Trace metal contamination of soil and groundwater in the Rietvlei Catchment, Cape Town

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Dissertation submitted in fulfilment of the requirements for the degree *Masters of Science in Environmental Sciences with Hydrology and Geohydrology* at the North-West University

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Graduation July 2019

24103500

Acknowledgements

The past two years has been such a ride. The topic, goals and intentions of this research shifted countless times. It taught me so much; not only about geohydrology but about myself. I have learned to allow situations and things to unfold and flow as they should. I was working harder than before while focussing on multiple other projects at once. I am so grateful for being granted this opportunity.

This degree is dedicated to my Grandfather, ***Chrisjan van Wyk***. Jack and ***Master*** of All Trades.

I would like to thank the following individuals for their support and guidance throughout this project:

First of all, I want to give all of my grace and appreciation to my God, the Universe. I am so thankful for the abilities I have, the continuous strength, discipline and success I gain through His power.

To Prof Ingrid; You came on board for the last six months of this project as my supervisor and I really enjoyed working with you. I come from a geology background but I learned so much about hydrology. A really big thank you for the advice AND patience. You gave this project direction.

Thank you Jaco Koch for being my co-supervisor, you helped save this project.

To Dr Gaathier Mahed; thank you for this opportunity. I really appreciate everything you have done for me while you were here, everything you have taught me. I have gained so many life lessons from you. You are the coolest lecturer, obviously after Sascha.

Sascha, you are the best person and friend. Thank you for always helping me out when I’m stuck. I appreciate you so much. Blessings on blessings on blessings.

Everyone who was in charge of the collection and processing of the data.

Last but not least, my family. My parents who taught me to always give my best, even when it is not as good as the next person’s and to finish proudly. Thank you for teaching me hard work and instilling in me with a strong work ethic. I have the deepest appreciation for your continuous love, belief, encouragement and support throughout my entire life and university career. More Life!

Abstract

Trace metal elements are naturally found in sediments, soils, water and plants. They occur at concentrations less than 100 mg/kg and are more commonly known as heavy metals. There are a number of anthropogenic sources where TMEs stem from mining and metal extraction, agricultural activities, oil, wood and coal burning, manufacturing, cremation and waste disposal.

Once trace metal elements are introduced into the environment by a specific method, it may move to different environmental components that can be a result of the nature of interactions that occurs in this natural system. Soil possess the ability to bind with various chemicals and contaminants which tends to accumulate in this medium. The movement of TMEs in soil is controlled by soil components, how it interacts with other solid states, environmental factors and its quantities. Trace metal elements can bound or sorb by specific natural substances, which can change the mobility. Sorption specifically plays the main role in controlling transfer, non-polar organic soil compound behaviour and toxicity. All chemical processes are directly and indirectly influenced by the soil solution pH and redox potential and therefore influence TME behaviour in soil. The transport mechanisms of TMEs through soil is an important factor. Topography mainly affects metal mobility and availability in floodplains. TMEs in soil leach into groundwater and generally contains pollutants.

Groundwater resources is a principle origin of water, due to good water quality. It plays a crucial part in aiding the geological environment, sustaining the ecosystem equilibrium and maintaining life. When groundwater has been polluted, it could persist that way for decades or even centuries due to the slow-going natural processes of through-flushing. Ground- and surface water bodies are linked to each other in a majority landscapes.

Rietvlei is a located about 5 km on the north side of Cape Town. To establish the spatial distribution extent of TMEs, Visible and Near-Infrared Reflectance Spectroscopy have been used. This research aims to establish the TMEs found within the soils and groundwater in the Rietvlei area and the sub-catchment.

Keywords: environment, transport, chemical processes, pollution, spatial distribution, remote sensing

Opsomming

Spoormetaalelemente (SME) word natuurlik in sedimente, grond, water en plante aangetref. Hulle kom voor by konsentrasies kleiner as 100 mg/kg en staan meer algemeen bekend as swaar metale. Daar is 'n aantal antropogeniese bronne waar SME stam, insluitend mynbou- en metaalontginning, landbouaktiwiteite, olie-, hout- en steenkoolbrand, vervaardiging, verassing en afvalverwydering.

Sodra spoormetaalelemente deur 'n spesifieke metode in die omgewing vrygestel word, kan dit na verskillende omgewingskomponente beweeg, wat die gevolg kan wees van die aard van interaksies wat in hierdie natuurlike stelsel voorkom. Grond besit die vermoë om te bind met verskeie chemikalieë en kontaminante wat geneig is om in hierdie medium op te bou. Die beweging van SME’s in grond word beheer deur grondkomponente, hoe dit fungeer in wisselwerking met ander vaste state, omgewingsfaktore en die hoeveelhede daarvan. Spoormetaalelemente kan gebind of sorbeer word deur spesifieke natuurlike stowwe, wat die mobiliteit kan verander. Sorpsie speel spesifiek die hoofrol in die beheer van oordrag, nie-polêre organiese grondverbandgedrag en toksisiteit. Alle chemiese prosesse word direk en indirek beïnvloed deur die pH-en redokspotensiaal van die grondoplossing en beïnvloed dus TME-gedrag in grond. Die vervoermeganismes van TME's deur grond is 'n belangrike faktor. Topografie beïnvloed hoofsaaklik metaalmobiliteit en beskikbaarheid in vloedvlaktes. TME's in grond lek in grondwater en bevat gewoonlik besoedelingstowwe.

Grondwaterbronne is 'n oorsprong van water, as gevolg van goeie watergehalte. Dit speel 'n belangrike rol in die ondersteuning van die geologiese omgewing, die handhawing van die ekosisteemewewig en lewe. As grondwater besoedel is, kan dit vir dekades of selfs eeue voortduur as gevolg van die stadige natuurlike prosesse van deurspoeling. Grond- en oppervlakwaterliggame word in 'n meerderheidslandskap met mekaar verbind.

Rietvlei is ongeveer vyf km noord van Kaapstad geleë. Om die ruimtelike verspreidingsgraad van TME's te bepaal, is VNIRS gebruik. Hierdie navorsing het ten doel om die TME's in die grond en grondwater in die Rietvlei-omgewing en die subopvanggebied te vestig.

Sleutelwoorde: omgewing, vervoer, chemiese prosesse, besoedeling, ruimtelike verspreiding, afstandswaarneming

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List of Abbreviations

Abbreviation	Name
pH	A scale of acidity from 0 to 14
Al/Al^{3+}	Aluminium
$–NH_2$	Amine
Sb	Antimony
As	Arsenic
Br	Bromine
Cd	Cadmium
Ca	Calcium
$CaCO_3$	Calcium carbonate
CCME	Canadian Council of Ministers of the Environment Quality Guidelines
CO^{2-}	Carbon dioxide
CO_3	Carbonate
–COOH	Carboxylic acid
Cl^-	Chloride
Cr/ Cr(III)/ Cr(VI)	Chromium
CoCT	City of Cape Town
Co	Cobalt
R^2	Coefficient of determination
Cu	Copper
CRD	Cumulative Rainfall Departure
d	day
δ	Delta
DEM	Digital Elevation Model
DWAF	Department of Water Affairs and Forestry
EC	Electrical conductivity
EARTH	Extended model for Aquifer Recharge and Soil Moisture Transport through the unsaturated Hardrock
ICP-MS	Inductively coupled plasma – mass spectrometer
Fe/Fe^{3+}	Iron
FeO	Iron oxide
GIS	Geographic Information System
GMWL	Global Meteoric Water Line
FeOOH	Goethite

Abbreviation	**Name**
ha	Hectares
OH	Hydroxide
H^+	Hydrogen
δ^2H	Hydrogen isotope
LIMS	Laboratory Information Management System
Pb	Lead
LPV	Little Princess Vlei
mamsl	Metres above mean sea level
Mg	Magnesium
Mn	Manganese
Hg	Mercury
MWL	Meteoric water line
Mg/l	Milligram per litre
Mm/a	millimetre per annum
Mo	Molybdenum
nm	Nanometer
Ni	Nickel
NO^{-3}	Nitrate
NDVI	Normalized Difference Vegetation Index
NE	North East
N/A	Not Applicable
OA-ICOS	Off-Axis Integrated Cavity Output Spectroscopy
OLI	Operational Land Imager
$\delta^{18}O$	Oxygen isotope
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
K^+	Potassium
WWTP	Potsdam Waste Water Treatment Plant
Eh	redox potential
Rb	Rubidium
SVF	Saturated Volume Fluctuation
Se	Selenium
SEP	Sequential Extraction Procedures
Na/Na^+	Sodium
SW	south-west

Abbreviation	Name
SLAP	Standard Light Antarctic Precipitation
Sr	Strontium
S^{2-}	Sulphide
TIRS	Thermal Infrared Sensor
–SH	Thiol
TDS	Total Dissolved Solids
TE/TMEs	Trace elements/ trace metal elements
USEPA	United States Environmental Protection Agency
VNIRS	Visible and Near-Infrared Reflectance Spectroscopy
–SH	Thiol
H_2O	Water
WHO	World Health Organization
Zn	Zinc

1 INTRODUCTION

1.1 Background

Water is essential to help all organism life and that it is usually obtained from reservoirs like lakes, rivers, streams, and groundwater. Water has the ability to for example “dissolve, absorb, adsorb or suspend different compounds” because of its polarity and hydrogen bonds (World Health Organization (WHO), 2007). Groundwater and soil contamination is seen as a significant environmental issue (Cundy *et al*., 2008). Aside from the various contaminants, trace metals are particularly concerning due to their toxicity (Marcovecchio *et al*., 2007). Trace metal elements (TMEs) weighs between 63.55 and 200.59 mg and a specific gravity higher than 4.0 which is about 5 times that of water (Momodu & Anyakora, 2010). They are present in dissolved, colloidal stages and in the form of minute separate particles in water (Adepoju-Bello *et al*., 2009). Trace metal elements occur in water either naturally or by anthropogenic forces (Marcovecchio *et al*., 2007).

Calcium, magnesium, potassium, and sodium are vital to prolong life and, therefore, needed for basic biological activities. Some of the metals required for enzyme functions include iron, copper, zinc, manganese, molybdenum, and cobalt (Adepoju-Bello *et al*., 2009), but in a surplus, it can be toxic. Trace metal elements, when ingested in an excess concentration, can result in health impacts coupled with various symptoms (Khan *et al*., 2008). They are toxic because they structure networks with proteins, where carboxylic acid (–COOH), amine ($-NH_2$), and thiol (–SH) groups are present (Momodu & Anyakora, 2010). It results in the malfunctioning, in some cases even the death of the cell because the altered biological unit cease to work. This toxin has the ability to form radicals, which are harmful chemicals responsible for biological molecules oxidation (Momodu & Anyakora, 2010).

Diagomanolin *et al*. (2004) stated that environmental degradation is the result of elevated consumption and exploitation of raw materials, and exponential population growth. Tong and Che Lam (2000) and Sanderson *et al*. (2002) put into words that developing countries, such as South Africa, with rapid industrialization and urbanization, are responsible for the high level of environmental pollution and consequently metal enrichment of soil. Brady and Weil (2008) defined soil as organic material and unconsolidated minerals, which is an ecosystem component and a plant growth medium. Heavy metals accumulate in topsoil from atmospheric deposition by interception, sedimentation, and impaction because several industrial and municipal wastes are deposited on it. It mostly contains metals (Phillips, 1981; 1999; Yusuf *et al*., 2003). Odjegba and Sadiq, (2002), Merkl *et al*., (2005), Osuji *et al*. (2005) and Nabulu *et al*. (2006) all stated that unrefined oil and its secondary products are dumped on roads, near soils or in water. Clevers *et al*. (2004) stated that remote sensing is useful to observe and track TME contamination of soils.

Groundwater abstraction is carried out for various uses like water supply, farming, and industrial activities (Foster *et al*., 2007). The evaluation of groundwater quality is universally aimed at parameters that have an influence on the pumped groundwater to determine whether it is safe for human consumption, and, agricultural and industrial use (WHO, 2007). The main intention of a groundwater quality evaluation plan is to derive a thorough understanding of the groundwater quality spread in an area, and the natural or anthropogenic evolution thereof (Wilkinson & Edworthy, 1981).

1.2 Problem statement

Trace metal elements are found in multiple mediums. The TMEs that are found in the soil have the ability to contaminate the groundwater. This may lead to the contamination of the groundwater which consequently adversely impacts the water quality.

1.3 Hypothesis

The soil and groundwater of the Rietvlei catchment is contaminated by certain sources found within the vicinity of the area. There is a correlation between the excessive TMEs that are found in the two mediums (soil and groundwater) that arise from the responsible sources. The contaminants will move from the sources, polluting the soil and subsequently the groundwater.

1.4 Aims and objectives

- To determine spatial distribution of TMEs, present in the soils through analysing a Landsat 8 hyperspectral image.
- To determine the groundwater quality of the eight boreholes in the Rietvlei and the sub-catchment of the quaternary catchment.
- To simulate the movement of the TMEs in the groundwater systems.
- Develop a mitigation plan.

1.5 Layout of dissertation

This dissertation provides an overview of TMEs found in the soil and groundwater. In addition, a methodology is developed that can be used to assess as well as rehabilitate affected area. The layout of the dissertation is as follows:

- Chapter 2 – Literature review
  - Properties and behaviour of the TMEs.
  - Mediums wherein TMEs occur.
  - A review of investigations already conducted relating to the mobility and transportation of TMEs in soil and groundwater.
- Chapter 3 – Study area
  - A review of the (sub)catchment, climate, topography, vegetation, soils, geology, hydrology, geohydrology and the possible pollution sources.
- Chapter 4 – Methodology
  - Data collection and analysis of groundwater.
  - Water quality parameters like pH, TDS and TME content.
  - Hyperspectral analysis of TMEs.
  - Stable isotope examination was done to discover the groundwater composition.
  - Numerical modelling of groundwater of the study area and sub-catchment was done to determine the groundwater flow.
- Chapter 5 – Results and discussion
  - Hyperspectral analysis of the soil to determine TME content.
  - Water quality
  - Data evaluation and interpretation of information obtained through the MODFLOW software to determine contamination results.

- Chapter 7 – Conclusion and recommendations
    - Conclusions with respect to the hypothesis.
    - Recommendations based on results, remediation and for future studies on how to improve on this study.

2 LITERATURE REVIEW

2.1 Trace metal elements

The chemical elements in soil are known as trace elements (TEs) since they occur at concentrations that are less than 100 mg/kg and have a density exceeding 6 g/cm (Hooda, 2010). Synonyms for trace elements are 'toxic metals', TMEs or '*heavy metals*', although none of these terms are entirely acceptable from a chemical viewpoint. Not all TEs are metals. Trace metal elements have the ability to interact with the natural complexes and change shape (Hooda, 2010).

Trace metal elements are found everywhere; in sediments, soils, water and plants. Once trace metal elements are introduced into a natural medium in a specific way, they can move to different part of the ecosystem (Sherene, 2010). Some examples of natural sources are vegetation, sea spray, lake and river sediments. Anthropogenic sources include mineral extraction, mining, coal burning and industrial activities. Assigning the source of a metal to a certain area is troublesome. Trace elements like Bromine (Br), Selenium (Se) and Antimony (Sb) are usually from volcanic activity. Zinc (Zn) can be from fertiliser production, a power station and vegetation, but it is dependent on the location (Nagajyoti *et al*., 2010). The contribution of TMEs in the biosphere have grown due to industrialisation and urbanisation. Trace metal elements are more available in terrestrial ecosystems and less in the atmosphere (Nagajyoti *et al*., 2010).

The metal contaminants most commonly associated with water, according to Wright and Welbourne (2002) include: Zinc (Zn), Copper (Cu), Aluminium (Al), Iron (Fe), Nickel (Ni), Manganese (Mn) and Lead (Pb).

According to Hoefs (2009); Halder *et al*. (2013) and Petrisic *et al*. (2013), new technologies, like environmental modelling, GIS (Geographic Information System) and isotope tracing instruments are applied more to understand metal pollution and migration.

2.1.1 Trace metal elements in soil

Contaminants gather in soil because it possesses the capacity to attach to a variety of substances with certain forces. The substances have the ability to occur in many configurations in soil (Nagajyoti *et al*., 2010). Trace metal element movement in soil is controlled via soil components, how it interacts with other solid states, environmental factors and its quantity (Nkobane, 2014). The accumulation of TMEs in soils is unsettling due to the negative impacts that it has on crop growth due to phyto-toxicity, soil organism health and food safety (Nagajyoti *et al*., 2010).

Gambrell (1994) gave a list of common chemical forms of elements in soils and sediments:

- "*water-soluble metals, as free ions, inorganic or organic complexes;*
- *exchangeable metals;*
- *metals precipitated as inorganic compounds, including insoluble sulphides;*
- *metals complexed with large molecular-weight humic materials;*
- *metals adsorbed or occluded to precipitated hydrous oxides;*
- *metals bound within the crystalline lattice structure of primary minerals."*

Climate change and anthropogenic impacts mostly change the soil properties. Scientists from different disciplines has investigated acid rain influence on soils and the sorption attributes of soil complexes. Overall, it was found that the ability of binding trace metal elements to soil particles is decreased by acid rain. The impact of acid rain for naturally high acidic or very weak soils is much smaller. The soil matrix complexity makes it difficult to select interactions that mostly subscribe to the adsorption of a particular metal (Dube *et al*., 2001). Wuana and Okieimen (2011) stated when the trace metal elements are in the soil, they are adsorbed by initial reactions which can take minutes to hours, followed by slow adsorption reactions which takes days to years and are redistributed into various chemical forms with varying toxicity bioavailability and mobility. This distribution is governed by trace metal element reactions in soils like

- "*mineral precipitation and dissolution,*
- *ion exchange, adsorption, and desorption,*
- *aqueous complexation,*
- *biological immobilisation and mobilisation,*

- *plant uptake.”*

2.1.2 Trace metal elements in ground- and surface water

Klavinš *et al*. (2000) and Li and Zhang (2010) both noted that ground and surface water in agricultural regions in most countries in the world, is at dire risk of metal pollution. According to Smail *et al*. (2012), metals from urban runoff, automobile emissions, and agricultural sources have the ability to migrate to the surface water through rainwater or surface runoff. Bichet *et al*. (2013) stated that the metals can infiltrate into deeper soil horizons, and ultimately groundwater. Trace metals in water-requires monitoring since they cannot decompose and stay available for extended periods (Buschmann *et al*., 2008). The risk of evaluating ecosystem TME contamination of a water body is vital for the management, and therefore, sources need to be identified and, in turn, restrict the possibility for adverse results (Wu *et al*., 2009). Sadler *et al*. (2011) stated that as a result of challenges in incessant metal observing with on-site sampling, there is an important requirement for proper expertise and ways to determine how metals behave in the environment, and predicting how they move and spread in an area. Groundwater becomes acidic due to acid rain and it leads to the mobilisation of TMEs. Trace metal elements are found to accumulate near the acidification front in water bodies (Kjøller *et al*., 2004).

2.1.3 Quantifying the movement of trace metal elements in both groundwater and surface water

Zimmerman and Weindorf (2010) stated that the quantification is usually performed by using mixtures of different yet particular strengths and reactivities to distribute metals from the distinct fractions of the soil that is under investigation. The TMEs present in soils can be determined through single reagent leaching, ion exchange resins, and sequential extraction procedures (SEP).

One SEP and guidelines should be appointed and used across fields. Tessier *et al*. (1979) has adapted the procedure that is widely used. The SEP hypothesis is that the TMEs with the most mobility are eliminated in the first fraction. Tessier *et al*. (1979) listed “*fractions exchangeable, carbonate bound, Fe and Mn oxide bound, organic* *matter bound, and residual*". They are usually as "*exchangeable, weakly absorbed, hydrous-oxide bound, organic bound, and lattice material components*", respectively.

2.2 Mobilisation of trace metal elements

Trace metal elements can bind or sorb to specific natural substances, which can change the mobility. Generally, they can show interaction with specific species and alter the oxidation states and precipitate. Speciation refers to the dissipation of trace metal elements (Hooda, 2010). The speciation is complex and can be understood in various ways and aspects. Chemical speciation is further classed as group, individual and distribution speciation, amongst others. Physical speciation is significant for chemical sorption and migration in soils since it considers different physicochemical shapes of the identical chemical. The transport mechanisms of trace metal elements through soil is an important factor (Hooda, 2010). Table 1 shows transport mechanisms of TMEs.

Atmospheric deposition can also be a contributing factor to soil and surface water contamination. The majority of present environmental levels and sanitation minimums for soils are still grounded on assessing the net trace metal concentrations (Du Liang *et al*., 2008). Net levels are not the only factor to evaluate environmental hazards since it does not show TMEs mobility, reactivity, and/or bioavailability that have the potential to be toxic. The actions of trace metal elements are greatly influenced by their chemical configuration of occurrence (Du Liang *et al*., 2008).

Du Liang *et al.* (2008) stated that topography mainly impacts metal mobility and availability in floodplains. Sorption processes like adsorption/desorption, pH and plant growth, organic matter, salinity, sulphur and carbonates are other process that also have an impact. (Hydr)oxides such as Fe and Mg are considered to be the principle transporters of Cd, Zn and Ni under states containing oxygen, while the organic fraction is significant for Cu (Du Liang *et al*. 2008).

Table 1: The transport mechanism of TMEs in soils

TMEs	Transport mechanism
As	Arsenic mobilisation under flooded situations includes 2 main processes: • Iron(II) oxide (FeO) undergoes reduction and As goes into solution phase; • Arsenate [As(V)] is integrated onto a solid state and undergoes reduction to As(III). As(III) is not absorbed as strongly as As(V) and has a considerable inclination to part into the solution state. (Tufano *et al*., 2008 & LeMonte *et al*., 2017)
Cd (cadmium)	It is held in soils via precipitation and adsorption. Precipitation is the main action, and the anion configuration are PO_4^{3-}, OH^-, CO^{2-}, and S^{2-}, and Cd adsorption on the soil mineral surface can transpire via non-specific and specific processes (Naidu *et al*., 1997 & Holm *et al*., 1996)
Pb	Pb distribution is led by reactions like • *"mineral dissolution and precipitation,* • *adsorption, ion exchange, and desorption,* • *aqueous complexation,* • *mobilisation and biological immobilisation* • *plant uptake."* The distribution and migration of Pb in soils is a result of activities including "*oxidation–reduction reaction, cations' sorption on exchange complex and chelated with organic matter*" (Kushwaha *et al*., 2018; Wuana & Okieimen, 2011)
Cr (chromium)	The Cr weathering mechanism has 2 phases: • From Cr (III) to chromium(III) hydroxide (hydrolysis), • Oxidation to Cr (VI) by manganese oxides (Mills *et al*., 2011; Morrison *et al*., 2009 & Oze *et al*., 2004)
Hg (mercury)	Hg fractions include 3 fractions: • *"mobile mercury,* • *semi-mobile mercury, and* • *non-mobile mercury"* (Han *et al*., 2003; Zhang *et al*., 2015 & Fernández-Martínez *et al*., 2005)

2.2.1 Sorption mechanisms

According to Hooda (2010), *sorption* is a universal term that basically explains a substance separating from another substance. The behaviour of non-polar organic complexes, toxicity and transport is controlled by sorption (An & Huang, 2015). It includes both adsorption and absorption. Adsorption is the activity whereby a lesser element in a solution cling to a hard surface. When a lesser element in a solution transmit into a permeable substance and attaches to the inside of the substance, this process is called absorption. Figure 1 shows the different mechanisms of sorption. There are many different mechanisms that cause elements to be removed from the solution (Hooda, 2010).

Hooda (2010) continued stating that in a more distinct definition, sorption occurs when matter accumulates at a surface without building up a three-dimensional structure. Where precipitation will cause the development of a solid phase whose molecular ordering is three-dimensional. Sorption of an ion may occur. due to three mechanisms:

- "*inner-sphere complexation,*
- *outer-sphere complexation, and*
- *diffusion swarm*".

When there is no water molecule present between a functional group on a solid surface it is termed inner-sphere.

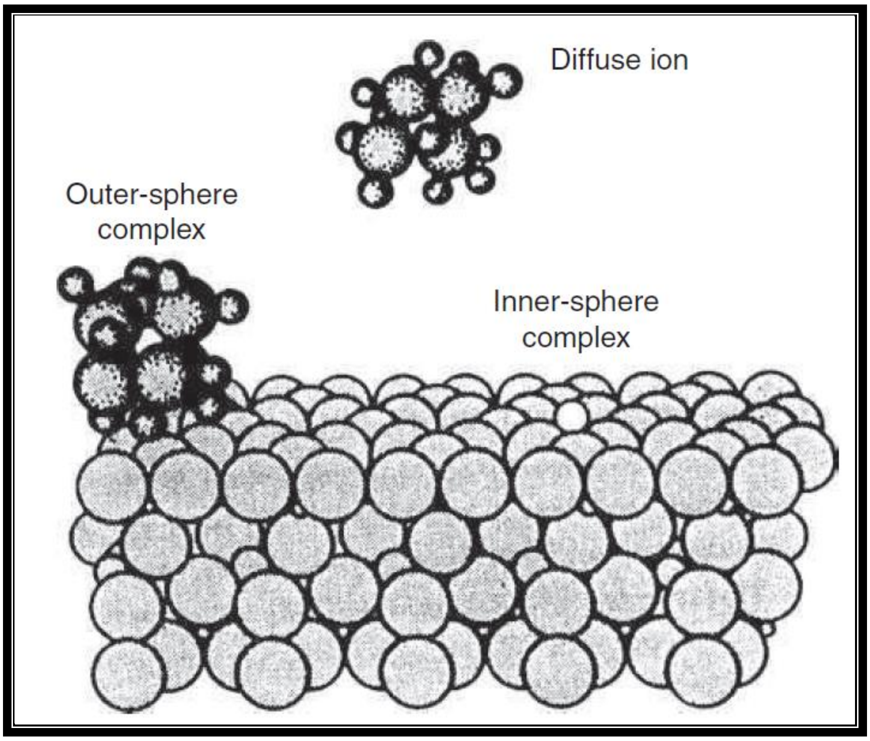

Figure 1: Different mechanisms of sorption (Hooda, 2010)

Manning *et al*. (1998) defined “inner-sphere compounds as links between the adsorbed ion and the reactive surface with no hydration water between the adsorbed ion and the surface functional group”. *Chemisorption* is used for this type of binding to a surface.

The stability of these bonds depends strongly on a number of specific properties of the cation such as ionic size and electronic structure, and on steric factors involved in the binding. This mechanism is the basis of specific or selective adsorption (Hooda, 2010). There are numerous factors that impact the selective sorption for example properties of the substance, steric factors, availability of pH-dependent sorption sites etc.

