Rating	Mitigation Measure	Revised Risk Rating
Low pH in Soil	Leaching through Soils	Shallow groundwater	Low	Low	Low	Not required	Not applicable
Low pH in Process Water	Leaking into Sub-Surface	Shallow groundwater quality	High	High	High During operation of the facility leakage of contaminants has been occurring in the area for the Cell Houses.	The facility is to be closed thereby all primary sources of contamination will be removed. No other action required.	Low
Low pH in Groundwater	Low pH facilitates mobilisation of metals within water.	Crocodile River, downstream water users, ecological health.	High	Mod	High Low pH waters have been determined to be present on site and migrating towards the Crocodile River without any natural attenuation increasing pH.	Increase pH of groundwater on site prior to groundwater leaving site.	Low

6.3 DISCUSSION

The process of developing a CSM has determined that a credible source-pathway-receptor (SPR) linkage exists with regard to site based low pH and high manganese impacted groundwater migrating in a northerly direction and negatively impacting upon the Crocodile River. The CSM has been continually updated through the course of the investigation based upon new site observations and in order to inform the next stage of investigation.

In developing conceptual site models for large potentially complicated sites it is important that a key individual remains involved in the project throughout the investigation and, if not gathers then at least, reviews all data from the various types of investigation being undertaken to ensure that the CSM is up-to-date and representative of in-situ conditions. All too often a conceptual site model is seen as an add-on to an investigation, instead of it being seen as the key to developing an appropriate understanding of the site, and as such is often only developed at the time of reporting. Such an approach limits the usefulness of a good conceptual site model.

A qualitative risk assessment has confirmed that the main receptor of concern is the Crocodile River and the contaminants of concern that may impact upon the river are low pH groundwater and elevated manganese groundwater. The qualitative risk assessment has been useful in focusing the attention of the author on proposals for remediation strategies that increase pH and lower manganese concentrations in groundwater. At this time, there is insufficient off-site water quality data to justify undertaking a detailed quantitative risk assessment. In this regard the off-site data water quality data is limited to four water samples obtained during a single sample event and it is not known if this data is truly representative of surface water quality throughout the year and/or if seasonal fluctuations change water quality significantly.

It was originally proposed by that author to develop a numerical groundwater model for the site using proprietary software to describe and model contaminant migration through the sub-surface towards the Crocodile River. However, during the study it became evident that development of such a model would not improve understanding of contaminant migration any further than that already developed through construction of a detailed conceptual site model. This was further confirmed through use of a simple 1-D contaminant transport analytical model.

Modelling of dilution of contaminants once they have entered the Crocodile River would however improve understanding of contaminant concentrations within the river to inform future development of a quantitative risk assessment should it have been required. However, such was not required as by this stage in the study the author had argued successfully that regardless of the possible dilution that would occur in the Crocodile River it remained unacceptable for such low pH and high manganese waters to leave site unaddressed. The development of the remedial strategy is discussed in Chapter 7.

CHAPTER 7:
SELECTION OF A REMEDIAL STRATEGY

This chapter discusses the decision making process that was undertaken by the author to determine what form of remedial strategy was required to be developed for the site. This was achieved by first determining the main drivers for remediation, identifying potential remediation strategies that would fulfil the requirements of the main drivers and finally, by undertaking geochemical modelling to assess the suitability of potential chemical amendments for achieving the remediation goal i.e. increase pH value and decrease soluble manganese content in groundwater.

7.1 DECISION MAKING

It was acknowledged at an early stage of the project that multiple remediation technologies exist which could potentially provide appropriate remedial solutions for the site. This may range from the "do-nothing" option, through to natural attenuation through to active in-situ remediation. Therefore, in order to justify the choice of remedial technique to be utilised it was proposed by the author to undertake a form of benefit analysis using the Analytical Hierarchy Process (AHP) which is a rigorous mathematical technique which allows the use of qualitative and quantitative criteria in multi-criterion decision making.

7.1.1 Method Description

The AHT was developed in the 1970s by Thomas L. Saaty, an American mathematician. The method represents a tool by which various options can be listed into order of preference based upon consideration of multiple factors affecting the decision making process (Saaty, 2008). The method considers both tangible and intangible factors and the "net-benefit" can be calculated to determine which option is considered to be most favourable to the project in achieving the end goal. The relative importance of each factor under consideration is determined by undertaking "pairwise comparison" by attributing a numerical value to each factor and then applying an appropriate numerical weighting. A figure describing the AHT process is provided as Figure 7-1. The figure shows how each of the various factors that influence the options under consideration are inter-compared.

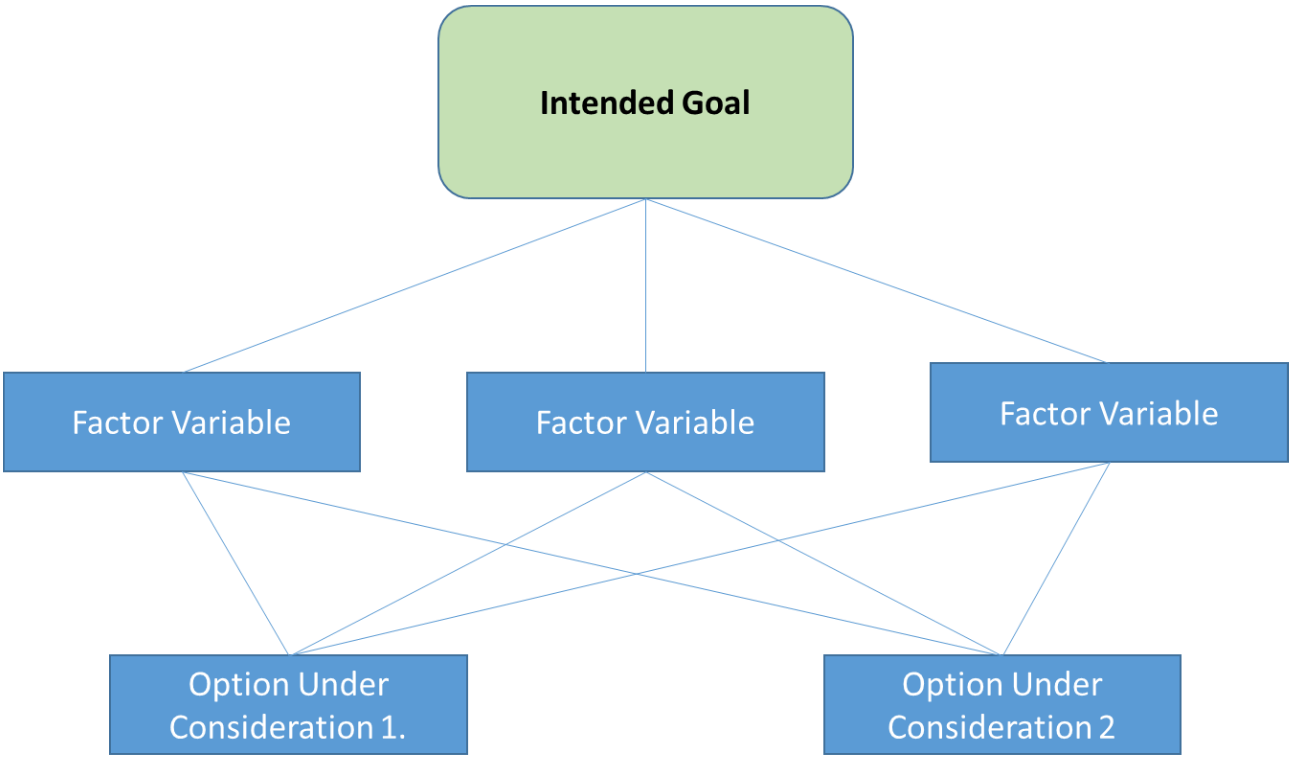

Figure 7-1: AHT Process (Modified after Wollmann et al., 2014)

7.1.2 Site Specific Assessment

After discussions with various stakeholders and in consideration of the potential impact upon the Crocodile River, the author determined that four main factors would likely affect the decision making process associated with the development an appropriate remedial strategy. The four factor variables are presented in Table 7-1 along with appropriate explanation for their inclusion.

Table 7-1: Factor Variable Assessment

Factor Variable	**Factor Variable 1**	**Factor Variable 2**	**Factor Variable 3**	**Factor Variable 4**
Title	Public Perception	Timeframe	Reduced Liability	Protection of River
Description	Potential for negative public perception if action is not seen to be taken.	Extensive on-site remedial works could delay the sale of the site to a new owner	On-going liability could have an impact on operating costs and reputation.	Successful remediation indicates that the client is a good citizen.

The author considered the relative importance to the project of the various factor variables and undertook pairwise comparison of each factor variable. The pairwise comparison is provided as Table 7-2. A scale of 1 to 9 has been used whereby a rating of “1” indicates that the two factors are considered to be of equal importance and a factor of “9” would indicate strong preference of one factor variable over the other. The comparison is subjective and where compromise is required over the two end positions then the user may choose any number between 2 and 8 to represent their opinions.

Table 7-2: Pairwise Input Table

Factor Variable Title (x)	Comparative Rating 1	Factor Variable Title (y)	Comparative Rating 2
Public Perception	3	Timeframe	9
Public Perception	3	Reduced Liability	9
Public Perception	1	Protection of River	5
Timeframe	4	Reduced Liability	9
Timeframe	5	Protection of River	3
Reduced Liability	9	Protection of River	3

For each pairwise comparison, the various values are divided to complete the comparison matrix which is presented as Table 7-3. To provide an appropriate weighted average to determine the priority scores each value within the matrix is divided by both the column total (see Table 7-3) and the four factors under consideration. The priority scores are presented in Table 7-4 and as Figure 7-2.

Table 7-3: Comparison Matrix

Factor Variable Title	Public Perception	Timeframe	Reduced Liability	Protection of River
Public Perception	1.00	0.33	0.33	0.20
Timeframe	3.00	1.00	0.44	1.67
Reduced Liability	3.00	2.25	1.00	3.00
Protection of River	5.00	0.60	0.33	1.00
Column Totals	12.00	4.18	2.11	5.87

Table 7-4: Determination of Priorities

Factor Variable Title	Public Perception	Timeframe	Reduced Liability	Protection of River	Total	Variables	Priority Score
Public Perception	0.08	0.08	0.16	0.03	0.35	4	**0.09**
Timeframe	0.25	0.24	0.21	0.28	0.98	4	**0.25**
Reduced Liability	0.25	0.54	0.47	0.51	1.77	4	**0.44**
Protection of River	0.42	0.14	0.16	0.17	0.89	4	**0.22**
Sum of Priorities							**1.00**
Inconsistency							**0.092**

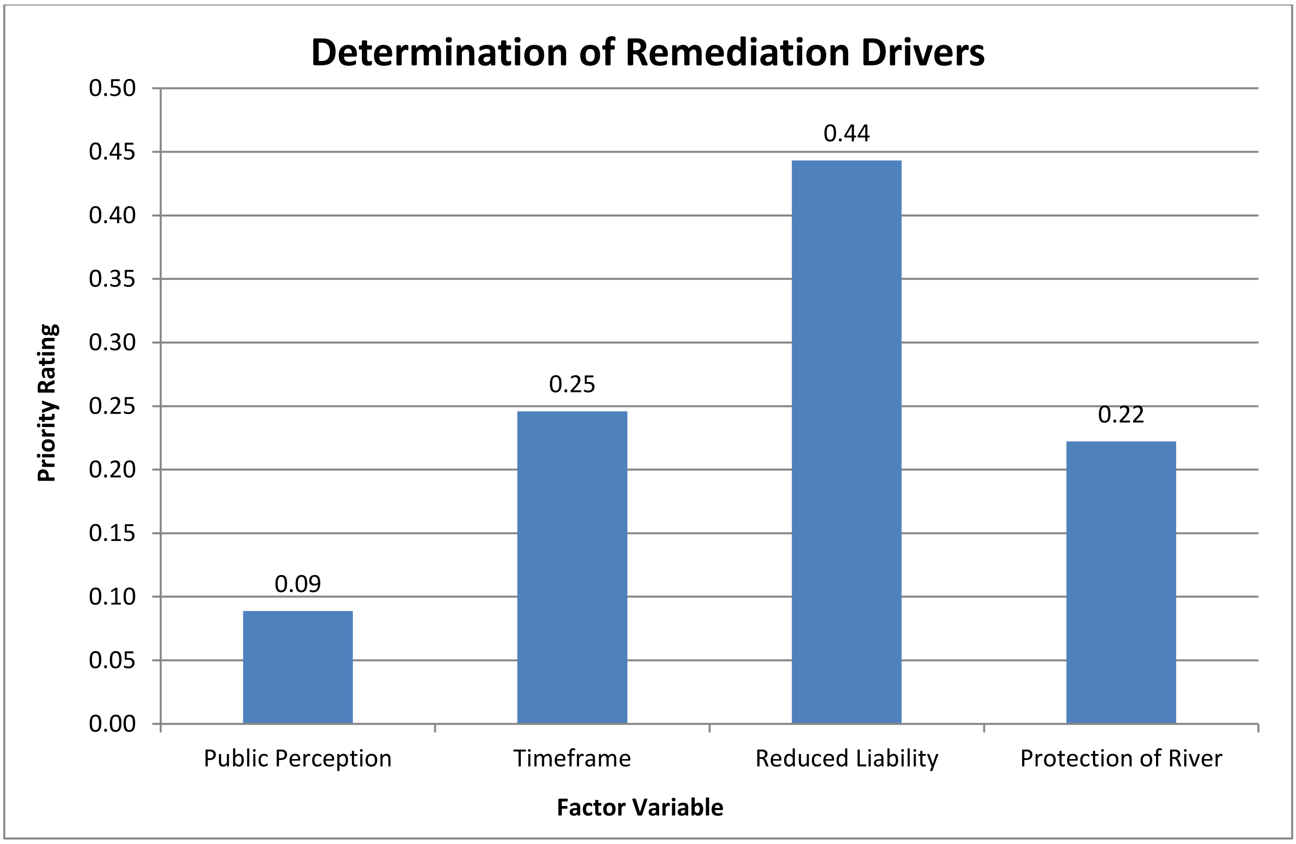

Figure 7-2: Determination of Remediation Drivers

7.1.3 Discussion

The assessment identified that the primary drivers accounting for over 60% of the decision making process were a) Reduction in Liability and b) Timeframes. Desire to provide actual protection of the Crocodile River accounted for 22% of the decision making process and public perception less than 9%.

The main driver has been determined to be a requirement to ensure that a reduction in liability occurs as a result of the remedial works to be undertaken. This is an easily measurable quantity that has both financial and criminal consequences for the owner or polluter of a contaminated land site. Similarly, timeframes for any proposed remedial strategy could impact upon both the timing of the sale of the land and the sale value.

The low percentage awarded to public perception surprised the author who had initial thought that such would provide greater stimulus to deciding upon a remedial strategy. However, the advantages of the AHP technique is that it is mathematically rigorous and reduces subjectivity in deciding upon options.

Having gained an understanding of the main drivers affecting the choice of remediation strategy and having gained an in depth knowledge of the site from the site investigation the author was able to undertake a qualitative assessment to determine the suitability of five proposed remedial options:

- Option 1. Monitored Natural Attenuation.
- Option 2. Excavation of an Interception Trench.
- Option 3. Pump and Treat.
- Option 4. In-situ Chemical Dosing (on-site).
- Option 5. In-situ Chemical Dosing (off-site).

Consideration of each option is presented in Table 7-5. The assessment determined that monitored natural attenuation and the excavation of an interception trench were not suitable due to extended timeframes, practicality and there being no substantial reduction in liability. Pump and treat was considered unsuitable due to the low quantities of groundwater that could be reasonable expected to be captured and that the weathered and fractured nature of the underlying strata would require a tight spacing of capture wells which would therefore represent a costly exercise. In-situ chemical dosing was determined to be viable with on-site treatment being preferable over off-site treatment for security and maintenance reasons although the latter would have reduced impact to the Crocodile River in a more-timely manner.

Table 7-5: Choice of Remediation Strategy

Remediation Options 1 to 5	**Suitability for the Site**
Option 1. Monitored Natural Attenuation	
Relatively cheap option estimated at R 200,000 per year for at least 20 years. However, it is unlikely to work as natural attenuation has not been shown to be occurring on site and this option therefore does not reduce liability nor deliver within appropriate timeframes. Further, this option is unlikely to meet with regulatory approval and any application would likely be dismissed resulting in delays to the project and limiting the ability of the owner to sell the site.	Not suitable
Option 2. Excavation of an interception trench for groundwater capture and disposal or treatment	
This would involve the construction of an interception trench along parts of the northern boundary of the site whereby migrating groundwater moving towards the Crocodile River would be intercepted and either discharged to sewer or undergo ex-situ treatment. However, there is limited room available between the site and the R2296 road to allow for construction of a trench and any excavation would need to extend to approximately 10 mbgl, which would be very difficult due to the inherent strength of the underlying strata. In addition, the liability would not be reduced as the contamination would remain on-site until it moves off-site and is intercepted. The timeframes are likely to extend to >10 years due to the low hydraulic conductivity and movement of groundwater across the site.	Not suitable
Option 3. Pump and Treat	
Groundwater capture for ex-situ treatment though chemical dosing is a proven technology for the treatment of low pH water and groundwater elevated with respect to manganese. Any system would involve the construction of groundwater capture wells and pipework to transport the water to areas for chemical dosing prior to disposal to sewer once appropriate groundwater quality criteria had been achieved. However, due to the fractured nature of the underlying strata a tight array of boreholes would be required to intercept contaminated groundwater moving through various fractures. This would represent a rather costly remedial strategy. Low capture quantity would result is a long period of treatment with no rapid decrease in liability. Further, disposal to sewer would attract local municipality disposal charges.	Not suitable

Option 4. In-situ remediation via Chemical Dosing (On-site)	
In-situ remediation through chemical dosing to increase pH and force the precipitation of manganese would likely work. This would involve undertaking in-situ treatment on-site to introduce chemical amendments to raise the pH of the groundwater and cause the precipitation of manganese, thereby reducing the quantity of contaminants leaving site. The remediation activities could be undertaken at the same time of site demolition thereby having no impact upon project timeframes.	Suitable
Option 5. In-situ remediation via Chemical Dosing (Off-site)	
Similar to Option 4. Treatment could be undertaken close to the river thereby reducing impact more quickly. However, the client would need to agree and maintain access to the land between the site and the Crocodile River for the duration of the remediation. This may require paying for land or access rights and maintaining security. Further, access to site is limited due to the steep terrain.	Not suitable

7.2 GEOCHEMICAL MODELLING

The solubility of manganese is dependent upon both ORP and the master variable pH. Hughes (2014d) noted that where groundwater is below 6 then manganese is most likely to be found is solution as the bivalent Mn^{2+} form. With increasing pH of groundwater, manganese may precipitate from solution, depending upon the ORP, as $MnCO_3$, MnO_2, Mn_2O_3 or less commonly as MnO.

As discussed in Chapter 5, the redox conditions across the site are generally oxidised although wide ranging with redox potential obtained during December 2014 and January 2015 ranging from -124 to 439.90 mV and pH ranging between 3.69 and 11.03. Where the combination of pH and ORP are not suitable then manganese will not precipitate from solution. To force precipitation of manganese from solution it is therefore necessary to adjust either pH or ORP, or both.

A standard Eh-pH diagram for manganese is provided as Figure 7-3. The predominant form of manganese in solution in Mn^{2+}. Under neutral to alkaline pH conditions (pH 7-12) aqueous Mn^{2+} does not exist, instead insoluble Mn oxide, hydroxides and carbonates are formed (Naicker, 2014).