Na^+, K^+, NO^{-3}, and Cl^- (Sodium, Potassium, Nitrate and Chloride) can show ion-specific inadequate interactivities at the interface of minerals and it is known as ion pair formation. The compounds are called outer-sphere complexes (Rahnemaie *et al*., 2006). The ion is involved in the binding as a hydrated species in an outer-sphere complex. The properties of the ion itself will be far less important in determining the binding because the ion is masked by the hydrated water. Hence, this mechanism will contribute to nonspecific sorption (Hooda, 2010). Outer-sphere complexation is less reliant on pH as opposed to inner-sphere (Rahnemaie *et al*., 2006).

2.2.2 pH and Redox Potential

Chemical activities are directly and indirectly influenced by the soil solution pH and redox potential (Hooda, 2010). The combined impacts of pH and Eh on TMEs mobility are highly element specific and complex. Trace elements solubility has the ability to transpire as available hydrated cations and usually increase with declining pH. Hooda (2010) gives explains this behaviour:

a) Sorption competition (If the soil solution pH decline, H^+, Fe^{3+}, Al^{3+} (Hydrogen, Iron, Aluminium) activity increase along with their positively charged hydroxide in the soil solution. These cations will be in competition with anions).

b) Decreasing pH-dependent negative charges of the sorption compound: (The total quantity of negative sorption sites declines as pH decreases. The pH-dependent negative charges on the solid phase are triggered by the surface hydroxide groups dissociation on minerals or functional groups on organic colloids, are neutralised by protonation. Positive charges are created by covalent binding of H^+ on organic functional groups or hydrated oxides of iron and manganese. The universal negative charge on the sorption complex therefore declines. The soil colloids get a total positive charge under the point of zero charges.) and;

c) Soil components dissolution (Several soil components become unstable with decreasing pH). While free $CaCO_3$ is just stable in soils with pH ≥ 7.5, hydroxides of aluminium will significantly dissolve at pH values below 5.5, and Fe when pH is < 3.5. When pH is decreased under 6, metal mobility decrease as follow: Cd > Zn > Ni > Mn > Cu > Pb > Hg. Anions like As, Mo (Molybdenum), Se, Cr(VI), are more mobile in alkaline conditions (depicted in Figure 2). Anions are increasingly sorbed with decreasing pH due to soil colloids that increasingly get an additional positive charge.

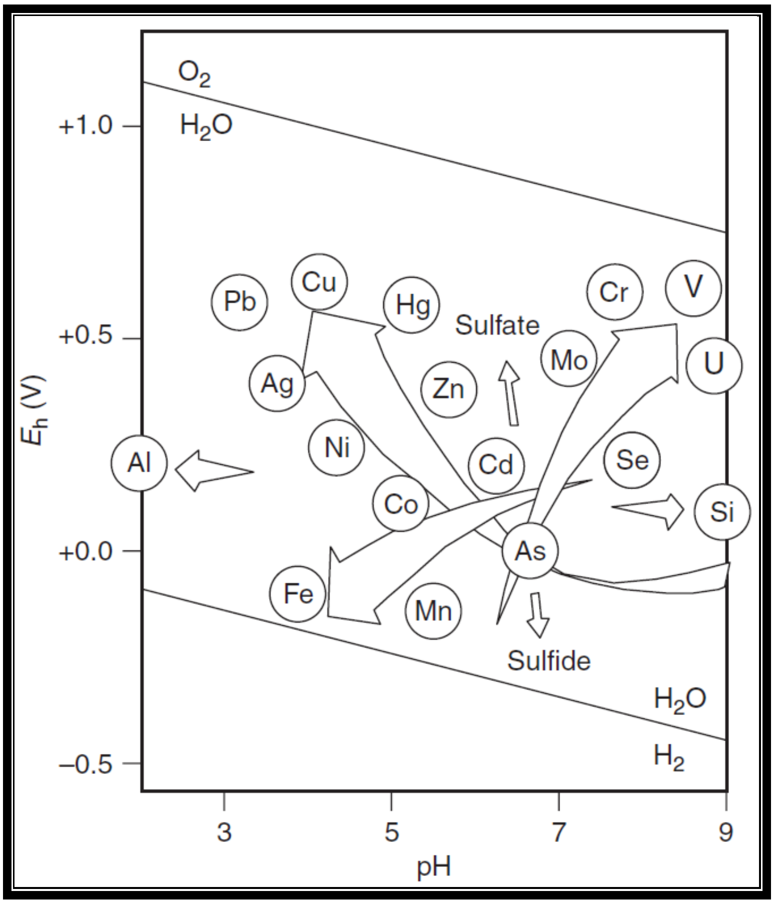

Figure 2: Major trends for increasing element mobility in soils (Hooda, 2010).

2.2.3 Transport

Trace elements in mobile forms which are in true solution and those associated with colloidal and suspended material, can migrate downward (Hooda, 2010). Taylor (1953; 1954) and Aris (1956) established the laws at the microscopic scale of solute transport along a single capillary from the combination of two independent mechanisms namely advection and molecular diffusion. Advection refers to the movement of dissolved or suspended particles along with the solution while hydrodynamic dispersion is the combination of molecular diffusion and mechanical dispersion (Hooda, 2010). Figure 3 shows the effect of mechanical dispersion. Molecular diffusion is created by Brownian motion of the particles. Particles tend to migrate from high-concentration zones towards places in the solution where the concentration is lower due to this random motion. The result of the irregular shape of the soil particles that causes individual particles to follow different pathways in the porous structure is seen as mechanical dispersion (Hooda, 2010). The true microscopic velocity of the particles, as a result, is different from the mean macroscopic velocity (Hooda, 2010).

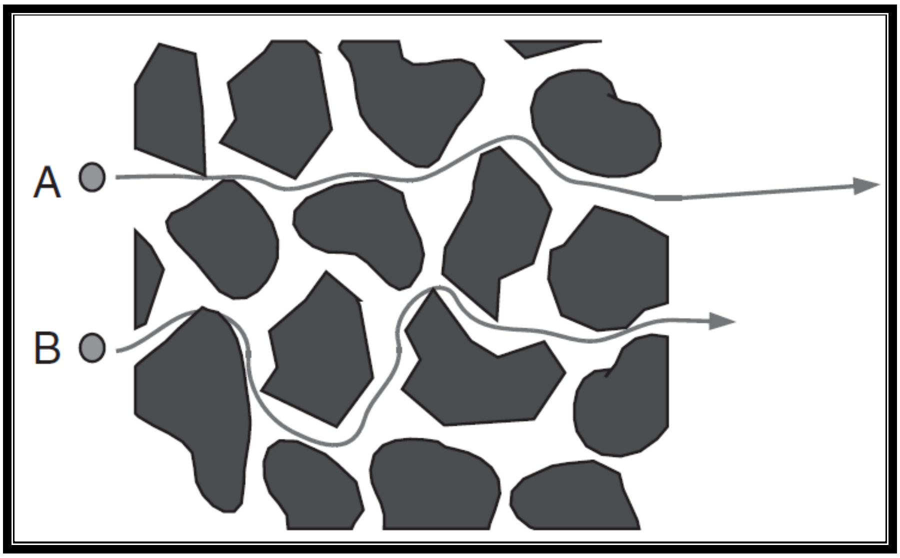

Figure 3: Illustration of the effect of mechanical dispersion (Hooda, 2010).

The hydraulic conductivity of soils depends on the soil texture, which largely determines advection. The hydraulic conductivities of borehole-sorted sands or gravel, permeable, are between 10^2 and 10^1 cm/s. The hydraulic conductivity of very fine sands and silt is around 10^2 to 105 cm/s, whereas clays have hydraulic conductivities below 10^6 cm/s, and therefore are they are almost impervious. Therefore, it is easier for metals to migrate downward or leaching to groundwater in coarser- than finer-textured soils. Sorption to the solid phase during percolation significantly impedes the migration of particles in comparison with the flow of the solution (Hooda, 2010).

A leachate usually contains pollutants that can be for example organic matter that has been dissolved or inorganic macro-components to name just a few.

2.2.4 Remote sensing and trace metal elements

Choe *et al.* (2008) stated that remote sensing is a method used in studies of trace metal dispersion for fast preliminary analysis. Wu *et al*. (2005) and Kemper and Sommer (2002) stated that TME levels present in soils could be determined by reflectance spectroscopy. Since trace metals are spectrally without characteristics in the visible and near-infrared (VNIR) at 350–2500 nm regions of the electromagnetic spectrum. Spectrometer data can be used for the indirect observation and mapping of metal dispersion by utilising the minerals spectral signatures that couples trace metals (Choe *et al*., 2008). Figure 4 is a typical VNIR spectrum that only range from 450 to 900 nm. The standard way of studying the trace metal contamination of soil is based on normal sampling followed by laboratory analysis and then geo-statistical interpolation to show how the trace metals are spatially distributed (Leenaers *et al*., 1990). This is an expensive and time-consuming method (Shi *et al*., 2014).

Soil reflectance is a progressive characteristic that stem from innate spectral response of the diverse mixture of soil physical and chemical features. Investigations indicated the moderate contribution of soil elements like clay minerals, FeO and organic matter to the reflectance spectra of soil (Sun & Zhang, 2017). VNIRS have been used in the field of soil sciences for longer than two decades because it estimates trace metal concentrations in soils. Guerrero *et al*. (2010) listed a number of pros for the VNIRS technology; it is constructive, extremely replicable, fast, and inexpensive when done in vast assessments, a small number of samples are required to be analysed. Soil spectral information can be applied to determine soil properties (Shi *et al*, 2014). Elements like Ni, Cu, cobalt (Co), and Cr with an empty *'d'* orbital, have the ability to show absorption aspects due to crystal field impacts in VNIR area (Sun & Zhang, 2017). Zinc is not spectrally mobile within VNIR area. Despite absorption aspects, TMEs is undetected with reflectance spectroscopy at moderate levels (Wu *et al*., 2007).

While TMEs at low concentrations do not possess spectral attributes in the visible and near-infrared area, estimations for the element levels in soil can be established through correlation with FeO, clay minerals and organic matter (Sun & Zhang, 2017). Al Maliki *et al*. (2018) stated that Pb is a spectrally inactive metal but the concentration obtained through correlating it with another soil component that is spectrally active, like soil carbon. Wavelengths between 500 and 612 nm are significant to detect Pb. At the interval of 600–800 nm and 800–1000 nm, organic matter and iron oxides are strongly absorbed and dominates soil reflectance in that area (Xu *et al*., 1991). Chen *et al*. (2015) and Viscarra Rossel *et al*. (2006) reported soil organic approximation bands are absorbed at 410 nm, 581–626 nm and 670–690 nm. The clay minerals indicate that kaolinite have strong absorption at 2200 nm, and 1400 nm and 1900 for vermiculite (Xu *et al*., 1995). Because of this, bands that are linked with organic matter and clay minerals were correlated with soil Zn through Zn adsorption of organic matter and clay minerals (Sun & Zhang, 2017).

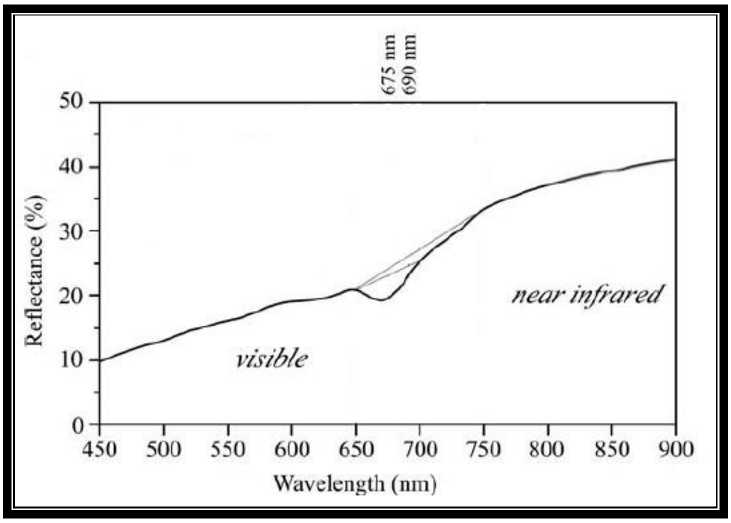

Figure 4: A typical VNIR spectrum (450–900 nm) graph (adapted from Wolfe *et al*., 2006).

Fe-oxides, like goethite (-FeOOH), in soils are absorbed in the VNIR (350–1100 nm) spectral regions. As a result of OH, water, and CO_3 overtones and mixture of vibrations, clay minerals are absorbed at the 1100–2500 nm region (Shi *et al*, 2014).

Soil organic matter absorption is prominent over the VNIR area because of the different chemical bonds like C-H (carbon-hydrogen), C-C (carbon-carbon), C-N (amide), and O-H (hydroxide). Ni, Cu, Co, and Cr has the ability to show absorption features in the VNIR areas under two distinct situations:

a) the elements are available at excessive levels (>4000 mg/kg); and
b) they possess an empty *'d'* shell.

The rationale is when a transition element atom is located in a crystal sphere, the electron will advance to a higher level (Shi *et al*, 2014). Therefore, the electron transition leads to the absorption of electromagnetic energy. According to Wu *et al*. (2007), Cr and Cu indicates spectral attributes at 610 and 830 nm at >4000 mg/kg. Trace metal elements that has absorption attributes can be determined through their direct correlation with the spectral attributes. When TMEs are available in small quantities, they lack spectral attributes within the VNIR areas, which makes it troublesome to determine the trace metal concentrations in the soil through soil spectral features (Shi *et al*, 2014).

2.3 Groundwater

Groundwater can be defined as water that is in the saturated zone where it occupies the empty spaces in geological formations. Mainly there are two groundwater body attributes that separate it from a surface water body.

1. The fairly slow water movement through the sub-surface. Once a groundwater body is polluted, it can stay that way for a long time period, due to the slow-going through-flushing.
2. There is a significant level of physico-chemical and chemical interdependence that links the water and the incorporated matter (WHO, 1996)

Seepage from the surface water may recharge groundwater although the surface water body is separated from the groundwater network by means of an unsaturated area. Since water can interchange between two components in the hydrologic system, any activity the one undergoes will impact the other (Winter *et al*. 1998). The movement of surface water and groundwater are governed by topography and the geologic composition of the region. Surface water seepage into the groundwater network during periods of elevated surface water phases can result in groundwater flow direction alteration, which is mostly driven by fluctuations in climate (Winter, 1999).

2.3.1 Quantifying groundwater flow

Groundwater usually flows from recharge areas to discharge areas. There are numerous methods to quantify groundwater, the most popular being analytical and numerical models or a combination of these two models (Spitz and Moreno, 1996). Darcy's Law, a well-known analytical model (Driscoll, 1986).

Numerical models dominate groundwater flow calculations and mass transport simulations in complex environments. In a numerical model, the study area is divided into a number of cells, for which aquifer parameters etc. are allocated. Computer programmes are then used to decipher the flow and mass transport. The steps involved in the development of numerical models includes the following (Spitz and Moreno, 1996): collecting relevant data and interpreting this to obtain an understanding of the system, setting up a model, calibrating the model and running predictive scenarios.

2.3.2 Groundwater recharge

Groundwater recharge is water supplementation to the saturated zone, by rainfall or surface water seepage and/or groundwater from adjacent aquifers. This section will however focus on the recharge from precipitation as shown in Figure 5. Xu and Beekman (2003) state that recharge can be classified as:

1. Origin of water direct/diffuse recharge: direct infiltration via unsaturated zone to a groundwater body or indirect infiltration by means of for example riverbeds or, localised recharge by means of localised surface water bodies and associated infiltration.
2. Flow mechanism via the unsaturated zone: piston flow where water is displaced downwards without altering the moisture distribution or preferential flow through preferred (e.g. fractures, burrows, fissures).

Recharge can be expressed in various forms but the most widely used are as a rainfall percentage, or mm/time. Groundwater recharge is significant in the replenishment of aquifers and the associated quantification of the availability of groundwater.

There are numerous methods to calculate recharge, including (Dennis *et al*., 2012):

- National recharge maps, there are currently three maps that are used to determine recharge, namely Vegter's recharge map (1995) where recharge is expressed as mm/a. Schulze generated an annual recharge of soil water into the vadose zone in mm/year in 1997 and the Groundwater Resource Assessment phase II recharge map developed in 2006, where the recharge was determined per quaternary catchment and expressed as a percentage of rainfall. It is important to note that these maps only provide an indication of average recharge over an area.
- The chloride mass balance method is widely used in South African and takes into account the relation between chloride in rainfall and that of groundwater to determine rainfall percentage.
- Water balance methods, including the Saturated Volume Fluctuation (SVF) method, the Cumulative Rainfall Departure (CRD) method and the Extended model for Aquifer Recharge and Soil Moisture Transport through the unsaturated Hardrock (Earth) method. These methods basically take into account groundwater inflows and out flows and aquifer parameters to determine the recharge.
- Isotope-based methods accept that oxygen-18 and deuterium occurs naturally. Recharge can be calculated taking into account the relationship between the deuterium isotopic compositions displacements from the local meteoric water line (MWL) and the inverse of the square root of recharge. It has been determined that in a $^{18}\delta - ^{2}\delta$ plot, the displacement of soil moisture is represented by a line parallel to the local MWL and is correlative to the inverse of the square root of the recharge rate (Xu & Beekman, 2003).

Numerical groundwater flow models are used to predict groundwater levels under different conditions. A groundwater model can therefore predict groundwater recharge as numerical groundwater models are based on water balances. See Section 4.3 for more information regarding numerical models.

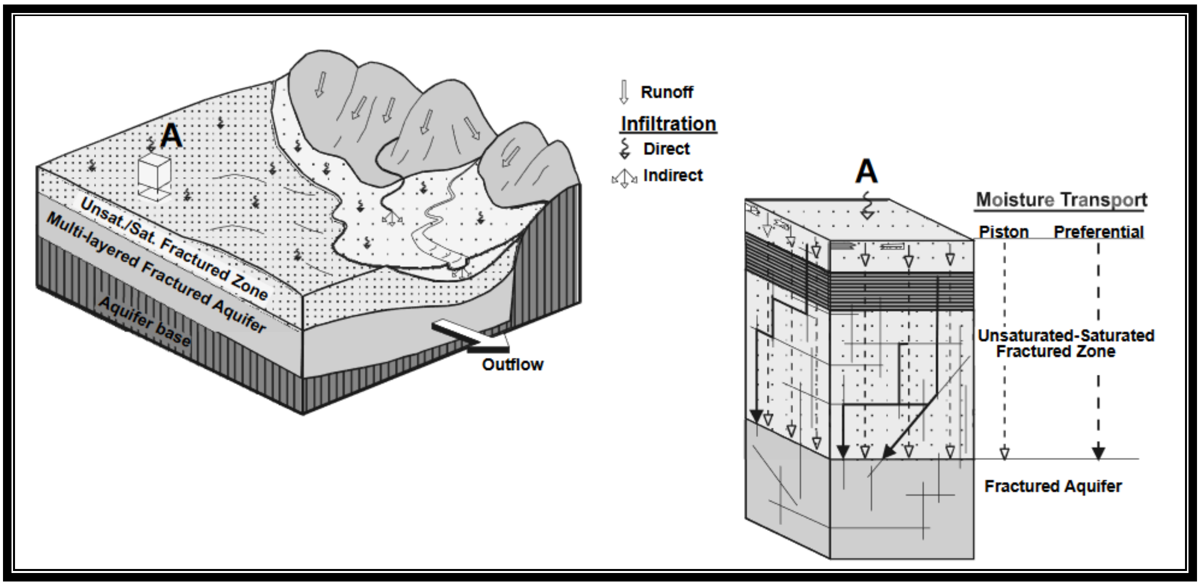

Figure 5: Mechanisms of infiltration and moisture transport (Xu & Beekman, 2003).

2.3.3 Quantification of groundwater pollution

A method to quantify pollution would thus be helpful for assessing groundwater contamination and for monitoring remediation success. A valid method is required for quantification of contaminant mass in the subsurface and would be useful for the implementation of natural attenuation as remediation strategy at a field site (Bauer *et al*., 2003). Simultaneously, the quantification of contaminant mass flow tempo and average contaminant concentrations at control planes that are established in advance, located at an angle of 90° to the average groundwater flow direction, and the determination of possible concentration spreading throughout the length of the control planes (Bauer *et al*., 2003) Contrary to point scale measurements, it is grounded on a sizeable sampling volume procured by pumping and therefore delivers more reliable results, because it is less susceptible to impacts of aquifer heterogeneity and contaminant spreading as a result of its integrating nature. Suppose the same amount of monitoring boreholes is used, the integral method always produces more information on the subsurface contamination than point samples, as these point samples are comprised in the measured concentration time series as first sample (Bauer *et al*., 2003).

Bockelmann *et al*. (2001) stated that this method had been used at a field site to quantify mass flow tempo of hydrocarbons leading to natural attenuation rates of these hydrocarbons. The method has further been successfully compared to other methods of mass flow tempo determination and been applied at other field sites to quantify mass flow rates of BTEX and polycyclic aromatic hydrocarbons and chlorinated hydrocarbons. The integral pumping test method used in this investigation puts control planes into impact downstream of suspected contaminant source areas. These control planes are perpendicular to the average groundwater flow direction and comprises multiple pumping boreholes (Bauer *et al*., 2003). Some factors like the borehole positions, pumping rates and pumping times are created to permit the borehole capture zones to shield the whole groundwater flow downstream of the contamination area. A well at the control plane is worked for a time frame of some days usually. Contaminants concentrations and other groundwater quality parameter values are calculated as a time function in the discharged groundwater of each borehole. The concentration time series produce information on contaminant plume(s) location and degree as borehole on the concentrations of the target substances within the plume(s). This permits the determination of mass flow tempo at the control plane and average concentrations in the borehole capture area at the local flow field (Bauer *et al*., 2003).

2.4 Mitigation

According to Reichenberger *et al*. (2007), mitigation is a term about reducing risk, exposure and/or effects. A successful mitigation strategy must consider the geological setting of groundwater, economic resources, and the feasibility of water treatment (Noubactep *et al*., 2003). For a mitigation strategy to be comprehensive, both human consumption of groundwater and the impacts it has on the environment at large should be examined (Reichenberger *et al*., 2007). There are a number of corrective actions that can be implemented to improve the quality of groundwater. These technologies that can be used for mitigation include:

2.4.1 Pump and treat

his system is grounded on the idea of removing contaminated groundwater to treat at the surface (Abd Ali & Faysal, 2016). The water that has been treated may replace the aquifer water; be discharged to a stream, river or a sewer system. Pump and treat networks (Figure 6) have been worked at many locations for numerous years. Data obtained from these locations have shown that this system is initially fruitful but the performance drastically declines after some time. Noteworthy quantities of residual contamination can persist after continuous treatment.

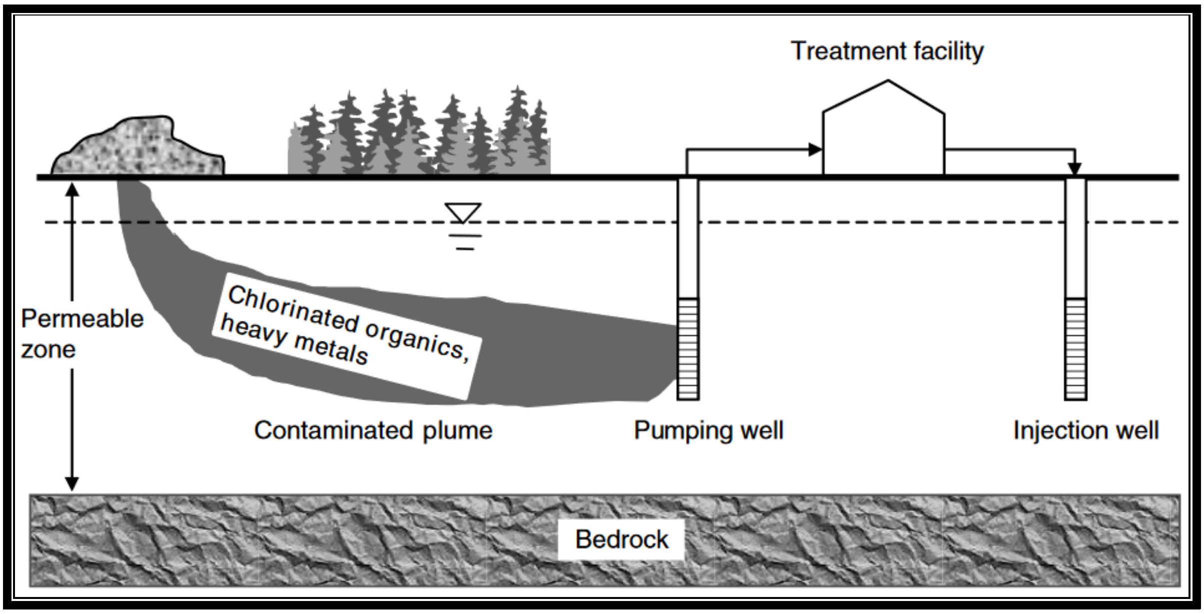

Figure 6: Pump-and-treat system (Simon *et al*., 2002).

2.4.2 In-situ flushing

This method includes pumping a substance into groundwater through boreholes. The flushing solution (normal water or meticulously created solution like co-solvent) moves with a gradient via the contamination area where it desorbs, solubilises, and removes the contaminant. The solution is pumped out through withdrawal boreholes situated at another incline when the contaminants have been solubilised. The contaminated solution is attended to though common wastewater treatment procedures at the surface and subsequently pumped back to the injection boreholes (Abd Ali & Faysal, 2016).

2.4.3 Monitored natural attenuation

United States Environmental Protection Agency (USEPA) (1999) defined natural attenuation as the "*use of natural processes to contain the spread of the contamination* *from chemical spills and reduce the concentration and amount of pollutants at contaminated sites*". Using this method, depicted in Figure 7, as a remediation plan includes applying for a formal regulatory request to allow biological, chemical, and physical activities to manage groundwater contaminants, and perform continuous management to confirm that these activities are successful (Bekins *et al*., 2001).