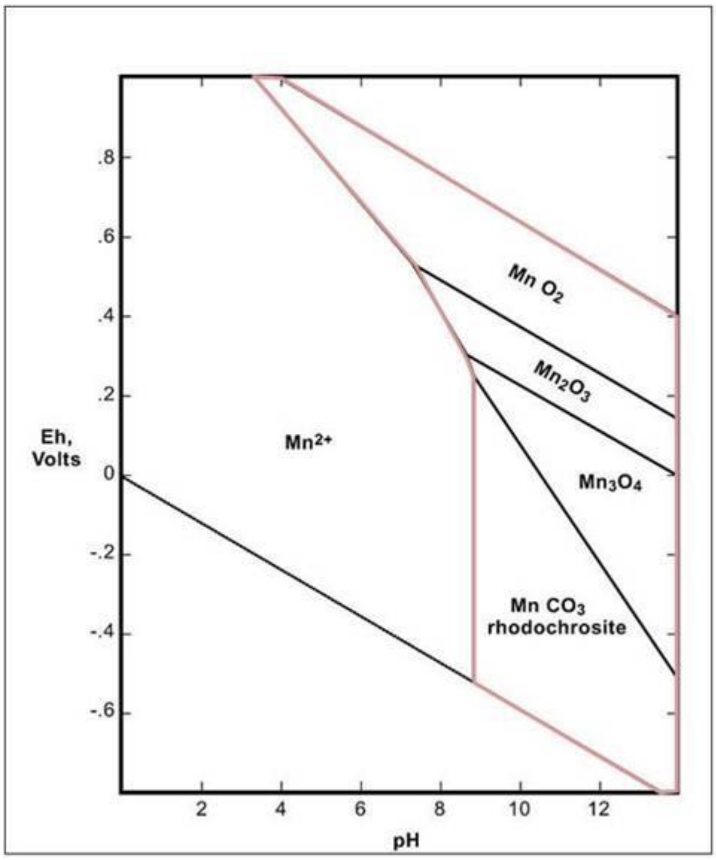

Figure 7-3: Eh pH Diagram for Manganese (Taken from Cincinnati University, 2017)

Plotting the Eh against pH for the various groundwater samples obtained during the investigation determined that conditions exist in which manganese would be predominately present in solution in the Mn^{2+} form. The plot is provided as Figure 7-4. Review of the plot suggests that precipitation of manganese could be achieved by increasing pH or decreasing or increasing ORP. As the goal of the remediation is to both precipitate manganese and increase the pH of the groundwater leaving site to circum-neutral it is therefore logical that any method used to facilitate manganese precipitation should be designed to raise pH. Figure 7-4 shows the combined plot of pH and ORP obtained during the December 2014 and January 2015 sampling event. The anomalous combination of pH and Eh shown to the right of Figure 7-4 is indicative of the part of the site underlain by backfill “Greenfill” which is naturally increasing pH in the area of the football pitch and which indicates that conditions are right for precipitation of manganese as the mineral Hausmannite Mn_3O_4 likely forming brownish-black pseudo-octahedral and pyramid crystals (Pellant, 1992).

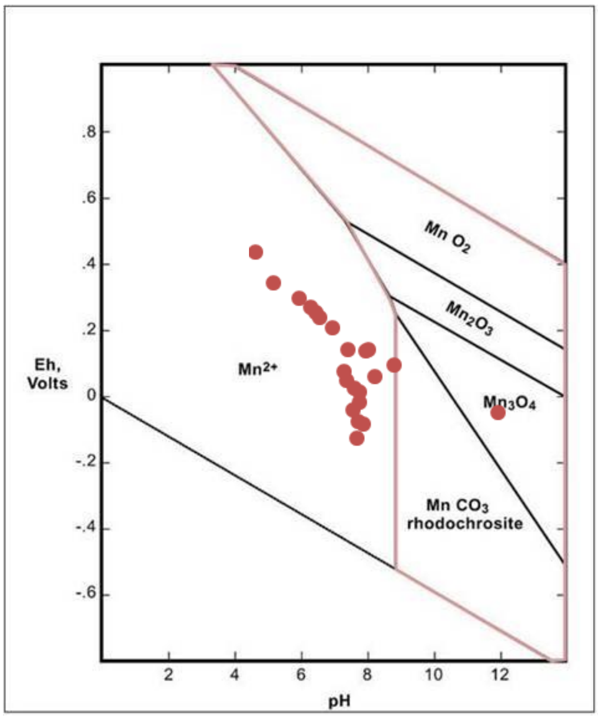

Figure 7-4: Plot of pH and ORP for site specific data

With the goal being to develop an in-situ remediation strategy to neutralise pH and force the precipitation of manganese from solution the author proposed that geochemical modelling be undertaken to determine the most appropriate amendment that could be added to improve groundwater quality. This is discussed in the followings sections.

7.2.1 Methodology

Geochemical modelling of the addition of potential chemical amendment to groundwater impacted by elevated concentrations of manganese and low pH was undertaken using PHREEQC geochemical modelling software using data as provided within the Minteq v4 database.

The groundwater sample collected from monitoring well GAA002-D was chosen to be the representative sample for this assessment. This sample exhibited the lowest pH of all the water samples obtained from site (pH = 3.64) and a relatively high manganese concentration of 682 mg/l. It was proposed to equilibrate the groundwater samples with four potential chemical amendments for comparison, specifically: a) $BaSO_4$; b) NaOH; c) $CaCO_3$; and d) CaO. These four chemical amendments were chosen as their addition represented little or no potential risk to human health or water quality.

7.2.1.1 Input

The initial groundwater quality data for the groundwater sample obtained from borehole GAA002-D was input into PHREEQC with the values presented in Table 7-6.

Table 7-6: Input Table

	Units	Value
pe*	s.u	7.28
pH	s.u	3.64
Temperature	Degrees Celsius	25
Alkalinity	mg/l	0.002 as Ca0.5(CO_3)0.5
Aluminium	mg/l	22
Calcium	mg/l	194
Iron	mg/l	0.43
Potassium	mg/l	12.5
Magnesium	mg/l	163
Manganese	mg/l	682
Sodium	mg/l	210
Silica	mg/l	62.9
Fluoride	mg/l	2.97
Chloride	mg/l	33.4
Nitrogen (5)	mg/l	18.5
Sulphate (6)	mg/l	3590

Cadmium	mg/l	0.0333
Copper	mg/l	0.162
Lead	mg/l	0.198
Uranium	mg/l	0.0225

7.2.1.2 Precipitation of Manganese

Assuming a continuous supply, the groundwater was then brought into equilibrium with each of the four individual amendments at a concentration of 0.1 mol/L. The suitability of the potential amendments was determined through review of residual manganese present in the groundwater.

Table 7-7: Groundwater Sample from GA002-D (Modified from Naicker, 2014)

Mineral/ Parameter	Chemical Formula Units	Equilibrium Solution	Reaction with 0.1 mol			
			$BaSO_4$	NaOH	$CaCO_3$	CaO
pH	s.u	3.64	3.76	5.15	5.75	9.38
pe	s.u	7.28	11.8	10.41	9.80	6.18
Approximate manganese concentration (after final solution)	mg/l	682	682	571	20	0.0048

The modelling determined that the addition of lime (CaO) had the greatest change on pH raising pH from 3.64 in the equilibrium solution to 9.38 in the final solution. CaO additionally had the greatest influence on manganese concentration resulting in almost 100% of manganese being removed from solution. The addition of $CaCO_3$ showed improvement in pH, rising from 3.64 to 5.75, and 97% of manganese being removed from solution. The addition of NaOH increased pH from 3.64 to 5.15 but removed only 16% of the manganese in solution. The use of $BaSO_4$ had no impact upon pH nor did it result in any manganese precipitation, but it did result in the development of highly oxidising conditions for Fe.

7.2.1.3 Mineral Forms

The mineral forms that would likely form following the addition of chemical amendments have been determined form review of the saturation index (SI) for the mineral form.

The saturation index is represented by the formula

$$SI = \mathrm{IAP}/\mathrm{K} \qquad \text{Equation 7-1}$$

where:

SI = Saturation Index

IAP = Ion Activity Product

K = Solubility Product

A saturation index lower that zero is indicative of sub-saturation and the chemical phase may dissolve into solution; a saturation index equal to zero indicates equilibrium between the mineral phase and the solution; and a saturation index greater than zero indicates supersaturation and may result in precipitation of the mineral phase. During this assessment apparent equilibrium was assumed at SI values between -0.5 and 0.5 to account for uncertainty (Naicker, 2014). The various saturation indexes calculated for the equilibrium solution and after addition of the four potential chemical amendments are presented in Table 7-8 with saturation with respect to various minerals highlighted.

Table 7-8: SI for manganese and selected Mineral Phases (Modified from Naicker, 2014)

Mineral Name	Formula	Saturation Index (SI)				
		Equilibrium Solution	$BaSO_4$	NaOH	$CaCO_3$	CaO
Manganese (II)Sulphate	$MnSO_4$	-7.3	-7.3	-7.3	-7.5	-7.7
Manganese (III) Suphate	$Mn_2(SO4)_3$	-41.8	-32.8	-35.7	-37.3	-45.0
Manganese (II) Chloride Tetrahydrate	$MnCl_2:4H_2O$	-11.7	-11.7	-11.7	-11.8	-11.9
Birnessite	MnO_2	-16.5	-7.5	-4.8	-3.6	3.5
Bixbyite	Mn_2O_3	-18.3	-9.3	-3.8	-1.5	12.8
Hausmannite	Mn_3O_4	-24.5	-15.4	-7.2	-3.8	17.6
Nsutite	MnO_2	-16.0	-6.9	-4.2	-3.0	4.1
Pyrochroite	$Mn(OH)_2$	-10.4	-10.4	-7.6	-6.5	0.7
Pyrolusite	MnO_2	-14.5	-5.4	-2.7	-1.5	5.6
Rhodochrosite	$MnCO_3$	-2.2	-2.2	0.5	1.6	5.3
Ferrihydrite	$Fe^{3+}10O14(OH)_2$	-3.6	-0.2	1.3	1.9	4.0
Gibbsite	$Al(OH)_3$	-2.3	-2.3	1.9	3.6	0.4
Calcite	$CaCO_3$	-4.6	-4.6	-1.9	0.0	-7.0

Gypsum	$Ca(SO_4)\cdot 2H_2O$	-0.4	-0.4	-0.4	0.2	15.1
Halite	$NaCl$	-6.9	-6.9	-6.6	-6.9	3.7
Hematite	Fe_2O_3	0.6	7.4	10.5	11.7	1.8

For the equilibrium solution the saturation index for gypsum (-0.4) falls within the allowable range (+/- 0.5) indicating apparent equilibrium with gypsum. However, the saturation index for hematite (0.6) is greater than zero and out of the assumed margin of error indicting that conditions are suitable for precipitation of the mineral. The addition of $BaSO_4$ resulted in the saturation index for hematite increasing from 0.6 to 7.4 indicting a strong preference for precipitation of the mineral. It also resulted in an increase of the saturation index for ferrihydrite (another Fe mineral) from -3.6 to -0.2 thereby indicting apparent equilibrium between the mineral and the solution. The addition of NaOH resulted in supersaturation with respect to rhodochrosite, ferrihydrite, gibbsite, and hematite. Of these minerals only rhodochrosite contains manganese. Precipitation of the latter three minerals would reduce concentration of aluminium and iron in on-site based groundwater. The addition of $CaCO_3$ resulted in increased saturation index values for rhodochrosite, ferrihydrite, gibbsite and hematite. With the addition of CaO, supersaturation occurred for seven manganese based minerals, specifically: birnessite, bixbyite, hausmannite, nsutite, pyrochroite, pyrolusite, rhodochrosite. The saturation index values for ferrihydrite, gypsum, and halite also increased indicting probable precipitation of those minerals. However, although remaining positive the saturation index values for gibbsite and hematite reduced with the latter to within the range of equilibrium.