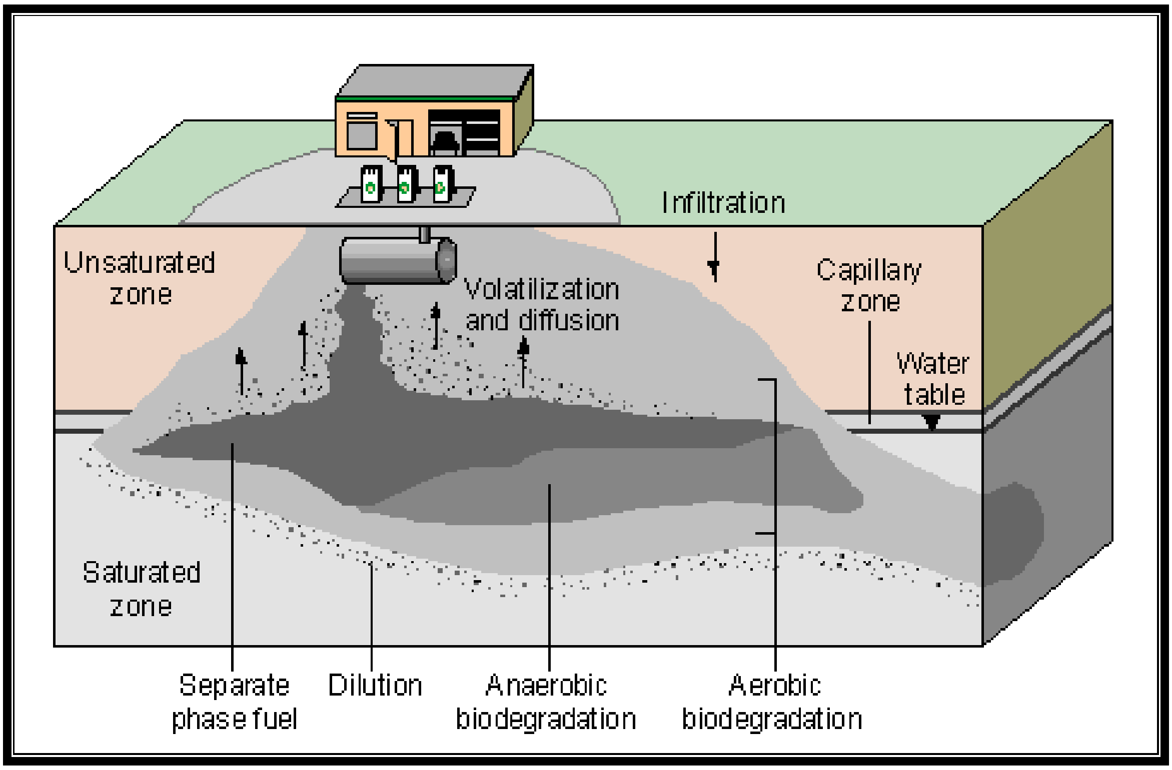

Figure 7: Illustration of the natural attenuation processes (Bekins *et al*., 2001).

3 STUDY AREA

3.1 The Diep River catchment

The Diep River catchment, forms part of the bigger Sand River catchment (Brown & Magoba, 2009). StatsSA (2011) reported that the catchment extends over a region of about 2000 hectares and accommodates approximately 41,000 people (Rohrer & Armitage, 2017). There is a minor lake of little depth, called Little Princess Vlei (LPV), it is a semi-natural "*vlei*" that acts as a retention pond situated downstream in the catchment. Little Princess Vlei is significant in terms of traditional and ecological importance (Kotzé, 2008; Anderson *et al*., 2014). Aside from the Diep River, the catchment has a number of rivers including Klapmuts, Sout, Modder and Mosselbank Rivers. Figure 8 shows a study region map with quaternary catchments delineated in red.

The catchment has experienced considerable urban progress between the period of 1970 and 1980. It leads to resulted in significant elevated flood peaks, which the occurring storm water system was incapable of handling, resulting in many drastic flooding events. As a way to alleviate, the City of Cape Town (CoCT) erected six restraining reservoirs alongside the Diep River and its upstream branches to decrease floods (Rohrer & Armitage, 2017).

3.1.1 Hydrology

The Diep River's origin is in the Riebeek-Kasteel Mountains, to the NE of the study region. The river moves in a southwesterly orientation via Malmesbury before entering Table Bay, with the total length of the river being about 65 km. It is a low lying area with some mountains on the eastern side, including the Perde, Kasteel and Paarlberg (*Department of Water Affairs and Forestry* (DWAF), 2002).

The Mosselbank River is a major Diep River branch, with its origin in the Skurweberg Mountains. This tributary runs through the southeastern part of the catchment, including Durbanville and Kraaifontein regions. The Klapmuts River is a Mosselbank branch. Other Diep River system branches includes (see Figure 8):

- Riebeek River

- Klein River, Swart River
- Platklip River
- Sout River

The study area falls within four quaternary catchments namely G21C, G21D, G21E and G21F. Information regarding these catchments is documented in Table 2.

Table 2: Information regarding quaternary catchments (DWAF, 2006).

Catchment	**Area (km^2)**	**Rivers/river reaches**	**Mean annual runoff (Mm^3/a)**	**%no flow**	**Present ecological status**
G21C	244	Kasteelburg/above Malmesbury	62	0	C[1]
G21D	484	Above Malmesbury/ Mosselbank Confluence	49	0	C
G21E	531	Mosselbank	68	0	C
G21F	242	Mosselbank Confluence/Mouth	24	0	B[2]

There are three flow gauges (G2H012, G2H013 and G2H014), with only one being close to sub-catchment namely G2H014, along the Diep River as Figure 15. Flow gauge G2HO12 is shown in Photo 1. The data from these gauges are used to determine the naturalised study area mean yearly runoff as 50×10^6 m^3. The present day conditions runoff is 45×10^6 m^3 (DWAF, 2002).

Viskisch *et al*. (2016) stated that several water quality investigations were done in the Diep River estuary. As urbanisation around the Diep River estuary increase, remarkable changes in the volume and quality of water flowing into the system have transpired (Jackson *et al*., 2011). Storm water drains and sewage works additionally flows into the Rietvlei.

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[1] Localised low level impacts, but no negative effects apparent

[2] Moderate levels of localised impacts – moderate or perceived impact on the environment

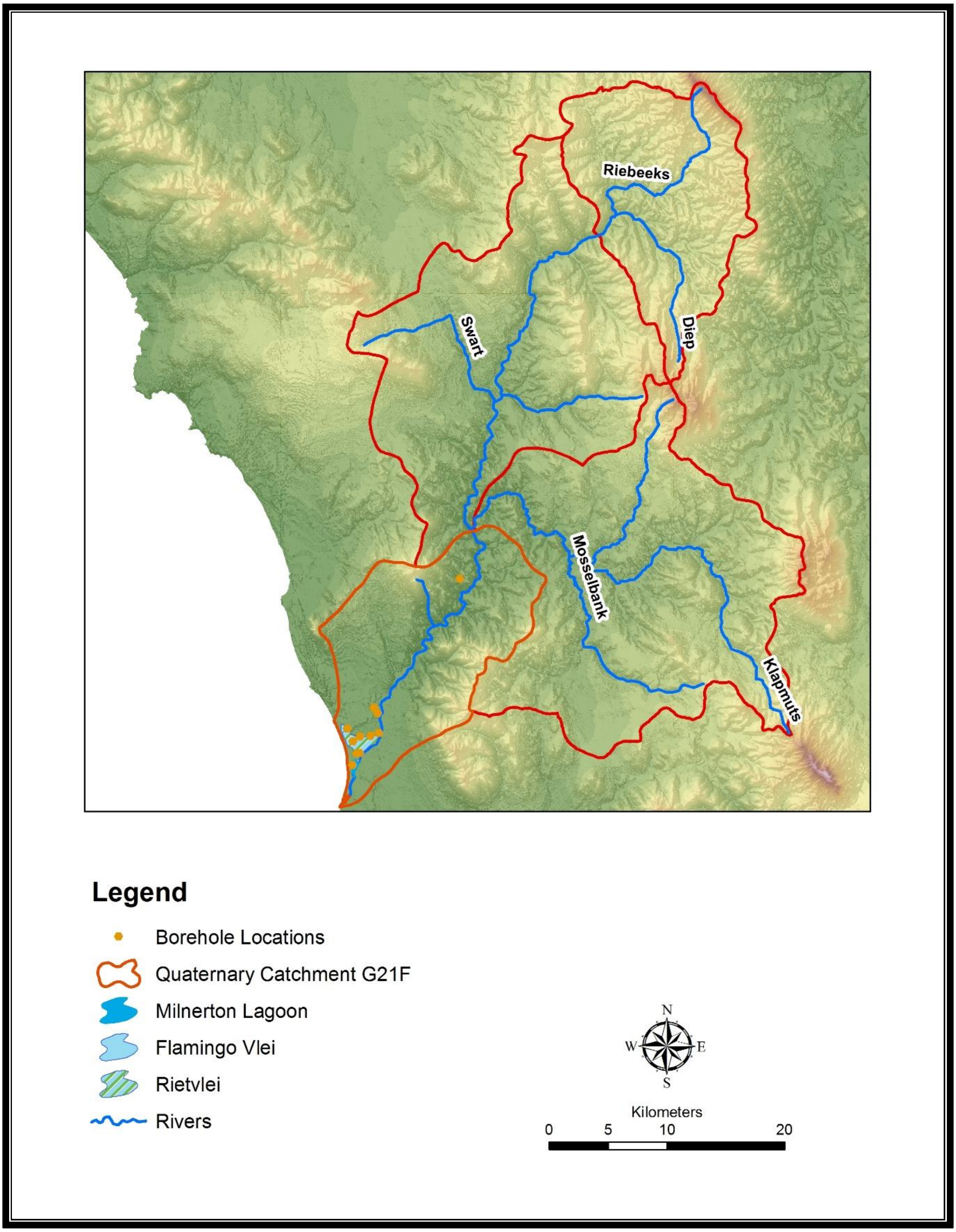

Figure 8: Tributaries of the Diep River system

Photo 1: Flow gauge G2HO12.

Harding (2008) stated that there is a direct relationship between the storm water flows and rainfall sequence. The Bayside Canal, which releases into the wetland side, has a varying flow of below 1000 m^3 per day in summer months, and ranges from 7000 and 10000 m^3 per day.

The Potsdam Waste Water Treatment Plant (WWTP) discharges the water along the Rietvlei which transports the outflowing stream to the lagoon at the Otto du Plessis bridge. In order to obstruct the pollutants that flows from the WWTW, a channel was constructed to ensure that it does not contaminate the Rietvlei. Consequently, during rainfall seasons the channel has a tendency to overflow and the effluents move into the vlei (Jackson *et al*., 2008). Potsdam had a volume of 32 mℓ /day, and the net daily from the WWTW was about 30 mℓ/day (Botes, 2004). Flow tempos measured between 0.15 m^3/s and 0.45 m^3/s over a day (Jackson *et al*., 2008). Storm water runoff from an oil refinery (Chevron Refinery), and the significant suburban storm water discharge in the NE part of Rietvlei (Brown & Magoba, 2009; Jackson *et al*. 2008; Retief, 2011; Taljaard *et al*. 1992).

Cd, Hg, Pb and As in fish and invertebrates from the Rietvlei–Diep system also indicated a comparable pattern to the sediments and surpassed most South African and global restrictions for food (Hutchings & Clark, 2010). Jackson *et al*. (2011) suggests that the Milnerton Lagoon water has been inappropriate for recreational use since 2001. Paulse *et al*. (2009) have studied microbial contamination at three different locations along the Diep River. It was found that at all of the microbial totals were higher than the water quality recommendations in those locations. Jackson *et al*. (2009) and Ayeni *et al*. (2010) furthered the study to establish the metal contamination extent alongside the lower Diep River.

3.2 The Diep River sub-catchment

The study area is located about 5 km north of Cape Town. The Rietvlei wetland comprise of 561 ha between the Otto du Plessis Drive and Blaauwberg Road bridges. The vlei depth is generally not more than 2 m when it is at its capacity (Harrison, 2010). Jackson *et al*. (2011) stated that the Rietvlei is a significant region for water birds in the area and is acknowledged as a prominent area by *Birdlife International*. The Rietvlei sediment is mostly muddy, because of large-scale siltation which is the result of erosion in the catchment region (Millard & Scott, 1954). Comprehensive data on the biophysical properties of the study region were gathered in the 1960s and 1970s. Alkaline pH values were found, varying between 9.4 - 9.6 and 100 mg/l - 400 mg/l (Heydenrych, 1976). These results are ascribed to the brackish water of the Diep River and the catchment geology (Kalejta-Summers *et al*., 2001). Figure 9 depicts the sub-catchment.

The Diep River moves via the Rietvlei and the Milnerton Lagoon, before entering the sea. Together they cover a region of about 900 ha. These two features together comprise the "*Estuary*" (Jackson *et al*., 2011). Land use within the catchment is mostly agricultural, residential and industrial. Nutrients are vital for all living organisms. Particularly plants grow rapidly in excess of nitrogen and phosphorus (Haskins, 2013). The Diep River catchment has been extensively investigated to better understand catchment water quality in general (Table 3). These studies also cover the characterisation of the catchment from various perspectives.

Table 3: Some of the previously completed major studies in the area.

Author	Year	Focus of study
Grindley and Dudley	1988	Situation assessment of the Rietvlei
Jackson *et al.*	2008	Estuary health
Jackson *et al*.	2009	Heavy metal contamination in the Diep River
ICE	2011	Improving storm water quality flowing into the Diep River

3.2.1 Climate

The Diep River and its associated tributaries occur within the winter rainfall region (DWAF, 2002). The climate is characterised with winter rain and high evaporation rates in the summer. The winter cold fronts are usually the source of precipitation. These cold fronts approach the catchment from the west. Seasonal rainfall with warm, dry summers and mild, wet winters are experienced. The mean rainfall ranges between 800 and 1400 mm/year. This exceeds the mean yearly rainfall of the CoCT which is around 515 mm/year (Rohrer & Armitage, 2017). The average rainfall per quaternary catchment is documented in Table 2. The most rainfall occurs between May and October with more than 50% of the rainfall falling in these months. The average yearly evaporation tempo is about 1600 mm. The minimum temperatures in the winter are approximately 7^{o}C, with maximum temperatures of 30^{o} in the summer. However, when berg winds blow the temperature can reach 40^{o}C (DWAF, 2005).

3.2.2 Topography

The study area is located within the western lowland region of the Western Cape. The region is divided into the Swartland and on the direct opposite side, the Sandveld. The Swartland has oscillating lowland with quite abrupt river valley gradients, whereas the Sandveld is more level and has broader river valleys with little depth (DWAF, 2002). Topography is depicted in Figure 9.

Rietvlei has a triangular form, about 2 km wide and 1.5 km long. The area has a level surface between 1 - 2 m above sea level (mamsl), excluding the section that was removed with a power shovel in the 1970s (Grindley & Dudley, 1988). Duvenage (1983) stated that the estuary covers roughly an area of 428 ha from the opening to the Blaauwberg Road Bridge. The region of the Rietvlei and Milnerton Lagoon under the Otto du Plessis Road Bridge is included. Part of this area is known for primary dunes with a peak height of around 10 mamsl while most of the region is predominantly flat (Schalke, 1973).

3.2.3 Vegetation

Jackson *et al*. (2008) stated that the Rietvlei reserve includes prominent wetland plant species, namely; "*perennial wetland, reed marsh, sedge marsh, open pans, sedge pan, and some strandveld*".

The perpetual wetland consists of open water regions of the estuary and both regions with more saline water nearby the opening, and the deep water lakes of Flamingo Vlei that is basically freshwater. Two aquatic species, *Ruppia maritima* and *Potamogeton pectinatus*, have been noted and the latter is only found in Rietvlei. *Ruppia* is found in the upper lagoon but does not grow under hypersaline conditions. *Potamogeton* is usually found in vleis throughout our country, and serves as habitation and food source for various communities. In eutrophic states it has the ability to grow abundantly and can become an annoyance to recreational users (Jackson *et al*., 2008).

The reed marsh primarily comprises of *Phragmites australis* and *Typha capensis,* commonly known as the bulrush. The reed-beds serves as a habitat for birds. The reed marsh has grown significantly lately in the region. This is regarded as a result of increased siltation from the catchment and more nutrients from various sources (Jackson *et al*., 2008).

Sedge marsh includes *Bolboschoenus maritimus* and *Juncus kraussii*. "*Sarcocornia pillansii*, *Triglochin bulbosa*, *Sporobolis virginicus*, *Zantedeschia aethiopica*, *Cotula coronopifolia* and *Senecio littoreus*" are linked with them. The vlei grass *Paspalum vaginatum* has invaded the sedge marsh. Species like *Chenolea diffusa* and *Sarcocornia perrennis* are found in more saline regions around the lagoon. They occur at a height of about 0.2 and 1 m and are generally flooded in winter. The *Sarcocornia* gives a reddish colour to the vlei when it is exposed (Jackson *et al*., 2008).

Open pans are of little depth in certain sections of the vlei are dry in summer but stays wet in winter. Sometimes when these sections are dry, there are surface salt deposits. In summer they usually have a scanty cover of macrophytes like "*Limosella capensis* and *Salicornia meyeriana*", contrary to when flooding occurred algae and other aquatic species like *Ruppia* becomes more dominant (Jackson *et al*., 2008).

The Strandveld is "*a terrestrial shrubland consisting of a scattered perennial overstory of spinescent species, succulents and moderately tall evergreen thickets*". *Asteraceae* (daisies) are widespread in exposed regions predominantly in spring, and a small amount of geophytes (bulbous species). The vegetation (Figure 10) is usually about 3 m high. The Strandveld intruded the Rietvlei by *Australian acacias* or *Pennisetum* (commonly known as rooikrantz/Port Jackson or kikuyu grass) (Jackson *et al*., 2008).

Sedge pans and open pans are comparable, but are shallower and have the tendency to be drier for long periods. They are known by *Bolboschoenus maritimus* in the dry periods, with many other species like *Aponogeton distachyos* commonly known as waterblommetjies and *Spiloxene aquatic* that appears after the first rains (Jackson *et al*., 2008).

3.2.4 Land use

According to Grindley and Dudley (1988), there are numerous urbanised areas and satellite settlements in the Rietvlei. Land use for the sub-catchment is displayed in Figure 11. These areas can have a negative impact on groundwater quantity and quality and surface water networks.

Mining sand, gravel and stone mining also takes place within the study area which has led to the alteration of the land surface. Most of the study region is being cultivated. There are vineyards and orchards which form a minor part of the cultivated lands, with the dominance of grain (mainly wheat) farming.

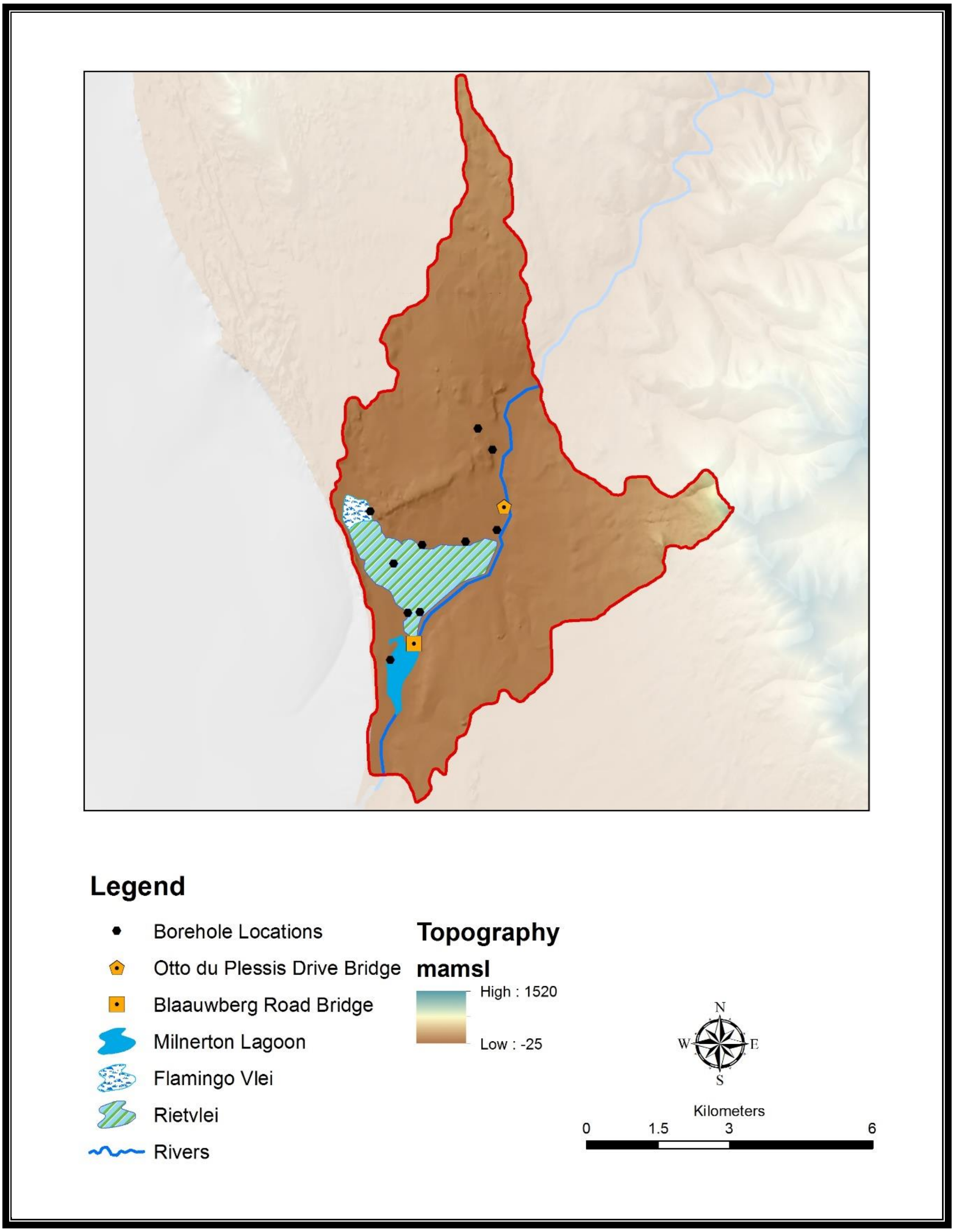

Figure 9: Topography of the study area

3.2.5 Soils

Mudumbi (2012) stated that the catchment consists of "*Malmesbury group (shale), Cape granite, Klipheuwel group (conglomerates) and sandy sediments*". The soils are classified as shale and granite clays, and rocky soils. It is a result of the weathering of Malmesbury Group shale, a deposition and compression product of silt and clay. Erosion is not usually a factor when it comes to these soils. Since these soils are high in nutrients and fertile, they are a proficient for agriculture. Figure 12 shows that the soil forms within the Rietvlei are Fernwood, Clovelly and Hutton. Soil textures are sandy loamy sandy and a small amount of sand clayey loamy.

3.2.6 Geology

The Malmesbury Group and the Cape Granite Suite are the dominant geological formation in the quaternary catchment (DWAF, 2002). The area geology is displayed in Figure 13. Lithology of the Diep River Catchment are shown in Figure 14. The Malmesbury Group includes dark, medium-grained, sub-greywackes with interbedded blue, and shales with a purple colour. The Cape Granite is light grey and is a porphyritic granite that invaded the Malmesbury Group. The Klipheuwel Formation outcrops at the village of Klipheuwel. At the contact zone of the Klipheuwel and Cape Granite Suite, the feldspars in the granite are weathered to kaolinite. The lower part of the catchment includes quaternary alluvial deposits that overlays the bedrock of the Malmesbury Group. The lagoon sediments are mainly made of weathering products from the Malmesbury Group because the Klipheuwel and Cape Granite Suite covers a fraction of the region. The Malmesbury Group sediments consists of multiple shales, greywackes, quartzites and grits, with conglomerate bands, limestone, dolomite and chert. In the Diep River catchment arenaceous greywackes vary by more argillaceous shales (Jackson *et al*., 2008). The sediments in the Milnerton Lagoon are rich with clay as a result of the prevalent Malmesbury Group within the catchment. At the mouth lagoon, the concentration of most elements had decreased. This is a result of more sediments weathering that leads to a loss of Ca (Calcium), Mg (Magnesium), Na, K, Rb (Rubidium) and Sr (Strontium) (Jackson *et al*., 2008).