7.2.2 Discussion

7.2.2.1 Modelling

The use of PHREEQC geochemical modelling has confirmed that precipitation of metals including: manganese, iron and aluminium can be achieved under alkaline and moderately oxidising conditions. It has also shown that three chemical amendments could be used for the precipitation of manganese from solution, specifically: NaOH, $CaCO_3$, or CaO. Of these amendments the only manganese containing mineral that would precipitate would be rhodochrosite with the majority of other metals precipitating being aluminium or iron based. The use of CaO however, would result in seven different manganese based minerals theoretically precipitating from solution and including: oxides, hydroxides and carbonates.

7.2.2.2 Remedial Techniques for the Removal of Manganese and increasing pH

Dissolved manganese can be removed from solution by a variety of methods including: ion exchange, biological oxidation, sorption and catalytic oxidation, direct oxidation and precipitation (Tobiason et al., 2016).

The work undertaken by the author determined that dosing the groundwater with 0.1 mol of calcium oxide (CaO) represented an appropriate solution to increase pH and precipitate manganese from solution. The process undertaken to produce calcium oxide from calcium carbonate is called calcination and involves the burning of calcium carbonate to release carbon dioxide leaving residual calcium oxide and is shown as Equation 8-1.

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g) \qquad \text{Equation 8-1}$$

The remediation strategy proposed by the author required that calcium oxide be hydrated on site to produce calcium hydroxide prior to injection into the sub-surface. Tsimas (2018) showed that the addition of water to calcium oxide is an exothermic reaction which results in the release of heat during reaction as indicated by Equation 8-2 and Equation 8-3:

$$CaO + H_2O\,(l) \leftrightarrow Ca(OH)_2 + 1{,}135\text{ kJ/kg of CaO} \qquad \text{Equation 8-2}$$

$$CaO\,(s) + H_2O\,(l) \leftrightarrow Ca(OH)_2\,(aq) \qquad \Delta Hr = -63.7\text{ kJ/mol of CaO} \qquad \text{Equation 8-3}$$

The addition of calcium hydroxide causes pH to increase through the generation of bicarbonate alkalinity and consumption of protons. With respect to manganese, the precipitation of rhodochrosite can be expressed by the following (Equation 8-4 and Equation 8-5).

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad \text{Equation 8-4}$$

$$Mn^{2+} + CO_2 + Ca(OH)_2 \rightarrow MnCO_3 + Ca^{2+} + H_2O \qquad \text{Equation 8-5}$$

Other remedial strategies involving active dosing are possible and have been discussed by others. Younger et al. (2002) discussed various methods of active dosing with alkali to increase pH and precipitate metals used in active mine treatment. These methods included:

1. Addition of Calcium based reagents
   This involves the addition of calcium hydroxide to raise pH and cause the precipitation of metal hydroxides.

2. Addition of Sodium based reagents
   This involves the addition of sodium based reagents including NaOH and Na_2CO_3 by which their addition raises groundwater pH allowing for the precipitation of metal hydroxides or carbonates.

3. Addition of Magnesium Hydroxide

   Magnesium hydroxide $Mg(OH)_2$ can be added to neutralise acidic groundwater as indicated by Equation 8-6. However, magnesium hydroxide will not readily raise pH above 7 which may limit the precipitation of some metals and reaction times can be quite long when compared to calcium hydroxide or calcium oxide.

   $Mg(OH)_2$ (s) + $2H_3O+$(aq) ↔ Mg^{2+} (aq) + 4 H_2O (l) Equation 8-6.

4. Addition of Ammonia gas

   This method involves bubbling of ammonia gas through water to form NH^{4+} consuming protons as shown as Equation 8-7.

   NH_3 (g) + H^+ (aq) = NH_4^+ (aq) Equation 8-7

Chen et al. (2015) reported upon the use of carbon dioxide and alkaline additives to precipitate manganese as carbonate. The authors compared different types of alkaline additives and determined that precipitation rate for manganese increased with increasing amounts of alkaline additives. The authors found that carbonate precipitation by CO_2 with CaO could covert soluble manganese to rhodochrosite within stability zones determined via Eh and pH conditions (See Figure 7-5) and explained in Equation 8-8, Equation 8-9 and Equation 8-10.

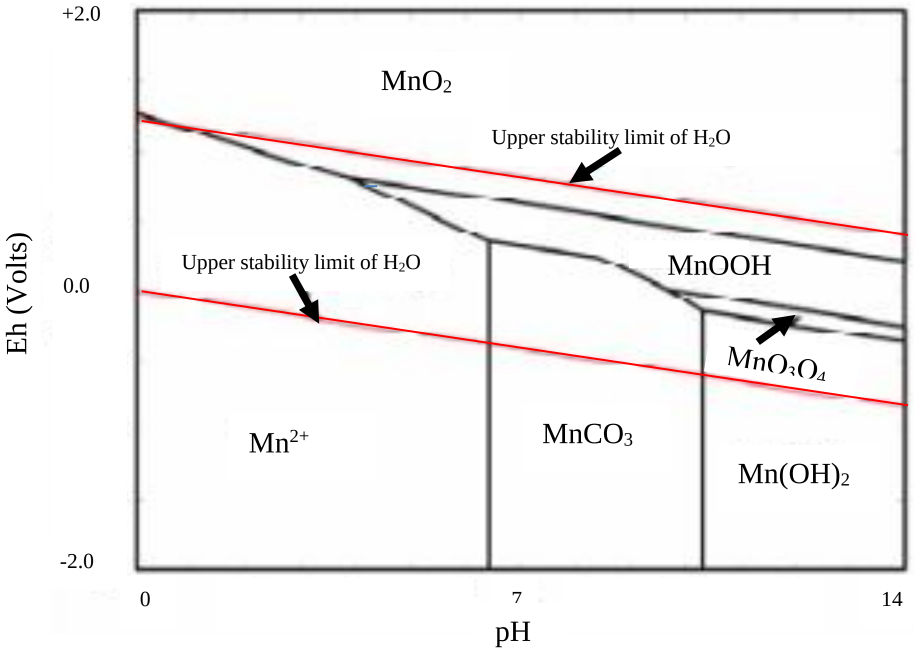

Figure 7-5: Eh-pH diagram for manganese carbonate formation (Modified from Chen at al., 2015)

$CaO + H_2O \rightarrow Ca(OH)_2$ Equation 8-8

$Mn.SO_4.H_2O + CO_2 + Ca(OH)_2 \rightarrow MnCO_3 + CaSO_4.2H_2O$ Equation 8-9

$(NH_4)_2Mn(SO_4)_2.6H_2O + CO2 + Ca(OH)_2$
$\rightarrow MnCO_3 + (NH_4)2SO_4 + CaSO_4.2H_2O + 5H_2O$ Equation 8-10

Often manganese removal from solution can be achieved as a by-product of other treatment undertaken to improve water quality with respect to some other defining features. Tobiason et al. (2016) reported upon manganese removal being achieved as a by-product of water softening whereby lime-soda was added for the removal of hardness.

Kurtz et al. (2009) discussed methods of metal abstraction through precipitation of manganese which involved the oxidation of Mn^{2+} thereby raising the Eh prior to neutralisation to increase pH and precipitate manganese in the Mn^{4+} form as MnO_2 and exemplified as Figure 7-6.

The process being described by the equations Equation 8-11 and Equation 8-12 with changes in pH and Eh associated with microbial action.

$Mn^{2+} + 0.25O_2\ (g) + 1.5\ H_2O \rightarrow MnOOH\ (s) + 2H^+$ Equation 8-11

$Mn^{2+} + 0.5O_2\ (g) + H_2O + 2H^+$ Equation 8-12

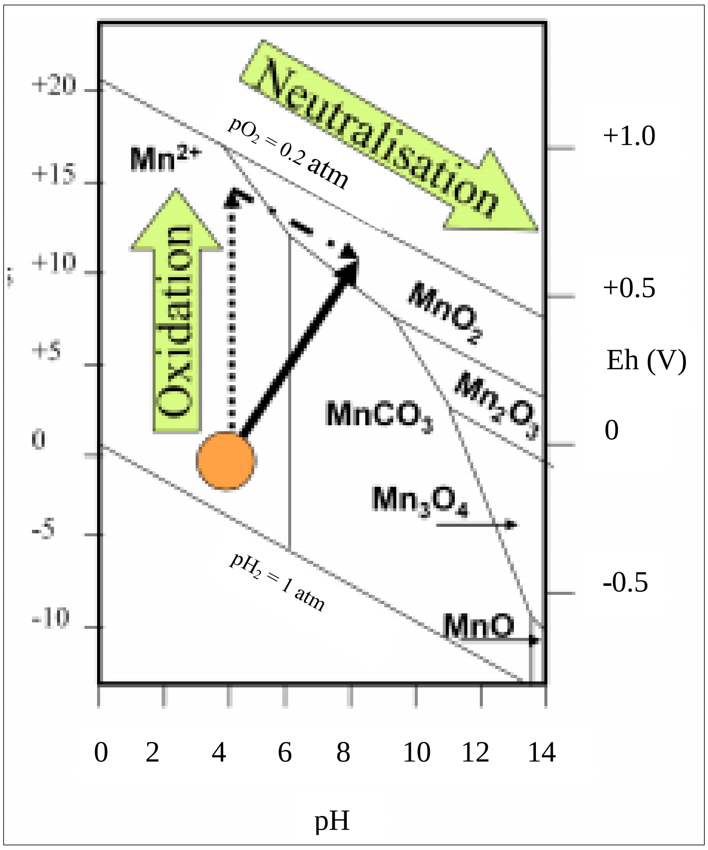

Figure 7-6: Eh Ph Stability Diagram (Modified from Kurtz, 2009).