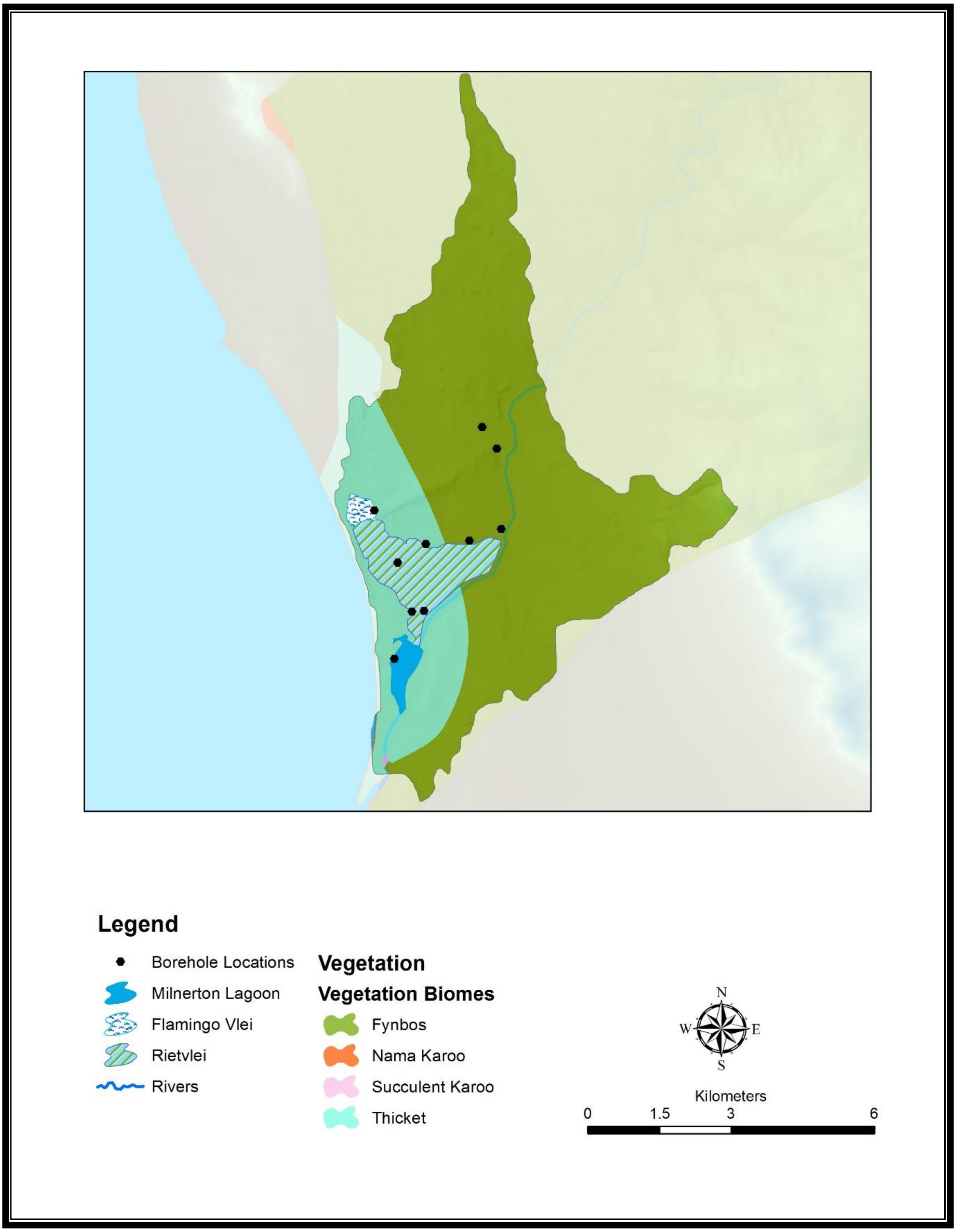

Figure 10: Vegetation

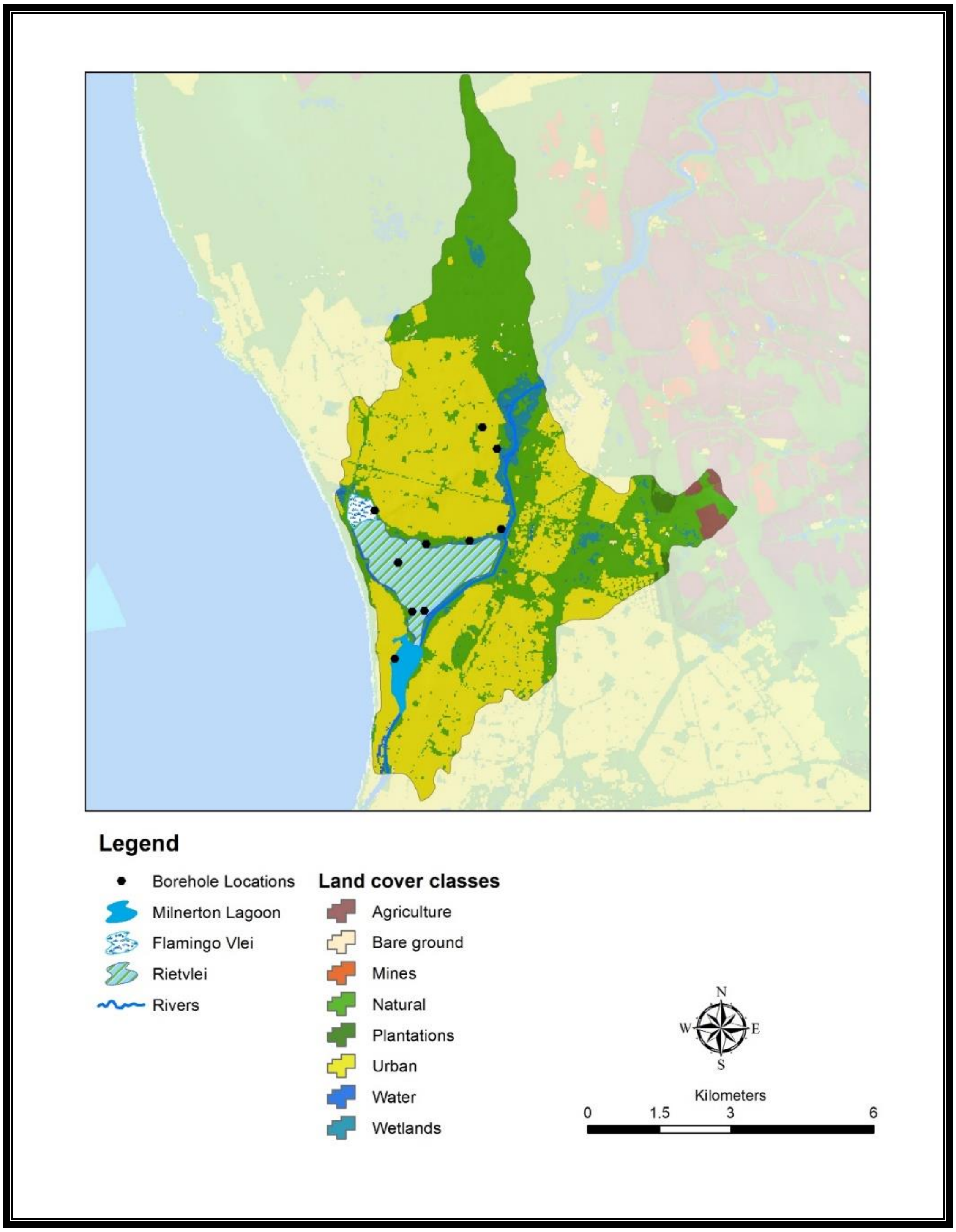

Figure 11: Land use for the study area

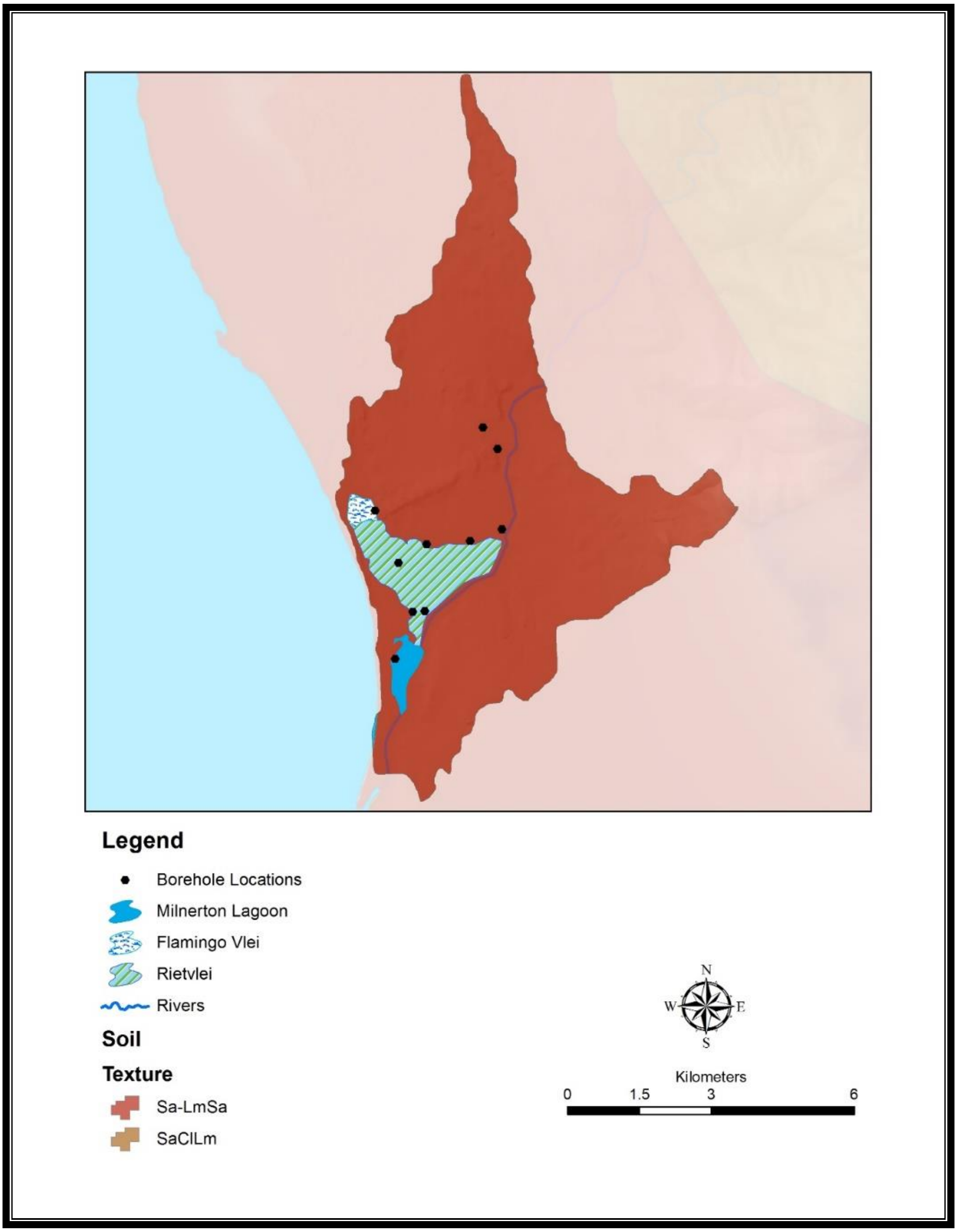

Figure 12: Soils within the study area

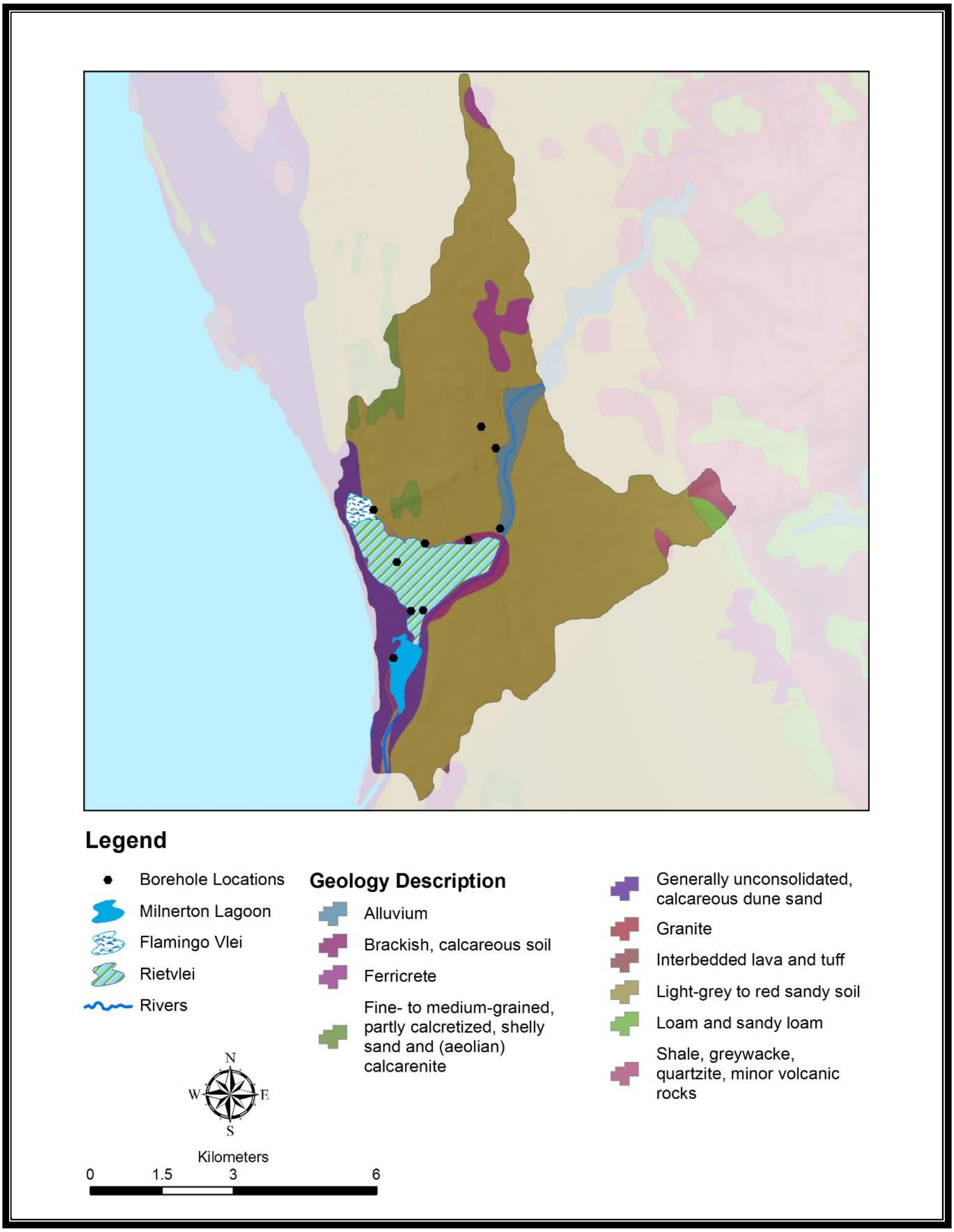

Figure 13: Catchment geology

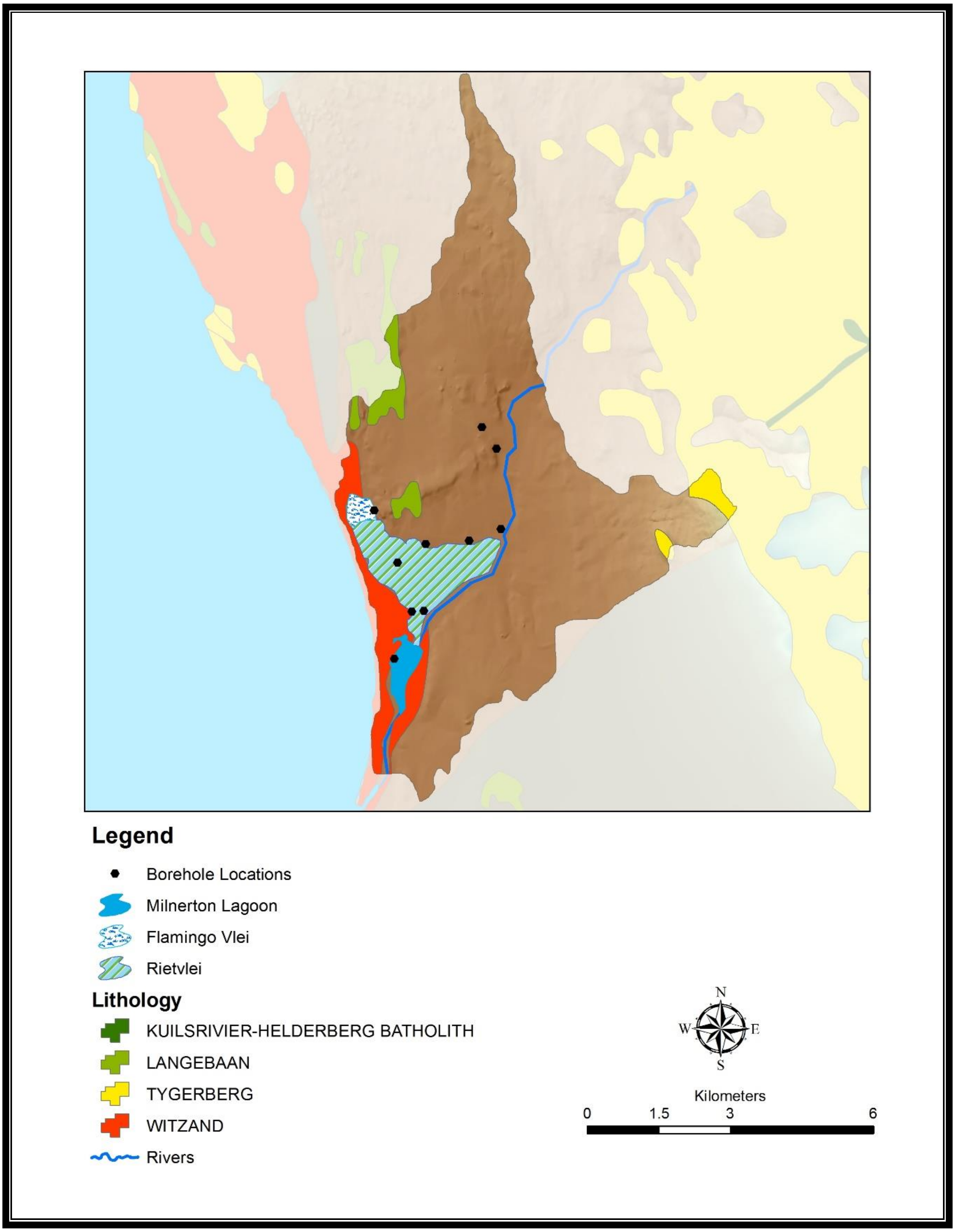

Figure 14: Lithology of the study area

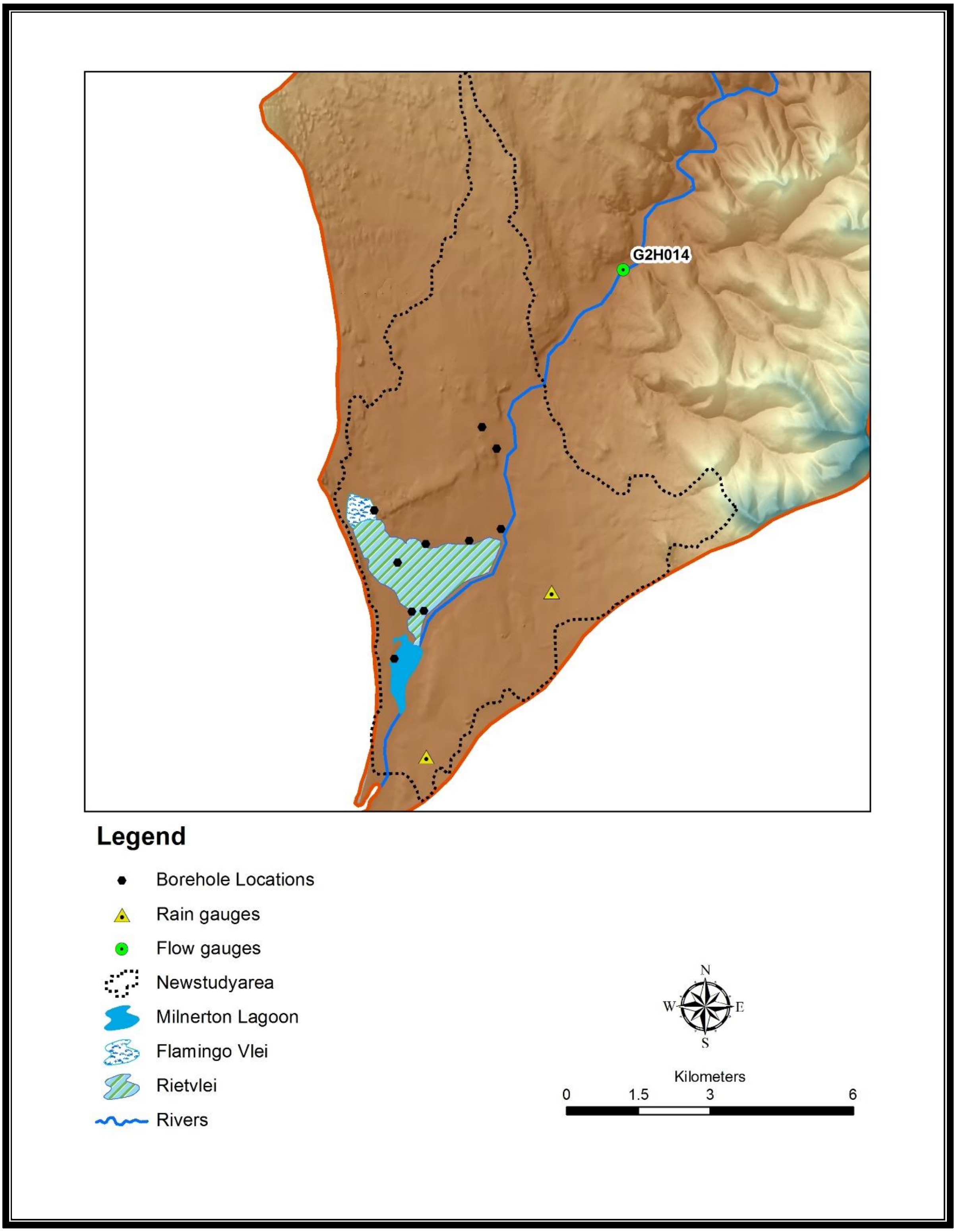

Figure 15: Location of flow and rain gauges

3.2.7 Geohydrology

This region has two prominent aquifer systems, as a result of the geology (DWAF, 2002), namely an upper unconfined primary aquifer (intergranular, consisting of unconsolidated sediments along the coastal plan) and a semi-confined deeper secondary aquifer (fractured/weathered aquifers of Malmesbury and Cape Granite bedrock underlying the Swartland and areas of the coastal aquifer). The two aquifers are parted by a clay aquiclude, that is non-existent when the rock layers form outcrops at the surface (Jackson *et al*., 2008). The main aquifer is barely formed in the Diep River catchment. Nevertheless, the quaternary deposits that are linked do exist NE of Kalbaskraal and alongside the Milnerton shore. The sands are not regarded as an important aquifer (DWAF, 2002). The primary aquifer serves as a groundwater storage unit for some insignificant releases into Rietvlei when summer starts as the levels within the vlei begin to decrease. Overall, the underlying bedrock of the catchment will have a minimal contribution towards sustaining the Diep River flow. Porosity and specific yield for the different aquifer materials are documented in Table 4. Groundwater yield is depicted in Figure 16.

Table 4: Porosity and specific yield of geological materials.

Material	**Porosity (%)**	**Specific yield (%)**
Unconsolidated sediments		
Gravel	25-35	15-30
Sand	25-45	10-30
Silt	35-50	5-10
Clay	45-55	1-5
Sand and gravel	20-30	10-20
Glacial till	20-30	5-15
Consolidated rocks		
Sandstone	5-30	3-15
Limestone and dolomite	1-20	0.5-10
Karst limestone	5-30	2-15
Shale	1-10	0.5-5
Vesicular basalt	10-40	5-15
Fractured basalt	5-30	2-10
Tuff	10-60	5-20
Fresh granite and gneiss	0.01-2	< 0.1
Weathered granite and gneiss	1-15	0.5-5

Sources: Freeze and Cherry, 1979; Todd, 1980; Driscoll, 1986

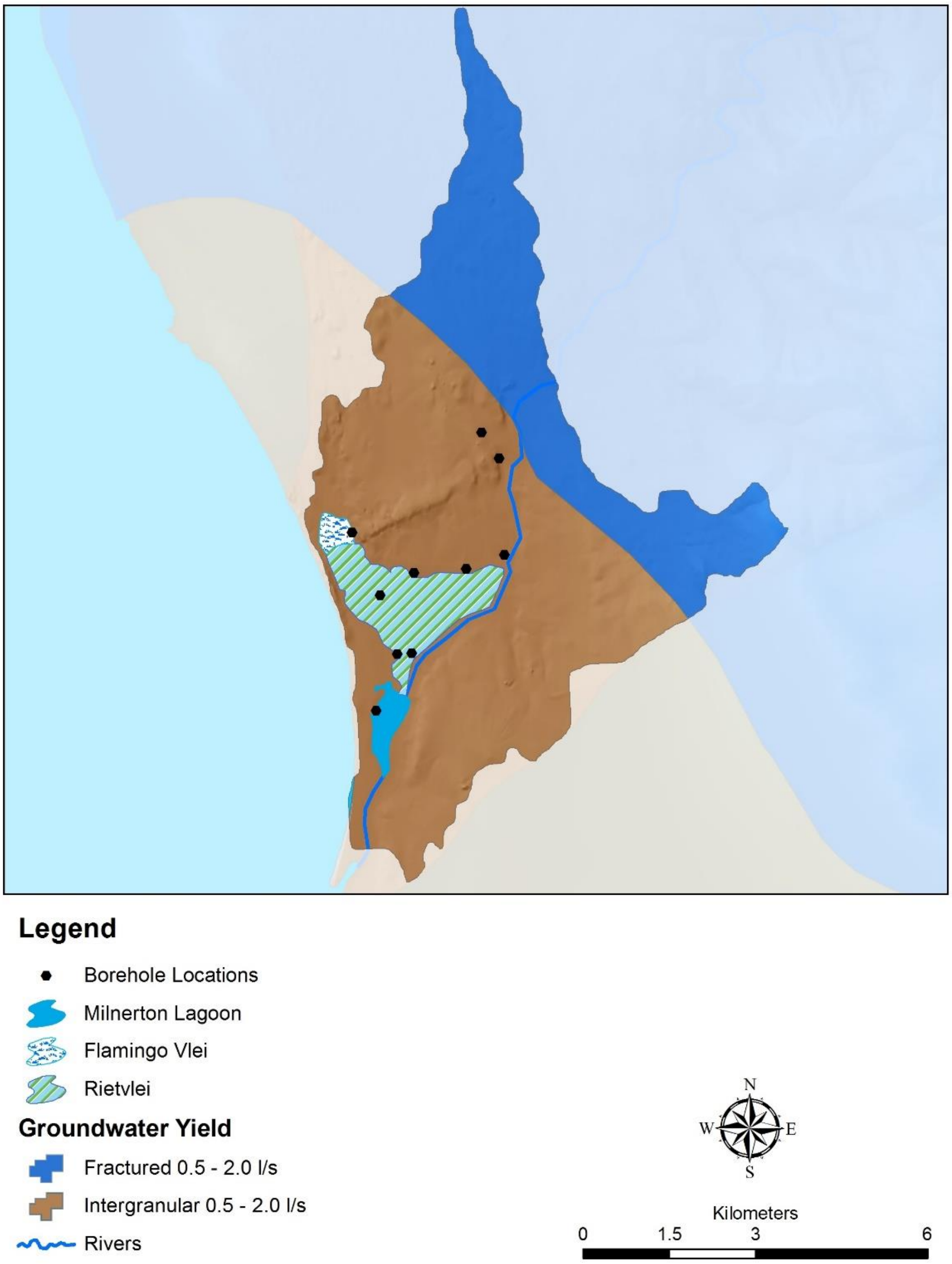

Figure 16: Groundwater yield

3.2.8 Possible pollution sources

Possible pollution sources within the Rietvlei area include the Chevron plant, Potsdam Waste Water Treatment Plant, a vast variety of manufacturers including Universal Cosmetic, Crous Chemicals, and other. Chevron is the third-largest crude oil refinery in South Africa that produces petrol, diesel, jet fuel and other products. Table 5 summarises the possible health impacts of Cu, Zn and Pb with their uses/incidences.

Table 5: The uses and health effects of the metal contaminants most commonly associated with water.

Metal	**Uses/occurrence**	**Possible health impacts**
Cu	• Building industry. • Animal feeds and fertilisers. • Sewage treatment process • Metal production	• Impedes human nervous- and cardiovascular systems (skin, bone, immune and reproductive systems). Impedes particular microbes' growth. • Low levels can cause heart and circulatory issues, bone irregularities and immune system difficulties (Bost *et al*., 2016). • High levels leads to gastrointestinal distress, as borehole as kidney- or liver damage (National Research Council, 2000) • Decrease in biological diversity (Medina et al., 2005).
Pb	• Plumbing materials and water services, • Pb paint chips • Cosmetics • Pesticides • Automobile exhaust (Little & Wiffen, 1977)	• Decrease in IQ (intelligence), anemia, leads to deafening, and irregular growth of kidneys, heart and brain. • Exceedingly high concentrations lead to ataxia, cerebral oedema, paralysis, coma and, even death. • Hyperactivity, poor attention span, IQ shortcomings and palsy, or wrist drop Pb-contaminated drinking water - increase in blood pressure, kidney problems. • Problematic pregnancies, reproductive, digestive and memory problems, nervous disorders. • High blood-lead levels (Cui *et al*., 2005; Van der Kuijp *et al*., 2013; Huang *et al*., 2012; Taylor *et al*., 2010).
Zn	• Conductor of electricity.	• Essential element in plant and animal growth.

Metal	Uses/occurrence	Possible health impacts
	- Galvanising. - Deodorants, wood preservative, suntan lotion. - From worn rubber tyres on vehicles	- Hair loss, skin lesions, diarrhea, withering of body tissues and ultimately death, brain development is hindered in utero and in infancy, malfunctions in cerebral activity are all results of deficiencies. - High levels suppress Cu and Fe absorption (Zhang *et al*., 2012; Taylor *et al*., 2010).

Groundwater vulnerability is an idea "*that some land areas are more vulnerable to groundwater contamination than others*" (Vrba & Zaporozec, 1994). Figure 17 shows that the groundwater vulnerability is very high. This means that the areas easily transmit pollution to groundwater. There are multiple ways to establish groundwater vulnerability (Ewusi *et al*., 2016). The technique used in South Africa is the DRASTIC approach formulated by Aller *et. al*, (1998), the inherent vulnerability dependents upon the hydrological, geological and hydrogeological properties of the areas (Zwahlen 2004).

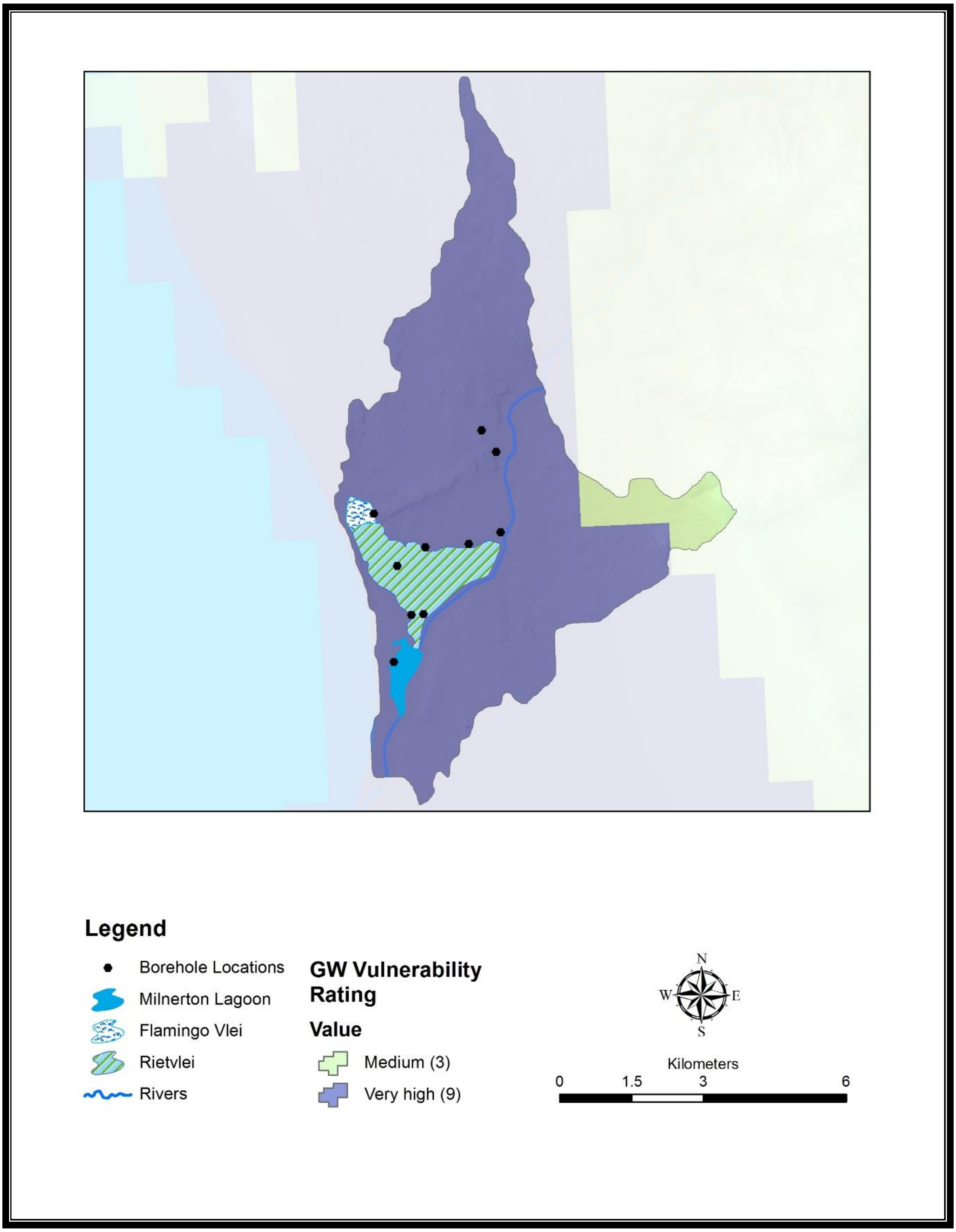

Figure 17: Groundwater vulnerability

4 METHODOLOGY

4.1 Data collection

In any investigation, collection of the relevant information pertaining to the investigation, is done first. However, before the data collection the study area extent was reduced to a sub-catchment of the Diep River system focusing on the tracer metal issues in the vicinity of the Rietvlei and Milnerton Lagoon.

In this study, work related to the groundwater characterisation in the Rietvlei area has been undertaken to compliment the generation of a groundwater model. This was underpinned by the following work:

- Eight piezometers of appropriate design (or borehole points) were installed across the study area (see Figure 18).
- The piezometers were dug into the subsurface and thereafter further penetrating the unsaturated zone with a column of PVC (Polyvinyl chloride). The manual drilling technique continued until the saturated zone was reached. Finally, the slotted borehole casing was installed below the level of saturation.
- Each piezometer had a combination of water quality and level logger. The logger was set to take a reading every 30 minutes.
- Manual measurements of water groundwater levels and water quality were taken to verify the logger readings.

In order to delineate sub-catchments, a digital elevation model (DEM) was imported into Global Mapper. The create water shed function within Global Mapper was then used to delineate a sub-catchment as shown in Figure 18.

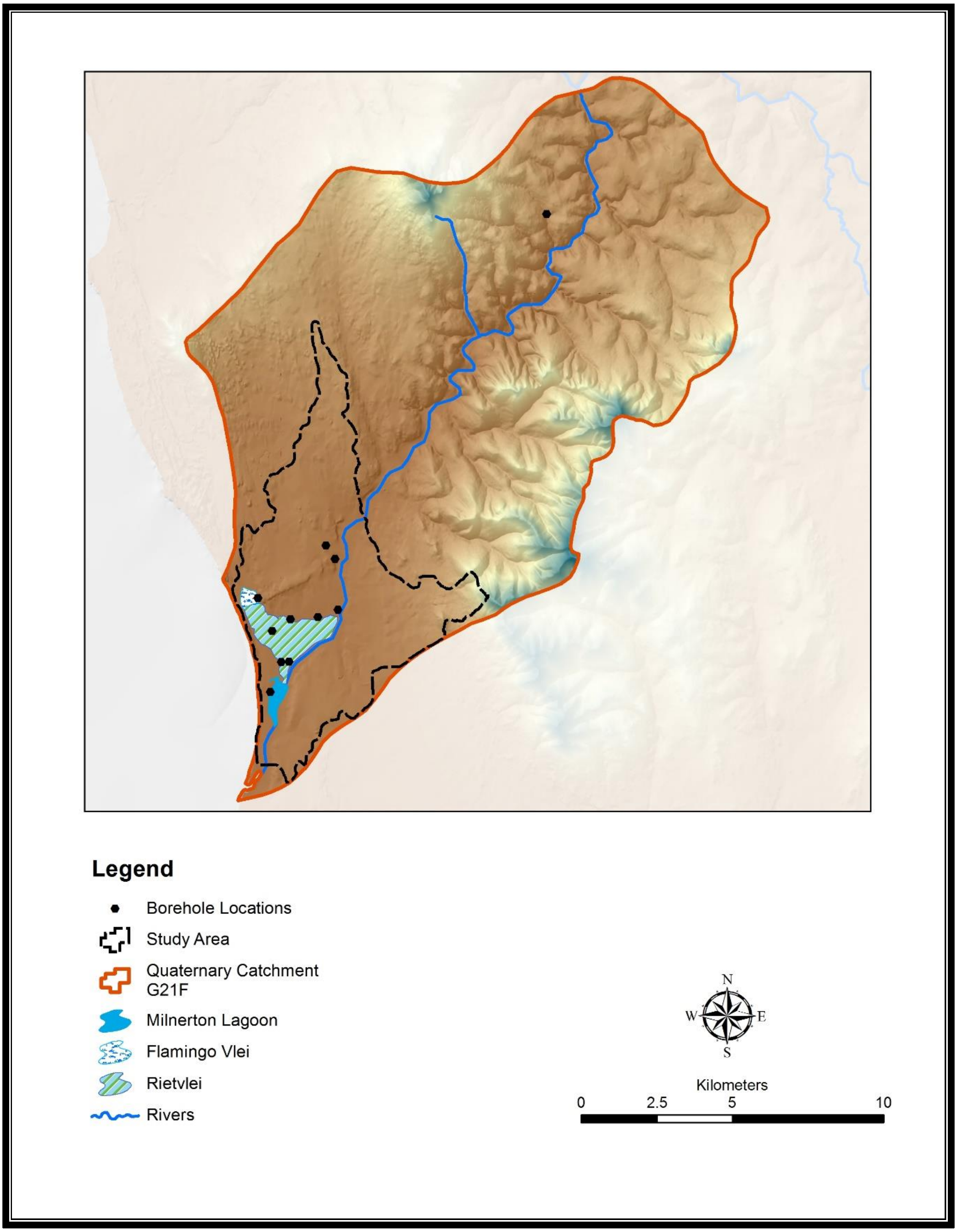

Figure 18: Sub-catchment with borehole locations

4.1.1 Collection of existing data

There are a number of existing data sets/reports that can be accessed for information. A summary of these is documented in Table 6.

Table 6: Data Sources (Dennis *et al*., 2012)

Data needed	Data and information	Source
Study area	Quaternary catchment boundaries	WR2005
Water sources	Flow-gauging stations	Department of Water Affairs and Sanitation
Physiography	Topographical maps – 1:250 000 – 1:50 000 (if needed)	Dir. Surveys and Land Information
Climatic information	Rainfall Evaporation	WR2005 Department of Water Affairs and Sanitation Consultant reports
Geology	Maps	Council for Geoscience
Soils	Maps	Department of Agriculture, Forestry and Fisheries Agricultural Research Council WR2005 Landsat 8 OLI Hyperspectral image
Drainage	Flow data	Department of Water Affairs and Sanitation WR2005
Vegetation and land-use		SANBI WR2005
Geohydrology	Maps – national groundwater maps – groundwater vulnerability map – 1:500 000 maps	Water Research Commission Department of Water Affairs and Sanitation
Geohydrological information	– national groundwater database – reports – aquifer parameters	Consultant reports National Groundwater Archive
Catchment study reports	Common and documented information about water resources	Consultant reports Department of Water Affairs and Sanitation

Figure 19 depicts surface water bodies located in the study area.

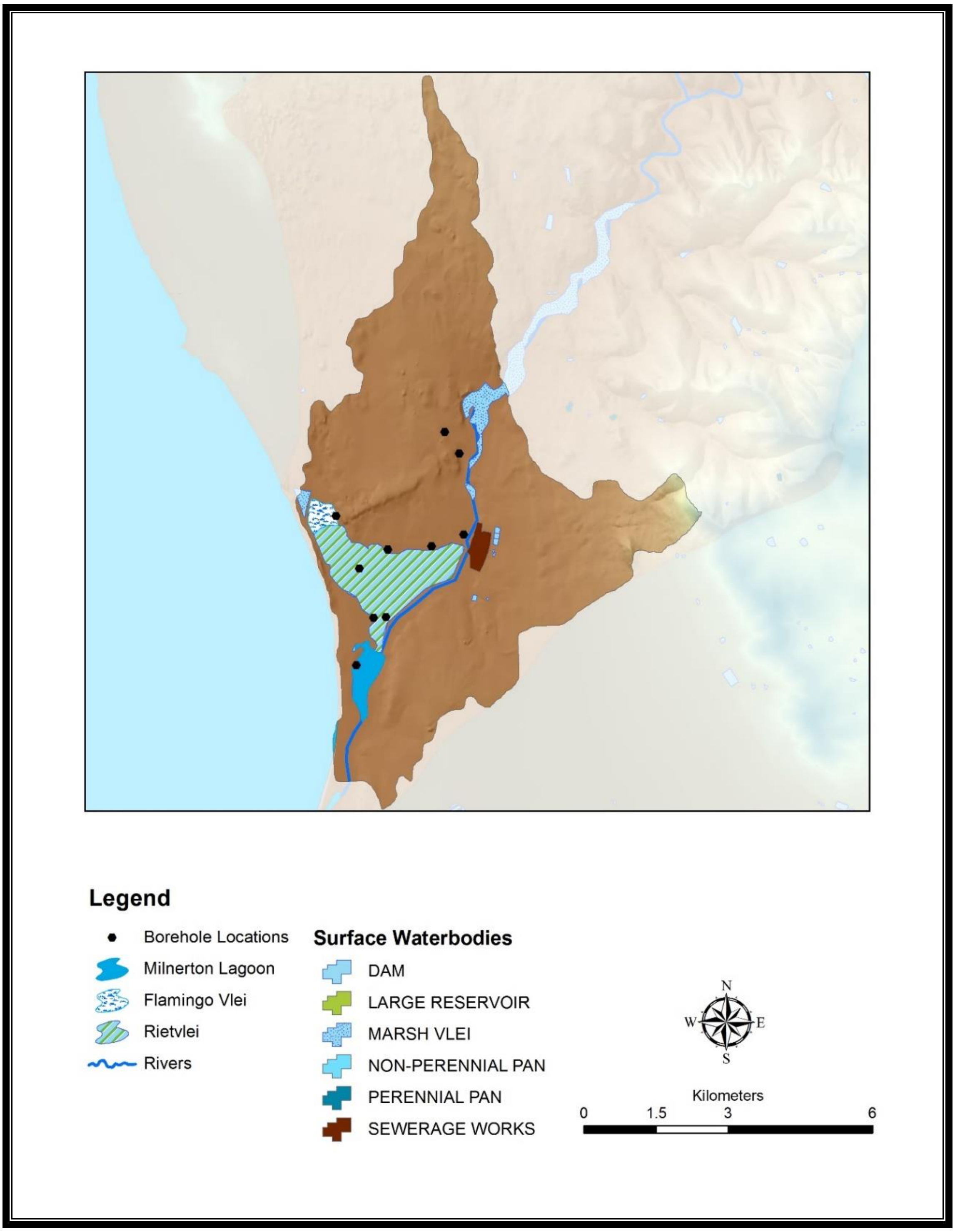

Figure 19: Surface water map

4.2 Data assessment

4.2.1 Hyperspectral analysis

Landsat 8 Operational Land Imager (OLI) and Thermal Infrared Sensor (TIRS) hyperspectral images comprise of a total of nine bands with a spatial resolution of 30 m for Bands 1 - 7 and nine. The eighth band is also known as the panchromatic band and has a 15 m spatial resolution. Band 1 and 9 are useful for coastal and aerosol studies and cirrus cloud detection, respectively. Bands 4 (Red) and 5 (Near Infrared) provides vegetation indices. Bands 10 and 11 are thermal and provides more accurate surface temperatures, they are collected at 100 meters. The estimated location size is 170 km north-south by 183 km east-west (Barsi *et al*., 2014).

The image data used in this study was acquired using Landsat 8 OLI. To establish spatial distribution of Zn, Pb and Cu concentration, the images had to be analysed and processed through ArcGIS (version 10.3.1) and Scyven (Scyllarus Visualisation Environment, version 1.3.0) software. Song *et al*. (2010) stated that these data are only applicable to barren soils and therefore, to separate barren soils on a space capsule image, the Normalized Difference Vegetation Index (NDVI) must be calculated.

Figure 20 shows approaches to estimate trace metal concentrations in soils using VNIRS. To statistically assess the correlation between the image and groundwater dataset, regression was performed. Steps to obtain the spectral signature of the bands and ultimately Zn, Pb and Cu concentrations are as follows:

A. **ArcGIS** (to composite and clip the bands to a desired area)
   1. Open all seven bands in ArcGIS.
   2. Windows > Image Analysis > Select all seven bands > Composite bands and clip to the study area > New image in table of contents > Export composited and clipped image and save as tiff.

B. **Scyven** (to analyse the spectral signature of the study area)
   1. Open composite image > Settings > Pre-processing: check Filter box and select Savitzky Golay (spectral) > OK
   2. Draw polygon around the study area > Right click > Plot polygon spectra > Run Analysis > Results will appear in the Plots section > Export results.

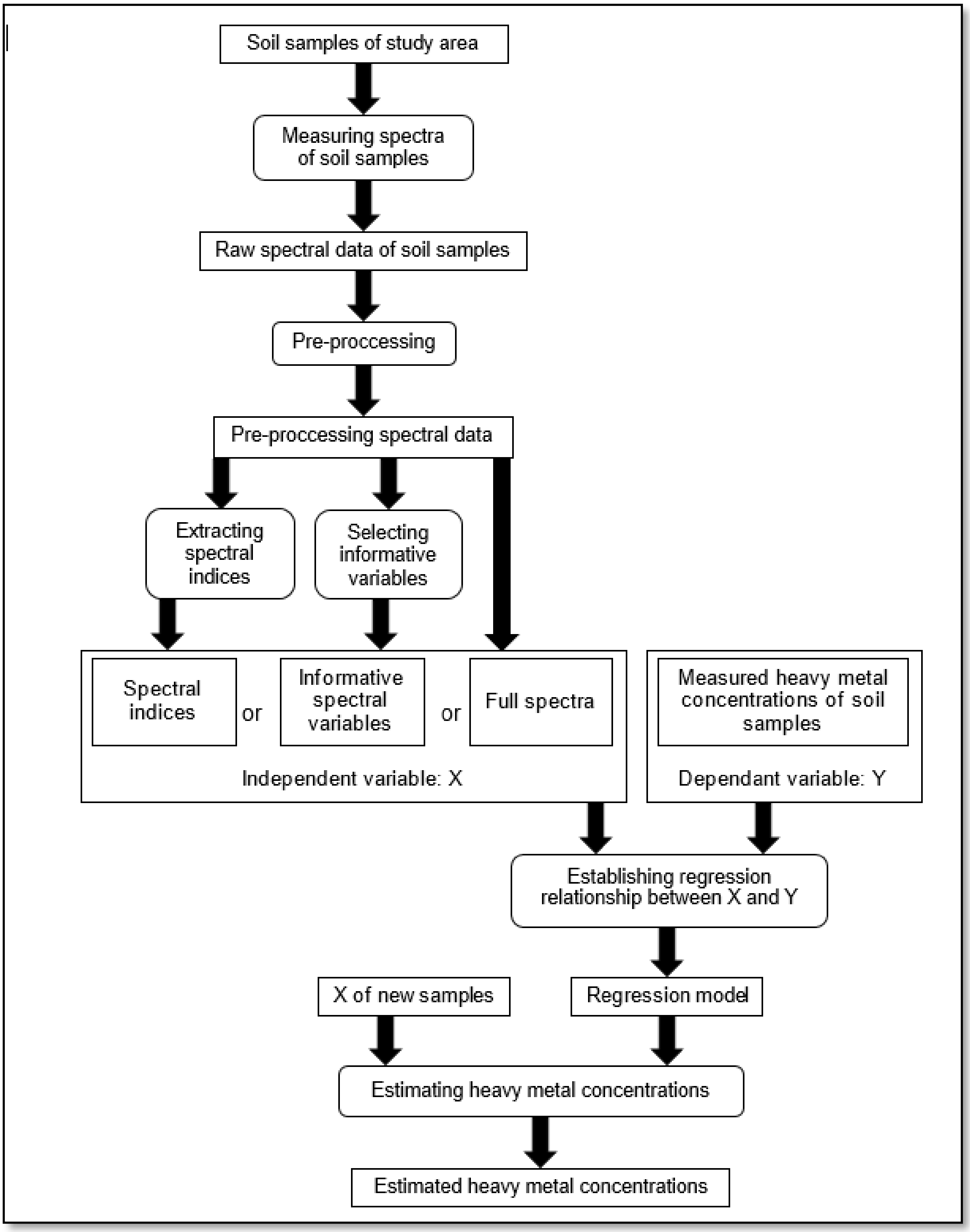

Figure 20: Approach to estimating TME concentrations in soils using VNIRS (from Shi *et al*., 2014).

C. **ArcGIS** (to generate two maps of concentrations in the study area to compare with ground data)
   1. Calculating the NDVI: Windows > Image Analysis > Select composite image > Make sure in Options that NDVI Red band = 4 and Near Infrared band = 5 > Processing: NDVI
   2. Toolbox > Spatial Analyst Tool > Map Algebra > Raster calculator > (Near Infrared – Red)/ (Near Infrared + Red)
   3. Calculate concentrations by using linear equations for Zn, Pb and Cu (from Asmaryan *et al*., 2014):

      (i) Zn = 0.9552 x Spectral Irradiance Values (Reflectance) – 149.69
      (ii) Pb = 0.3458 x Spectral Irradiance Values (Reflectance) – 75.527
      (iii) Cu = 0.7098 x Spectral Irradiance Values (Reflectance) – 129.12

   4. Generate spatial distribution maps for Zn, Pb and Cu concentrations.

D. Generate correlation graphs of Zn, Pb and Cu for the measured vs. predicted concentrations.

Figure 21 shows the reflectance spectra from the hyperspectral image.

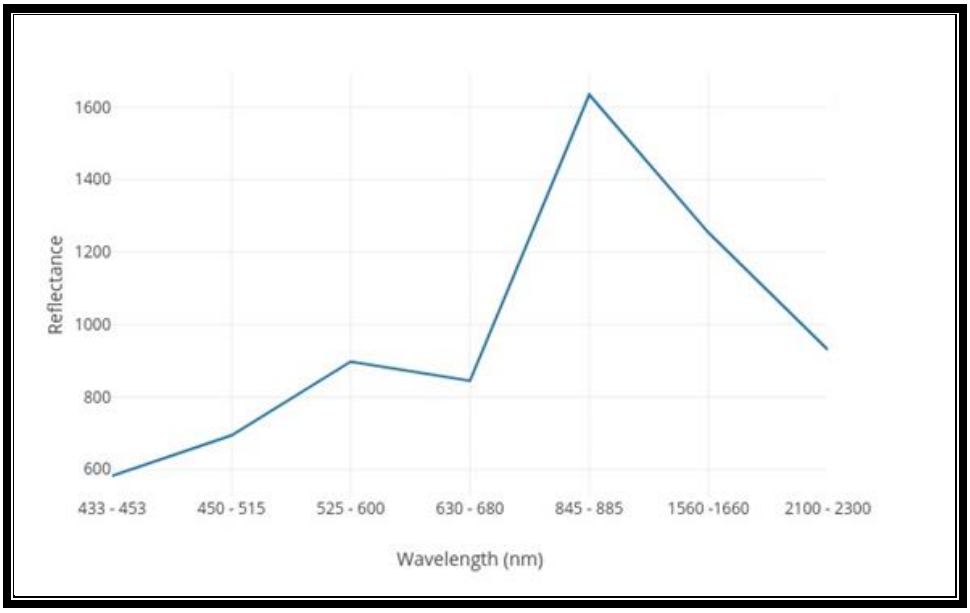

Figure 21: Reflectance spectra from the hyperspectral image

4.2.2 Water quality

The majority of the data used for this study are secondary data acquired over a period of time. Samples from eight boreholes with varying depths ranging from in various locations within the Rietvlei wetland area. The parameters like dissolved oxygen, pressure, salinity, pH, TDS, temperature and redox potential were calculated.

In order to determine what mechanism is dominant in the area, the Na^+, Ca^{2+} (in mg/L) and TDS concentrations must be plotted (Gibbs diagram) against each other for the specific borehole. Na:(Na^+/Ca^{2+}) was then plotted. The variation in TDS (mg/L) was then plotted on the y-axis.

4.2.3 Stable isotope analysis

Fifteen water samples were submitted for stable isotope analysis ($\delta^{18}O$ and δ^2H). The water sample analyses for this study were done with the help of the off-axis integrated cavity output spectroscopy (OA-ICOS) method. This was performed on an LGR (Los Gatos Research) DLT-100 liquid water isotope analyser (model 908-0008) manufactured by Los Gatos Research Inc. This is linked to a LC PAL liquid auto-sampler (model 908-0008-9001) by CTC Analytics for the simultaneous measurement of $^2H/H$ and $^{18}O/^{16}O$ ratios of water samples. The auto-sampler was either inserted with a Hamilton 1.2 µl syringe (model 26P/-mm/AS, 7701.2N) by Hamilton Company (Reno, USA) or a SGE 5µl (model 5F-C/T-0.47/5C) for the injection process of the water samples into heated injector block (85°C). The DLT-100 Liquid-Water Isotope Analyser model provides a 1-sigma precision below 0.6‰ and 0.2‰ for δ^2H and $\delta^{18}O$, respectively.

4.2.3.1 Analytical procedure

Every water sample and laboratory guideline were inserted into glass vials (2ml capacity) with PTFE (Polytetrafluoroethylene)/silicone/PTFE septum vial screw caps. The vials were filled with 1-1.5ml of water sample leaving approximately 0.5ml headspace and positioned into 54 set tray holder on the auto-sampler. All of the samples were then injected 10 times where the first few (5) are ignored and the average of the non-ignored values is taken as delta value. Three guidelines that bracket the samples isotopic composition are done sequentially with the samples. Between each injection the sample chamber is flushed with air that is drawn via a desiccant column for water molecules to be removed.

All values are expressed in the standard delta notation in the per mill (‰) relative to VSMOW as:

$$\delta = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000$$

Where R is the heavy to the light isotope ratio ($^{18}O/^{16}O$) of the sample and the standard. For data normalisation, three standards were adjusted exactly against VSMOW2 and SLAP2 (Vienna Standard Mean Ocean Water–Standard Light Antarctic Precipitation) international standard waters. The data were normalised to the VSMOW/SLAP scale.

The following laboratory standard procedures are undertaken in the following order to obtain high quality delta $\delta^{18}O$ and $\delta^{2}H$ values for every analysis:

- The raw data files are imported into LGR's LWIA Spectral Contamination Identifier™ (version 1.0.0.69) to identify any samples that may have organic contaminants (alcohol, plant and soil water extracts, etc.) that have the ability to lead to severe spectral interference, causing poor isotopic estimation outcomes.
- The data is then incorporated into LIMS (Laboratory Information Management System) for Lasers 2015 (version 10.088) software which functions as a data processing pre-screening tool to outline the following:

    1) Identifying bad samples based on poor $H_2 0$ injection concentrations
    2) Correcting for between-sample carryover (or memory)
    3) Correcting for linear and nonlinear instrumental drift
    4) Normalisation of data to VSMOW/SLAP scales using lab standards
    5) Tracking quality assurance or quality control of the tool on a daily and long-term basis
    6) Keeping track of all samples and projects

Trace metals were analysed at Stellenbosch at their Central Analytical Facility on an ICP-MS (Inductively Coupled Plasma Mass Spectrometry).