Other Methods to reduce Sulphate and Metal concentration in Groundwater

Teclu et al. (2009) reported upon the use of sulphate reducing bacteria (SRB) to remediate groundwater impacted by heavy metals. SRB converts sulphate to sulphide whilst simultaneously oxidising a carbon source (Malik, 2004). Dissolved phase metals are then able to bond with the sulphate causing the precipitation of sulphide. Similarly, Vanbroekhaven et al. (2007) studied a heavy metal contaminated site in Belgium for which column experiments were undertaken using soy oil, cheese whet and sodium lactate to reduce heavy metals contamination in groundwater. Vanbroekhaven et al. (2007) determined that both cheese whey and lactate amended with nitrogen and phosphorus represented the most efficient amendment for the precipitation of cobalt as a sulphide. Jacobson et al. (1999) discussed experimentation that had been used to remove elevated concentration of manganese from groundwater using spent mushroom compost columns. Their work was associated with assessing the effectiveness of passive systems for the removal of manganese and/or using manganese as an indicator system. The authors found that the behaviours of manganese was complicated and noted both increases and decrease in manganese concentration occurring when pH and sulphide concentrations increased. Importantly the authors noted that “manganese can be retained under sulphate reducing conditions but retention is not related to sulphate reduction” (Jacobson et al., 1999).

Tobiason et al. (2016) noted that manganese removal can be achieved via sorption and catalytic oxidation at circum-neutral pH and where glauconite can be used as an ion exchange mineral. Similarly, the same result can be achieved by catalytic oxidation with chlorine. Ion exchange may also be utilised where divalent Mn^{2+} is removed from solution through replacement of monovalent cations e.g. Na^+ or H^+.

7.2.2.3 Proposed Remedial Strategy for the Delta E.M.D. Site

Recharging groundwater from the south of the site has been shown to be improving groundwater quality through neutralisation of acidity and providing favourable conditions for the precipitation of manganese from solution. However, relying upon this alone would likely require a period of 8 to 32 years to meet with requirements for groundwater quality compliance and as such would not provide sufficient neutralisation within the required timeframes. In order to reduce the timeframe for the remediation works to a period potentially reduced to a period of between 3 to 12 years the author proposed that on-site chemical dosing with CaO be undertaken to provide the groundwater system with additional alkalinity to reduce pH and result in the precipitation of manganese.

The author also proposed that the remediation strategy included the following key components:

1. Construction of large diameter chemical dosing wells immediately up-gradient of the sources of contamination. Hydrated CaO would be mixed on site and injected into the wells and natural groundwater flow would allow the chemicals to migrate in a northerly direction through the areas impacted by contamination facilitating neutralisation of pH and resulting in the precipitation of manganese.
2. Construction of large diameter chemical dosing wells within the middle of each contaminant zone to allow for the injection of hydrated CaO into the main source areas. Natural groundwater flow would then allow alkalinity to migrate towards the northern boundary of the site and reduce acidity and precipitate manganese.
3. Construction of medium diameter perimeter barrier wells along the northern boundary of the site within the zones of contamination. Initially these wells would be used as monitoring wells and then as injection wells into which hydrated CaO would be injected to form a barrier through which on-site contaminated groundwater would migrate and be neutralised and any unused alkalinity would migrate off-site in a northerly direction along preferential pathways neutralising acidity between the northern site boundary and the Crocodile River.
4. Construction of on-site and off-site monitoring wells and monthly monitoring to determine the effectiveness of the remedial strategy through measurements of heavy metal content and pH and re-assess the chemical dosing quantities required based upon site observations.
5. Construction of very shallow monitoring sumps adjacent to the Crocodile River at the end of the sub-surface geological structures connecting the contaminants on site with the Crocodile River. Sampling from these points would be undertaken on a monthly basis to determine groundwater quality and identify when groundwater quality had reached acceptable guidance criteria.
6. Continued up-gradient and down-gradient surface water monitoring along the Crocodile River on a monthly basis to determine any changes in water quality during the remediation period.

CHAPTER 8:
DISCUSSION

It is the author’s experience that most contaminated groundwater site investigations in South Africa are underfunded and therefore fail to provide the appropriate degree of information required to inform the design of the most suitable remedial strategy for a particular site. The remedial strategy that is therefore developed rather unfortunately often represents or includes:

1. An under designed strategy.
2. Over engineering solutions.
3. The wrong remedial strategy altogether.
4. Poorly constructed boreholes and monitoring wells.
5. An under estimation of timeframes required to achieve compliance.
6. Poorly worded contract with unfair conditions, excessive risk and financial liability.

The first five bullet points listed above are typically the result of under-funding and poorly executed investigations. The latter bullet point, however, is of particular importance in that the author is aware of a examples of industrial clients wanting clean-up of contaminated groundwater for which site information is limited and yet the proposed contractual conditions place an unfair proportion of risk onto consultants and remediation contractors. Recent but confidential examples of this practice in South Africa have resulted in substantial over-expenditure, over-design of remedial systems, failure to improve groundwater quality and extensive timeframe overrun. Further, often the over-engineered remedial systems that are failing to complete the works in the required period of time are replaced, or possibly “enhanced”, in the latter stages of remediation by low cost proven and commonly accepted technologies that could have been used in the first place!

The author notes that the knowledge and ability to execute thorough site investigations and design suitable remediation strategies is present in South Africa. However, all too often, the funds set aside for site investigation are limited and this results in the site investigation engineer only attaining a rather poor understanding of site conditions. This practice of underfunding is presumably to save client costs, however, such is usually ineffective as insufficient investigation typically leads to over estimation of remediation costs or insufficient remediation meaning for residual liability being incurred. Where clients attempt to pass on liability to consultants or contractors at the tender stage without sufficient site information they will typically receive a reduced number of bidders, very high costs and numerous changes to proposed contractual terms and conditions making comparison of tender returns rather time-consuming.

8.1 Proposal for Site Investigations for Remediation Design

Using a site investigation the author undertook during 2014 to 2015, for which appropriate funding was available, the author seeks to describe how contaminated groundwater investigations and development of remediation strategies for shallow fractured rock aquifers should be undertaken in South Africa.

8.1.1 Assessment

The author chose to undertake this study as he had identified that there was no consistency with regard to the quality and extent of site investigations undertaken in South Africa. Very often due to cost limitations an inadequate investigation will be undertaken which may, due to inadequacy, raise more questions than answers. The question therefore follows: “How should site investigations be undertaken in South Africa?”

The author considers that the focus of an investigation should be upon developing a detailed conceptual site model and then through logical and mathematical testing advance to prove the appropriateness of any proposed remedial strategy such that the quality of any remedial strategy can be calculated using the formula proposed below:

$$Quality\ of\ Remedial\ Strategy = \frac{(Ability + Knoweldge)\ x\ Desire\ to\ reduce\ liability}{Resistance\ to\ spend}$$

Ability and knowledge to undertake site investigations and design remedial strategies is available in South Africa and these can be supported by international best practice and guidance including ASTM D5730, BS5930:1999, Eurocode BS EN 1997-2:2007.

A desire to reduce liability is also present as shown by the AHT assessment undertaken by the author (see Chapter 7). There is however also a resistance, or reluctance, to spend the monies necessary to investigate a site properly and provide a suitable remediation strategy. This is probably due to a combination of limited understanding with regard to how much a site investigation can cost and the difficult financial times we are currently experiencing in South Africa. Regardless, under expenditure during the site investigation phase inevitably leads to over expenditure during remediation or failure to address the problem.

The author proposes that a twelve-step protocol should be followed for most site investigations in South Africa associated with the identification and design of a remedial solution for contaminated groundwater within shallow weathered/fractured aquifers. The twelve-step protocol is represented as Figure 8-1 with each step being discussed and described in the following sections. During each of the twelve steps the conceptual site model should be revised to ensure it is as up-to-date as possible. After each of the Steps 5 to 11 the user should review the information obtained and loop back into the twelve step guide to Step 4 in an iterative manner to determine if the information obtained is sufficient at that time to move forward or if additional surveys and assessments should be undertaken before moving to the next step. In undertaking this assessment the user must also consider the cost implications that any additional work may impose on the budget and weigh this against the potential benefit to be gained in determining the most appropriate remediation strategy for the site.

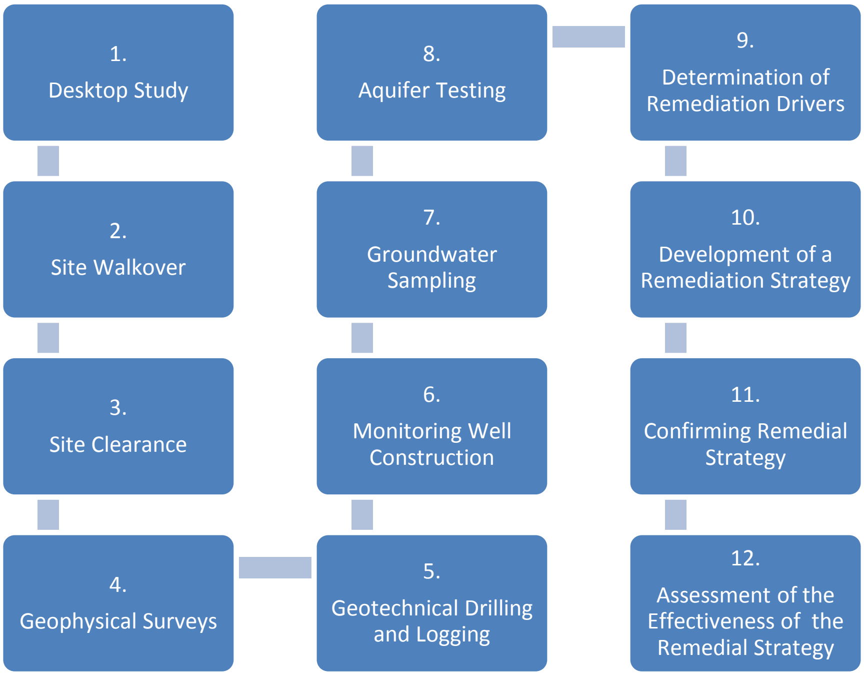

Figure 8-1: Twelve Step Guide to Detailed Site Investigation for Groundwater Contamination within Fractured Aquifers

STEP 1. Desktop Study

This step should involve a review of information available in the public domain including but not limited to: historical photographs, geological maps, hydrogeological maps, hydrology maps, geological memoirs, topographical maps, and various groundwater databases held by the national government. The purpose is to obtain an initial understanding of the site and provide sufficient information to develop an initial conceptual site model. The site investigation engineer should during this step start identifying those questions that must be asked whilst on site in order to understand the site further.