4.3 Numerical modelling of Groundwater

Bayesian interpolation and variational data are grounded upon Bayes' theorem. Both experience problems when represented in a linear form with related assumptions, and accordingly, one is disguisable. Bayesian interpolation is preferable acceptable to fit data randomly and distribute asymmetrically with obscure inaccuracy by not exerting the information to an unwanted (Leroy *et al*., 2012).

Bayesian interpolation is known as an application of Bayesian inference rank. "The first inference level is about x^2 fitting of predefined basis functions to data with a prior defined so as to penalize the overfitting of data. The following inference level appoints the best symmetry between misfit and overfit of the data". The outcome obtained is the most credible fit and these values can be used to compose maps when they are applied in two dimensions on a sphere. Bayesian interpolation anticipates negation of the systematic error problem since it fits data through position and time functions, it successfully acknowledge where anomalous data clusters occurs (Leroy *et al*., 2012). The water levels used are available in Table 7.

Table 7: Once off water levels with associated wells/boreholes.

	x-Coordinate	y-Coordinate	Water level (m)
Well 1	-47139.02	-3745262	7.59
Well 2	-46443.51	-3747414	3.2
Well 3	-46185.95	-3747409	3.52
Well 4	-46698.5	-3746373	2.43
Well 5	-46844.4	-3748385	2.18
Well 6	-46089.39	-3746007	3.12
Well 7	-45179.36	-3745975	4.01
Well 8	-44507.76	-3745758	4.54
BH 1	-44815.91	-3743612	10.22
BH 2	-44530.44	-3744073	5.73
BH 3	-37090.46	-3732949	49.99

The first step in Bayesian interpolation is where water levels are correlated with topography (Figure 22). The results indicate a correlation of approximately 98%

Bayesian interpolation is therefore valid and used to calculate groundwater levels for the study area as shown in Figure 23.

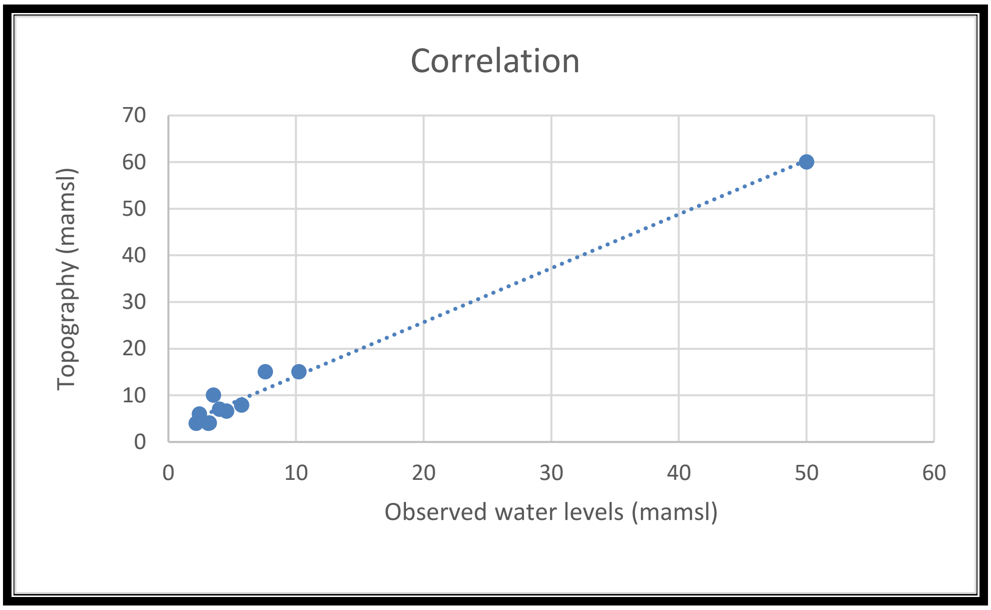

Figure 22: Correlation between topography and groundwater levels

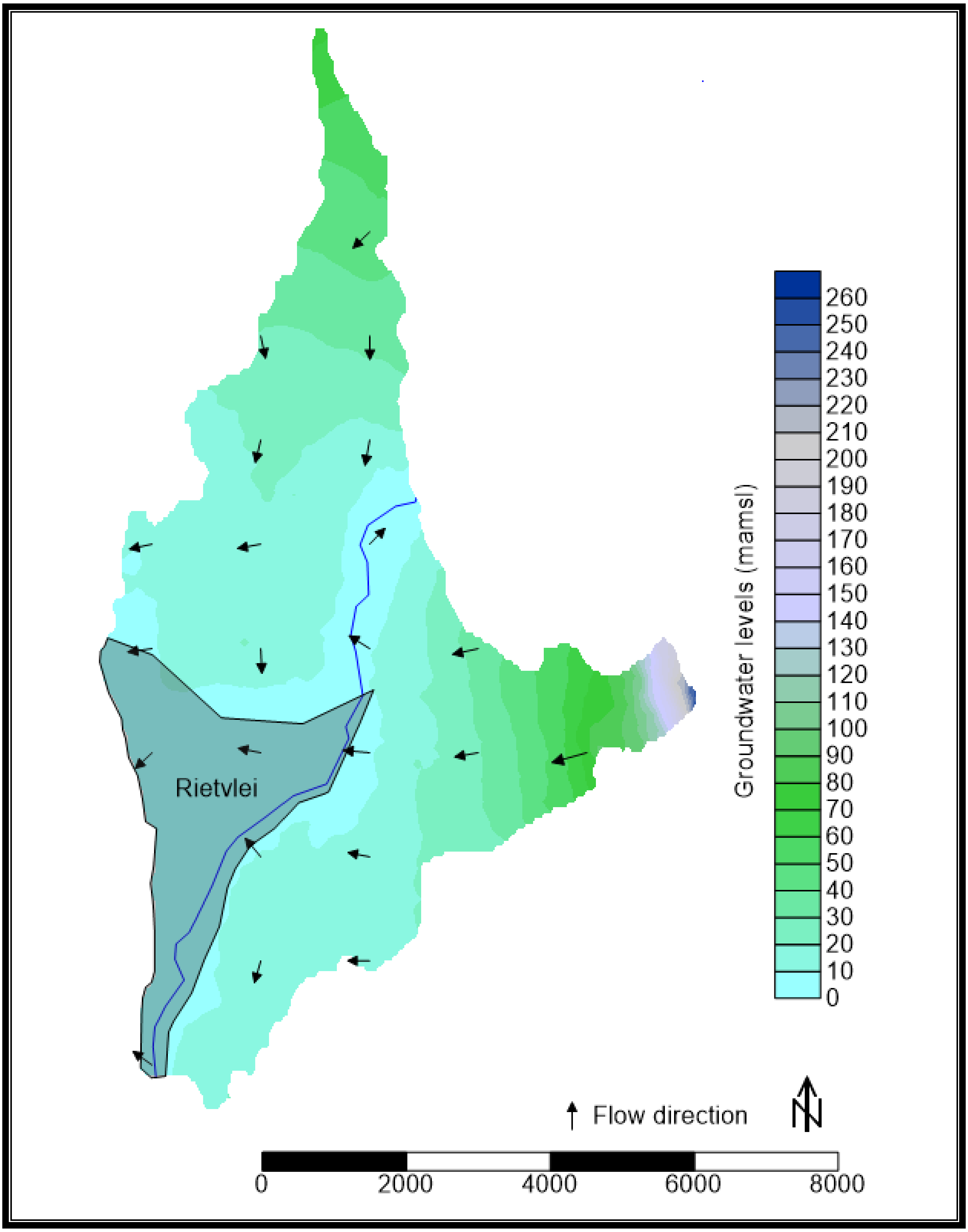

Figure 23: Groundwater levels and flow directions

A numerical groundwater water flow model was developed for the Rietvlei using the sub-catchment boundaries. A grid was generated for the study area using a finite difference approach. The grid consists of 468 cells in the x-direction and 384 cells in the y-direction. The dimensions of each cell are 50 m x 50 m. The modelling exercise should consider the recharge and geohydrological characteristics of the site - which include aquifer systems, aquifer parameters and possible exchange between surface water systems and the groundwater systems. Aquifer parameters for the model are listed in Table 8. The rivers in the Rietvlei region are fixed-head boundaries. Existing groundwater levels are used to calibrate the model. The calibration and correlation outcomes are displayed in Figure 24 and Figure 25.

Table 8: Model parameters

Model parameters	**Model values**
Transmissivity	200 m^2/d for sands 30 m^2/d for fractured rock
Storativity	1 x 10^{-3} for fractured rock
Specific yield	3 x 10^{-1} for sands
Porosity	3 x 10^{-1} for sands 1 x 10^{-1} for fractured rock
Rainfall	500 mm/year
Recharge	13.42 mm/year

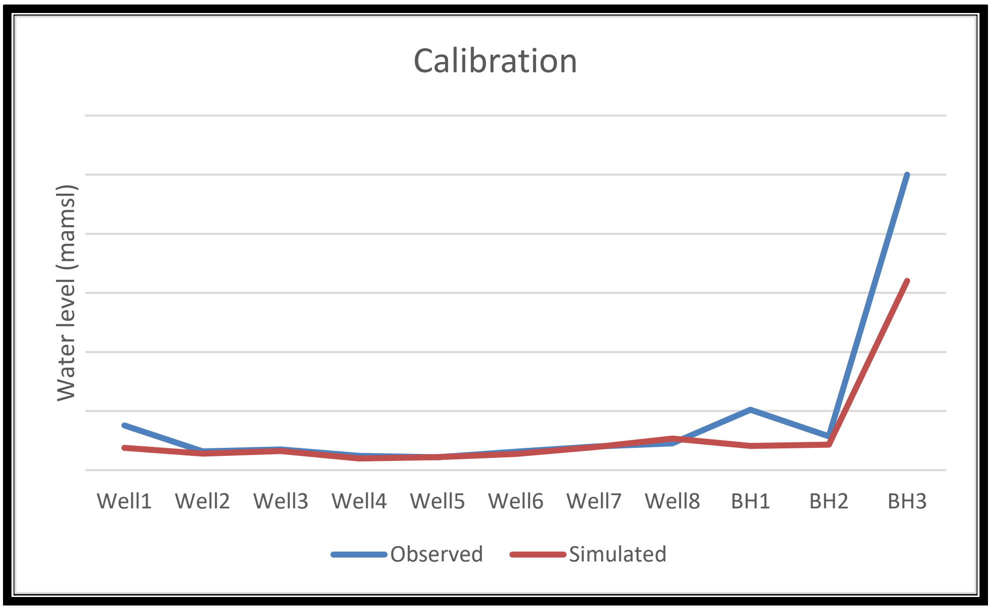

Figure 24: Calibration

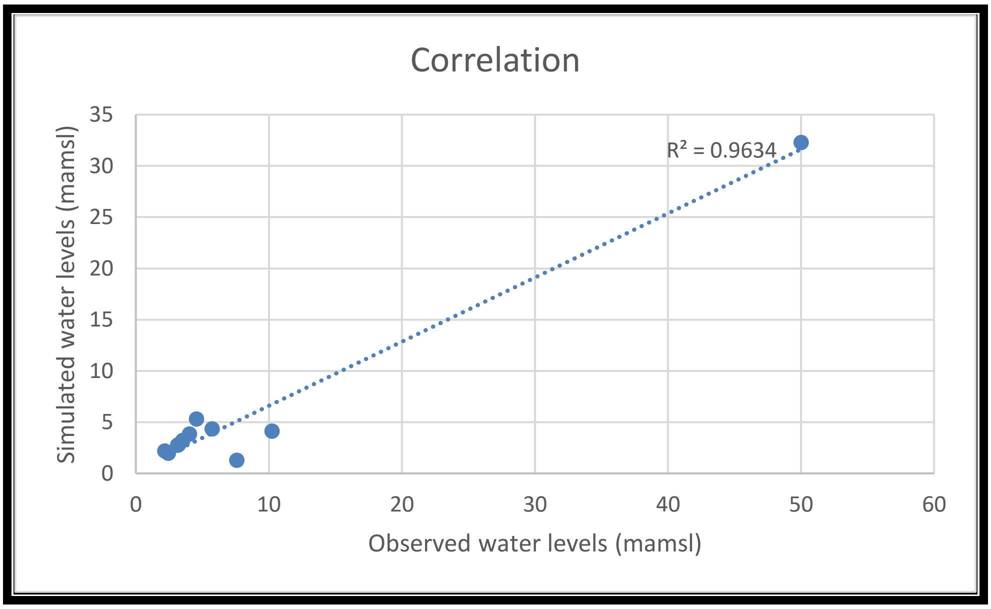

Figure 25: Correlation

4.4 Mitigation

Mitigation methods were discussed in Chapter 2. Three of them could be considered to reduce the pollution that occurred; namely "*Pump and Treat, In-situ flushing and Natural Attenuation*". The other two ("*Permeable Reactive Barrier and In-situ Air Sparging*") are not viable because they are either too expensive and/or the extent of the area is too large for it to be successful. Only the "*Natural Attenuation*" was used in MODFLOW to determine its efficacy. When it is done practically, the mitigation results will have to be examined over a period to establish the efficacy of the selected mitigation method.

5 RESULTS AND DISCUSSIONS

5.1 Hyperspectral analysis of soil

Reflectance spectra measured with Scyven are shown in Figure 21. Cu, Zn and Pb were analysed as an indicator of the contamination in the Rietvlei. Appendix 9.1 gives descriptive statistics of Cu, Zn and Pb of the measured groundwater samples.

The spatial distribution Zn, Pb and Cu in the Rietvlei are illustrated in Figure 26, Figure 27 and Figure 28.

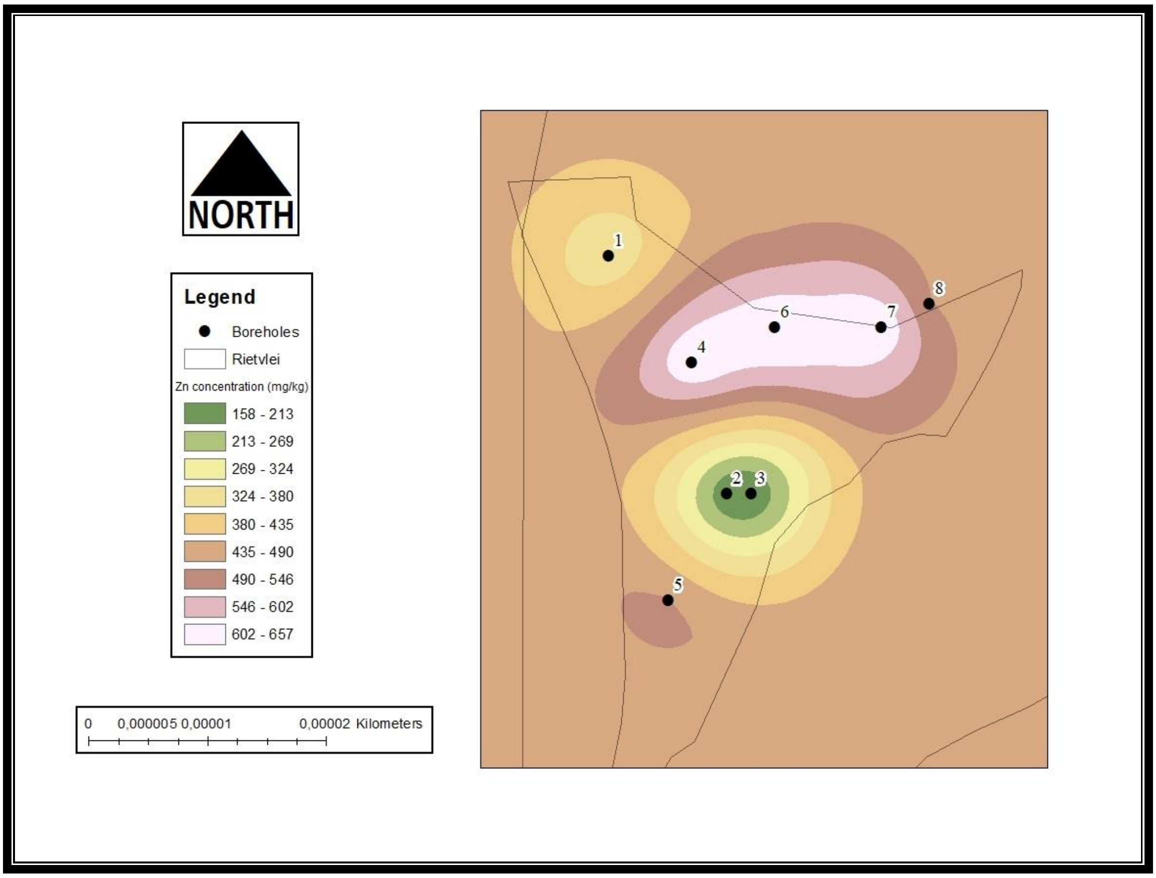

Figure 26: Spatial distribution of Zn in the Rietvlei

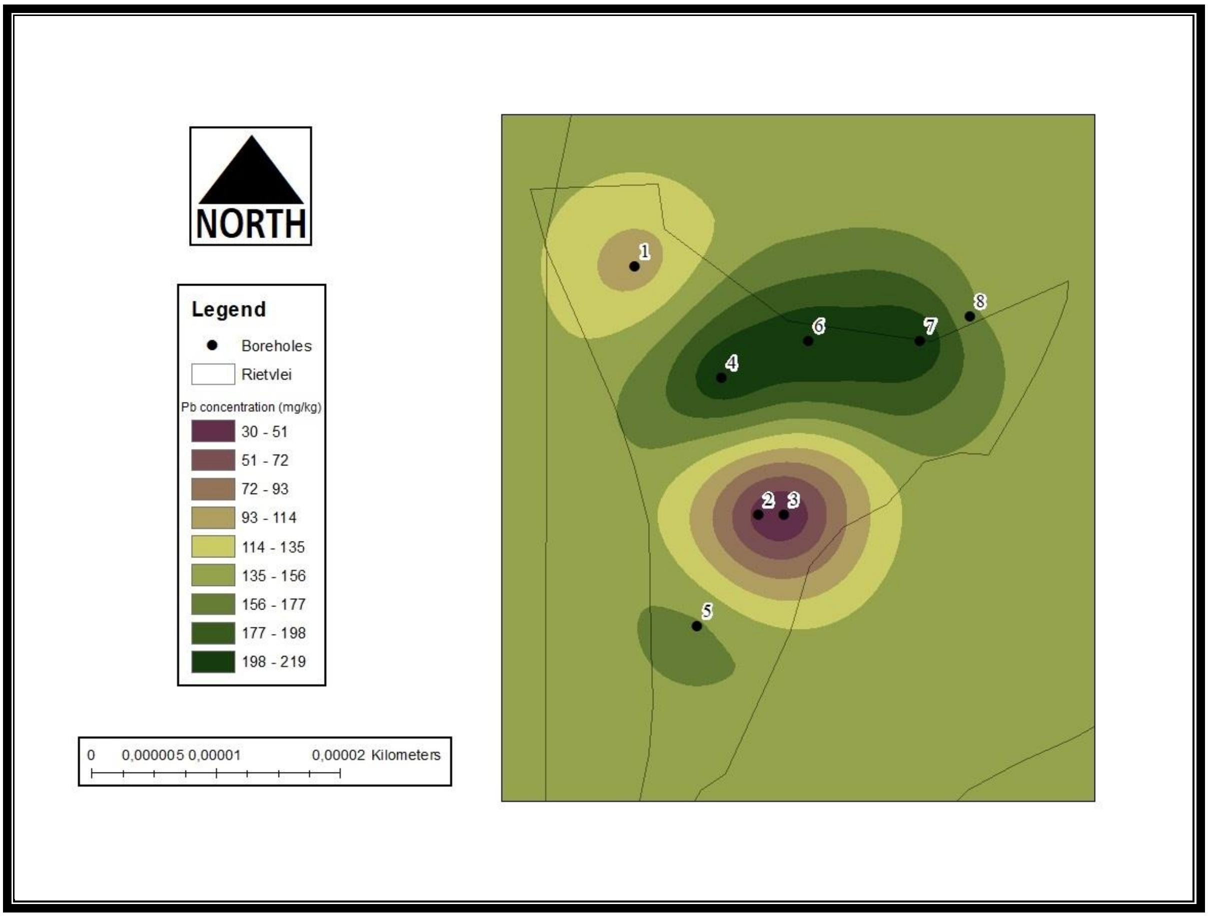

Figure 27: Spatial distribution of Pb in the Rietvlei

Regression analysis was performed between groundwater measurements and spectral data to estimate the relationship between the two variables. It is done to predict the accuracy of the remote sensing method. The results indicate the possibility of the spectra to predict the soil concentrations. The soil concentrations according to the hyperspectral analysis are much higher in comparison to that of the groundwater. Trace metals can be transported from the soil, causing groundwater to be enriched and contaminated. The Zn levels from the image range from ≤ 165 mg/kg to about 660 mg/kg. Whereas the concentrations for the groundwater is 0.69 mg/kg (lowest) to 50.1 mg/kg (highest). Although there is a vast variation between the soil and groundwater information, one can observe that the highest concentration measured (50.1 mg/kg) and predicted (660 mg/kg) is borehole 4. In the case of Pb; it ranges between ≤40 - 220 mg/kg, and groundwater 0.7 - 34.8 mg/kg. The regression analyses for Zn, Pb and Cu are shown in Figure 29, Figure 30 and Figure 31.

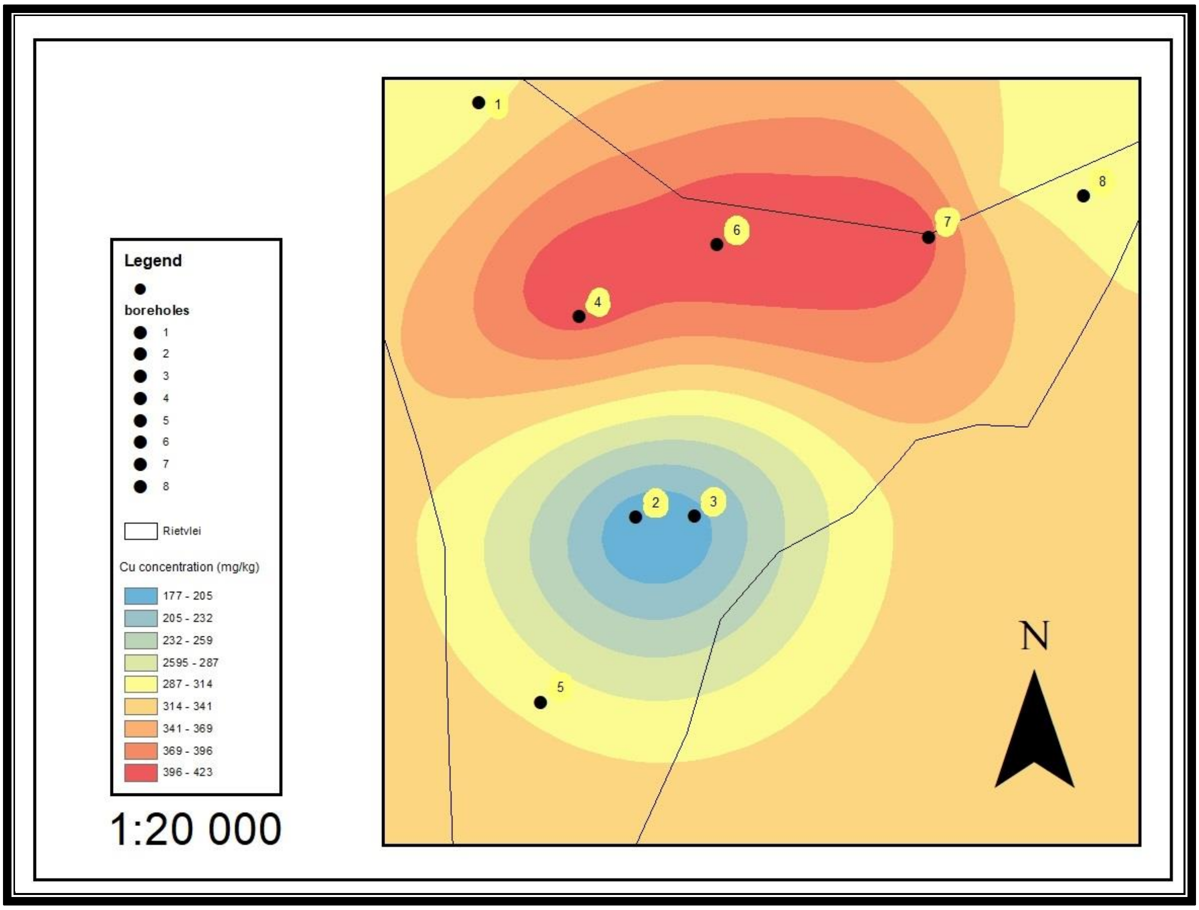

Figure 28: Spatial distribution of Cu in the Rietvlei

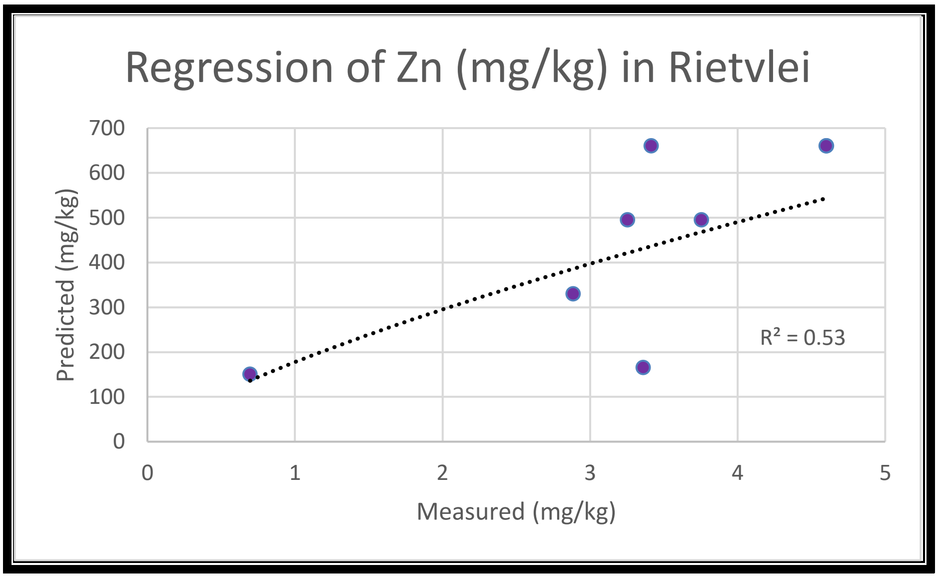

Figure 29: Regression of Zn between the measured concentrations and predicted concentrations.