STEP 2. Site Walkover

This is an essential part of any site investigation as the benefit of a site walkover is that it allows the site investigation consultant to gain a full appreciation of site activities/processes undertaken on site and determine if site observations indicate either poor or good site management activities/practices. The site investigation consultant is also then able to observe suitable changes in topography and vegetation which can provide an indication of the surface or near surface pathways through which contaminants may have migrated. As with all geological and hydrogeological site investigations the consultant would also be able to appreciate various changes in topography and vegetation which may act as a guide to the interpretation of types of geological strata present beneath the site. The author himself has substantial experience in mapping changes in geological strata where rock outcrops were poorly represented in the environment and instead changes in grass type indicated ground either underlain by dolomites or shales. The site visit walkover also is an opportunity to design the subsequent site investigation and determine various aspects including but not limited to: number of monitoring wells required, borehole spacing, and probable borehole casing requirements in addition to identifying access restrictions which may limit the ability of the site investigation consultant to undertake investigation in particular areas.

STEP 3. Pre-Clearance Site Survey

The risk associated with striking buried services during site investigations on industrial and commercial land is very high. Existing site drawings indicating the location of buried services or infrastructure should always be reviewed but treated with caution as very often diversions have been put in place which may not have been recorded or similarly extensions to existing services have been installed but not recorded. There are many service clearance contractors operating in South Africa able to locate and avoid electrical cables using cable avoidance tools and other buried services or obstructions using ground penetrating radar. To ensure the safety of all workers associated with instructive investigations it would seem prudent to appoint a qualified service clearance contractor prior to breaking ground. Further, buried infrastructure can represent a pathway for the migration of contaminants and therefore an understanding of the layout of buried infrastructure can inform the conceptual site model.

STEP 4. Geophysical Surveys

There are multiple geophysical techniques that can be used to determine the presence of geological structures or features at sites. The type of technique to be employed will depend upon to type of feature that site investigation engineer is attempting to locate e.g. gravity surveys for sinkholes in dolomites, or magnetic and electrical magnetic for dykes associated with identification of potential barriers or pathways for contaminant and groundwater movement. For industrial and commercial land where highly conductive contaminants are likely to be present in the subsurface then the author is firmly of the opinion that electrical resistivity tomography (ERT) provides the best value for money given the large areas of site coverage that can be achieved in a single day. The method is however, limited by availability of space in which generally 200 m of length is required for layout of electrodes. Should there be insufficient clear length of survey then vertical electrical survey (VES) represents an appropriate alternative. VES is generally more time consuming that ERT, however recent developments in technology now include a series of VES electrodes on a barrel which can take a series of surveys and which can then be plotted as point data to develop a contour plot of depth specific resistivity. Detailed review of the data allows the site investigation engineer the informed opportunity to site boreholes in areas of interest and to delineate area of contamination etc.

The Delta site exhibited low apparent resistivity to depths of greater than 30 mbgl. Possible geological explanations for such low resistivity were limited and as such it was considered that potential contamination had extended to considerable depth into the underlying bedrock. As such, it was necessary to consider this in development of a remediation strategy.

STEP 5. Geotechnical Drilling and Logging

In South Africa geotechnical boreholes are not normally drilled as part of contaminated land investigations due to the relatively high cost of mobilisation and drilling. However, the author considers that there is a lack of appreciation of the benefit that knowledge of geotechnical assessment can provide and how it can inform the CSM and the design of the remedial strategy. Combined geotechnical and contaminated land investigations are undertaken elsewhere across the world typically associated with the re-development of brownfield sites. Despite geotechnical drilling being a much slower form of drilling, compared to percussive drilling which is typically used to construct groundwater monitoring wells, it can provide substantial benefit in that it allows the site investigation engineer opportunity to undertake geotechnical logging to assess the depth of weathering and any fracturing within the subsurface and thus determine where groundwater flow and contaminant migration is most likely to occur. Further, descriptions of the fracture planes including the presence of any precipitates can help inform the remedial strategy by proving geochemical modelling predictions. By obtaining measurement of the number of fractures within a particular geological unit and an estimation of the fracture width the consultant is able to determine an effective porosity and then in combination with other measurements including hydraulic gradient and hydraulic conductivity determine the expected duration of time that any contaminant will require to migrate from one place to another.

STEP 6. Monitoring Well Construction

Currently, typical practice in South Africa for determining the depth that monitoring wells should be drilled and cased in estimated at the time of tendering and then adjusted on site based upon ground conditions identified. Usually, this involves varying the amount of permanent steel casing inserted into the boreholes. Final borehole depths are generally only reduced if additional casing is required and the drilling and casing budget/allowance needs to be re-balanced. In South Africa, it is not common practice to grout the initial casing into place to form a seal before advancing the borehole to greater depth. Rather the boreholes are drilled to the required depth for casing, casing installed, borehole advanced and only sometimes is a grouted seal placed between the annulus of the boreholes and the upper steel casing. This is poor practice for contaminated land and groundwater site investigations but is done so to avoid standing time charges that would otherwise be incurred should the drilling team be required to ensure that grout is placed around the initial casing and allowed to set before advancing further to depth. Failure to ensure an adequate grouted seal through upper strata, which is more likely to be impacted by contamination than deeper strata, essentially means that the monitoring wells and boreholes that are being installed on industrial and commercial site become pathways for the migration of contamination to deeper groundwater. Indeed, in the authors experience geo-environmental consultancies in South Africa are now commonly recommending that clients grout-up sections of boreholes or abandon monitoring wells that have been drilled without due consideration for ground conditions present or the potential for them to create pathways and larger contamination problems in the future. This fundamentally comes from failure to obtain non-intrusive site information and to develop an appropriate conceptual site model prior to undertaking intrusive drilling works. Given that geophysical surveys are generally a low-cost means of investigation whereas potential groundwater remediation costs associated with drilling boreholes and creating a pathway for migration of contamination will be very high it seems to the author that undertaking a pre-drilling geophysical survey would represent a rather important risk mitigation measure.

Indeed, the use of limited number boreholes with water sampling alone is unlikely to provide the data spread necessary to facilitate delineation of a plume of contamination within the sub-surface, particular within a fracture rock aquifer. The use of electromagnetic geophysical surveying at the Delta site may have improved understanding of underlying geological profile in the upper 2 m. This in combination with the ERT surveying would likely have improved upon delineation of geological structures and potential contamination within the very near surface. However, use of the technique would have been limited to areas not affected by the large amount of infrastructure present on site.

STEP 7. Groundwater Sampling

The techniques to be employed during groundwater sampling will be partially dependent upon the type of contaminant present and at what depth within the water column the contaminants is likely to enter the monitoring well used for sampling. For example, dense non-aqueous petroleum liquids (DNAPL) are likely to sink to the bottom of any well whereas light non-aqueous petroleum liquids (LNAPL) will float on the top of the water column. Similarly, due to density contrast and/or residence times contaminated water high in salts or metals entering the water column of a monitoring well along a fracture set at depth may rise or fall below the depth of ingress; failure to sample at the point of ingress may result in obtaining a water sample that is not representative of water quality with respect to contaminant concentration at the point of ingress due to in-borehole dilution. Selection of sampling depth should therefore be informed from detailed understanding of the conceptual site model which itself could be better improved by the use of down-the-hole geophysical and physiochemical logging prior to sampling. Low-flow sampling over bailing is recommended to ensure that physiochemical continuity is attained prior to sampling. However, there are depth limitations associated with this technique (typically 8 to 10 m bgl) and related to the use of small diameter pumps which have limited capacity in overcoming head. Physiochemical parameters should be measured at the time of sampling and as a minimum include: EC, pH, TDS, DO, ORP, and Salinity. Further, the type of equipment used to obtain the measurements should be stated in the report along with confirmation of calibration time and date for the equipment.

Regardless of the potential contaminants of concern, the author recommends that during initial sampling and chemical testing a full-suite of chemical analysis be undertaken to establish baseline conditions.

Such a suite should include:

Physical Constituents

- pH, Electrical Conductivity (EC), Dissolved Solids

Hydrocarbons

- MTBE; TAME; Benzene; Toluene; Ethyl Benzene; Xylenes;1,3,5 trimethylbenzene;1,2,4 trimethylbenzene; Naphthalene; GRO C6-C10; DRO C10-C14; DRO C14-C15; DRO C15-C40

General

- Total Alkalinity as $CaCO_3$, Total Hardness as $CaCO_3$, Fluoride (F), Sodium (Na), Potassium (K), Chloride (Cl), Nitrite (NO_2), Nitrate (NO_3), Sulphate (SO_4), Calcium (Ca), Magnesium (Mg), Ammonia as N

Metals

- Aluminium (Al), Arsenic (As), Barium (Ba), Beryllium (Be), Boron (B), Bromide (Br), Cadmium (Cd), Caesium (Cs), Chromium (Cr), Cobalt (Co), Copper (Cu), Iron (Fe), Lead (Pb), Lithium (Li), Manganese (Mn), Mercury (Hg), Molybdenum (Mo), Nickel (Ni), Selenium (Se), Silver (Ag), Strontium (Sr), Tellurium (Te), Thallium (Tl), Tin (Sn), Titanium (Ti), Tungsten (W), Uranium (U), Vanadium (V)

Other depending upon site history

- VOC’s, SVOC’s, phenols, PAH.

After review of the initial full suite of data and with consideration provided to the contaminants of concern likely associated with the activities undertaken on site the consultant may propose to reduce the suite of analysis.

Water quality type should then be mapped across the site using standard methods of typing including piper diagrams etc. Determination of contaminant location can then be determined through mapping and contouring of water type and concentrations using the appropriate interpolation method.

STEP 8. Aquifer Testing

Aquifer tests can be undertaken to determine aquifer properties and the depth of fractures sets along which preferential flow be occur. Although multiple tests in different strata are better and provide greater confidence with respect to determination of aquifer properties the author recognises the high cost of undertaking such tests. Therefore, for initial design purposes the author proposes that at least one aquifer test per geological strata or geological structure be undertaken. Wherever possible a secondary monitoring borehole should be located in order to aid with interpretation of the aquifer test analysis. Additional testing can then be undertaken to improve upon conceptual site understanding.

A tracer test should be undertaken to determine the pathways which groundwater and or contaminants may migrate within the sub-surface. The work undertaken by the author did not require a tracer test to be undertaken as the contaminants of concern acted in a similar manner as tracers and the author was able to determine the presence of structures and contaminants using ERT geophysical methods. However, tracer tests can also be undertaken to improve understanding of effective porosity and therefore time period for which contamination may continue to flow. The choice of tracer may depend upon ground conditions present but may include anything from a coloured dye, through to addition and salts and possibly radio-nuclide tracers.

STEP 9. Determination of Remediation Drivers

Step 1 to 8 described the process of identification of in-situ conditions and determination of the site conceptual model whereas Step 9 to 12 describe that required to inform the development of a remedial strategy. The first step in developing the remedial strategy is to determine the main drivers for the proposed remedial activity. Typically, geo-environmental consultants become involved with sites when there is either a) a proposed transaction associated with sale or purchase of a site; or b) when an issue of regulatory non-compliance with respect to discharge or pollution has been identified. The drivers in such instances may vary. It is therefore important, if not prudent, to identify the drivers for the development of a remedial strategy. Identification of the main drivers can be determined in a mathematically robust manner by undertaking an AHT assessment. The AHT assessment represents a mathematical tool which compares the various drivers against each other to determine the main drivers and which removes subjectivity from the equation. Within a mixed population, there are likely to be differing drivers for different groupings of people – detailed assessment of the data sets can be undertaken to determine the main drivers for various population sets. By using a technique such an AHT assessment support is provided for the development of a remedial strategy which is both scientifically defensible and supported by the population being served. Further, presentation of an AHT assessment may actually result in stakeholders achieving greater confidence in the remedial strategy being developed. If the drivers are compliance based targets i.e. meeting particular water quality criteria at point of discharge then this can be easily measured both with respect to quality and the potential financial fine that could be incurred for non-compliance. Measuring success can become a little more complicated and open to interpretation when the drivers are not easily measurable but intangible e.g. public perception. In such an instance, the client may desire to undertake works which are not technically necessary but rather represent over-engineering in order to ensure that there are no negative implications associated with public perception. Such an instance may even occur when a risk assessment determines that there is no active S-P-R and therefore no risk to the receiving environment but to ensure to be “seen to do the right thing” the client may require a degree of remedial activity to be undertaken.

STEP 10. Development of a Remedial Strategy

Once the main drivers have been determined the remedial design consultant may then consider the various technically viable options that are available. Any remedial strategy proposed therefore needs to be shown to work technically e.g. reduction of mass of metal with a water body, and within various determined criteria e.g. reduction in mass of metal within a water body within a period of two-years. Geochemical modelling should be undertaken to determine the potential chemical amendments that could be added to solution to achieve the required end-goal, or other defining criteria. Any remedial strategy developed must be technically viable and supported by calculations to ensure that the various government authorities accept the proposed strategy; otherwise time-delay may be incurred. Development of a remedial strategy should also consider the various costs associated with the strategy and the various options for undertaking treatment on-site, off-site or both, either sequentially or simultaneously. This means undertaking a design that has been considered in accordance with determining the best available techniques not entailing excessive costs a process commonly known as BATNEEC.

STEP 11. Confirming the Remedial Strategy

The proposed remedial strategy should be assessed via either laboratory testing or in-situ field trials. During the testing or trials variations in dosing of amendment can be made to ensure the most appropriate dosing is applied. Indeed, this is necessary to ensure that the effectiveness of the proposed remedial strategy is fully understood and may form part of any approval granted for the proposed remedial activity.

STEP 12. Assessment of the Effectiveness of the Remedial Strategy

Assessment of the effectiveness of the remedial strategy should be undertaken through compliance monitoring and sampling of designated groundwater monitoring wells and sampling points located at points of egress of contaminants along identified structures. The frequency of monitoring will be dependent upon the transmissivity of the sub-strata which may vary as an effect of the remedial activity undertaken, as a minimum however, the author suggests that consideration be given to monthly or quarterly monitoring for a minimum period of one-year to obtain a full set of data across the four seasons. After which, the data should be assess and if remediation goals have not been met then any requirement for extended monitoring should be considered. The suite of chemical analysis chosen should include that specific for the contaminants of concern as well as those required for general water quality criteria.

8.1.2 Reporting

As a minimum the factual and interpretative reporting should include the following components:

Factual Reporting

- Site location drawing and sampling location plans.
- Borehole drilling logs.

- Description of sampling techniques and equipment utilised.
- Surface water quality data.
- Groundwater quality data.
- Groundwater level data and description of any pumps being utilised.
- Topographical elevations for site locations and monitoring wells.
- Pumping test equipment and data.

Interpretative Reporting

- Identification of the source of contamination.
- Source concentration of contaminants.
- Description of geological, hydrogeological, hydrology and topographical setting.
- Determination of groundwater flow direction.
- Determination of water type distribution across the site.
- The area of influence from test pumping and estimation of aquifer properties.
- Confirmation as to whether geological structures represent a pathway or barrier (or both) for the migration of contamination.
- Updated Conceptual Site Model.
- Screening of chemical test data.
- Source-Pathway-Receptor model.
- Risk Assessment including data obtained from the source area.

8.2 Discussion

Review of available technology associated with the remediation of groundwater impacted by low pH and elevated manganese concentrations has been heavily informed by surface water treatment of mine waters prior to discharge. However, available information indicates that for this site in-situ remediation would be achieved by the addition of a chemical amendment that acts to raise redox potential and pH to create suitable conditions for the precipitation of manganese from solution. The addition of particular amendments can determine which precipitates of manganese will come out of solution e.g. oxides, hydroxides or carbonates. For this assessment the author has proposed that CaO be added to result in an increase in pH and provide sufficient availability of alkalinity to allow for the precipitation of result in precipitation of rhodochrosite ($MnCO_3$).

With all methods there remains potential for armouring to occur along fracture sets possibly reducing the effective fracture width and therefore reducing hydraulic conductivity along the fractures sets. This could have relevance when assessing the overall residence time associated with contaminants leaving site. Should armouring through deposition occur in the near-vicinity of the perimeter and should hydraulic conductivity be reduced then this will presumably increase the contact time available for the applied alkalinity to further reduce the contaminant load leaving site.

CHAPTER 9:
CONCLUSIONS

Elevated concentrations of manganese and sulphate and low pH values have been identified as being present in groundwater on site. It has been shown that an active source-pathway-receptor model exists and that elevated concentrations of manganese and low pH water may negatively impact upon water quality of the Crocodile River. The geophysical survey and review of groundwater quality from monitoring boreholes has allowed the locations and sizes of plumes of contamination groundwater to be determined. Knowledge of the location of the plumes has allowed the remediation plan to be focussed upon areas of concern. Precipitates of manganese and sulphate have been identified in soils immediately adjacent to the Crocodile River at the points where geological structures in connectively with the site outcrop.

An analytical hierarchy assessment technique was undertaken which determined that the main drivers for remediation were timeframes and reduction in liability. As such a remediation strategy has been developed that involves chemical dosing to neutralise low pH and cause on-site precipitation of manganese as rondochrosite ($MnCO_3$).

This proposed remedial strategy involving in-situ neutralisation is technically strong and represents a major improvement upon the original proposal of a shallow seepage water capture trench along the northern boundary of the site. The original proposal would not have worked as the geotechnical work has shown that it would not be readily possible to construct a trench to the required depth and the geophysical work has shown that it was not necessary to construct a trench along the full length of the northern boundary anyway as the contamination was localised to particular fractures zones. Furthermore, without active on-site remediation the main remediation drivers would not have been accommodated and it is estimated that it would take between 8 and 32 years for contaminant concentration in groundwater to reduce to acceptable levels with no substantial reduction in liability being achieved.

The work undertaken by the author has been successful in showing how gaining a detailed understanding of site specific conditions and developing a detailed conceptual site model can influence and allow the user to develop an appropriate remedial strategy for a contaminated industrial or commercial site impacted by contaminated groundwater within a shallow weathered/fractured phreatic aquifer.

9.1 UPDATED CONCEPTUAL SITE MODEL (JANUARY 2015)

The multi-technique site investigation undertaken for this site has allowed for an updated site conceptual model to be developed and which is described in the following text.

The site is a former industrial site in Nelspruit that operated from the 1980's and manufactured batteries using the electrolytic manganese dioxide process. As a result of leakages from wet-process section of the site (cell houses) low pH process water and various contaminants of concern including manganese and sulphate entered the sub-surface. The site is underlain by granitic gneiss that is weathered and fractured to approximately 15 mbgl and two linear fracture zones bisect the site in a generally northerly direction. Groundwater flow direction is in a northerly direction with recharge surcharge by an unlined canal forming the southern boundary of the site. The granitic gneiss has been determined to possess hydraulic conductivity of between 10^{-2} and 10^{-3} m/day within the weathered/fractured zones. The underlying fresh rock is estimated to have a hydraulic conductivity of between 10^{-7} and 10^{-9} m/day thereby limiting the depth to which contamination may migrate. The Crocodile River is located approximately 200 m north of the site and the linear fracture zones provide connectivity between the site and the river. The various contaminants of concern have been shown to be migrating in a northerly direction along the linear fracture zones and entering the Crocodile River.

The concentration of manganese in on-site groundwater varies between 0.005 mg/l and 2,406 mg/l. Sulphate at concentration in excess of 8,000 mg/l is leaving the site via the northern boundary. In addition to facilitating dissolve phase manganese as Mn^{2+} some other metals are also present in dissolved form at slightly elevated levels including Al, Cd, Cr, Ni and Se.

Recharging groundwater (and canal water) from the south is assisting in neutralising low pH waters particularly in the area to the southeast of the site where previously neutralised sludge ("Greenfill") had been placed in the area now occupied by the football pitch. Neutralisation of low pH groundwater as a result of seepage through the neutralised spoil has allowed for the precipitation of manganese from solution as rhodochrosite ($MnCO_3$) in the eastern most fracture zone (Zone B) (Figure 4-8). However, elevated manganese and sulphate and low pH remain present on site and along the perimeter boundary. No natural attenuation of low pH, manganese and sulphate elevated groundwater is occurring elsewhere on the site.

It is estimated that approximately 5 to 8 kg/day of manganese and 35 to 58 kg/day of sulphate is leaving site along the northern site boundary and reaching the Crocodile River and will continue to do so for at least 8 years after operations on site cease but possible up to 32 years although at much reduced loadings. In situ treatment on-site will reduce the impact upon the Crocodile River to that contamination that has already left site and reduce the period of impact to between 3 to 12 years.

A risk assessment has been undertaken and an active source-pathway-receptor model has been defined with elevated concentrations of site based manganese having been shown to be in connectivity with a shallow unconfirmed aquifer and entering the Crocodile River. Further, the concentrations of manganese have been shown to be elevated against various water quality screening criteria and therefore represent a risk to the aquatic environment. Thus the value of the conceptual site model is restated.