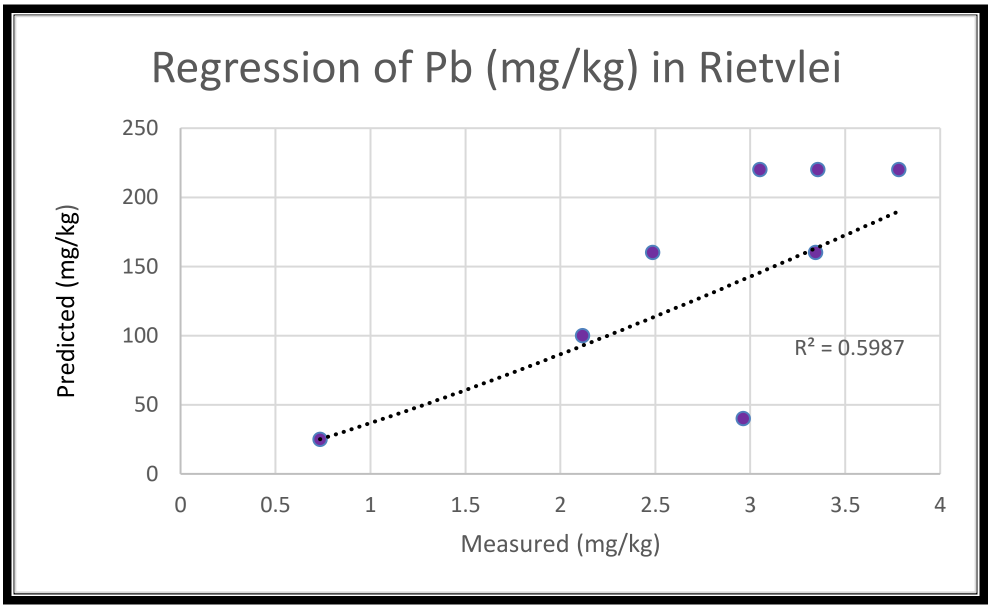

Figure 30: Regression of Pb between the measured concentrations and predicted concentrations

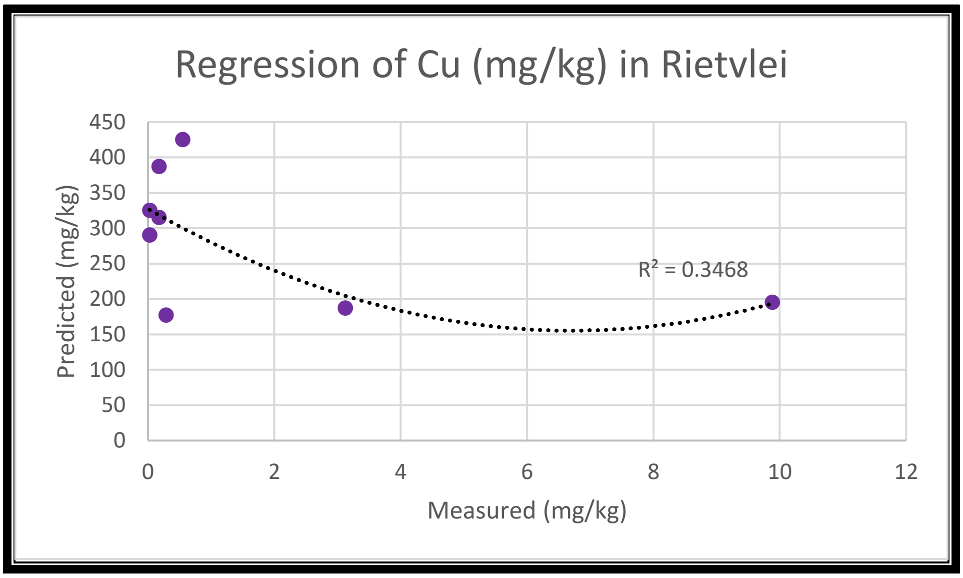

Figure 31: Regression of Cu between the measured concentrations and predicted concentrations

The Cu concentration obtained from the image range from 177 – 325 mg/kg. This is relatively high according to the guidelines in Table 9, whereas the concentrations for the groundwater is 0.25 mg/kg to 14.8 mg/kg. Regression between Zn, Pb and Cu from the groundwater and predicted concentrations is 0,53; 0,5987 and 0,3468, respectively. Pb and Zn prove to be > 0.5 which indicates a medium quality. Low R^2-values indicate imprecise predictions. The regression are low indicating a lack of correlation. The reasons for this may for example interactions and processes like surface water transportation, organic matter interactions, adsorption to clay and oxide surfaces. Data scarcity has also been a limitation.

Table 9: Guidelines for trace metals (mg/kg) (from Choe *et al*., 2008).

Element	**Guidelines**	
	Low	**Median**
Cu	34	270
Zn	46,7	218
Pb	150	410

Most of similar studies done all have more than at least 29 samples. Taking the guidelines (Table 9) into account for the predicted concentrations, Cu is relative high (177 – 315 mg/kg), Zn too (165 - 660 mg/kg) and Pb is relatively low (40 – 220 mg/kg).

The Zn concentration for groundwater (Figure 32) is relatively low variation whereas the predicted soil concentration are much higher in comparison. This could be because Zn may migrate and undergo a number of processes while being transported from the soil to groundwater. Borehole 2 and 3 has the lowest concentration at < 165 mg/kg and boreholes 4, 6 and 7 much higher at concentrations between at 660 mg/kg. Borehole 7 indicates the highest concentration for both groundwater and soil. This shows that there is a relationship. This borehole is located closest to the Chevron refinery where they produce a variety of chemical products. Depicted in Figure 32, Figure 33 and Figure 34 are the concentrations of groundwater and forecasted soil levels.

In Figure 33 borehole 7, again, indicates the highest concentrations for both soil and groundwater. Interestingly, borehole 2 has a Pb soil concentration of 40 mg/kg but a high Pb groundwater concentration at > 4.5 mg/kg. This borehole is located near a road. Years ago, petrol contained Pb and automobile emissions polluted the soil. The reason that the groundwater is enriched with Pb and not the soil could be that the contaminant has moved from the soil to the groundwater over time. Also, the cosmetic manufacturing company is located near this borehole and Pb has been used for decades as a colouring pigment in paints and other materials.

The groundwater Cu concentration (Figure 34) at borehole 1 is the highest (> 9 mg/kg). The Cu soil concentration is also high at 290 mg/kg. Borehole 3 has the lowest concentrations for soil and groundwater at 177 mg/kg and 0.0285 mg/kg, respectively. This could be a results of the processes and interactions like surface water transportation, organic matter interactions, adsorption to clay and oxide surfaces etch that could transpire while the TMEs are distributing or lack thereof between surface and subsurface data. Noticeable, boreholes 6 and 7 are low in Cu concentration for groundwater but high in the case of the predicted soil concentrations. The wastewater treatment plant is located near boreholes 6, 7 and which could explain the high soil concentrations.

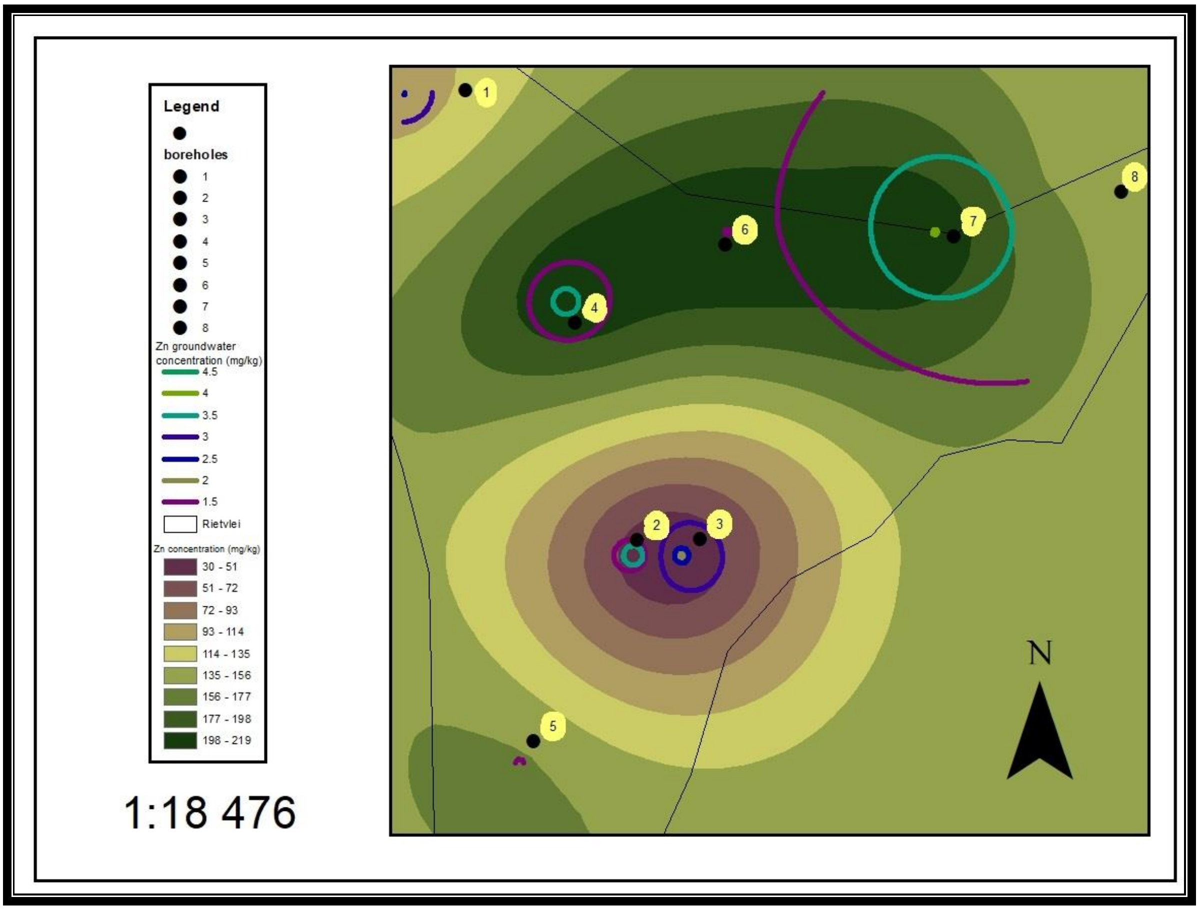

Figure 32: Relationship between predicted soil concentrations and groundwater concentrations of Zn.

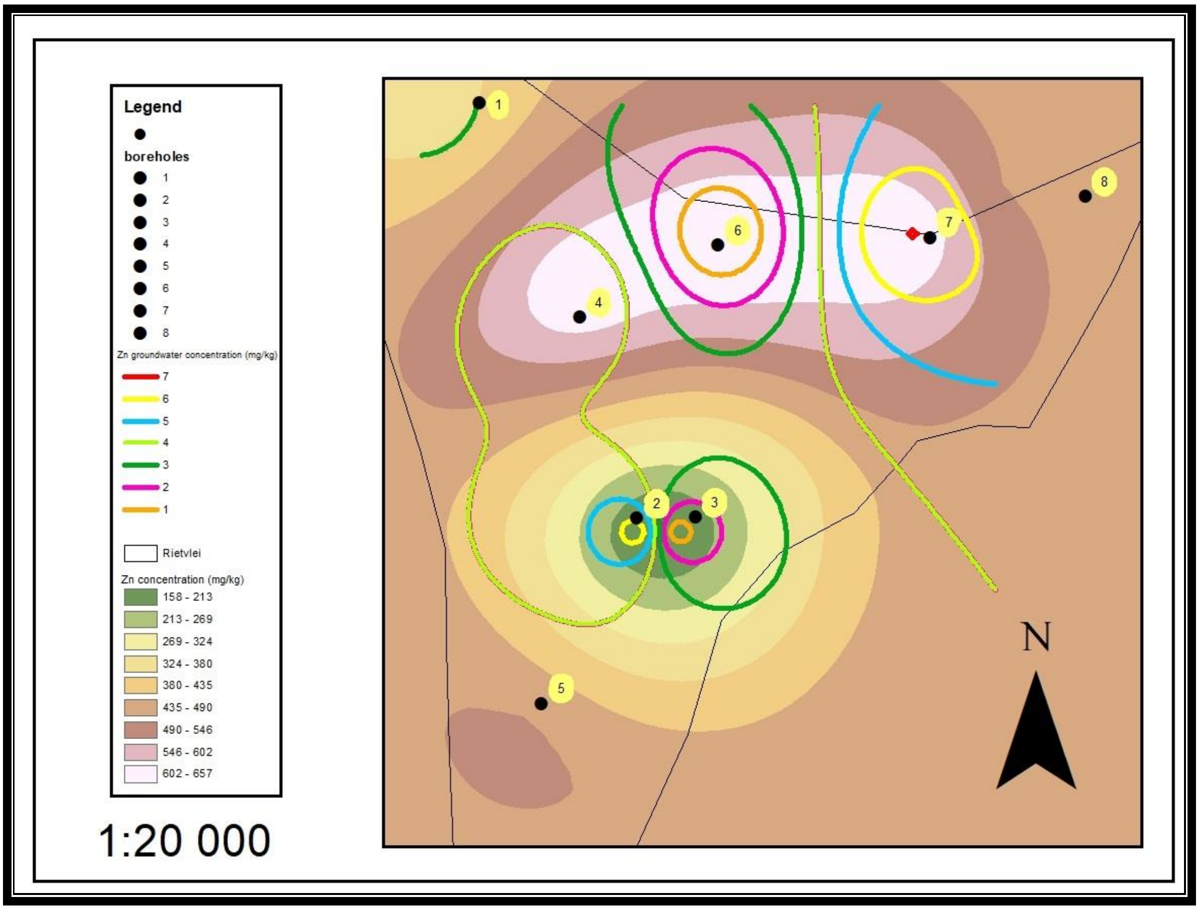

Figure 33: Relationship between predicted soil concentrations and groundwater concentrations of Pb

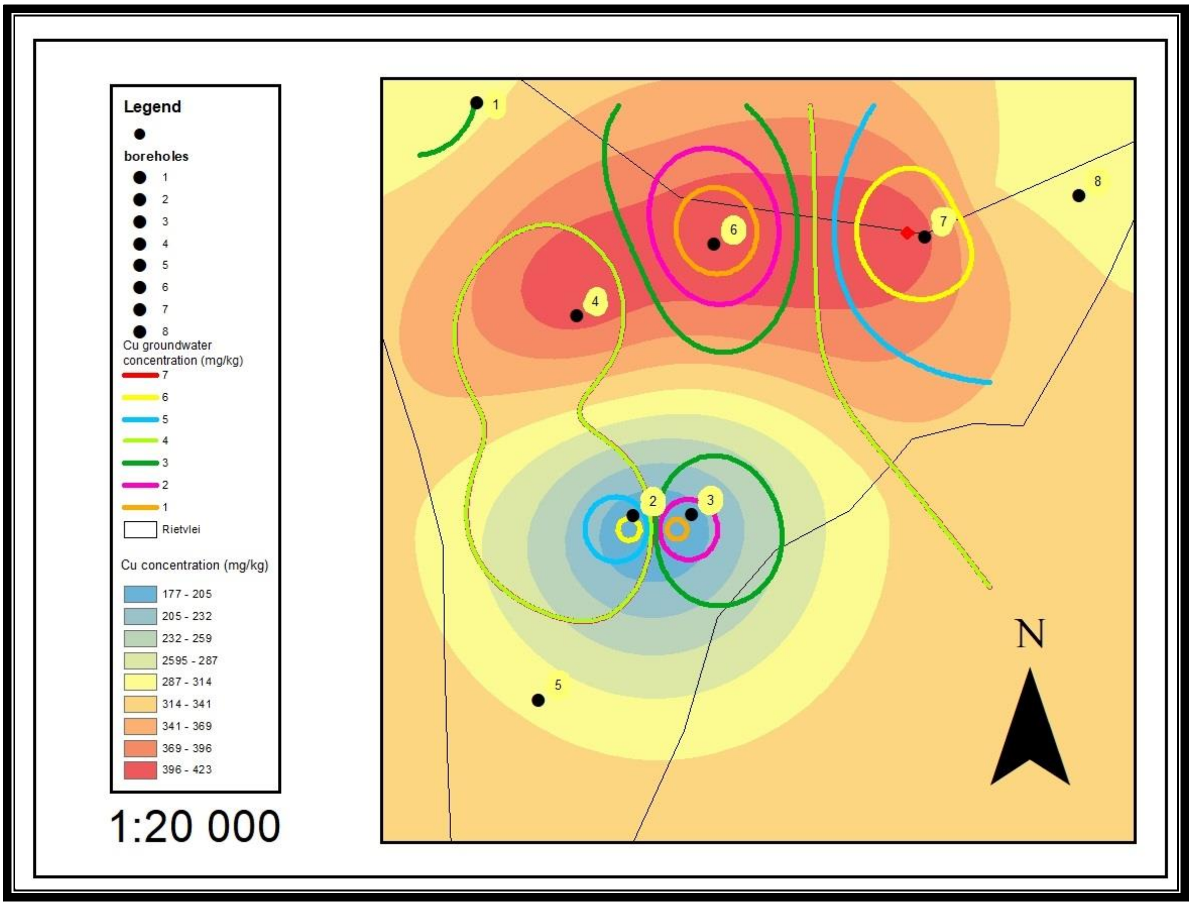

Figure 34: Relationship between predicted soil concentrations and groundwater concentrations of Cu

5.2 Water quality

5.2.1 Trace metal concentrations in the groundwater

Degradation of groundwater quality due to contamination is mostly due to anthropogenic activities but one must remember that groundwater contamination can occur naturally too. Table 10 represents the recommended safe metal concentrations in aquatic ecosystems as stipulated by the DWAF (1996) and the "*Canadian Council of Ministers of the Environment Quality Guidelines*" (CCME, 2001). It is important to adhere to the stipulated guidelines for metal concentrations in aquatic samples in order to determine whether the water is safe for utilisation. As seen in the table there are many trace metals in the boreholes that exceeds the acceptable values and therefore are not safe for human consumption. It may be troublesome to determine what the actual contamination source is, one can assume considering the positions of the boreholes. The elevated levels of certain TMEs in the boreholes can be linked to their commercial uses and possible health impacts (discussed in Chapter 3.11) and to where the boreholes are located in the area. Boreholes 1, 2, 5, 6, 7 and 8 are all situated near residential areas and/or roads while borehole 3 and 4 is near the Deep River and dam, respectively. All these boreholes are basically contaminated by the same trace metals; namely: Al, Fe, Mn, Pb, Zn while only borehole 7 indicated high Cu concentration.

Table 10: Trace metal concentrations in the groundwater

	DWAF (1996) (mg.l^{-1})	**CCME (2001) (mg.l^{-1})**	**BH1**	**BH2**	**BH3**	**B4**	**BH5**	**BH6**	**BH7**	**BH 8**
Al	0.1-0.15	0.005-0.1	0.59	0.18*	0.03	0.07	0.03	0.13	0.28*	0.04
Cu	0.002-0.012	0.002-0.004	0.01	0.01	0.005	0.02	0	0	1.24*	0.01
Fe	N/A	0.3	1.16*	0.28	14.45*	0.4*	1.06*	9.08*	4*	8.78*
Mn	1.3	N/A	0.07	0.42	3.21	2.45	0.3	0.4	0.41	8.24
Ni	N/A	0.025-0.15	0	0.01	0.01	0.02	0.01	0.02	0.02	0.03
Pb	N/A	0.001-0.007	0.00	0.01	0.06*	0.00	0.01	0.00	0.02	0.00
Zn	0.036	0.03	0.06*	0.09*	0.08*	0.44*	0.03	0.07*	0.14*	0.33

5.2.2 Gibbs diagram

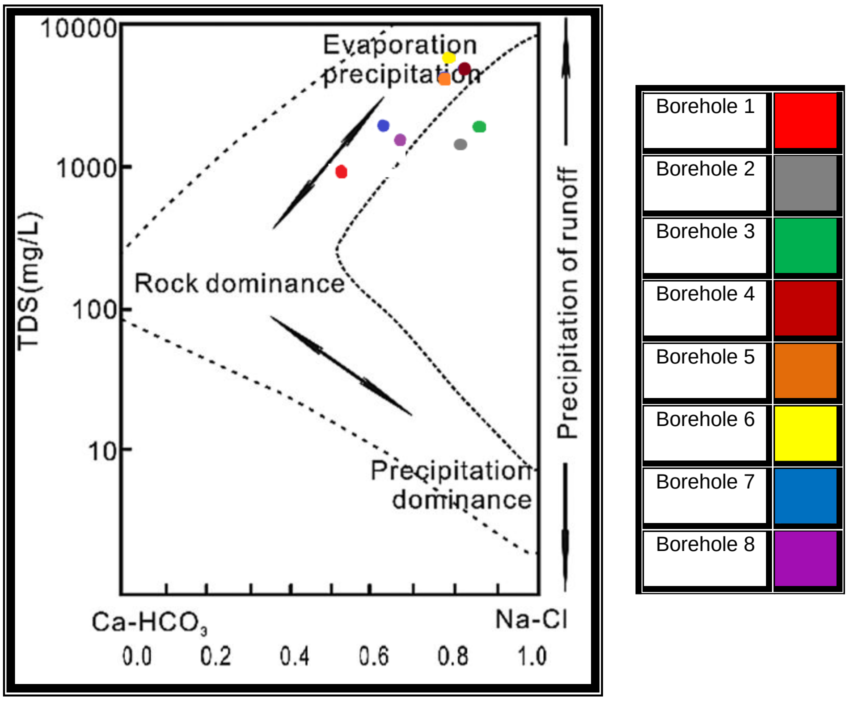

Figure 35: Gibbs diagram for controlling factor of groundwater quality with colours associated with the boreholes

Gibbs (1970) diagram was used to establish the dominant processes that control the groundwater chemistry. It is clear from

Figure 35 that all the water in the eight boreholes chemistry is predominantly influenced by the evaporation-precipitation mechanism, which explains the high salinity levels and poor groundwater quality. This type of mechanism can be expected due to the locality of the boreholes because they are situated near the coast. It is anticipated because evaporation substantially increases the ions concentrations produced by chemical rock weathering, causing elevated salinity. Ionic levels of major elements available in groundwater were analysed for comparable abundances and ionic affinity.

Field observations in the immediate vicinity of the Rietvlei allude to the excessive use of groundwater for irrigation of household gardens. This cumulative use could have a direct impact on the migration of the freshwater-saltwater interface further inland. This could also be the reason for anomalously high Electrical Conductivity (EC) readings at various groundwater boreholes in the area. The water in these boreholes is dominated by Na^+ and Cl^-. It also contains very high levels of dissolved solids. This is due to the high evaporation rate that causes the increase of salinity in the water. $CaCO_3$ precipitates from the solution and leads to an extreme raise in the relative proportion of Na to Ca. It seems that the ion chemistry of fresh groundwater evaporation was the primary factor. Borehole number one shows the lowest concentration of total dissolved solids, and it also shows the lowest concentration of $Na^+/(Na^+/Ca^{2+})$.

De Franco *et al*. (2009) categorised water quality into three classes in terms of EC, namely; salty (>5 mS/cm), brackish (2 - 5 mS/cm) and fresh (<2 mS/cm). According to Table 11, the water quality across the boreholes are predominantly salty which is to be expected since it is near the coast. This could also indicate that the saltwater-freshwater interface had an impact, and that saltwater intrusion played a part.

Table 11: Water quality in terms of EC.

Borehole no.	Date	EC (mS/cm)	Water class
1	2015/07/05	1.242	Fresh
2	2015/12/05	41.083	Salty
3	2015/12/05	55.413	Salty
4	2015/07/05	21.023	Salty
5	2015/07/05	13.683	Salty
6	2015/12/05	19.087	Salty
7	2015/12/05	5.732	Salty
8	2015/07/05	3.725	Brackish

Groundwater in this region is mostly saline and, therefore, not suitable for human consumption based on the water quality.

5.3 Stable isotopes

Isotope analysis gives the variation in the eight boreholes and rainwater. There is a correlation between average local MWL and average isotope composition of atmospheric precipitation. The analytical outcome for the water samples are shown in Appendix 9.2 and illustrated in Figure 36.

Average $\delta^{18}O$ value is -2.2025‰ whilst δH is -3.8625‰ (for the eight boreholes). The isotopic data in a $\delta^{2}H$ vs. $\delta^{18}O$ scatter gram, depicted that most analysed samples are located around the Global Meteoric Water Line (GMWL). Due to the heavy rainfall during the winter months, there was quick discharge increases and falling isotopic content due to winter rainwater infiltration, with a lower isotopic content.

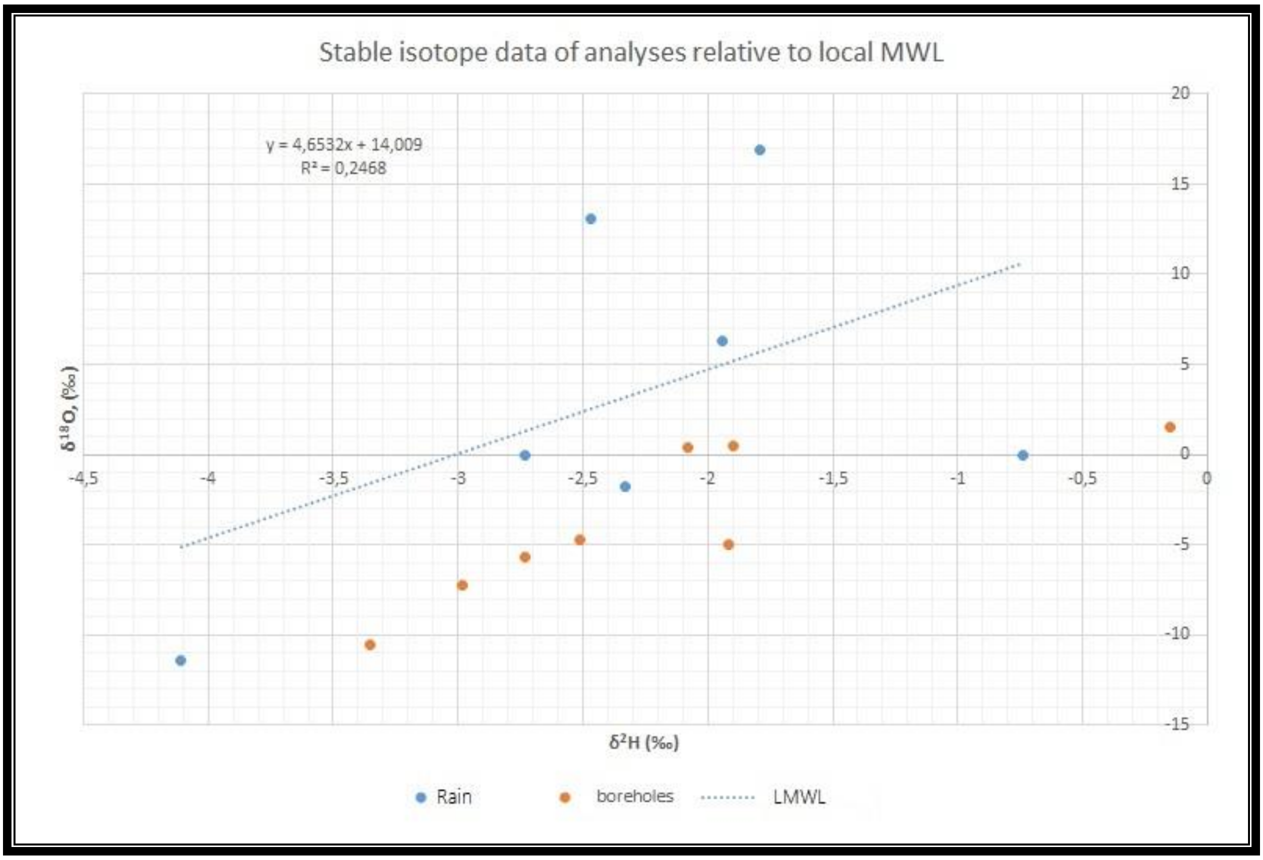

Figure 36: Stable isotope data of analyses relative to local MWL with a legend

Stable isotope composition of groundwater and rainwater shows the δ^2H and δ^{18}O compositions of groundwater and rainwater. The local meteoric water line for the Rietvlei was selected for comparative purposes because of its proximity. The δ^2H and δ^{18}O data fall into distinct groups, providing information on the secondary processes acting on the water as it travels from precipitation to groundwater. The rainwater samples plot higher in comparison with the groundwater on the local MWL. The majority of groundwater in the area fall close to or to the right of the local meteoric water line, indicating that these samples have not undergone some evaporation prior to infiltration.

The isotopic compositions δ^2H and δ^{18}O for the groundwater and rainwater are different. For example, the groundwater has a relatively enriched isotopic signature (less negative) where the rainwater is more distributed, however somewhat close. This indicates that infiltrating rainwater is the main source for the groundwater recharge. Recharge following large flood events could have such a depleted isotopic signature because heavy rain tends to have a relatively negative isotopic composition, and there is relatively less evaporation. A good linear relationship between measured ‰^{2}H and ‰^{18}O was observed for the series of groundwater water concentrates.

5.3.1 Groundwater recharge

The groundwater recharge (mm/year) was calculated using the isotope displacement method to determine the recharge for the area (Table 12). Boreholes recharge varies between 2.25 – 25 mm/year. The low recharge could be because of the clay content, and its retention ability, within the Rietvlei.

Table 12: Recharge within the area

BH	mm/year
Borehole 1	6.25
Borehole 2	25
Borehole 3	2.25
Borehole 4	11.08
Borehole 5	25
Borehole 6	8.16
Borehole 7	13.62
Borehole 8	16

5.4 Movement of contamination plumes

Three maps were created in Surfer for three different model scenarios. The contamination percentage seen in Figure 37, Figure 38 and Figure 39 over 10, 20 and 50 years indicates the contamination flow. These figures depict the movement of contaminants into the subsurface while the vector arrows indicate the direction and magnitude of migration. This was determined assuming the natural attenuation method. The Chevron refinery and an airfield (name unknown) were used as the main pollution sources within the area. It is clear that the contamination decrease away from the sources and the contamination flow direction minimally alternated over the 50-year period.

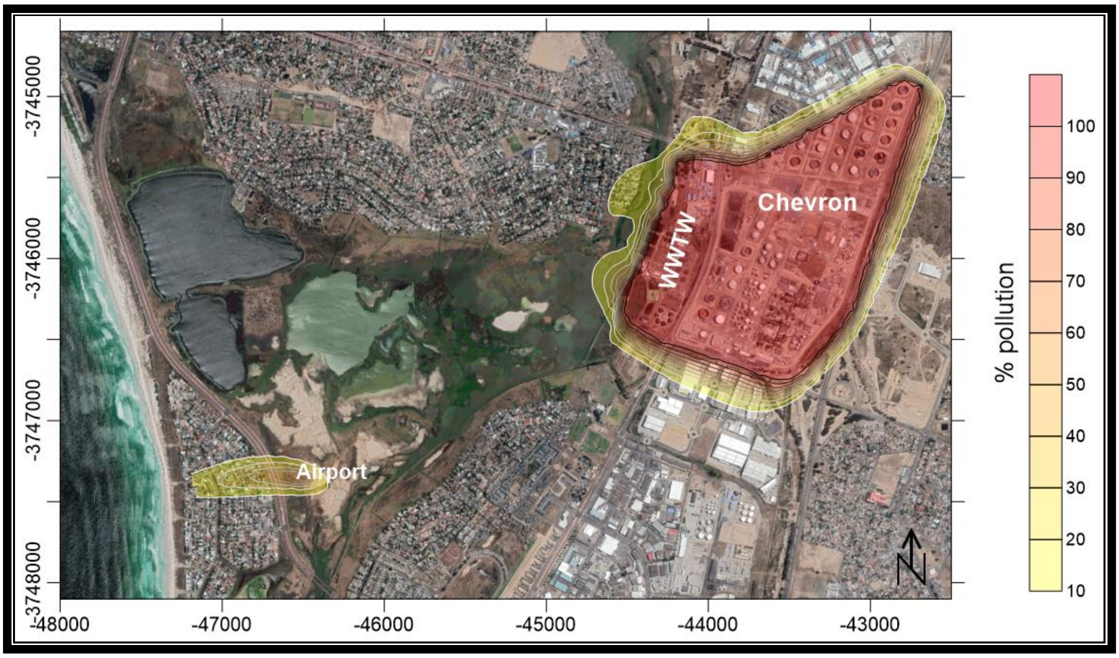

Figure 37: The simulation results for 10 years of the TMEs pollution

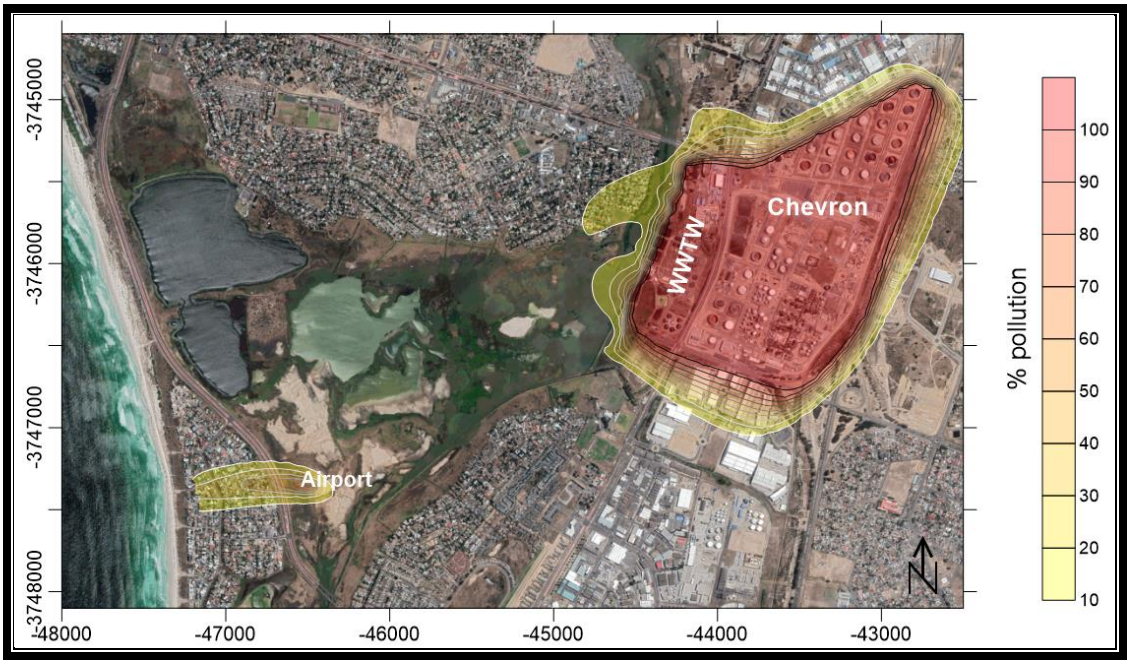

Figure 38: The simulation results for 20 years of the TMEs pollution

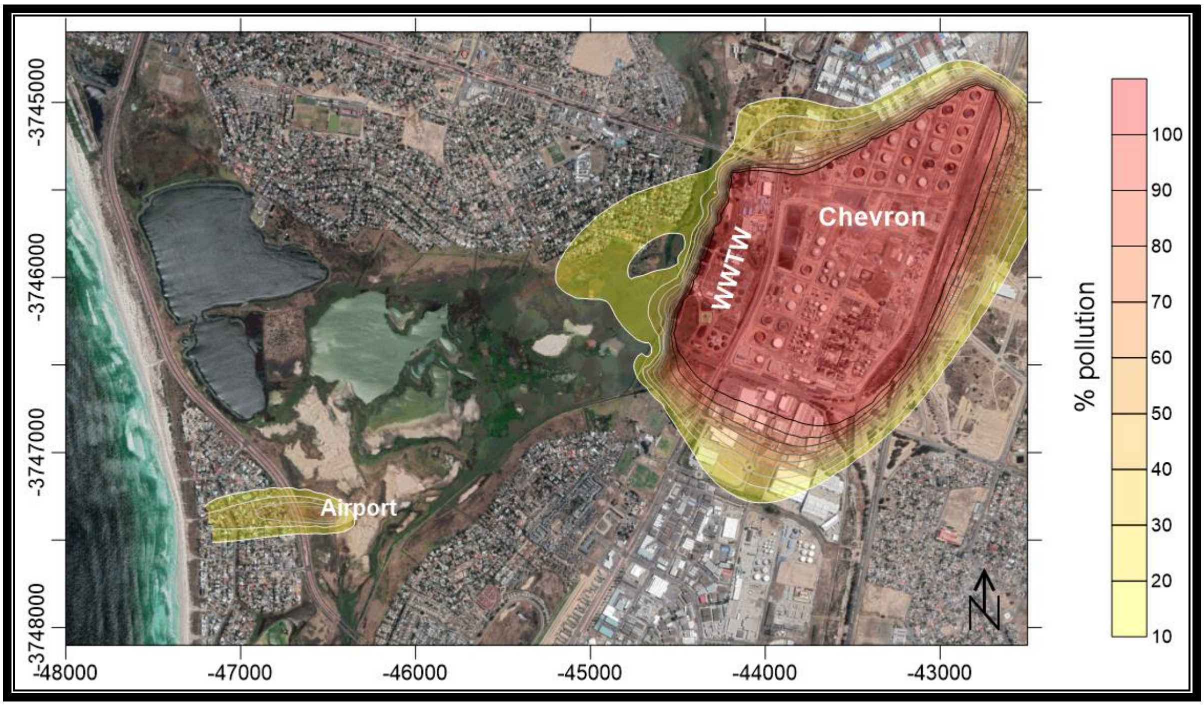

Figure 39: The simulation results for 50 years of the TMEs pollution

The change over time is represented by line graphs. Figure 40 and Figure 41 depicts Cu and Zn concentrations in each borehole. The concentrations decrease over days in each borehole. The same phenomenon is visible with lead (Figure 42). The concentrations decrease in every borehole except well 1 and 4.

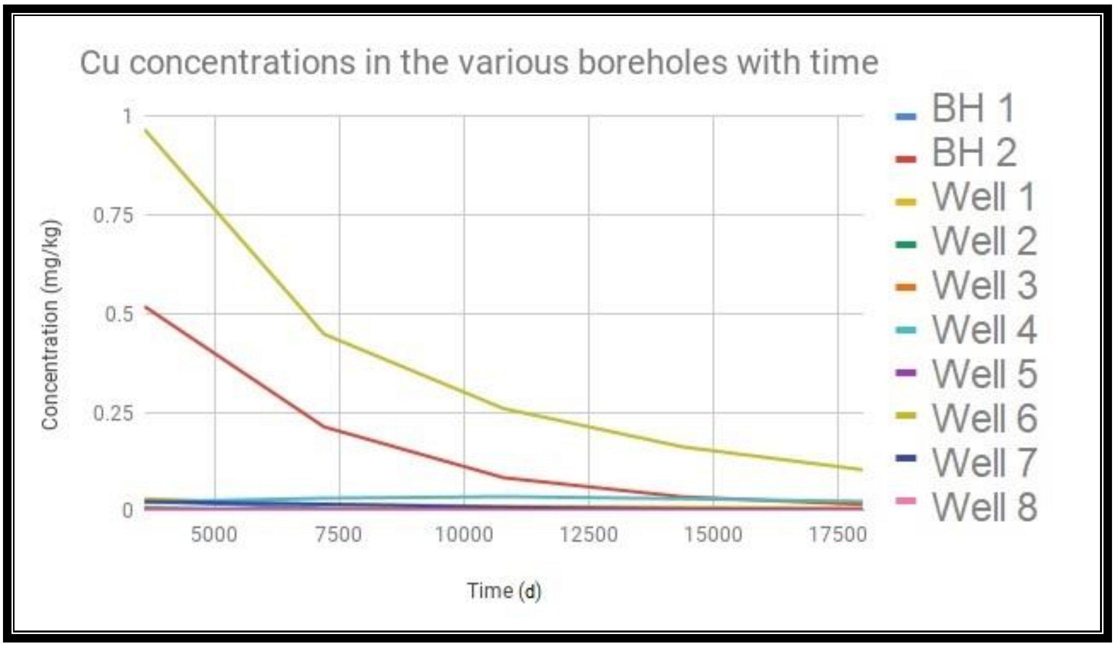

Figure 40: The change in concentration of Cu over time measured at different boreholes located within the contaminated region

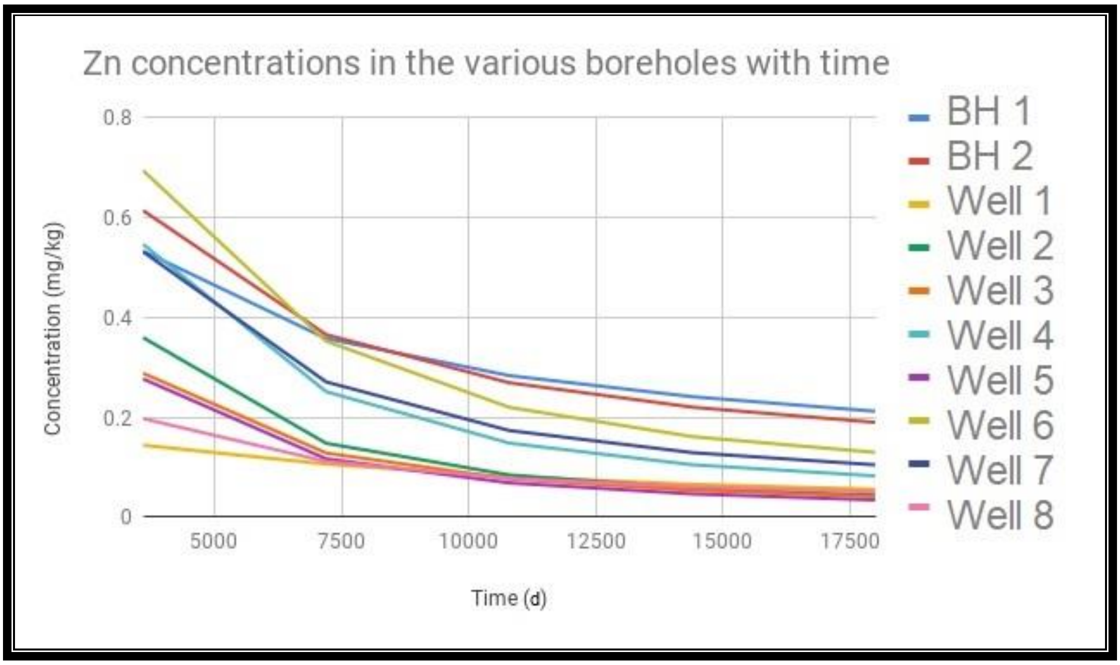

Figure 41: The change in concentration of Zn over time measured at different boreholes located within the contaminated region

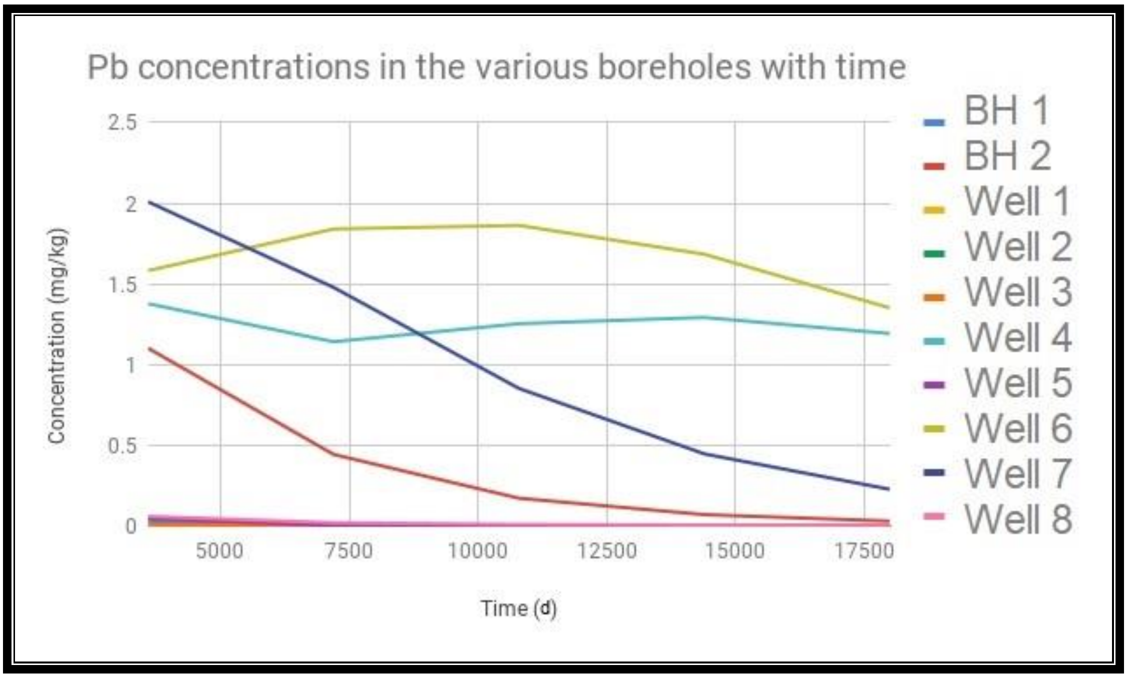

Figure 42: The change in concentration of Pb over time measured at different boreholes located within the contaminated region

At well one an there is an increase in concentration until it reaches a plateau between around 7500 – 11000 days and then subsequently decrease. In contrast, well four initially indicates a declining concentration until 7500 days followed by a minimal spike in concentration. This could be because of sorption.

6 CONCLUSIONS

The results obtained after the groundwater samples had been gathered and examined indicated that despite the way whereby TMEs are inserted into the soil and groundwater, the soil will retain or filter TMEs through into the groundwater. Trace metal element migration into groundwater or the atmosphere is not usually anticipated when the soil retention capacity is exceeded. The degree of TMEs movement downwards in the soil was found to be closely related to the chemical characteristics that are particular to each metal and solution.

The main findings follow:

- The aim of determining spatial distribution of TMEs within the Rietvlei and sub-catchment was to find an answer through remote sensing. The predicted concentrations gained from Landsat 8 through hyperspectral analyses indicated that the soils are enriched with Cu, Zn and Pb. The concentrations were used to indicate how TMEs are transported from the soil to groundwater. The concentration of TMEs found in the soil are much higher than what was measured in the groundwater. Although the Cu, Zn and Pb levels found within the groundwater were significantly less than what was predicted for the soils, it is safe to assume that a certain amount of the TME remained in the soils while the other moved into the groundwater. This could be a result of the processes and interactions like surface water transportation, organic matter interactions, adsorption to clay and oxide surfaces that could transpire while the TMEs are distributing.

- Regression analysis was performed between groundwater calculations and soil spectral data to estimate the relationship between the two variables. Detection showed that Zn, Pb and Cu concentration forecasting in spectral reflectance quantification, did not correlate with the groundwater concentrations. The reason for the lack of correlation between the measured and predicted concentrations could be due to the scarcity (number of samples = 8) of data available for the research area.

- Groundwater quality was compared to the standards of DWAF (1996) and CCME (2001). The concentrations of Al, Fe, Mn, Pb and Zn available in the respective eight boreholes exceeded the accepted limits. This implies that the environment and organisms consuming the groundwater will be negatively affected.

- The Gibbs diagram determined that the major processes controlling the groundwater chemistry is the evaporation-precipitation mechanism, which is to be expected considering that the study area is located near the coast. Weak groundwater quality is likely linked to high salinity. The groundwater across the boreholes are predominantly salty which is to be expected.

- The possible pollution sources in the Rietvlei area are the Chevron refinery, Airfield (name unknown), Universal Cosmetic Manufacturing, the Potsdam Waste Water Treatment Plant, Crous Chemicals and historic automobile emissions that contained Pb.

- It was found that the TMEs found in the soil moved into the groundwater. The concentrations whereby they occur within the two mediums differ. This could be because TMEs migrate elsewhere and/or are retained within the soil. Other reasons may include interactions and processes like surface water transportation, organic matter interactions, adsorption to clay and oxide surfaces, etc.

- Groundwater recharge was calculated using the isotope displacement method. Boreholes recharge δ^2H at 3.55 - 2500 mm/year and $\delta^{18}O$ 35,64 – 17773 mm/year. Rain δ^2H 0 – 123,43 mm/year $\delta^{18}O$ 23,68 – 730,46 mm/year

- The groundwater and contamination flow was performed over periods of 10, 20 and 50 years. The Chevron refinery and airfield was set as the main pollution sources in the region. The contamination decrease away from the sources and the contamination flow direction changes over the 50-year period. There is a daily change in concentration in each borehole. The concentrations decreased in every borehole except for wells one and four. At well one, there is an increase in concentration until it reaches a plateau between around 7 500 (d) – 11 000 (d) and then subsequently decreases. In contrast, well four initially indicates a declining concentration until 7500 (d) followed by a minimal spike in concentration. This could be that a limited source containing Pb was introduced into the system at that well at that given period. It proves that each borehole will reconfigure to attain its natural state.

- Certain methods are not viable because they are either too expensive and/or the extent of the area too large for it to be successful. The possible methods used in MODFLOW were used to determine efficacy. When done practically, the mitigation results must be supervised to establish the efficacy of the selected mitigation method. In order to mitigate the pollution and contamination in this case, the natural attenuation method was assumed.

The results obtained proved the hypotheses. The contaminants will flow from the sources, polluting the soil and subsequently the groundwater. There is a connection between the excessive TMEs found in the soil and groundwater and the product content of the responsible sources however the connection could not be quantified. The groundwater quality is therefore not suitable for human consumption.

7 RECOMMENDATIONS

To improve the current study, there must be more data available for the groundwater. Obtaining actual soil samples to analyse may give more accuracy and a preferable correlation between the soil and groundwater. Sufficient data and information will ensure that proper analyses, interpretations and conclusions are made.

There are numerous ways to this study could be furthered:

1. Determining the transportation of TMEs from soil to groundwater by sampling the soil within the area at different locations and over a defined period and groundwater samples.
2. Obtaining more samples and data for groundwater and soil within the Rietvlei area itself, and the larger catchment.
3. Determining the impact that the saltwater-freshwater interface may have with groundwater extraction and how it influences the groundwater quality.
4. A more extensive mitigation plan could be developed. When running a model, all the mitigation methods should be used as situations to see which will be most successful.

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9 Appendix

9.1 Groundwater samples

Table 13: Descriptive statistics of Cu, Zn and Pb of groundwater samples

Boreholes	**Statistics**	**Trace metal concentration (mg/kg)**		
		Cu	**Zn**	**Pb**
1	Average	5,48553	9,46795	7,319066667
	Highest	9,8822	17,1738	15,0211
	Lowest	3,162	2,8849	2,1167
2	Average	1,26727	4,94777	9,7545
	Highest	3,1238	6,3706	4,6983
	Lowest	0,025	3,3601	2,9625
3	Average	0,5226	4,23215	3,41075
	Highest	1,0503	7,2638	5,165
	Lowest	0,025	0,6954	0,7343
4	Average	3,0921	14,7597	10,08314
	Highest	14,8344	50,0728	34,7635
	Lowest	0,025	4,6031	3,3541
5	Average	0,0496	4,06422	3,66645
	Highest	0,1726	5,0753	4,0239
	Lowest	0,025	3,7542	3,3426
6	Average	0,0502	4,61878	4,395866667
	Highest	0,1762	5,8603	8,1842
	Lowest	0,025	3,4156	3,0504
7	Average	0,025	5,65312	4,161783333
	Highest	0,025	7,0111	4,5166
	Lowest	0,025	4,6	3,7812
8	Average	0,025	4,39614	3,07582
	Highest	0,025	5,645	3,5399
	Lowest	0,025	3,2543	2,4847

9.2 Stable isotope analysis

Table 14: Stable isotope analytical results

Lab ID	Sample ID	δ^2H (‰)	$\delta^{18}O$, (‰)	Aquifer	State or Province	Country Code	Other Info
W-1098	Borehole 1	-4.7	-2.51	Cape Flats	Western Cape	ZA	Groundwater filtered
W-1099	Borehole 2	-5	-1.92	Cape Flats	Western Cape	ZA	Groundwater filtered
W-1100	Borehole 3	1.5	-0.15	Cape Flats	Western Cape	ZA	Groundwater filtered
W-1101	Borehole 4	-7.3	-2.98	Cape Flats	Western Cape	ZA	Groundwater filtered
W-1102	Borehole 5	0.5	-1.9	Cape Flats	Western Cape	ZA	Groundwater filtered
W-1103	Borehole 6	-10.6	-3.35	Cape Flats	Western Cape	ZA	Groundwater filtered
W-1104	Borehole 7	-5.7	-2.73	Cape Flats	Western Cape	ZA	Groundwater filtered
W-1105	Borehole 8	0.4	-2.08	Cape Flats	Western Cape	ZA	Groundwater filtered
W-1106	Rain 1	16	-0.74		Western Cape	ZA	Rain water
W-1107	Rain 2	16.9	-1.79		Western Cape	ZA	Rain water
W-1108	Rain 3	13.1	-2.47		Western Cape	ZA	Rain water
W-1109	Rain 4	-11.4	-4.11		Western Cape	ZA	Rain water
W-1110	Rain 5	0	-2.73		Western Cape	ZA	Rain water
W-1111	Rain 6	6.3	-1.94		Western Cape	ZA	Rain water
W-1112	Rain 7	-1.8	-2.33		Western Cape	ZA	Rain water

Declaration

This is to declare that I, Annette L Combrink, accredited language editor and translator of the South African Translators' Institute, have language-edited the dissertation

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With the title

Trace metal contamination of soil and groundwater in the Rietvlei catchment, Cape Town

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