9.2 PROPOSED REMEDIATION STRATEGY

Initial geotechnical modelling determined that the addition of limestone or lime to the impacted groundwater will result in the neutralisation of acidic groundwater. A detailed remediation action plan has therefore been developed that is based upon chemical dosing using hydrated lime to neutralise low pH waters on site to facilitate the precipitation from solution of dissolved phase manganese as rhodochrosite ($MnCO_3$).

The proposed groundwater remediation has been designed to target areas identified as Zone A and Zone B on Figure 4-8. After demolition of surface infrastructure then across these two zones a series of 72 shallow small diameter boreholes should be drilled to depths of 15 mbgl on a 20 m centre to centre spacing. The wells will be utilised for the injection of hydrated lime. This alkaline dosing with neutralise pH and lead to the precipitation of manganese from solution. In addition, up to 35 shallow injection wells similarly drilled to 15 mbgl should be constructed along the northern boundary of the site within Zone A and Zone B. These perimeter wells will be injected with hydrated lime to neutralise any acidic groundwater's that manage to pass beyond the main treatment zone. The amount of saturated $Ca(OH)_2$ solution required to achieve an effective lime rate has been estimated at 50t/ha. Lime will be mixed on site until saturated and then injected into the dosing wells to a maximum volume of 4 m^3 per injection well in any day before moving onto the next injection well. This equates to 6.2 kg/m^3 of CaO injected per well per day or approximately 14 tonnes per month. The area for treatment has been estimated (2 x 100 m x 100 m) at 2 hectares and therefore based upon an estimate of 50 tonnes per hectare of CaO the remediation activity is anticipated to take approximately 7 months from commencement of injection. Including the pre-drilling the entire remediation is expected to take up to 9 months. The remediation will be considered to be complete when the concentrations of manganese at the site perimeter are below surface water quality guidelines for the protection of ecological health and when pH at the perimeter is between 6 and 8.

9.3 RECOMMENDATIONS

The author recommends that monthly groundwater and water quality monitoring be undertaken for the duration of the remedial action and for a period of 1 year after completion and then subject to satisfactory improvement consideration could potentially be given to bi-annually for a period of 5 years.

9.3.1 Water Quality Monitoring Locations

It is proposed that groundwater monitoring be undertaken on a monthly basis at established groundwater monitoring points along the northern boundary of the site and within the zones of identified contamination. The co-ordinates for the proposed monitoring points and the appropriate monitoring well designations are provided in Table 9-1.

Table 9-1: Groundwater Monitoring Points

Monitoring Point	Latitude	Longitude
GAA001-S	-25.45625	30.98222
GAA001-D	-25.45616	30.98219
GAA002-S	-25.45719	30.98532
GAA002-D	-25.45716	30.9852
GAA003-D	-25.45759	30.98566
GAA004-S	-25.45919	30.98733
GAA004-D	-25.45916	30.98721
GAA007-S	-25.45859	30.98673
GAA007-D	-25.45855	30.98668
GAA008-S	-25.45857	30.98644
GAA009-S	-25.45923	30.98592
GAA010-S	-25.45789	30.98501
GAA011-S	-25.45854	30.98502
BH1	-25.45836	30.98669
BH3	-25.45854	30.98668
P1-S	-25.45636	30.98171
P1-D	-25.45645	30.98173

It is also proposed that surface water quality monitoring be undertaken on a monthly basis at pre-sampled monitoring points within the Crocodile River beyond the northern site boundary as identified in Table 9-2.

Table 9-2: Surface Water Monitoring Points

Monitoring Point	Latitude	Longitude
GACROC01	-25.458300	30.990200
GACROC02	-25.456900	30.988100
GACROC03	-25.454500	30.986400
GACROC04	-25.454100	30.986100

9.3.2 Monitoring Methods

The proposed suite of analysis for surface and groundwater monitoring is presented in Table 9-3.

Table 9-3: Testing Suite

Timing	Testing and Analysis Suite
Field Measurements at time of sampling	pH, ORP, DO, TDS, EC
Laboratory Analysis	pH, ORP, DO, TDS, EC Cl, Mg, K, Na, Ca, SO_4, NO_3, NH_3, Total Alkalinity Mn, Al, Fe, Cr (3+ and 6+), Cd, F, Li, Pb

9.3.3 Further improvements to site understanding

Undertaking off-site geophysical surveys on the bush land between the northern boundary of the site and the Crocodile River would aid with defining the location of the fracture zones in connectivity with the site and the Crocodile River. This would improve the conceptual site model and identify additional locations for monitoring water quality and groundwater improvement during the remedial activity.

A detailed quantitative risk assessment (DQRA) could be undertaken to consider the effects of dilution of contaminants within the Crocodile River and determine if there is significant risk posed to down-gradient ecological receptors. An understanding of site specific target levels that would be gained from undertaking the DQRA would aid in establishing the point in time at which remediation could be considered to have been shown to be successful and remedial action and monitoring requirements can cease.

Development of a rehabilitation plan for the site included a public participation process which was undertaken by others. The author considers that undertaking an analytical hierarchy technique assessment with members of the public and with regard to determining their main drivers for remediation would have further improved the overall understanding of what drives the development of remedial strategies.

It was noted that with respect to soil, manganese accumulates in the subsoil rather than on the soil surface (ASTDT, 2000). The soil samples obtained off-site were generally from the very near surface (0 to 0.25 mbgl) due to a limited degree of soil cover overlying rock. It is possible that area of soils and vegetation accumulation within cracks and crevices in the surrounding strata may contain more elevated concentration of manganese. If future off-site works were to be undertaken then any sampling protocol should be designed to located areas of vegetative and soil accumulation and obtain suitable samples of soil for chemical analysis. The results should then be compared to the existing data set to determine if the original data remains representative of the off-site condition.

9.3.4 Closing

All the knowledge gained from this site investigation has been used to develop a guideline proposal for the future development of site investigations and remediation designs in South Africa specifically for contamination of shallow groundwater in weathered/fractured rock aquifers and which has been presented and discussed in Chapter 8. The author considers that the guideline provided therein should be followed by others when conducting future site investigations in South Africa associated with assessment of groundwater contamination where shallow weathered/fractured rock aquifers are present on site.

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APPENDIX A

POINT LOAD TESTING RESULTS

Table A-1: Point Load Testing for Borehole BH1 (Modified from Hughes, 2014b)

From (mbgl)	To (mbgl)	A/D	Height (mm)	Width (mm)	Estimated UCS (kN)*	Rock Strength Assessment	Notes
2.42	2.55	D		50	98	Strong	
2.42	2.55	A	48		89	Strong	
2.80	2.90	D		50	>250	Extremely Strong	
2.80	2.90	A	70		n/a	n/a	Incorrect Failure
2.96	3.04	D		50	134	Very Strong	
3.76	3.88	D		50	>250	Extremely Strong	Failure along joint @ 60 degrees
3.88	4.23	D		50	>250	Extremely Strong	
3.88	4.23	A	66		138	Very Strong	
3.88	4.23	D		50	>250	Extremely Strong	
3.88	4.23	D		50	>250	Extremely Strong	
3.88	4.23	D		50	>250	Extremely Strong	
3.88	4.23	A	58		>250	Extremely Strong	
6.00	6.23	D		50	>250	Extremely Strong	
6.00	6.23	D		50	>250	Extremely Strong	
6.00	6.23	D	52		>250	Extremely Strong	
6.00	6.23	A		50	>250	Extremely Strong	

*UCS=24*Is(50)

Table A-2: Point Load Testing for Borehole BH2 (Modified from Hughes, 2014b)

From (mbgl)	To (mbgl)	A/D	Height (mm)	Width (mm)	Estimated UCS (kN)*	Rock Strength Assessment	Notes
5.03	5.15	D		50	144	Very Strong	
5.03	5.15	D		50	162	Very Strong	
5.03	5.15	A	54		140	Very Strong	
6.95	7.12	D		50	54	Strong	
6.95	7.12	D		50	48	Moderate Strong	
8.12	8.32	D		50	12	Weak	Failure along vertical fracture
8.12	8.32	D		50	114	Very Strong	
8.92	9.22	D		50	134	Very Strong	
8.92	9.22	D		50	64	Strong	Failure along vertical fracture
8.92	9.22	D		50	118	Very Strong	
10.00	10.26	D		50	100	Very Strong	
8.92	9.22	D		50	134	Very Strong	
10.00	10.26	A	51		37	Moderate Strong	Failure along fracture
11.20	12.00	D		50	>250	Extremely Strong	
11.20	12.00	A	60		n/a	n/a	Incorrect Failure
12.00	12.38	D		50	>250	Extremely Strong	
12.00	12.38	A	67		>250	Extremely Strong	

*UCS=24*Is(50)

Table A-3: Point Load Testing for Borehole BH3 (Modified from Hughes, 2014b)

From (mbgl)	**To (mbgl)**	**A/D**	**Height (mm)**	**Width (mm)**	**Estimated UCS (kN)***	**Rock Strength Assessment**	**Notes**
5.50	5.60	D		50	42	Moderate Strong	
5.50	5.60	A	60		40	Moderate Strong	
5.60	5.70	D		50	34	Moderate Strong	
6.80	6.95	D		50	36	Moderate Strong	
6.80	6.95	A	58		36	Moderate Strong	
7.00	7.24	D			>250	Extremely Strong	
7.00	7.24	D			>250	Extremely Strong	
7.00	7.24	D			240	Very Strong	
7.00	7.24	D			203	Very Strong	Failure along a joint @ 60 degrees
7.00	7.24	A	65		>250	Extremely Strong	
7.00	7.24	A	75		>250	Extremely Strong	
7.24	7.32	A	66		n/a	n/a	Incorrect Failure
7.24	7.32	D		50	>250	Extremely Strong	
7.32	7.40	D		50	>250	Extremely Strong	
7.32	7.40	A	65		>250	Extremely Strong	
8.00	8.18	D		50	>250	Extremely Strong	
8.00	8.18	D		50	>250	Extremely Strong	
8.00	8.18	A	63		>250	Extremely Strong	
8.70	8.80	D		50	>250	Extremely Strong	
8.70	8.80	A	55		172	Very Strong	Failure along a joint @ 60 degrees
9.58	9.68	D		50	>250	Extremely Strong	
13.90	14.05	D		50	>250	Extremely Strong	

*UCS=24*Is(50)